CEEC-TAC5 & Medicta2019

BOOK
OF
ABSTRACTS

Editors:

Andrei Rotaru
Stefano Vecchio Ciprioti

5th Central and Eastern European Conference on
Thermal Analysis and Calorimetry
&
14th Mediterranean Conference on
Calorimetry and Thermal Analysis

27-30 August 2019
Roma, Italy

Book of abstracts of the 5th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC5) and 14th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2019).

5th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC5) and
14th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2019).
27-30 August 2019
Roma
Italy

Editors:
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The 5th Central and Eastern European Conference
on Thermal Analysis and Calorimetry
&
The 14th Mediterranean Conference on
Calorimetry and Thermal Analysis

CEEC-TAC5 & Medicta2019

27-30 August 2019 – Roma, Italy

is organized by the:

Central and Eastern European Committee for
Thermal Analysis and Calorimetry (CEEC-TAC),

Italian Association for Calorimetry and Thermal Analysis (AICAT),

Interdivisional Group of Calorimetry and Thermal Analysis (GICAT)
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Dear Participants at CEEC-TAC5 & Medicta2019 Conference,

Let us express our great pleasure to welcome you here in Roma - Italy, for attending the joint 5th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC5) and 14th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2019) between 27th and 30th of August 2019; we thank very much to all 371 of you for joining us! Since “All Roads Lead to Roma”, it was somehow natural to meet here this time! Roma is the largest city of Italy and also its capital. It is an impressive cosmopolitan city with an artistic, architectural and cultural history that has influenced the whole world and dates back to almost 3000 years ago.

Now, the joint event CEEC-TAC5 & Medicta gathers 371 registered participants from 38 countries and of 6 continents, presenting a total number of 449 scientific works. Of those, 4 are Plenary Lectures (PL), 3 are Award Plenary Lectures (APL), 16 are Invited Lectures (IL), 4 Parallel Sessions of Oral Presentations – 108 contributions (OP) & 3 Sessions of Poster Presentation – 318 contributions (PS). An important task of CEEC-TAC5 & Medicta2019 is the continuation of 2 distinctive directions the conference follows, with 2 Workshops (WS) introducing the subjects:
1) *Advanced Functional Materials;* 2) *Kinetics & Lifetime Prediction of Materials (KLTPM).*

At this edition, Awards will be offered to exceptional scientists: *i*) Prof. Janos Kristof from Hungary (Honorary Member of CEEC-TAC), *ii*), Prof. Vahur Oja from Estonia (Distinguished TA&C Researcher in Central & Eastern Europe); *iii*) Prof. Kestutis Baltakys from Lithuania (Outstanding Young TA&C Researcher in Central & Eastern Europe); three *iv*) “Andrzej Malecki” 2019 Grants for Best Young Researcher from Central & Eastern Europe in the field of Thermal Analysis and Calorimetry; four *v*) “Jaroslav Sestak” 2019 Travel Grant for Best Student from Central & Eastern Europe and from Mediterranean Area in the field of Thermal Analysis and Calorimetry.

We would like to express our thanks to the people who contributed and supported the organization of this event, especially to the members of the Honorary Committee, Scientific Committee, International Organizing Committee, National Associations for Thermal Analysis and Calorimetry from Central and Eastern European countries and those from the Mediterranean area, Executive Organizing Committee, Central and Eastern European Committee for Thermal Analysis and Calorimetry, Italian Association for Calorimetry and Thermal Analysis (AICAT), Interdivisional Group of Calorimetry and Thermal Analysis (GICAT) of the Italian Chemical Society, Sapienza University of Rome (SUR) and the Department of Basic and Applied Sciences for Engineering of SUR, University of Craiova, INFLPR-National Institute for Laser, Plasma and Radiation Physics, and Institute of Physical Chemistry “Ilie Murgulescu” of the Romanian Academy. We acknowledge the great support of our Sponsors: MPstrumenti & LINSEIS, METTLER TOLEDO, RIGAKU, HITACHI, DSC CONSUMABLES (Gold Sponsors), NETZSCH (Bronze Sponsor) and our Partners: ECO Ricerche, Thorn Scientific Services Ltd. A special acknowledgement has to be addressed to the *Journal of Thermal Analysis and Calorimetry*, *Ceramics International*, *Applied Clay Science*, *Journal of Mining and Metallurgy, Section B: Metallurgy*, where one of their volumes will be dedicated to research papers of our conference, presented as oral or poster contributions.

The 4-day meeting is hosted at the Rectorate Building of the Sapienza University of Rome, which is located close to the historic centre. The official language of the conference is English.

We hope that you will enjoy the city during your stay at the CEEC-TAC5 & Medicta2019 conference, and that you will leave Roma with the same good feelings and memories as those after attending the previous conferences. We expect that this conference will give you novel scientific and practical knowledge, and enrich you with a variety of new contacts.

Looking forward to seeing you at forthcoming thermal analysis and calorimetry conferences, and hopefully in 2021 for CEEC-TAC6 and Medicta2021!

Stefano Vecchio Ciprioti & Andrei Rotaru
Chairmen of CEEC-TAC5 & Medicta2019

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General Information

The joint event "5th Central and Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC5) & 14th Mediterranean Conference on Calorimetry and Thermal Analysis (Medicta2019)" has gathered **371 registered participants** from **38 countries** and of **6 continents**, presenting a total number of **449 scientific works**. Of those, 4 are Plenary Lectures (**PL**), 3 are Award Plenary Lectures (**APL**), 16 are Invited Lectures (**IL**), 4 Parallel Sessions of Oral Presentations – 108 contributions (**OP**) & 3 Sessions of Poster Presentation – 318 contributions (**PS**). Each session of oral presentations is comprised of 27 works, while each session of poster presentations includes 106 works.

An important task of CEEC-TAC5 & Medicta2019 is the continuation of 2 distinctive directions that the first conference follows, with 2 Workshops (**WS**) introducing the subjects:

1) *Advanced Functional Materials;*

2) *Kinetics and Lifetime Prediction of Materials (KLTPM).*

Plenary Lectures

- ***Kestutis Baltakys*** (Kaunas Univerity of Technology, Lithuania)
- ***Dimitrios N. Bikiaris*** (Aristotle University of Thessaloniki, Greece)
- ***Nobuyoshi Koga*** (Hiroshima University, Japan)
- ***Janos Kristof*** (University of Pannonia, Hungary)
- ***Vahur Oja*** (Tallinn University of Technology, Estonia)
- ***Crisan Popescu*** (KAO European Research Laboratory, Germany)
- ***Henrik Rudolph*** (Applied Surface Science, Elsevier, the Netherlands)

Invited Lectures

- ***Arnon Chaipanich*** (Chiang Mai University, Thailand)
- ***Svetlana Danilova-Tretiak*** (A.V. Luikov Heat&Mass Transfer Institute, Belarus)
- ***Ahmed El-Sabbagh*** (Ain Shams University, Egypt)
- ***Nathanael Guigo*** (University of Cote d'Azur, France)
- ***Tiit Kaljuvee*** (Tallinn University of Technology, Estonia)
- ***Dana Luca Motoc*** (Transilvania University of Brasov, Romania)
- ***Cheila G. Mothe*** (Federal University of Rio de Janeiro, Brazil)
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- ***Adriana Saccone*** (University of Genoa, Italy)
- ***Pablo Taboada*** (University of Santiago de Compostela, Spain)
- ***Paul S. Thomas*** (University of Technology Sydney, Australia)
- ***Ranjit K. Verma*** (Patna University, India)
- ***Anna Vykydalova*** (Slovak University of Technology in Bratislava, Slovakia)
- ***Kseniya Zherikova*** (Nikolaev Institute of Inorganic Chemistry, Russian Federation)

Tuesday, 27th of August	
$8^{30}-13^{00}$	***Short Summer School on TA&C***
$13^{00}-14^{30}$	*Lunch*
$14^{30}-16^{30}$	***International Conference for Young Researchers and Students on TA&C***
$16^{30}-17^{30}$	***Afternoon break***
$13^{30}-16^{30}$	***Registration of participants at CEEC-TAC5 & Medicta2019***
$16^{30}-17^{30}$	***Afternoon break***
$17^{30}-18^{30}$	**Opening Ceremony**
$18^{30}-19^{00}$	**Crisan Popescu, PL1**
$19^{00}-19^{30}$	**Henrik Rudolph, PL2**
$19^{30}-21^{30}$	*Welcome Cocktail*

Wednesday, 28th of August				
$9^{00}-9^{40}$	**Janos Kristof, APL1**			
$9^{40}-9^{50}$	**CEEC-TAC5 & Medicta2019**			
$9^{50}-10^{30}$	**Workshop Materials**			
$10^{30}-10^{50}$	*Coffee break*			
$10^{50}-11^{20}$	**IL01**	**IL02**	**IL03**	**IL04**
$11^{20}-11^{40}$	OP1.01	OP2.01	OP3.01	OP4.01
$11^{40}-12^{00}$	OP1.02	OP2.02	OP3.02	OP4.02
$12^{00}-12^{20}$	OP1.03	OP2.03	OP3.03	OP4.03
$12^{20}-12^{40}$	OP1.04	OP2.04	OP3.04	OP4.04
$12^{40}-13^{00}$	OP1.05	OP2.05	OP3.05	OP4.05
$13^{00}-14^{30}$	*Lunch*			
$14^{30}-15^{10}$	**Nobuyoshi Koga, PL3**			
$15^{10}-15^{20}$	**CEEC-TAC5 & Medicta2019**			
$15^{20}-15^{50}$	**IL05**	**IL06**	**IL07**	**IL08**
$15^{50}-16^{10}$	OP1.06	OP2.06	OP3.06	OP4.06
$16^{10}-16^{30}$	OP1.07	OP2.07	OP3.07	OP4.07
$16^{30}-16^{50}$	OP1.08	OP2.08	OP3.08	OP4.08
$16^{50}-17^{10}$	*Coffee break*			
$17^{10}-17^{30}$	OP1.09	OP2.09	OP3.09	OP4.09
$17^{30}-17^{50}$	OP1.10	OP2.10	OP3.10	OP4.10
$17^{50}-18^{10}$	OP1.11	OP2.11	OP3.11	OP4.11
$18^{10}-18^{30}$	OP1.12	OP2.12	OP3.12	OP4.12
$18^{30}-18^{50}$	OP1.13	OP2.13	OP3.13	OP4.13
$18^{50}-19^{10}$	*Evening break*			
$19^{10}-20^{20}$	***Medicta General Assemblies***			
$19^{10}-20^{20}$	***CEEC-TAC General Assembly***			

Thursday, 29th of August				
$9^{00}-9^{40}$	**Vahur Oja, APL2**			
$9^{40}-10^{40}$	**Poster session 1**			
$10^{40}-11^{00}$	*Coffee break*			
$11^{00}-11^{20}$	OP1.14	OP2.14	OP3.14	OP4.14
$11^{20}-11^{40}$	OP1.15	OP2.15	OP3.15	OP4.15
$11^{40}-12^{00}$	OP1.16	OP2.16	OP3.16	OP4.16
$12^{00}-13^{00}$	**Poster session 2**			
$13^{00}-14^{30}$	*Lunch*			
$14^{30}-15^{30}$	**Poster session 3**			
$15^{30}-20^{00}$	***Afternoon break***			
$20^{00}-24^{00}$	*Conference Dinner*			

Friday, 30st of August				
$9^{00}-9^{40}$	**Kestutis Baltakys, APL3**			
$9^{40}-9^{50}$	**CEEC-TAC6 / Medicta2021**			
$9^{50}-10^{30}$	**Workshop KLTPM**			
$10^{30}-10^{50}$	*Coffee break*			
$10^{50}-11^{20}$	**IL09**	**IL10**	**IL11**	**IL12**
$11^{20}-11^{40}$	OP1.17	OP2.17	OP3.17	OP4.17
$11^{40}-12^{00}$	OP1.18	OP2.18	OP3.18	OP4.18
$12^{00}-12^{20}$	OP1.19	OP2.19	OP3.19	OP4.19
$12^{20}-12^{40}$	OP1.20	OP2.20	OP3.20	OP4.20
$12^{40}-13^{00}$	OP1.21	OP2.21	OP3.21	OP4.21
$13^{00}-14^{30}$	*Lunch*			
$14^{30}-15^{10}$	**Dimitrios N. Bikiaris, PL4**			
$15^{10}-15^{20}$	**CEEC-TAC6 / Medicta2021**			
$15^{20}-15^{50}$	**IL13**	**IL14**	**IL15**	**IL16**
$15^{50}-16^{10}$	OP1.22	OP2.22	OP3.22	OP4.22
$16^{10}-16^{30}$	OP1.23	OP2.23	OP3.23	OP4.23
$16^{30}-16^{50}$	*Coffee break*			
$16^{50}-17^{10}$	OP1.24	OP2.24	OP3.24	OP4.24
$17^{10}-17^{30}$	OP1.25	OP2.25	OP3.25	OP4.25
$17^{30}-17^{50}$	OP1.26	OP2.26	OP3.26	OP4.26
$17^{50}-18^{10}$	OP1.27	OP2.27	OP3.27	OP4.27
18^{10}	***Closing Ceremony***			

Room A (Aula Magna)
Room B
Room C
Room D (MLAC)
Coffee Break and Poster Session region at SUR
Back side of the Rectorate Palace of SUR
Canteen at the Faculty of Economics of SUR
Hotel Quirinale
Room A, B, C, D are inside of the Rectorate of SUR
Rooms for various GAs are available at Department of Chemistry Building at SUR

Rectorate Palace of the Sapienza University of Rome (SUR), Piazzale Aldo Moro, No. 5, Roma
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Program of CEEC-TAC5 & Medicta2019

27-30 August 2019

Roma, Italy

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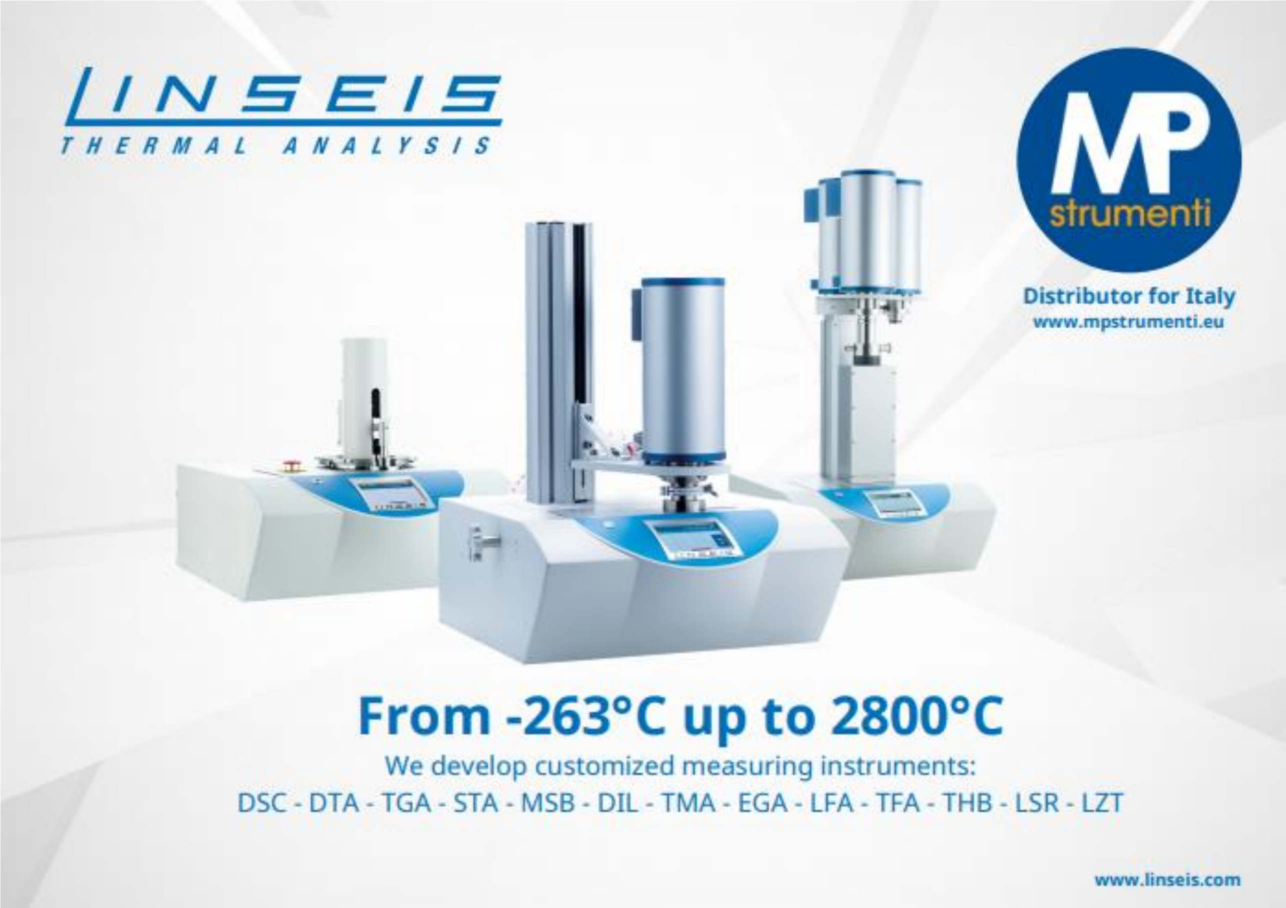


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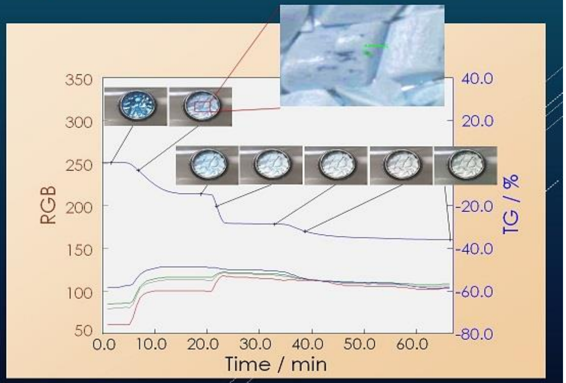
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Plenary Lectures

“Beauty” and the “Thermal Analysis”

Crisan POPESCU
KAO Germany GmbH, Pfungstaedterstr. 98-100, Darmstadt, Germany

The talk aims at showing how the use of thermal analysis concepts and methods helps the development of beauty industry, particularly of hair care.

Fibrous proteins, particularly keratin fibres, were among the first systems undergoing the explorations with thermal analysis means, when first instruments became commercially available. The investigations focused initially on discerning structural details and evaluating thermodynamic quantities. After decades of revealing incrementally the keratins intricate structure, the thermal analysis methods begin being increasingly used to substantiate product claims, to assist the development of hair care treatments and to assess the damage incurred by the action of various treatments.

Surveying various examples, the talk points out to hurdles in applying TA methods and underlines some of the problems of data interpretation, which may hinder the meaningful exploitation of the results.

Ethics in Scientific Publishing

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National laws are often considered to be a subset of the common ethical rules and rules of proper behaviour. Since national laws can differ greatly from country to country, so can ethical rules and rules of proper conduct. When we are talking about ethics in science, we are trying to apply "universally" valid scientific values, which are globally accepted in the scientific community. The presentation will start out with a small discussion of what ethics in science entails. It is obviously impossible to discuss all aspects of ethics in science in a 30-minute presentation. I will therefore focus mostly on ethics in publishing. This covers the role of authors (and co-authors) as well of that of the reviewers. I will also briefly touch on the role of funding agencies (departments) as well as the publishers (editors), but the main emphasis will be on the role of authors and reviewers.

Kinetic approach to complex reactions in solid–gas systems: A continuous challenge

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Kinetic approach to the complex solid-state reactions involving those in solid–gas systems is a challenging task, because simple probabilistic logic is not necessarily applicable due to significant physico-geometric constraints [1,2]. The kinetic behaviors of each or specific reaction step in the physico-geometrical multistep reaction are required to reveal for establishing the rigid theoretical basis for the formal kinetic description of the overall process using thermal analysis. The other possible cause of the complexities of the kinetic behavior is apparently owing to the impact of a gas in the reaction atmosphere and that evolved by the reaction on the apparent kinetic behavior. Because of a wide variety of the apparent changes in kinetic behaviors of the reactions with these gases, a unified theory of explaining the impact of gases on the kinetics is still missing. The further complexity may be caused by the mutual correlation between the physico-geometrical reaction mechanism and the impact of the gases.

In this lecture, we overview the current status of the kinetic understanding of complex reactions in solid–gas systems, and subsequently address each difficult problem in the following stepwise manner by referencing our recent achievements.

(1) Apparent features of the multistep reactions [1,2]
(2) Kinetic approach to multistep reactions [3-6]
(3) Multistep reactions comprising opposite thermoanalytical signals [7-11]
(3) Apparent features of the impact of atmospheric gas [11-13]
(4) Universal kinetic description over different atmospheric conditions [13]
(5) Mutual correlation between physico-geometrical reaction mechanism and impact of atmospheric gas [13]

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Thermal characteristics and decomposition mechanism of furanoate polyesters, a new class of biobased polymers

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In recent years, the potential replacement of fossil fuels for the production of appropriate monomers by inexpensive and renewable starting materials such as cellulose, starch, lignin, proteins and vegetable oils is increasingly being explored with the aim to develop a more sustainable bio-based economy. Polymers based on 2,5-furandicarboxylic acid (2,5-FDCA), which is a new biobased monomer, consist a new class of alipharomatic polyesters that can be prepared from monomers derived straight from renewable resources like furfural and hydroxymethylfurfural (HMF) [1]. The study for the production of such polyesters has now been extended and almost the whole series of poly(2,5-furan dicarboxylate)s have been prepared using aliphatic diols, sugar diols like isosorbide, benzylic structures like 1,4-bishydroxymethyl benzene, and bisphenols like hydroquinone, etc.

The macroscopic properties of these materials depend heavily on their microstructure and structural characteristics, which in turn are affected from the crystallization conditions and their thermal history. The thermal characteristics such as the crystallization and melting temperature determine their processing conditions and the potential uses in various applications. For this reason, the crystallization and melting temperatures of 2,5-FCDA-based polyesters have been extensively studied from our group.

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Award Plenary Lectures

Thermal analysis at surfaces and interfaces: studies on thin films and intercalation complexes

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Mixed oxide thin films are widely used in industrial electrochemistry (chlorine production, waste water treatment, galvanics, organic electrosyntheses, etc.) as well as in sensor development. Among the common preparation techniques (e.g. spin-coating, immersion, spraying) the sol-gel method is preferred when the composition of the film should be strictly controlled.

The evolution of the films on metal support via heat treatment of the precursor salts (mostly chlorides) from alcoholic or aqueous solutions can be followed by TG-MS and emission FTIR techniques. The formation and decomposition of intermediates (carbonyls, carboxylates, carbonates) can significantly affect the morphology of the surface. With the continuous monitoring of the evolution of both the solid and the gas phases the mechanism of film formation can be revealed.

With cascade intercalation the layers of the kaolinite mineral can be completely exfoliated. The nanolayers have photochemical activity that can be further enhanced with the deposition of silver nanoparticles onto the surface. The most critical part of the exfoliation procedure is the formation and structure elucidation of the kaolinite organo-complexes with different reagents (potassium-acetate, hydrazine, dimethyl-sulfoxide, etc.). The use of thermoanalytical techniques such as high temperature XRD, high and low temperature Raman microspectroscopy, controlled-rate thermogravimetry (CRTA) is indispensible in the discovery of the structure of the nanocomplexes. Mechanochemical activation of the clay is another way to induce active (defect) sites in the mineral structure contributing to photochemical activity.

Acknowledgement

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Application of thermal analysis to study vaporization parameters of narrow boiling range oil fractions

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One of the important group of thermodynamic parameters both for thermodynamic calculations and for assessment of chemical processes, also for transportation, storing or environmental impact assessment, are the parameters describing the volatility of the material. Unlike pure substances or their well-defined mixtures, oils consist of many organic compounds with different chemical structure and size. In terms of process design and environmental engineering calculations one way to simplify the calculations is to divide the oil into fractions with narrow boiling ranges (or pseudo-components), which can be described by mean characteristics. Thus, depending on the application, it would be desirable to describe the vaporization ability of the fractions with narrow boiling ranges either by the vaporization parameters (boiling point, vapour pressure, enthalpy) corresponding to the actual boiling point, or by the vaporization parameters (the average boiling point, its pressure dependence and the related conditional enthalpy of vaporization) corresponding to the average boiling point (vaporization parameters of the pseudo-component).

The goal of the presentation is to provide an experience-based overview of the application of thermal analysis, specifically based on the principle of ASTM D1782, for measuring vaporization parameters, both corresponding to the actual boiling point and the average boiling point, of oil fractions with narrow boiling ranges. The ASTM D1782 “Standard test method for determining vapour pressure by thermal analysis” is a pure compound vapour pressure measurement technique, where the vapour pressure curve is established by determining via separate experiments boiling points at different pressures. The each boiling point is determined from the onset of the thermogram corresponding to the sample evaporation through the pinhole from a hermetically sealed crucible, when the sample is heated at a constant rate to temperatures higher than the boiling point for the given pressure. For fractions with narrow boiling ranges, although the principle of ASTM D1782 is relatively directly applicable for measuring the vapour pressures corresponding to the actual boiling points (by finding the onset from thermogram), a prior experimental experience would be necessary for obtaining a thermogram with suitable height and shape (sharpness) in order to achieve good results. The thermogram should correspond to a left-scewed curve (corresponding to a left-scewed curve rather than a Gaussian curve). Application of the principle of ASTM D1782 for calculating the vapour pressures corresponding to the average boiling points of the fractions with narrow boiling range (pseudo-components) through converting the vaporization curve to the condensing curve and calculating the average boiling point, needs prior optimization of the experimental conditions (heating rate, amount of material), so that the vaporization from the capsule through the micro-opening could take place in conditions close to vapour-liquid equilibrium. The thermogram itself could correspond to a Gauss curve or a right-skewed curve.

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Eco-friendly calcium silicates: preparation techniques, thermal properties and application

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The main feature of environmentally friendly cementitious materials ("Celitement", "Solidia cement", "Calcium sulfoaluminate cement", "Magnesia-based cements," etc.) is that the energy consumption and the CO_2 emissions associated with cement production can be reduced within the range of 30–70 % [1, 2]. One of the most attractive ways to obtain mentioned materials are the production in a three-step process: 1) hydrothermal synthesis of higher basicity calcium silicate hydrate or calcium silicate (CaO/SiO_2 ratio from 1.25 to 2.0); 2) mechanochemical or thermal treatment of hydrothermal products together with siliceous raw materials such as sand, blast-furnace slag, glass, etc. or silica (usually 1:1); 3) cement curing in the water or CO_2 atmosphere [3-4]. It is known that the properties of environmentally friendly cementitious materials depend on the mineral composition of products obtained during hydrothermal treatment. For these reasons, the synthesis, structure and chemistry of the above mentioned compounds have been studied by many scientists, yet their opinions seem to differ.

Thus, this work aims to investigating an preparation technique for the production of environmentally friendly cementitious materials which combines the hydrothermal synthesis of precursors and their solid-state sintering at a low temperature. The preparation technique of the above mentioned materials requires a 600–1000 °C lower calcination temperature as well as a lower quantity of calcium carbonate, which leads to lower CO_2 emissions. The obtained results were confirmed by XRD, STA, FT-IR, SEM, TEM and BET analysis.

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Invited Lectures

In a search for advanced materials produced by MOCVD: thermodynamics, kinetics, functional properties, relationships

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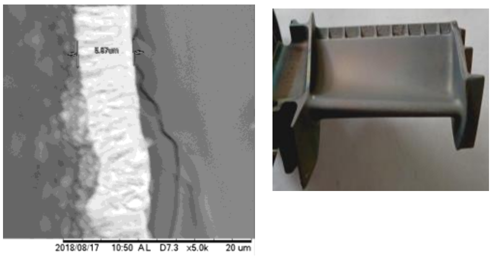
Nowadays MOCVD (Metal Organic Chemical Vapor Deposition) has become well-established material production technology and it is firmly associated with semiconductors. However, the potential of the method is far from being exhausted and it is being actively studied for the replacement of existing technologies to produce functional coatings with improved properties.

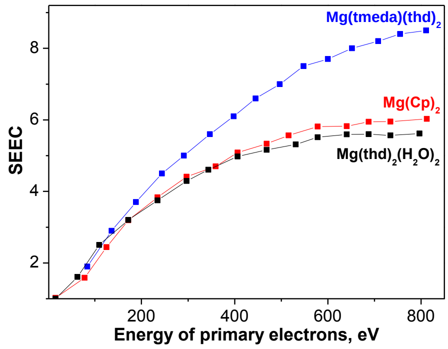
In focus of this lecture, there are two types of advanced composite materials obtained by Metal Organic Chemical Vapor Deposition (MOCVD): Thermal Barrier Coatings (TBC) and Secondary Electron Emission (SEE) systems.

Manufacturing the TBCs operating under extreme conditions is a challenging but vitally important task for various areas of industry due to their application as coating parts of gas turbines. Further performance improving their efficiency by the significant increasing in operating temperatures and pressures within the turbine section requires both novel high-strength and refractory materials and new highly effective manufacturing methods. The thermodynamics and kinetics factors effecting MOCVD of thermal insulated composite thick coatings on gas turbine blade are going to be highlighted.



SEM cross-section image of YSZ deposited in 15 min on gas turbine blade

High-emission materials are in demand in a wide field of practical application: from photomultipliers, electron multipliers, which are important elements of high-precision devices (mass spectrometers, night vision devices, thermal imagers, etc.) to plasma displays. Gas-phase processes are very promising for obtaining effective emitters which are multicomponent in most cases. Obviously, the well-developed and well-reproduced processes for obtaining such thin materials could be realized only on the base of study of the relationship between emission characteristics and the actual state of the deposited layers. The main factors responsible for the emission properties will be discussed.



Secondary electron emission coefficient (SEEC) of MgO films deposited from different precursors

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Characterization of anticorrosive bio coating in the plasma cure process by TG / DTG, DSC and AFM techniques

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The need for substitution or reduction of petrochemical derivatives in industrial production has generated the search for components from renewable sources. The synthesis of polymers from renewable resources has attracted the attention of scientists around the world and has shown a promising path to the sustainable development of new products. Therefore, an alternative process of coating or protection preparation minimizing the use of petrochemical derivatives has been strongly desired and studied. This fact motivated the development of anticorrosive phenolic bio coating (coating greem) for application on metal surface of 1020 carbon steel based on by-product of cashew industry, cashew nut shell liquid (CNSL). An innovative form of plasma curing was performed and its performance was compared to the conventional curing method, the use of Hexamethylenetetramine (HMTA). The bio coating samples produced were characterized by Thermal Analysis by TG / DTG and DSC techniques. Among all the samples characterized by Thermogravimetry, the CNSL-based resin cured with 1% w / w HMTA presented higher thermal stability, with a decomposition stage around 250 ° C. Followed by plasma-cured CNSL resin for 15 minutes with initial decomposition temperature at 200 ° C. The DSC analyzes of some samples cured with HMTA and plasma exhibited changes in the baseline, that is, changes in the values of the glass transition temperature (Tg), while other samples with different formulations presented an exothermic event, suggesting an incomplete cure process. The analysis of Atomic Force Microscopy (AFM) of the analyzed samples showed lower values of adhesion (7.6 nN) for plasma cured bio coating, suggesting a better cure performance. Corrosion tests showed that the plasma cured coating remained unchanged, with no point of corrosion during the initial cycle of the corrosion tests, while the other specimens showed corrosion points during the tests.

Application of thermal analysis techniques for studying the possibilities of utilization of oil shale ashes formed at electricity production in Estonia

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A circular economy became an object of an actual discussion as a sustainable alternative to current linear economy system. This is also new strategic interest in Estonia, especially in the context of electricity production. Approximately 70% of the electricity production in Estonia is based on the combustion of Estonian oil shale (OS), which contains approximately 30-35% of organic matter and inorganic matter contains mostly carbonates and sandy-clay minerals. The sulfur content is around 1.5%. Last year ~10 million tons of OS were used in electricity production and ~6 million tons of OS ashes were formed in Estonia. Only ~2% of the total amount of OS ashes are utilized in different areas (e.g., cement production, stabilization of road layers, agricultural purposes etc.) and the other part is left unused and landfilled.

A number of changes have occurred in Estonia`s OS based energy sector. On the one hand the implementation of circulating fluidized bed (CFB) boilers has improved fuel efficiency and lowered the greenhouse gas emissions. On the other hand, the changes in process conditions, in particular, the lowering of the temperature from 1200-1400°C (used in pulverized firing (PF)) to 750-800°C (used in CFB boilers) have negatively affected the physical and chemical characteristics of the OS ashes. In principle, the inorganic part of the OS undergoes a number of chemical transformations during the combustion process, including decomposition of carbonates with the formation of calcium and magnesium oxides. These oxides partially remain in the form of free oxides causing the alkalinity and partially take part in the formation of secondary minerals–mainly silicates with varying compositions.

One of the promising operations for the large-scale utilization of alkaline OS ashes is the liming of acidic soils. There are 350 000 ha of agricultural land that need to be permanently lime fertilized in Estonia. The granulation of OS ashes can be part of this solution by making better use of these wastes and the possible environmental contamination during the liming of soils can be eliminated. The granulation of OS ashes with accelerated carbonation technology can also be considered for the production of light-weight aggregates in the applications of construction materials. Above mentioned applications require determination of the physico-mechanical and physico-chemical characteristics of the end products and in order to investigate the relationships between these characteristics, thermal analysis (TA) methods were applied to granulated products.

The idea to replace expensive sorbents with OS ash has been raised and the cyclone ash which contains 20-25% free CaO has a proven ability to bind acidic gases. Today, commercial lime in addition to OS ash is used as a binding agent in the semi-dry $DeSO_X$ system of the Eesti Power Plant. Therefore, comparative investigation of the efficiency of activated ashes and the commercial lime used in the $DeSO_X$ system was carried out with TA methods. Analogical investigations for studying the possibilities of CO_2 mineralization was also carried and OS ashes and clinker dust (CD) as sorbents in CO_2 mineralization process were investigated at different operating temperatures and quantification study of the effects of pre-treatment (e.g. hydration and fineness *via* grinding) on CO_2 uptake was carried out. The clay based ceramics is also another application area of the utilization of OS ashes. OS ashes and CD were used by the clay replacement in different blends and TA coupled with evolved gas analyzer (MS or FTIR) was an excellent tool for the determination of the relationships between physical-mechanical and physical-chemical characteristics and the thermal behavior of the blends studied.

The (r)evolution of biobased polymers and sustainable materials by thermo-analytical means

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The transition to greener and more sustainable products is an important societal challenge. A worldwide global task force has been implemented by the United Nations between local and regional governments to define sustainable development goals (SDG) for 2030. The use of biomass feedstocks as carbon source for fabrication of chemicals and polymers has substantially grown in the past decades. Biorefinery processes have recently emerged to generate chemical building blocks from lignocellulosic biomass that can be further transformed into functional polymers. More precisely the roadmap to ensure the transition from fossil based polymers to biobased polymers implies to unlock numerous gateways. The thermal and mechanical behavior of these polymers is probably one of the most important issues since it drives their processing, their life as well as their end of life [1].

This lecture aims at highlighting how thermal analysis can give important informations both on the general knowledge of the biobased polymer and on the design of new properties. A special emphasis will be made on furanic polymers which are obtained from various constitutive sugars of vegetable biomass. Both thermoplastics and thermosets, can be prepared from furanic monomers. This is the case of Polyfurfuryl Alcohol (PFA) which is one of the rare available biobased thermosets. PFA represents an excellent eco-friendly solution for several material applications such as adhesives, corrosion protection, thermally-resistant nanocomposites [2-3] or in combination with natural fibers or wood pieces. The aromatic character of the furan ring is generally put forward to underline the good thermomechanical performances and/or chemical resistance of furanic polymers that can thus compete with other well implemented aromatic polymers (Terephthalate polyesters, phenolic resins etc.). To offer new or modified properties in PFA for instance, the already explored solutions consisted in adding co-monomers or nano-fillers. [2-3]

The biorefinery processes also produce side-stream products such as humins. The biorefinery humins have a polyfuranic structure and they need to find pathways of valorization. Here again, combination of various advanced thermo-analytical techniques helped to draw clear conclusions on how thermally induced cross-links are developing within the humins thus modifying the chains mobility and the visco-elastic properties. [4]

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Application of Thermal Methods to the Characterisation of the States of Water in Precious Opal

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Precious opal is a hydrous silica ($SiO_2.nH_2O$) that is formed through a dissolution-precipitation process forming hydrated silicas with variable water content [1]. The gemmological value of precious opal is defined by its microstructure where the prized play-of-colour (POC) observed is a result of the diffraction of visible light from an ordered arrays of silica spheres. The monodispersed colloid of silica spheres are formed through an Ostwald type ripening process. Once the colloidal particles have grown to a suitable size for Bragg diffraction of visible light (ca. 200 to 400 nm in diameter; i.e. $\lambda = 2dn\sin\theta$ where n is the refractive index of opal), aggregation occurs most likely through a homogeneous colloidal crystallisation process which results in the ordered array. Subsequently the array is solidified through precipitation of a second generation of silica which cements the array onto a solid coherent mineral specimen. The microstructure of the array can then be observed through the hydrofluoric etching of fresh fracture surfaces which reveal the ordered arrays of the monodispersed spherical particles.

As the process of opal formation occurs in solution, a hydrous silica is formed. The silica network itself can be of an amorphous nature (opal-A) or is paracrystalline (opal-CT; cristobalite containing tridymite stacking faults) and contains water in the form of molecular and silanol (bound) water. The molecular water is trapped in cages, capillary pores and interstitial voids while the silanol water is present at the surface, internal interfaces (e.g. at capillary or void surfaces) and in the silica network as isolated broken bridges. The type and amount of each of these species of water is dependent on the environment in which opal formation occurs (e.g. temperature and pH) and hence water may be used as a probe to characterise the morphology structure of opal.

Both thermal and spectroscopic methods have been used to successfully characterise the types of water present in opal and given the range of types of water, multiple characterisation techniques are required. This paper will outline the application of both thermal and spectroscopy methods in the characterisation of opal. TG data are presented to identify the total water content (molecular and silanol), low temperature DSC data is used to characterise the proportion of crystallisable water present in opal and thermoporosity based on DSC is used to determine the characteristic pore size of water filled pores. The silanol water content is determined from the ^{1}H-CP-^{29}Si MAS NMR while the distribution of molecular and silanol water is also gleaned using FT-NIR. The total water content is not indicative of the origin and formation environment of opal, however, the distribution of the different types of water present in these hydrous silicas is strongly dependent on the formation environment. The distribution of species type coupled with a knowledge of the origin of the opal allows the development of a fundamental model for opal genesis.

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Notes about the flow behaviour of cellulosic fiber thermoplastic composites

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Understanding the flow behaviour of the cellulosic fiber thermoplastics composites, CFTC, is necessary for simulating high shear processes like injection moulding and extrusion [1]. Building a simulation model requires, besides to the process parameters, full characterization of CFTC namely the properties of density, thermal expansion, viscosity, Pressure-Volume-Temperature, pvT., thermal conductivity, thermal degradation, polymer structure, specific heat and dynamic mechanical properties. In comparison to the synthetic fiber thermoplastic composites, characterization of CFTC suffers from the non-reproducible quality and the irregular geometry of the cellulosic fibres [2]. Modeling of fibers during flow is difficult because cellulosic fibers show complex behavior of splicing, fragmentation and mass change due to the thermal decomposition. Therefore, a comprehensive study considering a wide scope of fibers is necessary to simulate the flow behavior and hence the end-product properties. This work investigates different fiber types namely bast, leaf and regenerated celluloses. Fibers are then extracted to investigate the effect of fiber type and processing parameters on the change in fiber dimensions. A spiral mold is used in the injection molding experiments to test the simulation process on a one-dimensional model [3]. The effects of the following parameters are considered such as fiber type (regenerated cellulose, sisal, hemp, wood fiber, wheat straw and kenaf), fiber content (10 and 30 wt.-%) and fiber length (0.5 and 1.5 mm for regenerated cellulose). The rheological behaviour of the CFTC is correlated with both the fiber type and the fiber size. The work discusses other auxiliary phenomena concerning the constancy of fibre content along the injected products and the pore formation due to the inevitable gas evolution from the cellulosic fibres.

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Thermal behaviour of cement bypass dust revalorization

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Cement bypass dust (CBPD) is a by-product of Portland clinker manufacturing. It consists of calcite, free lime and other compounds such as SiO2, AL2O3, MgO and Fe2O3, but due to increased substation of fossil fuels with alternatives (waste materials), it may contain also compounds with relatively high chloride content, as well as SO3, K2O, what presents a high environmental risk. Therefore, cement bypass dust is considered as a solid waste unsuitable for direct return into feedstock. Evidently, the increased waste production contributes to a highly negative environmental impact of the cement industry.

There are different approaches to revalorize CBPD [1-2], but some of them are timely consuming or too expensive. This paper presents a promising technology of lightweight ceramic aggregate production with CBPD as a raw material component. CBPD can reach up to 30 mass % of the raw material composition for the lightweight ceramic aggregate production, depending on its chemical and mineralogical characteristics [3]. Formation of new phases during the thermal treatment was followed by mass spectroscopy (TG-MS) up to 800°C, which temperature was identified as a frontier parameter considering the retention of Cl2 inside the designed systems. The influence of thermal treatment, ranging from room temperature to 800°C, on the final products characteristics was evaluated, including: thermal expansion, weight loss, porosity, compressive strength, changes of morphology and colour.

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Hydrogen-bonded complexes in binary mixtures of pyridine and its methyl derivatives with water

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Molecular order in aqueous solutions of nonelectrolytes and weak electrolytes with molecules having non-polar moieties is commonly discussed in terms of hydrophobic and hydrophilic interactions. Although general agreement has been achieved that this approach is adequate, various experimental methods and theoretical considerations may lead to different, sometimes inconsistent, conclusions. A reliable assessment of molecular arrangement in liquid phase requires somewhat eclectic approach rather than strict reasoning based on one method, even if very elegant.

Aqueous solutions of pyridine, 2-, 3-, and 4-methylpyridine, and 2,6-dimethylpyridine has been a subject of such investigations. Empirical studies included thermodynamic quantities: the enthalpies of mixing, molar volumes, and compressibilities, determination of solid-liquid equilibria by DSC and visual methods, small-angle neutron scattering, and the attenuation of ultrasounds. These were complemented by quantum chemical calculations of stabilization energies of hydrogen-bonded complexes. The results were compared with those for cyclic rather than aromatic amines: piperidine, pyrrolidine and its *N*-methyl substituted derivatives.

The observed phenomena, such as the formation of microheterogeneities in liquid phase and congruent or incongruent melting of solid hydrates, led to an idea of water as an active solvent that makes aggregation possible due to hydrogen bonds that join water-amine complexes together: RN...HO(H)...HOH...NR, rather than because of London dispersion forces between non-polar parts of the amine molecules. In more detailed analysis, a quasi-chemical reactions model was applied, which related experimental enthalpies of dilution and the stabilization energies of the water-amine complexes calculated theoretically.

DSC insights into thermooxidative phenomena: from ferrites to mustard oil

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DSC throws light on all phenomena involving heat changes and this brings versatility in its applications. Crystallization, polymeric conversion, curing, decomposition (oxidative or otherwise), annealing and, phase changes (solid-liquid-gas, glass transition, denaturation etc.) are all integral parts of preparations, processing and applications in our lives. Two fields shall be covered in the presentation. Amongst the multifunctional materials, the cases of ferrites (magnesium, barium, cobalt and samarium) are taken up to explain how for low temperature syntheses of nanoparticles of ferrites for their unique and useful magnetic, electrical and optical properties (recording, data storage, sensor, photoluminescence etc applications), studies of thermooxidative phenomena using DSC could make things easy. The properties of such materials (hence their applications) as well as their particle size have been found to be greatly depending upon the method of preparation and the annealing/ sintering temperature.

Similarly, the thermooxidative decomposition in edible oils is of concern. While being used for frying during food preparation, many changes (oxidation, isomerisation, polymerization, hydrolysis etc.) may take place in the cooking oil. The formation of volatile and non-volatile compounds does also influence the fried food quality and the nutritional parameters. Autooxidation (since exposed to air during storage and oil processing for extraction, food production etc) is a big problem. Susceptibility to oxidation (photo oxidation, enzymatic oxidation, auto oxidation do affect the flavour and the nutritive value of fried food) affect the stability of oils. As a case study, mustard oil which is an important ingredient of Indian foods has been taken which is also used as a frying medium during food preparation. This exposes it to thermooxidative decomposition. The studies have been extended to turmeric doped mustard oil. Turmeric has been used for doping the mustard oil since it is the most commonly used Indian spice which is used along with mustard oil during cooking. Thermal stability of pure and doped sample was studied using oxidation induction period method [1] presuming that any sort of chemical change will follow the same equation. Plots were obtained for stability of the sample in air and oxygen atmosphere under different isothermal temperatures. It has been found that stability of the oil increases with decreasing partial pressure of oxygen in the reaction atmosphere at lower temperatures. In air atmosphere, the stability is approximately 3 times higher than in O_2. At higher temperature, the stability is practically independent of the partial pressure of oxygen. With a rise in temperature the shelf- life of mustard oil lowers exponentially as has been calculated by the present method, it comes down from 145 days at 0^oC to 0 day at 100^o C, thus the packaging of mustard oil in oxygen free container/vessel should be made essential. The T_{on} remains the most important and primary parameter for assessing oxidation in edible oil which may also effect other valuable kinetic parameters. In the presence of turmeric, the stability of mustard oil gets disturbed, apparently, on account of reactions involving curcumin and different fatty acids. Stability of the doped samples was found to be independent of partial pressure of O_2, at higher temperature. This may be because of reactions involving curcumin and different fatty acids

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Thermal analysis techniques applied to rare earth alloys investigation

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Thanks to the ample spectrum of their unique properties, rare earth metals have become a basic component for a vast array of alloys and compounds that are essential in many applications, as nowadays several technologies, including hybrid electric vehicles, generators in wind power plants, low energy light bulbs, etc. depend on them to achieve higher efficiency and lighter weight.

This talk will highlight the role of thermal analysis techniques on the experimental investigation of phase equilibria, phase transformations, thermodynamics of formation of rare earth alloys, which are the basic tools for understanding properties that are fundamental for their technological applications [1].

The experimental determination of equilibrium diagrams is frequently a matter of some difficulty, often requiring a combination of several techniques (among them thermal analysis and calorimetry playing a central role) always essential for the unambiguous definition of the equilibrium relationships. The number of phases, their stoichiometry and structural identification, the equilibria in which they partake, the temperature and composition along the boundary lines or surfaces are key information that can be attained.

In general, the investigation of alloy phase diagrams meets with a number of difficulties that are especially remarkable with rare earth alloys [2-5]. These are in particular: the high reactivity of rare earth metals with oxygen, crucible materials, etc, requiring special handling precautions and a protective atmosphere; the high sensitivity of the constitutional properties of their alloys for even small quantities of the most common impurities, and therefore the need for really pure rare earth metals; the high melting temperatures of several rare earth metals and alloys (particularly those with noble metals and semimetals); the high vapour pressure and volatility of several of them; the existence, for several rare earth metals, of different allotropic transformations and their complex interactions with other metals. These difficulties, several of which are common to other groups of metals such as alkaline earths and actinides, often having analogous behaviour and reactivity, will be particularly considered with reference to the systems investigated by the University of Genova research group, with particular emphasis on differential thermal analysis and calorimetric measurements.

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Compressive strength and phase characterizations of Portland limestone calcined clay cements

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Today production of Portland cement exceeds 4,000 Mt/y. For every 1 t of Portland cement produced, approximately 1 t of CO_2 is emitted. Therefore, the research to find other sustainable materials to replace Portland cement is of great interest. In term of abundant and sustainability, limestone and calcined clay are seen as possible materials to be used to replace Portland cement in the long term. In this investigation not only the compressive strength was looked into but also the phase characterizations to understand the reactions of each material and also when used together. Calcined clay and limestone were used to replace Portland cement up to 50% by weight. Thermogravimetric analysis (TGA) of the mixes was carried out at 7 and 28 days to determine the hydration and pozzolanic reaction occurred during these ages. X-ray diffraction and scanning electron micrograph was also used in combination with TGA for phase characterizations. It was found that while calcium carbonate was detected in all the mixes with limestone, calcium aluminosilicate hydrate (C_2ASH_8) was found to increase with calcined clay which corresponds with a decrease in calcium hydroxide. Moreover, interestingly monocarboaluminate phase was found and became clearer when there was a combination of calcined clay and limestone in the mix.

UV-cured di/tri(methoxy) vinyl silane modified urethane acrylate blends for optical coatings: thermal and optical properties

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The increase interest on developing controlled optical properties of the acrylic resins to address a wide range of applications, including gradient-index optics, holographic data-storage, optical coatings, etc. urge for consistent studies on their material properties (1-3) for different UV exposure conditions.

The lecture aims to present consistent insights into several di/tri(methoxy) modified PFPE – urethane acrylate blends as were analysed by infrared spectroscopy, refractometry and DMA. Each combination was photopolymerized in the presence of 4.8 wt.% Omnirad 2100 photo-initiator with a 705 mW·cm^{-2} UV-LED light intensity and 390 nm emission, keeping a constant value of 12 mm for the sample-lamp distance and different curing times under controlled nitrogen atmosphere.

The polymerization progress was monitored on each side of the 300 μm films by real time infrared spectroscopy using a Nicolet 5700 FTIR spectrometer (Thermo Fisher). The refractive index evolution and thermo-optic coefficient was retrieved by aid of a refractometer at 633 nm. The films were measured within the prism without any high refractive index interfacial contact agent.

Dynamic mechanical analysis (DMA, TA Instruments) was employed within -40 up to 250 °C in tensile mode at a 1 Hz frequency and a 1 °C/min heating rate. The mechanical transition temperature was measured at the maximum of the tan δ whereas the storage and loss moduli were investigated.

The results are viewed as indispensable both for the targeted application and for establishing a route for the photopolymerization process applied to different blends.

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Thermal and thermophysical analysis of SiC influence on different polymer matrices

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A characteristic trend of many material-intensive industries is to reduce the weight and size characteristics of products, one of the ways to achieve this is to replace expensive and heavy metal materials with polymeric ones. It is actual for aerospace industry, microelectronics and a number of industrial applications. The problem is preservation of the functional quality of materials, such as mechanical, electrophysical properties. In some cases, thermal stability and thermophysical properties are equally important. One of the ways to change the thermal properties of polymers is the introduction of highly heat-conductive fillers.

Silicon carbide, due to its high strength, high thermal conductivity, thermal oxidative resistance and chemical inertness, is widely used in various areas of solid-phase materials science: as an abrasive, in creating heating elements in high-temperature furnaces, in sensors etc. Therefore, investigations aimed at the development of new polymer composite materials filled by silicon carbide are relevant. The thermal conductivity of crystalline silicon carbide is from 210 to 490 W/(m·K) depending on the polytype. There are papers in which the effect of different concentrations of silicon carbide on the thermal conductivity of some polymers has been studied and its increase has been established [1 – 4].

In the present lecture more general analysis is presented – the effect of dispersion and concentration of silicon carbide on the thermal behavior (TG-DSC) and thermophysical properties (mainly thermal conductivity) (of various polymers: polar and non-polar thermoplastics (polyamide and low-density polyethylene) and reactoplastics (epoxy resin). The industrial silicon carbide was used as well as silicon carbide obtained in HMTI by the method of carbothermic reduction of silica in electrothermal fluidized bed.

Comparison of polymer composites based on different polymer matrices with the same content of silicon carbide (60 wt.%) showed a different effect of the same filler on the thermal properties of the composite, which is due to the difference in the nature of the interaction of a particular polymer with silicon carbide particles and their influence on structure and crystallization of the polymer matrix.

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Study of the thermooxidative stability of aged beeswax using differential scanning calorimetry

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Beeswax represents one of the important materials used in the cultural heritage. Thermooxidative degradation has a bad influence on beeswax stability. Factors affecting the thermooxidative stability are temperature and oxygen. These factors lead to significant changes in chemical structures of materials and to the loss of their physico-mechanical properties. Thermooxidation occurs in two steps: induction period (IP) and oxidation itself. The IP is considered as a measure of material stability and at the end of the IP sudden changes occur in their properties [1].

The subject of the study was to explore the thermooxidative stability of several types of beeswax. The first type was beeswax taken from various parts of leg from Saint Ursula statue from 19th century. Trying to assess the degree of statue degradation we compared the results with the thermooxidative stability of unaged commercial beeswax and samples of beeswax after accelerated ageing: changing of temperature, three types of constant temperature and in the atmosphere containing NO_x. The thermooxidative stability of all samples was studied using non-isothermal DSC measurements. Kinetic parameters of the IPs were obtained from the experimental data by isoconversional method using Arrhenius temperature function and non-Arrhenian Berthelot-Hood temperature function [1, 2]. These parameters enabled to predict the thermooxidative stability of the materials. The use of Arrhenius equation gives unrealistically long IPs at room temperature while the Berthelot-Hood equation provides better results. As expected, the lowest stability had the sample taken from the surface of the statue, while the other samples from the inner part of the statue were approximately three times more stable. In addition, the thermooxidative stability of accelerated aged samples of the beeswax is comparable to that from the inner part of the statue.

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Chill sensitiveness and thermal analysis parameters relationship in hypo-eutectic, Ca and Ca-La inoculated commercial grey irons

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Previous experiments shown a specific distribution of Al, La and Ca on the section of complex (Mn,X)S compounds, found as major nucleation sites for graphite flakes in low-S cast irons (< 0.03%S), and a possible contribution of La to improve their capacity to nucleate graphite, avoiding carbides formation. [1] For general application, La,Ca,Al-FeSi alloy has a high efficiency in low S and Al and higher carbon equivalent grey cast irons, electrically melting, without any other active elements contribution. For specific applications, more complex La-bearing alloys are recommended, such as for higher dendritic austenite amount promotion [LaBaZrTi –FeSi alloy] or for lower eutectic recalescence [LaBaZr –FeSi alloy]. [2]

Thermal [cooling curves] investigations [2 – 7] were undertaken to explore Ca and La-Ca bearing FeSi alloys inoculation effects [0.25wt.% addition] on solidification parameters, in 3.7 – 3.8% carbon equivalent and optimum S and Mn relationship in electrically melted iron [0.046 – 0.056%S, (%Mn) x (%S) = 0.024 – 0.029]. Standard thermal analysis was applied to un - and inoculated cast irons [10 measurements for each inoculation system]. Representative temperatures on the cooling curves and under-cooling degrees referring to the meta-stable eutectic temperatures were determined and correlated with the chill [carbides/graphite formation sensitiveness], in different castings solidification conditions [1 – 4 mm cooling modulus, wedge shape castings, resin sand mould].

It appears that for optimum S and Mn relationship supplementary addition of La to Ca-bearing inoculants has specific benefits, such as lower eutectic recalescence and of the maximum recalescence rate, higher GRF_1 and lower GRF_2 graphitizing factors and lower value of the first derivative at the end of solidification, as premise for lower shrinkage formation; lower chill (carbides) sensitiveness, especially at the highest cooling rate (thin wall castings).

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KEYWORDS: solidification, thermal analysis, cooling curve analysis, grey cast iron, cooling modulus, inoculation, ceramic cup, carbides formation sensitiveness

Modulation of nanoparticle activity and associated complex biological responses by the nanobiointerface

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When designing a nanovehicle for a specific biomedical application such as diagnostic imaging or therapy it is necessary to bear in mind that these nanoplatforms will surely interact with the different components of biological fluids and, in particular, with proteins which will coat the particle surfaces forming the so-called protein biocorona [1]. In order to account and decipher the nature and complexity of protein-nanovehicle interactions isothermal titration calorimetry appears, in particular, as a very interesting experimental tool, which can help to put light in the events taking place [2,3].

On the other hand, these ensembles (nanovechicle + protein corona) will constitute what cells "see", and will determine the mutual cell‒nanovehicle interactions, their cellular uptake and intracellular trafficking, thus, conditioning both of their biodistribution and therapeutic response in vivo [4].

Hence, in this talk, we will present several examples on how the modulation of nanovehicle´s physical properties such as size, shape, surface roughness, or surface functionalization can drastically influence the interactions and physical-chemical bioactivity of the synthesized nanoplatforms as well as the induced biological responses.

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Oral Presentations 1

Theory & Methods, Kinetics & Catalysis, Fuels & Biofuels, Energetics and Applied Thermal Engineering

Doubts on popular Kissinger´s method of kinetic evaluation showing essential misfits such as the difference between the maximum of reaction rate and extreme of DTA peak

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The famous Kissinger´s kinetic evaluation method (Anal Chem 1957) is examined with respect to the feasible impact of the individual quantities and assumptions involved, namely the model of reaction mechanism, f(α) (with the iso- and noniso-thermal degrees of conversion, α and λ) the rate constant, k(T) (and associated activation energy, E), heating β and particularly when applied under cooling rate, which needs supplementing an additional thermodynamic term for the melt undercooling, ΔT, e.g., $(3\beta)/[T^2_m (\Delta T)^2] = df(\alpha)/d\alpha$ (A/B) exp $\{-B/T_m (\Delta T)\}$. Most of all, the association of the characteristic temperatures with the DTA peak apex adjusted with as cased T_p and corrected T_m peaks. It is shown that the Kissinger´s equation, is disparate to the results of Vold (Anal Chem 1949) while omitting the term of heat inertia arising from the true balance of heat fluxes, e.g.,$d^2\alpha/dt^2 = (K/H)(d\theta/dt)$, (where θ, is the difference in temperature of the centres of the two samples) explicitly showing the misfit between T_m and broadly implemented value of T_p. The absence of this term skews the evaluated values of activation energies. Despite a long lasting history of kinetic evaluation it is clear that such an important part of DTA peak analysis has been overlooked at everyday applications despite exhibiting as many as 6000 cutations. It is possibly caused by the obvious methods simplicity, which provides easy publishable values of activation energies. It is surprising that anybody who evolved various alternatives of the Kissinger method did not find any reasons for its criticism.

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Effect of delayed nucleation on crystallization kinetics of chalcogenide glasses

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Chalcogenide glasses are very interesting materials used for their optical and opto-electrical properties. These materials are used as optical fibres, lenses, sensors and phase change materials. The knowledge of crystallization process is important for their preparation and utilization. The crystallization process contains two steps, a creation of nuclei and their subsequent growth. Whereas the process of nucleation is almost undetectable due to a small size of nuclei, in order a few crystals. The subsequent crystal growth can be observed using differential scanning calorimetry (DSC) or differential thermal analysis (DTA). Nevertheless the character of nucleation process has a significant impact on resulting shape and position of crystallization DSC/DTA peak. Despite this fact, the nucleation process is rarely studied.

In this contribution the effect of nucleation on resulting DSC curves is analysed for chosen chalcogenide glasses Se-Te and Sb-Se [1-3]. The analysis is focused on effect of time delayed nucleation on observed crystallization kinetics studied by isothermal and non-isothermal DSC method. Also the impact of nucleation behaviour on apparent activation energy is discussed. The densities of nuclei and crystal growth rates are calculated on the base of model of filling space introduced in previous work [3] and compared with data obtained by direct microscopy experiments. Determined values are in a good agreement with direct observation by microscopy.

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Characterization of non-isothermal and isothermal vulcanization kinetics of natural rubber by fast scanning calorimetry

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Abstract: The vulcanization kinetics was studied by means of fast scanning chip-calorimeter (FSC) under non-isothermal and isothermal conditions. By fast temperature controlling, FSC enable to study non-isothermal vulcanization kinetics up to 9 orders in combination with differential scanning calorimetry (DSC). Fast heating rates can delay the decomposition process and lead it shift to higher temperatures. Then the vulcanization behavior even above decomposition temperature can be measured, which allows to obtain non-isothermal kinetics with broad range of heating rates. Meanwhile, the FSC chip sensor can largely reduce the heat capacity of holders comparing with DSC. This enables to quickly achieve equilibrium state when the sample is heated to isothermal temperatures. Then some thermal parameters can be precisely measured, i.e. induction time. In this study, natural rubber was used as a suitable sample and some first results will be shown for illustrating the method as well as validity.

Thermal degradation of Poly(N,N-dimethylaminoethyl methacrylate). Kinetics and mechanism

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Poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA) is intersting, relatively new polymer with large amount of important properties. It is a polycation containing tertiary amine groups and possessing bioactive properties. PDMAEMA is a weak polybase that has interesting temperature dependent solubility - it has a lower critical solution temperature (LCST), when the solid polymer is separated from the solution, because of hydrogen bond decomposition (thermosensitive properties). The LCST of PDMAEMA, which in aqueous solution at neutral pH is about 50°C, is higher than the human body temperature but could possibly be changed by its copolymerization with other co-monomers. PDMAEMA has been used in large numebr of different application including thermoactive.

In that presentation the thermooxidation and pyrolisis process of PDMAEMA was investigated. The relationship between average moclecular weight and thermal stability was analysed. The infrared analysis was performed to obtain information on the structure of the solid residue. The thermal degradation process has a multi step character. The limit temperature for all decomposition steps were measured. The order of disintegration of the macromolecules was determined. Activation energy values for each step in both processes have been calculated. The mechanism of thermooxidation and pyrolis was proposed.

Thermodynamic analysis and isothermal bainitic transformation kinetics in lean medium-Mn steels

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High requirements for high strength steels in the automotive industry increase a need for developing new steel grades. The steels should compromise very good mechanical properties with the cost of their production [1-2]. This situation put steel making industry with a lot of new problems concerning a chemical composition and a proper heat treatment of new generation steels. These problems require the upgraded knowledge of the influence of different heat treatments on a phase transformation kinetics of the advanced steels [3-4]. These problems need the use of thermal analysis methods and thermodynamic approaches to determine the effect of thermal profiles on final microstructure and mechanical properties. One way for this is the use of dilatometric analysis, which can determine the critical transition temperatures, its rate and various effects undergoing during the heat treatment [5-6].

The present work shows the use of advanced thermodynamic calculations for determination of continuous-cooling-transformation diagrams (CCT) for the process of projecting heat treatment routes for lean medium-Mn steels. The dilatometric analysis was carried out for the experimental analysis of phase transformation kinetics of 3Mn-1.5Al steel subjected to different isothermal holding conditions at a bainitic transformation range. The isothermal holding was carried out at different temperatures (between 350 and 450°C) and different isothermal holding times. Light and scanning electron microscopy were used for a detailed microstructure analysis.

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The kinetics of water freezing from inorganic salt solution confined in the mesopores

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Pore-confined cyclic water freezing is widely recognized a one of the major phenomena responsible for the deterioration of natural (stones) and man-made (concrete, brick) materials. Water solidification is accompanying with the volume expansion, which is the main force driving additional strain in the skeleton of porous material. The deeper insight into the physical phenomena related to water phase change allows for the development of the more efficient means and systems for the protection against the frost-induced degradation of materials.

The Gibbs-Thomson equation [1,2] gives the relation between the depression of water triple point and diameter of pore confining water. The high accuracy of that equation was verified in many experimental research, during which the existence of non-freezeable water film was also reported. The calorimetric technique are recognized as one of the most efficient to investigate the phase change of the material.

In our study we extended the Gibbs-Thomson equation with the case when the pore liquid is not the pure water but inorganic salt solution. The entropy equations for various phases of water: water vapour, liquid water in salt solution, ice were proposed. Combining the Laplace equation, which gives the mechanical equilibrium at the interface, we finally derived the equation describing the depression of water triple point assuming that the pore system is occupied with the inorganic salt solution. Pore system is hardly ever filled with pure water as usually many salt or other contamination are present. Therefore the equation developed by us more reliable responds to the real system. Further, using solution of sodium chloride in water, we made the series of experimental research proving the correctness of the proposed relation.

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Kinetic study of liquid sodium– calcium hydroxide reaction for safety assessment of sodium cooled fast reactor

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In an accidental condition postulated for sodium-cooled fast reactor (SFR), sodium–concrete reaction (SCR) may probably occur when liquid sodium from cooling system spilled into the floor may lead to fail the steel liner as protector of the structural concretes [1]. The structural concretes of SFR comprise siliceous concreate as main body of reactor structure and perlite concrete placed between the steel liner and the siliceous concrete serving as a protector and an insulator. Therefore, the reaction behaviour between the perlite concrete and liquid sodium in an early stage of SCR should be focused for obtaining the fundamental information of safety assessment on SCR. The perlite concrete includes portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$) as in Portland cement.

In this study, thermal behaviour of liquid sodium–calcium hydroxide was investigated using a differential scanning calorimetry (DSC) equipped with videoscope and placed in a glove box substituted with argon. The DSC exothermic peak for the Na–$Ca(OH)_2$ reaction systematically shifted to higher temperatures with increasing heating rate. Apparent activation energy and pre-exponential factor for the Na–$Ca(OH)_2$ reaction were estimated using Kissinger method [2]. Though there is no kinetic information of Na–$Ca(OH)_2$ reaction in the legacy database on sodium-limestone concrete reaction [3], the kinetic parameters for Na–$Ca(OH)_2$ reaction estimated in this study were comparable to those of Na–$CaCO_3$ reaction. For the Na–$Ca(OH)_2$ reaction, calcium oxide (CaO) and sodium hydroxide (NaOH) were detected as major solid products from XRD analysis, which was in good agreement with the phase diagram of Na–$Ca(OH)_2$ binary system calculated using FactSage [4].

Acknowledgments

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Influence of mechanical activation on kinetics and formation of spinel monitored by DTA

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Magnesium aluminate and other alumina-based spinels are refractory ceramics with excellent properties, such as high hardness, high mechanical strength, and low dielectric constant, applicable in many modern industries. $MgAl_2O_4$ was produced by solid state reaction between MgO and α-Al_2O_3 powders. Mechanical activation represents a very efficient method for increasing the reactivity of powders, accelerating chemical reactions and decreasing the sintering temperatures. Mechanical activation of mixed powders was performed in a high-energy planetary ball mill in air for 60 minutes. Sintering was performed in air at temperatures ranging from 1200°C to 1600 °C with a 2 h dwell time. Initial powders and sintered samples were characterized using X-ray diffraction and scanning electron microscopy.

Differential thermal analysis (DTA) and thermal gravimetry (TG) were used to determine the temperatures for synthesis reactions and phase transformations. Based on the DTA results, several different processes occured during heating, including evaporation of physisorbed water, decomposition of $Mg(OH)_2$, and spinel formation. With mechanical activation, all characteristic temperatures shifted to lower values, and peaks were more pronounced. Raman spectra were used to characterize the degree of inversion as a function of sintering temperature for all of the sintered specimens.

Temperature functions and induction periods

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Thermoanalytical methods, such as DSC, DTA, TG and chemiluminescence are highly suitable for the determination of thermal and thermooxidative stability of materials [1]. The stability can be assessed from the length of induction period (IP) which is a stage where seemingly no reaction is observed by the technique applied. At the end (or close to the end) of IP, sudden change of material properties takes place, mostly deterioration, so that the IP is often considered a measure of material stability [1].

The processes studied by thermoanalytical methods are accelerated by temperature. It should be an ambition to predict the material stability under application conditions from these accelerated tests. The predictions severely depend on the temperature function applied. The Arrhenius equation is known to overestimate the material stability [2] so that it is not suitable for the extrapolation of accelerated tests to application conditions at ambient temperatures. The Berthelot-Hood function and our new temperature function [3] appear to be most suitable. After the IP, the predictions are practically the same obviously due to the equivalence of the temperature functions in the temperature range of measurements [4]. The stability of material in the solid phase is higher than that in the liquid phase. Hence, if a phase transition (melting) precedes the main degradation stage, the assessment of material stability represents the lowest limit.

In accelerated tests, sometimes the IPs are not observed. However, when extrapolating the results to ambient temperature, it appears that the process exhibits an induction period [5]. This indicates that the induction period is a stage generally occurring in the processes in condensed phase.

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Estimating errors in the determination of activation energy by nonlinear isoconversional methods applied for thermoanalytical measurements

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Several linear and nonlinear isoconversional methods have been applied for following non-isothermal thermoanalytical data performed under constant heating rates: crystallization of $(GeS_2)_{0.3}(Sb_2S_3)_{0.7}$ (4 heating rates), decomposition of ammonium perchlorate (6 heating rates) and decomposition of poly(vinyl chloride) (PVC) (5 heating rates) and simulated data for two consecutive first order reactions (12 heating rates). It has been considered some pairs “linear isoconversional method + nonlinear isoconversional method”. Each “integral pair” corresponds to a certain approximation of the temperature integral. The values of activation energy (E), error of E obtained by linear method ($\Delta_L E$) and Fischer confidence interval obtained by nonlinear method ($\Delta_F E$) applying the procedure suggested by Vyazovkin and Wight [1] have been determined for each pair of methods, several conversion degrees, and the confidence level of 95%. It has been obtained that, for a certain pair of methods, (a) $\Delta_F E$ values are substantially greater than $\Delta_L E$ values, and (b) the values of E determined by linear method are identical with those determined by the nonlinear method. The statement (a) is explained by the procedure for $\Delta_F E$ evaluation in which it is assumed that $\Delta_F E$ correspond to maximum value of Fischer distribution function. According statement (b) it is expected that is a relationship between $\Delta_L E$ and $\Delta_F E$. Both statements suggest that the error in E determined by a nonlinear isoconversional method (ΔE) is equal with $\Delta_L E$. It has been obtained the following correlation between $\Delta_L E$ and $\Delta_F E$ valid for all pairs of isoconversional methods and all considered processes:

$$\Delta E \equiv \Delta_L E = 0.2447(\pm 0.0005)\mathrm{x}\Delta_F E + 0.00037(\pm 0.00001)\mathrm{x}(\Delta_F E)^2$$

This relationship has been verified also for the following sets of thermoanalytical data performed under arbitrary temperature programs: simulated sinusoidal modulated data, experimental TG data obtained in investigating thermal decomposition of HDPE under quasi-isothermal conditions and experimental TG data obtained in investigating thermal decomposition of LDPE under arbitrary temperature programs.

For thermoanalytical data performed under any temperature programs, the procedure for evaluation the error of activation energy determinate by a nonlinear isoconversional method consisting in the following two successive steps: the determination of $\Delta_F E$ for confidence level of 95%, and the evaluation of ΔE by using the above relationship between ΔE and $\Delta_F E$.

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In-situ visual observation thermal analysis: STA and DSC equipped with optical microscope

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Thermal analysis, STA or DSC has a wide range of applications to understand thermo-physical and chemical changes at a "macro-molecular level". The research focuses on the thermo-analytical methodology based on "*In-situ* visualization" with thermal analysers to approach the various material fields.

In-situ visual observation analysis that integrates the optical microscope with the thermal analysers to observe the change in the materials during thermal process does not only reveal the visible changes directly in sample shape, size, color and other property, but also is significantly useful to help the interpretation of an accurate chemical or physical transformation.1) The thermal changes in the sample status can be displayed in real time and because the optical visual images can be automatically linked with the data from the thermal analysers as well as the temperatures, the playback analysis can be carried out just by clicking the data curves. 2)

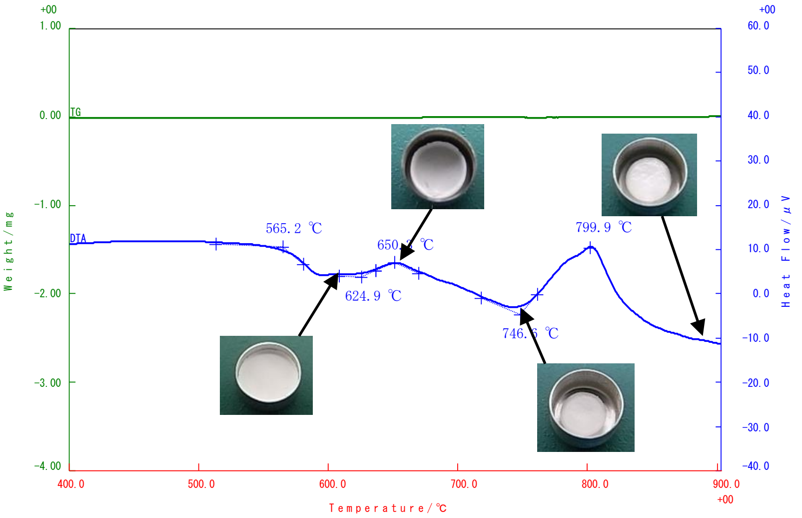

Fig. 1 Phase transitions of inorganic powdered glass by in-situ visual observation STA.

The STA result of inorganic powdered glass material obtained by Rigaku ThermoplusEVO2 TG-DTA8122 equipped with a sample observation attachment is shown in Fig.1. With the temperature range of RT～1000℃ at a heating rate of 10℃/min, we can roughly see the DTA baseline shift due to the glass transition is observed around 565°C followed by the exothermic crystallization peak around 746℃, without any mass losses during the heating. On the other hand, the changing complex baselines at 624°C and 650℃ on the DTA are observed between the glass transition and the crystallization. By introducing in-situ sample observation function, it was visually revealed that the shape changes of volumetric shrinkage take place greatly in this temperature region. To demonstrate the effectiveness of the developed unique *in-situ* visual sample observation function equipped with STA and DSC, the results of the application to several materials will be presented and discussed.

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Thermal analysis of the RFX-mod2 operating conditions for the design of the temperature measurement system

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Important modifications are under implementation in the RFX-mod fusion machine regarding the magnetic front-end, the vacuum confinement barrier, and the first wall [1]. The arrangement of the machine components changed by the removal of the former vacuum vessel, replaced by the larger toroidal support structure vacuum sealed, and by the containment in the vacuum environment of the shell for passive magnetic stabilisation of the plasma. The material of the first wall changed to high thermal conductivity polycrystalline graphite in order to reduce the surface temperature of tiles during plasma pulses; moreover, the first wall conditioning technique changed to pulse discharge cleaning with pulse frequency for heating within 0.2-0.5 Hz. The active control capabilities of the plasma improved by increasing the number of magnetic pick-up coils and electrostatic-magnetic field sensors [1]. All these modifications will allow to investigate new experimental scenarios in RFX-mod2 with different temperature field in the in-vacuum components to be monitored and controlled during plasma pulses and first wall conditioning.

Tree-dimensional non-linear transient finite element analyses shown attenuation and delay of the heat flux through the machine parts, and identified the passive stabilising shell as the instrumentable component closest to the plasma boundary able to follow the thermal behaviour by the detection of a temperature variation of 10 °C during a plasma pulse with a response time of about 200 s. The simulation of a full experimental day with 24 plasma pulses produced the thermal profiles with local values of the maximum temperatures achieved by the components, so verifying the compatibility with allowable limits of materials, in particular at the shell supporting rings made of polyamide-imide and at the vacuum sealing elements made of fluoroelastomer and acrylic foam [2]. Simulations of the pulse discharge cleaning demonstrated the capability of the system to provide the required power for first wall conditioning (18 MW) and the need to realise a duty cycle (1 hour on /3 hours off) limiting the average heat flux and the maximum temperature (60 °C) at the vacuum vessel sealing elements in order to minimise differential thermal deformations.

Some layouts with different spatial resolutions of the temperature sensors have been proposed and all of them are able to detect the maximum temperatures expected during operation; the final layout has been selected considering cabling technology and the design of the signal feedthroughs i.e. the number of available electrical contacts shared with mechanical and electrostatic-magnetic field sensors [3]. Cable routing and fixing technique of thermocouples have been tested on a mock-up of the modified machine so validating sensor realisation and installation.

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Quasi-equilibrated thermodesorption as a new method for studying adsorption of water in porous coordination polymers

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Quasi-equilibrated thermodesorption (or QE-TPDA – quasi-equilibrated temperature programmed desorption and adsorption) was developed by W. Makowski as an experimental technique dedicated for characterization of micro- and mesoporous materials. QE-TPDA of n-alkanes has been successfully applied in studies of zeolites [1] and mesoporous silicas [2]. QE-TPDA measurements are performed by cyclic heating and cooling of a tube containing the sample, through which the carrier gas (helium containing a small admixture of the adsorptive) flows. The QE-TPDA profiles contain desorption maxima observed during heating the sample and adsorption minima recorded while its cooling (Fig. 1).

Liquids showing limited volatility (e.g. water) may be used in the QE-TPDA experiments at saturation partial pressure corresponding to the lower temperature limit. In effect the QE-TPDA profiles cover the whole range of the pores and may exhibit features related to emptying and filling of the mesopores.

In a case study on STAM-1 completely different QE-TPDA profiles of polar and nonpolar molecules were observed (Fig. 1a and 1b), revealing differences in their adsorption mechanisms. Partially overlapping profiles of water recorded at different heating/cooling rates were attributed to a phase transition of the adsorbent/adsorbate system, resulting in the gate-opening effect [3]. Its experimental temperature was well reproduced in the GCMC molecular simulations (Fig. 1c).

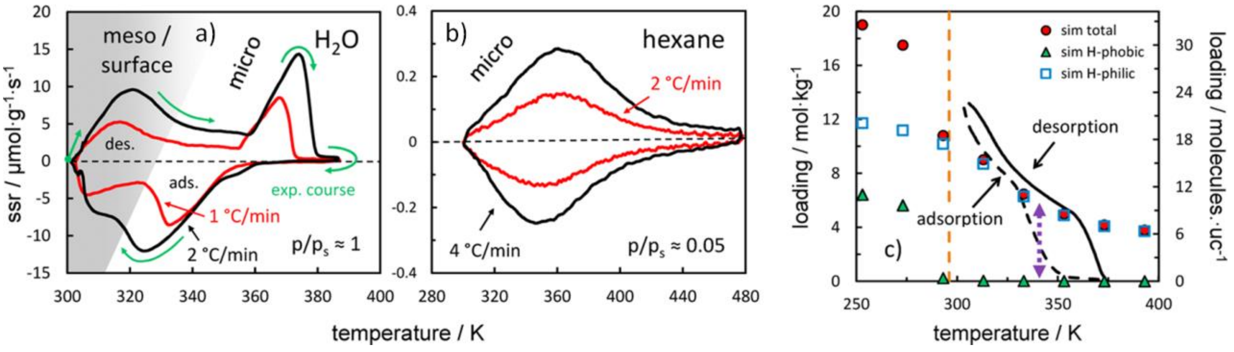

Fig. 1. The QE-TPDA profiles of water (a) and hexane (b) on STAM-1 represented as plots of the specific sorption rate (ssr). (c) Experimental adsorption isobars of water (2700 Pa) obtained from the QE-TPDA data, compared with the ones calculated in of GCMC simulations [3].

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Use of Thermal Analysis to predict the conditions for thermal explosion to occur: application to a Ce triethanolamine complex

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Knowledge of the conditions that must be met to predict the occurrence of thermal runaway is pertinent for a large number of applications [1]. The occurrence of thermal runaway is controlled by two competing phenomena: the exothermic reaction that tends to increase the local temperature, and heat dissipation that lowers the temperature through heat conduction [1]. Any thermal runaway must be initiated by a so-called “ignition” event. Two different igniting modes are considered [2]. In the “self-propagating high temperature” mode, ignition is created locally by an external and localized energy source [3]. In the “thermal explosion” mode, the reactants are heated to a temperature where the reaction becomes unstable [4].

Recently, a critical condition has been derived that takes into account reactant consumption, realistic geometries and constant heating conditions [5,6]. Therefore, the occurrence of thermal explosion can be predicted provided that the system parameters are known: mass, container geometry, activation energy, thermal conductivity, heat capacity, heat of reaction and density.

In this communication we will show that thermal analysis (TA) allows to determine the parameters related to heat generation and dissipation. In addition, TA allows to detect the occurrence of a thermal runaway during different temperature programs and sample masses. In particular, we will apply TA to analyse thermal explosion in a Ce triethanolamine complex.

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Decoupling between vitrification kinetics and molecular mobility in micrometric poly(4-*tert*-butylstyrene) (P*t*BS) by fast scanning calorimetry

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Polymer glasses confined at the nanometer scale may, in some conditions, show decoupling between non-equilibrium dynamics and molecular mobility [1]. This marks a difference with bulk glassy polymer, for which such decoupling is not observed and, instead, both aspects of the glass dynamics are fully related [2]. At the same time, recent works on various bulk glasses have reported another intriguing aspect of glass dynamics with the existence of different mechanisms of equilibration [3-4]. The observation of these mechanisms generally requires extremely long annealing times, whereas in confinement the annealing time scales are substantially reduced [5]. The existence of intermediate metastable states contrasts with the single decay toward equilibrium observed when physical aging is performed close to the glass transition [6].

In such context, we employed Fast Scanning Calorimetry (FSC) to investigate i) vitrification kinetics over a wide range of cooling rates and ii) molecular mobility of poly(4-*tert*-butylstyrene) (P*t*BS) confined at the micrometer scale. This polymer is known to show the largest glass transition temperature (T_g) depression under nano-confinement [7]. In this study [8], typical characteristic length were ranging from 6 down to 2 μm. Vitrification kinetics was characterized assessing the thermodynamic state achieved after a cooling rate ranging from 0.1 $K.s^{-1}$ to 1000 $K.s^{-1}$ through the limiting fictive temperature (T_f) [9]. The molecular mobility was analyzed using the complex specific heat obtained through the step response analysis [10].

Our results show an exceptional drop of T_f. This can be as large as 80 K for the smallest sample. Such depression is associated to a fast mechanism of (de)vitrification – well separated from the "standard" α process - which can show up 100 K below the glass transition region. In contrast, the molecular mobility is observed to behave bulk-like regardless of the sample size. The latter outcome highlights a marked decoupling between vitrification kinetics and molecular mobility.

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Fundamental study on thermal decomposition and hazard evaluation of periodate/fuel mixtures

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In order to clarify the fundamental properties of periodates, which are promising alternatives to perchlorates widely used as energetic materials, the thermal decomposition behaviour of KIO_4 and its mixture with lactose was investigated using differential thermal analysis (DTA; open system) and IR and Raman spectroscopy. In addition, their physical hazard was screened by sealed cell-differential scanning calorimetry (SC-DSC).

In KIO_4/lactose mixed at the stoichiometric composition of 81/19 by mass, three exothermic peaks at approximately 190, 340, and 450 °C were observed (Fig. 1b). Referring to the DTA result of KIO_4 alone (Fig. 1a) and the change in spectrum with heating temperature, the three peaks are considered to be attributed to oxidation of melted lactose (KIO_4 + lactose $\rightarrow$ KIO_3 + products) for the first peak, decomposition of unreacted KIO_4 ($KIO_4 \rightarrow KIO_3 + 1/2\ O_2$) for the second peak, and oxidation of decomposition residue of lactose by KIO_3 for the third peak. On the other hand, in a lactose-rich composition, the second and third peaks were hardly observed (Fig. 1c). The value of $\Delta T_1/\Delta T_2$, which is the ratio of maximum ΔT of the first peak to that of the second peak, became a maximum at 60/40 (Fig. 2a), suggesting that an ample amount of lactose can consume a majority of KIO_4 at comparatively low temperature (around 190 °C) in gas phase reaction. Also, when the predicted shock sensitivity (*SS*') was calculated based on Yoshida's method[1] using SC-DSC results, the samples having a mass ratio of 60/40−80/20 indicated positive *SS*' values (Fig. 2b), meaning that the shock sensitivity may be higher than that of the standard material, m-dinitrobenzene. The *SS*' value was the highest in a lactose-rich composition rather than stoichiometric composition.

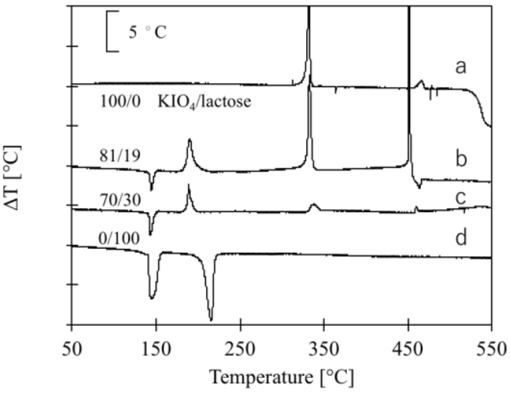

Fig. 1 DTA results of KIO_4/lactose mixture having various mass ratios.

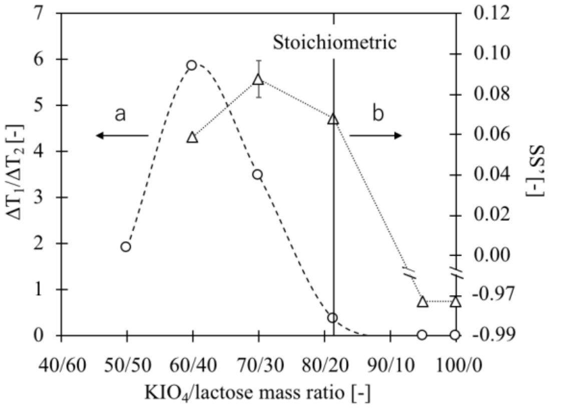

Fig. 2 Reactivity between KIO_4 and lactose and estimated shock sensitivity for various mixture mass ratios.

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Influence of copper compounds on thermal behaviour of ammonium dinitramide-based energetic ionic liquid

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Energetic ionic liquids (EILs), ionic liquids with high energetic materials, are promising new liquid rocket propellants as alternative of hydrazine due to their high energy content and low volatility [1]. We have been developing energetic ionic liquid propellants (EILPs) for small satellites based on ammonium dinitramide (ADN) which is one of the high energetic materials. Our past study [2] showed that some ratio of mixture of ADN (melting point = 93 °C), methylamine nitrate (MMAN) (melting point = 110 °C), urea (melting point = 133 °C) forms high energy and combustible EILs even below room temperature.

This study focused on exothermic reaction in condensed phase of the ADN-based EILs. It is known that CuO promotes the thermal decomposition of ADN [3]. In this study, the influences of copper compounds on condensed phase reaction were investigated by analyses of thermal behaviour and evolved gas. When the ADN-based EILs heated at 5 K min^{-1} under helium flow with thermogravimetry-thermal analysis-mass spectrometry (TG-DTA-MS), one exothermic peak with mass loss was observed at 140-230°C. Basic copper nitrate (BCN) dissolved in the ADN-based EILPs up to approximately 2 wt%. In the results of the ADN-based EILs with BCN, although the onset temperature of the exothermic reaction was almost same as the ADN-based EILs without BCN, a new exothermic peak which is thought to be from the decomposition of copper ammine nitrate was observed at around 180°C. In the case of presence of copper wool, the onset temperature was markedly lowered due to generation and decomposition of highly reactive compound, copper dinitramide. Since the EILs combusts using heat and evolved gas from the condensed phase reaction, these results contribute to the developing ignition system of rocket engine.

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Thermal decomposition mechanism of ammonium nitrate based on thermal analysis and computational chemistry

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Ammonium nitrate (AN) is widely used as a fertilizer ingredient because it is relatively inexpensive. Unfortunately, tragic accidental explosions involving AN have occurred in the past [1,2], including an incident at a West Fertilizer Company storage facility in Texas in 2013 that killed 14 and injured 260 [2]. Following this accident and others, the use and storage of AN have been strictly regulated. This background emphasizes the need to improve our ability to prevent accidental AN explosions. AN is also used as an oxidizer in industrial explosives because it releases almost 100% gaseous products upon reaction and has a positive oxygen balance (+20.0 g g^{-1}). In addition, AN has been considered as an alternative to ammonium perchlorate as a solid rocket propellant oxidizer. However, the poor combustion properties of AN, including low ignitability and sluggish burning rates under low pressure conditions, have prevented the application of AN-based propellants to date. As a result, there have been many studies aimed at improving the combustion characteristics of AN in combination with various catalysts or fuels Despite this prior work, the combustion properties of AN-based propellants still require improvement.

Fully understanding of reaction mechanism of AN is an essential factor at both views of safe and effective use. To this end, we examined decomposition mechanism of ammonium nitrate based on both theoretical and practical approaches. We developed and improved a detailed kinetic model based on quantum chemistry calculations with various level of theory, and then we simulated the AN decomposition to investigate the thermal decomposition behaviors. We then validated the model by comparison with results obtained from experimental thermal analysis (DSC) and evolved gas analysis (TG-DTA-MS), and proposed a theoretical mechanism for the decomposition of aqueous AN.

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Energy industry waste as a thermochemical energy storage resource

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Due to the ever rising demand for energy, the fossil fuel consumption has not decreased. Although aims are set towards new and sustainable energy sources, change of that scale takes time. Therefore, oil shale is still widely used and solid residues like ash are still produced in large quantities. As a result, new ways of utilizing the produced ash are being investigated. The properties of the different ash flows are well characterized and it is known, that oil shale ash contains high levels of Ca [1,2]. Different uses like recovery of metals and landfilling as well as cement production have been proposed.

The most important requirements for a thermochemical energy storage material are its ability to store heat through endothermic reactions and the possibility of an exothermic reaction between with a gaseous component. As shown by Jahromy *et al.*, due to the rich composition of oil shale ash, it is believed that ash could be used as a potential thermochemical energy storage material [3].

In this paper, we investigated the possibility and potential of utilizing Estonian oil shale ash, rich in CaO, as a thermochemical energy storage material. The investigated samples included the sources of main ash flow – furnace and electrostatic precipitator ash from two power plants utilizing circulating fluidized bed technology. Also the ash from the economizer was analyzed. The samples were characterized through elemental and chemical analysis and XRF, and subjected to thermal analysis in either mixtures or pure environments of N_2, CO_2 and H_2O.

The potential for TCES is analyzed mostly through calorimetry. The results indicate the existence of two endothermal peaks. As expected, mass loss steps for dehydration of minerals or some small traces of organics and the decomposition of carbonate minerals were noticed. The extent of decomposition of carbonate minerals is different due to the differences in the technologies – mainly the used temperatures. These results indicate that there is potential for utilizing Estonian energy industry waste as thermochemical energy storage materials.

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Efficient promoter for methane storage in hydrate form based on ethylene diamine: Thermochemistry and kinetics study

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Compared to heavier fossil fuels, which lead to emit large amounts of greenhouse gases into the atmosphere and accelerate the global warming, natural gas is considered as a much cleaner energy source. There are several procedures for the storage and transportation of natural gas, including adsorbed natural gas (ANG) compressed natural gas (CNG), solidified natural gas (SNG) and liquefied natural gas (LNG). Among these procedures, SNG technology is the most promising alternative to store and transport natural gas in the form of hydrates, which is based on hydrate formation and dissociation cycles. The SNG technology provide several great advantages, including: the hydrate formation is environmentally friendly due to the use of water and a small amount of additives, the molecular form of gas will be maintained in the hydrate form, 1 m^3 of hydrate will store ~160 m^3 of gas at STP condition and gas hydrates can be stored at ~-25 ºC and atmospheric pressure. Finally, the gas hydrate-storage strategy will provide a safer technology due to non-explosive nature of the gas hydrate. However, the most important limitation that hinders this technology for large-scale applications is the low rate of hydrate formation, which results in low final gas absorption. One of the ways to overcome this constraint is using some additives to enhance gas hydrate formation kinetics. In this work, ethylene diamine tetraacetamide (EDTAM) was developed as a new promoting agent for methane storage. The effect of EDTAM on methane hydrate formation parameters was evaluated by high-pressure micro differential scanning calorimeter (HP-DSC) and high-pressure autoclave cell at 2 °C and 8.0 MPa as the static and dynamic conditions, respectively. The results demonstrated that the onset temperature of methane hydrate formation was increased from −14 °C in the pure water system to −3 °C by adding 0.5 wt % EDTAM. The average conversion of water to hydrate was multiplied by a factor of 20.0 (from 3.2 wt % in pure water to 64.0 wt % in EDTAM solution) due to the presence of 0.5 wt % of EDTAM. Moreover, the EDTAM reduced induction time of methane hydrate formation by a factor of 4 in comparison with pure water in both static (DSC experiments) and dynamic (autoclave experiments) conditions. Also, EDTAM increased considerably the amount of consumed mole of methane, especially during the first stage of hydrate growth. Unlike surfactants, the addition of EDTAM does not induce formation of large amount of foam in the hydrate formation/dissociation process. All obtained results confirmed that the EDTAM is an efficient and prospective promoter for methane hydrate formation.

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Multistage process of gas hydrate growth in various media

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Gas hydrates are known as one of the major flow assurance issues [1]. The multistage of nucleation process can be due to various causes. The simplest event is the two-stage process of hydrates formation from gas mixtures, which can be explained by the sequential formation of two hydrates with different structures [2]. The interpretation of this process can be complicated if several events of primary and / or secondary nucleation can be present in the system. In water-in-oil emulsions it can be observed when each drop or an ensemble of drops acts as an individual microreactor. It can results in several exothermic effects on a thermal curve. Latent crystallization is also possible here, it will correspond to individual nucleation events on different drops, but without any detectable thermal effects [3]. If the process of secondary nucleation is possible in the sample, multiple exothermic effects can also be observed on the thermal curve [4]. In this case, the nature of the observed phenomenon will be completely different, namely crystallization on the newly formed nucleation centers (seeds), which are the crystals of hydrates. This behavior can be caused by: a) the germination of crystals from drop to drop; b) the entry into the reaction zone of unreacted water, for example, covered with a hydrate crust (it can be observed in water-in-oil emulsions when hydrate particles collide with each other). Other alternative to explain the multistage nucleation process can be the formation of supercritical nuclei on various surfaces, which are present in the system, or phase transitions in nuclei [5]. The identification of main stages of the process of gas hydrates nucleation in petroleum media allows determining the rate-limiting stages of this process and methods to influence them.

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Synthesis and catalytic activity of cyanophenoxy- substituted phthalocyaninates of *d*- and *f*- metals

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Phthalocyanines and their derivatives are used in such areas as catalysis, optics, electrical engineering, medicine. Highly effective catalysts, sensitizers, dyes and pigments, PDT applications, all of the above are not a complete list of specific examples of using materials based on compounds of this class. It is the structure of the phthalocyanine macro ring that causes the described structures to have promising spectral, fluorescent, catalytic, and many other properties. The study of these properties and the identification of the relation between them and the nature of peripheral substituents is a key factor opening the possibility of correct usage of materials based on phthalocyanine-type structures.

The work involved presents synthesis of cyanophenoxy- substituted phthalocyaninates of *d*- and *f*- elements of various structure as well as the study of their catalytic properties in the reactions of organic substrates degradation.

The synthesis of macrocycles was carried out by means of template fusion in the case of *d*-elements and under milder conditions in a high-boiling solvent, for complexes of *f*-metals. The complexes were purified by column and gel-permeation chromatography. The structure was confirmed using MALDI-TOF mass spectrometry, NMR, IR and electron absorption spectroscopy. Further, the spectral characteristics of the compounds in DMF, DMSO, pyridine, chloroform and acetone were studied. In a weakly coordinating solvent (chloroform), thermodynamics of the extra-coordination processes of small organic ligands was studied by the example of interaction with pyridine, pyrazine and DABCO. It was determined the complexes with the phthalocyanine : ligand = 1 : 1 ratio correspond to the most stable structure. The highest values of fluorescence quantum yields as a result of studies have shown zinc complexes. As a result of studying the catalytic properties using the example of a model reaction of sodium diethyldithiacarbamate degradation, it was found the values of catalytic activity decrease in the series Co > Cu > Zn > Ni. The study of the thermal stability of these catalysts has shown the possibility of their use in real systems.

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Hybrid material based on phthalocyanines compounds immobilized on silica matrix. Catalytic activity and thermal stability

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Tetramethylthiuram disulfide (TMDT) exhibit valuable properties in terms of synthetic or biological processes. They are used as fungicides, components of a drugs needed for healing alcohol addiction and human immunodeficiency. It is also known to use ADAM10 enhancers in the diagnosis of Alzheimer's disease. TMDT has an application of accelerator of vulcanization of rubber compounds on the basis of natural and synthetic rubbers of diene type and medicines against drug addiction. Synthesis of TMTD is easily performed via liquid-phase oxidation of N,N-diethylcarbamodithiolate (DTC) within alkali medium in presence of catalyst, although there are difficulties regarding oxidation process control.

Transition metal complexes with substituted phthalocyanines are known to be promising catalysts for the conversion of DTC to TMTD. The usage of metal phthalocyanine catalysts makes it possible to selectively oxidize DTC to TMTD under mild conditions. Giving solubility to metal phthalocyanines in aqueous solution is achieved by introducing sulfo- groups into peripheral substituents. However, a significant drawback of water-soluble metal phthalocyanines is a strong aggregation in solution, which leads to a decrease in their catalytic properties when conducting the reaction in a homogeneous liquid-phase medium.

Immobilization of metal phthalocyanines on the surface of solid phase carriers allows one to obtain hybrid materials for heterogeneous catalysis. In the present work, a series of hybrid materials was obtained by immobilizing a series of cobalt phthalocyanates on the surface of modified silica.

The resulting materials were tested as heterogeneous catalysts for the liquid phase oxidation of DTC to TMTD. It was found an increase in the size of the peripheral substituent in the phthalocyanine macrocycle and its removal from the surface of the silica leads to a decrease in the aggregation of the catalyst. The efficiency of catalytic action for materials reaches up to 90%.

The study of materials involved thermal stability using the DSC and TG methods showed the destruction proceeds in several stages. At the first stage, the adsorbed water is removed. The next stage for all compounds is in the temperature range of 300–500 °C and is due to the rupture of the bond between the active component of the catalyst and the solid phase carrier. In the range of 600-700 °C, the catalyst itself is completely destroyed. Thus, the resulting materials can be used in the process of obtaining TMTD, which flows up to 200 °C.

This work was supported by the Russian Science Foundation, the project 17-73-20017.

Use of methods of thermal analysis in study of metal-organic frameworks

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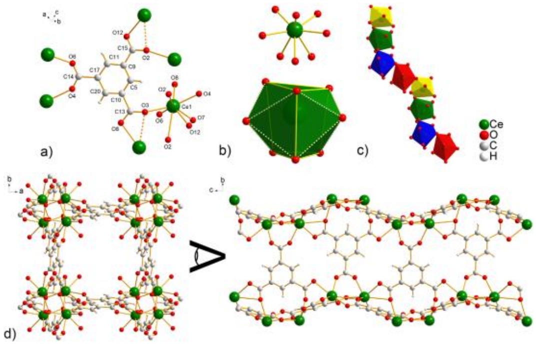
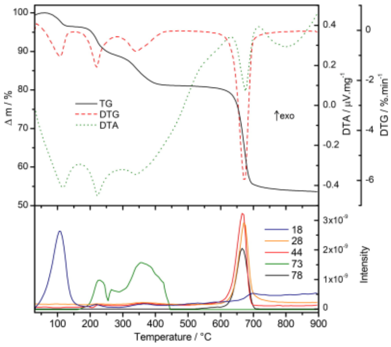
Topic of porous metal-organic frameworks (MOFs), has been one of the fastest growing fields in chemistry during the past decade. The driving force behind are superior characteristics and properties of porous MOFs compared to traditional inorganic porous materials as well as their applications in gas storage[1], catalysis[2], drug delivery[3] or other fields.

However, to prepare MOF with superior textural characteristics (large surface area, open and accessible porosity), the optimal conditions for sample activation have to be find. In our contribution we will show, how the methods of thermal analysis (TG/DTA-MS), can be used to optimise the textural properties of the MOFs. Thermal properties of novel MOFs were studied by simultaneous thermal analysis (TG-DTA) using Netzsch 409 PC apparatus, coupled with Aëolos Quadrupole Mass Spectrometer and powder XRD during *in-situ* heating.

In our contribution we will show, how the above-mentioned techniques were used to find optimal activation properties for MOFs, which touch the energy sector. The areas of our interest with MOFs and energetic applications concerned the magnetocaloric effect (MCE) and cryogenic magnetorefrigeration, where we studied three solvent (X) exchanged samples $[Gd(BTC)(H_2O)]\cdot X\}_n$. Another area, where MOFs touch the energy sector is gas adsorption and separation. From this point of view we will present the use of thermoanalytical methods in activation of several porous MOF, e.g. $\{[Pb_4(MTB)_2(H2O)_4]\cdot 5DMF\cdot H_2O\}_n$ or $[Ln(BTC)(H_2O)]\cdot DMF\}_n$ (Ln = Ho(III), Tm(III)), Ce(III), Lu(III)).





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Characterization and kinetics of coal combustion: Effect of particle size

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In this research, the effect different mesh size on the combustion of Saray (Thrace region-Turkey) coal sample is studied by thermogravimetry (TG-DTG) at different heating rates. TG-DTG curves revealed two main reaction regions known as evaporation of moisture and carbonization at each heating rate studied.

Two main reaction regions were identified in coal sample of different particle size known as evaporation of moisture and carbonization at each heating rate studied. Depending on the different particle size it was observed that reaction intervals and corresponding peak and burn-out temperatures are increased as the heating rate is increased.

Kinetic analysis of the Saray coal sample of different mesh sizes are determined using model fitting methods (Arrhenius and Coats & Redfern) and iso-conversional methods (Ozawa - Flynn - Wall and Kissinger - Akahira - Sunose). The results are discussed from the point view of heating rate and particle size. In general, there was no general trend in the activation energy values from the point of heating rate.

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Microwave assisted advanced oxidation process: kinetic analysis, temperature effect and activation energy

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The removal of pollutant molecules from industrial effluents has been receiving increasing attention, as legislation surrounding the release of contaminated effluents has become more stringent. Among numerous abatement techniques, Advanced Oxidation Process techniques (AOP) are gaining ground, as they are able to attack even the most recalcitrant compounds [1]. In the literature, a large number of these methods have recently appeared. Many of them use ultraviolet radiation (UV), either on its own or in combination with photocatalyzers, Fenton reactions and other similar methods [2].

Moreover, it is well documented that the simultaneous application of microwave (MW) power and UV light leads to better results in photochemical processes [3].

In this work an innovative photochemical reactor for simultaneous MW/UV delivery, with or without H_2O_2, is presented and results for photodegradation of some molecular pollutants are reported (Acid Orange 7, Atrazine, Rhodamine B).

In particular, kinetic analysis of the degradation process has been carried out, demonstrating that an indirect reaction of atrazine with an OH radical is dominant at low concentrations of H_2O_2 and a direct reaction of atrazine with H_2O_2 is dominant when the concentration of H_2O_2 is more than 200 mg/L.

The innovative configuration of the reactor allowed us to determine the activation energy of the Rhodamine B degradation process, even in the presence of microwave radiation.

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Thermoanalytical characterization and Microwave heating response of deep eutectic solvents

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Deep eutectic solvents (DESs) are an emerging class of green solvents, which are considered complementary to ionic liquids (ILs) [1]. Differently to these latter, DESs are not fully composed by ionic species; nevertheless they show physicochemical properties similar to imidazolium-based ILs [2].

DESs are usually high viscous liquids with a melting point lower than that of each individual component. The main peculiarity of DESs regards the capability of forming homogenous eutectic mixtures thanks to the formation of intermolecular hydrogen bonds between their components [1,2]. DESs belong to the green solvent family as a result of very attractive features such as their very simple preparation, low cost, high yields and the fact that further purification steps after their preparation are not needed. Some important current applications of DESs cover the following research fields: carbohydrates treatment like isolation, chemical transformation or modification of biomass, synthesis and fabrication of materials (polymers, metal processing and nanomaterials), novel extraction processes of bioactive compounds, and biotechnological and biological applications [1-4]. Particular attention must be paid to the combined use of DESs and microwaves (MWs); MW-assisted processes using DESs as solvent media can offer several advantages as for instance low energy consumption, fast processing times and high dissolving properties in a sustainable and green way.

In this work, a family of DESs based on choline chloride as hydrogen bond acceptor and two different kinds of hydrogen bond donors (polyols and acids) were prepared and their intermolecular arrangement was fully characterized by NMR (^{13}C, ^{1}H) and FTIR spectroscopy. The microwave interaction of all the DESs prepared and of their single components was evaluated by the experimental determination of the temperature profiles of the solvents under a constant MW power applied during a fixed time interval. The thermal behavior and the analysis of the evolved gas during the DESs thermal decomposition, which are not well described yet in the literature, were also assessed by TG-FTIR analysis, providing a further insight into the life cycle of DESs.

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Oral Presentations 2

Thermodynamics, Thermochemistry & Calorimetry and Thin Films & Nanomaterials

Homocoupling defects of a small donor molecule by rapid heat-cool differential scanning calorimetry

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In Organic photovoltaics (OPV), the active layer is constituted of a donor and an acceptor material. The phase structure and the interface between these two materials will strongly influence the performance. To improve the efficiency, the bulk heterojunction concept was developed, in which the active layer has a co-continuous nanoscale morphology. The phase behaviour of the components is therefore of high importance. During the synthesis of the molecules involved, side reactions, such as homocoupling defects, may occur. This can lead to a decrease in the final device efficiency [1]. It is therefore important to devise a way to detect and quantify them in the material.

Rapid Heat-Cool DSC (RHC) can be used as a dedicated technique for the construction of state diagrams of systems used in OPV active layers [2]. RHC allows for a relatively wide range of heating and cooling rates, thanks to its unique infrared furnace design and small sample size (ca. 250 µg). Using this technique, a state diagram was constructed for mixtures of p-DTS$(FBTTh_2)_2$ and its homocoupled side product, displaying a clear eutectic behaviour of the mixtures. This state diagram shows that even small amounts of these defects will have a significant effect on the thermal behaviour of the material. RHC proved to be a very useful technique for understanding the influence of the impurity on the processing of its OPV blends.

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DSC applied to the study of an “impossible” system: probenecid-benzamide

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We found that probenecid (PRO), an uricosuric drug [1], and the coformer benzamide form a cocrystal [2] that enhances the pharmaceutical properties (solubility and dissolution rate) of the pure drug. The study of this binary system gives an excellent example of the power and the limits of thermal analysis applied to the investigations of compounds of pharmaceutical interest.

The DSC curves obtained for the drug:coformer physical mixtures show a challenging pattern of endo/exothermal peaks heavily dependent on system composition and heating rate. Thermograms are so complicated that, at a first glance, their interpretation appears nearly impossible. We developed a thermodynamic model that addresses all the single processes which could take place during heating and should appear in the DSC curves if enough time was left to their occurrence and if they didn’t hidden reciprocally for kinetics reasons: melting of the metastable eutectic mixture formed by probenecid and benzamide (EU1) with composition x_{PRO} = 0.2; crystallization of the cocrystal (CC) with composition x_{PRO} = 0.5 and of the excess component with respect to the cocrystal composition; melting of the eutectic mixture formed by the cocrystal and benzamide (EU2) with composition x_{CC} = 0.4; melting of the cocrystal. The model has two variants: in the first one, the cococrystal can form only by crystallization from EU1 melt, while, in the second one, it is hypothesized that the cocrystal can form also by a liquid/solid reaction between EU1 and the solid component in excess respect to EU1 composition. The model here proposed well agrees with the enthalpy values measured for the physical mixtures of different composition.

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Role of the central metal ion in the formation of anion-templated Ln^{III}[15-metallacrown-5]$^{3+}$ complexes in aqueous solution

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Molecular capsules/compartments have gained considerable interest over the past decades as effective tools for selective molecular recognition and catalysis; the most widely studied are self-assembled architectures that use metal atoms to template the desired molecular environment [1-2]. One class of metallamacrocycles that has seen applications in guest recognition, molecular magnetism and luminescent spectroscopy is metallacrowns (MCs), which can be prepared with varying sizes but also can change the composition of metal and ligand and total charge. In particular, 15-MC-5 can be prepared as 3D structures with transition metals such as Cu(II) in the metallacrown ring position and lanthanides in the captured central position [3]. Most interesting are those complexes prepared with chiral ligands, such as phenylalanine hydroxamic acid, which lead to the formation of face differentiated metallacrowns that place five ligand side chains on the same face. These systems associate in the solid state forming chiral compartments when the proper guest is captured within these hydrophobic cavities; however, there is limited information on whether such dimeric structures exist in solution and are able to sequester guests into the generated molecular capsule.

To this end we have examined the binding features of a series of Ln(III)[15-$MC_{Cu(II)NpheHA}$-5]$^{3+}$ (Ln(III) = La, Nd, Sm, Eu, Gd, Dy, Ho) hosts with different dicarboxylate guest molecules having variable length, size and different degrees of unsaturation. We have explored to what extent Ln(III)MCs are still capable to form dimeric complexes in neutral aqueous solution through nano-ITC experiments [4]. The determination of the enthalpic and entropic contributions to the free Gibbs energy allowed us to unveil the driving forces of the molecular recognition processes in solution. We demonstrated that Ln(III) ionic radii trend as well as the chain length of the guests are the most important criteria for efficient recognition. Our results resolve the long-standing question as to whether these MC-based complexes exist in solution and show that their formation is a consequence of the host/guest interaction.

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Determination of the short time stability of polymers by fast scanning calorimetry

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Thermogravimetric Analysis (TGA) is a standard method to measure the thermal stability of polymeric materials. This technique is not sensible for degradation steps which are not related with mass loss. However, such reactions can significantly influence the mechanical behavior of material.

Here, the technique of stability estimation by crystallization analysis (SECA) and pseudo TGA which uses differential scanning calorimetry is shown. SECA measures the influence of decomposition on crystallization kinetics. This technique is very sensitive to decomposition. Using fast scanning calorimetry, SECA determines the short time thermal stability of semi-crystalline polymers. This property is essential for fast polymer processing like laser sintering or welding. Investigations are carried out on different materials developed for selective laser sintering like polyamides, thermoplastic elastomers and poly (ether etherketone).

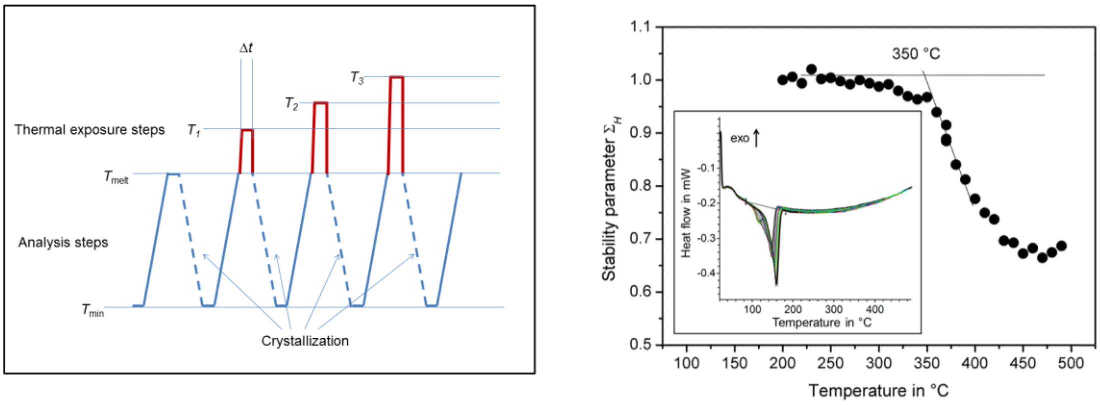

Fig. 1: **SECA:** Stability Estimation by Crystallization Analysis (left) and SECA of Polyamide 12 (right)

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Characterization of thermoreversible covalent networks for additive manufacturing

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The development of self-healing or remendable polymers has grown strongly over the past two decades. Our research in this field focuses on thermoreversible polymer networks based on the thermoreversible Diels-Alder reaction between furan (diene) and maleimide (dienophile) groups. To develop these materials and their processing for applications in self-healing (SH) soft robotic actuators, detailed knowledge about the reversible reaction kinetics and the connected chemorheological changes is required [1-3].

At high temperatures, the Diels-Alder/retro Diels-Alder reaction equilibrium shifts to a less connected state, while at low temperatures, the cycloadducts link the network together. Two stereoisomeric cycloadducts exist: a more thermodynamically stable exo-isomer, and a kinetically faster endo-isomer [4]. Detailed insight in the thermoreversible reaction kinetics is needed for optimizing temperature programs used during processing or healing. Combining this kinetic information with the conversion and temperature dependent visco-elastic behaviour facilitates the tuning of the material behaviour during processing and healing.

A comprehensive study of the thermoreversible reaction kinetics and the chemorheological changes, using DSC, microcalorimetry, FTIR and NMR spectroscopy, and dynamic rheometry. Combining kinetic information and chemorheology facilitates the careful selection of building blocks and aids development of filament extrusion and filament deposition modelling of these thermoreversible polymer networks [3,5].

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Calorimetry: a complementary method to study the mechanical energy conversion properties of nanoporous materials

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Different approaches may be investigated to use nanoporous materials for mechanical energy conversion. In the 1990s, Eroshenko first introduced the concept of using the mechanically forced intrusion of non-wetting fluids into mesoporous materials to transform the mechanical energy used in interfacial energy. Different mechanical behaviours have thus been obtained depending on the nature and texture of the material. In the case of specific hydrophobic zeolites in the presence of water a completely reversible behaviour for the intrusion and the extrusion could be observed and opens the door to molecular-spring type applications. In the case of hydrophobic mesoporous silica, most often the behaviour evidenced is a total or partial energy dissipation and leads to consider applications as bumper or damper.

More recently, studies have been conducted on hybrid materials as MOF (Metal Organic Framework) which possess a large variety of structures. The microporous materials: ZIFs or Zeolitic Imidazolate Frameworks are interesting candidates for water intrusion-extrusion since some possess a strongly hydrophobic character. [1]

The study presented here focuses on the energy involved during the intrusion-extrusion phenomenon of non-wetting fluid. A comparison is made between the results obtained with different fluids and in particular between mercury and water.

In addition, an experimental device based on the combination of a mechanical pump and a Tian-Calvet microcalorimeter makes possible to measure the complete energy balance during the intrusion-extrusion cycles. This assessment is essential before considering applications as dampers for example, since the heating of the system can degrade the mechanical performance.

Finally, the energy balances obtained by this system made of non-wetting fluid introduction in the porosity are compared with those obtained by a different approach. Indeed, recently flexible microporous MOFs have also been subjected to compression-decompression cycles in the presence of fluids that cannot penetrate the porosity and they have also shown their potential for the transformation of the applied mechanical energy. Most often an energy partially dissipative behaviour has been observed and the energy involved appears to be in the same order of magnitude as that of the previous systems.

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OP2.07

Miniaturized differential scanning calorimeter with integrated oven and reference (Chip-DSC)

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We announce the introduction of a miniaturized differential scanning calorimeter (Chip-DSC, Fig. 1a) with integrated oven in a ceramic sensor. Despite its small size of only 11 mm x 39 mm x 1.5 mm, all functions of a conventional DSC apparatus are integrated in this novel DSC sensor (Fig. 1b and c). In the sensor head the crucible, sample and reference temperature sensors, heater and reference are vertically integrated (Fig. 1b). Due to its small thermal mass, extremely high heating and cooling rates can be achieved (heating up to 1000 K/min; cooling down to room temperature in 4 minutes). The DSC chip is manufactured utilising in Low Temperature Co-firing Ceramics (LTCC) Technology to ensure high temperature stability allowing for DSC analysis up to 600 °C.

Due to the design, the time constant and sensitivity of the Chip-DSC are better or comparable to conventional instruments. We present unique rapid calibration procedure measuring 4 melting peaks in only one crucible allow a rapid calibration in approx. 15 minutes (Fig. 1d). Measured enthalpies are independent of the heating rate.

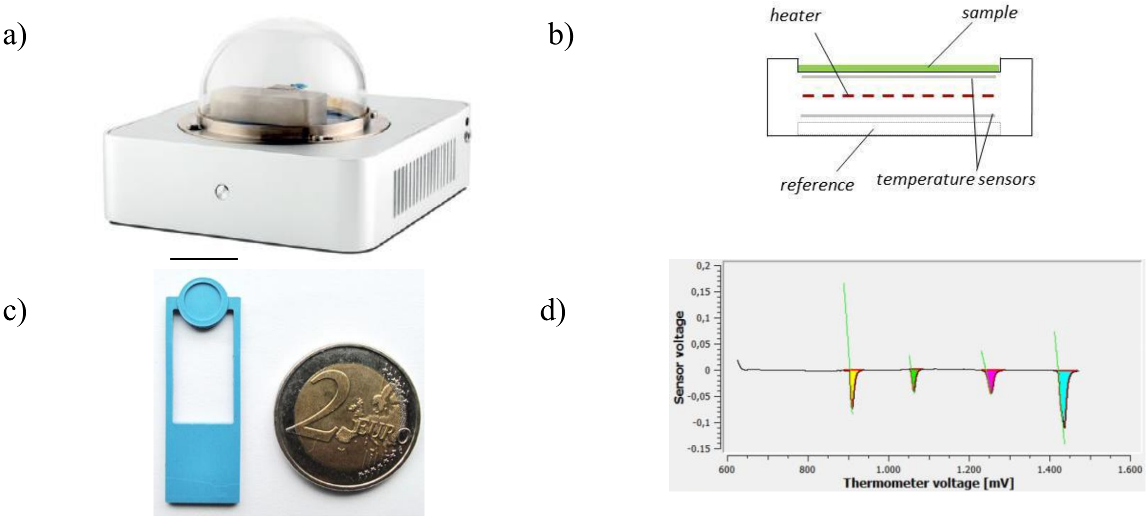

Fig. 1: a) Chip-DSC 1 device, b) vertical arrangement of functional elements in the sensor head, c) Chip-DSC 1 sensor, d) calibration by simultaneous measurement of 4 melting peaks

Following the introduction described above the talk will focus on experimental capacities of the device and on applications.

Thermal properties of photocatalytic and gas sensing carbon nanostructures and nanocomposites

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Our aim was to tune the photocatalytic and gas sensing properties of various carbon nanostructures by coating them with atomic layer deposition (ALD) grown oxide nanofilms and nanoparticles. As substrates, OH functionalized fullerene (C_{60}-OH), OH functionalized carbon nanotubes, graphene oxide (GO) synthesized with the improved Hummers method, carbon nanospheres obtained hydrothermally as well as carbon aerogels were used. Onto them, TiO_2, ZnO and Al_2O_3 thin films and nanoparticles were deposited by ALD.

The preparation and functionalization reactions of carbon nanomaterials were thoroughly monitored by thermal analysis (TG/DTA-MS). In addition, the thermal stability of the as-prepared carbon nanostructures in inert atmosphere was checked to determine what the maximum possible temperature was for the ALD reactions. The annealing in air was studied to determine what heating conditions are needed to remove the carbon cores to obtain hollow oxide nanomaterials. Besides thermal analysis, the nanomaterials were analyzed by XRD, SEM-EDX, TEM-ED, FTIR, Raman, XPS, UV-Vis.

Based on these studied we found that the C_{60}-TiO_2 composite was the first example of ALD prepared single molecule fullerene/oxide composite. The other depositions also meant the extension of the use of the ALD onto these important substrates. The photocatalytic and gas sensing of the as-obtained nanocomposites was investigated. Unexpectedly, amorphous TiO_2 grown by ALD had photocatalytic activity on these substrates - usually TiO_2 is considered to have photocatalytic activity only in crystalline state. The gas sensing of the substrates was considerably modified by the deposited oxide layers and multilayers.

Studies on the influence of environmental factors and composition on the thermal stability of paint coat deposited on pinewood

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Paints are products which color and protect the wood surface. It must resist over time and exhibit the same properties as the original layers applied even for months or years. There are very few studies analysing the influence of environmental factors on the quality of paint coat [1] as not deposited on wood, but other types of surfaces: metallic, ceramic etc. Most of the studies refer to testing the quality of paint layers exposed in laboratory conditions [2] or subjected to artificial aging [3-4]. In this study was considered three commercially types of paints: an alkydic paint which contains Teflon (SLT), an alkydic paint which contain an urethane component (LYP), and a paint which have an alkydic and also an acrylic component (ECM). Lacquers and paints are frequently used in ordinary life and this paper offers information on the influence of composition and environmental factors on thermal stability.

The study was realized for the fresh dry paint, for the paint subjected at laboratory conditions for six months, for the paint subjected at natural weather conditions for six months, and for the paints after one year of exposure at four different climate conditions. These coatings were thinly applied on dried fir tree wood pieces.

Thermogravimetric analysis was performed using a Mettler Toledo TGA-SDTA851^{e} derivatograph. The paint was removed from the wood surface with a scalpel and was supposed at temperatures between 25°C and 800°C at a 20 ml/min flow of synthetic air. The results was centralized and plotted to observe the changes resulting after exposure at natural weather conditions. The results obtained emphasized the influence of both composition and environmental factors on thermal stability. The best thermal stability was noted in the case of the SLT sample, which contains besides alkyd resin, Teflon. The thermal stability decreases once with the increase of the exposure time, especially in the case of samples exposed in Constanta and Nijmegen. The resistance over time of pinewood treated with the three types of paint to the action of environmental factors was also analysed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and by measuring the contact angle. All the applied techniques showed that a paint containing an alkyd and an acrylic component (ECM) is the most resilient to the action of environmental factors.

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Properties of poly(ethylene 2,5-furandicarboxylate) and its nanocomposites

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The talk will focus on a 100% biobased thermoplastic that can be produced from lignocellulosic biomass, the poly(ethylene 2,5-furandicarboxylate) (PEF), which presents a huge potential as a bio-based packaging material. PEF is often compared to polyethylene terephthalate (PET) due to some similarities in chemical structure and in their production. Indeed, PEF can be produced from 100% bio-based 2,5-furandicarboxylic acid (FDCA) in a chemically analogous way to PET.

PEF has gained increasing interest due to its intrinsically higher barrier properties, glass transition temperature and modulus. Furan based molecules are a very promising category of biobased platform molecules that can be obtained from non-food competitive carbohydrates. They have been referred to as "Sleeping Giants" because of their enormous market potential and their position in the US Department of Energy top 10 of high-potential biobased products [1,2]. FDCA is the bio-based building block for the synthesis of PEF [3]. PEF is then produced through direct esterification and polycondensation of 2,5-furandicarboxylic acid (FDCA) and mono ethylene glycol (MEG).

Crystallization of PEF from the melt and from the solid state, glass transition and mobility of amorphous PEF and influence of crystallites on the cooperative α-relaxation will be presented. Amorphous PEF presents a higher ΔC_p at the glass transition and a broader relaxation spectrum attributed to a higher free volume. The higher T_g of PEF is then purely related to segmental mobility and specific interactions in PEF. The creation of the rigid amorphous fraction (RAF) with crystallinity is lower in PEF than in PET. The difference in free volume also explains the lower coupling between the crystalline phase and the amorphous phase in PEF. Finally, nanocomposites based on PEF and organically modified Montmorillonite (Cloisite 11) obtained by solvent casting and extrusion method show interesting properties [4-10].

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Determination of the sublimation vapour pressure of thermally labile compounds with fast scanning calorimetry

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The determination of vapor pressure and corresponding enthalpy of sublimation lay within focus of many scientific fields and industrial applications. These values directly connected to the intermolecular forces in crystal state, provides the lattice energy and change in ordering by going from crystal to gas phase. In the present study, the fast scanning calorimetry was successfully applied for determination of vapor pressure and enthalpies of sublimation of low volatile organic substances.

In many cases, investigation of thermally labile systems e.g. biomolecules are accomplished with low thermal stability of them and application of classic techniques often fails by determining the decomposition rate of the system. Our technique is based on the determination of the mass loss rate of the sample from the experimental total heat capacity and preliminary determined specific heat capacity of the compound under study. Sublimation of the sample is carried out during repeated isotherms of pre-defined duration and at selected temperatures. Sample is heated to needed temperatures using high heating rates accessible by this technique, which allows reaching the sublimation temperatures without any mass loss during the heating time. From the other side in the proposed technique, the surface to volume ratio of the sample is so high, that sublimation mass loss rate is incomparably higher that decomposition rate. Thus, the sample of a few nano-grams sublimes without any thermal degradation.

Development and characterization of multifunctional YIG/epoxy nanocomposites

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Organic/inorganic nanocomposites combine the advantages of the inorganic constituent (i.e. mechanical strength, electrical/magnetic properties and thermal stability) and those of organic polymers (i.e. flexibility, dielectric, ductility and processibility). Nanocomposites based on ferrite-polymer mixtures constitute a wide active area of research, owing to their applications in electromagnetic interference shielding (EMI), drug delivery and targeting and as contrasting agents in magnetic resonance imaging (MRI) [1,2]. Magnetic nanoparticles possess unique physical and chemical properties compared to their bulk counter parts due to their nanodimension [3–5].

In the present study, YFe_2O_5/epoxy composite nanodielectrics were fabricated and studied. Specimens’ morphology was assessed via Scanning Electron Microscopy (SEM). The thermomechanical properties were investigated by means of Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA). The dielectric response was examined via Broadband Dielectric Spectroscopy (BDS). Magnetic characterization was conducted by means of a Superconducting Quantum Interference Device (SQUID).

The addition of the nanoparticles improves the dielectric and thermomechanical properties of the nanocomposites. Experimental data revealed increasing values of storage modulus with the addition of filler due to the enhancement of the materials’ stiffness. Relaxation phenomena arising in polymer composites are related to the polymer matrix and the presence of nano-filler. Three different relaxation mechanisms were recorded for all nanocomposites: Interfacial polarization, glass to rubber transition of the polymer matrix and re-orientation of polar side groups.

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Thermally-stimulated phenomena observed in isotactic polypropylene and high-density polyethylene matrices reinforced with graphene nanoplatelets and glass fibres

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The continuous demand for high-performing materials in the 20th century has led to the development of polymer composites. Polypropylene (PP) and High-Density Polyethylene (HDPE) are the most widely used thermoplastic polymers. Various fillers have already been incorporated in PP and HDPE matrices in an attempt to improve even more their properties. Graphene nanoplatelets (GNPs) and Glass fibres (GF) are two of these fillers since they can reinforce quite efficiently most polymeric matrices even at a small filler's content [1].

The thermal degradation of PP and HDPE polymers has been studied quite extensively using thermogravimetric measurements. For the kinetic description, most of the times single rate heating data and model-fitting methods have been used. Since the thermal degradation of the polymers is a very complex reaction, the choice of a reliable model or a combination of kinetic models is very important.

In this work, the thermal degradation kinetics of iPP-GF-GNP hybrid composites were studied using thermogravimetric analysis (TGA) and Analytical Pyrolysis Gas Chromatography/Mass Spectrometry (py-GC/MS). Conventional PP composites containing GNPs and GF were also studied for comparative reasons. The effect of GNPs size on the kinetics mechanism of HDPE was evaluated too. A detailed study has been performed for the calculation of the effective activation energy of polymers using the isoconversional differential method of Friedman. Finally, the kinetic model and the kinetic parameters of the thermal decomposition process were determined by a multivariate non-linear regression method.

It was found that the Isoconversional and model fitting methods were successfully employed for the study of the decomposition of PP and HDPE composites. The kinetic analysis results showed that the presence of GNPs altered the decomposition mechanism of the composites, while the mechanism of the PP-GF composite was identical to the one applied in the matrix.

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New organic-inorganic pigments as colorants for polymer composites

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Organic dyes are used in a wide range of products, including textiles, printing inks, plastics, rubbers and enamels. However, their applications are limited due to their tendency to migrate, low melting points and poor affinity to certain matrices. In some cases, these disadvantages can be overcome by the transformation of the dyes into pigments. There is currently great interest in organic-inorganic pigments, which can combine the advantages of both organic materials (such as versatility of color) and inorganic materials (high resistance to chemicals and light) [1-2].

The present study proposes a new precipitation method for preparing hybrid pigments based on organic dyes (with azo and anthraquinone chromophore) and aluminum-magnesium hydroxycarbonate (LH). The secondary ion mass spectrometry (TOF-SIMS) and X-ray photoelectron spectroscopy (XPS) were used to examine the interaction between LH and organic dyes. Dyes, LH and dye modified LH were also characterized via thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electronic microscopy (SEM) and UV–VIS spectroscopy.

The application of LH modified with azo dye as colorants for ethylene-norbornene copolymer (EN) also contributed to higher resistance of EN copolymer to unfavorable aging conditions. Adding 2 phr of the multifunctional organic-inorganic pigments to EN copolymer significantly enhanced the aging resistance of the resulting composites. The durability of EN copolymer was increased more than 4 times after replacement of the LH matrix in polymer with organic-inorganic pigments. These results offer a new way towards the facile preparation of multifunctional additives which may be beneficial for the development of the new colored polymer materials with improved UV resistance.

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Modelling polyurethane reactions by combining differential scanning calorimetry and micro-calorimetry

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Using thermal analysis techniques, like differential scanning calorimetry (DSC) and micro-calorimetry, the heat flow generated during polymerization reaction can be measured as a function of time and temperature. As the heat flow stands in direct correlation with reaction rate, the kinetics of the polymerization can be measured. Here a combination of isothermal and non-isothermal measurements is used in combination with different mixing rations of the initial compounds, to have a broad range of condition during which the reaction can take place. The polyurethane has higher order kinetics. Meaning that in isothermal conditions a high reaction rate at the start of the reaction which quickly slows down and is followed by a long tail. To accurately measure the initial reaction, DSC which as fast stabilization time is used. The disadvantage of using DSC that no absolute baseline is measured. Because of the long tail the difficult to assess if the urethane formation has stopped and the baseline can be recorded. Measuring the urethane formation in micro-calorimetry, the initial first hour of reaction cannot be measured due to stabilization, but from then onward the reaction is measured with a near absolute baseline. By combining the initial heat flow measured in DSC with the heat flow measured in micro-calorimetry, by doing a time and heat flow-shift, accurate measurements of reaction heat from the urethane formation are done. These measurement can then be used for modelling. Using a mechanistic model, where the global polyurethane reaction is subdivided in a set of (elementary) reaction, a heat flow can be simulated. Using a least squares curve fitting algorithm on the experimental and the simulated heat flows, the reaction rate parameters of the kinetic model can be determent. An advantage of this mechanistic modelling approach is that the concentrations of the different functional groups, like primary and secondary alcohols, presence of ether groups, catalysts, … are explicitly calculated and can be used to study different compositions.[1]

When the all different conditions can be predicted at reasonable accuracy a robust model is obtained. In a next step the mean molecular weight can be estimated using a statistical method, the so-called “in-out recursive analysis” developed by Macosko and Miller [2,3]. The growth of the molecules is calculated based on the conversion of the materials, leading to molecular weight, gelation, crosslink density and elasticity modulus calculations.

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Simulation of crystalline morphology from calorimetric crystallization curves

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Kinetic evaluation of crystallization is an evergreen topic of thermal analysis because kinetic models can provide valuable information about the mechanism and other characteristics of the studied processes. There are numerous methods for evaluation of crystallization kinetics under isothermal or non-isothermal conditions in the literature. These models result in characteristic constants like Avrami exponent, overall rate constant, apparent activation energy of crystallization, as well as the pre-exponential factor. These quantities can be efficiently used for comparing the process in different samples. The main drawback of the conventional kinetic evaluation is that they cannot provide any information about the supermolecular structure forms during the crystallization process. Since the properties of the polymers depend strongly on their crystalline structure, detailed knowledge is essential for understanding their behaviour. Usually, microscopic techniques are applied to study the morphology, but these techniques mostly provide local information only and the experimental conditions arefar from the practical conditions used in the real processing practice. Accordingly, the prediction of crystalline structure from calorimetric curve is useful, because a modern calorimeter can study the crystallization process under more realistic conditions then a microscope.

This work reports a novel method, which can simulate a morphological structure of semicrystalline polymers from the crystallization curve recorded by calorimetry. Nucleus density (N) is one of the morphological structure parameter of our calculation. There are several techniques in the literature for obtaining the nucleus density from calorimetric curves, but all of these techniques are difficult to use [1-4]. The main drawback of these models that only average N can be obtained using these methods, but the average size and size distributions of supermolecular units are still not known, which is essential for example from the point of view of optical properties of the polymers. In this recent work, we developed a program code which can simulate morphological structure including nucleus density and also the average size and size distriubution of supermolecular units based on the crystallization curve recorded by calorimetry. The results indicated good agreement between the simulated morphology and the crystalline structure formed in the microscope under the same conditions.

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Calorimetric and X-ray studies of RE tantalates and hafnates

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Thermal Barrier Coating (TBC) materials are gaining much attention recently, mostly because of prospects of their application in modern energy production plants and turbo-jet engines. Currently, new materials based on ***yttria-stabilized zirconia*** (YSZ) and other oxide materials with improved properties are being actively designed [1]. Rare-earth tantalates ($RETaO_4$) and hafnates ($RE_2Hf_2O_7$) considered now as the promising candidates for TBC application.

Specimens of RE tantalates and hafnates for calorimetric and X-ray studies were synthesized by a reverse co-precipitation from aqueous-alcohol solutions followed by calcination at 1700 K for a few hours. Identification of obtained substances was carried out by X-ray powder diffraction, ICP-MS, X-ray fluorescence analysis and SEM. It was found that RE tantalates were obtained in monoclinic M’ and M structures, while RE hafnates have structure of pyrochlore (for Ce-subgroup lanthanides) and fluorite (for Y-subgroup lanthanides). Studies of thermal behaviour of $RETaO_4$ and $RE_2Hf_2O_7$ were conducted using a Netzsch STA 409F1 Jupiter simultaneous thermal analyzer in the region 330-1500 K. Heat capacity measurements were carried out using a BKT-3 adiabatic calorimeter in the range 10-340 K and using a Netzsch STA 409F1 Jupiter thermal analyzer in the range 330-1273 K.

DSC studies show the absence of any endothermic and exothermic effects in the studied temperature range. Heat capacity curves in the low and high-temperature regions were fitted jointly to calculate smoothed thermodynamic values (heat capacity, entropy, enthalpy change and derived Gibbs energy).

High-temperature X-ray studies of $RETaO_4$, and $RE_2Hf_2O_7$ were carried out on a SHIMADZU XRD-6000 diffractometer (CuK_α radiation) in the 2Θ range from 10° to 60° using an HA-1001 Shimadzu attachment. Based on the data obtained temperature dependences of lattice parameters and coefficients of thermal expansion in the region 298-1173 K were determined. Results of X-ray studies demonstrate satisfactorily agreement with the available literature data.

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Thermodynamics of bistable metal complexes

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Of critical importance for the miniaturization of functional materials are molecular and molecule-based materials that can be switched between distinguishable electronic states by application of an external stimulus. Systems that can be switched in this way include spin crossover complexes, heterometallic complexes that exhibit electron transfer coupled spin transitions, and valence tautomeric complexes. The phenomenon of the reversible metal-to-ligand electron transfer (redox-isomerism or valent tautomerism) in crystals of *o*-semiquinonato complexes was firstly discovered in the early 1990s. It was shown that the external excitation such as temperature, pressure, and magnetic field causes a shift of the equilibrium of interconversion of isomers that differ in the structure, valence and spin states of metal and ligands. Redox-isomeric transformation is accompanied by the phase transition. Thus, change in the electronic structure of molecules leads to changes in the physical properties of solid phases (e.g., magnetic susceptibility, absorption spectra etc.). The particular and unique physical properties associated with different valence tautomeric systems will undoubtedly see them making an important contribution to the future progress in this scientific field [1, 2].

In this work, the temperature dependences of the heat capacities of (TEMPO-Im-Py)Co(3,6-DBSQ)$_2$ (**I**), cocrystallized (Phen)Co(3,6-DBSQ)$_2$ (**II**) and (Dipyridyl)*bis*(3,6-DBSQ)$_2$ (**III**) complexes were determined by precise adiabatic calorimetry and differential scanning calorimetry in a wide temperature range. The low-temperature heat capacities of compounds were analyzed on the base of the multifractal model, and the structure topologies of the studied complexes were established. The experimental results were used for calculating the standard thermodynamic functions, namely the heat capacity, the enthalpy, the entropy and the Gibbs energy of complexes **I–III**. The standard thermodynamic properties of the studied compounds were compared with the previously reported data for different metal complexes. Some conclusions on the influence of nature of the central atom and ligands on physico-chemical properties of bistable metal complexes were made.

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Solvation enthalpy and how it can be useful

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Enthalpy of solvation is an important parameter for chemical equilibrium and chemical reactions in the solvent. Prediction of thermodynamic properties of organic compounds by using additive scheme is a standard procedure for chemical engineering. The main idea of such scheme is the assumption that property of molecules can be calculated as a sum of structure fragments or atoms [1-3]. Thereby, in order to develop an additive calculation scheme, it is necessary to have a reliable set of experimental values and to propose a reasonable approach for dividing the property of a molecule into structural fragments.

The present study is aimed at developing and testing a unified additive scheme of estimation of solvation enthalpy of saturated and unsaturated aliphatic hydrocarbons, alcohols, ketones, aldehydes and nitriles in *n*-heptane. Structural fragments for hydrocarbons group contributions and functional groups are independent of nature of neighbouring atoms. In most cases, observed deviations of literature and calculated data do not exceed of 1-2 $kJ\cdot mol^{-1}$.

The second objective of our work is to extend the range of thermochemical properties which can be estimated with the solution calorimetry. Recently, we have shown that the combination of the solution calorimetry and high level ab initio calculations (DLPNO-CCSDC(T)) can be used for evaluation of the solid or liquid phase enthalpy of formation for cyano-substituted benzenes [4]. Using additive scheme of estimation of solvation enthalpy and the experimental values of solution enthalpies, the formation enthalpies in the condensed state for some classes of organic compounds were determined. The gas phase enthalpies of formation were computed at DLPNO-CCSD(T)/def2-QZVP level of theory. All experimental and calculated values were in good agreement with the most reliable literature data.

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Prediction of sublimation functions of molecular crystals based on melting points

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On the basis of the values contained in the literature published in 1900−2016, we have developed an experimental database including sublimation Gibbs energies, enthalpies, and melting temperatures of 1515 compounds. We have also suggested an algorithm of database fragmentation which includes groups/clusters with structurally similar compounds. For this aim we used Tanimoto similarity coefficients. Clusterization was carried out for each substance of the test set. All the points within a cluster were smoothed by a linear function in the coordinates of Gibbs energy vs melting temperature. Using the training and test sets, it has been shown that the algorithm suggested by us describes experimental data well (rms = 3.89 kJ·mol−1). We have developed quantitative structure−property relationship models based on HYBOT physicochemical descriptors and melting points in order to predict sublimation Gibbs energies and enthalpies of molecular crystals. The developed approach was applied to determine cocrystal formation thermodynamics. Twenty nine out of 30 seven cocrystals selected in the literature have been predicted correctly (78% of the correct matches).

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Chemical thermodynamics of carbosilane dendrimers and siloxane nanogels as promising macromolecular nano-objects

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Modern scientific and technological progress is largely determined by advances in physics, chemistry and technology of nanostructures. In recent years, special attention has been paid to the synthesis and study of properties of a new class of polymers – dendrimers, which are spherical macromolecules, characterized by regular and highly branched three-dimensional tree-like architecture, monodispersity and functionality of the surface layer. The most promising carbosilane dendrimers are thermodynamically stable macromolecules, which possess low characteristic viscosity, exceptional solubility, high flexibility and low glass transition temperatures. As a result of their unique properties, dendrimers are suitable for a wide range of biomedical and industrial applications.

Nanogels are nanosized hydrogel particles with three-dimensional networks formed by chemically or physically cross-linked polymer chains. In contrast to monodisperse dendrimers, nanogels are polydisperse systems both in terms of their molecular mass characteristics and branching factors. They possess high thermal stability, adjustable mechanical properties and biocompatibility. These advantageous properties make nanogels ideal carriers for their applications in biomedicine as targeted drug delivery systems, regenerative pharmacology and tissue engineering.

The fundamental thermodynamic study of dendrimers and nanogels is an actual direction in the field of chemistry of nanostructures. In the present work, the heat capacities of seven carbosilane dendrimers of the first (G1), third (G3) and sixth (G6) generations with different functional terminal groups, as well as two polysiloxane nanogels were determined in the temperature range from 6 to 520 K by precise adiabatic calorimetry and differential scanning calorimetry (DSC). The low-temperature structural anomalies were revealed for G1 and G3 dendrimers as well as nanogels; the high-temperature relaxation transition («nanosized effect») was detected for G6 dendrimers; the glass transition was observed for all studied compounds. The nature of these transformations was investigated, and its thermodynamic characteristics were determined and analyzed. The obtained experimental results were used for determining the standard thermodynamic functions, as well as the qualitative and quantitative dependences "thermodynamic property – structure" for the studied dendrimers and nanogels.

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Thermodynamics of formation of hybrid organic-inorganic perovskite-type halides

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Hybrid perovskite-type methylammonium lead halides have received great attention in recent years due to high conversion efficiency obtained in solar cells based on such materials. Since the time of the first demonstration photovoltaic devices based on the hybrid perovskites $CH_3NH_3PbX_3$ (X = Cl, Br, I) have showed huge progress in increase of conversion efficiency reaching currently 20.1%. However, despite very promising achievements fundamental chemistry and physics of hybrid organic-inorganic (HOIP) perovskites is far from being completely understood. In particular it is true for thermodynamic properties of HOIP perovskite-type halides ABX_3 and A_2BX_4(A=CH_3NH_3, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I). Moreover, reported results of DFT calculations aiming at estimating the stability of these materials often give controversial results. In addition, some of the HOIP perovskites (for example, $CH_3NH_3PbX_3$ (X = Cl, Br, I)) are known to be entropy-stabilized phases. Therefore experimental verification of the stability trends in HOIP perovskite-type halide systems is strongly required. This is especially important for assessment of the stability of these materials under particular working conditions. Therefore, the main aim of this work was to study the thermodynamics of formation of HOIP perovskite-type halides ABX_3 and A_2BX_4 (A=CH_3NH_3, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I). Their standard formation enthalpy at 298 K was measured by solution calorimetry. Heat capacity was measured in the temperature range 2-298 K using PPMS system. Standard entropy was obtained by integration of the Cp/T vs T curve. Standard Gibbs free energy of ABX_3 and A_2BX_4 (A=CH_3NH_3, formamidinium, Cs, Rb, etc; B=Sn, Pb, 3d-element; X = Cl, Br, I) was evaluated using measured formation enthalpy and entropy. Trends in variation of the thermodynamic functions with chemical composition and crystal structure of HOIP perovskite-type halides were analyzed and compared with available results of DFT calculations.

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Decomposition of metal-organic compounds: films versus powder

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Chemical solution deposition (CSD) is a versatile and low cost technique that has been extensively used to synthetize functional oxide films [1]. CSD involves several steps: i) preparation of precursors, ii) deposition of the precursor solution, iii) film drying, iv) pyrolysis to remove the organic ligands and v) film crystallization at high temperature.

Thermal analysis (TA) is especially suited to monitor and to disclose the processes that take place during pyrolysis. However, despite the fact that CSD is used to synthetize films, TA is customary performed on precursors in the form of powder. We have analysed experimentally, theoretically and numerically heat and gas transport in films and powders. In this communication we will show that, to know what occurs during film pyrolysis, the behaviour of films cannot be extrapolated from experiments done on powder [2,3].

We will present several cases showing that the thermal behaviour of a compound in the form of powder may differ greatly from that of the same compound in the form of a film. Since thermal decomposition of a metal-organic precursors is usually a solid-gas reaction, the transport of gaseous reactants or volatile by-products plays a crucial role on its kinetics [4] and decomposition mechanism [4]. Given that gas transport is easier in films, precursor pyrolysis is faster in films (the decomposition temperature is lower) and that may trigger different decomposition paths. Additionally, the good thermal contact of films with the substrate ensures sample thermalisation. In the case of a highly exothermic decomposition, the precursors in the form of powder may undergo a thermal runaway when placed inside a crucible, while combustion is prevented when the same precursors are analysed in the form of films.

To sum up, our contribution wants to emphasize that TA of samples in the form of films enables the in-situ monitoring of the processes that take place during CSD film pyrolysis and that TA of films is a necessary condition to disclose the mechanisms that take place during film pyrolysis.

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Application of isothermal and isoperibolic calorimetry to assess the effect of zinc on hydration of cement blended with fly ash

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The amount of zinc in the clinker or in the secondary raw materials has been increasing in last years. Zinc can get to Portland cement from solid waste or tires which are widely used as a fuel for burning in a rotary kiln. Zinc can be introduced to cement also by using of secondary raw materials.

The aim of this work was to determine the effect of zinc on hydration of Portland cement blended with fly ash (FA). This effect was studied by isothermal and isoperibol calorimetry. Zinc was added to the cement in the form of two-soluble salts of $Zn(NO_3)_2$, $ZnCl_2$ and a poorly soluble compound ZnO. The concentration of zinc added was chosen as 0.05, 0.1, 0.5, and 1wt. percent. The amount of FA replacement is 15 % of cement dosage. The newly formed compounds during hydration were identified by X-ray diffraction method (XRD) and Differential thermal analysis method (DTA).

Characterization of nitrogen groups on carbon surface by TG-MS

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The recently published quantitative TG-MS method [1] derived for the determination of oxygen containing groups on the surface of carbonaceous samples was applied and expanded for the characterization of nitrogen containing groups. The method is based on the linear relation between the amount of evolved gases and the MS peak area via proportionality constant (*K*) which gain the similar values for all evolved gases. These fundamentals were tested on the compounds which evolves the nitrogen groups during their thermal decomposition, concretely $(NH_4)_2CO_3$ and NH_4NO_3. The TG-MS measurements of the studied compounds were performed under an argon atmosphere (flow rate 40 ml min^{-1}) with heating rate 10°C min^{-1}. The monitored MS signals were selected according to the expected gaseous products evolved during the thermal decomposition of the individual compound.

The results for $(NH_4)_2CO_3$ confirmed validity of this method. The values of the *K* for the evolved gases gain similar values (3.78×10^7 for H_2O, 4.24×10^7 for NH_3 and 3.82×10^7 for CO_2) and it confirmed the suitableness of the TG-MS method also for the nitrogen containing groups. During the thermal decomposition of this compound, the nitrogen groups are evolved as ammonia and the overall decomposition process is quite simple, which results in very good agreement (Table 1) between the theoretical and experimentally determined elemental composition of all evolved gases. In the case of NH_4NO_3, the quality of the gaseous products evolved during the decomposition differs from the theoretical expectations (decomposition only to N_2O and H_2O) and plenty of the other nitrogen compounds were detected. The decomposition process is more difficult and the disagreements presented in the Table 1 implies that some other decomposition products not included in the calculations has to be present. However, it can be concluded that this method seems to be valid and suitable for the determination of nitrogen species. Finally, this method will be applied on some real carbonaceous samples modified by nitrogen and oxygen groups.

Table 1. The theoretical and the experimental composition (mol.%) of studied compounds.

sample	*evolved gases*	*m/z*	*composition of gaseous products (mol.%)*		
				theoretical	*experimental*
$(NH_4)_2CO_3$	H_2O, NH_3, CO_2	18, 17, 44	*H*	57.1	56.1 ± 0.2
			N	14.3	13.6 ± 0.1
			C	7.1	7.5 ± 0.1
			O	21.4	22.8 ± 0.2
NH_4NO_3	H_2O, NH_3, N_2, NO, NO_2, N_2O	18, 17, 28, 30, 44	*H*	44.4	50.7 ± 1.1
			N	22.2	21.3 ± 0.3
			O	33.3	28.0 ± 0.9

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The DSC monitoring of oil melting to follow the oil curing

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The drying of an oil paint is due to the polyunsaturations of the oil in the binder. Polyunsaturated oils dry trough an autoxidation process in which the double bonds of linolenic and linoleic acids naturally react with the oxygen present in the atmosphere. The gradual conversion of the liquid oil through a soft gel to a rubbery solid occurs as a result of a multistep free radical chain reaction. During the propagation step, hydroperoxides are formed.[1] A method frequently used to follow the oil curing is the DSC monitoring of the peroxide decomposition peak during time. [2, 3, 4]. Since the oil polymerization affects its crystallinity, we propose here an alternative method to asses the oil curing. The melting peak of linseed oil samples is measured at different times of curing and compared with the profile of the peroxide decomposition peak over time. The comparison shows that the two phenomena are strongly correlated and that, when the maximum of the peroxide content is reached, the melting peak disappears. The study of the DSC melting peak is therefore proposed as a valid alternative tool to monitor the curing of an oil paint.

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ISG-like membrane thermodynamics: a stepwise calorimetric investigation

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Cells and vesicles functionalities, as well as membrane proteins' one, are strictly correlated to membrane lipid composition because of its influence on membrane thermodynamic stability [1-2]. Despite the numerous studies on model membranes carried out through calorimetric, spectroscopic and imaging techniques, model systems were considered with simple composition which does not keep into consideration the complexity and the asymmetry of the real bilayers [3] and the lipid thermodynamic reorganization [4-5].

In this frame, simulating the composition of real cell membranes might be a key point for the correct interpretation of membrane-based mechanisms in cells since each lipid modification might produce modifications of the molecular structure of such systems, which in turn might lead to variations of their physicochemical properties [6].

In this work we selected Insulin Secretory Granules (ISGs), vesicles located in the pancreatic Langerhans β-cells and which are responsible for insulin and amylin storage and secretion in response to nutrients intake, as reference system and we dissected the influence of several factors that may influence the physicochemical behaviour of real cell membranes, as membrane curvature, phospholipid tails' length and unsaturation, phospholipid headgroup, etc. We performed a thermodynamic study of different vesicles at physiological pH by using the micro-DSC technique. An ISG-like membrane was therefore obtained by mixing fourteen different lipids, achieving a composition which represents the 80% of the headgroups and an average of 80% of the tails in real ISGs [7]. The influence of cholesterol and different FFAs (stearic acid, oleic acid and elaidic acid) was investigated highlighting the magnitude of the effects on such a detailed membrane.

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Oral Presentations 3

Materials: Functional Materials, Ceramics, Metals & Alloys, Cements, Glasses and Composites

The use of thermo-mechanical technique to support the development of novel materials for additive manufacturing

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Additive manufacturing (AM) has been increasingly accepted in industry [1]. The filament-based technology known as Fused Deposition Modeling (FDM) is one of the widely used, mostly for functional parts [2]. In Fused Deposition Modeling, thermoplastic filaments for both model and support are fed into the heated extrusion print head, enabling three-dimensional (3D) dispensing of the resulting polymer melts on a platform, which is lowered step-by-step once each object's layer is completed. Layer by layer, the object is then printed. Knowledge of the impact of material properties and the mechanical properties of printed parts is of paramount importance to further expand the use of FDM. The FDM process is controlled by many parameters, which range from material filament type to machine setting such as: nozzle diameter and temperature, printing speed, feed rate, bed temperature, raster angle and width, etc. A completely different widespread 3D printing technique is Digital Light Processing (DLP) that relies on the use of photocurable resins [3]. DLP builds each layer by projecting each ones on a vat filled with resins. For both this two techniques there is the need for a detailed analysis about the rheological behavior of polymer melts to rationalize the effect of melt behavior on printing quality. Moreover a thermo-mechanical characterization of the blends is important in order to optimize the printing process.

In the present work, three different commercial polylactide (PLA) filaments were selected and printed with a commercial FDM printer, selecting a challenging 3D geometry with overhang printing. The filaments were thoroughly characterized by rheological, microscopic, and thermal techniques to explain the differences in the printing and tensile properties observed.

Moreover we present the use of polymer blends based on the use of epoxy resins thermally cured to enhance the thermal and mechanical properties of daylight curable resins suitable for DLP printing.

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Thermochemical characterization of polybenzimidazole with and without nano-ZrO_2 for ablative material application

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During the ballistic atmospheric re-entry a space vehicle has to withstand huge thermo-mechanical solicitations because of its high velocity and the friction with the atmosphere. According to the kind of the re-entry trajectory, the heat fluxes can be very high (> 10 MW/m^2) thus an adequate thermal protection system is mandatory in order to preserve the structure of the vehicle, the payload and, for manned mission, the crew. [1]

Ablative thermal shields have been used since the first Apollo mission and, after 50 years, they still represent the best choice to permit the ballistic atmospheric re-entry. Among ablative materials the Light-weight Ceramic Ablators (LCA) have been selected for several missions because of their low density and high efficiency. In particular carbon phenolic ablators are composite materials consisting of a phenolic resin matrix and a carbon felt as reinforcing phase. An example is represented by PICA, the carbon-phenolic ablator manufactured by NASA, and ASTERM, the European counterpart which is still in a developing phase. [2]

The carbon phenolic ablator decomposes at high temperature in absence of oxygen with an endothermic pyrolysis reaction: the solid reaction product is a carbonaceous residue with good mechanical strength and the gaseous products can flow throughout the porous material and hinder the convective exchange (blockage effect). Although this satisfying performance, the use of the phenolic resin presents environmental drawbacks and by new European rules its employment will be forbidden in the next years. For this reason a more environmental friendly solution was conceived and an high performance thermoplastic material, polybenzimidazole, was employed instead of phenolic resin. [1, 2]

Polybenzimidazole (PBI) was selected because of its good performance at high temperature and its high char yield: some PBI-ablative material samples were manufactured with and without the addition of nano-ZrO_2 and tested with oxyacetylene flame exposure showing promising performance in terms of recession rate and thermal insulation.

In order to understand the polybenzimidazole behaviour during the exposure at high temperature in a reducing atmosphere thermogravimetric analysis were conducted at different heating rates. [3]

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Thermal and multi-analytical investigations of the towers from Corvins' Castle, Hunedoara, Romania

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The present work is focused on the characterization study of ancient pottery shreds excavated recently from Corvins'Castle from Romania. The archaeometric study of some samples from the New Gate Tower, the main gateway to the Corvins'Castle, Romania, is presented in this paper, in order to identify the provenance of the raw materials, the manufacturing and weathering / deterioration processes of this tower.

Modern and performant analytical techniques, as Fourier-Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy, X-Ray Fluorescence (XRF), X-ray diffraction (XRD), optical microscopy (OM), Scanning electron microscopy (SEM-EDS), petrographic analysis, Induced Coupled plasma with mass spectrometry (ICP-MS), colorimetry and ion-chromatography are used and the results are discussed, too. All these results are correlated with thermal analysis techniques: Thermogravimetry (TG), Derivative Thermogravimetry (DTG) and Differential Scanning Calorimetry (DSC) with applicationa in the field of art and archaeology. The results obtained in this work by TG and DSC have been related with Fourier Transform Infrared Spectroscopy (FTIR), a well-established technique, confirming the relevant complementary nature of thermal analysis. Thermogravimetry (TG) allows for quantitative analysis of thermally stable volatile additives, and weight-difference curves offer a novel means for assessing oxidative stability. Also, the other used techniques that have been used for structure, composition and morphology evaluation, revealed the presence of quartz, dolomite and feldspar and plagioclase with varied size, as albite and microcline minerals. For the first time in the literature, for this monument the species hydroxyapatite has been identified and could be explain the consolidated resistance structure inside of the tower, identified at the tower bottom and at the pre-historic layer.

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Thermal and spectroscopic characterization of original and modern restoration mortars at Herculaneum archaeological site

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Mortar can be defined as a composite material composed of crystalline and amorphous phases containing inert as well as reactive aggregates in a calcitic binder. Its composition and characteristics can deeply change depending on construction period, location and function. Roman mortars, for their extraordinary durability, have attracted several researchers interested in developing the most effective way to restore ancient monuments [1]. Currently, the use of materials similar in composition and properties to the original ones for the restoration of masonry structures is strongly recommended. The purpose of this study was to evaluate mineralogical, elemental and thermal differences among Roman and modern mortars to find the critical aspects which facilitated the degradation.

A multianalytical approach, based on TGA/DTG, XRF and petrographic analysis, was used to analyse 33 bedding mortars, 31 plaster mortars and 30 joint mortars, collected from various houses at Herculaneum.

By triangulating the results of the three analytical techniques some correlations could be observed within each class of mortars.

Bedding mortars: foot traffic of visitors and the conservation conditions/location induce decay on mortar-based. All the samples collected from floors placed under shelters which let rainwater penetrate and pool showed peaks relative to sulphurous and chlorine compounds which increase degradation processes [1].

Plaster mortar: The sampled plasters could be sorted into two groups, based on their aggregate composition. However, a similar aggregate composition did not induce superimposable thermal behaviour, underlining the different ageing processes of the samples, with consequent changes in the ratios of components due to the conservation conditions [2].

Joint mortars: Original Roman and modern restoration mortars showed several common aspects in terms of mineralogical composition. However, Roman mortars and restoration mortars differ in terms of aggregate grain size distribution, binder/aggregate ratio even if similar raw inorganic materials were used (different Ca:Si ratio but identical Si:Al ratio). The use of incompatible restoration mortars have induced degradation processes as indicated by significant different amount of some elements, such as chlorine, sulphur and phosphorus [3].

All these differences affect mortar durability favoring the contamination agents attack and inducing crumbling.

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Multiferroic ceramic materials prepared by flash sintering methods

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Recently, it has been reported that by applying a modest electrical field, typically ~100 V cm^{-1}, across a sample while heating it into a furnace, produces a sharp increase in conductivity and electroluminescence accompanied of sudden sintering at low furnace temperatures [1]. This method is known as flash sintering and has become a hot topic in materials processing. Here, we show that even unstable compounds, such as $BiFeO_3$, which is a quite interesting mutiferroic ceramic for novel devices such as sensors or memories, could be prepared as a dense pure ceramic by flash sintering starting from $BiFeO_3$ nanopowders [2]. It should be taken into consideration that at temperatures required for preparation and processing of $BiFeO_3$ this material is unstable and decomposes into secondary phases that deteriorate it properties. Moreover, it is shown that nanostructured, pure and electrically homogeneous $BiFeO_3$ ceramic pellets are obtained by reactive flash sintering from a stoichiometric mixture of Bi_2O_3 and Fe_2O_3 applying a small electric field within seconds and at furnace temperature 200 ºC lower than that required in conventional solid-state reaction [3].

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New materials for environmental remediation: synthesis and characterization of LDH's REE–doped (REE= Rare Earths Element) for lanthanides recovery from waste

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At the Libiola mine site, an abandoned Cu-Fe sulphide mine located near Sestri Levante (Genova-Italy), the formation of Cu-rich precipitates immobilise not negligible amounts of rare earth elements (REEEs). These compounds are in equilibrium with neutral mine drainage (6,6<pH<7,8 and Eh≈230,5 mV), formed by the sulphides oxidation to generate acidic and metal-rich solutions, then buffered by surrounding (basic) rocks and/or diluted by alkaline stream water. The precipitates are mainly constituted by two different minerals: allophane, $Al_2O_3(SiO_2)_{1.3\text{-}2}\cdot 2.5\text{-}3H_2O$, and woodwardite, $(Cu_{1-x}Al_x)(OH)_2(SO_4)_{x/2}\cdot nH_2O$ which belongs to the LDHs (Layered Double Hydroxides). The crystal structure of LDH minerals consists of brucite-type layers in which a trivalent cation partially substitutes a divalent cation, both occupying the octahedral sheets. Due to their properties, such as their ability to easily exchange interlayer anions, these compounds are promising materials for different applications as carriers or scavengers of potential toxic anions [1]; just for this purpose, the study of the relationships between REEs and woodwardite is fundamental to allow the use of these minerals as REEs getter for both georemediation and georecovery exploitation.

In this work we report the results obtained in the synthesis, at different pH values, and the characterisation of Cu-Al-SO_4 LDHs doped with both light (La, Ce, and Nd) and heavy (Y and Gd) REEs. The aim is to determine the seizure mechanism of REEs, discriminating between structural incorporation/co-precipitation and absorption. The interesting compounds have been synthesised via co-precipitation route (direct method) [2] obtaining nanoscopic crystallites with a partially disordered (turbostratic) structure. The compounds carachterization has been performed by means of the following techniques: thermo gravimetric analysis (TG), X-ray analysis on powders (XRPD), scanning electron microscope analysis (SEM), infrared spectroscopy (IR), ICP chemical analysis. The concentration of REEs in the solid fraction was in the range of 3.5-8 wt %. The only REEs not incorporated in the LDH was La, which formed co-precipitated segregated phases. Heavy REEs showed a higher affinity than the light REEs, probably because of their lower ionic radius. Increasing the pH in the synthesis routine lead to an increase of REEs incorporated by the LDH, especially heavy REEs, but caused the oxidation of Ce (from 3+ to 4+) with the consequent formation of ceria. The REE-doped Cu-Al LDHs could be used as a precursor in the production of Cu- and REE-containing oxides through thermal decomposition. Due to its ion-exchange properties, the REE-activated synthetic LDH was also a promising material for Li batteries.

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Synthesis and crystallization pattern of lead-free perovskites by sol-gel and hydrothermal routes

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Inorganic perovskites are considered as emergent materials, both as nanopowders and thin films, in several research fields, ranging from photovoltaic applications [1], ferroelectric ceramics [2], piezoelectric devices for energy harvesting and sensing [3].

Among inorganic compounds displaying perovskitic structure, barium- and lead-containing materials are currently employed for their electronic performances. Two main drawbacks characterize these materials, namely the required high temperature annealing in order to develop the perovskitic structure, especially for multicomponent oxides, and the presence of toxic elements that have a significant impact on both production and disposal of materials.

For these reasons, the research turned to the development of lead-free perovskites, obtained from low-temperature synthesis methods, like sol-gel or hydrothermal routes [4].

In this work, lead-free titanium-based nanopowders are obtained by sol-gel synthesis performed in reverse micelle, together with a hydrothermal process. In particular, sodium and potassium bismuth titanates are investigated in terms of thermal evolution of the starting powders; at the same time, nanopowders based on Cerium and titanium oxides are produced and studied. In both cases, annealing temperatures lower than 600 °C allow the development of the desired perovskitic structures. A comparison between the powders obtained with and without the hydrothermal step is also presented, together with the preliminary evaluation of the electrical properties of the final powders.

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Thermal behaviour and microstructural characterization of natural clayey materials, sands, volcanic ashes and geopolymer composites

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This work was carried out as a part of a project aimed at the design and characterization of tailor-made geopolymers and their application and validation in the structural strengthening of architectural heritages. Geopolymers are ceramic-like inorganic polymers, consisting mainly of aluminosilicates, obtained from natural as well artificial materials (such as industrial wastes). These formulations are able to withstand aging, thermal stress (up to 1200 °C) and mechanical stress. The design of the geopolymer formulations include the selection of raw materials as well of industrial and/or natural wastes; the possible suitability of the following materials was therefore verified: clayey sediments, volcanic ashes from Etna Mount (currently considered as natural wastes), palagonitized tuffs, sediments used in various historical periods, non-dangerous industrial wastes.

The selected raw materials were characterized with a multi-analytical approach using, thermogravimetric analysis (TG), TG coupled with both evolved gas analysis by Fourier transform infrared spectroscopy (TG-FTIR) and differential scanning calorimetry (TG-DSC), and gas-volumetric measurements of the loss of CO_2 content.Thermogravimetric curves were recorded in a variety of experimental conditions. A TA Instruments thermobalance model Q5000IR equipped with an FTIR Agilent Technologies spectrophotometer model Cary 640 for evolved gas analysis (EGA) was employed. TG measurements were performed from 30 to 950 °C under air or nitrogen. TG-FTIR measurements were performed at a rate of 20 °C/min in the same temperature range under nitrogen flow from 600 to 4000 cm^{-1}. TG-DSC analysis on selected samples representative of each group of materials was performed from 30 to 950 °C by using a Netzsch STA 449 Jupiter instrument under nitrogen flow (25 mL/min). In general, natural clayey materials exhibit three or four different step of weight loss at about 60 °C, 250 °C, 500 °C and 700 °C. The first decomposition step is due to hygroscopic water. The other decomposition steps are related, respectively, to the structurally bonded water and decarbonation phenomena. In combination with gas–volumetric measurements of the loss of CO_2, a precise determination of bonded water was also possible. The data obtained were used to evaluate the specific features of possible raw materials and select the most suitable ones to use in formulations. The thermal stability properties and the physical chemical properties of geopolymer formulates based on metakaolin were then analyzed through thermogravimetry, DSC, and X ray micro-tomography.

The thermogravimetric profile of these samples shows a weight loss at about 60 °C caused by the evaporation of free water which is absorbed and trapped in small pores. The continuous weight loss from 200 to 800 °C was attributed by the condensation of hydroxyl group. Micro computed tomography analysis was performed by using a Bruker SkyScan 1174v2 and the results are under evaluation.

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Phase relations in the Al_2O_3-TiO_2-SiO_2 system

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Rutile (TiO_2) coatings deposited on corundum (Al_2O_3) are supposed to actively filter the $MgAl_2O_4$-spinel phase from Al-based molten alloy. Al melt can then react with TiO_2, reducing it into sub-oxides and metallic titanium. In Si-containing Al alloy, $Ti_5(Si,Al)_3$, $Ti(Al,Si)_3$, and ternary phases can form. Therefore, to model chemical reactions at the interface between ceramic filter and Al melt, thermodynamic database of the Al-Mg-Ti-Si-O system is necessary. As a part, the thermodynamic description of the Al_2O_3-TiO_2-SiO_2 system is needed to model oxide melts.

The binary Al_2O_3-TiO_2, TiO_2-SiO_2, and Al_2O_3-SiO_2 systems were repeatedly studied experimentally, and their thermodynamic databases are available. The Al_2O_3-TiO_2-SiO_2 system was poorly investigated [1,2]. For the vertical Al_2TiO_5-SiO_2 section [1], there are contradictions to the phase rules. The system was also assessed thermodynamically, including the modelling of liquid miscibility along the TiO_2-SiO_2 side [3,4]. Thus, the present work is aimed at an experimental study of the phase relations in the Al_2O_3-TiO_2-SiO_2 and Al_2TiO_5-SiO_2 systems to verify the inconsistencies, and their thermodynamic modelling using new experimental data as well as literature data on thermodynamic functions.

Samples were prepared by the controlled co-hydrolysis [5]. To investigate phase equilibria, samples were annealed and air-quenched followed by XRD examination. The microstructure characterization was carried out using SEM/EDX. Solid phase transformations and melting behaviour of the samples were studied by DTA.

Isothermal sections of the Al_2O_3-TiO_2-SiO_2 system at 1250 and 1400°C and its Al_2TiO_5-SiO_2 section were constructed based on the obtained results. On liquidus of the ternary system, the temperatures of invariant reaction were detected. To model the system using the CALPHAD approach, CEF was used to describe the solid solutions and a two-sublattice partially ionic model was used for liquid.

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Development of phases in the sol-gel derived mixed-metal-oxide (Al_2O_3-TiO_2-ZnO) functional sorbent material

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Currently the most thermodynamically efficient power conversion technology; integrated gasification combined cycle (IGCC), reposes on turning conventional cheap carbon based fuels into syngas. Syngas can be stripped from impurities (primarily sulphide based) to achieve process efficiency and turbine protection in the high temperature desulfurization process (HTGD). Zincite was already shown as proven constitute of major regenerable HTGD sorbents.

Here we investigate Aluminium-Titanium-Zinc mixed-metal-oxide system as a candidate for HTGD sorbent material. We expand composition to alumina and titania to facilitate mechanical durability and thermochemical stability, respectively.

Sol-gel samples were prepared in wide compositional range from gahnite to Zn-titanate spinel; i.e. gahnite was Ti-doped on the account of Al (0-100%). We monitored the thermal and structural evolution, to observe different mechanisms of phase formation, as a function of doping and temperature conditions.

The significance of this work is the precise identification of the stability ranges of observed solid-solutions, whereas gahnite spinel and zinc-titanate spinels can interchange cations only in limited amounts, depending on the conditions, as confirmed from the structure refinement. It was observed that at high-temperatures solid-solutions exhibit quite different stability. More important, observed partial phase-separation at low-temperatures (which occur on behalf of different hygroscopy of the (Al,Ti)-Zn gels) significantly precludes the mechanisms of phase development at high-temperatures. Thereof, intermediate Zn-based phase was found to be responsible for the facilitated early zincite crystallisation. Microstructure and texture were commented accordingly.
Performed characterisations allowed discussion what are the best compositions and conditions for the preparation of the ultimate sorbent.

Impact of thermal analysis in the study of composite photocatalysts with layered type of structure

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Photocatalysts with layered type of structure are known as materials for hydrogen production by water splitting using sunlight energy. Interactions of crystalline oxides with different water solutions lead to processes which can influence the properties of oxides: intercalation of water and other molecules into the interlayer space and ion exchange of alkali cations to protons typically affect the photocatalytic activity.

The way to increase the photocatalytic activity of layered oxides is to use composites as organic-inorganic hybrids. They present a promising class of materials for electronics, chemical technology, environment due to the combination of organic and inorganic properties within the molecular scale. Recent developments in the preparation of inorganic–organic hybrid materials from layered compounds focus on the intercalation and grafting reactions.

Thermal analysis is an effective way to investigate composite materials. Thermochemical investigation is powerful not only from point of view of thermal stability but to determine the composition of samples and in case of intercalates to reveal the nature of bonding of inserted molecules with crystal structure as well.

Herein it will be reported results of the study on thermal stability and determination of composition of protonated, hydrated and hybrid organic-inorganic materials based on perovskite type layered titanates belonging to Ruddlesden-Popper phases with different thickness of perovskite blocks. As hybrids it will be considered crystalline complex oxides intercalated by methylamine, butylamine, methanol, ethanolamine etc.

Simultaneous thermal analysis (TG+DSC) coupled with mass-spectrometry (QMS) for gas evolution, FTIR-spectroscopy, powder XRD, SEM were used for the characterization of synthesized hybrids and investigation of their thermodegradation. Advantages of TG coupled with MS for the quantitative analysis of the composition of new hybrid organic-inorganic perovskite type compounds will be considered in comparison with ICP and CHN-analysis.

The basic for the discussion will be the content of organic and water molecules intercalated in the interlayer space of layered structure, the evolution of cell parameters and distances between perovskite blocks accompanied the formation of hybrids, possibility of grafting with formation of covalent binding, the relative thermal stability of organic-inorganic compounds depending on the type of structure, the nature of rare-earth atoms, the type and size of the organic intercalate. Results of the investigation of photocatalytic hydrogen evolution from different solutions and significant increasing in photocatalytic efficiency of hybrids will be presented.

Research was performed at the Research Park of St.Petersburg State University: Center for Thermal Analysis and Calorimetry, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Chemistry Educational Center. This work was supported by the Russian Science Foundation (grants № 19-13-00184).

Thermolysis of organic-inorganic perovskite-type layered titanates

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Organic-inorganic perovskite type compounds present the promising class of materials for electronics, chemical technology, environment due to the combination of organic and inorganic properties within the molecular scale. Recent developments in the preparation of inorganic–organic hybrid materials from layered compounds focus on the grafting reactions and preparation of two-dimensional hybrids and monolayers through exfoliation. Using of these compounds in different areas of application depends on their thermal and chemical stability.

It will be reported results of thermal stability of organic-inorganic materials based on protonated forms of perovskite type layered titanates $HLaTiO_4$ and $H_2La_2Ti_3O_{10}$ (Ln = La, Nd) belonging to Ruddlesden-Popper phases with different thickness of perovskite blocks. Objects under investigation are crystalline complex oxides intercalated by methylamine, butylamine, methanol and ethanolamine.

Thermal analysis (TG+DSC) coupled with mass-spectrometry (MS) for gas evolution, FTIR-spectroscopy, powder XRD, SEM were used for the characterization of synthesized oxides and investigation of process of their thermodegradation. Advantages of TG coupled with MS for the quantitative analysis of the content of new hybrid organic-inorganic perovskite type compounds will be considered in comparison with XPS and CHN-analysis.

It will be discussed the content of organic and water molecule intercalated in the interlayered space of layered structure, the evolution of cell parameters and distances between perovskite blocks accompanied the formation of hybrids, possibility of grafting with formation of covalent binding, the relative thermal stability of organic – inorganic compounds depending on the type of structure, the nature of rare-earth atoms, the type and size of the organic intercalate.

Scientific research were performed at the Research Park of St.Petersburg State University: Center for Thermal Analysis and Calorimetry, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Magnetic Resonance Research Centre, Center for Optical and Laser Research and Interdisciplinary Center for Nanotechnology

This work was supported by Russian Foundation for Basic Research (grant 18-03-00915) and Russian Science Foundation (grants № 19-13-00184).

Investigation of structural, optical and magnetic properties of $Ni_xZn_{1-x}Fe_2O_4$ ($0\leq x\leq 1$) spinel based nanopigments

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Considering the high resistivity, permeability, surface area, Curie temperature, mechanical hardness and chemical stability and low dielectric loss in high-frequency devices, mixed nickel-zinc spinel ferrite has attracted wide interest, showing a high potential in applications such as catalytic degradation of organic/inorganic pollutants, magnetic resonance imaging, hyperthermia treatment, drug delivery systems, magnetic heads, electric transformers, high-frequency data transfer, charge particle deflection yoke [1,2,3,4].

$Ni_xZn_{1-x}Fe_2O_4/SiO_2$ nanocomposites were synthetized using a modified sol-gel method. The thermal analysis revealed the formation of Ni-, Zn- and Fe-succinate precursors at 130–200 °C and their decomposition to ferrites at 220–400 °C. Fourier transformed infrared spectroscopy confirmed the formation of succinates and their decomposition into ferrites. The transmission electron microscopy images revealed spherical shape nanoparticles with size increasing with annealing temperature. The magnetic properties such as saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c) and anisotropy (K) depended on the Ni content and annealing temperature. The shape of hysteresis loops revealed the dependence of superparamagnetic behaviour on the structure, and a strong correlation between the ferrite-based pigment colour and annealing temperature.

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Spotting the difference of the thermal behaviour of structurally-related mono- and dicationic ionic liquids

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Ionic liquids (ILs) are salts composed of an organic cation and an organic or an inorganic anion which are liquid at or near room temperature. ILs have attracted a great deal of interest in the last 20 years due to some unique physicochemical properties such as the large electrochemical window, the chemical and thermal stability, and the negligible volatility, to mention a few [1]. Dicationic ionic liquids (DILs), a subset of the ionic liquid (IL) family, have attracted growing interest in recent years, and the range of applications within which they are investigated is constantly expanding. These ILs seem to differ from the traditional monocationic ones in many ways offering a growing portfolio of possible applications [2, 3].

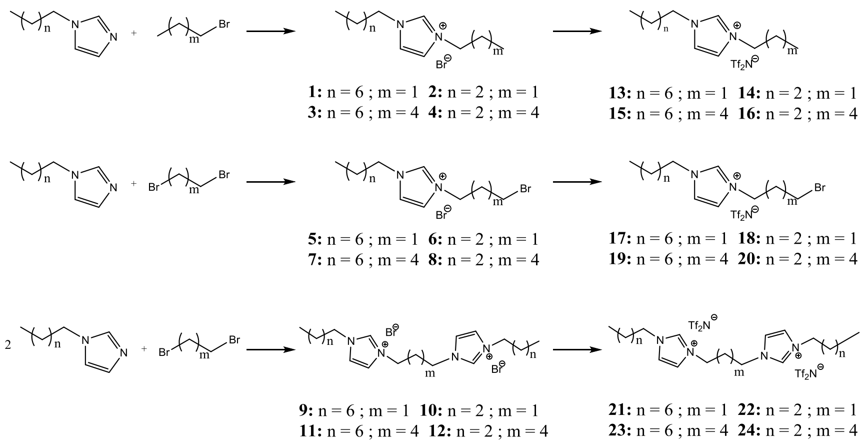

Figure 1. Synthesized mono- and dicationic ionic liquids.

Herein the thermal behavior of 24 ILs, belonging to two structurally-related families with either bromide or Tf_2N as counteranion, was analysed (Figure 1). For bromide mono- and dicationic ionic liquids (DILs), thermal gravimetric analysis showed similar decomposition events, while all Tf_2N DILs displayed higher stabilities than the corresponding monocations. Differential scanning calorimetry analyses of most of the (D)ILs only showed glass transition temperatures, a behavior in agreement with the broad liquid range of ILs. The impact of the cationic structure and/or of the type of anion on the above-mentioned transition temperatures has been studied.

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GUL cement degree of hydration of mortars with & without SCMs

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Cementitious materials degree of hydration is a key measure for quantifying the properties of concrete and mortar, including compressive strength and durability. Experimental studies of Portland cement hydration with and without supplementary cementitious materials (SCMs) using Calorimetry and thermogravimetric analysis (TGA) have been reported in the scientific literature. Furthermore, statistical and phenomenological models have been postulated to estimate the cementitious materials degree of hydration based on binder composition, chemical/physical properties, water to binder ratio, curing condition and age. The aim of this study is two folds; firstly to experimentally measure the effects of SCMs on the hydration of Portland-limestone cement, and secondly to evaluate the accuracy of cement hydration models, specifically the models developed by Riding et al. [1], Schindler and Folliard [2], and Wang [3] referred to in this study as Models A, B and C, respectively.

Four mortar mixes containing Portland-limestone (CSA type GUL) cement with and without 8% silica fume (SF) and/or 30% ground granulated blast-furnace slag (GGBFS) were studied. The binder hydration was quantified using Calorimetry and TGA methods up to 220 hours. Calorimetry and TGA experimental results were found to be consistent. Models A and B results at all ages were found to consistently underestimate GUL cement hydration degree up to 220h. The exception was Model B's good estimates of the mix containing GUL+SF+GGBFS. Model C results were found to overestimate the GUL cement hydration degree up to 50h and to have good estimates thereafter to 220h. Closer examinations reveal that all 3 models fail to capture the peak of the heat flow at early ages. Model A was then modified to analogously follow Model C accounts for limestone in cementing materials by considering the extra water available for cement particles (dilution effect) and the extra surface area provided by limestone for hydration products to grow. Comparing the results of Model A and modified Model A, referred to as Model D, a significant improvement in the estimates is observed. Model A and D peak of heat flow for GUL, GUL+GGBFS, GUL+SF, and GUL+SF+GGBFS percent errors decreased from 44%, 37%, 40%, and 28% to 4%, 1%, 8%, and 9%, respectively. The percent errors of Model A and Model D estimates of the binder hydration degree at 220h for GUL, GUL+GGBFS, GUL+SF, and GUL+SF+GGBFS decreased from 14%, 12%, 10% and 0% to 6%, 4%, 3% and 6%, respectively. The experimental results revealed that cement hydration model with specific account for limestone, such as Model D, is required to estimate hydration of mixes containing GUL cement.

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Simultaneous thermogravimetric and differential thermal analysis determination of products formed during hydration of blended Portland cement doped with zinc

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With the increasing use of secondary raw materials and alternative fuels in the cement production industry, the amount of present trash elements rapidly increases. Most of these problematic elements affect the quality of produced clinker or blended cement. This study focuses on zinc and his influence on the hydration process and the formation of new products. Zinc was added in the form of $Zn(NO_3)_2$, $ZnCl_2$ and ZnO) in higher concentration (1 - 20 % weight) for modelling of the formation or modification of newly formed products. These new phases were precisely characterized via simultaneous thermogravimetric (TG) and differential thermal analysis (DTA). Infrared spectroscopy (FT-IR) and X-ray diffraction method (XRD) with a high-temperature chamber was used for complementary analyses and more accurate analysis of newly created phases and compounds during the whole period of hydration.

Thermal and biological properties of several composite materials prepared by sol-gel method

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Zirconia/hydroxyapatite composites were synthesized by means of the sol-gel method. The aim of this work is to identify the temperature able to induce specific degradation phenomena or structural reorganizations, which are essential information to explain the relationship between the different biological responses recorded after exposure to the materials to the temperatures of the applied post-synthesis heat treatments.

The zirconia matrix and pure Hap were synthesized using Zirconium propoxide solution and calcium nitrate tetrahydrate and phosphorus pentoxide as precursors. Finally, the composites were obtained by adding different amounts of zirconia sol to the HAp one. The thermal behavior of all the materials was studied. The TG/DTG curves of all the samples, before thermal treatment and after 120° heating, suggest that the thermal treatment at relatively low temperature does not modify the thermal behavior of these composites. The results of the FTIR spectra of the gaseous mixture evolved during the TG experiments of fresh samples and their composites at different temperatures show that in all the samples the heating up to about 600 ° C allows the complete degradation of the organic substance and of the nitrate ions. SEM microscopy suggests that all samples, regardless of the thermal treatment, are homogeneous composites. Furthermore, the XRD spectra of the composite materials treated at 120°C revealed that they are amorphous, while at 600 and 1000°C, their crystallinity decreases with increasing the content of zirconia; the presence of HAp favours the crystallization of the zirconia matrix in the tetragonal phase [1].

The effects of the HAp content and heating on the biological performances of ZrO_2 were evaluated using NIH-3T3 cells. The biological results suggest that the materials heated to 100 °C improves the cellular vitality compared to those treated to 600°C [2]. Probably these effects are due to the modification of the materials' structure induced by heating.

In conclusion, the results of the study of thermal behavior and biological characterization allow to identify the best temperatures able to improve cell proliferation and vitality.

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Early hydration stages of iron ore and high initial strength Portland cement composites: a study by non-conventional DSC and calorimetry

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This work presents a study of the early stages of the hydration of composites formed by iron ore tailings and a high initial strength Type V Portland cement. Initially analyses by Non-Conventional Differential Thermal Analysis (NCDTA) [1-3] were compared with those performed by using a conventional isothermal calorimetric instrument, made by Calmetrix model ICAL2000. Two types of iron ore tailings (IOT) from a large Brazilian Iron Ore Unit Beneficiation were evaluated: **RF** and **RL,** respectively, from flotation and hydrocyclone steps. For both methods, the composite hydration reaction was analyzed on real time at 27°C, during the first 24 hours of hydration. The cement mass substitution degrees by the tailings were: 0% (cement paste), 5%, 15% and 30%. Despite the operating differences between the methods, the results showed good similarity and, as a good data correlation factor was found in between, NCDTA data were transformed to Non-Conventional DSC (NCDSC) data.

The different cement substitution degrees by tailing do not cause significant changes on respective pre-induction, induction and acceleration times, being perceptive only a little time increment on the accelerating period for one case (30% RF). However, this generates 50-60% more heat, when compared to the reference case, on same calorific capacity basis. Effects of RF and RL were very similar, but the latter seem to be more important, probably due to their finer grain sizes. A perfect linear correlation (R2 > 0.99) was found between the substitution degree and the energy generated during hydration for all cases, with good prediction for other IOT's contents, which indicates that the tailing components react during the early stages of hydration. The demand for sustainable applications of these tailings is huge, and this study brings important contributions for its practical application.

Keywords: Iron ore tailing-cement composites, Hydration, Isothermal Calorimetry, NCDTA, NCDSC

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Early hydration stages of iron ore tailings and high initial strength Portland cement composites: a study by thermogravimetry

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Thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to analyze the early stages of hydration of Iron Ore tailings and High Initial Strength Portland Cement Composites within the first 24 h of setting. This paper complements a previous calorimetric performed study of the same stages. Two types of iron ore tailings (IOT) from a large Brazilian Iron Ore Unit Beneficiation were evaluated: **RF** and **RL,** respectively, from flotation and hydrocyclone steps. The cement mass substitution degrees by the tailings were: 0% (cement paste), 15% and 30%. Thermal analysis was performed by using a SDT Q600 from TA Instruments, with and initial isothermal step at 35ºC to release free water, followed by a 10 ºC.min^{-1} constant heating rate step, up to 1000ºC, at the ages of 1h (only reference paste), 8 h and 24h. A discussion of original cement analysis and that of 1h hydration cement paste allows interesting observations and original gypsum content calculation [1].

For an appropriate comparative analysis between composites and the reference, the original thermal analysis curves were converted from the initial sample mass basis to their initial cement mass basis [2-3]. Converted curves showed good similarity for onset and offset times and peak positions, and furthermore, the observations and conclusions are in line and corroborate with the previous calorimetric study. The use of the tailings caused an acceleration of the first hydration reactions, especially for the aluminates, which leaded to the formation of calcium mono carboaluminate. For 30% of cement substitution, the measured water loss percentage of RL and RF pastes, due to ettringuite, tobermorite and other alluminated hydrated phase dehydration, was more than 180% higher of that of the reference. It was noted a higher effect for RL type tailings, probably due to their finer grain sizes. The results corroborate the importance of understanding the tailings effects on cement-based materials hydration.

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Thermal debinding of multicomponent binder used for powder injection moulding of Al_2O_3 powder

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The aim of this research was to produce biomaterials by injection moulding and powder sintering. This technology requires the use of a precisely selected binder which not only plays an important role in injection moulding process but also can not cause contamination resulting from the binder removal process, which would lower the functional properties. In this work, the binder plays two different roles. One as a conventional binder used for PIM and second as pore-forming material. For that reason, the multicomponent binder system based on thermoplastic polymers (PP, HDPE and EVA), paraffin wax (PW) and stearic acid (SA) were used. The moulded green samples were subjected to solvent and thermal debinding. After binder removal, the brown samples were sintered at five different temperatures in the range of 1200-1600°C using heating rates, which provides a large open porosity and relatively high strength and low shrinkage. DSC studies have shown that HDPE/PP, EVA/PP and HDPE/EVA/PP blends have quite stable melting points of individual components. The melting point of HDPE or PP used in the blend drops only by about 1 °C relative to the pure polymer. Only the addition of paraffin has a stronger effect on the plasticisation of the main ingredient of the blends.

The thermogravimetric test results show a narrow range of homopolymer degradation, and the use of HDPE/PP blends does not change much. The use of the EVA copolymer tends to be more interesting due to the wide temperature range thermal degradation, which depends also on the atmosphere used. Torque measurement during mixing and rheological behaviour of feedstock has been analysed. Results of rheological behaviour confirm that the increase of SA causes the lowering of polymer-powder slurry viscosity. The optimum stearic acid content of 6% was selected based on the torque curves of the various mixtures. The tested polymer-powder slurry is undoubtedly characterised by good rheological properties, and the performed DSC and TGA tests enable the selection of conditions for the homogenization of mixtures and degradation of the binder, respectively.

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Effect of cooling rate on characteristic temperatures and microstructure development of AlSi9MgMn alloy

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Aluminum alloys are widely applied in automotive, aircraft, food and building industries. Multicomponent AlSi9MgMn alloy intended for high pressure die casting (HPDC) has not been classified in international norm, neither EN nor AA, only briefly described in manufacturer norm [1]. Addition of particular alloying elements such as magnesium as well as manganese and iron can improve mechanical and technological properties of casting in dependence from solidification behaviour. Therefore, it is necessary to understand the influence of low cooling rates on characteristic transition and precipitation temperatures in relation to microstructure development.

Thermodynamic calculation and thermal analyses revealed solidification sequence with corresponded temperatures in correlation to microstructure investigation as follows: development of primary dendrite network, precipitation of high temperature $Al_{15}(Mn,Fe)_3Si_2$ phase, main eutectic reaction, intermetallic iron-magnesium phase precipitation $Al_8Mg_3FeSi_6$ and secondary eutectic phase $\alpha_{Al} + Mg_2Si$ as a final solidifying phase [2].

Solidification behaviour was investigated *in situ* through establishing the characteristic temperatures of phase transition and precipitation at low cooling rates started with the lowest 0,17 K/s till highest 19,49 K/s compared with those obtained by numerical simulation for HPDC at 63 K/s. Increase of cooling rate lower the characteristic temperatures and narrow the solidification interval of AlSi9MgMn alloy. It also changes the solidification manner and morphology of microconstituents. Higher cooling rate influences on refining of microconstituents in particularly primary dendrite network in particularly secondary dendrite arm spacing (SDAS). Correlation of microstructure features investigation and cooling rate reveals significant morphology change of intermetallic $Al_{15}(Mn,Fe)_3Si_2$ phase from irregular coarse morphology at lowest cooling rate, Chinese script morphology at medium one and globular morphology at highest cooling rate [3].

Correlation of characteristic temperatures during solidification process and obtained microstructure of multicomponent AlSi9MgMn alloy in low cooling rate conditions comprehends to evaluation of applicability of this material for thick-walled safety critical parts and sets in automotive industry.

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Thermal stability of retained austenite in isothermally held 0.18C-4Mn-1.7Al bainitic steel

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Medium manganese steels are a new grade of automotive sheet steels, which usually contain from 3 to 12% of manganese [1]. The manganese content should increase the amount of thermally stable retained austenite at room temperature [2]. Retained austenite is an important structural constituent of this group of steels because it is responsible for the transformation induced plasticity effect (TRIP effect) enhancing the steel ductility [3]. That's why it is important to know how different heat treatment schedules influence the stability of retained austenite. For this kind of analysis the dilatometric study is a very good way to determine a phase transformation kinetics and its effect on the amount and thermal stability of retained austenite [4].

The present work aims at using dilatometric tests for the analysis of phase transformation kinetics of the steel with untypical 4% manganese content. The steel was subjected to isothermal holding treatments at temperatures of 400 and 350°C for different holding times, from 15 min to 1 hour. The obtained results showed the influence of temperature on a rate and time of bainitic transformation, which directly affect the thermal stability of retained austenite. The microstructure analysis was performed by means of light and scanning electron microscopy. The microstructure analysis and advanced XRD studies allowed to determine the phase composition and other morphological features of the multiphase microstructures.

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Thermodynamic consideration of Al-2,2Mg-2,1Li alloy behaviour

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The mechanical properties of aluminum (Al) – magnesium (Mg) – lithium (Li) alloy are the result of microstructural constituent's development during solidification [1, 2]. During solidification, development of microstructural constituents' is influenced by chemical composition, thermodynamic parameters and processing parameters.

This research was conducted in order to assess the influence of thermodynamic parameters on solidification of Al based alloy containing 2,2 mass.% Mg and 2,1 mass.% Li. Solidification under equilibrium and non-equilibrium conditions were comprehended, respectively. Equilibrium considerations were obtained using Computer Aided Thermodynamic Diagram Calculation (CALPHAD), while microstructural analysis under more realistic conditions required combination of Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD). The equilibrium solidification calculations obtained using CALPHAD are given in Table 1.

Table 1. Equilibrium solidification sequence of Al-2,2Mg-2,1Li alloy

Reaction No.	**Reaction**	**Temperature,**
1	$L \rightarrow \alpha_{Al}$	640
2	$\alpha_{Al} \rightarrow \alpha_{Al}'$+AlLi (δ)	380
3	$\alpha_{Al}'+\delta \rightarrow \alpha_{Al}''$+ Al_2LiMg (T)	290
4	$\alpha_{Al}''+\delta \rightarrow \alpha_{Al}'''$+ Al_8Mg_5 (β)	89

Equilibrium solidification begins with transformation of α_{Al} dendritic network at 640°C followed by precipitation of stabile δ phase at 380°C. Precipitation of δ phase is a result of reduced solubility of Li in α_{Al} and high Li/Mg ratio (0,95). The ternary T phase precipitates at 290°C from balked α_{Al}'' matrix reach in Mg. The solidification ends with precipitation of secondary eutectic β phase at 89°C.

However, microstructural analysis under more realistic conditions indicated precipitation of metastable Al_3Li (δ') phase that was not covered by the predications. Metastable δ' phase precipitates after transformation of α_{Al} matrix as a result of reduced solubility of Li due to the Mg influence. The δ' phase presents a main strengthening precipitate in Al-Mg-Li alloys.

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Effects of homogenization conditions on the microstructure evolution of aluminium alloy from series 8XXX

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Industrial production of products, such as foil and aluminium alloy strips, begins with the production of semi-finished products in the form of bars. These are produced by the continuous casting process, which is quick and does not allow equilibrium conditions of solidification. Non-homogeneity, such as micro and macro segregation, non-equilibrium phases and microstructural constituents, as well as stresses arising during non-equilibrium solidification, are eliminated by means of homogenization annealing. In this way a number of technological difficulties in the further processing of semi-finished products can be avoided.

The aim of the study was optimization of the homogenization annealing of the EN AW 8006 alloy. With the Thermo-Calc software, a thermodynamic simulation of the equilibrium and non-equilibrium solidification was performed and the equilibrium phase diagram was calculated. Differential scanning calorimetry (DSC) was made on selected samples in as-cast state and after various regimes of homogenization annealing and also used for simulation of homogenization annealing. Using the light microscope (OM) and the scanning electron microscope (SEM) the microstructure of the samples was examined, whereas the microstructural components were analysed using the energy dispersion spectrometer (EDS). On the basis of all the results was concluded that the homogenization annealing has already been carried out after 8 hours at 580 ° C to the extent that the material is suitable for further processing.

Crystallization behavior of Co-9Al-9W superalloy

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The aim of the study is to determine the crystallization behavior of γ–γ′ Co-9Al-9W (at.%) superalloy by thermal analysis methods. For description of casting solidification and crystallization process the thermal derivative analysis (TDA) was utilized.

The alloy with composition Co-9Al-9W (at.%) was produced via induction vacuum melting using furnace VSG 02 Balzers. In order to differ the crystallization conditions, different types of molds were examined. First casting was made using cold graphite mold. For further casting processes aided by TDA analysis, sand molds with different temperature (respectively room temperature and 500 °C) were used. The solidification process was recorded by a Crystaldigraph PC-8T apparatus. During crystallization of sand castings, the temperature was recorded by S type thermocouple mounted in the mold. Each casting was further evaluated in view of primary microstructure by optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction analysis (XRD). Moreover, in order to investigate the thermal behavior of obtained casts and verify the *solidus* temperature obtained via TDA method, the differential thermal analysis (DTA) was performed up to 1500 °C using NETZSCH STA 449 F3 Jupiter thermal analyzer. The measurements were carried out under Ar. atmosphere with heating rate 20 °C s^{-1}.

The analysis of TDA curves allowed to determine *liquidus* and *solidus* temperatures under different cooling rates. In each case, the *liquidus* temperature was ca. 1450 °C, whereas *solidus* was approximately 1380 °C. The results obtained via TDA method were in accordance with DTA cooling curves, which showed similar values of *solidus* temperature. Moreover, TDA analysis revealed some slight thermal effect at temperature above 900 °C. At similar temperature, DTA analysis revealed occurrence of effect corresponding to γ′-precipitation.

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Effect of Ni on solidification of duplex low-density steels

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Recently, low-density Fe–Mn–Al–C steels have attracted attention, as they have low density with excellent combinations of strength and ductility. They can be classified into three categories: ferritic steels, duplex steels and austenitic steels, depending on the microstructure. Solidification of two duplex low-density steels was investigated. Two steels Fe–15Mn–10Al–0.8C and Fe–15Mn–10Al–5Ni–0.8C steel were produced in vacuum induction furnace under Ar atmosphere and re-melted in a simultaneous thermal analyser. The influence of Ni on the solidification process was analysed with thermodynamic calculations and differential thermal analysis. The samples were analysed with light optical and scanning electron microscopy. The distribution of elements between the ferrite and austenite phase were determined. Thermodynamic modelling was done by Thermo-Calc using the CALPHAD method. Good correlations were found between the theoretical values and the experimental results.

Evolution of Fe based intermetallic phases during homogenisation of Al-Fe hypoeutectic alloy

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Homogenization is the first heat treatment that is performed for most aluminium alloys prior to any deformation process. Homogenization is performed to counter microsegregations, which are the result of non-equilibrium solidification caused by diffusion rate differences between solid and liquid state during solidification. For the purpose of this paper, a hypoeutectic Al-Fe alloy containing 1.1 wt.% Fe was homogenized at 600 °C for up to 12 h in an electric furnace. After the homogenization heat treatment differential scanning calorimetry (DSC) was performed and the homogenized samples were compared with the as-cast state. The results were compared with thermodynamic calculations using Thermo-Calc software in order to determine the differences between the microstructure in equilibrium and non-equilibrium state. All samples were analysed using optical and electron microscopy, where intermetallic phases were qualitatively assessed with both methods. Furthermore, energy dispersive spectroscopy (EDS) was required to determine the type of phases present in all samples and a difference between the as-cast and homogenized state was apparent. The presence of metastable phases in the as-cast state and the transformation of such phases during the process of homogenization was confirmed. A homogenization process, lasting 12 h at 600 °C was also performed with a DSC instrument. The experiment confirmed a larger heat transfer at the beginning of homogenization which is in agreement with all previous analysis. All results have shown that after 6 h of homogenization, the effects of non-equilibrium solidification in this alloy have been sufficiently countered.

Oral Presentations 4

Polymers, Bio(macro)molecules & Biocomposites, Life science and Organic & Functional complex compounds

Use of thermogravimetry for qualitative and quantitative analysis of microplastics in soils

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Fragments of plastics (microplastics) are currently considered as contaminants harmful for various environmental compartments and biota. In soil, their analysis is hampered by soil matrix complexity and certain chemical and physical similarities between some plastics and soil organic matter. For this reason, the methods for identification are time consuming and laborious due to the need to separate the microplastics from soil matrix, and therefore, approaches for direct microplastics analysis are of importance.

Recently, we have reported several approaches for direct analysis of microplastics in soils including analysis of gases evolved from thermally degraded plastics (evolved gas analysis) [1] and comparison of mass losses obtained by thermo-oxidative degradation (thermogravimetry, TG) [2]. The latter includes two approaches, the first one uses non-contaminated soil, while its TG record is subtracted from the TG record of soil containing microplastics. In the second approach, the uncontaminated soil is replaced by a combination of equations, which reflect the mutual relationship between various soil compartments derived from natural soils and represent a soil universal model.

In this work, we describe the development and validation of the TG approaches for detection of a wide range of microplastics including PET, PE, PVC, PS and PHB. In particular, we show the development and testing of all possible scenarios and discuss the weaknesses and positives of the developed approaches.

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On the trail of heat - Isothermal microcalorimetry as a real-time monitor for bacterial contamination

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The detection of bacterial contamination is one of the most important and incessant aspects of quality control in pharmaceuticals [1], water [2] and food [3]. Standardized techniques rely on the optical alteration of samples in the way of so-called colony forming units (CFUs) that grow on selective culture media. The colony-forming units to be counted with the eye thus allow conclusions to be drawn about the initial bacterial concentration of the samples. The basic assumption is that one colony is formed per bacterium in the sample.

A temporal advantage would be the detection of a physical quantity that behaves additive and already dependent on the initial number of bacteria of the respective contamination. This kind of physical quantity would be, for example, the metabolic heat produced by every living bacterial cell. A suitable detector would be a thermocouple that could track the heat flow generated during the growth of bacteria in real time. These considerations find practical application in a high-performance isothermal microcalorimeter (IMC) which can detect the smallest traces of microbial contamination [4].

In our study, we investigated the practicability of classical cultivation techniques in the context of IMC measurements using *Lactobacillus plantarum* and *Pseudomonas putida* as model bacteria for an anaerobic and aerobic system, respectively. For this reason, we have monitored bacterial growth on and in solid and liquid culture (SC and LC) media using IMC. Our results demonstrate that IMC monitoring provides a reduced detection time in both SC and LC. In addition, the use of classical enrichment methods such as membrane filtration offers another possibility to detect bacterial contamination even earlier. By using a simple physical model, we were able to confirm that the initial bacterial concentration (determination via CFUs) allows a linear correlation with the detection time regardless of the cultivation technique used. The latter enables the quantitative determination of specific bacterial contaminations on the basis of classical cultivation conditions within the framework of microcalorimetric monitoring.

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Peculiarities of the calorimetric monitoring and thermokinetic analysis for anaerobic, microbial growth and product formation – from laboratory to technical scale

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Microbial driven biological conversions are used to synthesize industrial relevant products from readily available feeding materials. Anaerobic bioconversions are particularly favourable because a large proportion of the energy of the feeding material is found in the final products. This makes anaerobic bacteria for example interesting for the production of gaseous and liquid biofuels. Real time monitoring tools are essential to effectively control such industrial applications to increase productivity, product quality, and process stability. Given that metabolic heat flux measurements reflect changes in stoichiometry and kinetic of bioconversion processes immediately, calorimetry has the potential to be a great tool for monitoring such processes [1, 2]. However, the higher energy content, lower level of oxidation, of the products of anaerobic bioconversions also means that less energy is dissipated as heat throughout the conversion process. These tiny heat production rates are challenging the calorimetric monitoring and difficulties may arise to apply enthalpy balances for data interpretation. Particularly in the development of thermokinetic models, the combination of metabolic heat signals with metabolic reaction sequences from traditional reactor sampling and monitoring could prove to be intricate.

For exploring the information content of calorimetric signals of anaerobic bioprocesses and their suitability for bioprocess control the production rates of metabolic heat, protons and gas of *Clostridium acetobutylicum* was monitored using a high resolution reaction calorimeter. The on-line measures were analysed and related to conventionally derived kinetics of microbial growth and product formation during the different metabolic phases of the acetone-butanol-ethanol (ABE) fermentation.

Changes between different metabolic phases can easily be retraced by the production rates of heat and gas and partially from the evolution of pH. However, the quantitative heat data interpretation based on advanced kinetic models combined with enthalpy balances proofed to be very challenging. Small errors in chemical analysis of intermediates and products lead to huge differences in predicted enthalpies easily changing the whole conclusion of a model. This means that the calorimetric measurement provides much more accurate process information than the chemical reference analysis (on- and off-line). However, the combination of heat and exhaust gas signals allows the real-time quantification of the main metabolic fluxes and thus provides proof of a future bioprocess control strategy. Simple mathematical heat flow models reveals that the strategy should be transferable to the technical scale.

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Cyclophosphamide treatment evoked side effects on skeletal muscle monitored by DSC

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Polyneuropathy is defined as a simultaneous malfunction of several peripheral nerves, which could be a side effect of cancer therapy as well. Well-known, that polyneuropathy is caused by chemotherapeutic drugs in patients with malignant tumour. Many kinds of drugs supposedly cyclophosphamide also can induce a disease classified as toxic polyneuropathy.

Cyclophosphamide is a widely used cytotoxic drug, it can cause polyneuropathy as one of its wide side effect spectrum. Cyclophosphamide importance is shown by the appearance on the most important drugs list published by WHO.

In present study we analyse this side effect on skeletal muscle (*m. gastrocnemius*) by DSC (differential scanning calorimetry), as an established thermoanalitical method, to follow the possible consequence of drug treatment. We used cyclophosphamide treated in vitro animal model (Guinea pig) with a comparable dosage and time handling of human protocol to show evidences of this drug-induced effects.

According to our results, we could show a dose-dependent difference between thermal parameters (denaturation temperature and calorimetric enthalpy) of untreated and treated samples in their contractile proteins (actin and myosin), which can be detected by DSC. It proved that we can create new possibilities in the detection and prognosis of expected and unwanted side effects of cyclophoshamide such as polyneuropathy.

Comparison of effects of sauna and cryotherapy treatments on body temperature mapping in elite athletes

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Bathing in the sauna or cryostimulation are often used as a part of training plan of elite athletes. In this work we present comparison of thermal mapping results obtained from the same athletes, after different wellness treatment (sauna and cryostimulation) in two training cycles far away from each other in time.

The group of 10 students from Katowice Physical Education Academy who are also part of the Polish national team of ski-runners was selected to our experiment. We collect thermograms of participants performing experimental training using camera Flir System E60. The skiers thermograms were registered, before, immediately after and 10 minutes after endurance training including one hour running on the treadmill, on a threshold load. Thermal mapping was analysed four times: before the treatments in the sauna and after 10 visits there, and before visit in cryochamber, and after 10 visits in a remote time. Blood samples were drawn from the antecubital vein into test tubes anticoagulated with heparin at rest and immediately following the run to assay biochemical parameters.

It was obtained that in upper part of body changes of temperature were similar for applicate both wellness treatments. Nevertheless temperature drops immediately after training as well as 10 minutes after training were a little bigger after visit in cryogenic chamber than after sauna. Temperature changes of muscles of lower body were more complicated. Immediately after training changes were generally positive and higher after cryostimulation (except vastus lateralis, tibialis anterior), but these changes do not show statistical significance. However, 10 minutes after training drop of temperature was observed for all muscles zones. Temperature effect of stay in cryogenic chamber lasts longer than bathing in sauna.

Some differences were also observed in physiological and biochemical parameters due to using different wellness. The work rate (WR) after sauna treatment was definitely higher than after cryotherapy. An increase in uric acid (UA) immediately after exercise in regards to before exercise is a little bigger after cryostimulation compared to bathing the sauna. However haemoglobin (Hb) is slightly lower after cryostimulation than sauna treatment. The changes in lactate dehydrogenase (ΔLDH) and creatine kinase (ΔCK) due to training are markedly lower after the cryostimulation than sauna bathing. These results may suggest that cryotherapy is more desirable than the sauna because of lower changes of LDH and CK, which are known as markers of microdamage of muscle.

Modification of blood serum DSC profiles by sauna treatments in cross country skiers during the exercise cycle

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Sauna is a physical treatment, originating from Scandinavian countries such as Finland, and now widely used throughout the world [1-2]. This treatment is used in sports medicine, recreation and rehabilitation, mainly for the regeneration of tired muscles, hygiene and cosmetology, cleansing the body of toxins or relaxation [1-3]. The aim of the conducted research was to compare changes in athlete's blood serum during two exercise sessions: before and after ten sauna treatments.

Serum samples were collected from the blood of 9 athletes (3 women and 6 men) well trained in cross-country skiing in four stages in both exercise sessions: at rest, after exercise and after 1h and 24h rest and additionally only at rest after the first sauna treatment. Differential scanning calorimetry (DSC) measurements of aqueous serum solutions were made in the temperature range 20 - 100 ^{0}C with a heating rate of 1 ^{0}C min^{-1} and a pressure of about 1.8 atm using the VP-DSC microcalorimeter (MicroCal Co, Northampton, MA).

The results obtained by DSC allowed to register characteristic post-exercise changes in thermal transitions of serum denaturation, similar in nature, regardless of the use of sauna treatments. Comparison of DSC curves of athletes' sera demonstrates a stronger reaction to the effort in the exercise session after the sauna treatments. It was revealed especially in the part of serum denaturation transition at higher temperature range. The post-exercise changes in the low-temperature transition region were similar. Another observation from our study was quite a significant variation in the recovery process after the exercise among the athletes.

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Calorimetric investigation of an equilibrium reaction of glycolysis for the determination of cell mimicking kinetic and thermodynamic parameters

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One of the most investigated biochemical pathways is the glycolysis. Surprisingly, some publications studied the thermodynamics of the glycolysis and postulated that this pathway is not thermodynamically feasible [1, 2]. Strongly positive Gibbs energy changes for the combination of reaction 5 and 6 as well as for some single reactions taking the recent knowledge about metabolite concentrations, activity coefficients and equilibrium are the reasons. In order to identify the causes, equilibrium data, activity coefficient concepts and models of irreversible thermodynamics are newly determined or developed.

In this contribution a reversible reaction of glycolysis was exemplarily calorimetrically monitored, thermokinetically interpreted under cell mimicking instead of standard conditions. In addition a new thermokinetic approach using irreversible thermodynamics was suggested overcoming the weakness of the conventional Michaelis-Menten kinetics. This weakness is the neglect of the backward reaction from the product to enzyme-substrate-complex. Obviously, there are already some models overcoming this weakness (e.g. the Hoh and Cord-Ruwisch approach [3] or the reversible Michaelis-Menten mechanism [4]) however our suggestion needs less parameter and reflects the natural cell conditions better. The influence of different cell mimicking conditions (e.g. temperature, pH-value, ionic strength, concentration of magnesium and biopolymers [crowding agents] on thermodynamic and kinetic parameters was determined and will be discussed.

In the further course of the study, we want to apply the determined calorimetric data to a new thermodynamic feasibility analysis model to explore the predictive potential of thermodynamics for systems biology.

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Applications of thermal analysis for testing elastomeric composites

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Thermal analysis (TA) is one of the group of techniques, which is used in a broad spectrum of scientific disciplines. At present, it is one of the mainly utilized methods in the characterization of polymeric materials to give information, which are often unavailable via using other techniques [1].

Elastomeric composites are widely used in various industries, such as the defense, aerospace and automotive industries. They are applied in manufacturing of tires, tubes, seals, coatings, dampers and many other products. Therefore, thermal analysis is a perfect and versatile tool for characterizing such materials in a wide temperature range.

In the rubber industry, different components have been used for years, which can be employed as fillers, coagents, plasticizers or can modify the physical properties of elastomeric composites [2]. The analysis of the latest literature reports indicates that ionic liquids (ILs) are increasingly being used as a new class additives for various applications in elastomers. ILs are organic salts with a melting temperature lower than 100 ^{o}C. Due to good thermal stability, negligible vapour pressure and non-flammability in the temperature range for the processing of elastomeric composites, they can be effectively used in the field of elastomer technology [3].

This work presents current applications of thermoanalytical methods for testing elastomeric composites of acrylonitrile-butadiene rubber (NBR). Thermogravimetry (TG), differential scanning calorimetry (DSC) and dynamic-mechanical analysis (DMA) were used to characterize the influence of ILs and fillers on the curing characteristics of rubber compounds, as well as the thermal and dynamic-mechanical properties of vulcanizates. NBR composites were filled with carbon black or nanosized silica. ILs, such as tetrafluoroborates with pyrrolidinium, pyridinium and piperidinium cations, were used to improve the dispersion of filler particles in the elastomer matrix and to increase the efficiency of NBR vulcanization.

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Analysis of polymers and polymer mixtures using differential scanning calorimetry and advanced software

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Differential Scanning Calorimetry (DSC) is a very commonly used analytical technique to quickly characterize polymers, blends and mixtures. Inspection of incoming goods, production and quality control as well as research and material development are typical application areas for DSC. To cope with the challenge of automated routine analysis procedures on one hand and highest flexibility in usability and evaluation on the other, an advanced software was introduced recently [1, 2].

Comparing analysis results with reference data is an established procedure in research and materials characterization. Spectroscopic techniques such as infrared spectroscopy (FT-IR) or mass spectrometry (MS) allow those comparisons via the software for decades. Numerous spectra libraries are available to compare measurement results with reference data. With the new evaluation tool of the NETZSCH *Proteus*® software, this capability is now also available for thermoanalytical data. Along with reference data, this thermoanalytical library allows for visual comparison of measured data with reference data. Recent works could demonstrate the use of this library functionality for different polymers, polymer mixtures and even for recycled polymers [3, 4]. The measurement results obtained with DSC, of course, strongly depend on the compatibility of the mixture. In case the single components do not form mixed phases, mixtures will present DSC signals of each single component according to its quantity. This work presents examples for the characterization of polymer samples and mixtures by means of DSC results and subsequent comparison of these results with library data.

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Evaluation for Degradation of Polymer Materials using Sample Observation TG-DSC System

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In case of the conventional thermal analyzer, the specimen is installed in a closed furnace during the measurement. Therefore it is difficult to directly observe the specimen behaviour, such as change in color, expand/shrinkage, melt flow, decomposition, etc., with temperature change and/or time lapse.

We developed TG-DSC system having a furnace of the structure that was available for the specimen observation and the image recording during measurement. The availability of this system was published last year [1].

The polymer materials degrade by heating and/or UV irradiation over time. As such, the color and the shape will change with progress of this degradation.

In this study, the influence of the heating and the time lapse on the degradation behavior of the polymethylmethacrylate (PMMA) was examined by imaging analysis using sample observation TG-DSC system.

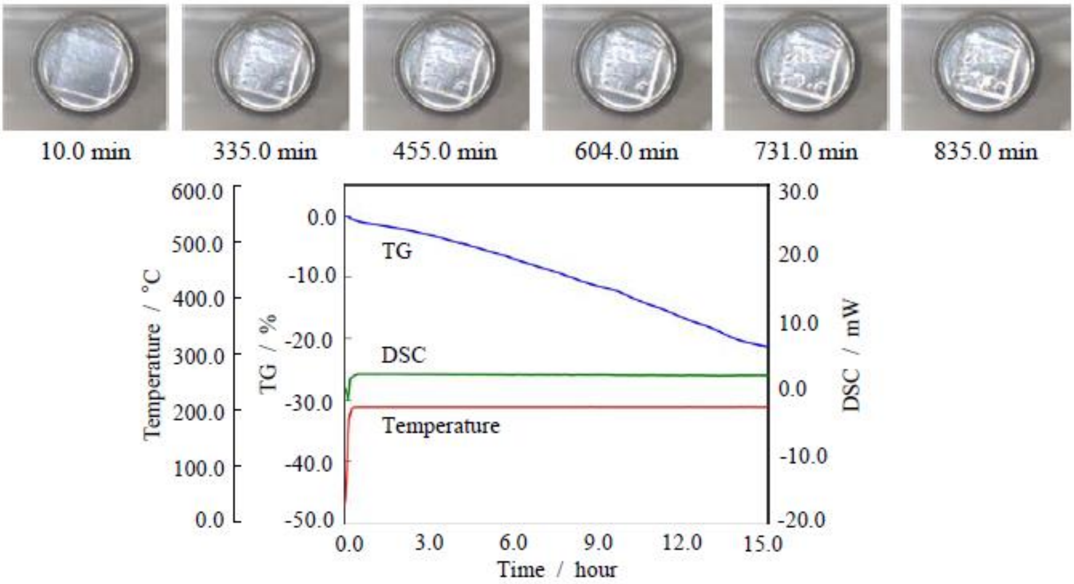

Fig. 1 TG, DSC and temperature curves, and images for PMMA by Sample Observation TG-DSC System

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New insights into the polymorphic changes of Metoprolol Succinate

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Metoprolol tartrate (MT) and metoprolol succinate (MS) are widely used to treat cardio-related medical conditions, there is a paucity of data in the scientific literature relating to the existence of other polymorphic forms. Paoli et al. [1] reported an anisotropic lattice expansion/contraction for MS and isotropic for MT effect of temperature on the lattice parameters of the salts. Upon cooling, both salts recrystallized to the original form. However, MT took 6 days to fully recrystallize to the starting form. Zhou et al. [2] synthesized a second crystal form of MS using solvent evaporation method. Data obtained from thermal analysis revealed that the new form has lower melting temperature (~ 126 ºC) and that it transforms eventually to the first (original) crystal form.

The aim of the present work is to better understand the thermal behaviour/ thermostability of metoprolol succinate and tartrate and to report any solid-state changes and possible polymorphic forms of the salts.

Differential Scanning Calorimetry (DSC) was method of choice for this investigation. Serval experimental procedures involving varying heating and cooling rates were applied to assess stability of different crystalline forms, creation of an amorphous form as well as recording existence of various polymorphs.

Metoprolol tartrate presented a relatively simple thermograms, melting on 1st heating cycle and glass transition (Tg ~ -5˚C) on the second heating cycle. Formed amorphous phase was stable and material didn’t undergo cold crystallisation.

On the other hand, MS presented complex and very much heating rate (heating treatment) dependent behaviour. Several recrystallisation processes were observed along with several melting points suggesting potential formation of up to three unstable polymorphic forms (Tc ~ 85˚C, 113˚C, 125˚C) and an amorphous phase (Tg ~ -5˚C) which is usually crated upon cooling of a molten MS.

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Nucleating agents with dual nucleating ability in isotactic polypropylene

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Isotactic polypropelene (iPP) is a semi-crystalline polymer used in various application fields. The properties of iPP depend mainly on its crystalline structure, which can be manipulated by the application of nucleating agents. Since iPP is a polymorphic polymer, these additives can enhance the formation of either one polymorphic modification of iPP or both (α- and β-iPP) of them. A well-known and commercially available example for dual nucleating agents is *N,N'*-dicyclohexyl-2,6-naphthalenedicarboxamide (sold under the trade name of NJ Star NU 100), which is an efficient additive in the preparation of iPP samples rich in the β-modification. However, it was shown that it is not selective for the β-iPP, since it also the α-iPP forms in its presence [1].

The aim of this work is to describe two other examples for dual nucleating agents of iPP, namely *N,N'*-dicyclohexyl-terephthalamide [2] and dibenzoyl-terephthalic acid dihydrazide, which were synthesized in our laboratory. In our research we used simultaneous thermal analysis to determine the melting temperature and the decomposition temperature of the compounds, since these characteristics are crucial from the viewpoint of applicability of a material as a nucleating agent. Then we introduced the additives in iPP in a wide concentration range, and investigated the thermal properties of the as prepared samples, by using differential scanning calorimetry. We proved that these compounds possess a dual nucleating ability in iPP, since they enhance the formation of both of the two polymorphic modifications already mentioned. Polarized light microscopy was also used to follow the crystallization process and to observe the presence of the iPP modifications.

Since the crystallization conditions (thermal conditions, presence of additives, etc.) influence the crystalline structure and consequently also the properties of the polymer, targeted manipulation of the structure by adding nucleating agents creates an opportunity to tune the properties of the polymer so that they fit our standards.

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Thermal analysis of aliphatic polyesters stabilized by polyphenols

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Thermal methods of analysis, including differential scanning calorimetry (DSC), as well as thermogravimetry (TGA), are significant for estimating the stabilization effect of polyphenols in polymer matrix. The effectiveness of selected antioxidants of plant origin incorporated into material can be proved, inter alia, by means of Oxidative Induction Time (OIT) calculation on unaged samples [1]. Longer Oxidation Induction Time (OIT) of polymers with antioxidants than of pure material confirms stabilization effect of natural antioxidants. Moreover, many thermograms reveal a difference between oxidation temperature of pure polymer and polymer with natural antioxidants, which also provides information about selected natural substances as stabilizers for polymers. In many cases it can be proved that materials with selected antioxidants have higher oxidation temperature than the pure ones, which confirms that these substances protect polymers from oxidation process.

Naturally occurring antioxidants, including polyphenols, can be applied as pro-ecological additives for aliphatic polyesters, which are bio-based and biodegradable polymers. Incorporation of natural stabilizers into polymers, such as polylactide (PLA) or polyhydrixybutyrate (PHB), leads to obtaining fully environmentally friendly materials which can be used in packaging industry [2,3].

Table 1. Exemplary values of oxidation process temperature range for pure aliphatic polyester and polyester with natural antioxidant.

Temperature range of oxidation process [°C]					
Poly(lactic acid)			Poly(lactic acid) with flavone (PLA+flavone)		
Onset	Peak	Endset	Onset	Peak	Endset
226	252	260	279	303	305

Acknowledgments
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Wood biocomposites with different epoxy systems. Thermal behaviour

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Wood is a raw, renewable and limited bioresource. Hence, the preservation of wood products has become a major concern [1-3].

The study describes the obtaining of coatings from epoxy derivatives of both natural and synthetic origins. The biocomposites were obtained by immersing wood or wood modified with succinic anhydride in different formulations of glycidyl methacrylate, diglycidyl ether of bisphenol A, epoxidized grapeseed oil and salicylic acid, as antifungal agent. The compounds were then subjected to a complex UV and thermal crosslinking protocol. The coated wood biocomposites were characterized in terms of their thermal behaviour.

Thermal decomposition behaviour and the identification of released gaseous entities were studied on a TGA/FT–IR/MS system. Non–isothermal kinetic studies were also undertaken. The biocomposite containing epoxidized grapeseed oil showed the highest thermal stability. The samples thermally decomposed following complex mechanisms in two or three stages.

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Unfolding and refolding of lysozyme dissolved in glycerol by fast scanning calorimetry

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Protein folding is one of the key problems in molecular biology [1]. Due to the relatively short duration of the folding process, experimental observation of folding is complicated. Lysozyme is a small globular protein, which finds applications in the food and medical industry. It was found that lysozyme folding proceeds via two parallel pathways with a fast direct folding and a significant population of the misfolded intermediate, which slowly folds into native protein [2].

We have used fast scanning calorimetry (FSC) and conventional differential scanning calorimetry (DSC) to investigate the unfolding of lysozyme in glycerol at scanning rates up to 500,000 K/min [3]. The apparent activation energy of the unfolding process is close in both cases: 261±13 kJ/mol (FSC) and 251±9 kJ/mol (DSC) and is smaller than the enthalpy of unfolding, indicating that the unfolding is not a single step two-state process. It was also found that the thermal unfolding was irreversible in the short term. However, after thermostating the sample at room temperature for several minutes, the unfolding peak reappeared in the heating scan, indicating a slow refolding process.

To further investigate the refolding we have used a temperature program which involves (a) fast heating and cooling of the protein, which probes the initial amount of the native state and produces unfolded protein, (b) an isotherm at the temperature well below the onset of the unfolding to initiate protein refolding in controlled conditions, and (c) a second heating scan to probe the state of the refolded protein.

We have found that at the shortest isotherms (<5 s) no endotherm due to unfolding of lysozyme is observed. At intermediate times (5 – 20 s) two endothermic peaks are observed. At longer isotherm (>30 s) a single endotherm is present. The appearance of the second endothermic peak is apparently due to the presence of a folding intermediate. The peak of the intermediate appears at lower temperature and has a comparable enthalpy to the unfolding of the native protein, which implies that the entropy of unfolding is greater than in the case of the native state.

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Thermogravimetric and evolved gas analysis of polymer materials designed for 3D printing

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Digital Light Processing (DLP) technology and Additive Manufacturing (AM) [1,2] have been widely adopted in the rapid prototyping and tooling areas for the creation of initial models by 3D printers. One of the possibilities of using 3D printing is the production of molds for casting manufacturing process. Owing to the unique layer-wise production method, many studies are focused on additive manufacturing of materials that often require superior properties. A variety of polymeric materials properties allows use of liquid resins for the additive manufacturing process. The efficient casting process requires intense and complete destruction of molds during combustion at the lowest possible temperature.

For this purpose, four polymeric materials were synthesized. In order to evaluate the characteristic properties of these samples thermogravimetric (TG) and infrared spectroscopy (FTIR) analyses were performed. During decomposition of samples, it was observed that all polymer samples were destroyed at temperatures of 300 - 460° C. The released volatile compounds were investigated using FTIR spectroscopy with TGA-IR module. The analysis showed that the main chemical compounds were: ethane, methane, carbon dioxide, methylacrylate. It was established that the material, which was synthesized with urethane methyl acrylate monomer, is being decomposed most intense at lowest decomposition temperature. The low ash content and decomposition temperature of the sample indicate that the materials synthesized from urethane acrylates have the appropriate thermal properties for the casting process technology.

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Thermal analysis of components of mechanochemical interaction of quercetin and glucose

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Flavonoids and their soluble in water glycosides have perspective biological activity. Receiving glycosides quercetin polyphenol interaction with carbohydrate glucose in solution is labor-consuming and expensive owing to multistage character. Earlier the possibility of glycosides synthesis by mechanochemical activation (MA) was shown for receiving the specific product which is not demanding high purity. At the same time the natural components containing quercetin such as buckwheat peel were used.

In [1] formation of glycoside bond of quercetin with glucose under MA is shown. One of preferable products of this interaction is isoquercitrin (quercetin-3-β-D-glucopyranoside). It exists as natural substance too. Reaction proceeds in mechanochemical reactor – drum of planetary mill in the conditions of controlled heating. There is a question of thermal stability of the reacting and formed components in the conditions representing mechanochemical interaction (temperature and the atmosphere).

The aim of the work is to research the thermal decomposition of substances used in reaction of receiving glycosides in the conditions of mechanochemical activation

For comparison and as initial substances commercial reactants are chosen: glucose, quercetin. MA of powders mixture of glucose and quercetin is in the AGO-2 mill-activator, regime of 1 W/g, air atmosphere. Conditions and the choice of gas carrier when carrying out the thermal analysis were chosen brought closer to conditions of mechanochemical synthesis.

Thermogravimetric curves of reagents of quercetin and glucose show multistage decomposition. In the interesting temperature range 373-723K stages at 409, 637K and 508, 602K are noted, respectively (speed of heating 10K/mines). Values of activation energy of decomposition stages of reagents in the called conditions are defined. Comparison with literary data for these substances are satisfactory. Temperature range of existence of a target product is defined. For stages of its thermolysis energy of activation is also demonstrated.

IR-spectra of formed glycoside were simulated quantum chemically in Gaussian (B3LYP/6-31G*) and measured experimentally on the Tensor 27 (Bruker) spectrometer, in potassium bromide. Glycoside-type bonds formation according to IR-spectroscopic data under mechanochemical activation of quercetin and glucose was presented. It is shown that addition of alkali catalysts entered into reaction mix intensifies process of thermolysis.

The conclusion is made that in the conditions of carrying out mechanochemical synthesis thermal stability of reaction mixture is limited to value 420-450K. On the basis of results of work some needs of restriction of temperature when carrying out mechanochemical synthesis are defined.

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Thermal stability of hen egg-white lysozyme in aqueous-organic mixtures

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Aqueous-organic solvents have several advantages in comparison with water as media for enzyme-catalyzed reactions. However, it is necessary to keep the enzyme in the native state during the reaction. Therefore, it is important to know how the nature and concentration of the cosolvent affects the stability of proteins.

In the work, we have studied the thermal stability of hen egg-white lysozyme in the mixtures of water with common organic solvents (acetone, acetonitrile, dimethyl formamide, dimethyl sulfoxide, 1,4-dioxane, tetrahydrofuran, methanol, isopropanol, tert-butanol) using capillary differential scanning calorimetry (DSC). The protein concentration in the experiments was 1 mg/ml, the scan rate varied in the range 0.5 – 2 K/min. Additionally, the circular dichroism (CD) signal of lysozyme at 290 nm was followed in the temperature range 10-90 °C at the heating rate 0.5 K/min.

In all the studied systems, addition of the organic cosolvent leads to a decrease in the denaturation temperature of lysozyme. For the mixtures with the same mole fraction of cosolvent, the denaturation temperature decreases in the following order: dimethylsulfoxide (weakest denaturant) > methanol > acetonitrile, dimethylformamide > acetone > isopropanol, 1,4-dioxane > tert-butanol > tetrahydrofuran (strongest denaturant). This series qualitatively coincides with the ability of solvents to suppress the hydrophobic effect [1].

In the presence of organic cosolvents, the temperature of disruption of the tertiary structure of lysozyme determined from the near-UV CD experiments is lower than its temperature of denaturation in DSC experiments. It can be suggested that increasing concentration of the organic cosolvent favors formation of a partially unfolded state with disrupted tertiary structure and mostly preserved secondary structure.

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Characterization of thermal properties of fat extracted from ruby chocolate by using DSC, PDSC and TGA methods

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Ruby chocolate is a new type of chocolate, made from the Ruby bean with a strictly secret procedure developed by the world's leading manufacturer of high-quality chocolate and cocoa products. The discovery of the fourth type of chocolate is modern breakthrough. The taste of chocolate is described as a mixture of sweetness, smoothness and fruitiness. Currently, there is no literature data on composition and thermal properties of ruby chocolate.

The purpose of the study was to analyze ruby chocolate fat using differential scanning calorimetry (DSC), pressure differential scanning calorimetry (PDSC) and thermogravimetry (TGA).

DSC measurement of melting characteristic and kinetics parameters of fat were carried out with a TA DSC Q200. Samples of 3–4 mg were placed into aluminium pans with a lid and were hermetically-sealed. An empty sealed aluminium pan was used as a reference and the experiments were performed under a nitrogen atmosphere at normal pressure. The melting profiles were obtained by heating the samples from -80°C to 80°C at a heating rate of 10°C/min. Fat samples of 3–4 mg were placed in aluminium pans and were heated at rates of 2.5, 4, 6, 7.5, 10 and 12.5°C/min. Experiments were performed in an atmosphere of oxygen. For each programmed heating rate (β,°C/min), at least triplicate determinations were carried out. When the run was completed, the onset and the maximum oxidation temperature (t_{on}, t_{max}) was determined. PDSC experiments were carried out using a DSC Q20 TA Instruments, coupled with a high-pressure cell. The sample was placed in aluminium pan, under oxygen atmosphere, being pressurized in isobaric module (1400 kPa). The isothermal temperature (from 100 to 140°C), used for the data collection. The oxidative induction time was obtained from the PDSC curves [1]. Measurements were made under nitrogen and oxygen at a flow rate of 25 ml/min. Samples were placed in platinum containers. Measurements were made at a temperature range of 50-700° C with a heating rate of 10° C/min. TGA curves were obtained for temperature dependence on mass loss, first derivative (DTG) was calculated [2].

The presence of polymorphic forms in melting characteristics of ruby chocolate fat was indicated. Value of activation energy for maximum temperature was lower than for onset temperature. The same correctness for pre – exponential factor was observed. The profiles of the TGA and DTG curves in oxygen showed stages of decomposition for ruby chocolate fat.

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On the investigation of co-crystals of 2,4-diaminopyrimidine based dihydrofolate reductase inhibitors

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Pharmaceutical co-crystals have emerged in recent years as alternative solid forms of active pharmaceutical ingredients, APIs, for enhancement of desirable physicochemical properties and/or biopharmaceutical performance [1,2]. They are multicomponent solids made up of an API and of one or more co-formers, all solid when pure at ambient conditions, joined together in a stoichiometric ratio in a new crystalline structure [1,3]. The supramolecular synthons responsible for supramolecular association involve, in most of the cases, hydrogen bond interactions, although other kind of (weaker) interactions may also play a role [1,2]. Therefore, besides the potential practical application, research on co-crystals can also give valuable contributions for fundamental understanding of supramolecular interactions and molecular recognition.

Dihydrofolate reductase (DHFR) inhibitors, such as pyrimethamine, Figure 1.a, trimethoprim, iclaprim, metoprine, share a common 2,4-diaminopyrimide (24DAPM) core structure, Figure 1.b [4]. In a co-crystallization experiment, although the same type of supramolecular H-bonded synthons are expected for DHFR inhibitors and 24DAMP, the molecular complexity of the former may also play a role in the co-crystallization trial outcome.

As part of an ongoing project aiming to get insight on these effects, in this work results are presented and discussed for the investigation of co-crystallization of pyrimethamine and of the core fragment 24DAPM with two closely related co-formers, theophylline and caffeine, Figure 1. As an highlight, thermal analysis was crucial in discovering polymorphs of both (1:1) pyrimethamine:caffeine and pyrimethamine:theophylline co-crystals.

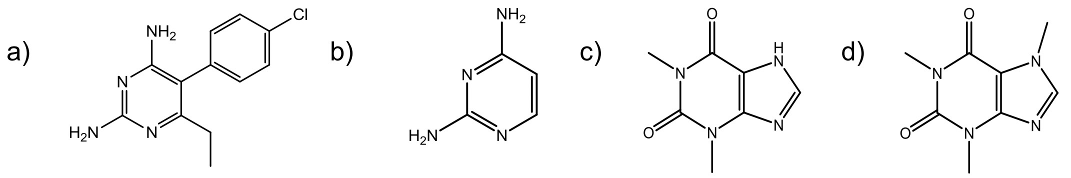

Figure 1. Molecular structures: a) pyrimethamine, b) 2,4-diaminopyrimidine, c) theophylline, d) caffeine

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Evaluation of stabilizing effect of potential antioxidants in polymers by DSC

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Thermal oxidation of polymers exhibits an induction period (IP), i.e. the stage where seemingly no chemical reaction takes place. The length of IP is often taken as a measure of the material stability [1]. In our previous paper [2] an integral isoconversional method based on non-Arrhenian temperature function was proposed for obtaining the kinetic parametres of IP from the onset temperatures of nonisothermal DSC runs with linear increase of temperature.

Antioxidants are commonly incorporated into the materials to prevent the deterioration of properties, resulting from the thermooxidation process [3]. To characterize the stabilizing effect of individual antioxidants in rubber compounds, the protection factors, *PF*s, can be used. The protection factor is defined as the ratio of the lengths of induction period of stabilized and unstabilized material [4]:

$$PF = \frac{t_i(\text{stab.})}{t_i(\text{unstab.})} \tag{1}$$

From Eq.(1) it is obvious that if the value of *PF* is greater than 1, the additive exhibits a stabilizing effect on the studied material. The greater the value of *PF*, the higher is the antioxidant effectiveness of the additive. Based on the obtained values of *PF*s, it is possible to calculate another criterion characterizing the stabilizing effect of the additive – antioxidant effectiveness *AEX* [4]:

$$AEX = \frac{PF - 1}{X} \tag{2}$$

where *X* is the concentration of the additive expressed in parts per hundred parts of rubber (phr). Physical meaning of *AEX* is that it expresses the additional stability brought about by a stabilizer, normalized per a mass unit of the stabilizer.

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Glassy dynamics of polymer and other materials by fast scanning calorimetry

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In the present contribution, we show how new generation fast scanning calorimetry (FSC) [1], allowing cooling/heating rates as large as several thousand K/s, can deliver simultaneous information on the molecular mobility and the vitrification kinetics of glass-forming systems. Regarding the former aspect, FSC allows accessing frequencies from the sub-Hz region to more than 100 Hz. Within this context, we will first show how these aspects can be applied to study the glassy dynamics of geometrically confined polymers, that is, polymer nanospheres [2]. Measurements of the molecular mobility indicate that the molecular mobility of these systems is essentially bulk-like. In contrast, the study of vitrification kinetics in these systems shows suppressed glass transition temperature in comparison to the bulk. Such depression is larger for nanospheres with smaller diameter. Hence, these results provide compelling arguments on the decoupling between molecular mobility and vitrification kinetics. Interestingly such outcome is also found in a gold based metallic glass, which shows cooling rate dependent glass transition deviating from the temperature dependence of the molecular mobility. The main consequence of these results is that the paradigmatic view on the connection between these two aspects of glassy dynamics must be revisited.

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The effect of pressure during cure on the thermal conductivity of epoxy composites filled with boron nitride

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There are many parameters which affect the thermal conductivity of composites of epoxy and boron nitride (BN), including BN content, BN particle size and shape, cross-linking system, and surface treatments [1]. In earlier work [2-3], we have demonstrated that the thermal conductivity of epoxy-BN composites can be enhanced in several ways: increasing BN content, including using hybrids; increasing particle size; using agglomerates rather than platelets; using thiol as a cross-linking agent rather than an amine, to improve the matrix-filler interaction. Here we investigate the effect of pressure during cure as a further possibility for increasing the thermal conductivity of epoxy-BN composites.

Epoxy-BN composites were prepared for stoichiometric epoxy-thiol and epoxy-amine systems. The BN filler (platelets) of size 2, 30 and 180 μm was added in a controlled proportion to give volume percentages of 37.3 and 42.2 for the epoxy-amine system and of 34.2 and 44.7 for the epoxy-thiol system. The components of each sample were mixed by hand, and a cylindrical mould of diameter 15 mm was filled with about 6 g of the mixture. A pressure of 175 kPa was applied by placing a weight on top of the piston, and the mixture was cured isothermally under pressure in an oven at 70 ºC for 3 hours. The density of the cured cylindrical samples was determined by Archimedes principle, and the thermal conductivity was measured by the Transient Hot Bridge method.

The results show a number of interesting aspects. First, for all the epoxy-BN composites prepared without the application of pressure, the thermal conductivity increases with increasing density, while the thermal conductivity of the composites with the larger particles (30 μm and 180 μm) is higher than that for the composites with the 2 μm particles. Second, for a given BN particle size and vol%, the thermal conductivity of the epoxy-thiol composites is always greater than that for the epoxy-amine composites. Third, and most importantly in the present context, the thermal conductivity and the density both increase for the samples cured under pressure, whether epoxy-amine or epoxy-thiol; in fact, the greatest increase when cured under pressure occurs for the epoxy-amine system. This establishes clearly the relationship between thermal conductivity and density. The increase in thermal conductivity results from the densification of the sample, and the consequent improved interface between matrix and filler. The greater effect of pressure observed for the epoxy-amine composites is because the epoxy-thiol composites already have a better interface resulting from the Lewis acid-base interaction between the boron and sulphur.

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Calorimetric study of host-guest complex formations of crown ethers and cyclodextrins with biologically important molecules

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Studies on the complexing properties of synthetic macrocycles such as crown ethers and cyclodextrins are of considerable importance for applications and make it possible to simulate molecular recognition processes occurring in biological systems. Low solubility and low bioavailability of some biological molecules make their application difficult. In order to increase the solubility of poorly soluble compounds in water, a complex formation with cyclodextrins and crown ethers can be applied. It is assumed that targeted selection of the solvent will allow creating optimal conditions for selective complexation and solubilization by macrocycles.

Our finding on the effect of H_2O-EtOH, H_2O-DMSO and H_2O-Me_2CO solvents on the enthalpy and entropy of molecular complexations of 18-crown-6 with glycine, D,L-alanine, L-phenylalanine and glycyl–glycyl–glycine on the stability of the resulting complexes and the literature data for related systems were analyzed. The ratios between the thermodynamic parameters of complex formation reactions and the reactant solvation were applied to reveal the key factors that are crucial for the increasing stability of the complexes and the increasing exothermicity of the processes under study in water- organic solvents.

Unlike molecular complexes of crown-ethers with amino acids and peptides, the additions of ethanol to water up to X (EtOH) = 0.20 mol. fr., leads to an decrease in the stability of the molecular complexes between quercetin (QCT) and hydroxypropyl-β-cyclodextrin (HPβ-CD), and benzoic acid (BA) with β-cyclodextrin (β-CD). For the [QCT HPβ-CD] and [BA β-CD] complex formation reactions there are an increase in the exothermicity and a decrease in the entropic contribution to the reaction’s Gibbs energy changes.

However, the changes in the Gibbs energy of molecular complexes formed by the “host’s” molecules 18C6 and βCD are due to the resolvation of “guest” molecules. In the cases of complexes with 18C6 the desolvation of “guests” is observed and in the [BAβCD] complexes the increase of BA solvation takes place.

Furthermore, the increase of exothermisity of both types of complex formation reactions in H_2O-EtOH mixed solvents is observed. An increase in the concentration of ethanol leads to an increase in the entropy contribution of [BAβCD] complex formation reaction which decreases the stability of [BAβCD].

The calorimetric measurements reported in this work were carried out at the Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemistry and Technology (ISUCT) using the equipment of the Centre for Collective Use of ISUCT.

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Synthesis and characterization of crosslinked polyethylene/graphite composite for geothermal heating/cooling pipe applications

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Geothermal energy is a cost-effective and environmentally friendly energy source which can be exploited in domestic heating/cooling systems by geothermal heat pumps [1]. The main goal of these systems is to achieve high efficiency combined with low cost. For geothermal heat pump systems, this can be accomplished with piping materials with high thermal conductivity and low-cost maintenance. Crosslinked polyethylene (PEX) is a widely used piping material with increased molecular weight, elastic modulus and impact resistance [2]. However, its low thermal conductivity is the main problem to be solved. It is well known that the addition of carbon filler materials in a polymeric matrix leads to higher thermal and electrical conductivity and improved mechanical properties [3]. In this work, PEX/graphite composites were prepared by the melt mixing process. A commercial graphite powder GraphTHERM® (by Luh GMBH) with 23μm in diameter was used as a filler in various concentration (0,5-5 wt. %). The thermal stability of PEX and composites was studied by using Thermogravimetric Analysis (TGA) while the degradation products were identified by Analytical Pyrolysis Gas Chromatography/Mass Spectrometry (py-GC/MS). The degree of polymers' crystallinity was calculated by Differential Scanning Calorimetry (DSC). The thermal diffusivity of the samples was measured by Laser Flash Analysis (LFA). Finally, the mechanical properties testing was performed to determine Young's modulus, tensile strength at yield, tensile strength at break and elongation at break. PEX composites were found to present higher thermal stability and conductivity compared to neat PEX.

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Investigating noncanonical DNA structures by calorimetry and spectroscopic techniques

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Aside from the well-known double helix, DNA can adopt a large variety of different conformations, which delineate its function. Based on sequence composition and environmental conditions, DNA can form alternative structures like parallel/antiparallel duplexes, hairpins, triplexes, tetraplexes, and branched architectures. These so-called non-B DNA structures have been demonstrated to participate in a number of cellular processes, and their formation has also been associated with several human diseases [1-2].

Beside the biological significance of non-B DNA structures, their unique nanoscale geometry, biocompatibility, biodegradability, and molecular recognition capacity have made non-B DNA motifs promising candidates for the construction of novel functional nanomaterials and nanodevices [3].

Undoubtedly, most of the attention in non-B DNA-forming sequences is currently paid to G-rich motifs with potential to form unprecedented structural arrangements like G-quadruplex, G-triplex, and G-hairpin, as well as to their C-rich counterparts, which are able to form the so-called i-motif structures.

Understanding of the energetic aspects concerning the structure and stability of such DNA arrangements is extremely important in view of biomedical and nanotechnological applications. In this context, we investigated, by combining calorimetric and spectroscopic methods, noncanonical DNA structures and their interaction with some molecules of therapeutic interest [4-6]. In particular, the thermodynamic characterization of a G-triplex, a G-hairpin, a number of G-quadruplex–duplex hybrids, as well as the preliminary results on the characterization of an i-motif structure will be discussed.

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Insights in thermal transitions of polymers by Modulated Temperature FTIR

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Because of its importance, the definition of polymer thermal properties is one of main issue in overall material characterization. This encourages fundamental and applied researches to the development of innovative instrumental techniques and interpretive models. As far as the thermal analysis, in 1993 a new experimental apparatus, called Modulated Temperature Differential Scanning Calorimetry (MTDSC) has been proposed [1]. By applying a modulated temperature program comprising of a periodic temperature variation superimposed to a linear heating or cooling ramp, MTDSC offers the great advantage of the identification of the equilibrium and out-of-equilibrium processes involved in materials' thermal transitions. However, modulated temperature protocols could be profitably combined with other investigation techniques in order to characterize the thermal behaviour of materials in greater detail. Infrared spectroscopy, as an example, is sensitive to inter- or intra-molecular interactions, conformation or structure changes occurring during sample transformation. Therefore, the investigation of intensity variations of different absorption bands as a function of temperature can be adopted to explore the sample thermal transitions at molecular level. The present contribution aims to introduce a new technique, called Modulated Temperature FT-IR (MTFTIR) [2,3], able to improve the description of the thermal behaviour of polymers. It is based on the sequential acquisition of sample spectra during a modulated temperature program. By processing selected bands, the total signal variation as well as its reversing and non-reversing components as a function of the mean temperature are obtained. The reversing component is related to the sample transformation that can be reversed by temperature modulation while, the non-reversing component, to the spontaneous processes that, once started, can't be reversed. In this way we explored the complex conformational and structural transformations involved in some transitions of polymers, such as the glass transition of poly(L-lactide) [2] and poly(ethylene terephthalate) as well as the crystallization of isotactic poly(propylene) [3]. The obtained results evidenced that MTFTIR is able to give new insights on polymer transformations otherwise not accessible by other conventional thermal analyses.

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Poster Session 1

Thermodynamic properties of binary mixtures of cyclohexanone + polychloroalkane

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In this paper, we report excess molar enthalpies, H^E, and molar excess Gibbs energies , G^E, for Binary mixture of cyclohexanone + 1,2 - dichloroethane, 1,1,1 - trichloroetrhane, 1,1,2,2-tetrachloroethane, these measurements were performed in order to complement the data on VLE and excess molar properties of mixtures containing polychloroethane [1,4]

Binary systems of alkanones (Ketones) with chloroalkanes are often characterized by negative deviations from ideality due to the presence of specific interactions between the carbonyl group of the alkanone and the chlorine atoms of the chloroalkane , H-bond type interactions are also present between the carbonyl group and the hydrogen atoms of the partially chlorinated methyl. The excess molar Gibbs énergies G^E (as derived from vapor liquid equillibrium measurements) are known to give conclusive evidence concerning the interactions between the components of binary liquid mixture.

The vapor pressure of the pure compounds and the binary mixture were measured by means of a static apparatus [5], at temperatures between 263,15K and 343,15K.From these data, isothermal molar excess Gibbs energies, G^E, were calculated. The excess molar enthalpies of the binary mixtures have been measured at 303,15K and atmospheric pressure, using a C80 Setaram Calorimeter.

The data on excess molar enthalpies and Gibbs energies have been examined on the basis of the UNIFAC Model.

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Aromatic hydrocabons liquid-liquid extraction

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The purpose of this work is the extracting aromatic compounds, present in a very low concentration , from an aliphatic stream of the oil industry. Ionic liquids have raised special interest in the last years with a number of papers supporting their potential for this separation[1]

However, due to the large number of ionic liquids feasable to be synthesized, the selection of the most suitable candidates for the proposed work must be hampered by group contribution methods, correlations or equations of state.

COSMO-RS, a novel quantum chemical approach to describe the chemical potential in the liquid phase, has become a frequently used alternative to force field-based molecular simulation methods or group contribution methods [2,3]

The COSMO-RS model is the most progressive kind of a dielectric model where molecules are placed in a conductor as the reference state. Through its unique combination of a quantum chemical treatment of solutes and solvents, with an efficient statistical thermodynamics procedure for the molecular surface interactions, a efficient calculation of phase equilibrium and other thermodynamic properties are achievable. Thus, to screen the most suitable ionic liquid, COSMO-RS was used to predict the IL/aromatic/aliphatic system partition coefficient and selectivity.

The set of ionic liquids were further evaluated. We assessed Kp(partition coefficient) for each ternary system (toluene-heptane-ionic liquid.

The Experimental results obtained allowed to confirm the qualitative capability of the COSMO-RS and thus, to be confident and certain on the development of further experimental essays , using ionic liquids identified with the highest potential.

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Aggregate reactivity to the alkali-silica reaction (ASR) in ground aggregate-cement pastes

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A range of standard accelerated test methods for the screening of aggregates for susceptibility to the alkali-silica reaction (ASR) which causes deleterious cracking in concrete structures are available worldwide and two standard test have been recently adopted in Australia (AS 1141.60.1 (Accelerated mortar bar test (AMBT)) and AS 1141.60.2 (concrete prism test (CPT))). These accelerated test methods are empirical and based on expansion measurement correlated to field performance.

The mechanism of deleterious ASR resulting in cracking involves two processes; the chemical processes involved in the formation of the expansive ASR gel and the mechanical action of the ASR gel of the concrete in crack formation. Expansion tests, although empirical in nature are important as they probe the mechanical potential of the reactivity of aggregates. The chemical processes involved in the phase development are also important as they provide the gel responsible for cracking and understanding these processes canlead to more effective methods of mitigation of ASR as well as alternative methods for the screening of aggregates for reactivity to ASR. This paper focusses on correlating reactivity of aggregates determined using the standard test methods with phase development in paste tests using ground aggregate-cement pastes aged under accelerated conditions.

Two aggregates are investigated in this study, a micro-diorite (CPT non-reactive) and a greywacke (CPT reactive) which have been selected because of their relative reactivity to standard test methods. Both contain quartz as the phase potentially reactive to ASR. The aggregates were initially fine ground in a ring mill in order to make paste specimens using a general purpose Portland cement. Pastes specimens were prepared using a 3 to 1 aggregate to cement ratio with a water to cement ratio of 0.7. Pastes were initially hardened for 24 before stripping from the moulds and aging in alkali media (1 M NaOH) at elevated temperature (40, 60 and 80°C) for periods up to 84 days. Specimens were recovered, crushed and dried in a vacuum oven for 24 hours at 105°C prior to grinding in the ring mill and characterising using XRD, TG and FTIR for phase analysis.

Phase development with age based on the calcium hydroxide OH stretch in the FTIR, the decomposition step in the TG and the (101) peak in the XRD and the (101) quartz peak in the XRD is reported. Characterisation for the full aging period will be reported at CEEC-TAC5 – MMEDICTA 2019; however, results to date indicate that for these quartz containing aggregates, the relative reactivity can be correlated to the quartz reactivity and the calcium hydroxide consumption.

Influence of curing temperature on nanometer pore size distribution of hardened cement paste by low-temperature differential scanning calorimetry

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The influence of curing temperature on the microstructure and porosity of hardened cement paste, specifically calcium-silicate-hydrate (C-S-H) mineral foam, is a topic of major interest and strongly linked to the strength development of concrete and concrete structures [1].

In the past, mercury intrusion porosimetry (MIP) was extensively used to characterise the pore size distribution of hardened cement paste, but criticized in the paper [2]. In addition to measuring artefacts (bottle neck effect), the main disadvantage is the necessary drying previous to testing, altering pore volume and pore sizes.

In this presentation we show that low-temperature differential scanning calorimetry (LT-DSC) [3, 4], is a suitable method to analyse the influence of curing temperature on pore size distribution of C-S-H mineral foam. For hardened cement paste (w/c = 0.6) several exothermic peaks are visible in the cooling run (+5 °C to -60 °C) of the thermograms. These areas, when interpreted Jennings colloidal model-II is the scopes of C-S-H [5], are assigned to water freezing in capillary pores (from 0 °C to -20 °C), large gel pores (-20 °C to -35 °C) and small gel pores (from -35 °C to -55 °C). The results show that there is a significant increase in the capillary porosity when comparing cements cured at 20 °C, 40 °C and 60 °C. This can be linked to the decrease of the final compressive strength of concrete. The results presented here closely match those using other methods [1, 6].

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Graft copolymers of chitosan with caprolactone: synthesis and thermal analysis

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An important place among natural polymers is occupied by chitosan (CS) due to its high adsorption capacity, biodegradation, biocompatibility and low toxicity. However, CS is insoluble in most of organic solvents as well as in aqueous solutions with physiological pH that limits its use [1]. Grafting polyesters to CS contributes to the formation of new amphiphilic copolymers, which consist of hydrophilic CS backbone and hydrophobic site chains of polyester. These copolymers are completely biodegradable, and form micelles with a hydrophilic outer shell and a hydrophobic inner core in an aqueous medium. Such copolymers are relevant as wound healing materials, implants and targeted drug delivery systems [2].

A series of chitosan-graft-polycaprolactone copolymers have been synthesized by grafting polycaprolactone (PCL) to hydroxyl groups of CS through ring-opening polymerization using methanesulfonic acid as a solvent and catalyst. The thermal behaviour of the copolymers was investigated by TG, DTG and DSC analysis (see table 1).

Table 1. Results of thermal analysis of graft copolymers of CS and CL.

CS:CL[1]	$\langle T_{fus} \rangle$, °C[2]	χ, %[3]	T_{max}, °C[4]	
			1	2
CS	-	-	300	
1:8,7	57	38	311	477
1:4,3	-	-	223	315
1:13,0	49	30	256	409
PCL	60	79	414	

[1]Molar ratio of CS and caprolactone used in synthesis. [2]Average melting point calculated from DSC curves. [3]Degree of crystallinity, calculated based on $\Delta_{fus}H$ of PCL with a degree of crystallinity of 100% of 133 J / g. [4]Temperature of the maximum decomposition rate in the first (1) and second (2) stages, calculated from the TG curves.

The presence of thermal decomposition steps of both CS and PCL on the thermogram of the copolymer confirms the successful grafting of PCL to CS. According to the obtained values, the degree of crystallinity of PCL in the copolymers is lower than in the homopolymer, which points to the formation of the graft copolymer. Moreover, the formation of graft copolymers was confirmed by IR spectroscopy. In this study, the dependence of the graft copolymers solubility in CH_2Cl_2 on the length of the PCL side chains was established.

Further research will be focused on the modification of the terminal hydroxyl groups in graft copolymer for copolymerization with thermoresponsive vinyl monomers.

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Thermal analysis of shungite containing PA- and LDPE-based composites

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Shungites are unique natural polymineral raw materials containing carbon in their composition which has an unusual structure. It is based on a graphene fragment <1 nm, which sequentially forms several structural levels: stackes, globules and 3D grids which are released in various media determining the specific properties of shungite carbon (electrical conductivity, permeability, strength, difility, etc.). Highly dispersed crystalline silicates are evenly distributed in this amorphous carbon matrix. The presence of uniformly distributed carbon and mineral phases of different polarity (nonpolar carbon, polar silicates, aluminosilicates, etc.) imparts the ability to be combined with substances of inorganic and organic nature to shungite. Therefore, shungite is proposed to be used as a filler in composite materials on various binding bases. A characteristic feature of micron shungite powders is good compatibility with polar and non-polar polymers, associated with the mosaic structure of the shungite surface including hydrophobic and hydrophilic regions. This property of shungite allows obtaining on its basis the compositions with a high degree of filling. At large fillings, the nucleating effect of shungite occurs that is evident through increase in the crystallization temperature of the composite material, decrease in the size of spherulites and an increase in the fraction of the crystalline phase.

This paper presents the results of thermal analysis of polymer composites based on polyamide and polyethylene filled with shungite nanosized powder. The carbon content is 28-30 wt.%. The average particle size is ~ 100 nm, the specific surface area is ~ 100-120 m^2/g.

The study of thermal behaviour (melting and crystallization) of polymer composite materials was carried out on STA449F3 Jupiter (NETZSCH). The measurements were carried out in the temperature range from 25 to 300 °C for samples based on polyamide and to 220 °C for polyethylene composites in a nitrogen atmosphere in aluminium crucibles. The heating and cooling rate is 5 K/min. Sample weights ranged from 30 to 35 mg.

A change in crystallization temperature in the presence of fillers reflects changes in the nature of relaxation processes occurring in thin layers at the polymer-phase interface. The molecular mobility of chains is changing. The magnitude of maximum crystallization temperature shift on DSC-curve can serve as characteristic of such change. This shift is determined by the nature of the polymer. The most marked change in regularity of the polymer component is detected in a polar polyamide as a result of a stronger interaction with the filler and thermodynamic affinity.

Phase transitions in Ti-Ni after ultrasonic treatment

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Recently, it has been found that ultrasonic vibrations can initiate the shape memory effect in alloys with thermoelastic phase transitions [1]. It was shown that the shape memory effect and its realization peculiarities depend on the parameters and conditions of ultrasonic influence [2].

The effect of ultrasonic treatment on phase transitions of the Ni – 50.7 at.% Ti shape memory alloy was studied. It allowed formulating the mechanism of high-energy impact on shape memory alloy properties. Shape memory phenomena were determined as a result of ultrasonic influence on TiNi alloy in a pre-deformed state.

It was found that the ultrasonic vibrations have the greatest impact on TiNi alloy subjected to annealing at a temperature of 800 ºC with the subsequent aging at a temperature of 430 ºC. The martensitic transformations take place according to scheme B2 → R → B19′ when cooling alloy and according to scheme B19′ → R → B2 when heating. The ultrasonic vibrations increased the value of the transformation temperatures B2 → R and decreased the value of the transformation temperatures R → B19′. Enthalpy of transitions B2 → R values 3,8 J/g, enthalpy of transitions R → B19′ values 6,6 J/g. The ultrasonic treatment influence on the characteristics temperature and they consist: M_s = -21 °C, M_f = -29 °C, A_s' = 34 °C, A_p' = 35 °C, A_p = 41 °C, A_f = 48 °C.

The results of the study showed that the ultrasonic vibrations might be successfully used for the initiation of the shape memory effect in actuators and for the change of the functional properties of the shape memory materials.

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Study of the thermal behaviour of the aceclofenac complexes of praseodymium and neodymium

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Research on molecules with pharmacological actions containing metal ions are widespread in several areas of research, such as chemistry, biology and biochemistry. The use of rare earth metals, are of great scientific importance, since these metals can be used in various types of materials [1,2]. The objective of this work was to characterize thermally the aclofenac of praseodymium and aceclofenac of neodymium. The TG-DSC analyses of the praseodymium complex indicate that the first mass loss occurs in the temperature range of 50 - 115 °C, with an endothermic peak at 110 °C. The anhydrous praseodymium compound is stable at 195 °C and above this temperature the thermal decomposition occurs in two consecutive stages, with a temperature range between 195- 300 °C and no thermal event in the second step, attributed to the thermal decomposition and pyrolysis of the compounds, although the mass losses are still observed up to 1000 ° C. The TG-DSC curves of the neodymium compound indicate that the first mass loss occurs between 50 - 115 °C, with endothermic peaks at 95 °C and 110 °C. The anhydrous compound presented thermal stability up to 195 ºC and above this temperature the thermal decomposition occurred in two consecutive stages, between 195-300 ºC (fast process) and 300 - 950 ºC (slow process), with losses of 45.77% and 36. 15%. It was concluded that the TG-DSC analysis allowed to characterize the thermal behavior of the synthesized compound, as well as to establish its stoichiometry. It has been determined that the praseodymium and neodymium compounds have 2.5 hydration waters, and three metal binders. Simultaneous TG-DSC curves provided information on the thermal behavior of these compounds (dehydration, stability, thermal decomposition steps) and show that the decomposition of the compounds occurs in four (Pr) and five (Nd) stages. The DSC curves allowed to quantify the energies involved in the processes of dehydration, oxidation and transformations of physical phenomena

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Obtaining specific heats of cementitious and construction materials by Modulated DSC

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Non-Conventional Differential Thermal Analysis (NCDTA) [1-4] and Calorimetric studies of hydration of cementitious and construction materials, such as cement and plaster of Paris, use pastes and/or composites with different components, which specific heats (c_p) must be known and considered, to have more accurate and precise results. Therefore, the main objective of the present work is how to obtain and to present the specific heats of usual raw materials used in these studies, as a function of temperature, by Modulated Differential Scanning Calorimetry (MDSC) by using single runs.

The analyses were performed by using samples in sealed aluminum pans, in a TA Instruments 2920 MDSC equipment, using the following method: cooling at 2°Cmin^{-1} from ambient temperature to –15°C, then heating at 4°C/min up to 60°C, with 0.5°C temperature modulation, and a modulating period of 100 seconds.

Contributing to the disclosure of respective c_p data with NCDTA or calorimetric study researchers, this work may save them time to design sample compositions with same initial heat capacity in case of isothermal calorimetric studies, as will allow them to correctly obtain and to consider their different heat capacity (C_p) sample analysis data, when using NCDTA systems.

Specific heat linear correlations from 20 to 50°C were obtained for different materials, which is the usual hydration study temperature range. These were directly obtained from MDSC cp data for different types of cement, for hydrated and non-hydrated plaster of Paris, as well as for some other materials used in authors research activities referring to cement and mortar hydration studies, such as solid wastes, clays, sand, lime derived products and metakaolinite.

Keywords: Modulated DSC, specific heat, cement, construction materials

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Influence of temperature on the content of degradation products of a soybean biodiesel oxidation

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Biodiesel has been widely used as an alternative fuel in diesel engines. However, although its physicochemical properties make it a substitute for traditional diesel fuel, biodiesel is more susceptible to oxidation and degradation during storage than the former one [1]. The high content of unsaturated fatty acid methyl (or ethyl) esters present in biodiesel causes its fast oxidative degradation when in contact with precursor agents as oxygen [2]. The reaction products are highly unstable, resulting in a mixture of different species, some of them of high molecular weight producing sediments and undesirable polymer compounds [3].

In this study, a sample of commercial soybean biodiesel was aged at 50 °C, 110 °C, 150 °C and 200 °C in a Rancimat equipment. This was performed bubbling air into the sample (10 L/h air flow rate), for 5h. The original biodiesel samples and the aged samples were analyzed by **thermogravimetry** (TG/DTG), under nitrogen atmosphere, and the data were compared with those obtained from the analyses performed by size-exclusion chromatography (SEC). Infrared (IR) spectroscopy analyses were also performed. The objective of this work was to evaluate the effect of the aging temperature on the oxidation of biodiesel and on the degraded product composition, and to quantify the gums and sediments formed.

The results show the formation of degradation products more volatile than biodiesel (light fractions) and heavier ones (heavy fractions). As expected, an increase in the content of the degradation products is observed with increasing temperature. The TG/DTG curves of samples aged at 150 °C and 200 °C show higher formation of heavier products than biodiesel. These sediments have higher thermal stability compared to those obtained in the lower temperature tests. The data obtained by SEC analysis confirm the same trend observed in the TG/DTG results. Higher aging temperature promote a higher sediment content and molecular weight. The IR spectra, specifically the carbonyl stretch band, confirm the degradation of biodiesel into acids, ketones and other compounds containing this functional group. The region corresponding to the fingerprint shows the formation of heavy products (gums and sediments).

The results indicate that the composition of the degradation products formed in the aged biodiesel is strongly dependent on the temperature employed in the aging process.

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TG/DTG study of the effect of lime and fly ash slurry milling on portland cement V type hydration

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The hydration of Portland type V cement pastes containing lime sludge (waste from the pulp and paper industry) and fly ash (thermoelectric waste) was investigated by thermal analysis. This study aims to evaluate by thermal analysis the effects of lime mud and fly ash in the early stages (4, 12 and 24 hours) and at older ages (14, 28 and 90 days) of cement hydration. Portland Type V High Initial Strength.

Different degrees of cement substitution were made with each aggregate to prepare the water / cement ratio pastes, in mass of 0.5, which was the same ratio used to prepare the control pastes having only type V cement and demineralized water. To follow the evolution of the hydration reactions of the pastes, thermogravimetric analysis (TG) and derived thermogravimetry (DTG) were performed. The quantification of the hydration phases of the cement was performed through the loss of mass that these phases present during the analysis, they are the free water content and chemically combined with the hydration products and the carbonic anhydride volatilization in the calcium carbonate decomposition. Results were compared based on the initial cement mass of each sample. The equipment used was a simultaneous TG / DSC model SQT 600 device from TA Instruments. The tests were carried out in a 100 mL.min $^{-1}$ atmosphere of N_2, with a heating rate of 10 ° C.min^{-1} and a temperature ranging from 35 °C to 1000 °C. Prior to this heating, the samples are kept at 35 °C for one hour in the equipment itself to eliminate any remaining free water.

The results show that both aggregates favor the hydration of type V cement during the analysis period and, apparently, lime mud has a higher action than fly ash. During the simultaneous use of the two tailings in the hydration process, a synergistic effect was found, which also favored the cement hydration process. It was observed that lime sludge contributed greatly to the calcium carbonate content generated and it appears that their porosity encourages greater carbonation over time, as the nucleation effect of lime sludge increased the production of calcium hydroxide that may have been the cause of the highest carbonation.

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Qualitative and quantitative characterization of Brazilian iron ore tailings by thermal analysis

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Iron ore tailings derived from mining activities in Brazil have a huge and important demand for their destination in other productive industries. Evaluation and indication of the best options of application in civil construction, between others, begins with an accurate mineral characterization.

This work presents and discusses the results of an alternative method, used to characterize qualitatively and quantitatively the chemical and mineral composition of the tailings by using thermogravimetry (TG) coupled with X-ray fluorescence and X-ray diffraction data. The analyzed samples are from a large Brazilian Iron Ore Unit Beneficiation, which are representative of tailings generated after flotation and hydrocyclone steps.

In the present case, TG analysis allows a precise quantification of the water mass percentage lost from the thermal decomposition of some mineral constituents [1], such as goethite and kaolinite. Consequently, their content in the sample can be calculated directly from TG data, but moreover, since the chemical and mineral composition are known, the mass percentage of other minerals in the constitution of the sample can be found by solving a system of equations, which in turn is obtained from stoichiometric correlations (even for constituents present in minor contents) [2]. The results found were compared with those obtained by the Rietveld refinement technique and a reasonable similarity was noted.

Rietveld Method is undoubted one of the most spread and reliable techniques for quantitative crystalline mineral composition from XRD data. But it should be noted that this method requires a highly specialized knowledge, whereas the proposed quantification, once a well-defined pattern is established, can be more easily implemented. This means that, for the study in question – characterization of ore tailings for applications in other production processes -, the presented method represents an easier and helpful tool for engineering students and researchers.

Keywords: Iron ore tailing, Mining Industry, Mineral Characterization, Thermal Analysis

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Densified alumina obtained by two-step sintering: Effect of the microstructure on the mechanical properties

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A defect-free alumina presenting high density and low grain size shows improved properties and reliability [1]. For example, fracture strength is significantly higher for fine-grained alumina than for coarse-grained alumina [2]. The two-step sintering technique has been used successfully for the refinement of ceramic grains, including alumina [3]. Lóh et al. [4] applied this technique to evaluate three commercial alumina powders of different purity (92, 96 and 99 wt% of Al_2O_3) and particle size (between 0.73 and 2.16 µm) by using optical dilatometry. Higher D_{rel} values and lower grain size of alumina were obtained with higher T2 and lower t2. The suppression of grain growth was obtained for 99 wt% purity alumina sintered at T1 of 1550 °C for 5 min and T2 of 1500 °C for 4 h, showing higher densification (~96% relative density) and reduced grain size (0.94±0.15 µm). However, the relationship between microstructure and mechanical properties must be evaluated.

Thus, this work aims to compare the mechanical behavior between alumina obtained by two-step sintering and conventional sintering regarding to density and grain size. Different two-step treatments were applied in a commercial alumina (99.7 wt.%-Al_2O_3 content, 0.73 µm average particle size) and compared with conventional sintering.

The powder was formed by uniaxial pressing (140 MPa specific pressure). The samples were heat treated (10 °C/min heating rate and 50 °C/min cooling rate in the second step). The microstructural analysis was performed in a scanning electron microscope. The mean grain size was determined the intercept method [5]. Porosity was determined by relation between apparent density of the sintered alumina and theoretical density. The bending strength test was performed based on ASTM 1161-13. Fracture toughness was measured based on the notch method. The microhardness test was performed by the Knoop technique.

Mechanical properties were significative improved, such as flexural strength (from 286 to 303 MPa), fracture toughness (from 4.09 to 4.35 MPa.$m^{0.5}$) and Knoop microhardness (from 17.5 to 17.6 GPa), in comparison to the conventional sintering, even with higher porosity, 2.36% in samples obtained by two-step sintering and 1.80% in the conventional sintering. By means of factorial analysis, relative density shows that temperature and holding time of second step individually influence relative density, but temperature has a greater effect. On the other hand, the temperature and holding time interaction of the second step presents the highest effect on the average grain size.

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Study of C3S phase evolution by DSC for the development of an endodontic tricalcium silicate

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Endodontics calcium silicates-based cements are the mostly used materials in the root-end filling or perforation. However, drawbacks the high cost highlights the need for improvements in their manufacturing process by the development of alternative products. In this way, differential scanning calorimetry (DSC) and high-temperature powder X-ray diffraction (HT-XRD) studies of C_3S phase are reported to identify and quantify important parameters of the hydration reactions, such as the hydration degree. A C_3S reference was prepared with pure chemical reagents for the development of a novel biomaterial calcium silicate-based cements, which have been defined in order to keep the positive properties and clinical applications typical of calcium silicates. The results indicated that such material could be obtained by botton-up synthesis routes aiming at the proper balance between the C_3S phase and the use of other cementitious materials. DSC proved to be a very useful technique to accompany this development.

Rosmarinic acid conjugated hemocyanins: synthesis and stability

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Hemocyanins (Hcs) are large copper-containing oxygen-transporting proteins that present in the hemolymph of arthropods and molluscs [1]. Numerous studies reveal their potential as immunostimulants, vaccine adjuvants and protein carriers [1]. In addition, various native and chemically modified Hcs exhibit cytotoxicity to some types of cancer.

Here, we report the preparation of conjugates of rosmarinic acid with *Rapana thomasiana* Hc (RtH) and *Helix lucorum* Hc (HlH). Rosmarinic acid is a secondary plant metabolite that along with other biological activities exhibit anticancer, antiangiogenic, antiinflammatory, antioxidant, and antimicrobial activities [2]. The two Hc-rosmarinic acid conjugates were obtained in a two step reaction and were purified by gel filtration using Sephadex G 25 column. Thermostability and thermal denaturation of the RtH-rosmarinic acid and HlH-rosmarinic acid conjugates was studied using a high-sensitivity differential scanning microcalorimeter DASM-4 (Biopribor, Pushchino, Russia), with a sensitivity > 0.017 mJ K^{-1} and a noise level < ±0.05 µW. We observed that the chemical modification did not affect significantly the thermal stability of the two Hcs. For the two Hcs-rosmarinic acid conjugates, the obtained DSC curves show an asymmetrical peak, which implies the existence of more than one structural unit in the analyzed samples. The DSC profiles of the modified hemocyanins differ than those of the corresponding native Hc, which is an indication for a structural rearrangement in the molecule. To assess the differences in the secondary structure of the native and conjugated with rosmarinic acid Hcs was applied attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. Changes in the Amide I band (1700 cm^{-1}–1600 cm^{-1}) were monitored. The chemically modified Hc seems to be less prone to aggregation and the side-chains of the amino acid residues are found to be buried inside the protein not so exposed to the solvent. Tested in vitro at concentrations up to 1 mg/mL, the native and the rosmarinic acid modified Hcs are not toxic to normal mice fibroblasts (3T3).

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Effect of ketoprofen-based ILs on secondary structure and thermal stability of human serum albumin

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Ionic liquids (ILs) based on active pharmaceutical ingredients are of current interest for the pharmaceutical industry. They have potential to overcome some classical problems of solid state drugs e.g. polymorphism, low bioavailability that is attributed to low solubility of hydrophobic drugs in aqueous media, IL is an approach to reduce the toxicity of the classical drugs and to offer an alternative drug delivery [1]. A series of ILs comprised of amino-acid alkyl ester (AAE) cations and a ketoprofen anion has been synthesized in three steps: 1) the corresponding amino AAE hydrochlorides were prepared; 2) the free AAE were obtained; 3) the target ketoprofen amino alkyl ester salts were syntheiszed. The ILs are characterized by FTIR, H^1- and C^{13}NMR, TGA, etc In vitro cytotoxicity assays show that the synthesized ketoprofen amino alkyl ester salts are less toxic to mice macrophages than ketoprofen. Under physiological conditions, interactions between the ILs and human serum albumin (HSA) were investigated using fluorescence and FTIR spectroscopies.

Thermostability and thermal denaturation of the HSA in presence of ketoprofen amino alkyl ester salts was studied using a high-sensitivity differential scanning microcalorimeter DASM-4 (Biopribor, Pushchino, Russia), with a sensitivity > 0.017 mJ K^{-1} and a noise level $< \pm0.05$ µW. Similar DSC profiles were observed for all HSA-IL complexes. The obtained DSC curves have an asymmetric shape with a main endothermic event cantered at 75ºC and a shoulder centered at 50-52ºC.

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Effect of sulphur-acid pre-treatment on the thermal properties of mixtures of ash from the biomass and chicken litter

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Industrial methods applied in poultry define the generation of large amounts of waste to a small production area. The situation in certain areas is complicated by the remoteness of farmland and shortage of good techniques for treatment and recovery of waste. That raises animal hygiene and environmental problems [1, 2].

In Bulgaria there are very few realized practices for using biowaste on poultry as a secondary raw material or energy resource [2]. This problem has not found the best solution and globally.

This work is devoted to studying the possibilities to minimize waste generated by poultry farms by developing and offering new approaches to converting them into useful products through which to implement a closed life cycle [3, 4].

The proposed new solution is constructed on the basis of waste from poultry farms with additional waste products from other industries and biomass. On the basis of this developed compositions containing poultry excrement and ash from the biomass, which has been acid -treated with sulphuric acid in various ratios. The aim is to do integrated recovery of several wastes. These thermal investigations have attempted application of the solid phase poultry waste and identifying the phases in it, in order to obtain organic products for agriculture.

It was found that the selected wastes and other raw materials have a structure and composition, which defines them as carriers of essential micro-nutrients without excessive content of heavy and toxic elements, which allows them to be classified as suitable components for obtaining soil improvers

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Effect of high-energy dry milling in the structural and thermal properties of biphasic ceramic

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Hydroxyapatite is included in the group of biochemicals together with tetracalcium phosphate ($Ca_4P_2O_9$), amorphous calcium phosphate, alpha-tricalcium phosphate ($Ca_3(PO_4)_2$), beta-tricalcium phosphate ($Ca_3(PO_4)_2$). These materials are often studied to modify and improve their properties for the application in medicine.

In the present study, samples of nanoparticulate sintered biphasic calcium phosphates - hydroxyapatite - $Ca_{10}(PO_4)_6(OH)_2$ and β-tricalcium phosphate - $Ca_3(PO_4)_2$ subjected to high energy milling activation with a different duration from 5 hours to 100 hours activation on dry conditions.

The effect of high energy milling activation on the compositional and structural changes of biphasic ceramic is studied by means of XRD, Fourier Transformed Infrared (FTIR) measurements as well as thermal analyses (TG-DTG-DTA). The HEM activation was carried out in a planetary mill ('Pulverisette'6 Fritsch) at 600 rev min^{-1} with Ahate milling balls (10 mm diameter) in standard mass of 30 g of sample.

The study on activation effect shows that the mechanical activation impacts at the micro-level is as following: (i) change the strength of chemical bond; (ii) deformation of polyhedrons; (iii) smaller size of crystallites with increased degree of structural defects leading to metastable phosphorite with increased dispersity.

The obtained results show correlation in the behavior of the studied samples in regards of the incorporated in the structure of OH-apatite carbonate ions. After HEM activation of the raw sample, the A-, B- and A-B type carbonate-apatite are formed. The new isomorphic phases (A-and A-B type carbonate-hydroxyapatite) are decarbonized at temperature of 650-1600 K.

Keywords: bioceramics, high energy milling activation, carbonate-apatite, thermal effects

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Thermodynamic characteristics of red blood cells derived from women with miscarriage. The aging effect

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Knowledge of the biophysical characteristics of red blood cells (RBC) during aging is of particular interest since this complex physiological phenomenon is related to human health and pathologies. In this work we apply differential scanning calorimetry to study the thermal stability of hemoglobin and specific plasma membrane proteins of RBC during the course ageing. The cells are derived either from women shortly after miscarriage or from healthy (pregnant and non-pregnant) women.

The calorimetric profiles of freshly collected RBC derived from the studied patients do not differ from those of healthy women, however in the course of ageing the temperature of hemoglobin unfolding gradually decreases more rapidly and the transition assigned to the cytoplasmic domain of band 3 protein disappeares at an earlier stage for women with miscarriage than for healthy ones. Sequential heating (to 60 °C)-cooling cycles, causing denaturation of spectrin, led to hemoglobin destabilization in the case of women with miscarriages, while to negligible effect on the hemoglobin stability of healthy women.

Data strongly suggest that the ageing of RBC derived from women that underwent a miscarriage proceeds faster than from healthy women as evidenced by the thermal destabilization of hemoglobin and the structural band 3 protein.

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Thermal Stability Study of Hemocyanins

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Many natural proteins act as a functional basis of biologic drugs. One of the first steps, required to outline the design of the therapeutic properties of protein drugs, is their thermodynamic characterization. Hemocyanins (Hcs) are oligomeric copper-containing glycoproteins that function as oxygen carriers in the hemolymph of several molluscs and arthropods. Besides their important biological function, a variety of medical applications of molluscan Hcs emerged.

The thermal unfolding of hemocyanins, purified from garden snails Helix aspersa maxima (gastropod) (HaH) and garden snails Helix lucorum (HlH), was investigated by differential scanning calorimetry (DSC). Denaturation of these hemocyanins was found to be an irreversible process. One transition, with an apparent transition temperature (Tm) at 79.8 °C and 82.7 °C, respectivelly, was detected in the thermograms of HaH and HlH using scan rate of 1.0 °C min^{-1}. The scan rate dependence of the thermograms indicated that the thermal unfolding of investigated hemocyanins was kinetically controlled. The thermal denaturation of the Hcs was described by the two-state irreversible model, and parameters of the Arrhenius equation were calculated.

The results of the present study of the Hcs, allow classifying these Hcs as thermostable proteins (T_m ~80 °C). The high degree of oligomerization of hemocyanin molecules in general is one of the reasons for their increased thermal stability. The obtained data will facilitate the further investigation of therapeutic properties and medical applications of these dioxygen-binding proteins.

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Hydration of mortar with EPS foam using Calorimetry & TGA

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Lightweight architectural and structural cementitious cladding elements are generally manufactured using mortar mix with low water to cement ratio (w/c) and incorporate expanded polystyrene (EPS) foam with a density of approximately 24 kg/m^3. Although EPS is a closed-cell foam, it is not waterproof. The removal of any water due to absorption has detrimental effects on the mechanical and durability properties of low w/c mortar. This study employs two thermal analysis techniques, isothermal calorimetry and thermogravimetric analysis (TGA), to investigate the effects of adding EPS foam on the hydration of low w/c mortar mixes.

A self-consolidating mortar mix with a w/c of 0.30, fine aggregate to cement ratio of 1.1, and cement content of 900 kg/m^3 was investigated with and without EPS foam. The samples consisted of 11.6±1.0 mm thick EPS foam sandwiched between two 15.9±2.5 mm thick layers of mortar. Isothermal calorimetry tests were performed for 24h at 20.1^{o}C. After 2h, 4h, 6h and 24h from the start of the test, samples were removed from the calorimeter, ground to a powder form, and tested using the TGA. The total heat of hydration and degree of hydration were used to assess the effects of EPS foam on the mortar properties. The degree of hydration was calculated based on the heat released [1, 2] and from chemically bound water [3]. The TGA values were adjusted to compensate for the fine aggregate, with the ratio of fine aggregate to cement assumed constant [4]. The isothermal calorimetry results showed a 4.6% decrease in the peak heat flow and a 2.8% decrease in the total heat of hydration at 24h when compared with the same mortar mix without EPS foam. The TGA results showed that the EPS foam has no statistical effects on the cement degree of hydration. The quantified cement degree of hydration of mortar with EPS foam was 45.8±2.9% compared to 45.6±3.5% without. In brief, the experimental results from the calorimetry and TGA were consistent. Moreover, they revealed that the water absorption of EPS foam insert is statistically negligible and therefore has no significant effects on the cement degree of hydration.

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Kinetic deconvolution analysis applied to liquid sodium–calcium carbonate reaction

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In this study, the reaction of liquid Na with $CaCO_3$ was studied kinetically as one model reaction of the liquid Na with structural concreate [1-3] by postulating a severe accident in a sodium-cooled fast reactor (SFR). The reaction, $4Na + 3CaCO_3 \rightarrow 2Na_2CO_3 + 3CaO + C$, that occurred in the temperature range of 650–850 K was tracked by the exothermic DSC peak and morphological observations for Na–$CaCO_3$ powder and Na–$CaCO_3$ pellet samples. Details on the kinetic and mechanistic features of the reactions are demonstrated in this presentation.

In the case of liquid Na–$CaCO_3$ powder reaction, four exothermic peaks appeared by overlapping partially. Changes in the distribution of $CaCO_3$ powder in liquid Na and in the contact area of the reactants as the reaction advances are possible reasons for the apparent multistep reaction. From the overlapping reaction steps, the first reaction step was extracted using mathematical deconvolution analysis [4], which is a statistical peak shape analysis. The first reaction step, recognized as the reaction at the first contact area between liquid Na and the surfaces of $CaCO_3$, was characterized by the first-order rate law with $(E_{a,1}, A_1) = (117 \pm 8$ kJ/mol, $(2.9 \pm 0.1) \times 10^5$ 1/s)

For the liquid Na–$CaCO_3$ pellet reaction, a single DSC exothermic peak was observed as the result of the one-dimensional regulation of the reaction geometry. The kinetic behavior was described by a two-step physico-geometrical consecutive process comprising the initial and main reaction steps. Through morphological observations, these two reaction steps were characterized as the surface reaction and subsequent internal reaction, respectively. The kinetic deconvolution analysis (KDA) [4] was applied to characterize the kinetics of each reaction step. A systematic decrease in the contribution of the first reaction step with heating rate was expected from the results of KDA. The first reaction step indicated a monotonous acceleration at a constant temperature with $(E_{a,1}, A_1) = (150 \pm 2$ kJ/mol, $(9.3 \pm 0.3) \times 10^7$ 1/s). During the second reaction step, the maximum rate appeared midway through the reaction step, in which the deceleration during the second half of the reaction step was interpreted as being caused by the consumption of liquid Na. The apparent Arrhenius parameters for the second reaction step were estimated to be $(E_{a,2}, A_2) = (66 \pm 1$ kJ/mol, $(7.6 \pm 0.5) \times 10^3$ 1/s).

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Thermal properties of some locally produced edible oils

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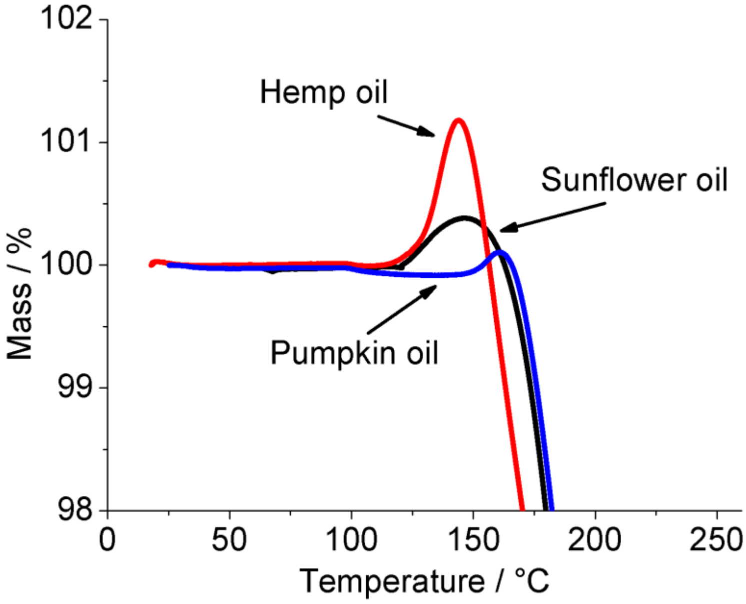
The importance of vegetable oils as valuable commodities for human nutrition is well recognized. Vegetable oils are usually used for frying, where they work as a heat transfer medium and contribute to flavour and texture of food.

In this study thermal and oxidative stability of several locally produced edible oils were tested: extra virgin olive oil, sunflower oil, pumpkin seed oil, hemp oil. During thermogravimetric measurements in air atmosphere at heating rate 1°C min^{-1} the highest mass increase due to oxidation was notified in hemp oil while sunflower oil displayed second highest mass increase but both samples displayed the mass increase maximum at similar temperature around 150 °C. When tested in nitrogen atmosphere all oils showed very similar thermal stability. Accelerated oxidation tests using the Rancimat method were performed at two temperatures 110 °C and 150 °C. Results are in good agreement with TG measurements where the lowest oxidation stability displayed hemp oil (3 h at 110 °C) and sunflower oil (4.7 h at 110 °C). Also, DSC was used to study high and low temperature properties of oils.



Increase of mass caused by oxidation during heating (1°C min^{-1}) in air atmosphere.

Study on the properties of electrospun polycaprolactone/silk fibroin scaffolds

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For centuries silk fibroin has been used as a textile fiber. Beyond textiles, silk fibroin has also been used in biomedical applications as a surgical material for decades. Because of his good mechanical properties, biocompatibility and biodegradability silk fibroin is being further developed for various emerging applications. In this work, tissue engineering scaffolds composed of polycaprolactone (PCL) and silk fibroin (SF) were prepared by electrospinning technique. Morphology, chemical composition, thermal properties, thermal stability and hydrophobicity of the PCL/SF scaffolds were characterized to evaluate the effect of SF by means of scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA*)* and water contact angle analysis. Electrospinning resulted in uniform fibers morphology, with thinner fibers in case of the PCL/SF scaffolds and a homogeneous SF distribution throughout the fibers. The FTIR results showed that the silk fibroin was successfully introduced to the PCL scaffolds. The hydrophilicity of the PCL modified scaffolds was enhanced. Results obtained with DSC analysis showed that with addition of the silk fibroin, glass transition temperature of the PCL increases, while the melting temperature and degree of crystallinity decreases, because of the less organized crystal structure with addition of silk fibroin. The thermal stability of the PCL/SF scaffolds also decreased with the addition of the SF.

Thermokinetic study of magnesium hydroxide obtained from seawater

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Magnesium hydroxide ($Mg(OH)_2$) is a very important inorganic compound with good physical and chemical properties. It has wide application in many fields, such as flame retardant in polymers, special ceramics, wastewater treatment, in the paper industry, as a catalyst, additive. Magnesium hydroxide can be produced by different methods such as precipitation, solvothermal and hydrothermal methods, microwave methods, electrochemical methods, the sol-gel method, dehydratation and hydration of commercial forms of $Mg(OH)_2$ and MgO, and the use of dolomite or sea water[1-2]. The precipitation crystallization method is the most economic one for industrial continuous production, having a simple process and low energy consumption [3]. In this paper magnesium hydroxide has been obtained from seawater by a well-known industrial process [4] which involves the chemical reaction between magnesium ions of seawater with dolomite lime to produce the magnesium hydroxide precipitate.

Furthermore, the precipitate was modified by ultrasound of high intensity. The purpose was to obtain magnesium hydroxide with high purity and reduced particle size without agglomeration. The precipitated magnesium hydroxide is characterized by the particle size distribution determined by the laser scattering method in the range of 20 nm to 200 mm, and by the SEM/EDS analysis.

Likewise, in order to investigate the effect of particle size on the thermal stability, thermokinetic study of magnesium hydroxide samples was performed by non-isothermal thermogravimetry in an inert atmosphere at different heating rates. The obtained data were used for the kinetic analysis of the degradation process. Kinetic analysis was performed using the isoconversional Friedman method in combination with the multivariate nonlinear regression method. Kinetic analysis revealed the complexity of the thermal degradation process for both investigated samples. Likewise, for each degradation stage of investigated samples, kinetic parameters (activation energy, pre-exponential factor and kinetic model) were calculated and compared.

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The role of amino acids (G, A, N) in the wet chemistry synthesis and thermal development of gamma alumina with specific morphology

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Alumina (Al_2O_3) is critically important material in variety of applications such as catalysis, due to chemical stability and mechanical durability over the wide temperature range. Furthermore, gamma alumina powders having defect cubic spinel structure with nanocrystalline character can be prepared using only moderate thermal treatment to facilitate catalyst support application. Reaching out to advanced morphological features is becoming increasingly important, as the limits of the nano-seized powders have been reached.

Here we bring about wet chemistry synthesis using aluminium nitrate nonahydrate (ANN) precursor combined with different amino acid fuel. The amino acids; glycine (G), alanine (A) and asparagine (N) have been specifically selected in order to show the role of gradual increase of their: 1) molar weight, 2) enthalpy of combustion, 3) amine groups content and 4) ratio to ANN, on the derived morphologies. Namely, the conditions leading to development of different morphologies from gels to powders were found to be heavily under the influence of fuel/oxygen ratio, i.e. on the smouldering vs flaming mechanism of the combustion. Thereof, the thermal evolution of the alumina precursors was monitored in details.

Higher content of nitrates (predominately from amino rich amino acids) strongly promoted auto-combustion behaviour. As-derived alumina precursors have been thermally treated at various temperatures (quenched and soaked), to monitor gamma and alpha alumina crystallisation, with respect to the development of morphology.

It was shown that this combustion synthesis allows facile tailoring nanocrystalline gamma alumina with different morphological features. Different textures types have been observed, such as porous wormhole, porous particulate and porous flakes. Detailed structural (XRD, FTIR), microstructural (SEM, EDS, BET N_2 A/D, PSD) and thermal (DTA, TGA) characterisations confirm the nanocrystalline character, thermomechanical stability and were not diminished for different porous morphologies in the course of this synthesis.

Hydrothermally-derived ceria doped with manganese in various amounts

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Ceria (CeO_2) is utilized as a catalyst in various environmental applications. Its catalytic properties are mostly attributed to high oxygen storage capacity. Ceria has flourite structure in which oxygen vacancies occur due to occurrence of cerium in two stable oxidation states, Ce^{4+} and Ce^{3+}. The easiness of shift between Ce^{3+} and Ce^{4+} enables the creation of oxygen vacancies, high oxygen mobility and oxygen storage capacity within the lattice. [1]

Doping of cerium oxide improves its catalytic properties in relation to pure cerium oxide. Manganese oxides are known for being capable of storing oxygen and forming many oxides with various oxidation states. MnO_x compounds are highly catalytically active and it is believed that incorporation of Mn atoms in ceria crystal lattice will also improve its catalytic properties. Cerium oxide both doped and pure can be prepared in many ways. The advantages of hydrothermal process are one-pot synthesis, cost-effectiveness and eco-friendliness since it allows obtaining of nanoparticles at low temperatures in just one step. [2]

Therefore, nano-ceria doped with manganese in various amounts was prepared via hydrothermal synthesis and the obtained ceria samples were thermally treated at 500°C for 2h. Both, as-prepared and thermally treated samples were investigated using X-ray diffraction (XRD). It was determined that in the diffraction patterns of as-prepared doped samples, beside ceria, birnessite ($Na_{0.55}Mn_2O_4 \times 1.5H_2O$) lines appear. In the course of thermal treatment birnessite transforms to α-MnO_2. Ceria lattice constant and crystallite size, as well as birnessite share, were obtained through whole powder pattern decomposition. It was established that the share of Mn entering ceria lattice, or forming birnessite varies with nominal composition. However, introduction of Mn in ceria is evident from the slight decrease of ceria lattice constant while crystallite size does not change significantly. Decrease of ceria lattice constant with the increase of Mn share could also be observed in thermally treated samples. Also, although thermal treatments yield with coarsening of crystallites, the decrease of ceria crystallite size with increase of manganese share is evident. Thermally induced changes were monitored via differential thermal analysis and thermo-gravimetric analysis (DTA/TGA) giving insight into birnessite dehydration. Calculation of birnessite share via TGA yield with similar values as obtained using XRD. The compliance of samples composition with nominal was confirmed using energy dispersive X-ray spectroscopy (EDS) while the scanning electron microscope (SEM) analysis revealed birnessite layered formations surrounded with ceria nanoparticles.

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Thermal properties of polylactic acid/modified magnesium hydroxide composites

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Polylactic acid (PLA) has become interesting for research because of its possible use in various application fields due to its biodegradability. PLA belongs to the polymers derived from the renewable resources such as sugar cane corn. The application of this polymer, as well as other polymers, is often limited by their flammability. This problem can be solved by adding flame retardants.

Flame retardants should prevent the start of the combustion reaction or quickly stop the reaction if it has already begun. Magnesium hydroxide ($Mg(OH)_2$) is an environmentally friendly metal hydroxide that is increasingly used as a functional inorganic filler and in this case as a flame retardant for PLA. $Mg(OH)_2$ is possible to produce by extraction from ores, such as magnesite, dolomite, or serpentinite, and from brine/seawater [1]. Inorganic fillers are often surface modified for better interaction with a polymer, i.e. better adhesion, and hence better polymer properties.

The aim of this study was to prepare PLA/modified $Mg(OH)_2$ composites of the satisfactory thermal properties and the thermal stability to extend the PLA application field. $Mg(OH)_2$ was obtained from seawater as an unlimited source of this material. Modification of $Mg(OH)_2$ was performed with 5 and 10% of stearic acid relative to the hydroxide. Using infrared spectroscopy with Fourier transformation (FT-IR) successful chemisorption of stearic acid on the filler surface was confirmed, after which two series of PLA/modified $Mg(OH)_2$ composites were prepared using a laboratory single-screw extruder. The amount of the modified $Mg(OH)_2$ was up to 20 wt %. Differential scanning calorimetry (DSC) was used to investigate the effect of the modified filler on the thermal properties of PLA. Addition of the modified inorganic filler has a complex effect on the PLA thermal properties, with a clear reduction in PLA crystallinity for both composite series. Thus, modified $Mg(OH)_2$ doesn't act as a nucleation agent in the PLA composites. The amount of stearic acid doesn't make noticeable influence on the thermal characteristics of PLA. The thermal stability of the composites was investigated using thermogravimetry (TG). PLA degrades in one degradation stage and the both modified $Mg(OH)_2$ in two. The both PLA/modified $Mg(OH)_2$ composite series degrades up to four degradation stages. With the increase of the modified $Mg(OH)_2$ content in both composite series their decomposition becomes the more complex and the thermal stability of PLA is getting worse. Different amounts of stearic acid used for filler modification didn't produce any influence on the thermal stability of PLA.

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DSC and SEM analysis of Poly(ethylene oxide)/ Polyhedral oligomeric silsesquioxanes (POSS) nanocomposites

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Poly(ethylene oxide) (PEO) as a semi-crystalline, biocompatible, water-soluble polyether finds considerable application in many different branches of industry. PEO based electrolytes are among the most extensively studied polymer ionic conductors, but high crystallinity of PEO limits ionic conductivity of these electrolytes at room temperatures. One of the possible ways to reduce the crystallinity of PEO is the incorporation of nanoparticles such as polyhedral oligomeric silsesquioxanes (POSSs) in the PEO matrix. The use of POSSs for making polymer composites has grown exponentially since the last few years of the 20th century. In comparison with the other most commonly used fillers, POSSs possess the advantage of being molecules. Thus, this allows us to combine their nano-sized cage structures, which have dimensions that are similar to those of most polymer segments and produce a particular and exclusive chemical composition. These characteristics linked with their hybrid (inorganic–organic) nature allow researchers to modify POSS according to particular needs or original ideas, before incorporating them into polymers [1].

In this work PEO nanocomposites with different hepta isobutyl polyhedral oligomeric silsesquioxanes (hib-POSS) were prepared and the influence of hib-POSS on PEO melting was investigated. It was observed that the glass transition temperature, melting temperature and crystallinity of PEO decrease when hib-POSSs with methyl, fluorine or chlorine substituents on phenyl group are present. Taking into account the mass ratio of the components, values of melting enthalpies suggest decrease of PEO crystallinity in the composites, probably due to the formation of POSS-POSS aggregates. Furthermore, hib-POSSs with methyl, fluoro and chloro substituents on phenyl ring narrow the melting and crystallization regions of PEO.

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Phase transformations in commercial hot deformed Al–Zn–Mg–Cu(–Sc–Zr) alloys

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In the present work the effect of hot deformation (300 °C/60 min) on mechanical, thermal properties, microstructure and recrystallization behaviour of the commercial AlZnMgCu(ScZr) alloys was investigated. Microhardness together with differential scanning calorimetry measurements was compared to microstructure development that was observed by transmission and scanning electron microscopy, electron backscatter diffraction and positron annihilation spectroscopy.

Microstructure observation proved eutectic phase at (sub)grain boundaries in the mould cast and hot deformed alloys. The grain size was ~ 20 μm in the mould cast AlZnMgCuScZr and ~ 1000 μm in the mould cast AlZnMgCu alloy. Hot deformation has no influence on the grain size of the alloys. Primary multilayer $Al_3(Sc,Zr)$ particles precipitated during casting and subsequent cooling in the alloy with Sc,Zr-addition. These particles were stable up to 450 °C.

Guinier-Preston zones and/or solute clusters were dissolved during the annealing up to ~ 170 °C in the mould cast alloys. In the hot deformed alloys no thermal effects connected with the dissolution of Guinier-Preston zones and/or solute clusters were observed. The hardening effect in the Sc,Zr-containing alloys observed after annealing above 300 °C is caused by the precipitation of the secondary $Al_3(Sc,Zr)$ particles. Deformation has no significant effect on the apparent activation energy values of thermal processes. Sc,Zr-addition has a significant antirecrystallization. No recrystallization was observed in the hot deformed AlZnMgCuScZr alloy neither after annealing at 350 °C/10 hours nor after annealing at 450 °C/10 hours. A partial recrystallization effect of the hot deformed AlZnMgCu alloy is clearly registered after annealing at 350 °C/10 hours and occurs very strongly after annealing at 450 °C/10 hours.

PS1.031

The effect of organic bases on thermal degradation of peroxo-titanates

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The nanostructured TiO_2 with leaflet structure, prepared from peroxo-titanic acid using ammonia shows unique photocatalytic abilities [1]. The use of various organic bases during preparation can result in the presence of organic components in the peroxo-titanate system and change the material's properties. The aims of this study were to specify the influence of used amines on thermal degradation of peroxo-titanates and the quantification of contained organic species. Various types of amines (primary, secondary, tertiary, quaternary ammonium hydroxides, tri- and tetramines) were used during synthesis. Samples were characterized with TG-DTA, high temperature XRD and SEM microscopy.

All materials share a very similar two-step shape of TG curves when heated in argon atmosphere to 1000 °C. Moisture, CO_2 adsorbed on surface and oxygen from peroxo groups are released during the first endothermic step up to ~170 °C, with mass loss of 9-15 %. This is followed by a second step, which is accompanied by exothermic reaction with peak maximum around 220 °C and corresponds to decomposition of organic species. Second degradation step continues until the temperature reaches a range of 400-470 °C.

Three different types of TG curves were observed in oxidizing atmosphere. Materials based on secondary, tertiary amines and compounds with more amino groups show the same behaviour in inert and oxidizing atmosphere. It suggests that organic species are removed by simple decomposition to volatile products. Samples with primary amines used during synthesis have in oxidizing atmosphere the third step occurring at 470-510 °C with mass loss of about 4-6 %. Similar third exothermic step was recorded in the systems which were based on quaternary ammonium hydroxides, but at lower temperature (450-480 °C) and with lower mass loss (1-2 %).

In some measurements crystallization of amorphous phase to anatase at temperatures 350-400 °C was observed, but change to rutile could not recorded. High temperature XRD confirmed this temperature range of crystallization to anatase, which then starts to pass to rutile in temperature range between 800-900 °C.

Calculated content of present organic components in dry materials were similar for materials from secondary and tertiary amine, i.e. 16 % and 19 % respectively. Using polyamines lead to higher content of organics, beetween 21-25 %. Amount of organics in samples prepared from primary amines was 18 % and from quaternary ammonium hydroxides 13-15 %.

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Non-stoichiometry in Cs_2HfCl_6 material and study of its influence on the CsCl-$HfCl_4$ phase diagram using DSC-TG analysis

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The cesium hafnium chloride (Cs_2HfCl_6) is a ternary halide, which melts congruently at temperature 826 °C. It is formed by cesium chloride (CsCl) and hafnium chloride ($HfCl_4$) mixed together in stoichiometric ratio 2:1 and crystalizes in cubic structure (space group *Fm-3m*) with lattice parameter $a = 10.42 \pm 0.01$ Å [1]. Due to high effective number Z = 58, high light yield around 54,000 photons MeV^{-1}, energy resolution of 3.3 % at 662 keV, high proportionality, moderate density 3.86 g cm^{-3}, and low hygroscopicity, the Cs_2HfCl_6 is considered as a suitable candidate for cost-effective detectors of ionization radiation [2].

This paper reports on the investigation of the undoped Cs_2HfCl_6 with stoichiometric and non-stoichiometric composition by DSC-TG thermal analyses. Five set of Cs_2HfCl_6 samples were studied: one stoichiometric with content of CsCl and $HfCl_4$ 2:1 and four non-stoichiometric with deficit (5 and 10 mol%) and excess (5 and 10 mol%) of $HfCl_4$, respectively. All five samples of Cs_2HfCl_6 material were enclosed under vacuum in sealed quartz ampules and measured by the non-isothermal simultaneous differential scanning calorimetry and thermogravimetry (DSC-TG) analysis.

The goal of this work is to investigate the behaviour of Cs_2HfCl_6 in enclosed system and evaluate the influence of Cs_2HfCl_6 non-stoichiometry on its thermal properties, i.e. characteristic temperatures of various phase transitions. This analysis contributes to the improvement and optimization of the conditions for crystal growth of the Cs_2HfCl_6 from the melt by the Bridgman method.

Acknowledgement

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Optimization of carbon yield from biomass pyrolysis based on kinetic analysis

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Pyrolysis of biomass based lignocelulosic materials is well established industrial process for production of either liquid (biooils) or solid (biochars) products. In last period the importance of biomass as precursor of special porous carbonaceous materials dramatically increased with increasing application potential of porous carbons as active matter of supercapacitors, electrodes in fuel cells, reservoirs for gas and energy storage and in many other applications. Thus, determination of conditions for effective conversion of biomass based material to carbons has attracted significant attention.

Based on earlier published approach [1-2], our contribution aims to describe the methodology of finding appropriate kinetic equation sufficiently describing pyrolysis of biomass based materials.

For the basic adopted mechanism (direct carbonization combined with parallel two step decomposition) kinetic equation was constructed with the use of Arrhenius equation for temperature term and simplified Sestak–Berggren equation for dependence on conversion. The parameters of kinetic equation were found by non-linear regression, comparing the theoretical TG curve with experimental ones obtained under various heating rates (1–20 K/min) with residual sum of squares used as the fitting criterion.

The kinetic equations were obtained for pure cellulose, wood powder and their derivatives obtained by impregnation with K_2CO_3 solution. With their use, the pyrolysis could be theoretically modeled including opposite dependence of carbon yield on heating rate for cellulose and wood based samples.

We expect that presented methodology can be used for successful prediction of thermal behavior of biomass during pyrolysis under various temperature programs including non-linear and isothermal heating and consequently optimization of temperature program steps for obtaining maximal carbon yield.

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Formation of belite-based binder from waste materials

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The present work deals with the preparation of belite-based binders using a mixture of sludge waste from mining and washing of limestone (source of $CaCO_3$ and SiO_2), and waste material from acetylene gas cylinders filler containing hydrosilicates - tobermorite and xonotlite. These wastes are of suitable oxide composition for the preparation of belite cements. The materials were mixed together in different proportions and burned at temperatures from 800 to 1300 °C. K_2O was used as dopant to stabilize the reactive belite modification. The main interest was focused on the process of belite formation related to its reactivity. During burning of waste material mixtures, limestone is decomposed providing CaO, while tobermorite and xonotlite are transformed into wollastonite. Then, belite is formed by reaction of SiO_2 and CaO, as it is typical in Portland clinker, but also by reaction of wollastonite and CaO. The process of belite formation influences its hydraulic properties to a great extent. Carbonation of calcium silicates was studied as well. Phase composition of burned products was studied by X-ray powder diffraction. Isothermal calorimetry was used to evaluate the hydraulic activity of belite binders. Hydration and carbonation products were identified by differential thermal analysis.

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Evaluating the impact of polymer chain length on API solubility using DSC-based methods

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A high percentage of new and current active pharmaceutical ingredients (APIs) demonstrate poor oral bioavailability. According to the Biopharmaceutics Classification System, these are Class II/IV compounds which are exhibitive of high/low permeability and low solubility. The formulation of so-called amorphous solid dispersions (ASDs), in which a hydrophobic drug substance is integrated into a hydrophilic excipient matrix, is a promising technique for enhancing the API's solubility and dissolution. For both rational component selection, in terms of miscibility, and prediction of their ASD's long-term physical stability, knowledge of a temperature–composition phase diagram (complete with liquid-liquid equilibria (LLE), solid-liquid equilibria (SLE) and glass-transition temperature (T_g) curves) is imperative to reduce time-consuming and often challenging experimental efforts.

Three procedures for predicting drug–polymer solubility at elevated temperatures using differential scanning calorimetry (DSC) have been discussed in the literature: melting point depression (MPD) [1], recrystallization [2] and melting enthalpy [3]. Likewise, three equations for calculating the T_g at different API concentrations, which are of interest in this study, have been proposed: Couchman–Karasz (C–K) [4], Fox [5] and Gordon–Taylor [6].

In this work, the solubility of four Class II APIs (carbamazepine, ibuprofen, indomethacin and naproxen) in a series of glycol-derived solvents (monomer, dimer, trimer, etc.) will be determined using three DSC-based methods (MPD, recrystallization and melting enthalpy). In addition, the heat capacity (C_p) value of each API will be obtained from micro-DSC measurements and applied to the C–K equation for T_g modelling. Thus, the influence of chain length will be realized and a comparison of the aforementioned thermal protocols and T_g models will be made. Furthermore, the APIs will be subjected to an extensive set of temperature profiles using DSC to probe for polymorphic forms, which could significantly alter their solid-state properties.

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Lithium, Sodium and Potassium Metatitanates and their Application as Heavy Metal Adsorbents

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Titanates have been used as adsorbents for heavy metals owing to their stability and fast adsorption kinetics. Nevertheless, the synthesis of such materials requires extreme reaction conditions. In this work, synthesis of titanates via fast, easy and cost effective way is described. The obtained materials were tested for heavy metal sorption through kinetics and equilibrium batch tests indicating that the prepared adsorbents can be considered as really promising for removal of heavy metal ions from water.

A method of synthesis of advanced hydrated metatitanate pseudomorphs obtained *via* extraction of sulfate ions from the crystals of titanyl sulfate dihydrate and their replacement with hydroxyl groups of NaOH, LiOH and KOH solutions leaving the Ti-O framework untouched has been proposed [1, 2]. It was observed that while material precipitated by KOH was thermally stable up to 150 °C, the decomposition of LiOH and NaOH materials started right at the beginning of the heating. With the increasing temperature, the amorphous materials started to crystallize into various lithium, sodium and potassium titanates and furthermore the growth of larger crystals and nanowhiskers on rods during the crystallization process was observed. The structural changes (especially crystallization into anatase, resp. titanates) during heating up to 1000°C were studied together with adsorption properties of prepared and annealed materials towards heavy metals (Pb(II), Cu(II) and Cd(II)).

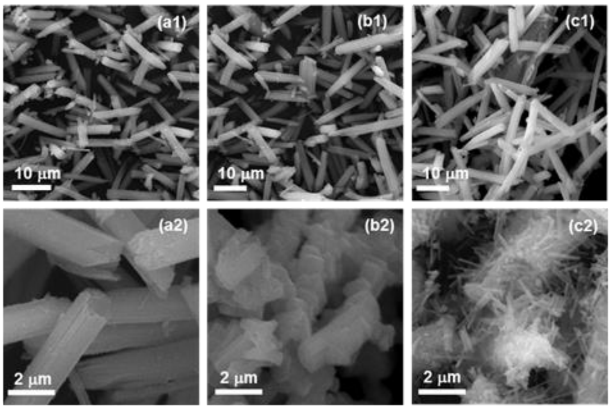

Figure 1. SEM comparison of non-annealed (a1, b1, c1) and annealed materials at 1000 °C (a2, b2, c2) of *TIG-LiOH* (a1, a2), *TIG-NaOH* (b1, b2) and *TIG-KOH* (c1, c2).

The influence of annealing temperature of prepared materials on sorption of Pb(II), Cu(II) and Cd(II) was tested with a result that prepared samples seem to be highly efficient sorbents. The maximum adsorbed amount for Pb(II), as calculated from the Langmuir adsorption model, was 497.3 mg g^{-1} for lithium materials, 469.4 mg g^{-1} for sodium materials, and 476.6 mg g^{-1} for potassium materials. However, the higher the annealing temperature the lower the adsorbed amount of heavy metal ions. Based on the results of adsorption experiments with material characteristics leads to conclusion that (for studied titania based adsorbents) the heavy metal ions adsorption efficiency increase with i) increasing amount of present exchangeable cations and with ii) decreasing degree of crystallinity.

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Crystal growth in $Se_{95}Te_5$ bulk samples and thin films

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Chalcogenide based glassy materials are used in many materials for example: optical fiber, materials with permeability in the infrared region and also in phase changing materials *PCM* (CD, DVD). Between of the most significant processes that occur in these glassy materials is the crystallization. [1].

The crystallization is a temperature dependent process that enables the growth of crystals. In this work we have studied the different mechanisms of crystal growth and their dependence on the thickness of the samples, and how all these parameters can affect the crystal growth rate.

The crystal growth rate is based on two different terms: the kinetic term and the thermodynamical term. The kinetic term expresses how the structural units move trough the interface between the undercooled melt and the glass. This term is often defined by the Stokes-Einstein equation that dictates that exists a correlation between the diffusion coefficient and the coefficient of viscosity. In the other hand the thermodynamic term defines the thermodynamic barrier that the system must overcome in order the crystallization can occur. This barrier is determined by the change of the free Gibbs energy.

Using the crystal growth rate temperature dependence allows to understand more about the crystal growth mechanisms. These mechanisms are based on how the structural units are attached to each other and then how the crystals grow. Between the different mechanisms that has been already observed are:2D-nucleated surface, normal crystal growth and the screw dislocation mechanism.[2,3,4]

As it has been mentioned above the crystal growth in $Se_{95}Te_5$ has been studied in bulk samples and thin films. It should be mentioned that even though that the samples are based on the same elements the crystallization mechanisms change. Studying the crystal growth in the bulk samples it has been observed that the crystals start growing alongside the surface and then as long as the surface is completely homogeneous then is starts to grow to the inner part of the sample. The crystal growth in the thin films is affected by the dimension of the sample (1μm) and it can be compared to the crystal growth at the surface of the bulk.

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Fermentation of non-dairy milks by commercial starter cultures: microcalorimetric approach

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The demand for vegetarian and vegan alternatives to dairy products is constantly and significantly growing all over the world. Fermented plant based foods (yogurt and cheese analogues) offer attractive prospects within the market of non-dairy products, since they can be valuable sources of good quality fats, proteins, dietary fiber, and other phytochemicals important for human health. The choice of lactic acid bacteria for fermentation of milk analogues is limited to strains that can ferment the sugars typically found in the raw materials. The objective of the present study was to evaluate the technological potential of cultures specially formulated for the plant-based fermented products.

Commercial starter cultures were grown in pasteurized retail non-dairy milk (soy, oat, coconut and almond) and bacterial growth was studied using isothermal batch microcalorimeter TAMIV. Maximal specific growth rates, heat produced during different growth stages and lag–phases duration were determined by processing calorimetric curves. In parallel to calorimetric measurements the changes of concentrations of carbohydrates and lactic acid were determined and pH measurements were carried out in order to obtain additional information for the interpretation of calorimetric power-time curves. The sensory characteristics of fermented plant-milk based yogurts were evaluated by a trained panel of assessors using descriptive analysis for their sensory qualities including taste, colour/appearance, odour, texture, and overall acceptability. Gas chromatography coupled with mass spectrometry (GC-MS) were applied to describe the production of aroma compounds.

As a result of this study, suitable starter cultures were selected for the fermentation of each non-dairy milk. It was found, that starter cultures can produce several undesired off-flavors and -aromas, which indicates that dairy starters cannot be directly used for the fermentation of non-dairy analogues. As a casein matrix is not formed during the fermentation of plant milks, the formation of desired texture relies on the starters' ability to produce polysaccharides or on the addition of suitable thickening agents. Further studies are required to select suitable stabilizers for each non-dairy yogurt.

Isothermal microcalorimetry as an innovative *in vitro* approach for assessing the effect of food fibres on human gut microbiome

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Sufficient fibre consumption is essential for normal gut microbiome function. However, the amount of fibre is not the only factor to consider – diverse fibre profile is also needed to assure diversity of the gut microbiome and to maintain the balance among microbial species. While the benefits of fibre consumption have been widely shown [1, 2], the effect of different fibres on individuals has not been thoroughly studied. Combination of isothermal microcalorimetry (IMC) together with chemical analyses (utilization of fibres, production of metabolites), gas production and pH measurements, and metagenomic sequencing of the bacterial communities gives a comprehensive overview of the interactions between gut bacteria and food fibres.

In vitro evaluation of the effect of fibres on human gut microbiome was carried out by inoculating fibres with bacteria from human faecal samples followed by fermentation at 37°C up to 48 h. Heat production patterns differed significantly among studied fibres and were dependent on the microbial consortia used in the IMC experiments. Inulins (fructose polymers) were shown to promote the growth of *Bifidobacterium* and *Bacteroides* species more compared to other fibres. Also, the most prominent production of organic acids, compounds with reported health benefits, was seen in the case of inulins. Polyols, which are commonly used as sugar substitutes, were shown to enhance the growth of *Enterobacteriaceae*, which are correlated with poor gut health and can be linked to health problems [3]. Gas production induced by the fibres was dependent on the composition of the bacterial community of the tested gut microbiome samples. Hence, fibres consumed with food can vary significantly in their influence on gut microbiome and thereby affect the function of gastrointestinal tract.

Isothermal microcalorimetry combined with omics methods is an excellent platform for the food industry to evaluate the effect of foods and ingredients on human gut health and select the most suitable components for novel product development.

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Monitoring Crystallization and Melting with Millisecond Time Resolution: In-situ Combination of Micro-Focus X-ray Scattering and Ultra-Fast Scanning Chip Calorimetry

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A custom-made fast scanning chip calorimeter (FSC) was designed and made compatible with the environment of the micro- and nano-focus X-ray beamlines such as the ID13 beamline at the ESRF (Grenoble) [1-2]. The advent of fast single-photon-counting X-ray detectors enabled in-situ coupling of the two techniques with a possibility of conducting continuous synchronous acquisition of the thermal and 2D X-ray scattering data with time exposures on the order of one millisecond. The designed setup was used to re-explore the early stages of crystallization of HDPE in order to evaluate the morphology and exact supercooling at the crystal growth front. Also, the phenomenon of multiple melting, which constitutes one of the long-standing issues in polymer science, was revisited. In the present work, by using heating and cooling rates much higher than the rates of recrystallization, the structural transformation corresponding to each of the observed thermal events was extracted from X-ray data analyzed in detail [3-5].

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High-Throughput screening of PCM with IR-Thermography

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The storage of heat energy becomes more and more importance. The possible storage materials must satisfy various criteria: e.g. the melting point should be in the required area of application, the substances must be chemical stable and be available in large quantities to an economical price [1]. Further properties like a reversible and congruent melting behavior or low supercooling are of importance for long-term use.

With latent heat storage materials (PCM) high storage densities with low temperature differences are achieved. For the determination of thermal properties with established standard methods (e.g. DSC) a high experimental effort is necessary. For further optimization of latent heat storage systems, a high throughput screening of PCM`s has been aspired and could be realized by infrared thermography. With this measurement procedure the heat radiation of a surface is detected. The software converted image represented the surface-temperatures of the measuring field in different colours or contrasts, fig. 1.

The constructed measuring setup is focused on a high sample throughput to measure the melting and crystallization behaviour of PCMs and their mixtures in the temperature range –20 to 60 °C. IR-thermography measurements of mixtures from two fatty acids (e.g. palmitic acid and capric acid) show a good agreement with the data from the DSC measurements, fig. 2, but the agreement with the literature is modest [2]. There are some differences, but the general phase diagram can be depicted.

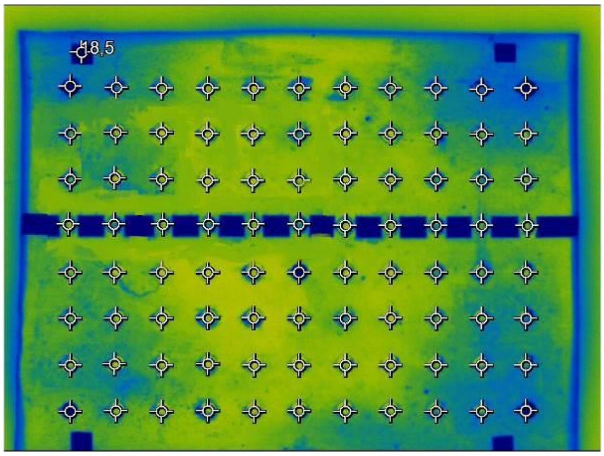

Fig. 1 image from the IR-thermography with all measurement points

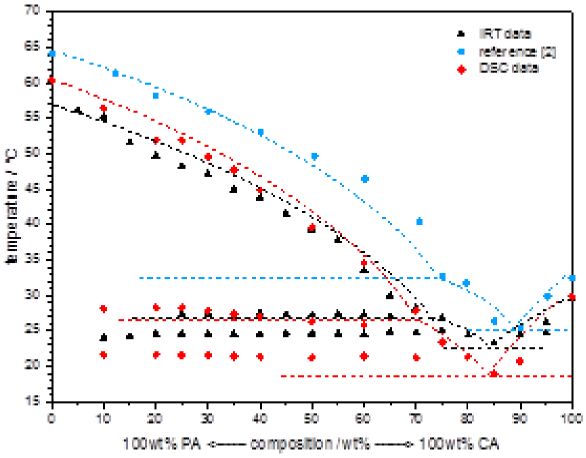

Fig. 2 resulting phase diagram of palmitic acid and capric acid with data from different sources

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Thermodynamic assessment of crystal growth in the system Gd-Te

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Smart syntheses of binary gadolinium tellurides Gd_xTe_y necessitate an exact view of all phase equilibria and the phases stability ranges in the system Gd-Te. With CalPhaD-method, thus thermodynamic modelling, we pioneer efficient experimental planning and their optimization. By steering clear of “trial-and-error-methods”, resource-saving syntheses and analyzes of inorganic materials can be predicted and performed.

The basis of all calculations are formed by collected and optimized data sets. With some previous described methods [1], we are enabled to enlarge commonly, appropriate tables, find and correct inconsistencies.

Initial point for transport calculations is the ternary phase diagram with Iodine. After evaluating the equilibrium constant K yield that both endotherm and exothermal transports are conceivable, fig. 1. Considering a possible condensation of Te_2 and GdI_3 and thus an equilibrium breakdown, we select primarily exothermic vapor transports. In further steps we enlarge the system to a quaternary one with sodium, fig. 2, and introduce NaI as transport agent. In this extended system $NaGdI_4$ and Na_2GdI_5 exist as gas phase complexes. For inclusion in the calculations, the thermodynamic properties must also be estimated - based on the results from [2].

The conditions for chemical vapor transport were calculated [3] for each known binary phase in the system Gd-Te. The temperatures T_1 and T_2 as well as a possible starting composition are indicated. Only for GdTe, no possible transport parameters could be determined.

The four phases $GdTe_3$, $GdTe_2$, Gd_4Te_7 and Gd_2Te_3 were selected by way of example and synthesized on the basis of the previous calculations: crystal growth by chemical vapor transport [4, 5]. The resulting products were analyzed by XRD and SEM - EDX.

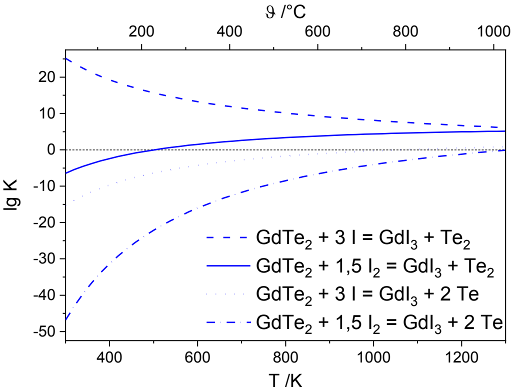

Fig. 1 equilibrium constant K of possible transport reactions

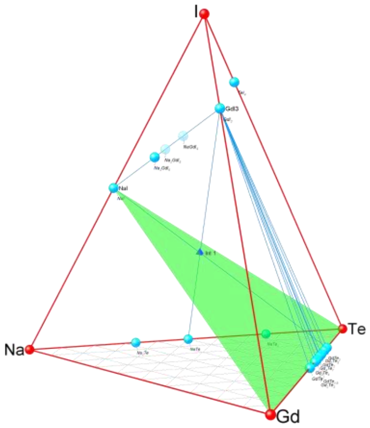

Fig. 2 quaternary phase diagram Gd-Te-Na-I

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Phase relations in the Al_2O_3-TiO_2-SiO_2 system

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Rutile (TiO_2) coatings deposited on corundum (Al_2O_3) are supposed to actively filter the $MgAl_2O_4$-spinel phase from Al-based molten alloy. Al melt can then react with TiO_2, reducing it into sub-oxides and metallic titanium. In Si-containing Al alloy, $Ti_5(Si,Al)_3$, $Ti(Al,Si)_3$, and ternary phases can form. Therefore, to model chemical reactions at the interface between ceramic filter and Al melt, thermodynamic database of the Al-Mg-Ti-Si-O system is necessary. As a part, the thermodynamic description of the Al_2O_3-TiO_2-SiO_2 system is needed to model oxide melts.

The binary Al_2O_3-TiO_2, TiO_2-SiO_2, and Al_2O_3-SiO_2 systems were repeatedly studied experimentally, and their thermodynamic databases are available. The Al_2O_3-TiO_2-SiO_2 system was poorly investigated [1,2]. For the vertical Al_2TiO_5-SiO_2 section [1], there are contradictions to the phase rules. The system was also assessed thermodynamically, including the modelling of liquid miscibility along the TiO_2-SiO_2 side [3,4]. Thus, the present work is aimed at an experimental study of the phase relations in the Al_2O_3-TiO_2-SiO_2 and Al_2TiO_5-SiO_2 systems to verify the inconsistencies, and their thermodynamic modelling using new experimental data as well as literature data on thermodynamic functions.

Samples were prepared by the controlled co-hydrolysis [5]. To investigate phase equilibria, samples were annealed and air-quenched followed by XRD examination. The microstructure characterization was carried out using SEM/EDX. Solid phase transformations and melting behaviour of the samples were studied by DTA.

Isothermal sections of the Al_2O_3-TiO_2-SiO_2 system at 1250 and 1400°C and its Al_2TiO_5-SiO_2 section were constructed based on the obtained results. On liquidus of the ternary system, the temperatures of invariant reaction were detected. To model the system using the CALPHAD approach, CEF was used to describe the solid solutions and a two-sublattice partially ionic model was used for liquid.

The study was financially supported by the German Research Foundation within the scope of the Collaborative Research Centre CRC920 (subproject A03).

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Thermal analysis of materials showing thermochromism (Chip-DSC)

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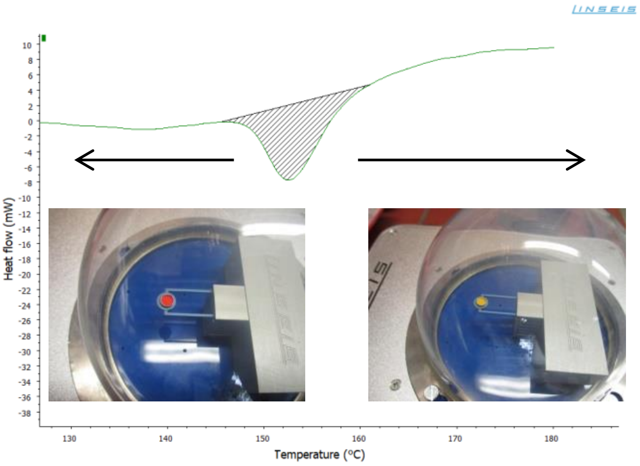
Thermal analysis is a very useful tool for the analysis of various compounds. Differential Scanning Calorimetry (DSC) gives information about the energy change during phase transitions and chemical reactions. Some phase changes and reactions are accompanied by color changes which can't be observed in most DSC instruments. In contrast, Chip-DSC 1 and Chip-DSC 10 with their transparent cover are useful for observing the sample during measurements and thus gaining further information during the heating, cooling or at isothermal segments.

Mercury(II)iodide exists in at least two enantiotropic modifications, a red low temperature modification and a yellow high temperature phase. This phenomenon (reversible phase transitions with color change) is called « thermochromism ».

Figure 1 shows the DSC diagram and photos during the heating run. It can be clearly seen that the endothermic event is a solid-solid phase transition with color change. Figure 2 shows the Chip-DSC 1 device.



Experimental data:
19.8 mg of HgI_2 were heated with 20 K/min in open aluminium pans under air in a Chip-DSC 1.

Thermal analysis of cholesterol by a Peltier-cooled DSC instrument

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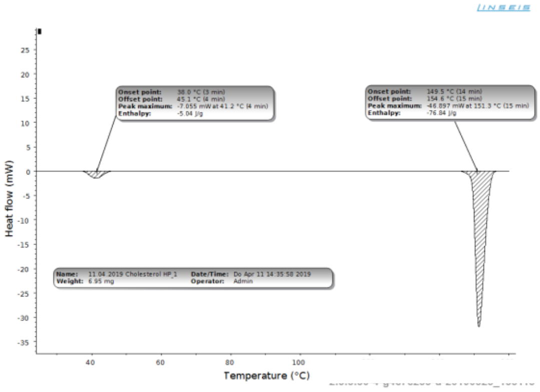
Thermal analysis is a very useful tool for the analysis of various compounds. Differential Scanning Calorimetry (DSC) gives information about the energy change during phase transitions and chemical reactions. Some phase changes occur at temperatures below room temperature and require thus previous cooling of the sample. This is often done by cooling with liquid nitrogen or a circulation cooler (« intracooler »). Both methods require additional equipment, high investment and lab space.

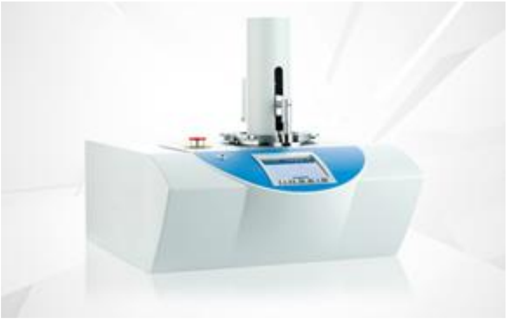
Linseis unique Chip-DSC sensors integrates all essential parts of DSC (furnace, sensor and reference) in a small chip wich can be cooled by Peltier effect. The advantage of this cooling is a low invest, maintenance free operation and no requirement for extra lab space.

Figure 1 shows the DSC profile of 6,95 mg of dry cholesterol that was analyzed from 0 °C up to 160 °C with a linear heating rate of 10 K/min using a Chip-DSC 100 with Peltier cooler. The first effect that can be observed is the endothermic solid phase transition at 38 °C that occurs only if the cholesterol sample is completely water free. Therefore, it can be used as an indicator of substance purity.

The second effect is the endothermic melting peak at 149 °C. The melting enthalpy and melting temperature can give additional information about substance purity in quality control and can also be used as a tool to identify the substance in general of drug identification.

Figure 2 shows the Chip-DSC 100 with peltier cooler and autosampler.





A novel method for global access to photosynthetic energy conversion efficiency based on calorespirometry

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One key parameter for assessing the CO_2 fixation in aquatic ecosystems but also for the productivity of photobioreactors is the global energy conversion efficiency (PE) by the photosynthetic apparatus. PE strictly depends on a range of different fluctuating environmental conditions and is therefore highly variable. PE is the result of complex metabolic control. At the moment PE can only be determined indirectly. Furthermore, the currently available techniques either capture only short time processes, thus reflecting only parts of the photosynthetic engine, or quantify the total process but only with limited time resolution. To close this gap, we suggest for the first time the direct measurement of the fixed energy combined with respirometry, called photocalorespirometry (Photo-CR). The proof of the principle of Photo-CR was established with the microalga *Chlamydomonas reinhardtii*. The simultaneous measurement of oxygen production and energy fixation provides a calorespirometric ratio of (437.9 ± 0.7) kJ mol^{-1} under low light conditions. The elevated calorespirometric ratio under high light conditions an indication of photo-protective mechanisms. The Photo-CR delivers the PE in real time, depending on the light intensity. Energetic differences less than 0.14 % at radiation densities of up to 800 µE m^{-2} s^{-1} can be quantified. Other photosynthetic growth parameters (e.g. the specific growth rate of 0.071 h^{-1}, the cell specific energy conservation of 30.9±1.3 pW $cell^{-1}$ at 150 µE m^2 s^{-1} and the number of photons (86.8) required to fix one molecule of CO2) can easily be derived from the Photo-CR data.

Evaluation for melting behaviour of polymer materials using sample observation DSC system

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Since a sample is put in the furnace generally, it's too difficult to directly see the sample's condition visually during measurement. Therefore, we have suggested a thermal analyzer equipped with camera function to easily understand the sample's reaction recently[1].

Same polymer materials with different molecular weight were measured. A shapes of melting peaks were different between low molecular and high molecular. The smaller a molecular weight become, the lower a melting temperature shows in general.

Low molecular polypropylene (PP) showed a shape change around peak top, and it was observed the sample flowed and spread in the sample pan. The high molecular weight PP also changed its shape near the peak top, but it maintained its shape even after the end of the peak. It is assumed that the smaller a molecular weight become, the easier a sample flowing (Fig. 1).

We also evaluated those fluid flow characteristic quantitatively by image analysis.

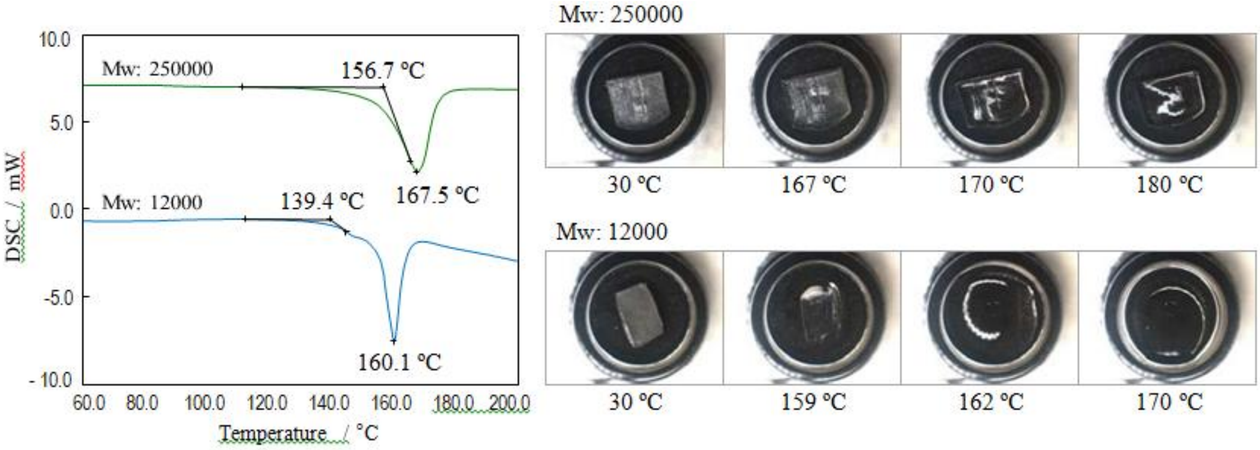

Fig. 1 Measurement Results for PP by Sample Observation DSC System Molecular weight: 25000 and 12000

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Influence of cell mimicking conditions on the results of a thermodynamic feasibility analysis

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Systems biology is trying to construct mathematical models of the metabolic activities in living cells for the investigation and prediction of metabolic pathways using the metabolic flux analysis (MFA). The biggest disadvantage of this method is that often underdetermined equation systems are obtained.

Thermodynamics might help with reducing the solution space by eliminating solutions that fulfil mass balances but violate the second law of thermodynamics. In this work, an algorithm called thermodynamic feasibility analysis (TFA) is applied to the glycolysis as an example for a metabolic pathway. This pathway was chosen because it is well understood and therefore poses a good model system for testing the method. TFA breaks up metabolic networks into individual pathways and analyses the thermodynamic feasibility every single reaction and combinations of reactions of the network [1].

An analysis of the feasibility of the glycolysis already exists but leads to the conclusion that, using the available literature data of the reactions, the whole glycolysis pathway is not feasible which is obviously wrong [2]. Reasons for this could be that the literature data was not determined under the conditions present in the cell or that the activity coefficients were neglected in the analysis. Therefore, new determinations and predictions of physical and thermochemical basis data of pure metabolites, reaction equilibria of single reaction steps, kinetic data and reaction heats under cell mimicking conditions (e.g. macromolecular crowding, ionic strength) are necessary. The reaction heats and kinetics were identified using isothermal titration calorimetry. The new data collection can be used to establish a TFA model which includes activity coefficients, protonation and complexation of the metabolites, new $\Delta^R g^{0\prime}$ values and new calculated $\Delta^R g$ values.

In the further course of the study, we want to apply the determined calorimetric data to a new thermodynamic feasibility analysis model to explore the predictive potential of thermodynamics for systems biology.

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Isothermal and non-isothermal copolymerization kinetics of hydrogels based on OEGMEMA or OEGMA and AAc

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Monomers composed of a polymerizable methacrylate moiety connected to a short poly(ethylene) glycol (PEG) chain are versatile building-blocks for the preparation of ‘‘smart’’ biorelevant materials [1]. Hydrogels based on these PEG methacrylates are a very important class of biomaterials with several applications. The radical polymerization kinetics of two such oligomers, namely oligo(ethylene glycol) methacrylate (OEGMA) and oligo(ethylene glycol) methyl ether methacrylate (OEGMEMA) was investigated previously in our group [2]. Synthesis of novel statistical copolymers based on oligo(ethylene glycol methacrylate), oligo(ethylene glycol methyl ether methacrylate) and acrylic acid, is presented here. The in situ bulk radical polymerization technique was used with various initial molar ratios of the monomers employed each time.

Experimental polymerization rate and monomer conversion data were measured using Differential Scanning Calorimetry (DSC) operating under non-isothermal conditions, at several constant heating rates, or isothermal, at different constant reaction temperatures. Isoconversional techniques were employed to estimate the variation of the polymerization effective activation energy as a function of the extent of reaction. It was found that, depending on the monomer structure and particularly on the presence or not of hydroxyl groups, the copolymerization mechanism and the activation energy is totally different. This is ascribed to side reactions taking place during copolymerization. From thermogravimetric analysis, it was verified that the presence of acrylic acid in poly(OEGMA-co-AAc) and poly(OEGMEMA-co-AAc) enhances the thermal stability at certain initial monomer molar ratios. Additionally, the presence of PEGMA enhances slightly the thermal stability of poly(OEGMA-co-OEGMEMA) in some initial monomer molar ratios. The swelling ratio and gel fraction was determined gravimetrically and shown that the homo-polymers, except P(AAc), exhibit high swelling properties, which decrease with increasing amounts of AAc in the copolymers. Poly(OEGMA-co-OEGMEMA) copolymers show an intermediate gel fraction yield and swelling ratio compared to their corresponding homo-polymers.

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Waste plastic packaging recycling: Pyrolysis of polymer blends

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It is widely known that one of the major challenges nowadays, concerning environmental issues, is the proper handling of plastic wastes produced in large amounts by modern societies. Among them, polymers used in plastic packaging are characterized by short life span and large volumes in the waste stream. Thus, proper and environmentally friendly recycling approaches are necessary to manage the situation. Thermochemical methods of treating polymers and pyrolysis in particular, appear as a promising alternative, since complex organic macromolecules of different compositions turn into useful products (usually monomer(s) and other secondary value-added organic components) and enable energy recovery. Catalytic cracking is an alternative to recycling of neat or mixed polymeric waste with a budge of chemical and energy advantages. The objective of this work is the decomposition of widely-spread polymeric blends used in plastic packaging and composed of PET, PS, PE and identification of the molecules or fragments yield when the materials are subjected to various thermal degradation conditions.

The specimens studied included the widely-found polymer packaging materials which were blended using the solution casting technique. Conventional or catalyrtic pyrolysis were performed on a Frontier Laboratories Multi-shot Pyrolyzer (EGA/PY-3030D) with a carrier gas selector (CGS-1050Ex) coupled with GC/MS QP-2010 Ultra Plus. The NIST 11 Search analysis library was used to identify products. The Single Shot analysis conditions involved an Ultra Alloy 5% diphenyl-95% dimethyl polysiloxane filled metal capillary column, flash pyrolysis lasted for 0.5 min, at preselected temperatures, while column oven program varied. Depending on the polymer type different compounds were detected ranging from various-structured hydrocarbons (when polyolefins were employed) to monomers or oligomers in the case of polystyrene and to oxygenated compounds such as benzoic acid or terephthalic acid when polyesters were pyrolized. Decomposition happens through radical processes. The fragments are complicated when degradation takes place at low temperatures, whereas they get simpler at high temperatures.

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Preparation of expanded microspheres from hydrous rhyolitic glass

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Hydrous rhyolitic glass constitute and abundant material of aluminosilicate composition and considerable amount of water in molecular and OH form that can reach up to 10 % wt. It is used as source material for the production of expanded granules for various applications. Except to the chemical and mineralogical composition, the water content of the glass affects its expansion potential.

In the current study, volcanic glass of different water content are prepared through sophisticated dehydration of rhyolitic glass, and subsequently subjected to thermal treatment towards the production of lightweight expanded microspheres using a Vertical Electric Furnace prototype. Extended characterization analyses are implemented towards determination of the main physical properties of the expanded material and their morphology/microstructure. It was found out that the optimum water content of the volcanic glass range between 3 and 5.5% and coincides with that of perlite. The expanded microspheres are characterised by closed-structure, limited porosity and high sphericity.

Thermal activation of bentonite and zeolite; kinetic analysis and characterization

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Bentonite and zeolite constitute abundant industrial minerals that are widely used as sorbents in various industrial applications. Scoping to increase their performance as sorption media, different types of activation are implemented, including simple heat treatment. Objective of the current study constitutes the kinetic analysis of activation process of both natural Ca-bentonite and zeolite through thermogravimetry under different heating rates and up to temperature of 1000 °C. The analyses will be accompanied by thorough characterization of surface properties, sorption capacity and porosity of samples that have been treated at different temperature levels.

Structural and Thermal study of a bio-based unsaturated polyester resin: Two-step *vs* one-step polymerization procedures

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Unsaturated polyester resins (UPRs) consist a significant category of thermoset polymers in industry, due to their easy processability, their low cost, their high chemical resistance and foremost their exceptional mechanical properties, leading to their extensive utilization in different industrial sectors such as in the automotive, marine, aerospace and construction industries [1-2]. However, both the growing public awareness related to environmental issues and the demand of sustainable alternatives to fossil based monomers, have led to the need of introducing bio-based UPRs.

In this study, bio-based UPRs were synthesized based on succinic acid, ethylene glycol and maleic anhydride. The synthesis was conducted both via two-step and one-step polymerization. The structure of the materials was studied by means of Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (^{1}H NMR) and X-ray photoelectron spectroscopy (XPS). Furthermore, thermal properties of the obtained materials were studied by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

The materials which were synthesized by the two-step polymerization procedure were not miscible with the reactive diluent. On the contrary, the materials which were synthesized by the one-step polymerization procedure were miscible with the reactive diluent and they were successfully cross-linked.

Acknowledgments

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Production technology and compositional analysis of archaeological ceramics by combination of TG/DTG-DTA and other analytical techniques

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Ceramics usually consist of a large number of minerals, including mixtures of different clay minerals and clastic grains (temper and inclusions). They undergo physical and chemical alterations during firing, which depend on the mineralogy of the raw materials, their grain size distribution, maximum heating temperature, duration of firing and kiln redox atmosphere. The components of ceramic artefacts include solid phases formed during firing. Therefore, the mineralogical composition of the ceramic paste is one of the parameters that contribute to the characterization of a certain production technology [1].

Clay minerals, as the main material for the production of ceramic artefacts, show some characteristic reactions (dehydroxylation, decomposition, transformation) during heating and several thermoanalytical criteria can be used for the reconstruction of manufacturing conditions. Heating also affects the contact between the fine-sized clayey matrix and mineral clastic grtains, as well as the microstructure of the clay minerals [2].

This work is focussed on the physical–chemical characterization of four ceramic objects which belong to the Museum of Byzantine Culture of Thessaloniki in Greece, by combination of supplementary analytical techniques, with the aim of deriving information about their main components and production conditions (firing temperature and atmosphere). Two of them, a fragment of a vessel that looks like a handle and an oil lamp, date back to the 6th century A.C., while the other two, an ottoman and a western type tobacco pipes, belong to the 17th century A.D.

Micro-morphological, elemental and mineralogical analyses were conducted with the help of Optical Microscopy, Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS), X-Ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The information derived on composition and production conditions was validated by SEM observations concerning the extent of vitrification. The minimum concentration of $CaCO_3$ in the original ceramic paste and the highest firing temperature were estimated by TG/DTG-DTA.

As it was concluded, the examined ceramics are utilitarian objects that exhibit differences both in the composition of the raw materials, and the firing process applied for their fabrication.

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Acknowledgements
We are grateful to the Museum of Byzantine Culture of Thessaloniki, Greece, for supplying the samples from the ceramic artefacts belonging to its collections.

Mechanical and thermal properties of polymethyl-methacrylate resins reinforced with calcium β-pyrophosphate

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Polymethyl-methacrylate (PMMA) is widely used in dentistry due to its biocompatibility. Moreover it is lightweight, colorless and has a good fracture toughness and low cost. However, it exhibits low impact and tensile strength and therefore it is necessary to reinforce it with a filler material. Variable methods have been used to enhance PMMA acrylic resin, such as the incorporation of various types of fibers, metal oxides, noble metals, metallic elements, and carbon-based fillers. B-pyrophosphate (β-Ca2P207, β-CPP) is biocompatible, non-toxic, stable at low PH, has a low rate of degradation and offers hardness comparable to tooth enamel[1].

Interim restorations are essential in fixed prosthodontics as they provide temporary protection of teeth before the permanent restoration. For their proper function, they must resist to occlusal and abrasion forces without fracture, and their materials must be non-toxic without causing allergenic reaction or irritations.

In the present study β-pyrophosphate was selected as reinforcing material for the PMMA acrylic resin [2]. Three point bending test was performed to study flexural strength. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) experiments were performed to study thermal properties. Fourier Transformation (FTIR) and X-Ray Diffraction (XRD) experiments were performed to investigate the structure of the materials. Finally, for the morphological study, Scanning Electron Microscopy (SEM) was applied. Composite specimens were prepared according to ISO 10477:2004 (E) and the mixture of β-CPP with the PMMA powder was performed on a ball milling device for 1 and 6 hours. A statistically significant increase in flexural strength was found in almost all composite groups, relative to the control, with six-hour specimens presenting the highest flexural strength values. The brittle fracture type was common to all groups. An improvement in the thermal stability of the composite materials was also observed as the β-pyrophosphate content was increasing.

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Thermal and Morphological characterization of phenol formaldehyde adhesive reinforced with textile waste and wood

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Phenol formaldehyde (PF) resin-based materials have been widely used in many fields, due to their high rigidity, good corrosion resistance, and less toxicity when burning. However, the environmental stress caused by petroleum-based phenol obtained from fossil resources has limited the application of PF. Therefore, industry efforts have been focused on identifying phenolics from renewable resources [1].

In this work, proteins derived from the recycling of textile waste and wood were used as a raw material in the synthesis of thermosetting polymers suitable to be used as adhesives for the production of wood-based panels (particleboards). Both types of proteins were polymerized with some eco-friendly aldehydes (glyoxal). For comparison, PF control resin was produced. The thermal properties of the PF control and PF/textile waste and wood composites were determined with Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) measurements. The chemistry of their structure was studied with Fourier Transform Infrared Spectroscopy (FTIR) measurements. Lab-scale panels were produced with a process similar to that of the industrial practice while Scanning Electron microscopy (SEM) technique was applied for the study of the interaction wood-resin.

The PF resin composites were successfully prepared. The maximum curing temperature of the PF/textile waste and wood composite shifted to higher values compared to the control PF. Moreover, the PF resin composite reinforced by textile waste and wood loses mass with a lower rate, and thus, they are more thermally stable than the PF control. The above results show that proteins can effectively replace part of the petrochemical phenol in the synthesis of PF resins, increasing so the bio-content of these resins and making them more friendly to people and the environment.

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Thermal and microscopic studies of a 17th century gilded wood-curved iconostasis from Greece

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The Assumption of Virgin Mary is an 11th century Orthodox church, placed in the village of Aetolofos, Thessaly, Central Greece. A unique gilded wood-carved iconostasis, made in the 17th century, separates the sanctuary from the nave. The portable icon under study -placed on the iconostasis- depicts Virgin Mary in half-length, embracing the infant Christ with her left arm. Samples collected from the icon and the iconostasis were examined for the identification of pigments, binders and related materials, as well as their state of preservation. The study aims to the documentation of Northern and Central Greek ecclesiastical art [1,2].

The samples were examined by means of thermal analysis; thermogravimetry (TG-DTA) and differential scanning calorimetry (DSC)- were applied, in order to give insights about the synthesis and the state of preservation of the painting layers. Additionally, microscopic techniques were applied, for the full microstratigraphic discrimination and characterization of the samples: Optical microscopy, micro Fourier infrared spectroscopy (μ-FTIR), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and X-ray photoelectron spectroscopy (XPS). The plaster layers of the icon consist of gypsum, anhydrite and basanite, with a small participation of calcite and quartz, while animal glue was used as the binding medium. The identified pigments are vermilion, red lead, green earth, lead white and hematite. The binding medium is identified as egg yolk, indicating that egg tempera was the applied technique, while a gold and silver alloy was used for the gilding of the icon. As a varnish layer, a resin of plant origin was used, probably sandarac or mastic. Regarding the sample collected from the iconostasis, its stratigraphic analysis shows that the gilding was applied on a white preparatory layer, consisting of anhydrite, gypsum, basanite and animal glue. The leaves used for the gilding of the iconostasis also consist of a gold and silver alloy.

The present study shows that the applied materials, pigments and techniques indicate the use of traditional and well-established methods in eastern orthodox ecclesiastical iconography, both for the portable icon and the gilded wooden-curved iconostasis. This work -while focusing on the documentation of the late post-Byzantine art of Central and Northern Greece religious art- shows that the iconographer of Aetolofos retained the traditional materials and techniques of eastern orthodox iconography.

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Unsaturated Polyester Resins: The effect of different types of initiators on cross-linking process and thermal stability

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Unsaturated polyester resins (UPRs) are the most widely used thermoset resins, with more than 1.5 million tonnes being consumed during 2018 globally, for the production of a wide variety of products [1]. UPRs are obtained by radical polymerization of unsaturated polyesters with unsaturated monomers which act as crosslinking agents. UPRs, also, contain initiators, accelerators which promote the curing process, etc. Thus, the manufacturing process of unsaturated polyester resins evolves different types of chemical reactions, leading to a plethora of industrial applications.

The cross-linking process is the most crucial stage of the UPRs manufacturing, since during that procedure, a three-dimensional network structure is created, urging the resin to be transformed into solid. Several types of initiator systems are used in order to induce cross-linking. The thermal homolytic dissociation of initiators is the most widely used mode, with the most extensively adapted initiator being benzoyl peroxides (BPO) which acts at elevated temperatures. There is, also, another category of initiators, those which induce curing at room temperature, such as methyl ethyl ketone peroxide (MEKP).

The purpose of this study is to deal with the effect of initiator systems (BPO and MEKP) on the curing process of unsaturated polyester resins and on the thermal stability of the corresponding cured materials. The resulting characteristics are revealed by Differential Scanning Calorimetry (both in isothermal and dynamic mode) and Thermogravimetric Analysis.

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Linear Low Density Polyethylene/Maleic Anhydride Grafted Polyethylene/Microcrystalline Cellulose composites: Structural, Thermal and Mechanical Properties

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Over the last years, remarkable attention has been paid to eco-friendly, sustainable materials for various applications. In this context, microcrystalline cellulose (MCC) with micron sized diameters was used as reinforcing element in green polymer composites. MCC is characterized by its abundance, renewability, low-price, low density and high strength to weight ratio [1-2]. Nonetheless, its polar surface arises issues concerning the interfacial adhesion state of matrix-MCC, when it is introduced in non-polar matrices. Among other methods of removing the aforementioned impediment, the incorporation of functionalized polyethylene into the composite has been found to be quite effective.

In this study, linear low density polyethylene (LLDPE) composites containing MCC (filler content 5-30 wt%) were prepared by the melt-mixing technique, where maleic anhydride grafted polyethylene (PE-g-MA) was used as a compatibilizer. The dispersion of the filler was studied with the assistance of micro Fourier-transform infrared spectroscopy (μ-FTIR) mapping, structural characteristics were determined by means of Fourier-transform infrared spectroscopy (FTIR) and X-ray diffractometry (XRD) and thermal measurements were conducted by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Finally, both tensile and impact Izod tests were carried out, while Scanning Electron Microscopy (SEM) was employed for the study of the fractured surfaces of the composites after mechanical testing.

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Development and thermomechanical characterization of carbides / epoxy, or graphite/epoxy composites: A comparative study

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Polymer matrix composites form an important class of technologically important materials mainly because of their thermomechanical and dynamic mechanical behavior. This advantage makes them one of the most sought-after class of structural materials suitable for many industrial applications [1]. In the present study, three series of composites were manufactured varying the filler type and content. Epoxy resin was used as a matrix, while particles of Boron Carbide (B_4C), Titanium Carbide (TiC) and Graphite (C) were acting as filler. The morphological characterization was conducted using Scanning Electron Microscopy (SEM). Subsequently, the dynamic mechanical behavior of materials was studied by means of Dynamic Mechanical Analysis method (DMA), while the thermal response was examined via Differential Scanning Calorimetry (DSC).

The results from thermomechanical measurements showed that the addition of the filler enhances significantly the mechanical properties of the composite systems. Storage modulus, in all cases, increases systematically with filler concentration due to the enhancement of the materials' stiffness. However, the optimal performance varies not only with filler content but also with filler type [2]. Specifically, composites with Boron Carbide, Graphite and Titanium Carbide show their optimal performance at higher, intermediate and lower filler concentration, respectively. Relaxation phenomena arising in polymer composites include contributions from both the polymer matrix and the presence of filler and reflect the interactions between the matrix and the filler [3]. In all reinforced systems, the transition from glassy to rubbery state, shifts to higher temperatures, implying enhanced interactions between matrix and reinforcement due to the strong adhesion between the matrix and the nanoparticles.

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Hybrid nanodiamond/ magnetite/ polymer nanodielectrics: Development, dielectric response, thermomechanical properties and energy storage

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Polymers exhibit a number of advantages, which include ease processing and forming, thermomechanical stability, high dielectric breakdown strength and low cost. Conductivity, dielectric and magnetic properties of polymers can be substantially altered by embedding suitable reinforcing inclusions [1-3]. Although carbon allotropes have been extensively used as nanoinclusions in polymer matrix composites, mainly due to their mechanical and electrical properties, there are relatively limited amount of studies concerning the dielectric and thermomechanical behaviour of nanodiamond reinforced polymers [4,5].

In this study series of nanocomposites, consisting of nanodiamonds and magnetite nanoparticles incorporated into a commercially available epoxy resin, were developed varying the filler type and concentration. Their electric response was investigated by means of Broadband Dielectric Spectroscopy in the frequency range of 100mHz to 10MHz and temperature range from 30 to 160°C and the thermomechanical characterization was conducted by means of Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA), respectively. The capability of storing and retrieving electrical energy was examined by performing DC current charge/discharge tests.

Experimental data revealed that the addition of fillers enhances both the thermomechanical properties and the induced polarization. Three distinct relaxation modes were recorded, arising from both the filler and the polymeric matrix, which are attributed to interfacial polarization (IP), glass to rubber transition (α-relaxation) and motion of polar side groups (β–relaxation). The energy storage/harvesting performance of the nanocomposites was assessed by calculating the coefficient of energy efficiency.

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Assessing the effect of Fe_3O_4 nanoparticles on the thermomechanical performance of different forms of carbon allotropes/epoxy hybrid nanocomposites

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Carbon nanostructured/polymer nanocomposites are in the focus of research efforts because of their improved mechanical characteristics, enhanced heat resistance, and advanced optical and electrical behaviours. The unique properties of the allotropic forms of carbon predetermined the wide variety of their application fields [1–4]. The incorporation of ceramic nanoinclusions in carbon nanocomposites can induce additional functionality in the field of magnetic properties, piezoelectricity etc. [4,5]. Among other transition metal oxides, iron oxide receives increased attention due to its abundance, low cost, corrosion resistance, high chemical stability and ecofriendly nature [6].

In this study series of nanocomposites, consisting of different carbon nanoinclusions (Carbon Black, MWCNT's, Graphene nanoplatelets, Nanodiamonds) and magnetite nanoparticles incorporated into a commercially available epoxy resin, were developed varying the filler type and concentration. Aiming to investigate further the structure-properties relationship, specimens' morphology and thermomechanical properties were examined by means of Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis respectively (DMA). Experimental data showed enhanced thermomechanical properties with the addition of filler. Investigation of nanocomposites' glass to rubber transition, revealed the types of interactions occurring between the constituents. These interactions may depend on the filler concentration, and the fillers' type and geometry.

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Study of thermal stability, thermal conductivity, and mechanical properties of crosslinked polyethylene/graphene nanocomposite

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Geothermal heat pumps are widely used as an eco-friendly and cost-effective house heating/cooling system. Crosslinked polyethylene (PEX) materials have been successfully used in domestic hot and cold water piping due to their good properties such as high-temperature strength, good elastic modulus and high impact resistance [1]. However, the main disadvantage of PEX is the low thermal conductivity which limits its application. The need for high efficiency of geothermal heat pumps systems has led to the development of nanocomposite polymeric materials with improved thermal conductivity and mechanical properties for piping applications. Different types of graphene such as graphene oxide and graphene nanoplatelets (GNPs) are often used as a multifunctional reinforcement filler material to improve the electrical, mechanical, gas barrier and thermal properties of a polymeric matrix [2].

In this work, PEX/GNPs nanocomposites were prepared by the melt mixing method, using GNPs with 5μm in diameter and 6μm in thickness (GNPs M5) at 0.5, 1, 2.5 and 5% wt. filler's concentration. X-Ray Diffraction (XRD) was used to study the structure of neat PEX and the corresponding nanocomposites. The crystallinity, the melting and crystallization temperatures of PEX/GNPs nanocomposites were calculated by Differential Scanning Calorimetry (DSC). The thermal stability of the samples was examined by Thermogravimetric Analysis (TGA) and the degradation products were identified by Analytical Pyrolysis Gas Chromatography/Mass Spectrometry (py-GC/MS). The thermal conductivity of the PEX and its nanocomposites was estimated using Laser Flash Analysis (LFA). Finally, mechanical properties testing was performed to determine the influence of the filler's content on Young's modulus, tensile strength, and elongation at break of PEX matrix. LFA results and tensile testing showed that the nanocomposites exhibited higher thermal conductivity and increased Young's modulus than neat PEX.

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Thermal and mechanical properties of poly(butylene 2,5-furan dicarboxylate) nanocomposites

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Poly(butylene 2,5-furan dicarboxylate) (PBF) is an alipharomatic polyester that can be prepared using monomers derived from renewable resources such as 2,5-furan dicarboxylic acid and 1,4-butanediol. Polyesters bearing furan moieties like poly(ethylene 2,5-furan dicarboxylate) (PEF) and poly(butylene 2,5-furan dicarboxylate) (PBF) are considered as the biobased alternatives of terephthalates. The mechanical properties, thermal properties and crystal structures of PBF are similar to petroleum derived poly(butylenes-terephthalate), PBT [1,2].

In this work, PBF nanocomposites containing 1 wt% of various types of clays were synthesized with the *in-situ* transesterification and polycondensation method. The fillers used were the montmorillonites Cloisite 10A, 20A and 20A-Na. The catalyst used was Titanium (IV) butoxide. The prepared PBF and its nanocomposites were molded into amorphous and semicrystalline films, with annealing for 1 hour at 100 °C. The successful synthesis of PBF was confirmed with H-NMR spectra and molecular weight was calculated via intrinsic viscosity measurements in the range of 10000-20000 g/mol. The nanofillers caused a reduction in the viscosity and subsequently molecular weight values. Tensile strength was greatly influenced by the crystallinity of the films and X-ray diffraction patterns revealed intercalation of the polymeric chains between the filler layers. Differential Scanning Calorimetry was used to study the isothermal and the non-isothermal crystallization of the nanocomposites, which was accelerated in both cases.

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High-temperature oxidation resistance of higher manganese silicide-based materials

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Higher manganese silicides ($MnSi_{\sim1.7}$) are promising alternative materials for mid to high-temperature thermoelectric applications, combining low cost, eco-friendliness, high thermoelectric performance, oxidation resistance and chemical stability. They exhibit a figure of merit up to ZT=0.7 [1], while studies on different element additions have led to values of ZT~1 [2]. So far, synthesis of this material has been achieved by using various methods [3-5].

The current work examines the high-temperature oxidation resistance of both undoped and doped $MnSi_{1.7}$ powders under air environment using Thermogravimetric Analysis. $MnSi_{1.7}$-based materials were prepared by pack cementation process. Then, the thermal behaviour of the synthesized samples was examined under non-isothermal oxidation test up to 1200 ^{o}C and isothermal tests at selected temperatures. The effect of the element addition on the thermal properties of $MnSi_{\sim1.7}$ was studied too. All the powders were characterized considering their structure and the phases they consist of before and after oxidation by X-Ray diffraction analysis, while their morphology and chemical composition were examined using a scanning electron microscope equipped with an EDS analyzer. The materials were successfully synthesized and presented remarkable oxidation resistance in the desired temperature range for thermoelectric applications.

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Thermogarvimetric evaluation of Cr-Ni coatings deposited by electrodeposition and pack cementation

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Carbon steel is frequently used metals in the construction sector and mechanical applications due to its very good mechanical properties [1]. However, it has very poor efficiency in elevated temperature environments [2]. Nickel chromium alloys are known to be much more resistant to such exposure conditions [3]. In this work, Cr-Ni coatings were developed by a combination of two processes. An initial Ni layer was electrochemically deposited on steel followed by chromium deposition by pack cementation. During the first step, the substrates were Ni-plated using Watts' solution ($NiSO_4 \cdot 6H_2O$, 300 g/l; $NiCl_2 \cdot 6H_2O$, 40 g/l; H_3BO_3, 40 g/l). The plating temperature was 50°C and the cathode current density 5 A/dm^2. At the second stage, the Ni deposited samples were packed and sealed in ceramic crucibles with powder mixture consisting of chromium powder (donor material), NH_4Cl (the chemical activator of the process) and balanced Al_2O_3 (used as filler). The sealed crucibles were loaded inside an Ar purged preheated cylindrical furnace at 900^{o}C and 1000^{o}C for 120min and then left to cool down to ambient temperature without interrupting the Ar flow. The structure and phase identification were performed by the use of X-ray diffraction, while the morphology and chemical composition were examined using a scanning electron microscope (SEM) equipped with an EDS analyzer. The oxidation tests were performed by thermogravimetric analysis (TGA). Firstly, the coated samples were heated from room temperature up to 1000^{o}C at a heating rate of 10^{o}C/min under air flow of 50 mL/min in order to determine the critical temperatures where the oxidation rate has significant changes. Afterward, they were submitted under isothermal oxidation conditions in flowing air at 900^{o}C for the investigation of oxidation at long exposure periods.

SEM analysis showed that Cr-Ni and Cr-Ni-Fe alloys were formed on the main area of the coatings. At the same time, Ni interdiffused in the ferrous substrate creating Ni-Fe compounds at the coating-substrate interface, increasing the coating adherence. X-ray diffraction revealed the main presence of mixed Cr-Ni-Fe compounds with several Cr-Ni and some probable Ni-Fe phases. Non-isothermal and isothermal TGA results showed superior oxidation resistance of the coated samples compared with the bare steel at high temperatures.

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The role of thermal analysis in the development of iron-containing nano-kaolinite photocatalysts

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The development of clay-based catalysts requires the formation of defect sites in the mineral structure. The iron contamination of clays is generally present in the form of oxides, hydroxides and carbonates. In our case XRD analysis showed the presence of hematite (Fe_2O_3) and goethite (α-FeOOH) in the raw kaolin. Depending on the degree of crystallinity, the dehydroxylation of goethite takes place between 250 and 300 C°. The iron-containing mineral contaminants can be removed by acid treatment. However, with the exemption of HCl, acid treatment can slightly damage the mineral structure. At the same time, at the surface and at broken edges the OH-groups can be protonated, leading to exchangeable $–OH_2^+$ groups. The strength of the protonated OH-groups is comparable to that of coordinated water (falling in the range of 50-200 KJ/mol, based on atomic-scale structural and energetic simulations). Therefore, their dehydration/decomposition temperature is between those of adsorbed water and structural OH-groups.

Thermal analysis shows that the water evolution steps due to goethite decomposition, the removal of $–OH_2^+$ groups and the dehydroxylation of the mineral are closely overlapped. On the other hand, the study of the active surface sites (e.g. with TPD) can encounter significant difficulties since the $–OH_2^+$ groups can either block the unsaturated coordination sites, or decompose/desorb at the same temperature than the reagent used for surface titration.

In spite of these difficulties, thermal analysis can be advantageously used for the modelling of the formation of kaolinite-based oxide catalyst composites and hybrids with particular respect to the qualitative and quantitative evaluation of defect sites.

Acknowledgement

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Evaluation of the thermal behavior and mechanical properties of geopolymers containing different percentages of fly ash

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In recent years, geopolymers have attracted increasing attention because they have performance comparable to those of Portland cement, but are able to reduce CO_2 emissions. They consist of a geopolymer resin that acts as a glue for inert resources, thus improving the chemical properties, functionalizing and reinforcing the reactive inorganic raw materials, in particular the metakaolines. In this work, new geopolymers are synthesized in order to produce a composite geopolymer with fly ash recycling allowing both to decrease the environmental damage and to save on the costs of transport and disposal of waste.

Different percentages of Fly Ash (20, 50 and 70 wt%) and pure metakaolin were used to prepare the several geopolymers. This powder was subjected to alkaline activation, using a strongly basic solution consisting of sodium silicate. The dough was poured into plastic moulds and the consolidation phase carried out at 50°C for 24 h; whilst the hardening phase was carried out at room temperature for 7, 14 and 28 days. The chemical structure of the synthesized powders has been studied by FTIR. The different spectra show that after 28 days at room temperature, the synthesized samples have good geopolymerization, confirmed by the formation of bonds between the two components [1].

The XRD analysis suggests that no impurities were detected in the powders obtained after the geopolymerization process while in MK there were natural impurities. Furthermore, the ICP analysis highlighted the large presence of silicates in fly ash and metacaolina alumina.

Moreover, SEM images show that increasing the amount of fly ash the lamellar structure is reduced and the sample appears more compact. The transitions recorded by DMA were attributed to the devitrification of the curing network, which is formed during hardening at room temperature for 28 days. DSC analysis seems to confirm the behavior observed during the DMA. In fact, it is possible to observe a peak due to the mass loss caused by the presence of structural water in the geopolymer composition, that was less intense and shifted to lower temperature by increasing the fly ash content in the formulation.

In conclusion, the results suggest that the new synthesized geopolymer could be used as a building material, allowing the recycling of fly ash and reducing the amount of waste to be treated or disposed of in landfills.

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Biopolymer/HNTs nanocomposites with smart features

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Recent studies showed that the addition of nanotubular material such as halloysite nanotubes (HNTs) can generate changes in the material property by it-self or the lumen can be used as smart nanocontainer to produce smart features as stimuli responsive or self-healing ability. In particular the introduction of HNTs in a polymeric matrix can cause a conspicuous increase in its thermal and mechanical performance; in addition, due to the cylindrical pore (lumen) that can be loaded with chemically and biologically active substances, it is possible to introduce in polymers applications specific chemical inhibitors (antimicrobial, anticorrosion, flame-retardant, drugs, microcrack self-healing) that can be released in a sustained fashion.

HNT/polymer bionanocomposites showed excellent physico-chemical properties due to the synergetic effect of inorganic and organic components, HNT nanoparticles and biopolymer respectively. The potential applications of these materials are relevant in several fields.

A chemical-physical investigation [1] (contact angle measurements, dynamic mechanical analysis, thermogravimetry) is conducted to characterize the nanocomposites obtained combined three biopolymer with different charge to HNTs. Studies on activation energy of polymer degradation process are also conducted. Friedman's method is used to calculate E_a without making any assumption on the reaction mechanism [2]. All polymers used are nontoxic, biocompatible and biodegradable and HNTs are widely used for the development of systems for release of drugs, tissue engineering, decontamination and food additives [3].

The real applicability of these systems as drug carriers with specific functions, without that they may be themselves toxic to cells is investigated; in fact nanotechnology has promised invaluable progress in science and technology, the onus rests on the scientific community to predict the unknown outcome on the biological system for its safe proliferation. Films citotoxiciy study with CCK-8 are conducted. Surfaces are investigated by means of calcein AM/ propidium iodide experiments to clarify the cells proliferation on films.

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Spectroscopic and thermoanalytic studies on the complex formation between curcumin and hydroxypropyl-β-cyclodextrin

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Curcumin (CURC) is a natural phenol extracted from the rhizome of *Curcuma Longa Linn*, endowed with numerous pharmacological activities, including anti-inflammatory, antioxidant, antimicrobial and anticancer [1]. Unfortunately, CURC is basically water-insoluble and undergoes a rapid photodegradation, chemical degradation, and rapid metabolism. CURC stability and solubility can be improved by the complexation with cyclodextrins, which are cyclic oligosaccharides with a hydrophilic outer surface and a lipophilic cavity. In this work, the formation of the inclusion complex between the semisynthetic hydroxypropyl-β-cyclodextrin (CD) and CURC has been studied by phase solubility experiments and differential scanning calorimetry (DSC) at pH = 5 and 7.4. The inclusion complexes were obtained by adding increasing concentrations of CD in saturated CURC solutions.

The solutions were placed under agitation (100 rpm) at room temperature for 24h in the dark. Afterwards, the solutions were filtered (0.20 μm) and the solubilised CURC was quantified by spectrophotometric assay (λ = 426 nm). For DSC tests, the solutions have been lyophilized and the resulting solid mass scanned from 20 to 220°C at 10°C/min. Result of the thermal analyses of CURC, CD, and CD-CURC showed that the peak associated to CURC melting at 183°C was not evidenced, therefore confirming the formation of the inclusion complex. Phase solubility outcomes have shown that at pH = 7.4 the addition of CD up to a 15 mM concentration has allowed a 20.5-fold increase in CURC solubility. On the other side, at pH = 5, the solubility increase of the active molecule was 47-fold higher. Taken all together, results clearly indicate that the formation of the CD-CURC inclusion complex is strongly promoted at pH < pKa and with prolonged stirring times.

These results confirm and highlight the importance of the choice of the appropriate pH and mixing time on the formation of host guest inclusion complex with active ingredient(s) and CD.

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Liposomes for cutaneous delivery of curcumin: production, characterization and thermal analyses

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Curcumin (CURC), is a natural and lipophilic polyphenol extracted from the herbaceous plant *Curcuma longa* (1,2). Recently, antioxidant, anti-inflammatory, anticancer and antimicrobial activities of CURC have been proposed as a powerful and safe ingredient in wound healing (2). Unfortunately, the systemic bioavailability of CURC is curtailed by its low aqueous solubility, rapid first pass metabolism, and intrinsic instability, along with a limited skin penetration (3-4). Here, we hypothesize that a possible solution to these issues is the formulation of CURC-loaded lipid-vesicles for topical skin administration. 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC)-based liposome formulations encapsulating different CURC concentrations (0.1 to 10% w/w with respect to CURC:DPPC) were prepared by hydration of a thin lipid film followed by extrusion. The size of all formulations was 110-130 nm, with PI < 0.2 measured by photon correlation spectroscopy (PCS). High Performance Liquid Chromatography (HPLC) experiments revealed that CURC encapsulation efficiency was around 40% in all cases. To assess CURC influence on the arrangement of liposome bilayer, differential scanning calorimetry (DSC;10-80°C, 2°C/min) tests were run on 20 μL of liposome suspensions in distilled water (40 mg/mL), using equal volumes of water as a reference. Outcomes indicate that CURC presence in liposome bilayer weakly affects the transition temperature of the lipid bilayer of hydrated liposomes. This suggests that CURC arranges in DPPC bilayer with mild effects on its fluidity. *Ex vivo* skin permeation experiments carried out by a Franz Cells apparatus were performed to assess the efficacy of CURC-loaded liposomes for topical skin delivery.

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Thermal behaviour of phenyl-substituted dumbbell-shaped POSSs/PS nanocomposites

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Our group is engaged from some years in the synthesis and characterization of polystyrene (PS) – based nanocomposites, aiming to obtain both high thermal stability and good compatibility with the matrix, by using novel Polyhedral Oligomeric Silsequioxanes (POSSs) [1,2]. The aim was to investigate if and how much the POSSs physical properties were modified by the introduction of these groups in their molecules. In particular, for phenyl-substituted POSSs we found a higher resistance to thermal degradation than cyclopentyl derivatives, and for these last ones higher thermal stability than isobutyl substituted POSSs [3].

Many methods could be used to incorporate POSSs into polymers, it means: copolymerization, in situ polymerization, grafting, and many others. In every case loading POSS into polymer leads to the improvement of its physical and chemical properties, including increase of possible service temperature, of oxidation resistance, and, generally, of mechanical properties. Among various possible methods to prepare PS based nanocomposites, we choose in situ polymerization in the presence of 5% w/w of phenyl POSSs, in order to use a preparation method homogeneous with those employed for the preparation of isobutyl [4] and cyclopentyl [5] nanocomposites.

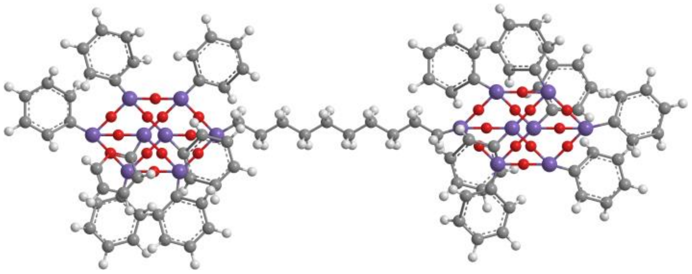

Fig. 1 Molecular structure of 1,10-bis(heptaphenyl-T8-silsesquioxyl)n-decane

On continuing our research in this field, in the present work we synthesized the PS based nanocomposites, having the 5% of fillers of Fig.2. In order to compare the results here obtained with those found for the nanocomposites previously studied [4,5].

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Chemical and textural fingerprint of natural stones for the use of construction and restoration stakeholders (CatSTONE project)

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Since thermal analysis (DTA/TG) needs small amounts of sample and provide extensive qualitative and quantitative information, it could be used as an approach in the study of natural stones of construction and restoration interest [1-3]. The methodology, presented within the CatSTONE project, intends to combine DTA/TG with Gas Chromatography and Mass Spectrometry (GC-MS), all supported by Image Analysis (IA), to be used as a mean for identification of lithotypes. Information about the chemical composition of the bulk rock and its impurities can be obtained through the DTA/TG GC-MS, while the automatized IA, based on images acquired by Scanning Electron Microscopy (SEM), allows the study of textural features. The project aims at defining the limits of investigation and the resolution of the original analytical method for natural stone materials and, within the Cultural Heritage setting, to verify the validity of the chemical imprint as a support to historical-artistic stakeholders. It is mostly addressed to the carbonatic rocks of the European database to-be, which encompasses a large amount of the market and built heritage. A first cluster of carbonate rocks widely employed as ornamental stones in Italy such as Carrara marble, Pietra di Vicenza and Breccia Aurora has been characterized following the designed protocol. The specimen preparation plays a crucial role in the overall analysis, *e.g.* the initial particle-size. The TG curves obtained on different granulometric fractions (A: $Ø > 1$ mm; B: $200\ \mu m > Ø > 120\ \mu m$; C: $120\ \mu m > Ø > 90\ \mu m$; D: $Ø < 63\ \mu m$) showed different behaviour; fine ground marble starts to decompose at lower temperature.

The significance of an advanced characterization has been demonstrated: the procedure, more based on instrumental data than the conventional, operator dependent, MOLP-based analysis, allows reproducibility of the measurements. All the data acquired will contribute to the European Innovation Partnership (EIP) NATUREUROSTONE *Building a harmonized European database on natural stones for the use of construction and restoration stakeholders* and will integrate the EN 12407:2007.

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Thermal stability of luminescent lead–free double perovskite $A_2B(I)B(III)X_6$

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In the last decade, lead halide perovskite (LHP) $APbX_3$ ($A = CH_3NH_3^+$, Cs^+; $X = Cl^-$, Br^-, I^-) materials have been widely studied for their excellent optoelectronic properties, which are particularly suitable for photodetectors, solar cells and light emitting diodes [1-3].

Unfortunately, these materials suffer from two major drawbacks: the toxicity of Pb and their poor stability against degradation induced by heating, moisture and device operation conditions. The heterovalent substitution of Pb^{2+} ions with a combination of a monovalent (B^+) and a trivalent (B^{3+}) metal has been explored and constitutes one of the most promising strategy both to have a lead – free compound and to increase the thermal stability. The resulting compounds are called double perovskites (DPs) or *elpasolites*. DPs are characterized by a 3D network of alternating $[B^+X_6]$ and $[B^{3+}X_6]$ corner-sharing octahedra, with an overall $A_2B(I)B(III)X_6$ stoichiometry [4].

Here, we present the recent results in the preparation of colloidal, powder and single crystals double perovskite where $A = Cs^+$, $B(I) = Ag^+$, Na^+, $B(II) = In^{3+}$, Bi^{3+}, $X = Cl^-$, Br^- and their thermal characterization by means of DTA/TG coupled with the evolved gas analysis in order to establish the influence of each metals on the overall compound stability.

The high emission, the thermal and light stability and the control of the stoichiometry candidate the halide double perovskites as promising materials for optoelectronic applications, such as LED and solar cell technology.

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Thermal Decomposition of Tetramethylammonium Iodide and Tetramethylammonium Lead Iodide Perovskite: A Kinetic and Thermodynamic Study

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Alkylammonium lead halide perovskites are currently considered with great hope as possible light harvesting materials for photovoltaic devices. However, it is now well-known that their low thermal and chemical stability is a serious drawback for large-scale applications. Therefore, the investigation of the thermal decomposition pathways of these materials is important to put in place effective protection strategies and to identify possible chemical modifications [1]. To this end, the study of the thermodynamics and kinetics of the thermal decomposition of simple alkylammonium halides, which has been the subject of a number of studies in the past [2], is becoming again of interest [3] as a first step to tackle the more complex study of the corresponding perovskites.

In this study, we present a multitechnique investigation of the kinetic and thermodynamic properties of the thermal decomposition undergone by tetramethylammonium iodide, $(CH_3)_4NI$, and the corresponding tetramethylammonium lead iodide perovskite, $(CH_3)_4NPbI_3(s)$, carried out by the TG-DTA (Thermogravimetry-Differential Thermal Analysis), XRD (X-Ray Diffraction), and effusion techniques (KEML: Knudsen Effusion Mass Loss, KEMS: Knudsen Effusion Mass Spectrometry).

The kinetics of the multi-step decomposition process of $(CH_3)_4NPbI_3(s)$ was studied by XRD measurements and by an isoconversional analysis method which is based on processing TG data recorded at various constant heating rates. The activation energy of the rate-determining step so obtained, namely the second one, is consistent with a mechanism involving the breaking of the C−N bond (see process (3) below). The vaporization/decomposition behaviour of the compounds under consideration was investigated by KEMS and KEML in the overall temperature range 435 - 550 K on the basis of the following processes:

$(CH_3)_4NI(s) = (CH_3)_3N\,(g) + CH_3I(g)$ (1)
$(CH_3)_4NI(s) = (CH_3)_4NI(g)$ (2)
$(CH_3)_4NPbI_3(s) = PbI_2(s) + (CH_3)_3N\,(g) + CH_3I(g)$ (3)

where $(CH_3)_4NI(s)$ may in principle follow two different decomposition pathways, depending on whether the N-C bond is broken or not. The possible occurrence of process (3) (vaporization as gaseous “intact ion pair” $R_4NX(g)$), often overlooked in the literature, is discussed with the help of theoretical calculations. From the partial pressures measured by KEML, thermodynamics of processes (1)-(3) were derived.

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Decomposition temperatures and vapour pressures of ionic liquids for electrochemical applications

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Ionic liquids (ILs) are salts with melting temperatures below 100°C. Typically they are formed by organic cations, like imidazolium, pyrrolidinium, ammonium or alkyl phosphonium, and organic/inorganic anions, like hexafluorophosphate, tetrafluoroborate, triflate, dicyanamide, tetracyanamethanide, bis(trifluoromethanesulfonyl)imide (TFSI) or bis(fluorosulfonyl)imide (FSI). The presence of such bulky and asymmetric ions decreases the ion-ion interactions and lowers the melting point with respect to more classical salts. ILs present peculiar physical and chemical properties: extremely low vapour pressure, high ionic conductivity, a high thermal, chemical and electrochemical stability, a high thermal capacity and good solvent capacity. Due to these peculiarities, ILs have been proposed for a large variety of applications in chemistry and physics, such as, for example, green solvents, electrolyte components for electrochemical devices, lubricants, ingredients for pharmaceuticals and heat exchangers.

Due to the possible applications of such materials, it is of great importance to investigate their decomposition temperatures and vapour pressures. In the present paper we report an investigation on these physical peculiarities for a few IL families based on the bis(trifluoromethanesulfonyl)imide or bis(fluorosulfonyl)imide anions and on quaternary ammonium or imidazolium cations. Ramp-temperature and isothermal thermogravimetric experiments were conducted in these compounds, after running a strict drying procedure, in order to ascertain their decomposition temperature and their vapour pressure in a wide temperature range, from 175 up to 325 °C, following well established procedures [1,2].

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The case study of the Medieval Town Wall of Gubbio in Italy: characterization of mortars using XRD, TG-DTA, PLM and SEM

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In the frame of the HERACLES project [1], a set of Cultural Heritage sites was studied to improve their resilience against climate events. Among these is the medieval Gubbio Town Walls in Italy.

The Town Walls of Gubbio represent a cycloptic structure and enclose the medieval city with a length of about 3 km. They are characterized by several gates and defense towers, walls of variable heights (up to 12 m) and thickness (from 0.5 to 3 m) made of multi-leaf stone masonries. During the centuries, several factors, including environmental actions and structural and material repairs have produced different criticalities, involving both structure and materials.

Consequently, Town Walls exhibit several issues related to the materials degradation used for building and restoration. These materials suffer of increased deterioration due to climate change effects coupled with pollution.

Another important problem is linked to the progressive degradation of the mortars binding the masonry. The wall body-structure behaves/reacts properly as greater is the cohesion between mortar and stones.

The present work focuses on the characterization of mortars of this monument and several samples relate to different parts of the Walls, corresponding to different historical periods and interventions, were collected. They were characterized to determine the corresponding mineralogical and chemical compositions along with morphological analysis. For that purpose, ex-situ laboratory techniques such as X-ray diffraction (XRD), Polarized Light Microscopy (PLM), Scanning Electron Microscopy (SEM), and Thermogravimetry and Differential Thermal Analysis (TG-DTA) were used to examine the mortars weathering and degradation state in order to organize appropriate restoration and repair actions

[1] HERACLES – HEritage Resilience Against CLimate Events on Site.

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Modelling of fast response surface thermocouples for fusion plasma facing components

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Surface eroding thermocouples have been studied to measure temperatures and heat fluxes in the divertor of the DTT facility [1]. Thermal measurements are performed on plasma facing components of fusion machines especially on the divertor to provide local temperatures relevant to the material surface (sensors embedded in the component under the exposed surface [2]), bulk calorimetry (time variation of temperature observed at the same sensor [3]), or the power density deposited on castellated modules (temperatures detected at the same time by sensors located at different distances from the heated surface [4, 5]). Signals of these temperature measurements will be used during pulse operation or first wall conditioning for parameters monitoring, component protection, and machine control.

Surface eroding thermocouples (or "self-renewing thermocouples") can be used to instrument plasma facing components in which the thermojunction is formed in a very thin layer at the surface of the sensor [6]. This construction leads to a fast thermal time response (10 ms), robust design against heat loads around 10 MW/m^2, and is particularly useful to characterize the surface temperature evolution of the plasma facing component with the carrier body made of the same material as the component. Surface thermocouples also enable a simple computation of the power density applied to the component. Arrays of surface thermocouples proved to be a vital component of the overall diagnostic set and can be installed to measure pulsed heat fluxes in the divertor of tokamaks [6].

The study deals with modelling the signal response of surface eroding thermocouples, developing a sensor design, and integrating the concept in the castellations of the DTT device divertor [7].

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Preliminary electrochemical study of carbon powder material obtained by high pressure water jet recycling process of tires and used as cathode in Lithium-Air batteries

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Lithium-air batteries, are an extremely attractive technology for electrical energy storage, because of their far higher theoretical specific energy than that of conventional batteries [1]. However, some issues, such as the stability of the electrolyte or the slow oxygen reduction reaction (ORR) during charging are still to be overcome. At the same time environmental problems push researchers to develop practical and convenient ways to perform useful materials recycling [2]. In this contest, this work evaluates an innovative high pressure water jet recycling method of tires followed by a pyrolysis process at three different temperature: 500 °C, 800°C and 1000 °C to produce three hard carbon materials to be used as cathode in lithium air batteries. The obtained materials were characterized by SEM, EDX, BET, Raman and XRD analysis, while the electrochemical characterization has been performed by charge/discharge cycles in galvanostatic mode. A comparison between the so obtained three carbon powder materials has been carried out. A specific capacity up to 1000 mA/g have been obtained in all cases even if the powder treated at 1000°C seems to have a better electrochemical behavior.

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Photo-induced oxygen scavenging in rubber nanocomposites with titania particles and silsesquioxane molecular fillers

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The hydrolysis-condensation reactions of organotrialkoxysilanes R'Si(OR)$_3$ with different R' organic functions under strictly controlled synthesis conditions allow the preparation of silsesquioxanes (SSQs) with tunable crosslinking degree, size, architecture and reactivity [1]. These features condition extent and nature of interfaces when SSQs are employed as molecular fillers in the preparation of nanocomposites (NCs), thus directing their final structure-related properties [2]. Moreover, molecular fillers can be used as dispersing aids for embedding inorganic nanoparticles (NPs) in polymer-matrix nanocomposites [3], reducing the number and size of aggregates and conferring new multiple functionalities characteristic of smart materials.

With the objective of tailoring barrier effect, photocatalytic and mechanical behavior simultaneously, novel rubber NCs including ladder-type SSQs and different amounts of TiO_2 NPs have been developed. The effect of TiO_2 addition on crosslinking degree and thermal stability of the prepared NCs was evaluated by thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses and the results were correlated to the information on structure and molecular dynamics obtained from solid-state nuclear magnetic resonance (NMR) experiments. Both oxygen barrier and photo-induced scavenging were studied by photoluminescence and correlated with the NCs structural features, aiming to point out the different activity of organic/inorganic components and hybrid interfaces on O_2 trapping process.

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Phase behaviour and rheology of multi-responsive soft microgels

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Soft colloids have attracted great interest in the last few years for both technological applications and theoretical implications. Indeed, they are very good model systems for understanding the general problem of dynamic arrest, since their larger tunability with respect to atomic and molecular systems leads to complex phase behaviours. Among them multi-responsive microgels, colloidal suspensions of micro- or nanometre-sized hydrogel particles, are very intriguing systems due to their high responsiveness to external stimuli such as pH, temperature, electric field, ionic strength, solvent, external stress and light pulses. These systems play an important role in several biophysics applications [1].

One of the most studied microgel is the thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) whose thermo-responsiveness is strongly related to the temperature induced coil-to-globule transition of the NIPAM polymer. At room temperature indeed, PNIPAM microgels are in a swollen state, due to the polymer hydrophilicity that leads to dominant polymer-solvent interactions and to the retention of a great amount of water. By increasing temperature, across the volume phase transition (VPT) (T~ 305K), the polymer becomes hydrophobic, polymer-polymer interactions become stronger, water is expelled and particles reach a shrunken state. In this work we study an Interpenetrating Polymer Network (IPN) microgel composed of PNIPAM and a pH-responsive polymer as poly(acrylic acid) (PAAc) [2,3]. The IPN preserves the same VPT temperature of pure PNIPAM microgel [4]. Here we report rheological and differential scanning calorimetry measurements on aqueous suspensions of PNIPAM-PAAc microgels as a function of temperature, weight concentration and PAAc content. The frequency dependent linear viscoelastic properties across the typical swollen-shrunken volume phase transition are deeply investigated [5] and a preliminary phase diagram is reported.

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Layered composite based on halloysite and biopolymers: a carrier for controlled release

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Recently, great efforts have been addressed to the design of biohybrid materials composed of organic moieties and inorganic clay minerals, which can present different features in terms of chemistry, aspect ratio, morphology and charge.[1,2] We have prepared new biohybrid materials based on halloysite nanotubes and natural polymers (alginate, pectin and chitosan) for the controlled and sustained release of bioactive species. A functional nanoarchitecture has been designed allowing to generate a layered structure with biopolymer/halloysite nanocomposite. The assembly of the raw components and the final structure of the hybrid tablet have been highlighted by the morphological and wettability properties of the prepared materials.[3]

Being that the biohybrid has been designed as a smart carrier, halloysite nanotubes have been firstly loaded with a model active molecules. The effect on the release kinetics has been investigated confirming that the delivery capacity can be controlled by modifying the structural features of the hybrid material. It was also demonstrated that this strategy is feasible for pH or other chemical stimuli triggered release of the payload. Therefore new routes are opened for a large range of applications such as protective films for cultural heritages or drug delivery systems where the proposed nanoarchitectures are suitable as functional material with tunable delivery capacity.

Characterization of aging of HDPE piping using DSC, DTA, DTA-TG techniques

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The lightweight, relatively high strength, anti-rust and the quite easy processability together with low cost candidate high-density polyethylene (HDPE) as an interesting material for piping for the transport not only of potable and wastewater but also of combustible gases and chemical and petrochemical products. However, various degradation mechanisms affect HDPE when exposed to different environmental situations such as low/high temperature, sun light, rain, soil, water [1, 2].The polymers can fail into three main stages. The first one is a ductile fracture due to an excess of external load. This situation could be avoided with a proper design of the component and of the in service conditions. As time in service increases, some flaws could form inside the material reducing the mechanical properties and leading to a fragile failure. Finally, the third stage is a fragile fracture due to the deterioration of the material. The determination of time to failure is of great interest to establish the component residual life. This work presents the results of an investigation on some HDPE commercial pipes aging, performed with DSC, DTA, DTA-TG techniques [3]. The fusion temperature, enthalpy and the OIT (*oxidation induction time*), obtained at different plateau temperature, are measured. The results are used to characterize and compare the materials as well as to evaluate the residual lifetime, before the onset of the third stage, of in service pipes [4, 5, 6].

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A DSC study on the heating phase transformations in the ASTM A213 T91 steel

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The results of a comprehensive investigation of several phase changes occurring in a standard ASTM A213 T91 steel are presented in this paper. The entire temperature range 25°C to 1500°C has been explored using differential scanning calorimetry (DSC) under various heating rates, and microscopic techniques (light optical microscopy and electron microscopy FEGSEM / EDS). (Fig.1) Results show that the austenitization process in T91 steel consists of two separate steps: 1) transformation from α to γ; 2) dissolution of the coarser chromium-rich carbides. A solid determination of the temperature at which the dissolution process of chromium-rich carbides reaches completion has been obtained at T = 1068°C. (fig.1) New data have also been acquired on γ-to-δ transformation. Results have been compared with theoretical phase equilibria calculations and other experimental data published in the available literature. Significant differences between experimental and theoretical determinations of temperatures, as well as within the pool of experimental data exist. We suppose that such discrepancies can be ascribed to kinetics, but some contribution, however is due to differences in the chemical composition of the examined steels

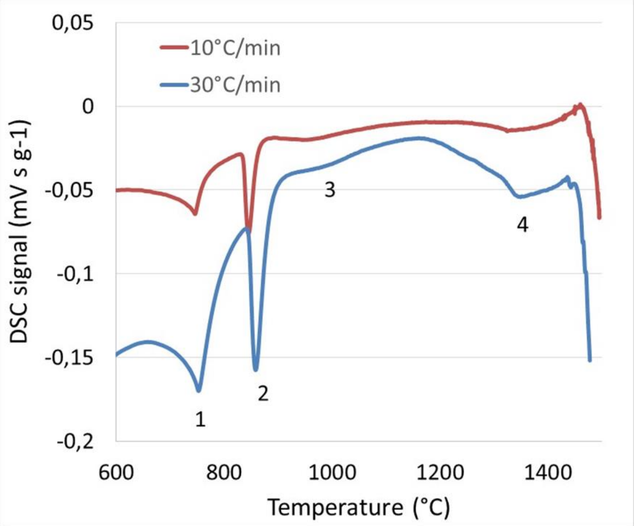

Fig.1 T91 Q+T DSC profiles in the range 600-1500°C, for two heating rates.

Poly vinyl alcohol (PVA) hydrogels: the effect of crosslinking density and molecular weight on water interaction estimated by thermal analysis (TGA-DSC)

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Hydrogels are semisolid crosslinked polymeric networks able to interact with water and swell when in contact with fluids. Water can represent up to 98-99% of their weight

Several polyvinyl alcohol based hydrogels were synthesized changing pH of the reaction, PVA molecular weight and crosslinking density. Thermal analyses (TGA-DSC) can be utilized to analyse hydrogel-water interaction as a function of pH, crosslinking degree and molecular weight of the polymer [1-3].

When materials are heated, they lose part of their weight as a function of the temperature. All materials lose their water component in 30-120°C temperature range and the temperature at which the greatest loss is detected is function of the strength with which it is bound to the structure. Hydrogels show three kind of water: freezable free water, freezable bound water and not freezable water. The last one can be detected upon heating sample (TGA) but cannot be quantified upon cooling (DSC) the sample. DSC analysis permits to quantify freezable water [4].

Hydrogels weight loss in the 30-120°C range confirms the presence of structures able to interact with different strength with water. Consistently with the increase in crosslinking density, a significant increase of the not freezable water, i.e. water strictly bound to the structured polymer network is found.DSC analysis confirms the poor structuration of low molecular weight hydrogels with the totality of water as freezable water. Moreover, freezable water in low molecular weight hydrogels is subdivided into freezable free water (97%) and freezable bound water (3%). Being the freezable bound water the layer bound to not freezable water, its percentage is very low. Matrices with the highest crosslinking density show different kinds of bound water as indicated by the presence of several temperature peaks [5].

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Thermomechanical behaviour of “ghiara”, a paleo-soil from Mount Etna, Italy

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A paleo-soil, the so-called “ghiara”, was discovered during the basaltic rocks mining process on Mount Etna in Sicily, Italy. It is characterized by an intense reddish hue due its high iron content combined with the high temperatures (800-900°C) reached in contact with the lava flow and so for the highly oxidising conditions. Ghiara is macroscopically heterogeneous with variable sizes up to coarse gravel and pebble. Usually, its aspect reproduces the origin of the sediments involved by the overflowing lava, deriving from epyclastic or pyroclastic deposits [1].

In order to evaluate the possibility to be used in the production of ceramics, alkali activated materials or concretes, the thermomechanical behaviour was investigated by means of heating microscope (Misura HSM, Italy), and simoultaneous DTA and TGA (STA 409 NETZSCH, Germany). The heating microscope is a horizontal furnace equipped with a camera capable of recording images of the profile of the specimen, obtained by pressing the pulverized ghiara, during heating [2]. The furnace reaches a maximum temperature of 1600°C in static air.

From the images of the sample profile it is possible to obtain a sintering curve that describes the volumetric variations of the sample thus providing data on the thermomechanical performance of the pressed powder. The dilatometric curve shows a good dimensional stability up to 1200°C, when the sintering of the material corresponding to its contraction begins. The appearance of the fluid phase, which leads to a rounding of the edges of the pellet, is recorded by the sofwtare around 1190°C. The complete loss of dimensional stability records at 1210°C.

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) are in good agreement with the data of the heating microscope, showing the absence of thermal events up to the sintering start temperature and the absence of weight loss up to 1300°C. The appearance of the liquid phase corresponds to the melting endothermic peak with a minimum posiitoned at 1220°C.

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Adsorption of platinum compounds for water treatment applications

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Cytostatic drugs (CD), characterized by their environmental persistence have been detected in water bodies at concentrations up to µg/L levels [1]. Several methods for the removal and degradation of CDs, have been developed [2]. However, these methods are expensive and sometimes inefficient for CDs complete removal from the treated water.

Platinum-based chemotherapy agents are widely used for the treatment of a variety of cancers and demonstrate a high toxicity and low biodegradability. Such drugs, after use, are excreted to hospital waste-water intact or as highly toxic derivatives in significant percentage [1]. The presence of Pt-based drugs in the µg/L range in hospital effluents rising concerns about the long-term exposure of living organisms to low levels of such toxic compounds [3].

A potentially effective strategy to treat such low levels of Pt-containing contaminants is to pre-concentrate the sample to be treated by selective adsorption with specifically designed materials. Then, the adsorbed compounds can be desorbed and treated by advanced oxidation processes. Desorption can be realized by changing the temperature of the system which would make more sustainable the process as no chemicals (e.g. strong acids, organic solvents) would be needed.

In this contribution, the adsorption of cisplatin and $PtCl_4^{2-}$ in the µg/L range by cysteine-modified silica is evaluated. The choice of this material is based on the high affinity of cysteine for Pt^{2+} [4].

Adsorption kinetics and isotherms have been built by analyzing the free concentration of Pt by using ICP-MS. Isothermal titration calorimetry has been then used to monitor the heat exchanged in the adsorption process.

Early results show that for $PtCl_4^{2-}$ equilibrium is reached within 30 minutes with a starting concentration of 500 µg/L at pH = 6. Adsorption of $PtCl_4^{2-}$ and cisplatin in the 250-1250 µg/L show a retention more than 90% and 60% respectively. Isothermal titration calorimetry (ITC) evidences an exothermic reaction that when a dispersion of the adsorbent material is titrated with a solution of the compounds.

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Characterization of 18650 Li-ion cell components before and after thermal abuse tests

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Lithium-ion batteries (LIBs) had a great development in recent years because they are the preferred option when high energy density, high power density and low self-discharge are required. For these reasons their use has grown quickly, above all for portable electronics, power tools and hybrid/full electric vehicles [1]. As a consequence of the large amount of the energy that is stored inside these cells, the aspect regarding the safety can't be ignored. In fact, in recent years, LIBs have been the source of several serious accidents. If during the normal operating condition a failure occurs, the cell could undergo into a process called thermal runaway, an unstoppable chain reaction during which a series of exothermic reactions takes place. The heat produced is greater than the one released so there is an uncontrollable increase in pressure and temperature that can lead to explosions and projections of fragments [2]. Various researches have been carried out to study the thermal stability of battery materials, usually using a cone calorimeter [3]. On the contrary only few works are focused on the characterization of the residues after the tests, which is important for a proper waste management [4]. Moreover, some documented cases are reported of ignition of battery pack subject to fire after its extinction. The characterization of the residues would make possible to understand also their role in the reignition. In this framework, this work aims to characterize cell components before and after thermal abuse tests performed in a Cone Calorimeter. To this purpose SEM-EDS and XRD are used to determine the structural, morphological, and compositional changes of the cell components and compared with previous studies [4]. SEM-EDS analysis shows that the mixed Li oxide and graphite particles are initially homogeneously distributed on the collector surfaces, while after the test the surfaces are not homogeneous, leaving the current collector uncovered in some areas. This evidences damage of the original lattice structure [5]. Panasonic 18650 Li-ion cell components are also investigated using a DSC before and after cone calorimetric tests. The results show at the anode two exothermic peaks at approximately 150°C-170°C and 250°C-270°C due to the exothermic reduction reactions involving the intercalated lithium and the electrolyte or ligand (PVDF). At the cathode, the exothermic peak is observed at 250-290°C, due to the decomposition reactions of the mixed oxide which constitutes the cathode and the subsequent oxidation reactions of the solvent with the formed oxygen.

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Characterization of cellulases produced by *Trichoderma longibrachiatum* DIBAF-10 using Differential Scanning Calorimetry

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Conversion of cellulose to soluble sugars by enzymatic hydrolysis is a key step for production of biofuels from lignocellulosic biomass. Efficient hydrolysis of cellulose requires the action of three different classes of enzymes: endoglucanase (1,4-β-d-glucan glucohydrolase [EC 3.2.1.4]), exoglucanase (1,4-β-d-glucan cellobiohydrolase [EC 3.2.1.91]), and β-glucosidase (β-d-glucoside glucohydrolase, [EC3.2.1.21]) [1]. *Trichoderma longibrachiatum* DIBAF-10 produced a cellulase cocktail tailored for the saccharification of milk thistle (*Silybum marianum*) with the potential to compete with commercial enzymes.

In this study, crude cellulase preparations from *T. longibrachiatum* DIBAF-10 were thermally studied by differential scanning calorimetry (DSC), to assess the conformational transitions between the folded and unfolded structure of the proteins and the relationship between them and the energetics of their stability. Generally, the aggregation can take place concurrently with the irreversible thermal denaturation and the conformational unfolding or accompanies an exothermal effect that results in formation of precipitation [2]. The study of thermal properties is essential to better characterize and understand the interactions between cellulase and its substrates and their dependence on temperature. In fact, enzyme thermo-stability is essential during saccharification reaction because steam is always used to make the substrates more suitable for the enzymatic hydrolysis [3].

The present work shows that DSC profiles of crude enzyme samples from *T. longibrachiatum* DIBAF-10 provide important thermodynamic information, about the thermostability of the included proteins. The thermograms of crude enzyme coktails, and of the commercial ones, show similar exothermic peaks at 52.45±0.90°C and 49.5±0.95°C, respectively, and comparable ΔH values. This is probably due to the same conformational change leading to aggregation of proteins.

DSC, moreover, is cost-effective tool to obtain “conformational fingerprinting” of the crude enzyme cellulase preparations.

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Thermal analysis as a tool for material characterization in conservation of wooden artefacts

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In recent years, inorganic nanoparticles have been proposed as efficient fillers for the consolidation and preservation of lignocellulosic art-works, such as paper documents and archaeological woods. A novel green protocol for the deacidifying consolidation of waterlogged archaeological woods through aqueous dispersions of polyethylene glycol (PEG) 1500 and halloysite nanotubes containing calcium hydroxide have been designed.

The controlled and sustained release of $Ca(OH)_2$ from the halloysite lumen extended its neutralization action over time allowing to develop a long-term deacidfication of the wood samples. TG experiments under CO_2 allowed us to characterize the carbonatation kinetics of $Ca(OH)_2$. A preliminary thermo-mechanical characterization of the clay/polymer nanocomposites allows us to determine the experimental conditions to maximize the consolidation efficiency of the wood samples. The penetration of the halloysite-$Ca(OH)_2$/PEG composite within the wooden pores conferred robustness on the archaeological woods on dependence of the clay/polymer composition of the consolidant mixture. Compared to the archeological wood treated with pure PEG 1500, the addition of the modified nanotubes in the consolidant induced a remarkable improvement of the mechanical performances in terms of flexural strength and rigidity. The pH measurements of the treated woods showed that halloysite-$Ca(OH)_2$ are effective alkaline fillers. Accordingly, the modified nanotubes provided a long-term protection for the lignin of the woods exposed to artificial aging under acidic atmosphere.

The attained knowledge shows that an easy and green protocol for the long-term preservation of wooden art-works can be achieved by the combination of PEG polymers and alkaline tubular nanostructures obtained through the confinement of $Ca(OH)_2$ within the halloysite cavity.

Thermal characterization of micro encapsulated polyphenols extracted from olive leaves

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Olive leaves are waste material of the olive industry; they are rich of polyphenols, especially oleuropein, with high antioxidant activity. These molecules are very sensitive to environmental conditions such as high temperature, pH and oxygen, limiting their applications as ingredients for healthy foods. Encapsulation techniques are proposed as a way to protect polyphenols from adverse conditions [1]. The aim of the present work is to study, by DSC, the thermal stability of different encapsulation systems for olive leaves polyphenols, in order to add them as ingredient for bakery products.

The phenolic extract was encapsulated in microbeads of sodium alginate, obtained by emulsification/internal ionotropic gelation, in combination with either plant or animal polymers (pectin, whey proteins and sodium caseinate). The thermal analysis was conducted on the original ingredients and on freeze-dried microbeads by DSC Q100 (TA Instruments, New Castle, DE, USA), heating from 25 to 350°C at a scanning rate of 10 °C/min.

Alginate and pectin ingredients showed a huge exothermic peak around 240 °C, previously associated to the biopolymers thermal breakdown [2]. The intensity of that peak was lowered after calcium gelation, indicating the higher thermal stability of the egg-box structure [2]. All the studied systems showed an endotermic peak, in the range 75-85°C, related with the water loss [3]. A single endothermic peak in the microbeads indicates the chemical interaction between polymers and extract and a good thermal stability [3]. The peak was observed at around 75, 77, 79 and 85°C, for alginate-whey proteins, alginate-caseinate, plain alginate and alginate-pectins microbeads respectively, in order of growing thermal stability [3].

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Thermal degradation of a $Fe^{2+}Cr_2O_4$ synthetic spinel

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Single crystals of $Fe^{2+}Cr_2O_4$ were synthesized using a flux-growth method. Previous studies showed that Cr completely fills the octahedral site, and that iron occurs almost exclusively as $^{VI}Fe^{2+}$.

As Cr should not be oxidized in spinels, we would expect that heating affects only the iron cation present in the T site. Heating in hercynite spinels, $FeAl_2O_4$, causes exchange of the Fe and Al cations between the two non-equivalent sites and oxidation of Fe^{2+} to Fe^{3+}.

Consequently, as Cr cannot fit into a tetrahedral site, the only possible effect is the oxidation of Fe^{2+} to Fe^{3+} and, possibly, the formation of T site vacancies.

To reach this purpose, crystals were put in a thin-walled quartz tube and heated in a vertical tube furnace at different temperatures from 600 to 1000°C. Heating runs were performed at room pressure in air. Run temperatures were accurately measured and controlled by means of a calibrated Pt/Pt-Rh thermocouple located near the sample; the uncertainty is estimated to be about ±5°C.

Since the cell parameter (a) and the oxygen positional parameter (u) changes with time and temperature, a strongly correlated relationship between the heating process and the iron oxidation was supposed.

At the end of the oxidation process the crystals were polished to about the median plane in order to see if and how the oxidation develops into the crystals.

In order to verify the presence of ferric iron, SEM EBS as well as EMPA analyses have been performed and successively compared with data obtained from single crystal XRD, EMPA and Mössbauer previously performed.

The interaction between the antimicrobial peptide Lasioglossin III and model membranes

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Antimicrobial peptides (AMPs) are evolutionarily conserved key effector molecules of the innate immune system which can be isolated from almost all living organisms, including plants and animals [1]. These peptides exhibit a broad-spectrum of activity against a wide variety of pathogens, including bacteria, protozoa, fungi, and viruses [2]. It is believed that, due their unique and non-specific action mechanisms which involve a direct destabilization and interaction with the lipid matrix of pathogens' membranes, they could help in fighting infections caused by multidrug-resistant (MDR) bacteria [3]. Further, a significant number of these bactericidal peptides have been shown to have anticancer activity.

Lasioglossin III (LL-III) is a cationic peptide (VNWKKILGKIIKVVK-NH_2) derived from the venom of the eusocial bee *Lasioglossum laticeps*, having both antimicrobial and antitumor activity. Moreover, it shows a low hemolytic activity and it has almost no toxic effect for eukaryotic cells [4]. Despite these features, the molecular basis of LL-III action mechanism is still unclear.

In this study, we report a calorimetric and spectroscopic characterization of the interaction of a LL-III with model membranes mimicking eukaryotic, bacterial and cancer cell membranes. Particularly, the antimicrobial and cancer cell membranes were modeled with liposomes constituted by a mixture of zwitterionic (POPC or DPPC) and anionic lipids (POPG or DPPG and POPS or DPPS). Liposomes composed of only zwitterionic lipids (POPC or DPPC) were used as simplified model of eukaryotic membrane.

Our DSC and fluorescence results demonstrate that the LL-III preferentially interacts with anionic lipids inducing a significant perturbation/reorganization of the lipid membrane structure. The type and the extent of such membrane reorganization is dependent on the membrane composition. These findings provide interesting insights into the action mechanism of this peptide.

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Thermodynamic properties of mixtures an ionic liquid + an organic compound

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ILs, are molten organic salts, in the liquid state at room temperature. The physical and chemical properties of ILs can be tuned by proper selection of the kind of anion, cation and substituting groups of both constituent ions. Nowadays, they are used in an increasing number of applications. Low chain alcohols and N-methyl-2-pyrrolidone, NMP, are organic liquid broadly used, especially as a solvent, in many processes both at laboratory and industrial scale. Several publications have been devoted to experimental and theoretical thermodynamic studies on pure ILs and their mixtures with common organic solvents [1] or water [2]. Because of the huge number of systems to be investigated, a systematic study and a full overview is far from be reached.

In this work we report the experimental measurements of excess molar enthalpies and excess molar volumes on 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide + ethanol or + NMP (2) mixtures. To the best of our knowledge, calorimetric and volumetric properties have not been reported in the literature for the selected binary mixtures.

Density measurements were carried out by means of a vibrating tube densitometer (model DMA 58, Anton Paar, Graz - Austria). Heats of solution were collected at 298.15 K, through a heat flow micro-calorimeter (Thermal Activity Monitor Mod. 2277, Thermometric, Sweden) by adopting the Isothermal Titration Calorimetry, ITC, technique that permits to obtain excess partial molar enthalpy of each component, $\overline{H_i}^{E}$, and hence HE, being: $H^E = x_1 \overline{H_1}^{E} + x_2 \overline{H_2}^{E}$.

This technique, differently from mixing-flow calorimetry, avoids errors due to incomplete mixing; a recurring problem in calorimetric determinations involving ILs that are intrinsically highly denser and more viscous than conventional organic solvents. Moreover, it permits to obtain more precise values of the partial molar excess enthalpy at infinite dilution, $\overline{H_i}^{E,\infty}$.

HE or VE vs. x1 data have been fitted by using the Meyers-Scott equation.

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Thermodynamic properties of binary mixtures containing alkanols

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Literature data on molar excess enthalpies (H^E), molar excess Gibbs energies (G^E), liquid-vapour equilibria (LVE) and activity coefficients at infinite dilution of components (γ_i^∞) concerning binary mixtures of *n*-alkanols, of general formula $CH_3(CH_2)_m$-OH, + *n*-alkane, are treated in the framework of the DISQUAC model, an extended quasi-chemical group contribution theory. The systems are characterized by two types of contact surfaces: aliphatic (CH_3, CH_2 and C groups) and hydroxyl (OH group).

Several group contribution models have been introduced to predict thermodynamic properties of binary mixtures containing organic compounds of different polarity, but the superiority of the DISQUAC model appears clearly when we consider the centration dependence of the molar excess functions in mixtures such as alkanols + alkanes. Indeed, assuming – as DISQUAC do – that the H^E is the sum of two contributions, dispersive and quasi-chemical, taken in adequate proportions, with the maxima situated at different values of mole fraction, x_1, we can reproduce much better the shape of the experimental H^E curves.

Several papers [1-2] report the application of the DISQUAC model to mixtures of linear or branched alkanols with alkanes using interchange energy parameters, dispersive and quasi-chemical, not structure-dependent.

In this paper, using a new set of interchange energy parameters – strongly dependent on the structure of alkanols – the model provides a fairly consistent description of the mixing thermodynamic properties as a function of concentration. The model may serve to predict missing data.

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Biodegradable compression moulded thermoplastic carbon based ashes/maize starch films for agricultural applications

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A controlled, easy and cheap method to process maize native starch, in order to obtain a highly performing thermoplastic polymer, was previously developed. A proper plasticizer such as the glycerol was added to a commercial maize starch at different concentrations corresponding to mass fraction from 50 to 70%. The samples containing 50% of plasticizer had the best thermal and physical performances [1].Starting from these interesting results, the aim of this work is the development and characterization of biodegradable thermoplastic waste carbon based ashes/maize starch films for agricultural applications. The carbon based ashes were added to glycerol and maize native starch at different amounts starting from a 10 wt%. The compounds were mixed at 130 °C for 10 min and then compression moulded.

The effect of the different amounts of carbon based ashes on the thermal and physical-mechanical properties of the moulded thermoplastic carbon based ashes/starch samples is assessed by using several techniques, such as rheometer, X-ray diffraction, scanning electron microscopy, differential scanning calorimetry, thermogravimetric analysis, moisture absorption and mechanical tests.

The presence of the waste carbon ashes allow to improve thermal and physical-mechanical performances of starch. In addition, the waste carbon ashes/maize starch films protect the crops from the excessive insolation and biodegrade into the soil, releasing the plant nutrients contained in the ashes.

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Comparison of all TG, DTG and DTA data files to evaluate, using chemometric methods, the different ages of fossil bones from two old cemetery sites

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In recent years various thermal analytical studies have been carried out in order to estimate the antiquity of fossil bones. In fact, the possibility of making this estimate on the basis of mass loss ratios as a function of temperature, has been highlighted for some time [1]. In recent years, however, it has also been shown that good results can be obtained by using not only some data obtained from the curves provided by the thermal analysis [2], but using the entire data file consisting of the curves themselves. However, until now a systematic comparison has never been carried out to establish which of the most well-known curves that can be obtained by means of thermal analysis actually provides the most valid information to distinguish the greater antiquity of a sample compared to another. This question was attempted to give an answer in the present research: for this purpose, both TG, DTG and DTA linear temperature scans of some samples of fossil bones from two different cemetery sites in the middle of Nile were carried out, known to archaeologists for the different antiquity of the burials present in them (respectively from the Mesolithic or Meroitic-Christian periods). Of all the samples, both the TG curves, the DTG curves and finally the DTA curves were carried out. With all the values of the points of each of these three types of curves, three respective data files were obtained, with which, after autoscaling, the principal component analysis (PCA) was performed. In short, the representation of the respective "scores", obtained from the file of all the TG, DTG and DTA curves, showed that both the files obtained from the TG curves and those from the DTG curves are able to separate into two respective clusters the samples belonging to one or the other of the two sepulchral sites; that is to separate the bone samples from each other with very different ages. Moreover this can be obtained using, for the representations of the "scores", both the main components 1 and 2, or components 1 and 3. Instead the data files of the DTA curves are not able to lead to a complete separation of the fossil samples of different ages. This result is in agreement with what has already been reported in the literature concerning, for example, the DTG curves [2], but it is not clear for now why DTA curves are less useful for the required purpose, even if different hypotheses can be formulated in this regard.

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Dynamical study of a model protein-polymer conjugate by differential scanning calorimetry

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Protein-polymer conjugates are important tools used in the biomedical field against severe and chronicle diseases [1]. The study of these systems, in terms of structure, dynamic and microscopic interactions is an innovative approach, different from the common studies present in literature, that mostly report the synthesis and the biochemical evaluation.

We propose the calorimetric characterization of bioconjugates made by a covalent linkage between the model protein Myoglobin and the polymer Poly(ethyl ethylene glycol) (PEEP) [2]. The polymer PEEP belongs to the class of poly(phosphoester)s, good candidates for the substitution of the "gold standard" poly(ethylene glycol) (PEG) in the bioconjugation field [3].

Samples in the dry form, with polymer of different length, and with a different number polymer chains attached, have been studied through differential scanning calorimetry, with heating and cooling scans from -85°C to 25°C. Calorimetry gives important indications on the interactions instituted between the polymer and the protein, that can be deduced by the shift in temperature and the changes in ΔC_p that occur in the glass transition of the polymer present in the conjugates respect to the polymer alone. The conjugates have been compared with the physical mixture to evaluate what's the effect of the covalent bound, and the effect of the polymer length and number has been evaluated recording the scan of samples with different composition.

The results obtained are supported by measures of elastic and quasi-elastic incoherent neutron scattering spectroscopy on the samples, that complete the picture with some considerations the relaxation dynamic of the samples.

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Thermomechanical properties of mandrels manufactured by 3D printing for the production of hollow FRP parts

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The manufacturing of hollow FRP (Fiber Reinforced Polymers) parts is carried out by using complex processes requiring extensive hand on processing or the use of tailored tools. The development of additive manufacturing technologies opened new perspective on the use of 3D printing as a production method for composite tooling [1,2]. If hollow parts are to be manufactured the use of mandrels produced by 3D printing is relevant as far as the materials used can withstand the curing temperature while allowing easy removal of the part itself after curing.

The present paper will present a novel approach developed by the authors which rely on the use of photocurable resin blends processed in a DLP/LCD printer. The thermomechanical properties of the resins are analysed by Dynamic Mechanical Analysis and Differential Scanning Calorimetry to determine the best post processing condition to guarantee the efficient use of the material as tooling for composites curing at 120-130 °C. The effect of material toughness is also discussed to show its effect on tooling removal.

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Pyrolytic valorization of the plastic residue of a WEEE treatment plant

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The total amount of waste electrical and electronic equipment (WEEE) collected in 2015 in Europe (EU-28) was 3.9 Mt [1] 10-50 wt% of which consist of plastic materials (mainly thermoplastics, but also thermosettings) depending on the kind of appliance [2]. In order to achieve the minimum recovery target established by WEEE Directive (70–80% of material and energy recovery), the treatment and recovery of plastics is getting commanding while, nowadays, WEEE material recovery facilities (MRF) are principally focused on metals recovery. The management of plastics is challenging, especially through the mechanical recycling, because the output streams are characterized by high polymeric heterogeneity and the presence of a large quantity and variety of additives used to modify the polymers properties such as inorganics and flame retardants [3].

The possibility of a pyrolysis process as a mean of recycling the residual plastic rich fraction (WEEE residue) derived from of a material recovery facility has been evaluated.

The unknown product composition of WEEE residue has been supposed through coupled thermal – infrared analysis (TG/DSC-FTIR) and ultimate analysis and resulted as PP 3 wt%, PVC 4 wt%, styrene-based polymers (principally ABS) 53 wt%, thermosetting resins (principally, epoxy/phenolic resins) 24 wt%, inorganic fraction (principally fiber glass) 16 wt%. DSC experiments showed that the overall energy, defined as the degradation heat, needed in order to completely degrade WEEE residue was about 4 % of the exploitable energy of the input material. The effect of temperature and different zeolite catalysts were investigated, in particular in terms of yield and quality of the produced oils during the pyrolysis process. Produced oils were potentially exploitable as fuels and almost all catalysts improved their quality. The best performance were reached by NaUSY(5.7) with the second highest production of light oil and the greatest total monoaromatics yield, plus 12 wt% in comparison to thermal pyrolysis experiments. Furthermore, light oil produced by NaUSY(5.7) has one of the best LHV (36 MJ/kg) and no halogenated compounds were detected by GC-MS analysis. The energy required for the thermal degradation of WEEE Residue could be supplied by char or pyrolytic gas combustion.

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Evaluation of VOCs adsorption/desorption on carbonized wood biomass by simultaneous hyphenated techniques of TG-MS and TG-FTIR

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Simultaneous hyphenated methods in thermal analysis such as STA, thermogravimetry-differential thermal analysis (TG-DTA) coupled with an evolved gas analysis technique such as mass spectrometry (MS) or Fourier transform infrared spectroscopy (FTIR) gives us a profound understanding of the volatile products evolving from a material during heating and provides an accurate qualitative interpretation of the thermal behavior of materials.

Recently, the use of carbonized biomass (charcoal) as an adsorbent for the improvement of indoor air quality has attracted much attention due to its high adsorption capacity of volatile organic compounds (VOCs) which is known as one of the causes of sick building syndrome causing undesirable health problems of headaches, asthma, etc.1) A few different aromatic and aliphatic VOCs were adsorbed on carbonized wood biomass derived from Japanese cedar charcoal (CC), hiba charcoal (HC) and charcoal of building waste wood (WWC, mostly cedar wood). The thermal desorption behavior of VOCs adsorbed on carbonized wood biomass are successfully evaluated by TG-MS (Rigaku/ThermoMass) and TG-FTIR (Rigaku/TG-DTA coupled with Thermo Scientific/FTIR). The results of the analysis revealed that carbonized wood biomass from CC showed a higher VOC adsorption capacity compared to the HC. The VOC characteristics of CC and WWC were very similar, and the effectiveness of WWC as a VOC adsorbent was shown. Additionally, VOC adsorption is a highly complex process and is dependent on the surface chemistry of the carbon material, the surface area, the presence of other compounds in the adsorption site, the type of VOC as well as the adsorption environment. Here, we have also examined the effectiveness of surface modification on biomass charcoal using acid solution of HCl at pH1, alkali solution at pH13 and H_2O treatments.

We conclude that TG-MS and TG-FTIR are complementary indispensable tools necessary for the identification of evolved gases as well as for elucidating the detailed reactions and the amount of VOC desorption.

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Kinetic analysis of spontaneous thermal polymerization of polymerizing substances

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The United Nations Recommendations on the Transport of Dangerous Goods (UN-TDG), Model Regulations, Rev.19 (2015) [1] has a new division of substances “polymerizing substances (PMs)”, which, without stabilization, would be forbidden from transport due to being liable to dangerously react under conditions normally encountered in transport. UN-TDG also has a new requirement for the determination of the Self-Accelerating Polymerization Temperature (SAPT) for PMs. Accordingly, PMs may be subject to temperature monitoring or temperature control depending upon their SAPT and type of transportation packaging. The requirement states the SAPT shall be determined in accordance with test procedures established for the determination methods of Self-Accelerating Decomposition Temperature (SADT) for self-reactive substances. Some of the methods involve reaction kinetic measurements with thermal analysis and then determining SADT by performing the heat balance calculation for the desired package. However, recent work [2] has shown that SADT results for materials with induction times can differ significantly depending upon which the SADT method was applied. Regarding PMs, the induction times depend on radical inhibitors added to PMs in order to reduce active radicals, which initiate spontaneous thermal polymerization. However, the effectiveness of inhibitors depends on the temperature, the nature and the concentration of the added inhibitors, the availability of molecular oxygen (aerobic inhibitors), the byproducts spectrum, and the concentration of impurities[3].

The aim of the present study is to obtain a better understanding of the kinetics of the spontaneous thermal polymerization of polymerizing substances. We prepared four monomers; acrylic acid, methyl acrylate, acrylonitrile, and vinyl acetate. Kinetic analysis of the four monomers using differential scanning calorimetry was conducted. The kinetic methods employed were the isoconversional kinetic (model-free) method and the Kissinger method with the autocatalytic reaction model ($f(\alpha)$). Finally, we verified whether these methods have applicability to the SAPT determination.

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Thermal behaviour and burning properties of ammonium nitrate/ammonium perchlorate-based solid propellant for combustion control by N_2O supply

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This study was aimed to prepare propellants capable of on/off control of combustion by an oxidizing gas (N_2O) supply. In the present work, we first prepared propellants composed of moisture-proof ammonium nitrate and 3% carboxymethyl cellulose ammonium by spray drying (AN/CMCA) [1] or by using commercial AN and ammonium perchlorate (AP) as oxidizers and hydroxyl-terminated polybutadiene (HTPB, molecular weights: 2800 and 1400) as a fuel. We then investigated their thermal behaviour and burning properties in N_2 or in N_2/N_2O atmosphere [2].

The propellants having different AN/AP mass ratios (AN/AP = 30/70, 40/60, 50/50, and 60/40) with 23.5 wt% HTPB were investigated by differential scanning calorimetry (DSC) and thermogravimetry-differential thermal analysis (TG-DTA). An exothermic peak derived from AN was observed in the range 300–350 °C for all the samples in the DSC scans. However, when commercially available AN and HTPB1400 was used, a sharp exothermic peak derived from AP was observed around 410 °C, in addition to the exothermic peak derived from AN. A sharp exothermic peak for HTPB1400 was also observed around 250 °C in the DTA curve.

The burning tests were performed under a N_2 atmosphere (0.3–6.0 MPa) for all the propellants prepared. It was found that the samples using commercially available AN were less likely to ignite than those using the spray-dried AN/CMCA at the same AN/AP ratio; the lowest burning rate was 0.6–0.7 mm/s. When HTPBs of different molecular weights were used, it was found that HTPB1400 was the most difficult to ignite, and the lowest burning rate was around 1.2 mm/s. Three of the samples (HTPB2800: AN/CMCA, AN/AP = 50/50; HTPB2800: AN, AN/AP = 40/60; HTPB1400: AN/CMCA, AN/AP = 40/60) did not ignite under 0.3 MPa N_2 but stably burnt under N_2 with N_2O supply at the same pressure. However, when the N_2O supply was stopped, the combustion was interrupted with a slight time delay, suggesting that the combustion of the prepared propellants could be controlled by regulating the N_2O supply. Only HTPB1400: AN/CMCA, AN/AP = 40/60 ignited in the thruster under N_2/N_2O supply. This behaviour could be related to the sharp exothermic peak of this sample around 250 °C in the DTA curve.

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Innovations in thermal analysis – the new Flash DSC 2+

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METTLER TOLEDO is a global manufacturer and marketer of precision instruments for use in laboratory, industrial and food retailing applications. The products and services are available worldwide in over one hundred countries. With more than 10,000 employees, most of them in sales, service and development, Mettler Toledo guarantees customers unique products and support of very high quality.

Thermal analysis has played an important role in METTLER TOLEDO since the early 1960s. The first commercially available TGA/DTA System, the TA1 was available in 1964. Since the beginning, we have offered innovative Thermal Analysis solutions, products, services and software.

Introducing the Flash DSC 1 in 2011, fast scanning calorimetry was revolutionized. In 2018, the new Flash DSC 2 + which allows an even higher temperature range (-95 to 1000 °C) and faster scanning rates (6 to 50,000 K/s) than the Flash DSC 1, was introduced. New measurement possibilities of this instrument will be shown.

Thermal analysis STAR^{e}-software provides unrivalled flexibility and unlimited evaluation possibilities for example with the reference library, quality control or data integrity software options. The reference library option allows to organize and store any type of sample information in a centralized location and three different search functions to identify thermal analysis data. Using the quality control option, it is possible to create a statistic template, perform a statistic evaluation and make a trend analysis. The latest software option data integrity allows to easily organize data for different users and define user rights.

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Non-isothermal decomposition kinetics of poly(ethylene oxide)/polyhedral oligomeric silsesquioxanes (PEO/POSS) nanocomposites

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POSSs are nanoparticles composed of inorganic Si_8O_{12} skeleton surrounded by eight organic groups. In this case the general formula is $R_7R'(SiO_{1.5})_8$ where R is isobutyl group and R' is phenyl group or monosupstituted phenyl group. The various POSS nanoparticles were prepared by corner capping reaction of isobutyltrisilanol with the suitable aryltrimethoxysilane [1]. Substituents on phenyl group are methyl, metoxy, fluorine and chlorine. As non-volatile molecular nanoparticles, POSS can be incorporated in polymer matrix to modify specific property.

In this work PEO nanocomposites with different hepta isobutyl polyhedral oligomeric silsesquioxanes (hib-POSS) were prepared by annealing method and the influence of hib-POSS type on the non-isothermal decomposition kinetics was investigated. The kinetic analysis of the non-isothermal data was performed using Netzsch Thermokinetics Professional software. The obtained results indicate that the non-isothermal decomposition of PEO is predominantly single-step reaction and therefore can be kinetically described by a single-step model. The non-isothermal decomposition process of all PEO/POSS samples is more complex compared to PEO and is kinetically described by a multi-step model. The kinetic parameters (activation energy, pre-exponential factor and reaction model/models) were calculated for PEO, each PEO/POSS sample and each decomposition step. POSS influences the beginning of the decomposition process while the main kinetic model for the characterization of PEO decomposition process remains the same in all samples.

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Thermal behaviour of GaSb system doped with Fe, Mn, Cd, Gd

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Gallium antimonide is considered to be a promising material for optoelectronic and thermoelectronic devices, due to the prohibited bandwidth, and the high solubility of the chemical elements in groups I-III. Due to the high concentration of its own defects (≈ 1017 cm^{-3}, the specific energy band structures and the high solubility of impurities in gallium antimonide, it was possible to create tunnel diodes and coherent radiation sources in the current spectral range for modern information systems. *GaSb* semiconductor, with a forbidden narrow band, is one of the most demanding materials for creating thermo-photovoltaic elements, luminescent diodes, photodiodes, solar cells and other microelectronic devices. Many uncertainties are related to the doping mechanisms, and the dopant's influence on the physical processes in the base material.

The atoms of the Group IV metals, in particular of Fe, substitute in the *GaSb* crystalline network the *Ga* atoms, forming as a whole the separate subnetwork of the *Sb* and *Ga* atoms.

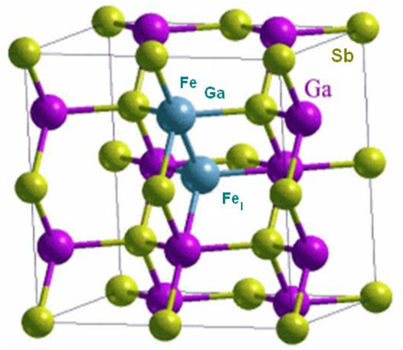

Fig. 1

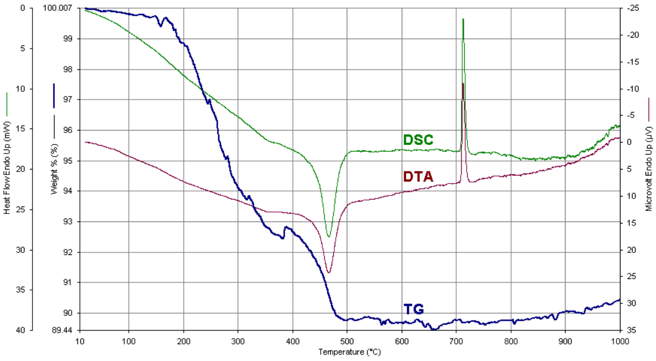

Fig. 2

In Fig. 1 is the structure of the semiconductor *Ga(Fe)Sb*: *Ga* - violet color, *Fe* blue color, *Sb* - yellow color. The GaSb system doped with Fe, Mn, Cd and Gd was thermally analyzed in air (150 cm^{3}min^{-1}) with a PerkinElmer DIAMOND TG/DTA thermobalance from room temperature to 1000 °C. In Fig. 2 is the result of the thermal analysis of a *Fe*-doped *GaSb* sample with an atomic concentration of 10^{18} cm^{-3}.

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Poster Session 2

Thermal characterization of gelation for aqueous methyl cellulose solutions containing polyethylene glycol and salt

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Methyl Cellulose (MC) and Polyethylene Glycol (PEG) are considered to be environmentally and biologically friendly materials, and they have been applied to industrial and biological uses as highly hydrophilic and viscous polymers. The gelation temperature of aqueous MC solutions is reduced by addition of PEG and/or salt [1]. To evaluate thermal characteristics, DSC can be used to measure gelation temperature. However, these measurements often were difficult to detect gelation peak in low concentration solution from aspect of DSC sensitivity.

In this study, we investigated the influence of PEG and/or salt on MC hydrogel formation using high sensitivity DSC [2].

Gelation peak of MC hydrogel was clearly detected. The gelation temperature and enthalpy decreased with the addition of PEG (Fig. 1). In contrast, the peak enthalpy increased with the addition of salt (Fig. 2). The impact on gelation temperature from the addition of $\mathrm{CaCl_2}$ was larger than from the addition of $\mathrm{MgCl_2}$.

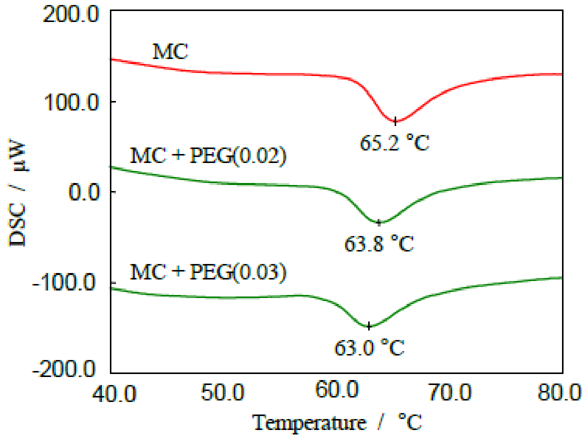

Fig. 1 Influence of PEG for MC
Molar fraction of Ethylene oxide unit of PEG : 0.02 and 0.03

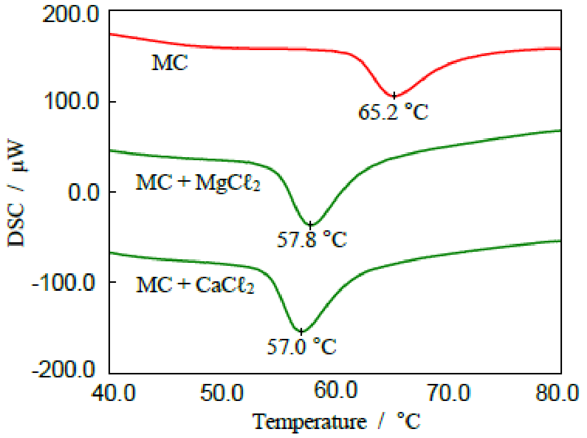

Fig. 2 Influence of Salt for MC
Concentration of $\mathrm{MgC\ell_2}$ and $\mathrm{CaC\ell_2}$: 0.1 mol/ ℓ

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Reactivity hazard evaluation of metal thin film - nitric acid system to prevent explosion incidents in metal stripping processes

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Explosion incidents in metal stripping processes using nitric acid have become to increase recently in Japan. Understanding the mechanism of these explosion incidents is needed to prevent similar explosion incidents. Thus, we focused a near-miss incident when metal thin films composed by Al, Ni, Ti, and Ag (hereafter laminated film) was dissolved in nitric acid, and we investigated a cause of this incident.

Exothermic peak at 25-200 °C was observed when the thermal behavior of the laminated film – nitric acid system was measured using DSC. Moreover, the sharp exothermic peak was observed (shown in Fig. 1) when the weight ratio of the laminated film and nitric acid was from 1:1 to 2:1. The laminated film was separated into 5 pieces along the laminated direction (hereafter separated film), and the thermal behavior of separated films – nitric acid system was measured using DSC. As a result, the sharp exothermic peak was only observed in some pieces of separated films. On analysis of the composition of the separated film, the amount of silver was small in the pieces that do not show the sharp exothermic peak. On the other hand, the amount of titanium was large in the pieces that show the sharp exothermic peak. Based on the result, it is safe to say that Ag and Ti are required to initiate the sharp exothermic behavior. Furthermore, as a result of investigation on the effect of Ag ion on the thermal behavior of metal thin film – nitric acid system, heat generation of only Al – nitric acid system accelerated by existent of Ag ion. Consequently, the dissolution of Al is likely to accelerate unintentionally by the existence of Ag ion and Ti metal, and this unintended dissolution of Al causes the large amount of heat generation and gas production.

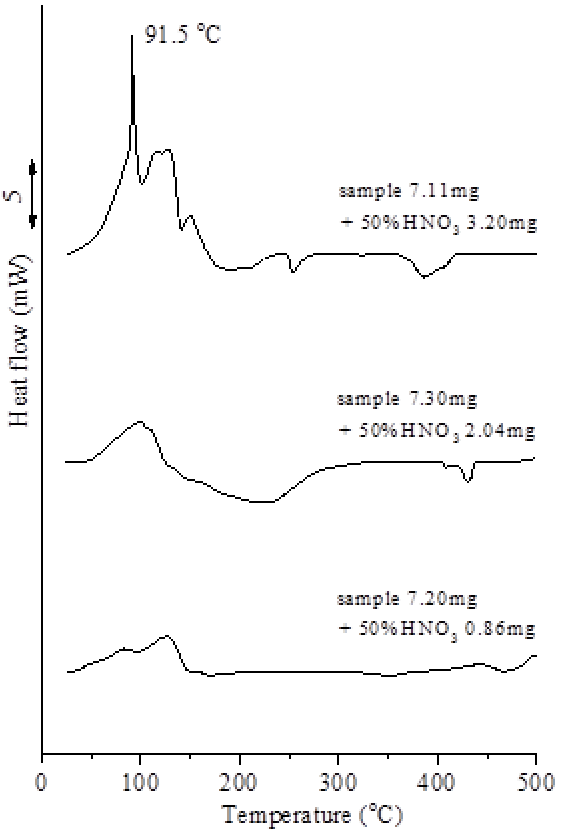

Fig.1 Thermal behaviour of the laminated film – nitric acid system measured using DSC.

The heat capacity and magnetic properties of $BaLa_2WO_7$ samples doped with samarium

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Samples with the general formula $Ba(La_{1-x}Sm_x)_2WO_7$, doped with samarium at 1 and 3 at.% (x= 0.01 or 0.03), were synthesized by high-temperature annealing up to 1200°C. The X-ray diffractograms of the samples were measured in the range of 2θ from 10° to 60° with a step of 0.02° on a Shimadzu XRD-6000 diffractometer (CuK_α radiation). According to the results of X-ray phase analysis no extraneous phases in appreciable amounts were detected. The crystal structure of the samples corresponds to the structure described in [1], and belongs to the monoclinic syngony with the space group $P112_1/b$.

The heat capacity of the samples was measured on a low-temperature adiabatic calorimeter [2] over the range from 4.5 to 320 K. In the temperature area below 20 K, the samples showed deviations from the normal course of the heat capacity curve, presumably due to the presence of a magnetic moment in samarium atoms. Anomalous components were identified by calculating the lattice heat capacity of compounds in the coordinates of $-\ln(C_p/T^3)$ vs. $-\ln(1-C_p/3Rn)$. The temperature maxima of the anomalies in both compounds were at 8.5 K, an excess contribution to the heat capacity up to 20–22 K was observed.

The magnetic properties of the samples were measured in two modes: Zero Field Cooling (ZFC) and Field Cooling (FC) on a Quantum Design installation over the temperature range from 4 to 400 K (ZFC) and from 400 to 2 K (FC) with an external field of 5000 Oe . As a result, we obtained the data on the magnetization and magnetic susceptibility of the compounds studied.

The visual appearance of the temperature dependences of the magnetic susceptibility χ of the samples is characteristic for the substances exhibiting ferromagnetic properties. The magnetic susceptibility curve measured in the FC mode runs higher than the curve obtained in the ZFC mode, which indicates the presence of ferromagnetic interaction between samarium atoms, manifested in a more precise orientation of their magnetic moments under the effect of an external field, what leads to increasing of magnetization.

A graphical analysis of the magnetic susceptibility curves makes it possible to determine the position of the Curie point at a temperature of about 25 K. The graphs of the inverse magnetic susceptibility $1/\chi$ show that the linear region in which the Curie-Weiss law holds is located at a temperature from 100 to 400 K. The approximation of this region by the straight line equation gives the Curie constant of 7.2 cm^3 • K/mol for these compounds.

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Texture properties and thermal stability of compounds formed in CaO-SiO_2-$Cu(NO_3)_2$/$Co(NO_3)_2$/$Cr(NO_3)_3$-H_2O system

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The rapid increase in industrial development resulted in emitting enormous amount of greenhouse gas and other pollutants [1]. In order to reduce the negative effect of mentioned gas on the environment, it is recommended to change manufacture process by avoiding pollutants and to use innovative recuperative waste removal technologies [2]. It is known that one of the most commonly used methods is the conversion of greenhouse gas (N_2O, CH_4, CO) to non-hazardous gas. By seeking this goal, the industry use large amounts of precious metal catalysts (Pt, Au, Pd), which are very expensive and their application are limited by low thermal resistance [3]. For this reasons, scientists and industry are looking for cheaper and more resistance catalysts, such as metal oxides (CuO, Co_3O_4 and others) [4].

Thus, this work aims to investigating the texture properties and thermal stability of compounds synthesized in CaO-SiO_2-$Cu(NO_3)_2$/$Co(NO_3)_2$/$Cr(NO_3)_3$-H_2O system under hydrothermal conditions.

Dry primary mixture with molar ratio of $CaO/SiO_2 = 1.5$ was mixed with $Cu(NO_3)_2$/$Co(NO_3)_2$/$Cr(NO_3)_3$ solutions ($c = 10$ g Me^{x+}/dm^3) to reach the solution/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis was carried out in unstirred suspensions at 175 °C temperature for 16 hours. It was determined that after hydrothermal synthesis all amount of metal ions (100 mg Me^{2+}/g) were intercalated to the structure of synthesis products. In situ X-ray diffraction study on the thermal stability of synthesized compounds was performed in a modular temperature chamber from RT to 1000 °C temperature. It was obtained, that the nature of metal ions changes both surfaces area and thermal stability of synthesis products. These results were confirmed by XRD, STA, FT-IR, SEM, TEM and BET analysis.

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The thermal stability of dibasic calcium silicates hydrates substituted with Cr^{3+} and Al^{3+} ions

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The growing generation of greenhouse gas and pollutants leads to huge environmental issues, like global warming, air pollution, water pollution, and climate change [1]. For this reasons, an intensive research and developments are carried out on the environmentally friendly and economically attractive synthesis technology of high selectivity and productivity adsorbents and catalysts [2]. It is known that lower basicity calcium silicates hydrates (gyrolite, xonotlite) have good adsorption properties for some metal ions [3]. Furthermore, these compounds with incorporated metal ions can be used for the production of environmentally friendly cementitious materials or utilized in ordinary Portland cement by improving its properties [4]. However, there is no data about the interoperation of chromium and aluminium ions, which can be used as catalyst, into the structure of dibasic calcium silicates hydrates.

Thus the aim of this work was to examine the thermal stability of dibasic calcium silicates hydrates substituted with Cr^{3+} and Al^{3+} ions, and their derivative physical and chemical properties.

Dry primary mixture with molar ratio of $CaO/SiO_2 = 1.5$ and $Al_2O_3/(Al_2O_3+SiO_2) = 0.05$ was mixed with $Cr(NO_3)_3$ solution ($c = 10$ g Cr^{3+}/dm^3) to reach the solution/solid ratio of the suspension equal to 10.0. The hydrothermal synthesis was carried out in unstirred suspensions, under saturated steam pressure at 200 °C temperature for 0-72 hours. The thermal stability and phase transformation of synthetic products were investigated by simultaneous thermal (Linseis PT1000) and in-situ XRD (with a high-temperature camera MTC-hightemp) analysis. The obtained results were confirmed by XRD, FT-IR and SEM analysis.

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Sol-gel synthesis and thermoanalytical study of $xBi_2O_3{\cdot}V_2O_5$ ceramics

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The different bismuth vanadates are well-known more than several decades and they exhibit a variety of interesting physical and chemical properties. Nowadays a great attention has been devoted to the study of the Bi–V–O system in view of its potential applications in many scientific and technological fields [1]. Such properties as pyroelectrics, ferroelectrics, water splitting ability, extensive stability against photocorrosion, benign to environment and less expensive are highly desirable and wide applicable [2]. Unfortunately, in the Bi–V–O system, different crystalline phases exist, depending on both the synthesis conditions and the molar ratio of Bi : V. This is the reason why various techniques have been applied that include precipitation, co-precipitation, sol-gel, polymeric precursor, oxidant peroxide, hydrolysis, hydrothermal and ultra-sonication methods. These synthesis methods are essential in their own prospective; variety of properties can be attained by shifting from one method to another and/or by changing the reaction parameters [3].

In this work, we have synthesized different double oxides depending from the initial composition of $7Bi_2O_3{\cdot}V_2O_5$, $5Bi_2O_3{\cdot}V_2O_5$, $3Bi_2O_3{\cdot}V_2O_5$, $Bi_2O_3{\cdot}V_2O_5$ by an aqueous sol-gel synthesis method. This study of obtained ceramics has been provided to see the effect of initial composition and applied synthesis technique on their size, shape and morphology. Beside this, we also described in detail the thermoanalytical behaviour of as prepared Bi–V–O gel precursor, which is the critical stage during the formation of final compounds. In addition, the conductivity of prepared ceramic for $5Bi_2O_3{\cdot}V_2O_5$ initial composition using broadband impedance spectroscopy was also performed.

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Aqueous sol-gel synthesis, structural and thermoanalytical study of a lithium lanthanum titanate ($Li_{3x}La_{2/3-x}TiO_3$, LLTO) solid electrolyte

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Lithium ion batteries have been widely used in portable electronic devices, electric vehicles, and emergency power systems because of their high energy density, high power density and long cycle life. Among oxide electrolytes, perovskite-type $Li_{3x}La_{2/3-x}TiO_3$ (LLTO) is a promising candidate due to its high ionic conductivity at various temperature [1]. In this case, sol-gel synthesis method opens a variety of possibilities for the preparation of such kind solid oxide electrolyte as lithium lanthanum titanate, with interesting morphological features and proper electrical properties. Moreover, according to the fact that this Li–La–Ti–O system has lots of different crystal phases depending from the molar ratio of corresponding metals, the right choice of synthesis technique usually determines the quality of the obtained ceramic. In this study, we propose aqueous tartaric acid-assisted sol-gel synthesis technique for the preparation of lithium lanthanum titanate ceramics with initial compositions $Li_{0.35}La_{0.55}TiO_3$, $Li_{0.4}La_{0.55}TiO_3$, $Li_{0.45}La_{0.55}TiO_3$ and $Li_{0.5}La_{0.55}TiO_3$. Additional, in this case the starting materials were chosen from the inorganic salts, otherwise than usually published reports in scientific journals. This gives strong additional novelty to this study. Besides this, the detail thermoanalytical investigation of Li–La–Ti–O tartrate gel precursors adds to this work significant remarks, and reveals the origin of the formation mechanism for final ceramics.

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The effect of mayenite structure properties on Cu^{2+}ion adsorption

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Mayenite ($Ca_{12}Al_{14}O_{33}$, C/A=1.7), have stimulated research interest because will have a better accelerator - rapid hardening activity, oxygen mobility, ionic conductivity and adsorption properties than other calcium aluminates. Mayenite can be synthesized during a solid state reaction between $CaCO_3$ and Al_2O_3 mixed powder at very high temperatures such as 1300 – 1500 °C for over than 40 h [1-3].

In previous work [4] it was proved that synthetic calcium aluminium hydrates are stable till 225 °C and at higher temperature recrystallized to mayenite, whereas the basic diffraction maximum intensity of mayenite significantly increased during calcination in a 650–900 °C temperature range. This fact confirms that the mayenite structure partially changes during calcination process. For this reason, the main objective of the present work was to determine effect of the calcination temperature on the mayenite structure as well as on Cu^{2+} ions adsorption capacity.

The synthesis of compounds has been carried out in unstirred suspensions (CaO/Al_2O_3 = 2.8, w/s = 10) within 4 hours at 130 ºC. The synthesis product were calcined in different temperature (1 h): CA1 - (350 °C temperature), CA2 - (550 °C temperature), CA3 - (900 °C temperature) and was used as the adsorbent to removal of Cu^{2+} ions from aqueous solutions. It was determined that a stable monolayer of absorbed N_2 was formed on the surface of samples. Straight lines were obtained for all samples in BET coordination ($0.05 \leq p/p_0 \leq 0.30$) and correlation coefficients R^2 remains very close to the unit, i.e. 0.999. It was found that calcination temperature has influence on products structure and specific surface area. It was found that specific surface area (S_{BET}) value after calcination 350 °C and 900 °C temperature have increased about 2 times: from 10.44 m^2/g to 19.46 m^2/g, respectively. It was determined that the largest amount of Cu^{2+} ions was adsorbet when using mayenite calcined at 900 °C temperature. The previous results were confirmed by XRD, STA, and FT-IR analysis.

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Synthesis, structural and thermoanalytical study of $Ca_{1-x}Sr_xMoO_4$ ceramic

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In the past decades, metal molybdates with scheelite type structure attracted many scientists attention due to their unique structural, electronic and catalytic properties. These properties could be modified incorporating other ions to produce binary solid solutions with better characteristic than individual compounds [1]. There are many different techniques to produce alkaline earth metal molybdates. Solid-state reaction, co-precipitation and Czochralski methods have some disadvantages such as harsh reaction conditions, high-temperature treatment, long diffusion paths and impurities. These drawbacks usually cause a low homogeneity of the final product because of the MoO_3 that has a tendency to evaporate at high temperature. In order to solve such kind of disadvantages during both the synthesis processing and quality of the final ceramics the aqueous sol-gel synthesis technique could be successfully applied. Besides, such kind of synthesis route offers the possibility to precisely control the final composition of obtained ceramics and produce materials with uniform dense structure. In addition, this synthesis technique also allows to ensure better homogeneity in the mixing at molecular level, which is the critical stage that strongly affects the properties of obtained crystalline compounds [2]. This is the main reason why in this paper we report environmentally friendly aqueous sol-gel synthesis method in order to produce nano-sized binary oxides with general formula of $Ca_{1-x}Sr_xMoO_4$. From the review of several articles there was found that interaction energy between powders and organic compound rises with increasing complexing agent functional groups. Such conclusion means that tartaric acid has more functional groups than, for example, either oxalic or acetic acids and it might exhibit better performance during the building of the chelate complex [3]. Thus, in this study all prepared Ca–Sr–Mo–O tartrate gel precursors were investigated by the thermogravimetry and differential scanning calorimetry (TG–DSC) to determine both the possible thermal decomposition of volatile compounds and the mechanism of the crystallization for $Ca_{1-x}Sr_xMoO_4$ ceramics. In order to complement the results obtained from the thermal analysis, the Ca–Sr–Mo–O tartrate gel precursors were additionally heat-treated at different temperatures and the final multicomponent metal oxides were investigated by X-Ray diffraction (XRD), Raman spectroscopy (RS) and scanning electron microscopy (SEM) techniques.

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Aqueous sol-gel synthesis and thermoanalytical study of alkaline earth metals doped $La_2Mo_2O_9$ oxide-ion conductor

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Fuel cells convert chemical energy to electricity in a silent and environmentally friendly way. Solid-oxide fuel cells (SOFCs) have the highest energy conversation efficiency and excellent fuel flexibility because of their high operating temperature [1]. Nowadays, most widely used materials for SOFC electrolyte are yttria-stabilized zirconia (YSZ) and gadolinium-doped ceria (GDC). However, these materials require high-operating temperature (1273 K) to obtain high oxide-ion conductivity. This condition could cause problems such as seal at high temperature, interface reaction between components, the sintering of the electrodes and more [2]. In 2000, Lacorre et al. discovered a new family of oxide ion conductors with parent compound $La_2Mo_2O_9$ [3]. At room temperature lanthanum molybdate exists in low-symmetry monoclinic α-phase, which, above 813 K of temperature, turns into cubic β-phase and this transition effect increases an oxygen-ion conductivity almost by two orders of magnitude. In order to stabilize β-phase of the lanthanum molybdate at room temperature, K^+, Sr^{2+}, Ba^{2+},Ca^{2+}, Bi^{3+}, V^{5+}, S^{6+}, Cr^{6+}, W^{6+} and other ions can be used as additives to suppress the reversible phase transition into the monoclinic structure. Moreover, the replacement of La^{3+} ion by divalent cation increases the amount of oxygen vacancies, such substitution effect slightly increases the ionic conductivity. This thin line between the properties of synthesized ceramic and dopant concentration determines its potential application. From this point of view, the choice of synthesis method plays an important role that enables the preparation of homogeneous product with well-expressed composition, structure and desired properties. An aqueous sol-gel synthesis technique has many advantages in case of above-mentioned tasks and it can be successfully exploited for the preparation of $La_2Mo_2O_9$ compound. Moreover, the use of the tartaric acid as a ligand in the sol-gel process gives this study and additional novelty, because similar investigations in scientific press are not published yet. In this report we applied an aqueous sol-gel synthesis technique to produce ceramic with initial composition of $La_{2-x}M_xMo_2O_{9-\delta}$ (M=Ca^{2+}, Sr^{2+}, Ba^{2+}). There is well known that the decomposition of as-prepared gel precursors plays a crucial role in frame of the formation for final ceramic, thus the thermoanalytical study of these metal tartrates was performed. The phase transition behaviour of the final ceramic by differential scanning calorimetry (DSC) was also investigated. The characterization of $La_2Mo_2O_9$ doped by alkaline earth metal was performed using X-Ray diffraction (XRD) and scanning electron microscopy (SEM).

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PS2.011

Porous montmorillonite heterostructure: synthesis, structural and thermal characterization

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Organically modified montmorillonites (OMMT) has found wide applications as absorbents of organic pollutants (1), fillers in polymer nanocomposites (2) and etc. The properties and application of OMMT mostly depend on the type of modifier (quaternary or primary alkyl ammonium ions, neutral amines, phenyl groups) and arrangement of organic cations in the interlayer space of OMMT. Furthermore, the length and the concentration of alkyl chains, the nature of intercalated modifier and the cation exchange capacity (CEC) of montmorillonite (MMT) are the main factors controlling the basal spacing of OMMT [3]. The specific application field of OMMT is their use as precursors for the synthesis of porous clay heterostructures (PCH). In these materials the orderly mesoporous network is formed during ionic surfactants interaction with inorganic ions and after calcination step the high specific surface area of PCH is generated [4]. Such a type of structure is beneficial for catalytic application.

The aim of this research was to evaluate the role and concentration ratios of each compound in the synthesis of OMMT and PCH as well as to obtain conditions for the formation of catalytically applicable compositions of PCH. To realise these objectives the series of OMMT compositions were synthesised using MMT with a CEC of 105 meq/100 g and different amount of quaternary ammonium salt – Noramium MB2HT.

The variation of the basal spacing (d_{001}) of OMMT depending on the concentration of modifier was investigated by X-ray diffraction technique (XRD). The XRD analysis revealed that at surfactant:clay (w/w) ratio of 1:1 the d_{001} of OMMT increased from the initial 1.23 nm to 3.91 nm after modification for 0.5 h at 60 °C. The OMMT composition with largest basal spacing (d_{001}=3.91 nm) was chosen for further synthesis of PCH.

The amount of modifier intercalated into the interlayer space of the OMMT and the calcination temperature of PCH were determined by TG/DSC. According to TG/DSC analysis the paraffin-type arrangement of alkyl chains originates when amount of modifier in the OMMT composition reaches 45 %. The calcination temperature of PCH formation should be held to about 650 ^{o}C. According to N_2 adsorption/desorption results specific surface area S_{BET} of synthesized PCH was 900 m^2/g. The PCH material of such a high specific surface area could be used as catalytic support for other catalytically active phases.

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Accelerated carbonation of C_2SH based dense concrete

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Carbonation of cementitious materials is a natural phenomenon that is caused by carbon dioxide in the atmosphere. About 19 % of the CO_2 produced during manufacture of cement is reabsorbed by the concrete over lifecycle [1]. The carbonation reaction of calcium silicates in the air is generally a slow process that is dependent on the relative humidity of the environment, temperature, permeability of the concrete, and concentration of CO_2 available [2]. For this reason an accelerated carbonation very often is used.

The objective of this work was to create an environmentally friendly technology for obtaining calcite based products which will combine hydrothermal synthesis of calcium silicate hydrate $Ca_2(HSiO_4)(OH)$ (α-C_2SH) and accelerated carbonation process. The mechanical properties of the formed concrete and the mineralogical composition dependency on the curing conditions were determinate too. Hydrothermal synthesis was carried out at 200 °C for 16 h from burned limestone and opoka (silica–calcite sedimentary rock) mixture with molar ratio $CaO/SiO_2 = 2.0$. The main product of the synthesis was α-C_2SH with small amount of quartz and portlandite. The thermal activation was carried out at 450 °C and 800 °C for 1 h. The concrete samples were pressed in a hydraulic press to form 36 × 36 mm cylinders. The carbonation process was carried out at different conditions changing the CO_2 (99.9 % concentration) pressure from 0.5 to 2.5 MPa, duration from 4 to 24 h, temperature from 25 to 55 °C, as well as different sample preparation: compaction from 5 to 17.5 MPa, water to binder (w/c) ratio from 0.15 to 0.4 and binder/sand ratio from 1:1 to 1:3. Products were analysed by DSC, TG, XRD and SEM analysis.

It was determined that all of the studied parameters have an optimal value, at which the highest compressive strength can be reached. Thus, the highest compressive strength of the concrete samples was reached after carbonation at 15 bar for 24 h at 45 °C, with 12.5 MPa compaction, w/c = 0.25 and α-C_2SH to sand ratio of 1:3. At these conditions the compressive strength value exceeds 25 MPa. The conducted DSC, TG and XRD analysis confirmed that the main component after the carbonation is calcium carbonate, mainly in a form of calcite that is directly related to compressive strength development. It was shown for the first time that not only calcium silicates, but also their hydrated forms, e.g. α-C_2SH as a binder material is suitable for carbonation curing and could be used to produce carbonated construction materials. It is very attractive from economic point of view – avoids the high energy consumption that the calcination process requires.

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Influence of buckwheat hulls on the sintering of porous ceramics

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In Lithuania, the most widespread quaternary clay deposits are predominantly illite with limited quantity of montmorillonite and kaolinite. They contain little Al_2O_3 (~15 %), a lot of CaO (~10 %) and belong to fusible clays group, have a refractoriness of 1170–1250 °C, a sintering temperature of 1130–1150 °C, and a sintering interval of only 30–50 °C [1], making it difficult to produce high-value sintered ceramics. These clays are mainly used in the production of porous ceramic blocks. More and more sawdust is used in other areas, so manufacturers have to look for new unconventional burning additives. New raw materials usually change the course of ceramic body formation reactions.

The objective of this work was to investigate the influence of buckwheat hulls on the thermochemical processes during firing and to determine the main properties of the obtained porous ceramics. Taurage deposit (Lithuania) clay was mixed with 0–10 wt% buckwheat hulls or their ash (JSC EKOFRISA). Plastically formed samples were dried at 105 ±1 °C and fired in the 900–1075 °C temperature range. The mechanical properties of the ceramic body and the mineralogical composition dependency on sintering temperature were determinate. Materials and products were analysed by DSC, TG, dilatometry, XRD and SEM analysis.

According to the DSC data (exothermal effect at 300–500 °C), a higher amount of heat is released during the firing of clay with buckwheat hulls than in the case of clay with sawdust. As a result, a ceramic body begins to form sooner. In samples with these additives, new crystalline compounds start to form at ~60 °C lower temperature than in pure clay. Dilatometry data show that a thermal expansion in the temperature range of 200–700 °C is more pronounced in the clay with buckwheat hulls. This enlargement results from the emission of gaseous dissociation products which is due to oxidation of organic additives. In the dilatometric curves of the samples containing buckwheat hulls the initial progressive shrinkage, indicating the appearance of the vitreous phase, was noted at a temperature 725–735 °C, e.g. ~100 °C lower than in clay (~830 °C). It is likely that this additive accelerates the breakdown of the clay minerals structures. As a result, the fluxing elements (Na_2O, K_2O and Fe_2O_3), which most affect the formation of the vitreous phase, are released.

Buckwheat hull have been found to reduce the plasticity of the clay-forming mass as well as the drying/firing shrinkage of the samples. The compressive strength of the ceramics depends heavily on the quantity of buckwheat hull additive, its fineness and firing temperature and is ~10 % higher than of the samples without additives. Mineralogical composition studies have shown that the following crystalline compounds prevail in the ceramic body: quartz, hematite, anorthite and augite.

The results showed that the buckwheat hulls could be used in the production of porous ceramic blocks in the range up to 10 wt%, as a partial replacement for natural clay material.

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Synthesis, Characterization and Thermal Studies of new Zn(II) monomer based on 4,4´-diaminodiphenylmethane

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The understanding of driving forces for self-assembly in the solid state has emerged as an attractive approach to the fabrication of new materials, and considerable effort has been made towards the supramolecular networks assembled by covalent and hydrogen bond [1]. The assembly of these complexes strongly depends on the selection of both the metallic centers and the ligands. Compared to 4,4´-bpy, the advantage of 4,4´-diaminodiphenylmethane (dadpm) molecule as a bidentate-bridging ligand is the possibility to form the hydrogen bonds via terminal amino-groups, that is why it is selected as a good candidate for ligand in supramolecular architecture [2]. Herein we report the synthesis and characterization of the $[Zn(dadpm)_4(H_2O)_2](NO_3)_2\ (H_2O)_2$ (**1**) mononuclear complex. Compound **1** was obtained as a result of the reaction between $Zn(NO_3)_2{\cdot}2H_2O$ and dadpm in CH_3OH solvent and has been characterized by IR spectroscopy, single crystal X-ray diffraction and thermal analysis. In the IR spectrum of **1** the ν_{as}(NH) and ν_s(NH) bands and δ(NH) deformation vibrations of dadpm molecule are observed at 3399, 3326 cm^{-1} and 1610 cm^{-1}. The $\nu(CH_2)$ vibration bands are observed at 2857, 2805 cm^{-1}. Compound **1** crystallizes in triclinic *P*-1 space group and represents mononuclear Zn(II) complex where dadpm works as a monodentate ligand (Fig. 1). The Zn atom is coordinated by N atoms from four dadpm ligands and O atoms from two water molecules, forming a distorted octahedral coordination of ZnN_4O_2.

Thermal analysis curves of the title compound are shown in figure 2. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses show that the thermal decomposition of **1** includes a few steps. The loss of uncoordinated and coordinated water molecules was observed as a well resolved process completed at 203 °C, and accompanied by two weak endothermal effects observed at 112 °C and 148 °C in DTA. Subsequent heating leads to the thermal degradation of the ligand. The remains residues correspond to ZnO with no change to 1000 °C.

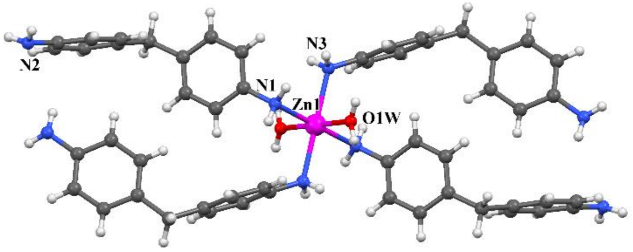

Figure 1. View of the Zn(II) environment

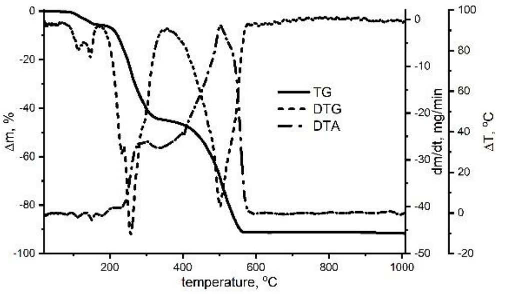

Figure 2. TG/DTG/DTA plots of **1**

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Thermal analysis study of trinuclear homo- and heteroatomic iron clusters

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Trinuclear μ_3-oxo clusters have been widely studied in the last decades due to their structural particularities and their large spectrum of properties [1]. An important role in the application of this class of compounds plays the possibility of synthesis of iron oxide and mixed iron oxides nanoparticles [2-3].

In this study we report the study of two trinuclear iron based clusters with the composition $[Fe_3O(C_4H_3OCOO)_6(CH_3OH)_3]\cdot NO_3\cdot 2CH_3OH$ (**1**) [4] and
$[Fe_2CrO(C_4H_3OCOO)_6(CH_3OH)_3]\cdot NO_3\cdot H_2O$ (**2**) by the thermogravimetric method.

The thermal analysis study (Figure 1) shows that the decomposition of complexes occurs in several steps with the formation of corresponding iron oxides $Fe_3O_{4.5}$ and $Fe_2CrO_{4.5}$.

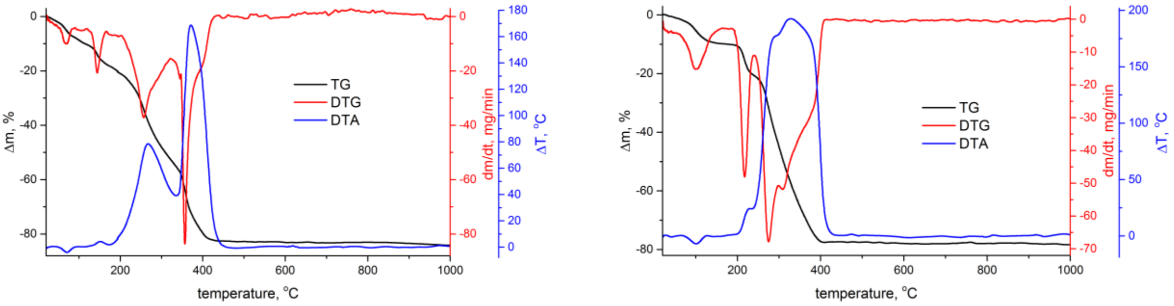

Figure 1: Thermoanalytic curves for $[Fe_3O(C_4H_3OCOO)_6(CH_3OH)_3]\cdot NO_3$ (left) and $[Fe_2CrO(C_4H_3OCOO)_6(CH_3OH)_3]\cdot NO_3\cdot H_2O$ (right) measured at air in the 20 – 1000 °C temperature range at a 10 °C/min speed.

Both compounds are stable only up to 50 °C after what begins the decomposition process through the elimination of solvent molecules (water and methanol) in the temperature range 50 – 160 °C. At higher temperatures occurs the furoate ligand decomposition up to 400 °C. The final products are obtained at 400 °C as iron oxide $Fe_3O_{4.5}$ for **1** and mixed iron chromium oxide $Fe_2CrO_{4.5}$ in the case of **2**.

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The action of Fe_2O_3, Fe_2ZnO_4 and Fe_2CuO_4 nanoparticles on micromycetes

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The development and investigation of metal oxide nanoparticles has attracted a lot of attention due to their useful applications in catalysis, energy storage, magnetic data storage, sensors, and ferrofluids [1].

Recently it was reported the possibility to obtain iron oxide nanoparticles from μ_3-oxo trinuclear clusters as precursors [2]. The TG analysis data have shown that the mixed iron oxides are obtained through thermal decomposition processes at temperatures above 500 ºC.

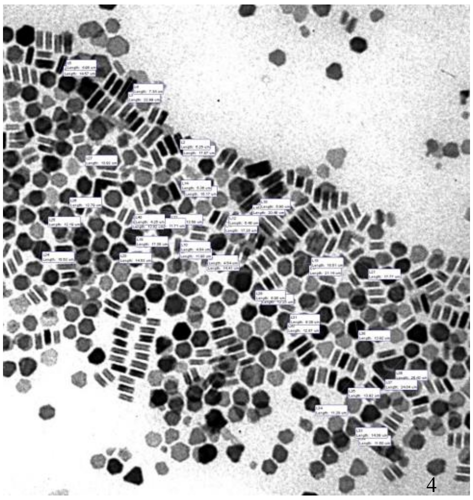

Fig. 1 TEM image of Fe_2ZnO nanoparticles

In this work we report the study of the influence of Fe_2O_3, Fe_2ZnO_4 and Fe_2CuO_4 nanoparticles on the morphocultural and biosynthetic properties of micromycetes. The following phytopathogens were taken as test cultures for the performed experiments: *Aspergillus niger, Alternaria alternata, Borytis cinerea, Fusarium solani, Fusarium oxysporum*.

At the cultivation of these submersed strains, in the Czapek medium supplemented with Fe_2O_3, Fe_2ZnO_4 and Fe_2CuO_4 nanoparticles, the accumulated biomass increased more significantly in the Fe_2O_3 and Fe_2ZnO_4 cases. In the presence of Fe_2CuO_4 nanoparticles, biomass stimulation was recorded in only 2 of the 5 studied *Aspergillus* strains, and in 3 strains a decrease in biomass accumulation ranging from 7-15% compared to the control was observed. Nanoparticles of Fe_2O_3, Fe_2ZnO_4, and Fe_2CuO_4 have been more beneficial for the growth and accumulation of biomass of strains belonging to the *Penicillium* genus.

Treating phytopathogens with the obtained metabolites of the *Trichoderma* strains has demonstrated antifungal activity stimulation. The most significant stimulation of antifungal activity was in the case of Fe_2ZnO_4 nanoparticles.

Thus, we can conclude that nanoparticles of Fe_2O_3, Fe_2CuO_4 and Fe_2ZnO_4 can alter the morphocultural and biosynthetic properties of micromycetes.

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Thermal analysis of Cd(II) coordination polymers assembled from bridging sulfate anions and N,N'-donor Schiff base ligands

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Coordination polymers are a promising class of materials. Sulfate anions with rigid tetrahedral geometry are widely employed to prepare extended network structures. The variety and diversity exhibited by this class of compounds has been reviewed by Rao et al. [1]. To increase and adjust the metal-metal distances, we used the bridging Schiff base ligands of the N,N-donor type, *1,2-bis(pyridin-4-ylethylidene)hydrazine)* (4-bpmhz) and *1,2-bis(pyridin-3-ylethylidene)hydra- zine)* (3-bpmhz). Following the reaction between the $CdSO_4 \cdot 8/3H_2O$ salt and the mentioned lingands, two coordination polymers were obtained, 2D coordination network $[\{Cd(4\text{-}bpmhz)(SO_4)(H_2O)\} \cdot 0.5H_2O]_n$ (**1**) and the 3D coordination grid, $[Cd(3\text{-}bpmhz)(SO_4)(H_2O)]_n$ **(2)** whose crystal structures were confirmed by single-crystal X-ray diffraction analysis.

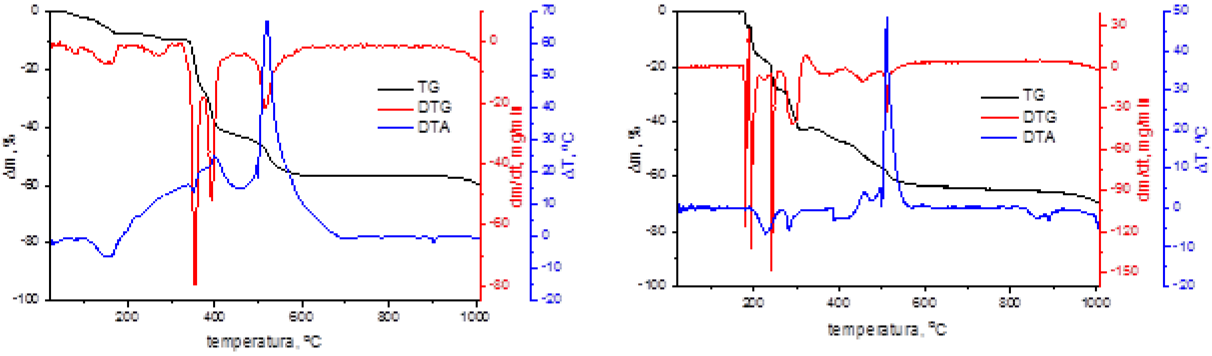

Figure Thermal analysis curves of compound **1** (left) and **2** (right) under a flow of air with the heating rate of 10 °C min^{-1}

The thermal decomposition of compounds begins with the loss of crystallization and coordination water molecules (Figure). For compound **1**, crystallization water molecules are eliminated in the temperature range 55-95 °C, 2 %, (1.9 % calcd.), then removing a coordinated water molecules, 100-160 °C, 4.2 %, (3.8 % calcd.). The slow oxidative decomposition of the 4-bpmhz ligand starts at ~ 250 °C but a significant loss of mass is recorded in the range of 340-620 °C, 50 %, (50.3 % calcd.). The constant mass remaining stable up to 920 °C is assigned to cadmium sulfate, 43.5 %, (44 % calcd.). Compound 2 is thermally stable up 174 °C, then the removal of water molecules takes place, 175-184 °C, 5 %, (3.9 % calcd.). 3-bpmhz ligand decomposition takes place in the range 190-496 °C, 51.5 %, (51.2 % calcd.). The remaining cadmium sulphate, 43.4 %, (44.8 % calcd.) is stable up to ~ 1000 °C, then begins to decompose.

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Thermal behaviour of ozone treated activated carbons

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Currently is a tendency to obtain activated carbons (ACs) from cheap and renewable raw materials by methods requiring low energy consumption. A perspective research line in this context is the use of microwaves in the process of ACs preparation. The employment of microwaves is finding a widening application in various fields because of the many advantages of microwave heating in comparison with traditional methods, such as fast heating, lack of inertia in heat transfer and activation time reduction, which in turn lead to diminished consumption of energy and activation agents. The oxidation of ACs aims at the formation of various functional groups on their surface for a stronger interaction with nanoparticles or biological active compounds. Acid and base functional groups are also formed during the production of ACs, depending on the activation methods employed. However, the amount of these groups is very small, mainly because of their instability at the elevated temperatures at which the activation process takes place. The advantages provided by gaseous ozone oxidation cannot be achieved by using other oxidizing agents: the process takes place at room temperature, the structure of the activated carbon is not contaminated with heteroatoms as a result of oxidation, functional groups of a certain type are formed and the surface of the AC is sterilized during the process. These features make it possible to obtain ACs suitable for use in medicine.

ACs from walnut shells were obtained by microwave treatment. To increase the functionality of the adsorbent, the ACs were oxidized with ozone, resulting in an adsorbent containing aliphatic and aromatic carboxylic groups. There was a considerable decrease in the specific surface of the activated carbon after the oxidation process. Nitrogen adsorption was used to determine the structural parameters of the ACs. A simultaneous thermal analysis was used to study the thermal behaviour of intact and oxidized activated carbons.

In order to estimate the thermal stability of the oxidation-based functional groups and to observe the reversibility of the chemosorption process, a thermal analysis of the intact and oxidized samples was performed. The correlation of the results obtained from the thermal analysis and nitrogen adsorption indicated that the ozonization process led to the formation of functional groups of predominantly acidic nature on the surface of activated carbon; the oxidation took place homogeneously throughout the surface, leading to the blocking of pores and a considerable reduction of the specific surface; ozone chemosorption was partially reversible after desorption at elevated temperatures leading to incomplete restoration of the specific surface, while the morphological structure of the adsorbent underwent insignificant changes.

Hydrophilization of the pyrolysis residue of tires to obtain water-miscible pigments

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Pyrolysis is a widespread recycling technology of polymeric waste. Used tires being pyrolysis lead to the formation of three components: fuel fraction which being subjected to purification to yield gasoline and diesel fuel, steel wire which is recycled and carbon black that is accumulated contaminating the environment. This is explained by the specific properties of carbon black: small, hydrophobic particles that easily disperse and pollute the environment, is a possible carcinogen for humans, and short-term exposure to high concentrations can cause discomfort in the upper respiratory tract. At the same time, the carbon black obtained from tire pyrolysis contains a significant amount of fuel and is not miscible in polar solvents such as water. This makes the field of use of carbon black is narrow - is needed remove adsorbed fuel from particles and render them hydrophilic properties, thus obtaining a black pigment, the fields of use of which substantially increase: pigment for the production of pavement, decorative mortar, lacquers and paints, supplement for construction and repair of road.

Studied tire pyrolysis residue is a homogeneous, finely dispersed, water-immiscible black substance. In order to assess the thermal stability of the residue, thermal analysis was performed in a dynamic air atmosphere. The results of thermal analysis show that the residue is stable up to 320 °C and total thermal degradation takes place at 750 °C, the carbon black begins to lose weight as soon as heating begins, the process continuing at temperatures above 300 °C; this is explained by the increased content of volatile substances that have not been completely discharged during pyrolysis. From thermal analysis was established that the carbon black contains 15% flammable volatile substances, oxygen oxidation of the surface in the air begins at 320 °C and total degradation takes place at temperatures above 430 °C. As a result of thermal degradation of soot no solid residue is formed. Based on the results of the thermal analysis, preventive degassing of the soot at 200-250 °C is recommended for evacuate volatile substances to prevent their accumulation and explosion. Oxidation with air is recommended to be carried out at 350-400 °C by continuous mixing to obtain a homogeneous product.

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Physical-chemical and biological properties survey for Cu(II) complexes with nitrogen-donor heterocyclic ligands

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The Cu(II) complexes with nitrogen-donor heterocyclic ligands are intensively studied concerning their biological activity such as antimicrobial, anti–inflammatory and anticancer ones [1]. Some species display an interesting thermal behaviour as well [2, 3].

In order to combine the redox ability of Cu(II) with stability induced by chelate ligands a series of Cu(II) complexes with formula $[M(N\text{-}N)_2pmtp](ClO_4)_2$ (pmtp: 5-phenyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine; N-N: 2,2`-bipyridine (**1**) or 1,10-phenanthroline (**2**)) were synthesized. Their mononuclear nature was proved by single crystal X-ray diffraction. The compound (**1**) crystallize in monoclinic system *P*a space group while compound (**2**) crystallize in triclinic system *P*-1 space group.

Thermal behavior of all complexes has been studied using TG/DSC–MS analysis in air. The TG curves show that complexes stepwise decompose in several stages, associated with perchlorate transformation, fragmentation and oxidative degradation of heterocyclic ligands. All these modifications end with black CuO stabilization.

The ability of the complexes to trap reactive oxygen species like O_2^- was tested by EPR spectroscopy in KO_2 presence. The rate constant of complex (**1**) could not be determined as result of fast decomposition while complex (**2**) showed a reaction constant of 0.018 s^{-1}.

Complex (**2**) exhibits a large spectrum of antimicrobial activity both on planktonic and biofilm embedded strains.

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Thermal analysis of new copper(II) dithiocarbomethoxyhydrazone complexes

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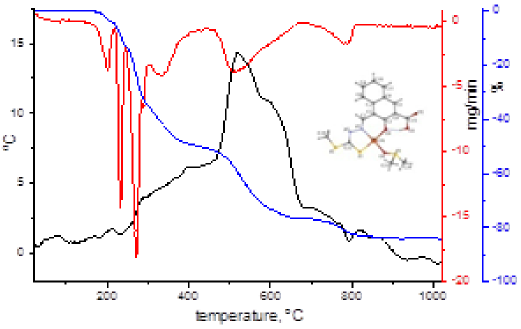
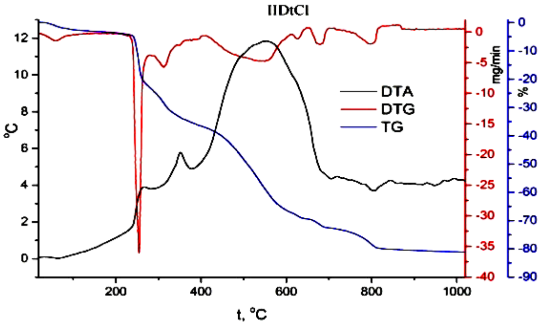
The methods of the thermal analysis are useful for studying physical and chemical properties of coordination compounds. In this work we are using thermal analysis data to describe the composition, thermal stability and the way of decomposition of a new series of copper(II) dithiocarbomethoxyhydrazone coordination compounds, namely $[Cu(H_2L)X]\cdot Solv$, where X=Cl, Solv=H_2O (**1**), dmso (**4**); X=Br, Solv= $0.5C_2H_5OH$ (**2**), dmso (**5**) and [Cu(HL)Solv] where Solv= H_2O (**3**), dmso (**6**), dmf (**7**), some of which were characterized structurally [1]. The combined thermal analysis (TG-DTG-DTA) of the compounds were performed in the temperature range 20-1000°C in air atmosphere with a heating rate of 10 °/min. The thermal decomposition takes place in several stages, for all compounds. In the temperature range of 20-250 °C, one (**1-5**) or some (**6, 7**) endothermic effects are observed, which, from the mass loss are attributed to the elimination of external or internal solvent molecules: H_2O -3.8% (**1**), 4.0% (**3**); $1/2C_2H_5OH$ - 4.7% (**2**); DMSO - 17.81% (**4**), 13.89% (**5**), 12.95% (**6**) and DMF - 13.84% (**7**). In the temperature range of 250-800 °C, a series of exothermic effects related to the gradual burning of hydrazone ligand follows.





The final decomposition temperature of the investigated compounds is: 840 (**1**), 780 (**2**), 810 (**3**), 780 (**4**), 790 (**5**), 780 (**6**), 778 °C(**7**). The TG, DTG decomposition profiles of the complex **7** and **6** (structurally characterized) are similar and show quite high temperature of decomposition beginning at 180-200°C (fig. 1a), corresponding to the elimination of *dmso* and *dmf* internal molecules, respectively, and suppose a similar structure for these compounds. Compared to those, **1-3** species of complexes, synthesized in alcohol medium, show very week endothermic effects in the region up to 50-70°C (fig.1b). Thermal analysis data for complexes **1-7** are in agreement with elemental and X ray data analysis and suggest the proposed composition.

Acknowledgments: Dr. O.Petuhov (Institute of Chemistry, R. Moldova) for thermal measurements.

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A novel cooper(II) 2D coordination polymer and its thermal decomposition

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Coordination polymers are multidimensional periodic structures of metal ions interconnected through organic ligands, which, through their specific structure and properties, have been of great interest to researchers in the fields of chemistry and technology sciences, as well as in other areas [1]. The two-dimensional polymer of Cu(II) of molecular formula $\{[NH_2(CH_3)_2]_2[Cu_3(HIDA)_4]\cdot H_2O\}_n$ was synthesized following the reaction of iminodiacetic acid (H_3IDA) and copper(II) acetate monohydrate in the presence of dianilineglyoxime ($DAnH_2$) in a molar ratio of 2: 1: 2 and methanol-DMF-water environment in a volumetric ratio 2: 1: 1. The coordination polymer compound has been studied by single crystal X-ray diffraction and combined thermogravimetric analysis (TG, DTG and DTA). The cation $[NH_2(CH_3)_2]^+$ were probably obtained from (H_3IDA), also dianilineglyoxime didn't coordinate to the metal, its role being just to create a suitable environment for the reaction to occur. The termogram was recorded in the range of 20-1000°C in air atmosphere, at a heating rate of 10°C/min. (Figure). From the thermogram can be noted that only several stages of decomposition have taken place, since the given polymer has a relatively simple chemical composition, consisting only of amino acid anions and dimethylammonium cations. From the first decomposition stage at 85°C, the loss of the water molecule from the external sphere is observed, the mass loss constituting approximately 4.87 %. In the range of 85-215°C, the IDA protonated molecules with gas release (CO_2, N_2O, etc.) and a mass loss of 30.38 %, are completely decomposed. At a higher temperature range of 215-590°C, breakage of the metal-ligand linkages occurs with the total decomposition of the 4 iminodiacetic acid molecules, the mass loss constituting 48.46 % of the total mass of the polymer. Following the whole thermal decomposition process, CuO residue with a mass fraction of 16.29 % is formed.

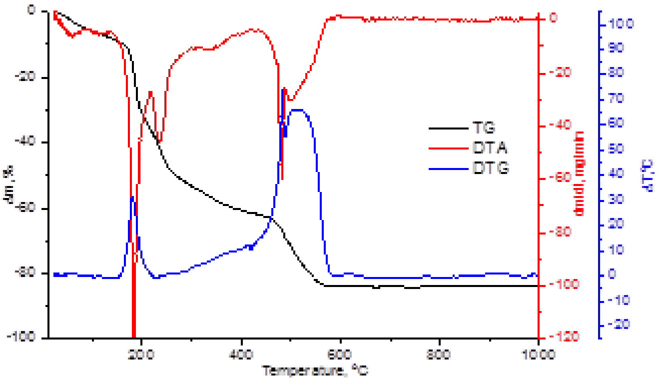

Figure. TG/DTG/DTA patterns of Cu(II) 2D polymer.

Figure. TG/DTG/DTA patterns of Cu(II) 2D polymer.

Acknowledgements: The author is grateful to Dr. Oleg Petuhov (Institute of Chemistry of Moldova) for thermal measurements.

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A novel Co(II) porous coordination layer: synthesis, structure and thermal analysis

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The design of porous coordination polymers (PCPs) that show selective adsorption or high adsorption capacity is an important topic in research on applicable porous materials. 2,2'-Dithiodibenzoic acid (H_2dtdb) is a multifunctional ligand containing two carboxylic groups and two thio donor atoms, which may coordinate to the metal ions by diverse modes, and allow of different coordination polymer topologies. The twisted binding site of the S–S bond makes the ligand flexible and in combination with 1,2-bipyridine ethane (bpe) spacer and Co(II) salt gave us the opportunity to obtain new PCP:–$\{[Co_4(Htb)_4(tb)_2(bpe)(H_2O)_2]\cdot 2(dmf)\cdot 9(H_2O)\}_n$ (**1**). Surprisingly, H_2dtdb was split into two molecules after cleavage of S–S bond forming the thiobenzoate ligand (tb^-).

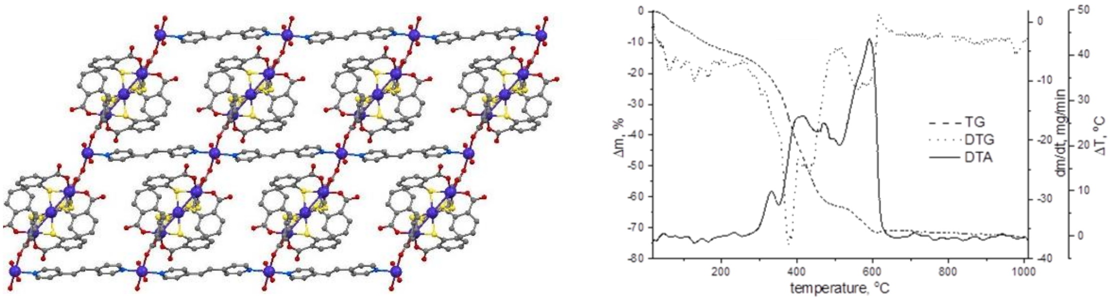

Figure 1. Fragment of 2D layer (a) and TG-DTA pattern of **1**(b)

The compound crystallizes in centrosymmetric triclinic space group *P*-1: *a*= 10.3970(4), *b*= 13.7039(5), *c*= 13.7672(7) Å, α= 66.058(4), β= 88.257(4), γ= 75.025(3)°, V=1725.71(13) Å^3. Compound **1** is a three-dimensional polymer that could be used to adsorb small molecules and also, shows a theoretical interest because it contains a high number of molecules of water and dmf, which can be removed by degassing and track the changes in porosity and structure. To determine the adsorption properties, it is necessary to know the temperature at which the structure of the compound remains unchanged and its thermal behavior. For this, the simultaneous thermal analysis was used, figure 1b. Received results gave us information about thermal stability and temperatures of reactions during the heating in the wide temperature ranges. Due to the high solvent content in the external sphere, compound **1** begins to lose weight once the heated is start. Up to 240 °C, the sample loses all water and dmf molecules. Using the obtained data, compound **1** was degassed at three different temperatures: 20, 120 and 150 °C, after which the adsorption isotherms of nitrogen were measured. The influence of degassing temperature on the adsorption properties will be presented and discussed.

Protective properties of Al_2O_3 scale growing on the FeCrAl alloy covered with a thin layer of Y_2O_3 during cyclic oxidation in the air

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On the FeCrAl alloy foil, single-layer Y_2O_3 coatings were deposited by the sol-gel method. Thin films were deposited from containing yttrium(III) acetate hydrate ($C_6H_9O_6Y{\cdot}x{\cdot}H_2O$) as a precursor to Y_2O_3. The molar ratio of the precursor:alcohol in the sol was: 1:50, 1:250 and 1:500. Samples with the obtained ceramic coatings were given cyclic oxidation in air at 900°C. Changes in the morphology and chemical composition of the FeCrAl alloy surface layer during cyclic oxidation were determined using: TGA/DSC, XRD, SEM-EDS, AFM and BET. It has been shown that the yttrium present in the coating changes the morphology, chemical composition and degree of surface area development (BET) of the scale. After 10 cycles of oxidation (each cycle lasted 24 hours), the thickness of the scale was from about 0.5 μm to 3.4 μm. It was shown that the deposited thin film Y_2O_3 on the FeCrAl alloy surface lowers the surface area of the scale (about 2-3 times), reduces the pore size in the Al_2O_3 layer (up to about 2-3 nm) and reduces the roughness of the scale (about 7.5 times smaller compared to the uncoated substrate). Gravimetric studies showed a parabolic law of the relationship between the mass increase of samples and the time of oxidation. The most favorable protective properties were the scale increased on the Y_2O_3 coated alloy, which was obtained from the sol with highest dilution (ratio of precursor:alcohol = 1:500). Its protective effectiveness against scales formed on uncoated substrate was 84%. Heat resistance of FeCrAl foil covered with this coating was more than 4.5 times higher than the uncoated alloy.

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Disorder in solid AgCl and AgBr

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Ionic transport properties in the silver halides have attracted special attention for a long time. There were two main questions concerning understanding of experimental results on these materials. The first one – what is the mechanism of ion transport in each of these compound, and the second one – how does the property of ion conducting relate to other physical properties. The motivation for the study of these compounds is their challenging physics and application potential in the areas of batteries, electrochemical sensors, fuel cells and electrochemical devices.

It was found that unusually high increase of ionic conductivity of AgCl and AgBr with temperature is the result of predominant Frenkel-defects formation[1-3]. Some Ag^+ ions leave their lattice sites and occupy interstitial sites in the interior of the crystal. Two disorder centers (vacancy and interstitial ion) are formed per misplaced lattice ion [1]. The experimental methods most commonly used for testing disorder models and for the quantitative determination of disorder data are conductivity, diffusion measurements and heat capacity measurements.

The only existing older numerical heat capacity data on AgCl and AgBr, which could be helpful in disordering interpretation, were Pankratz [4] experimental data and Kubaschewski [5] estimation. However, big discrepancies appear between these data. We have decided to carry out heat capacity measurements of AgCl and AgBr by means of Differential Scanning Calorimetry. Comparison of our results with literature data leads to the conclusion that both Kubashewski [5] and Pankratz [4] data are incorrect.

Correlation of precise heat capacity data with transport properties would be of considerable interest in respect of disorering of crystal lattice of the compounds under investigation. Therefore, we have decided to undertake the investigation of transport properties of AgCl and AgBr compounds. The present work reports the analysis of excess heat capacity of silver halides in terms of Frenkel defects formation as well as the electrical conductivity of silver chloride and bromide and its correlation with heat capacity.

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The work was financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wroclaw University of Technology.

Modification of blood serum DSC profiles by sauna treatments in cross country skiers during the exercise cycle

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Sauna is a physical treatment, originating from Scandinavian countries such as Finland, and now widely used throughout the world [1-2]. This treatment is used in sports medicine, recreation and rehabilitation, mainly for the regeneration of tired muscles, hygiene and cosmetology, cleansing the body of toxins or relaxation [1-3]. The aim of the conducted research was to compare changes in athlete's blood serum during two exercise sessions: before and after ten sauna treatments.

Serum samples were collected from the blood of 9 athletes (3 women and 6 men) well trained in cross-country skiing in four stages in both exercise sessions: at rest, after exercise and after 1h and 24h rest and additionally only at rest after the first sauna treatment. Differential scanning calorimetry (DSC) measurements of aqueous serum solutions were made in the temperature range 20 - 100 ^{0}C with a heating rate of 1 ^{0}C min^{-1} and a pressure of about 1.8 atm using the VP-DSC microcalorimeter (MicroCal Co, Northampton, MA).

The results obtained by DSC allowed to register characteristic post-exercise changes in thermal transitions of serum denaturation, similar in nature, regardless of the use of sauna treatments. Comparison of DSC curves of athletes' sera demonstrates a stronger reaction to the effort in the exercise session after the sauna treatments. It was revealed especially in the part of serum denaturation transition at higher temperature range. The post-exercise changes in the low-temperature transition region were similar. Another observation from our study was quite a significant variation in the recovery process after the exercise among the athletes.

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The influence of high-temperature treatment of granular activated carbon on its behaviour in direct carbon solid oxide fuel cell

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The comprehensive studies in regard to various types of direct carbon solid oxide fuel cells (DC-SOFCs) supplied with charcoals and pyrolysed in situ wood-chips were carried out. The tests performed with these fuel cells showed that charcoals are suitable and attractive fuels for the DC-SOFC providing sufficiently high power density. Their properties were very important. In such kind of experimental studies, the problem to obtain the set of activated carbons of strongly differentiated porous structure appears. This can be achieved in several ways. For example, during the production of activated carbon by changing activating agent or activation process conditions (temperature or time). However, heat treatment of activated carbon at high temperature provides the best results. Commercial granular activated carbon R_3-ex (Norit) was demineralized with conc. HF and HCl acids and then heated in an Ar atmosphere at various temperatures (1500, 1800°C). The maximum heat treatment temperature was the factor of differentiating the samples. The specific surface areas (S_{BET}) calculated on the basis of low temperature N_2 adsorption isotherms were 1390, 970, 550 m^2/g respectively for unmodified, and heated at 1500, 1800°C activated carbon. The Norit activated carbon samples were used as solid fuels in direct carbon fuels to determine the mechanism of electrochemical oxidation of carbon particles in SOFCs. The results obtained from electrochemical tests were compared with data obtained from DTA/DSC-TG analysis performed in the N_2 and CO_2 gas atmosphere in the temperature range of 25-850°C. It was found that the Boudouard reaction and electrochemical oxidation of CO had great impact on the DC-SOFC performance. The results were also compared with other types of charcoal derived from waste-biomass samples (pistachio shells), which were prepared by means of the thermal treatment in temperatures of 400, 600 and 850°C in ambient gas atmosphere for 1 hour. The tests demonstrated that DC-SOFCs supplied by chars derived from pistachio shells as well as the granular activated carbon had provided stable operation with reasonably satisfactory current and power density levels (70-120 mW/cm^2).

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Design of thermal and mechanical properties of materials for selective laser sintering technology based on results obtained via the DTA/DSC-TG method

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Additive manufacturing is the one of the most rapidly developing manufacturing technologies today, offering a wide range of possibilities for fast, cost-effective production of materials. The most commonly used technology in the AM area is selective laser sintering (SLS), enabling freedom of design and low-cost production of plastic parts.

Knowledge of the thermal properties of polymers is essential for the development of optimal parameters for the processing of materials into useful products using SLS technology and for predicting the performance of these products during their lifetimes. In order to produce good functional SLS parts, the powder on the part's bed surface must receive a sufficient amount of energy via the laser sintering process. Sufficient energy density is produced when the energy input increases and is applied to the bed surface, which increases the temperature, resulting in improved melt flow. An average of 80% of the powder in the build chamber is not sintered during the SLS process and may be re-used. However, the properties of sieved but non-sintered powder deteriorate due to exposure to various temperatures for extended periods of time during the three-stage SLS system material build process, which involves warm-up, build, and cool-down stages; this process may take up to 40–80 hours for big jobs.

The aim of this paper is to determine the impact of the thermal properties of selected polymers (PA 2200, iglide I3-PL, Vestosint 3D 6644) as well as of composite materials consisting of a polymer matrix (iglide I3-PL with additions of molybdenum disulphide

MoS2 + C, Innov'PA 2550 GBAL, and Sinterit Smooth, FlexaBlack and FlexaBright). All of these samples were investigated using the DTA/TG or DSC/TG method within the temperature range 25–200ºC. It was found that the addition of MoS2 caused a change in sintering temperature. To ensure flexibility in the application of such materials, 3D printers are constructed in various ways. The analysed results of DTA/TG or DSC/TG investigations were compared with the mechanical and geometrical properties of printed shapes. The correlation between the parameters of thermal properties of the starting powders used in 3D printing and the quality of the obtained products is analysed and discussed. The results can be used in practical applications to assist SLS users in improving the sintering process and obtaining surface-printed materials of higher quality.

Heat capacity studies of triblock semifluorinated alkanes

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A series of triblock semifluorinated alkanes of the general formula: $H(CH_2)_m(CF_2)_6(CH_2)_mH$, abbreviated as $H_mF_6H_m$, where m = 6, 12, 18, 20 and 30, have been synthesized in two steps, by radical addition of 1,6-diiodoperfluorohexane $I(CF_2)_6I$ to two equivalents of an appropriate terminal alkene $CH_2{=}CH(CH_2)_{m-2}H$, followed by subsequent deiodination [1,2].

Heat capacity measurements of the synthetized compounds were carried out in the temperature range of 1.8 K - 360 K, by means of the heat capacity (HC) option of the Quantum Design physical property measurement system (PPMS).

Temperatures of the observed individual phase transitions were derived and the corresponding entropic contributions were estimated. The obtained values were critically compared with those found earlier [2] by DSC method. The temperatures of transitions from crystal to smectic phases agree rather well in both methods. However, our present investigations show that below melting points, additional rather broad anomalies appear for all samples except for the longest molecule (H30F6H30). No phase transitions were detected in low temperature regions, between 1.8 and 230 K.

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Evaluation of osteoclastogenesis inhibition by binding sRANKL with fermented and unfermented chickpea sprouts extracts using isothermal titration calorimetry (ITC)

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Osteoporosis is a disease that affects people of all ages, it is characterized by a loss of bone mass, weakening of bone spatial structure, which can lead to bone fractures. The disturbed RANK, RANKL and OPG (osteoprotegerin) system is responsible for the disease [1]. OPG is a ligand binding to sRANKL that inhibits osteoclastogenesis, but its level may decrease in pathological conditions. The use of ligands binding to sRANKL instead of OPG increases the concentration of osteoprotenan inhibiting bone resorption [2,3].

The analysis was carried with chickpea (*Cicer arietinum*) sprouts extracts cultivated under different types of light. The sprouts were fermented by *Lactobacillus casei* 0979. The profile of isoflavones was analysed using LC-ESI-MS technique. The thermodynamic parameters of binding of sRANKL to isoflavones as standards or as a mixture in extracts was evaluated by isothermal titration calorimetry (ITC) and compared with docking simulation.

The study showed that fermentation with lactic acid bacteria increased the content of isoflavones in chickpea sprouts, especially after seeds cultivation under blue light for 10 days and 4 days fermentation, were the concentration of isoflavones amounted 3.81 g/100 g d.m. The high concentration of isoflavones methoxyl derivatives in extracts resulted in the high affinity to sRANKL. The highest affinity and stability of complexes with sRANKL showed extract of chickpea sprouts cultivated for 8 day under UVB light (ΔG= -15.78 kJ/mol; ΔH= -17.17 kJ/mol) and cultivated for 4 day under blue light (ΔG= -13.86 kJ/mol; ΔH= -21.61 kJ/mol), both fermented for 4 days. The isoflavones contained in chickpea can be potential ligands that can limit the binding of RANK to RANKL and osteoclast formation. The research was funded by National Center of Science (project No. UMO-2016/21/B/NZ9/00898).

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In vitro evaluation of the activity of grained extracts as inhibitors cholinesterases, reducing choline uptake

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Acetylcholinesterase (AChE) is the main enzyme that hydrolyses acetylcholine. This neurotransmitter is deficient in Alzheimer's disease (AD) starting from the early stages of the disease due to the deposition of α- and β-amyloid proteins and the development of senile plaques that limits transmission of nerve impulses. The use of AChE inhibitors may improve cognitive functions as well as reduce the symptoms of this disease [1-2].

Our previous studies have shown that coffee extracts and their various fractions are potential AChE inhibitors, prompting us to investigate how bioactive coffee extracts digested in the simulated gastrointestinal tract will interact with this enzyme [3]. The aim of the study was to assess the affinity for AChE coffee extracts after *in vitro* digestion and enzyme inhibition efficiency. The digestion of coffee extracts from roasted beans to various degreases (green, light and dark) was carried out in a simulated digestive system, reproducing physiological processes of the gastrointestinal tract introducing a mixture of selected probiotic bacteria. The evaluation of AChE inhibition was assessed for coffee extracts taken after digestion on each of the four sections of gastrointestinal tract, i.e. in the stomach, small and large intestine and colon, and performed using an isothermal titration calorimetry that allowed to determine the most effective coffee extract limiting the enzyme activity that protects acetylcholine from degradation.

Studies have shown that the highest bioavailability of compounds with high affinity to AChE was characterized by green coffee due to the high content of hydroxycinnamic acids and it was additionally increased in the presence of microbiota. The research was funded by National Center of Science (project No. UMO-2018/29/N/NZ9/01160).

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Thermal insulation properties of monolayered and DCL type of TBC systems based on rare La zirconates: numerical simulations and laser-flash analysis

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The insulation properties of different types of TBC (*thermal barrier coatings*) systems based on $ZrO_2 \times 8Y_2O_3$ and $La_2Zr_2O_7$ ceramic materials were analysed in this investigations. From the morphological point of view the analysed TBC systems can be classified as an monolayered systems of $ZrO_2 \times 8Y_2O_3$ and $La_2Zr_2O_7$ type and double ceramic layer (DCL) systems with outer $La_2Zr_2O_7$ sublayer and inner $ZrO_2 \times 8Y_2O_3$. In this type of coatings additionally the DCL system with additional composite $ZrO_2 \times 8Y_2O_3 + La_2Zr_2O_7$ sublayer was included. The thickness of all systems was in the range 250-350 µm. All analysed systems were deposited by atmospheric plasma spraying from commercial feedstock powders after spray drying process of manufacturing. The ceramic coatings were additionally sprayed on In 626 Ni-based superalloy with the bond coat of NiCrAlY type with the thickness 125 µm.

The basic goals of investigations was as follow: (1) characterization of feedstock materials; (2) characterization of insulation layer microstructure with special attention to pores and cracks architecture; (3) characterization of thermal insulation properties expressed by thermal diffusivity and thermal conductivities in the function of temperature and finally (4) simulation of temperature and stress distribution on monolayered and double layered systems.

In research part the feedstock powders were primary investigated. The granules size and its top surface and internal morphology were analysed by laser diffraction method and SEM/EDS/EBSD coupled methods. Final TBC systems of 4 types (two monolayered and two DCL type) were described also form morphological point of view as well as the quantitative analysis of microstructure and pores were made by automatic images analysis. Additionally the internal stress level was analysed by XRD method. The final investigations was related with thermal insulation properties characterized by laser flash analysis in temperature range from 25 to 1100°C with step of 100°C. Obtained data (thermal diffusivity) were the base of thermal conductivity calculations.

The final element of investigation was numerical simulation of thermal and stress distribution in ceramic insulation layer calculated by FEM method with physical and mechanical data from temperature 25°C and 1100°C.

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Thermal insulation properties of composite $La_2Zr_2O_7$+8YSZ thermal barrier coatings

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The composite thermal barrier coatings (TBC) were characterized in this investigations from thermal insulation points of view. The base materials were powders of 8YSZ and $La_2Zr_2O_7$ type with similar chemical composition but different ability to thermal insulation in TBC systems. The analysed TBC systems were sprayed by atmospheric plasma spraying process on In 625 superalloy with the bond-coat of NiCrAlY type. The thickness of ceramic top-layers was ca. 300 µm in each case. The composite character of coatings was related with microstructural features. All coatings were deposited from the mixture of feedstock powders to the form of dual phase coatings with ration of each powders 25 to 75, 50 to 50 and 75 to 25 in weight %. The basic goal of investigation was characterization of thermal insulation properties expressed by thermal diffusivity and conductivity.

In first step of presented investigations the microstructural feature's of ceramic sublayer were presented such as porosity level, and fraction of each phase. The quantitative characterization of 8YSZ and $La_2Zr_2O_7$ phase in the coatings was the most important parameter analysed in this investigations. The special attention was took on the thickness of each type splats and was expressed by average 8YSZ and $La_2Zr_2O_7$ splat thickness. This parameter is the most important data for 1-d model of heat transfer in composite systems. The next parameter dedicated for this model is the thermal conductivity of each type of materials. In this case the thermal diffusivity and conductivity for monolayered systems of 8YSZ and $La_2Zr_2O_7$ type were used (presented in other investigations). The last parameter used in this calculations is the intersplats heat transfer coefficient (the methodology of IHTC value was showed in other publications on ICASS 2019 Conference). The final result of this calculation is the characterization of thermal resistance of each TBC system in the function of temperature as well as the determination of IHTC value for interfaces of $La_2Zr_2O_7$/8YSZ type in temperature range 25-1100°C. Additional element presented in this investigations is FEM analysis of composite systems and characterization of its thermal insulation properties by simulation methods.

Analysed TBC systems were described form morphological point of view (porosity, phase constituent, microstructural aspects etc.) by XRD, SEM and EDS analysis. The final investigations was related with thermal insulation properties characterized by laser flash analysis in temperature range from 25 to 1100°C with step of 100°C. Obtained data (thermal diffusivity) were the base of thermal conductivity calculations.

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Analysis of Re influence on solidification kinetics and heat treatment

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Thermal analysis of the crystallization process allows accurate calculation of the latent crystallization heat of various phases crystallizing during solidification. Based on the assumption that the latent crystallization heat is proportional to the share of various phases in the alloy microstructure, the thermo-derivative analysis also allows the calculation of the amount of the crystallized phases. Calculation of the above-mentioned properties is based on the characteristic points determined in a differential curve. Properly selected chemical composition of the alloy as well as appropriate cooling rate and heat treatment conditions lead to improvement of functional properties of manufactured elements. Therefore it is essential to know the changes of the cast structure in the relation to the change of the chemical composition [1].

The purpose of the presented research work is to investigate the thermo-derivative interdependences occurred in the copper alloys analyzed using Universal Metallurgical Simulator and Analyzer (UMSA) [2]. Moreover the influence of the heat treatment conditions on the structure of chromium copper alloy has been also the research subject.

The conductivity and microhardness of the tested alloys have been also measured in the function of the chemical composition and the state (i.e. heat treatment).

Keywords: Cu-Cr, Microstructure, Thermal-derivative analysis, Crystallization kinetics

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The influence of silver on the crystallization kinetics, microstructure and properties of Cu-Ni alloys

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Keywords: Copper alloy, Microstructure, Thermo-derivative analysis, Crystallization kinetics, Phase composition

The scientific aim of the paper is to determine the influence of Ag addition to Cu-Ni-Si alloys on the crystallization kinetics and to outline thermal and plastic treatment parameters on the structure and mechanical properties and electric conductivity of modified Cu-Ni-Si alloys. In the work the influence of the mass concentration of Ag on the properties of the copper alloys has been investigated. The applied thermo-derivative analysis has allowed for determination of both: range of the temperature values of the beginning and the end of crystallization, its phases and eutectics and effects of the modification on the solid fraction of the solidified alloy. In addition to the crystallization kinetics, the microstructure morphology, mechanical properties under real operating conditions as well as electric conductivity have been also investigated. Moreover, the conducted research have included the impact of heat treatment and plastic deformation on the alloy structure with consideration of the type, share and distribution of intermetallic phases as well as structural stresses caused by coherent phases and the effect of occurring dislocations on the reinforcing phases during aging.

Knowledge of phenomena occurring in the solidified Cu alloys is important for forming the microstructure and as a result - the functional properties of alloys. It also affects the process parameters of heat and plastic treatment such as temperature and time.

Strengthening the cobalt-modified copper surface

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In the paper the influence of the mass concentration of cobalt – introduced at the surface of the copper in the time of the laser modification – on the structure and strengthening has been presented. Both structure and strengthening have been analysed with application of the measurement of hardness and abrasion resistance.

The applied thermo-derivative analysis has allowed for definition of the range not only of the temperature of the crystallization beginning (T_L) but first of all the temperature of the crystallization end (T_{Sol}) for the alloy of the Co mass concentration similar to the Co mass concentration on the surface of the laser alloyed copper. It will enable the optimization of the heat treatment temperature.

In addition to the research on crystallization kinetics, the microstructure morphology in the modified zone, the diffusion zone and heat-affected zone have been investigated. One has also analysed the influence of the initial state of copper (after annealing and plastic processing) on the strengthening taking into account type, sharing and arrangement of the intercrystalline phases as well as matrix deformation.

The research have involved thermal-derivative analysis, scanning electron microscopy with analysis of chemical composition, X-ray phase analysis, abrasion resistance and microhardness testing methods.

1. Keywords: Copper, Surface modification, Alloying, Cobalt

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Modified Zn-Al-Cu alloys

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The primary purpose of the work was an attempt to answer the following questions: how will the addition of rare earth metals affect the crystallisation kinetics of the tested alloys? What will be the relationship between changes in the shape of the derivative curve and the microstructure and the same - properties of Zn-Al-Cu alloys? To improve properties of the zinc alloy modification of the structure consisting of the change of the morphology of alloy structural constituents has been applied, primarily by reducing the interfacial eutectic $\alpha'+\eta$, reduction in the size of fundamental components as well as the modification based on the change of the grain morphology of the solid solution with the aluminium phase [1, 2].

To describe the phenomena that occurs in the material during solidification as a result of the application of modifiers, both thermal-derivative and structural analysis using scanning and transmission electron microscopy method was used.

Keywords: crystallisation kinetics, Zn-Al-Cu alloy, microstructure modification

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The influence of phase change materials (PCMs) on thermal and mechanical properties of polyurethane-based bone scaffolds

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Polyurethanes (PUs) are nowadays one of the most investigated synthetic polymers for biomedical applications. The synthesis of polyurethanes typically includes three compounds: long-chain polyols, di- or triisocyanates and chain extenders. By changing chemical composition of the polyurethane, the properties of the final product, such as mechanical properties, biocompability, biodegrability etc. can be tailored to the specific purpose [1].

Phase change materials (PCMs) show a high enthalpy of fusion. During phase transitions they can store/release a considerable amount of thermal energy. In order to obtain the best results, the temperature range of phase transition of chosen PCM should be within the temperature range of an application [2].

Among vast variety of PCMs, poly(ethylene glycol) (PEG) seems to be a promising candidate. PEG is a semi-crystalline polymer with high degree of crystallinity, which causes large heat of fusion. PEG can store energy during solid-liquid or after shape stabilization solid-solid phase transition, whereby exhibiting small volume change. Melting temperature and heat of fusion strongly depend on molecular weight of PEG. With an increase of molecular weight of PEG, enhancements of previously mentioned properties are observed [2].

The incorporation of PCM into polyurethane matrix can be useful in the biomedical application for injectable bone scaffolds. During polymerization of PU large amount of heat is released, which can cause thermal necrosis of surrounding tissue. After an addition of PCM the temperature peak of exothermal reaction could be decreased [2].

In this work, polyurethanes modified with magnetic (Fe_3O_4) particles and phase change material (PEG) prepared in the two-step bulk polymerization were investigated. As a chain extender next to commonly used 1-4-butanediol, sodium alginate was applied in order to improve PUs bioactivity. An influence of various concentrations and different types of PEG on thermal properties of the final product was investigated. Samples were tested by mechanical (compression, DMA) and thermal (DSC, FSC, TG) methods. The obatined materials may be considered as novel bone scaffolds with improved thermal properties.

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Thermal properties of polyurethanesaccharides modified with magnetite and hydroxyapatite

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Among synthetic polymers, polyurethanes (PUs) are considered as the most biocompatible ones. PUs are easy to modify, and such modifications influence their properties – they can be used for various applications [1]. Polyurethanes can be obtained via one- or two-step polymerization process. In a two-step polymerization firstly isocyanate-terminated prepolymer is formed. Then it reacts with the chain extender to yield the final product [2].

Chain extenders are typically low-molecular-weight compounds. If compound is bifunctional, then it is called chain extender, for the higher functionality, the compound is considered as a cross-linker. An introduction of chain extender significantly changes properties of polyurethanes, such as mechanical properties and stability. It is caused by the fact that chain extender is a part of hard segment of the polyurethane. The most commonly used chain extender in elastomeric systems is 1,4-butanediol (BDO), which contains two hydroxyl groups [2]. In order to improve biocompability of the polyurethane scaffold, natural compounds can be used. Sodium alginate (SA), polysaccharide derived from brown algae, is widely used for biomedical application, due to its non-toxicity. Alginates contain hydroxyl groups that can be utilized as cross-linking sites for a polyurethane prepolymers [1] and as a result polyurethanesaccharides can be obtained.

Hydroxyapatite (HAp) is a calcium phosphate mineral. HAp is a good alternative for synthetic bone materials due to the fact that bone consists of around 65% HAp-like compounds. An addition of HAp to the PU-based material can not only enhance osteogenesis, but also improve mechanical properties such as Young modulus or tensile strength [3]. Another modification can be an addition of magnetic particles, which can simplify MRI examination and allow magnetic hyperthermia treatment.

In this work, polyurethanes modified with magnetic (Fe_3O_4) and HAp particles, and manufactured in the two-step bulk polyaddition process were presented. As a chain extender BDO and SA were used. The influence of various HAp content was investigated. Samples were tested by mechanical (compression, DMA) and thermal (DSC, FSC, TG) methods.

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Effect of temperature on dielectric relaxation alloxan-induced lenses from of healthy and diabetic rabbits

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The aim of the article is to present the results of in vitro tests of dielectric properties of a lens sample taken from healthy rabbits and rabbits subjected to hyperglycaemia in vivo. Dielectric experiments were carried out in a cylindrical chamber filled with air atmosphere [1].The values of dielectric parameters for these two groups of lens samples were obtained using AC 1V voltage (RMS) in the alpha electric dispersion region at temperatures from 22 to 200°C. The rabbits in this study were injected with elevated blood glucose induced by alloxan in the range of 485-506 mg/dl. Earlier, other authors [2] also used a rabbit model to study the thermal properties of various glycated tissues in vitro at temperatures of 25 to 90°C.

In the full temperature range for each frequency, the relative permittivity and conductivity values for a diabetic lens are higher than those recorded for a healthy lens. This suggests that diabetic samples have a higher density of relaxing active sites and free protons under the influence of the electric field as a result of crosslinking the protein molecules of the lens with dicarbonyl intermediates of advanced glycation end-products (AGEs). The occurrence of a peak temperature of about 80 °C for these two parameters is related to the decomposition of water absorbed by these tissues from an environment with a relative humidity of 65-70%. The activation energy of the conductivity up to 80°C is 30 kJ/mol and 40 kJ/mol, respectively, for a healthy and diabetic lens, indicating that glycation leads to an increase in the energy needed to change orientation and break the hydrogen bond in the lens-water system. As a consequence, the thermal stability of the diabetic lens due to protein aggregation [3] can be affected by higher electrical power dissipated in the form of heat compared to a healthy lens. The results of these measurements prove that dielectric spectroscopy is biomedically useful as a physical method in assessing the differences of electrical conductivity at low and high temperatures between a normal and pathological lens.

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Comparative analysis of temperature dependence of dielectric parameters in selected dry tissues from rabbits

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The main objective of this study was to compare the behavior of dielectric relaxation in two types of rabbit tissues, such as tendon and cornea. In our in vitro studies we used the ambient temperature of these biological materials in values above and below the physiological range due to the medical application of these temperature ranges in the therapy and diagnosis of human tissue dysfunctions.

Dielectric measurements of rabbit dry tissues were carried out using the LCR bridge made by HIOKI in the frequency range of 500 Hz-100 kHz and temperatures in the range from 22°C to 200°C. The dry state concerned tissues lacking water absorbed from the environment, called loosely bound water, in by heating these tissues at 150°C for about 1 hour and immediately cooling them to room temperature [1].

The temperature dependences of loss tangent for both the tendon and the cornea represent the relationship between the loss and storage of electricity in the biological system. The differences between thermal behavior of this dielectric parameter for these materials relate to the beta-relaxation process associated with the rotation of the polar side chains of collagen molecules, which is a typical protein in these animal and human tissues [2]. In the case of the cornea, there is a reduction in the amplitude of this relaxation and a shift of about 15°C to higher temperatures compared to the temperature of the tendon. The values of relative permittivity and conductivity at the same temperature for constant frequency are higher in the tendon than in the cornea. Power-low [3] responses are observed in the area of alpha conduction dispersion of both tissues, indicating proton conduction processes. The results of this study suggest that the density of relaxing polar sites and protons is smaller for the cornea than for the tendon over the entire frequency range of the electric field.

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Influence of polymer type on rheology and debinding temperature of powder injected maraging steel

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Powder injection moulding (PIM) is a relatively modern and mass production method of near-net-shape elements with complex geometry and small dimensions. High efficiency of this method influenced its dynamic development and wide field of industrial applications in recent years [1]. The ceramic or metallic powder and polymer binder are homogenised firstly, and then the slurry is formed by the injection moulding process. The green parts next are subjected to partial or complete debinding to remove the polymer. This step requires the use of very slow heating and long-annealing in thermal debinding temperature. To avoid many technological disadvantages (distortions or cracks), binders consisting of two or more polymers with different degradation temperatures are increasingly used. Moreover, the different types of polymer give the possibility to use other methods of debinding, e.g. solvent debinding.

The use of maraging steel powder for injection moulding is interesting because of the unique combination of high strength, and high toughness of maraging steel has made them irreplaceable in many industrial applications. These steels are a particular class of low-carbon alloys that derive their strength from precipitation of intermetallic compounds [2]. That is why it is so important to minimise the residual carbon remaining after degradation of the binder. The main goal of the research is to choose the components of the polymer-powder slurry that will enable its formation, quick and easy degradation of the binder, which does not leave residual carbon. For that reason, the multicomponent binder system based on thermoplastic polymers (PP, HDPE and EVA), paraffin wax (PW) and stearic acid (SA) was used. The initial selection of the components of the binder was based on measuring the torque of the blades of the mixer Rheomex CTW100p of Haake company which was read both the pure polymers and their blends, and the ready-made polymer-powder slurry (feedstocks) produced at a temperature of 170 °C at a rate of rotary blades 40 r.p.m. Binder polymers and their blends were tested by differential scanning calorimetry under nitrogen. To select the thermal degradation conditions, thermogravimetric tests were performed on the Perkin Elmer Pyris 1 thermogravimetric analyser at a temperature range of 50–600 °C under nitrogen. Rheological experiments were carried out in a capillary rheometer Haake Rheocap S20.

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Liquid salts deposits assisted decomposition processes in the systems $Sm_2Zr_2O_7$ + (ZrO_2, CeO_2, HfO_2)

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The motivation of the presented study was characterization of high temperature decomposition process in composite coatings of $RE_2Zr_2O_7$+8YSZ type (where RE = Sm, Nd, Gd and La) identified during investigation under hot corrosion conditions of selected thermal barrier coatings (TBC) systems in environment of liquid salt deposits of Na_2SO_4. The analysis revealed presence of decomposition of pyrochlore phase to the form of fluorite type of lattice on the surface of ceramic sublayer. No other structural effect where observed. Basing on this observation, the modeled systems of $Sm_2Zr_2O_7$ with ZrO_2, CeO_2 and HfO_2 oxides were designed and analyzed. The selection of oxides was related with its application as materials used in TBC systems.

The three types of mixture with equimolar fraction of basic phase were made via mixing and milling of powders in alcohol. The powders were then dried and pressed to the pellet form. Additionally, the same equimolar composition of $Sm_2Zr_2O_7$+ZrO_2 (CeO_2, HfO_2) powders were mixed with 10 % wt. of Na_2SO_4 salt. Fabricated mixed samples were analyzed by differential thermal analysis (DTA) method for identification of thermal effects related with observed structural phenomena. The DTA analysis was carried out in the temperature range 40–1200°C. Moreover, the phase constituent changes of prepared samples after long term exposure at temperature range from 900 to 1200°C with thermal step 50°C were investigated by X-ray diffraction method. The microstructural investigations were made by scanning electron microscopy (SEM). The plan-view observation was performed as well as the investigation of the prepared cross sections. For chemical composition analysis across the surface and cross sections, energy-dispersive X-ray spectroscopy (EDS) measurements were carried out.

Obtained data for model samples, corresponding to real TBC systems confirmed information about accelerated decomposition in $Sm_2Zr_2O_7$+8YSZ composite systems as an effect of liquid sodium sulphate assisted reaction between Sm_2O_3 and ZrO_2 oxides as well as between Na_2O and gaseous SO_3. The observed reactions are in accordance with so called fluxing mechanism typical for hot corrosion process.

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Determination of thermal diffusivity of TBC systems by laser flash measurement

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Thermal diffusivity measurement by laser flash method is recently very popular technic for insulation properties determination especially in the case of thermal barrier coatings (TBC). This method based on the temperature measurement of rare surface of sample inducted by laser impulse in wide range of temperature. As an answer the signal corresponding to the temperature changes is measured. This signal (or rather it half time) is the base of thermal diffusivity determination. The laser flash analysis gives wide range possibilities of different materials measurements from metallic good thermal conductors to ceramic material with very good insulation properties. The most interesting features of this method is possibility of thermal diffusivity determination for multi-layered materials by application of two or three layered models available as a software supplement of laser flash apparatus.

In presented publications the process of thermal diffusivity measurement in TBC three-layered system will be presented on an example of 8YSZ based coatings with thickness ca. 300 µm, and bond-coat of NiCrAlY type with thickness of ca. 125 µm. All types of coatings were sprayed by atmospheric plasma spraying process on In626 Ni based superalloy. The procedure of thermal diffusivity determination includes the samples preparation in the form of square samples with size 10×10×2 mm. In first step the thermal diffusivity measurement was made on the TBC (8YSZ/NiCrAlY/In625) sample treated as 1-layered materials. The Cowan model was used for final calculations. In second step the substrate alloy with NiCrAlY bond-coat was used for calculations, and finally the pure In625 was analysed.

Basing on the results of measurements the PROTESU^{TM} software was used the thermal diffusivity calculations of each sublayer separately. In firs step the results for In625 and 2-layered system of NiCrAlY/In625 was used for thermal diffusivity calculations of NiCrAlY bond-coat. This calculations were made with 2-layer model available in PROTESU^{TM} software. Obtained results was compared to data obtained for bulk materials with the same chemical composition. Another calculations were made for 3-layered system of 8YSZ/NiCrAlY/In625 system with known data for NiCrAlY bond-coat. In this case the thermal diffusivity was calculated for outer ceramic top-coat. Finally the NiCrAl/In625 system was treated as a first layer and outer 8YSZ layer as a second layer with thermal diffusivity calculation based on 2-layered model. Obtained data for top-coat of 8YSZ type were compared to data for 8YSZ bulk ceramic with similar porosity and to data obtained for measurement for so called free standing 8YSZ coating, obtained by mechanical removing of insulation layer from TBC system.

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Microstructural phenomena in TGO zone in $RE_2Zr_2O_7$ based thermal barrier coatings – analysis of modelled powder and real TBC systems

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Thermal barrier coatings (TBC) are the strongly complicated materials systems built from three different layers and materials. The outer sublayer is responsible for thermal insulation effect which is related with the type of ceramic materials used to deposition of TBC. The interlayer (so called bond-coat) is oxidation/corrosion resistant coating with the basic mission such as protection of substrate alloys to oxidation and/or corrosion processes and additionally elimination the effect of differences between thermal expansion coefficients between ceramic layer and metallic substrate. The last element of this system is substrate alloy responsible for mechanical answers on external loading.

The most important microstructural processes in TBC systems are located in the interfaces area between ceramic top coat and bond-coat (built usually from Ni-based heat resistant alloys). During the operating conditions in this interfaces the thermally grown oxides (TGO) zone is formed and this effect decides on the overall durability of whole system. The basic parameters of TGO zone, influenced on microstructural phenomena related with TBC durability, are the thickness of the oxide scale and it phase constituent. The most beneficial effect is obtained when the thickness is low and basic scale oxide is Al_2O_3. When the more complex oxides are formed, with simultaneously TGO growth, the durability of TBC systems rapidly decreased. Usually in standard TBC systems the 8YSZ is used to deposition of ceramic top-coats. This material is based on ZrO_2 and is chemically stable with Al_2O_3 in all temperature range. The problem is significant when the new materials dedicated to ceramic top-coats are used in TBC systems such as zirconates of rare earth elements. In this case the tertiary system is presences such as Gd_2O_3-ZrO_2-Al_2O_3 or similar. In this case the most reactive phase is RE_2O_3 type of oxide which has strong tendency to reaction with Al_2O_3 and formation of complex oxides such as GdAlO3 with perovskite type of lattice.

In presented investigations the microstructural phenomena`s in TGO zone of different types of TBC systems such as $Gd_2Zr_2O_7$, $Nd_2Zr_2O_7$, $Sm_2Zr_2O_7$ and $La_2Zr_2O_7$ were investigated with special attention on the formation of perovskite type of oxides such as REAlO3. Additionally the model tests on equimolar mixture of powders of RE_2O_3-ZrO_2-Al_2O_3 and RE_2O_3- Al_2O_3 type were made with special attention to thermal analysis method such as DTA and DSC. In this investigations the high tendency to complex transition oxides was confirmed.

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Dilatometric study of the phase transformation kinetics stimulated by recrystallized and non-recrystallized austenite in 3Mn-1.5Al steel

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Medium-Mn steels are extensively investigated due to their beneficial combination of strength and plasticity, which are required by the automotive industry. The trend is to use lean chemistry strategies due to low cost pressure and technological limitations, related to weldability, galvanizing behaviour, forming, etc. [1]. Manganese is a major alloying element, which enables obtaining retained austenite in a final microstructure. This structural constituent is crucial for mechanical behaviour of such multiphase steel sheets, when is distributed as blocky grains or layers within ferritic, bainitic or martensitic matrices [2]. The stabilization of retained austenite requires a multi-step heat treatment from the austenitizing temperature. Thus, proper heat treatment profiles during cooling need to be designed using thermal analysis methods and thermodynamic calculations. One of the ways for this is the use of dilatometric analysis to determine critical transformation temperatures [3].

The work addresses the austenite decomposition and subsequent phase transformations during cooling the 3Mn-1.5Al steel. The phase transformation kinetics is stimulated by different conditions of recrystallized and non-recrystallized austenites. The pseudo-binary Fe-C diagram was calculated using thermodynamic calculations. Ferritic, bainitic and martensitic phase transformations are investigated in detail in respect of their temperature range forming and microstructures produced under various conditions of continuous and isothermal cooling. The tests included the determination of the continuous-cooling-transformation (CCT) diagram and the DCCT diagram of the steel deformed prior to cooling. The dilatometric analyses were conducted with the use of DIL805 dilatometer. Deformation of samples at 900 and 1050°C was to determine the effect of austenite state on temperatures of phase transitions.

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Interspalt heat transfer coefficient determination in composite thermal barrier coating systems of $RE_2Zr_2O_7$+8YSZ type

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The problem of thermal insulation properties of thermal barrier coatings (TBC) systems is related with many technological and materials aspects such as physical properties of base ceramic materials (Um-klapp processes), the presences of cracks and pores and internal architecture of the ceramic sublayer (multi-layered structure, segmentation etc.). One of the most important factor is internal morphology of ceramic sublayer related with multiphase structure as a consequence of application of composite feedstock powders or deposition of coating with two or more different (from chemical point of view) powders. As a result the composite type of TBC systems are obtained with complex chemical and phase formula. The properties of those coatings are more beneficial in comparison to standard monolayered coatings as well as layered TBC systems such as DCL TBC (double ceramic layered TBC) both from mechanical point of view (better fracture toughness) as well as theirs thermal insulation behaviour, expressed by thermal conductivity/thermal diffusivity coefficient. Much lower value of thermal diffusivity and thermal conductivity of composite multiphase TBC systems are related with presents of interphases splats boundaries of two different ceramic materials and the key factor deciding about beneficial thermal effects is interphase (intersplat) heat transfer coefficient. The value of this parameter is not described in scientific literature, and this investigations showed the simple method to it determining. The base data used to calculations are: thermal diffusivity (by laser flash method) of monolayered TBC systems with re-calculation of thermal conductivity value for ceramic layer in function of temperature, voids architecture characterization by images analysis method as well as the thickness of the ceramic layer and mathematical models for effective thermal conductivity calculations dedicated for composite materials. Presented article showed the simple method of interphase (intersplat) heat transfer coefficient calculation in composite TBC systems of $Sm_2Zr_2O_7$+8YSZ type. As an referential materials used to calculation the monolayered $Sm_2Zr_2O_7$ and 8YSZ TBC coatings were used. The three different types of composite systems were investigated. The ratio of feedstock powders used in atmospheric plasma spraying process was 25/75, 50/50 and 75/25 in weight %. The mathematical models of Maxwell, Maxwell-Eucken, Rayleigh and Hasselman-Johnson were examined for spherical and spherical with horizontal voids. The calculation revealed that value of interphase (intersplat) heat transfer coefficient was on the level 10^5 [W/m^2K], and was thermally stable at temperature range 25-600°C.

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Thermogravimetric investigations of new Co-Al-Mo-Nb-X (X = Cr, Ti) cobalt-based superalloys

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The aim of the presented study is characterization of high-temperature oxidation behavior of new tungsten-free Co-based superalloys by thermogravimetry (TG) analysis. The following alloys have been taken into account: Co-10Al-5Mo-2Nb (at.%) alloy as a referential material, Co-20Ni-10Al-5Mo-2Nb (at.%) alloy as and Ni-modified version and 2 new alloys with composition not presented in literature modified by Ti and Cr Co-20Ni-10Al-5Mo-2Nb (at.%) and Co-20Ni-10Cr-10Al-5Mo-2Nb (at.%) respectively.

Recent investigations showed that there is possibility of γ/γ′ structure creation in Co-based superalloys of Co-Al-X type, where X=W, Mo, Nb and Ta. The main strengthening element in those alloys is ordered $L1_2$ phase with overall formula $Co_3(Al,X)$. The γ′ precipitates and the low-energy γ/γ′ interface provide high-temperature strength and stability to these alloys similar to the Ni based superalloys. Intensive investigations in area of alloying strategy (in order to increasing γ′ solvus temperature as well as increasing of strength and yield stress) get the beneficial effect, and at this moment of new Co-based superalloys development, the creep properties and flow stress of tertiary, quaternary and quinary Co-based superalloys of new type are comparable to Ni-based superalloys of first and second generation at temperature approaching 900°C. But there are still challenges that require further research such as: decreasing the density of alloys and improvement of theirs oxidation resistance.

The thermogravimetric analysis was carried out in the temperature range 40–1200°C of heating rate 5°Cmin^{-1}. The investigation was performed using the thermal analyzer NETZSCH STA 449 F3 Jupiter. TG–DTG plots showed oxidation behavior up to 1200 °C and indicated the temperatures of further isothermal oxidation examinations. The oxidation behavior of basic Co-10Al-5Mo-2Nb (at.%) alloy was compared to Ni-modified Co-20Ni-10Al-5Mo-2Nb alloy and new Cr and Ti added alloys of new-types. The obtained data showed different oxidation behavior dependably on the type of alloying elements. Moreover, the effect of Ni, Cr and Ti addition on oxidation performance was determined. The scales grown on Co-base superalloys after thermogravimetry were evaluated by means of scanning electron microscopy and energy dispersive spectroscopy.

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Dynamic Mechanical Analysis of aliphatic polyesters with stabilizers of plant origin

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Dynamic Mechanical Analysis (DMA) is a powerful tool which is usually utilized to reveal the viscoelastic and rheometeric properties of polymers. In the present study this method has been used to characterize the mentioned properties for aliphatic polyesters with polyphenolic stabilizers. The selected polymers and their blends with substances of plant origin have been tested in terms of viscoelastic behaviour in a function of temperature. Moreover, results obtained from this method have been correlated with other data received, for instance, from infrared spectroscopy (FT-IR ATR) and colour measurement.

The selected polymers belong to the group of aliphatic polyesters. These polymers, including polylactide (PLA), polyhydroxybutyrate (PHB) and their blends, are biodegradable thermoplastics which can be simultaneously obtained from renewable resources. Thus, these polymers are considered to be environmentally friendly thermoplastics, dedicated especially for packaging sector [1]. Utilizing stabilizers of plant origin instead of conventional ones contributes to obtaining completely pro-ecological materials.

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Thermal properties of porous polyurethane scaffolds for bone reconstruction and regeneration

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Polyurethanes (PUs) since the late 1990's were applied in particular as scaffolds, injectable void fillers, cement and drug delivery systems. PUs attract attention thanks to physical or chemical modification possibilities. Properly designed PUs have excellent physiochemical and mechanical flexibility as well as they are biocompatible, non-toxic and promote calcification in vivo. PUs are synthesized by polyaddition of three main components: polyol, polyisocyanate and chain extender. The conventional chain extenders used in PUs synthesis are m-phenylenediamine, 1,2-ethanediamine and 1,4-butanediol. In medical application other compounds are used, e.g polysaccharides [1]. Polysaccharides are ubiquitous and can be classified as either heteropolysaccharides or homopolysaccharides. Polysaccharides can be found in plants (e.g. cellulose, starch, guar gum), algae (e.g. alginate), animals (chitosan) and microbes (e.g. dextran). Alginates, due to their features including non-toxicity, biodegradability, biocompatibility and relatively low cost, are used in the fabrication of sustainable biomaterials [2, 3]. Therefore PU–sodium alginate compositions are potential materials for tissue engineering.

In our studies, PU/sodium alginate with nano-hydroxyapatite (HAp) and magnetic nanoparticles were obtained in a two-step polymerization. FTIR, DSC, TOPEM DSC, TG and microscopic methods were used for characterization of the obtained PUs composites. The assessment of the bioactivity and biodegradation in vitro was also performed. FTIR results confirmed the structure of synthesized polyurethanes and prove that the –NHCOO– bond has been formed. The TG/DTG analysis results showed that the obtained polyurethane composites exhibited thermal stability up to 234°C. Magnetic nanoparticles enhanced stability and biological durability of the PUs composites.

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Synthesis and thermal properties of PEG-based polyurethanes modified with hydroxyapatite for biomedical applications

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Polyurethanes (PUs) are traditionally used as elastomers, films, foams, adhesives, varnishes and coatings, and in recent years they have also been used as orthopedic scaffolds or vascular prosthetics. This is due to their good surface and mechanical properties, good hemocompatibility, hydrolytic resistance to bacterial enzymes and low cytotoxicity. The type of isocyanate raw material from which PUs composites are produced is relevant to tissue biocompatibility. Therefore, PUs obtained from diisocyanates such as TMDI, HDI or HMDI are more favourable in biomedical applications [1]. In the last decade, the preparation of novel biomaterials by using renewable resources has found an increasing interest. In view of their features, such as non-toxicity, biodegradability, biocompatibility, easy availability, high reactivity and low cost, several natural polymers such as proteoglycans and proteins (fibrin, collagen, keratin, gelatin), polysaccharides (chitin, chitosan, starch, alginates, cellulose) are broadly used, especially in biomedical field. It had already been proved that addition of starch in PUs reinforced the polymer's mechanical properties [2, 3].

In this work PU/starch composites with a phase change material (PCM) and hydroxyapatite (HAp) were obtained in a two-step polymerization process, where starch was applied as PU cross-linker and poly(ethylene glycol) (PEG) as a PCM. FTIR-ATR, TG, DTG, SEM, DSC techniques were used for characterization of the obtained PU/starch composites. FTIR results confirmed the structure of the obtained PU/starch composites. FTIR results confirmed the structure of obtained PU/starch composites. The TG/DTG analysis results showed that the modified composites exhibited higher thermal stability than the unmodified materials. PCM and HAp enhanced stability and biological resistance of the PUs.

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Thermo-analytical investigation of Dominican ambers

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Fossil resins are living products of various types of trees that have been embedded into sediments. Depending on the botanical origin, geographical location and geological conditions, different resins can be distinguished and classified into five main groups according to Anderson *et al.* [1]. The deciduous trees similar to Acacia (*Hymenaea* genus) have been suggested as the botanical source of Dominican ambers, whereas the main constituents of the resins labdatriene diterpenoids have been identified.

Mineable quantity of amber in the Dominican Republic occurs in two geographical localities: in the northern part of Cordillera Septentrional (north from Santiago de los Caballeros) and in Cordillera Oriental (eastern from Santo Domingo, El Valle) [2]. Despite the scientific popularity of Dominican amber [3-5], there is still confusion regarding its age. The modern analytical techniques and preserved insects found inside the material indicate that it is considerably younger than 40 Ma, which is the most frequently reported age by geologists.

In our studies, Miocen Dominican amber samples from aforementioned deposits were analysed by microhardness (Vickers method), Fourier-transform spectroscopy (FTIR), Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) analysis. Besides, the gases evolved in elevated temperatures and inert gas atmosphere, were characterized by FTIR coupling device (TG-FTIR). TG results showed that Dominican ambers present relatively high thermal stability under oxidative conditions till about 200°C. After heating to 270°C, the mass of the Dominican − El Valle sample decreased by only 5 wt%, due to decomposition or volatilization of less stabile components of the resin structure, probably non-polymerized compounds [6]. The profile of first DSC heating scan shows variation of heat capacity related to the physico-chemical changes in the reactive resin material, such as exothermic post-curing reactions, evolution of volatiles, relaxation and partial melting.

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The influence of thermal treatment on Li and Co leaching efficiency from spent lithium-ion batteries

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A commercial lithium ion battery (LiB) consists of a cathode, an anode, a separator (fine porous polymer film), and electrolyte (lithium salt solution in an organic solvent). The cathode assembly mainly consists of Al foils, active cathode materials, black carbon, and a binder PVDF (Polyvinylidene Fluoride), while the anode mainly consists of Cu foils, graphite and a binder PVDF. Presently, the cheap and safe layered cathode materials $LiMO_2$ (M = Ni, Co and Mn) are one of the most widely used active cathode materials on the market.

Currently, both pyrometallurgical and hydrometallurgical processes have been used in the recycling of spent LiB. As applied to the spent LiB battery materials, the process must facilitate the complete separation of the powdered active materials from the current collector (metal foils) and the binder PVDF as well as promote efficient recovery of the valuable metals or their compounds from the active materials by leaching.

In many of the proposed hydrometallurgical recycling processes, the active cathode materials are separated from the cathode current collectors by dissolving the Al foils with NaOH, and the binder PVDF, is removed with organic solvent N-methylpyrrolidone (NMP). The dissolution of the binder PVDF from the cathode materials with NMP is difficult and expensive. Recycling efficiency can be increased by applying appropriate thermal treatment before leaching.

In this paper, the effects of thermal treatment (thermolysis: argon flow 100 ml/min, 400 0C, 5 h) on the separation of the active materials from the current collectors and decomposition of PVDF are presented. The behavior of the cathode and anode materials during thermal treatment was investigated by FTIR, TGA-MS and HT-XRD. The morphology and chemical compositions of the cathode and anode materials before and after the thermal treatment were analysed with a scanning electron (SEM) and powder X-ray diffraction (XRD), respectively.

It was found that the thermal processing of electrodes does not create new waste, but improves the separation of the active material from the metal foil. Thermolysis causes a significant increase in Li and Co leachability.

Keywords: lithium-ion battery, recycling, thermal treatment, thermolysis

The use of thermal hydrogen decrepitation to recycle Nd-Fe-B magnets from electronic waste

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Rare earth magnets based upon neodymium-iron-boron (NdFeB) are employed in many clean energy and high tech applications, including hard disk drives (HDDs), motors in hybrid and electric vehicles and electric generators in wind turbines.

The key elements in manufacturing NdFeB magnets are rare earth elements (REEs) such as neodymium and dysprosium. These elements have been subject to significant supply shortfalls in the recent past. Recycling of NdFeB magnets contained within waste of electrical and electronic equipment (WEEE) could provide a secure and alternative supply of these materials. Despite the obvious need for a viable recycling route for rare earths, at present less than 1% of rare earths are currently recycled [1].

Various recycling approaches for the recovery of sintered NdFeB magnets have been explored by industry and academia. These include direct reuse, waste-to-REE, waste-to-alloy, and magnet-to-magnet approaches. Except direct reuse, these processes may use hydrometallurgical or/and pyrometallurgical methods. The advantages and disadvantages of these methods are discussed elsewhere [1,2].

It has been reported [3,4] that hydrogen can be used as an effective method of recycling NdFeB by utilising the hydrogen decrepitation (HD) process to turn solid sintered magnets into a demagnetised powder for further processing.

In this work, sintered Nd-Fe-B magnets, dismantled from HDDs, were processed without prior removal of the Ni protective layer using the thermal HD process as an alternative recycling method.

The gas sorption analyser have been used to determine the quantity of the hydrogen absorbed by a samples of magnets, under controlled pressure (1, 2, 3 and 4 bar) and temperature (room, 100, 300 and 400 ^{0}C) conditions, using Sieverts' volumetric method. The composition and morphology of the starting and the extracted/disintegrated materials was obtained by ICP, XRD and SEM-EDS analysis.

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Application of the DSC and spectroscopy methods in the analysis of the interaction of lipid membranes with phosphatidylcholines containing anisic acid

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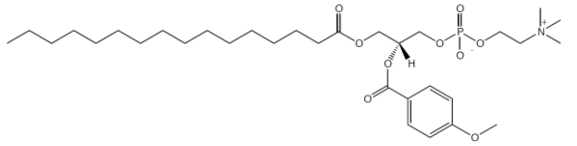
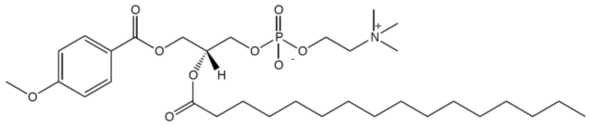
Cancer is one of the main causes of death rate in the world. The problem with traditional chemotherapy is that by acting on cancer cells it also destroys the normal ones. Therefore, new effective anticancer compounds are sought, the use of which does not cause side effects. Many studies indicate that such compounds include synthetic, anti-cancer lipids [1,2]. New structured lipids which are chemical compounds with physicochemical and biological properties modified in relation to natural phospholipids are constantly being tested. Due to the affinity to the membrane, they are able to build into it. As a result, biophysical properties are changed which probably results in modulation of the life processes of the cell.



1-PA-2-AN-PC



1-AN-2-PA-PC

The aim of this project is to study the effect of newly synthesized two phosphatidylcholines containing anisic acid at *sn*-1 and *sn*-2 position (1-AN-2-PA-PC and 1-PA-2-AN-PC) on thermodynamic parameters of liposomes formed from major membrane lipids (DPPC) using DSC and FT-IR spectroscopy methods. Synthesis and properties of these structured lipids were reported in previous paper [2]. It has been proved that the compounds show promising anti-proliferative properties against the tested tumor cell lines [2].

In addition to 1-AN-2-PA-PC and 1-PA-2-AN-PC, we tested the effect of anisic acid (AN) on phase transition of model membranes. It turned out that the compounds slightly change the temperature, half width and enthalpy of the DPPC main phase transition which may indicate on different location in the lipid bilayer.

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The use of a DSC in the Institute of Agricultural Engineering of Wrocław University of Environmental and Life Sciences is gratefully acknowledged. This work was sponsored by the statutory activities of the Department of Physics and Biophysics of Wrocław University of Environmental and Life Sciences.

Interaction between anticancer palladium(II) complexes with tris (2-carboxyethyl)phosphine and biomolecules – calorimetrical study

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In previous paper we reported that palladium(II) complexes with tris(2-carboxyethyl)phosphine (*trans*-$[PdCl_2(TCEP)_2]$ and *trans*-$[Pd_2(\mu\text{-}Cl)_2Cl_2(TCEP)_2)$ are promising agents against tumor cells. Cytostatic activity of these complexes was investigated against SK-mel (human, Caucasian, skin, melanoma), SH-4 (melanotic melanoma), Colo-829 (human, umbilical metastatis, melanoma) and C-32 (amelanotic melanoma) cell lines [1]. Melanoma is not the most common skin cancer, however, it is much more dangerous if it is not found in the early stages. It causes majority of deaths related to skin cancer. Especially due to the fact that metastatic melanoma is a disease difficult to treat. The 10-year survival rate for patients with this disease is below 10%. The therapies against melanomas have been recently improved, however, the survival rate is still low. Therefore, it is worthwhile to search for new agents against these tumors [1]. Our research of platinum(II) complex with tris(2-carboxyethyl)phosphine suggests that this compound does not cause membrane destruction and is not toxic to normal cells in a wide range of concentrations [2,3]. From the chemical point of view palladium(II) and platinum(II) componds show significant similarities. In order to approximate the molecular mechanism of palladium interaction with the cellular membranes, we carried out research on model systems for these complexes. What is more, in the study we investigated not only palladium complexes, but also the impact between TCEP (tris(2-carboxyethyl)phosphine) and biomolecules (phospholipid, human serum albumin).

All experimental results indicate that the biggest changes are in the hydrophilic part of the lipid bilayer. Microcalorimetric (DSC, ITC) experiments demonstrated that tested compounds slightly increase the phospholipids main phase transition temperature and decrease its cooperativity. Furthermore, *trans*-$[PdCl_2(TCEP)_2]$ and *trans*-$[Pd_2(\mu\text{-}Cl)_2Cl_2(TCEP)$ interact with albumin.

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Influence of basalt filler on the thermal, mechanical properties and toxicity of thermal decomposition gaseous products of ceramizable silicone rubber composites

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Recently, ceramizable composites were regarded as some novel fire-protection materials with wide application in electric wires and cables. Ceramizable composites ideally have the dual performance of composites at room temperature and ceramics at elevated temperature. They can resist high temperature of more than 1000 ^{0}C due to the formation of ceramic layers to protect the inner copper of the wires.

Silicone rubber, due to its extraordinary thermal and fire resistance properties, has been used as a continuous phase for ceramifiable composites. However, the principal reason for using silicone rubber as a matrix for ceramifiable composites is its ability to create inorganic silica during combustion in the presence of oxygen.

The ceramization effects of the silicone rubber composites could be obtained by sintering of filler particles such as e.g. silica, mica, alumina, wollastonite and montmorillonite or calcium carbonate. The formation of ceramic structure can be also result of chemical reactions between mineral filer particles. The main example of this mechanism is formation of calcium silicates from calcium-based fillers and the silica formed after silicone matrix burning. Formation of physical connections between particles of thermally stable fillers, as a result of addition low-softening/melting point fillers, such as glassy frits with softening point temperature of 374-525 ^{0}C or boron oxide or zinc borate with a melting point temperature of 450-550 ^{0}C have also a great influence on structure and mechanical properties of obtained ceramic structure.

The basic problem which limits the industrial application of ceramizable composites is not only their reduced resistance to fire and elevated temperatures, but also toxicity their thermal decomposition products and the insufficient mechanical durability of the former ceramic structure.

The presented results illustrates the impact of basalt filler, both in the form of basalt flakes and basalt fibers, on the thermal and mechanical properties as well as fire hazard, included toxicity of thermal decomposition product, of silicone rubber ceramizable composites. The investigated composites, apart from the basalt filler, contained in their composition mineral fillers in the form of silica and calcium carbonate, inorganic fluxes such as zinc borate and glass frit as well as cyanurate as a flame retardant.

Oxidation resistance of black glasses obtained from lader-like silsesquioxanes

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Black glasses, also called silicon oxycarbides, are amorphous materials where a part of oxygen ions have been replaced by carbon ions [1]. This substitution leads to improvement of mechanical, chemical and thermal properties and therefor attract attention of various scientific branches [1-3]. Usage of ladder-like silsesquioxanes, as preceramic materials, provides ease of synthesis and a possible to adjust the chemical and physical parameters of final glasses and adapt them to a specific application, e.g. protective coatings on metal substrates [3].

Black glasses were obtained by the means of pyrolysis of ladder-like silsesquioxanes, with different Si:O:C ratios, in Ar atmosphere at 800^{o}C in a tubular furnace. In order to determine the oxidation stability of as obtained silicon oxycarbide materials TG/DSC studies were conducted. On the basis of thermal studies black glasses were heat-treated in air atmosphere up to 1500^{o}C. Combined structural studies – XRD, FT-IR and Raman measurements gave insight about changes occurring during oxidation process. SEM with EDX investigation revealed changes to the microstructure and chemical composition of studied materials.

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Thermal properties and crystallization kinetics of fluoroindate glasses

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Fluoroindate glasses are materials present both broad transparency from the UV to the IR region and relatively high solubility of rare earth which can be incorporated into [1]. Additionally, low multiphonon relaxation rates makes that rare-earth doped fluoroindate glasses present high emission efficiencies. The phonon energy of fluoroindates is close to 510 cm^{-1} which is lower than the value of 580 cm^{-1} obtained for fluorozirconate glasses (ZBLAN). It should be also noted that they are characterized by better thermal and mechanical stability and resistance to chemical corrosion [2]. Compared to fluorozirconate glasses, these compositions present higher transparency in the mid-infrared range up to 8 μm and are also more stable against atmospheric moisture [3].

In the paper the investigation of crystallization kinetics of InF_3–ZnF_2–BaF_2–SrF_2–GaF_3–LaF_3 fluoroindate glasses co-doped with rare-earth ions using differential scanning calorimetry (DSC) was presented. Influence of the RE content and ratio on the thermal properties will be shown. Thermal analysis was performed using Friedman and Ozawa – Flynn - Wall methods. Activation energy and crystallization index were calculated. The glasses samples were subjected to additional controlled heat treatment in crystallization temperature in order to control crystallization parameters and obtain glass-ceramics matrials.

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Effect of ionic liquids on curing characteristics and thermal behaviour of butadiene-styrene elastomer

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The mechanism of sulfur vulcanization assumes that the zinc oxide (ZnO) surface acts as a catalytic reaction template by activating and joining reactants (sulfur, vulcanization accelerators). Therefore, the contact between ZnO particles and accelerators in the elastomer matrix should be maximised to improve the efficiency of vulcanization. This contact depends on the dispersion of ZnO particles in the elastomer [1]. Recently, owing to their unique chemical structure, ionic liquids (ILs) have been used to improve the dispersion of nanoparticles in polymers, particularly in elastomers [2]. Zinc oxide nanoparticles can be dispersed more homogeneously in the elastomer matrix when ILs are present [3], which increases their accessibility in reactions with vulcanization accelerator and sulfur.

In this work, different techniques of thermal analysis were employed to study the effect of zinc oxide and ILs on the cure characteristics, damping behaviour and thermal stability of butadiene-styrene elastomer (SBR). ILs from the group of GRAS (generally regarded as safe) compounds were used to improve the activity of nanosized ZnO in sulfur vulcanization of SBR. Applied ILs include anion of non-nutritive sweeteners such as saccharinate and acesulfame or pharmaceutically active anion – lactate. ILs are thought to catalyze the interfacial reactions; therefore, they can be assumed to play the same role in the vulcanization process.

Nanosized ZnO with ILs reduced the vulcanization temperature of rubber compounds. Their application resulted in the improvement of vibration damping ability of SBR vulcanizates. A slight decrease in the thermal stability of vulcanizates has been obtained, which should not affect the potential applications of these materials.

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The influence of functionalized hydroxyapatite on the thermal properties of polyacetal composites

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Plastics are currently the most commonly used materials in everyday life and in virtually all branches of the economy, also as biomaterials for bone substitute. The widespread use of plastics is primarily due to their useful properties, such as low density, high resistance to chemical agents, high mechanical strength etc. [1].

The subject of this research was focused on polyoxymethylene-based composites with functionalized hydroxyapatite (HAp). One of the disadvantages of POM based biomaterials is lack of bioactivity [2]. In our study bioactive modifiers have been used to improve bioactivity and biocompatibility of POM-based composites. HAp has been functionalized with poly(ethylene glycol) (PEG) using 1,6-hexamethylene diisocyanate as a linker. Functionalized HAp (HAp-g-PEG) has been incorporated to POM matrix using melt processing methods. POM composites with different contents of HAp-g-PEG were prepared (0.5%, 1%, 2%, 5%, 10%) and effect of HAp-g-PEG on the thermal properties were investigated using DSC, TOPEM-DSC and TG techniques. It has been found that incorporation of HAp-g-PEG leads to a significant increase of POM matrix thermal stability, in contrast to unmodified HAp where a dramatic decrease of thermal stability has been observed [3].

Acknowledgements

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Preparation and DMA investigations of polyoxymethylene modified with PEG-grafted hydroxyapatite

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Functionalization of fillers before dispersion in polymer matrix has many advantages over using conventional additives. The presence of an intermediate compound with similar chemical structure to the modifier and to the matrix leads to the strongest adhesion between them and better distribution of the modifier in the matrix, eliminating or reducing the formation of aggregates [1]. The functionalization process itself is more complicated and requires additional operations but allows the effective chemical surface modification of the filler.

The subject of our studies was preparation and DMA investigation of polyoxymethylene (POM) matrix composites with functionalized hydroxyapatite (f-HAp). POM is high-quality construction thermoplastic polymer characterized by high mechanical strength and low friction coefficient that can be used in biomedical applications. HAp was functionalized with poly(ethylene glycol) (PEG) using diisocyanate as a coupling agent and incorporated to POM matrix [2]. The thermal and mechanical properties were examined using DMA techniques in stretching and bending modes. It was observed that with the f-HAp content increase the loss modulus decreases and the storage modulus increases. The glass transition temperature also increases with the increase in f-HAp content. The DMA and microscopic results show a good dispersion of f-HAp in POM and suggest better adhesion between POM and filler compared to unmodified HAp.

Acknowledgements

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Structural and magnetic studies of nanosized Mn-Zn ferrites prepared by modified solution combustion route

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The nanosized Mn-Zn ferrite with $Mn_{0.6}Zn_{0.4}Fe_2O_4$ stoichiometry has been prepared by modified sol-gel autocombustion route from an oxalate precursor. The obtained manganese-zinc ferrite powders were characterized by powder X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), transmission electron microscopy (TEM) and superconducting quantum interference device (SQUID) magnetometry.

The pure spinel ferrite with average crystalline size at ~21 nm was obtained in proposed experimental conditions: the molar ratio of oxidizer (nitric acid) to fuel (citric acid and oxalate ions) was 2.5, and the molar ratio of the fuel to amount of metal ions = 2, pH = 7 adjusted by 25 vol% ammonia solution.

The synthesized material is characterized by metastable pure spinel phase. The particles have core-shell structure, where the roughly spherical ferrite crystallites make core surrounded by magnetically dead surface layer. The thermal variations of the magnetization in a field 0.5 T and inverse magnetic susceptibility product revealed that synthesized ferrite powders exhibit ferrimagnetic nature. The dynamic *ac* measurements demonstrated that the single domain particles behave like superparamagnet at high temperatures. The relaxation time (τ_o = $5.43 \cdot 10^{-10}$ s) determined on the basis of dynamic *ac* measurements is typical for superparamagnetic materials.

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Phase equilibria in the $ErPO_4$ – KPO_3 – $Er(PO_3)_3$ system

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Rare-earth phosphates have been extensively studied for many years mainly due to their thermal stability in high temperature and interesting optical properties. Increasing interest in these materials has been observed since binary and ternary lanthanide phosphates could be used as laser devices not only in the form of single crystals but also in the form of powder or glasses. That is why knowledge of the phase relationships (in a wide temperature range) in the phosphate systems play an important role in interpreting variations in properties with composition and could be helpful in searching for their potential applications.

The phase equilibria in the $ErPO_4 – KPO_3 – Er(PO_3)_3$ system was examined by thermoanalytical methods (DTA/TG/DSC), powder X-ray diffraction (XRD) and microscopy in reflected light. On the basis of the obtained results its phase diagram, not published previously, has been established for the whole range of composition up to a temperature of 1600°C.

The system is bounded by three susbsystems: $ErPO_4 – KPO_3$ [1], $Er(PO_3)_3 – KPO_3$ [2] and $ErPO_4 – Er(PO_3)_3$ [3]. In the first system an intermediate compound, $KEr_2P_2O_7$, occurs and in the second one $KEr(PO_3)_4$ occurs. Both melt incongruently at 1025°C and 712°C, respectively.
Two isopleth sections: (**I**) $KErP_2O_7 – KEr(PO_3)_4$ and (**II**) $KErP_2O_7 – Er(PO_3)_3$ have been found in $ErPO_4 – KPO_3 – Er(PO_3)_3$ partial ternary system. They are quasi-binary only in the subsolidus region. Three invariant points, two ternary peritectics P_1 (($t_{P1} = 855°C$) and P_2 ($t_{P2} = 640°C$) and one ternary eutectic E ($t_E = 530°C$) occur in the investigated region. The quasi-ternary peritectic and eutectic reactions proceed according to the equations:

$$ErPO_4 + L_{P1} \leftrightarrows KErP_2O_7 + Er(PO_3)_3$$
$$Er(PO_3)_3 + L_{P2} \leftrightarrows KErP_2O_7 + KEr(PO_3)_4$$
$$L_E \leftrightarrows KErP_2O_7 + KEr(PO_3)_4 + KPO_3$$

Solidification of alloys in $ErPO_4 – KPO_3 – Er(PO_3)_3$ system ends at the ternary eutectic point E, where three phosphates $KErP_2O_7$, $KEr(PO_3)_4$ and KPO_3 crystallize at a constant temperature of 530°C.

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Thermal behaviour and structural characterization of hydroxyapatite whiskers, obtained by hydrothermal synthesis with the use of calcium lactate pentahydrate

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Bioactive calcium phosphates ceramics exhibit excellent biocompatibility due to their chemical and crystallographic similarities with the mineral constituents of bones and teeth.

It's known that synthetic hydroxyapatite is often utilized as a biocompatible reinforcement for orthopaedic biomaterials and can provide improved mechanical properties in reinforced polymer composites. Synthetic HAp - in the form of whiskers - could be of particular importance as reinforcing fillers for composites because of its shape. Compared with available bio-inert whiskers or fibres, the most promising reinforcements seem to be HAp due to his biological properties [1]. Hydroxyapatite can be synthesized using different techniques such as precipitation, hydrolysis, and hydrothermal synthesis or can be extracted from natural resources, e.g. seashells, bovine bones.

This article describes the preparation of HAp whiskers as a result of the decomposition of calcium chelates under hydrothermal conditions. The main substrate for the synthesis was calcium lactate pentahydrate $C_6H_{10}CaO_6 \cdot 5H_2O$ (pure p.a., Chempur Company). Synthesis were carried out in various conditions with using a special stainless steel reactor. The effect of reagents concentrations, pH, reaction temperature and pressure on HAp whiskers morphology and composition was investigated. During the synthesis the following experimental parameters were varied independently: temperature (130,150,170, 200°C), stirring rate (0, 62.5, 125, 250, 500, 750 rpm), the reaction heating rate (0.2, 0.5, 0.7, 1.0, 1.5, 2.5 °C/min), time of synthesis (3, 5, 7h). The Ca^{2+} concentrations in starting synthesis solutions varied in range of $0.025 \div 0.2$ mol/dm^3. The molar Ca/P ratio in solutions was 1.67, which is equivalent to that of stoichiometric HAp. Synthesis were carried out under pressure in range of $5 \div 20$ bar.

The pH of the starting solutions and solutions after the synthesis was measured with a glass pH electrode (Eutech Instruments, CyberScan PCD 6500) at 25°C.

The products were characterized by qualitative and quantitative phase analysis using X-ray powder diffraction method (XRD, Bruker-AXS D8 DAVINCI). The morphology and microstructure of products were observed by scanning electron microscope (SEM, FEI, model Nova NanoSEM 200). Functional groups of the samples were identified by Fourier transform infrared spectroscopy (FTIR, TENSOR27 Bruker). After identification, the samples were subjected to thermal analysis (TA)(STA 449F1 Jupiter Netzsch, TGA/DTA) in temperature range of 25°C - 1550°C with a heating rate of 10°C min^{-1} in argon atmosphere.

Acknowledgments

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Preparation of calcium phosphates by hydrothermal precipitation using various chelating agents

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Calcium phosphate (CaP) bioceramics are widely used in the field of bone regeneration, both in orthopedics and in dentistry, due to their good biocompatibility, osseointegration and osteoconduction [1]. One of the well-known techniques to obtain of calcium phosphates in different forms, included hydroxyapatite (HAp) with excellent crystal quality and Ca/P ratio close to the stoichiometric value is hydrothermal method [2]. The synthesis is based on a chemical precipitation from an aqueous solution containing calcium and phosphate sources, carried out in an autoclave at elevated temperature and high vapour pressure. Various organic modifiers, especially chelating agents such as carboxylic acids or ethylenediamine tetraacetic acid (EDTA) are often added during the precipitation process to control supersaturation of CaP and thus the crystal growth rate. Upon heating, calcium chelates decompose and calcium ions are slowly and continuously released so that the degree of solution supersaturation is constantly low during the deposition process [3].

This article describes the preparation of calcium phosphates as a result of the decomposition of calcium chelates under hydrothermal conditions. The synthesis were carried out with using a special stainless steel reactor. The main substrates for the synthesis were calcium hydroxide $Ca(OH)_2$, calcium phosphate dibasic $CaHPO_4$ and chelating agents, such as DL-lactic acid, L(+)-ascorbic acid, DL-malic acid, L(+)-tartaric acid, citric acid and EDTA. Also, the hydrolysis of calcium phosphate dibasic $CaHPO_4$ was carried out.

The effect of reagents concentrations, pH, reaction temperature and pressure on calcium phosphates morphology and composition was investigated. The Ca^{2+} concentrations in starting synthesis solutions varied in range of 0.05÷0.2 mol/dm^3. Synthesis were carried out under pressure of 10 and 20 bar and at a temperature of 170 and 200 °C. The morphology and microstructure of products were observed (SEM). The phase composition of products was analyzed by X-ray diffraction method (XRD). Functional groups of the samples were also identified (FTIR). After characterization, the samples were subjected to thermal analysis (STA 449F1 Jupiter Netzsch, TGA/DTA) in temperature range of 25°C - 1550°C with a heating rate of 10°C min^{-1} in argon atmosphere.

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Determination of heat treatment parameters of new Co-based superalloys of Co-20Ni-7Al-7W type

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The new γ/γ′ Co-based superalloys are newly developed class of refractory alloys which may replace commercial Ni-based superalloys owing to their favourable properties at high temperature. This group of materials is typically described as a tungsten based and tungsten free alloys, which can consist the addition of γ′ phase forming refractory metals such as W and Mo, Nb and Ta respectively. The favourable structural form of γ′ phase is phase marked as $Co_3(Al,X)$ where X=W, Mo, Nb, Ta with $L1_2$ type of lattice. In case of new Co-based superalloys, the heat treatment gives the possibility to obtain microstructure composed of appropriate volume fraction of small cuboidal γ′-$Co_3(Al,X)$ precipitates within the γ-Co matrix. Due to tendency to increasing of thermal stability of γ′-Co3(Al,X) phase with $L1_2$ type of lattice and increasing the field of existence in ternary systems of Co-Al-X type the addition of alloying element Ni is also needed. Traditionally, due to a high tendency to interdendritic segregations of alloying elements in all multielement superalloys, the alloys based on Co–Al–X or Co-Ni-Al-X system should be thermally treated with followed processes: homogenization with next solutionizing and aging.

In this study, thermal analysis was applied for determination of temperature range for primary heat treatment of the Co-20Ni-7Al-7W (at.%) such as homogenization and solutionizing. The differential thermal analysis (DTA) measurements were carried out on the thermal analyser NETZSCH STA 449 F3 Jupiter. The base alloy was melted using induction vacuum furnace VSG 02 Balzers and casted under Ar atmosphere. In further part of evaluation, the phase composition of as-cast alloy and alloy after annealing operations was examined using X`Pert^3 Powder XRD system. Chemical composition and microstructure of alloy after solution heat treatment and aging were evaluated by means of scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) using Hitachi S-4200.

On the base of obtained results, the homogenization and/or solutionizing parameters were determined respectively. The basic criteria of homogenization treatment selection was the tendency or it lack to $D0_{19}$ undesirable phase formation with similar formula such $L1_2$, but with TCP (*topological close packed*) type of structure. Additionally the liquidus and solidus temperature were characterized and theirs value were compared to data obtained during numerical simulation model alloy with the same chemical composition. In the last part of thermal analysis the solvus temperature of γ′ phase was determined, as a thermal requirements to aging process. The final part of investigations was related with microstructural analysis of alloy after as-cast condition as well as after each step of thermal treatment.

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Microstructural stability in composite TBC coatings of $Gd_2Zr_2O_7$+8YSZ type

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Thermal barrier coatings (TBC) are the one of the most advanced engineering systems in materials engineering. The most important task they have to accomplish is related with insulation of metallic parts of hot sections of gas turbines in aircraft engines or in stationary units for example in power plants. The TBC system is usually built from outer ceramic layer responsible for decreasing of temperature with the thickness of 200 to 400 μm. The ceramic insulation layer is thermally sprayed by atmospheric plasma spraying or is deposited by physical method such as electron beam physical vapour deposition. The immanent feature of this coatings is porosity which gives the strong effect of thermal insulation. Another element responsible for decreasing of temperature is related with the scattering effect of ceramic. The most popular material used in this systems is 8YSZ ($ZrO_2 \times 8Y_2O_3$) with the one of the lowest value of thermal conductivity. Bur from practical point of view this value is not enough from current requirements point of view. Much better insulation effect is expected and confirmed for pyrochlore group of ceramic materials with overall formula $A_2B_2O_7$. The most popular materials from this group are zirconates of rare earth elements such as $Gd_2Zr_2O_7$. Many publication revealed that TBC systems based on this ceramic are characterized by much lower thermal conductivity than systems based on 8YSZ. The solutions based on monolayered $Gd_2Zr_2O_7$ insulation layer are effective from thermal insulation point of view, but overall durability of TBC based on it is low due to high value of Young modulus. In consequence the thermal barrier coating of this type showed high tendency to cracking and spalling with the effect of so called “white failure”. The solution of this problem can be application of two layered systems in the form of DCL (double ceramic layer – layer on layer) coatings or composite coatings where the internal morphology of ceramic layer consists mixture of two different phases. In this case the fracture toughness of ceramic zone is much better and the insulation effect is higher than can be expected due to intersplats boundaries scattering effect.

The basic problem in multiphase coatings is interphase thermal stability between used ceramic materials and between ceramic phase and Al_2O_3 which is the product of bond-coat oxidation (second element of TBC systems). In this publications the presented analysis are related with characterization of thermal stability between $Gd_2Zr_2O_7$ and 8YSZ oxides and between $Gd_2Zr_2O_7$ and Al_2O_3. Both analysis where made on the modelled powders and in real TBC system of $Gd_2Zr_2O_7$ + 8YSZ type. First investigations showed high level of thermal stability at wide range of temperature. In second case the formation of transition oxides of GdAlO3 type were confirmed both in the case of powder-based investigations as well as the real TBC composite system

This work was supported by Faculty of Materials Engineering and Metallurgy, Institute of Materials Science of Silesian University of Technology, as a part of Statutory Research BK-205/RM0/2019.

Solubility and miscibility of methylxanthines with polymeric excipients in theoretical and practical aspect

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Phase diagram reflects an equilibrium state in a mixture of ingredients. Construction of the phase diagram for mixture consisted of a crystalline active pharmaceutical ingredient (API) and an amorphous excipient, e.g. polymer, entails the calculation of the curves which predict a solubility of API in polymer and a mutual miscibility of ingredients. In the API-polymer solid-state system, solubility is refer to the maximum loading of the drug substance that creates a thermodynamically stable solid solution. Miscibility defines the upper limit of the drug substance loading which does not lead to spontaneous phase separation followed by the API crystallization [1-3]. Development of both curves is based on mathematical calculations in which the Hansen solubility parameters are used [2,4].

The objective of this study was to develop the phase diagrams for mixtures of methylxanthines (caffeine and theophylline) with hydroxypropyl methylcellulose (HPMC, hypromellose). It is important issue since both methylxanthines and HPMC are commonly used together in the solid dosage drug technology. Based on these diagrams, it is possible to predict what quantities of the crystalline active substances may be dissolved in the amorphous polymer at a given temperature. It is also possible to predict at what ratios the ingredients have a good miscibility.

DSC tests carried out using the heating-cooling-reheating cycle confirmed that in the solid-state mixtures of caffeine and theophylline with HPMC, the crystallinity of methyl-xanthines can be partially reduced. In addition, part of the active substance does not crystallize under rapid cooling. FTIR and Raman study revealed that all the characteristic signals for the crystalline API were found in the spectra. No shifts of the peaks or the appearance of new ones were observed. This confirms that there is no chemical interaction between methylxanthines and HPMC and no hydrogen bonds are formed. Thermomicroscopic study of mixtures showed that no formation of crystalline or amorphous forms, other than those characteristic for single ingredients, was observed.

Concluding, the DSC, FTIR and Raman study revealed that there was no chemical or physical interaction between methylxanthines and HPMC in the solid-state. Partially loss of crystallinity of active substances in a solid mixture with HPMC is caused by formation of the solid solution and the miscibility of ingredients.

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A new DSC approach to compatibility/incompatibility study between ingredients of pharmaceutical mixtures

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An inability to mix the ingredients of drug formulations homogenously results from the interactions (incompatibility) between them. Incompatibility can occur both at the stage of dosage form formulation or during long-term storage, bringing changes in the physical, chemical or therapeutic properties of an active pharmaceutical ingredient (API). Since methods of thermal analysis provide valuable information about API and excipient interaction, they have been commonly used for the assessment of the compatibility/incompatibility since 1970.

The aim of this study was to develop a new approach for compatibility examination, combining differential scanning calorimetry (DSC) with advanced multivariate statistical methods. In order to this, the binary physical mixtures of acetazolamide as an model API and selected excipients, such as β-cyclodextrin, chitosan, lactose, magnesium stearate, mannitol, meglumine, methylcellulose, polyvinylpyrrolidone and starch, mixed at the 7:3, 1:1 and 3:7 molar or mass ratios, were investigated by the DSC (DSC 822e, Mettler Toledo, Schwerzenbach, Switzerland). The study were based on the heating-cooling-reheating test using the following temperature program: heating samples at a rate of 10°C/min from 25 to 250°C, isotherm for 2 min, cooling at a rate 40°C/min from 250 to −25°C, isotherm for 2 min and the second heating at a rate 10°C/min to 250°C.

The advanced multivariate statistical methods, such as principal component analysis (PCA) and cluster analysis (CA) were used for interpretation of the data acquired from the DSC scans. Out of large number of the DSC data, heating and cooling parameters such as melting point, crystallization point, melting and crystallization enthalpies, and peaks height were selected. The statistical model was built using Statistica 13.3 software (StatSoft Inc., Tulsa, OK, USA). The CA dendrogram was constructed by the Ward's method (agglomerative hierarchical clustering) using Euclidian distance with the Sneath's index criterion, at 2/3 of the maximum distance to select the number of significant clusters. PCA calculations were done by applying correlation matrices and an algorithm without a rotation of factors.

The compatibility between acetazolamide and excipient can be confirmed by two large clusters on the CA dendrogram, from which one groups acetazolamide and mixtures with a high acetazolamide content. The second cluster encompasses excipient and physical mixtures with a high excipient concentration. In the case of the PCA score plot, creation of a cluster by acetazolamide and mixtures with a high acetazolamide content confirms compatibility between ingredients. Concluding, the DSC coupled with PCA and CA revealed that acetazolamide was incompatible with β-cyclodextrin, lactose, magnesium stearate, mannitol, meglumine and starch.

Thermodynamic properties of phase transitions of two substituted benzaldehydes

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Syringaldehyde is a phenolic compound that occurs in trace amounts broadly in nature. It is useful as ingredient in fragrance and flavor industries and also as building block in the synthesis of some second-generation fine chemicals, such as 3,4,5-trimethoxybenzaldehyde [1]. This latter compound is a precursor of an antibacterial agent applied in Parkinson's disease treatment [1]. The crystalline and liquid (including supercooled liquid) vapour pressures of syringaldehyde were measured in the following temperatures ranges: T = (350.7 to 380.3) K and T = (374.3 to 425.5) K, respectively, using a diaphragm manometer static method [2]. Moreover, the sublimation vapour pressures of this compound were also measured in the temperature interval T = (337.2 to 359.2) K, using a Knudsen mass-loss effusion method [3]. This technique was also used to determine the vapour pressures of the crystalline phase of 3,4,5-trimethoxybenzaldehyde over the temperature range T = (315.2 to 335.3) K. The standard molar enthalpies, entropies and Gibbs energies of sublimation of the two compounds studied and of vaporization of syringaldehyde were derived from the experimental results. The thermal analysis of the two compounds was also performed using differential scanning calorimetry. The enthalpy of the O−H···O intermolecular hydrogen bonds present in the crystals of syringaldehyde was determined.

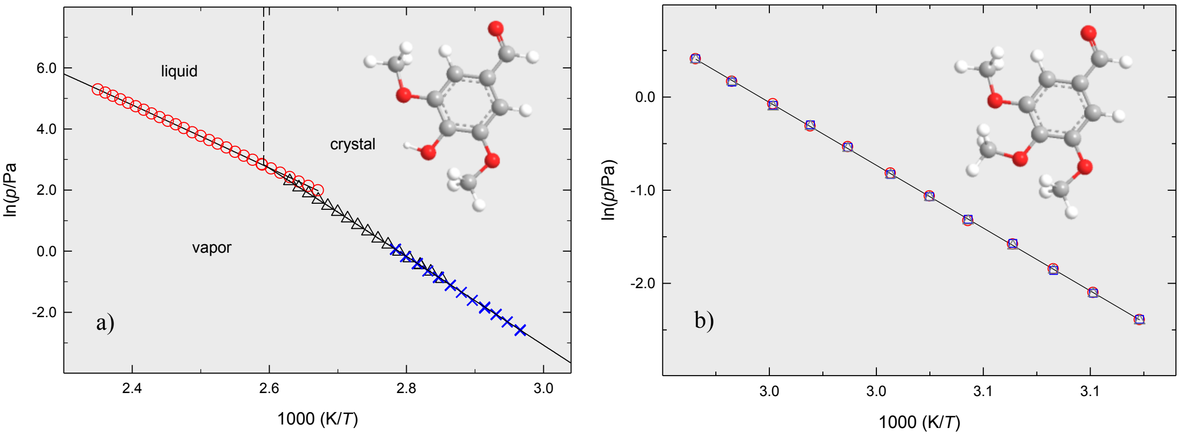

Figure 1. a) Phase diagram of syringaldehyde: ○, vaporization (static); Δ, sublimation (static); ×, sublimation (Knudsen effusion). b) Plot of vapor pressures against reciprocal temperature for 3,4,5-trimethoxybenzaldehyde: ○, small; □, medium and Δ, large effusion orifices.

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Thermochemical study of γ-lactone derivatives

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This work is part of a project whose main objective is the development of experimental and computational studies to provide accurate structural, thermodynamic and electronic properties of fragrances, to fill data gaps for most of these kind of compounds, building a solid data base information to design robust and accurate group contribution models allowing to estimate reliably properties of other related compounds. From this knowledge, it will be possible to do a correct prediction of fragrances environmental partitioning (air, water and biota) and consequently to take preventive actions and solve problems [1].

The γ-lactones are an important class of fragrance compounds found in a wide variety of products we use every day. Results from experimental and computational thermochemical studies for γ-butyrolactone and γ-valerolactone (figure 1), are reported. Experimentally, static bomb calorimetry was employed to measure their standard molar energies of combustion, at T = 298.15 K, while high temperature Calvet microcalorimetry was used to obtain their standard molar enthalpies of vaporization, at the same temperature. The results gathered from these experimental techniques were used to derive the standard molar enthalpies of formation of the two γ-lactone compounds, in the gaseous state, at T = 298.15 K. These parameters were also estimated from G3(MP2)//B3LYP calculations for the enthalpies of hypothetical reactions, as common practice in computational thermochemistry.

The values of the experimental and computational enthalpies of formation of each compound in the gaseous phase will be compared and discussed. The structural changes and the energetic costs, associated with the substitution of the hydrogen's ring by a methyl group will be analyzed.

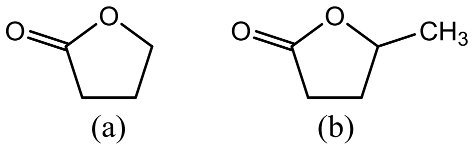

Figure 1. Molecular structure of γ-butyrolactone (a) and γ-valerolactone(b).

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Thermodynamic properties of *o*-phenanthroline and *o*-phenanthroline monohydrate

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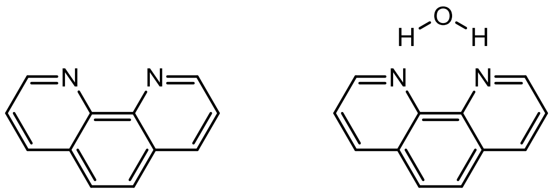
o-Phenanthroline has key geometric and chemical properties, as rigidity, planarity, aromaticity, basicity and chelating capability. Owing to the last property, o-phenanthroline is a classic bidentate ligand in coordination chemistry, being able to coordinate metal centers through the nitrogen atoms (Figure 1).

It is well known that the absorption or adsorption of water molecules in the structure of one compound can affect its physical-chemical properties. The current study addresses a thermodynamic study regarding *o*-phenanthroline and *o*-phenanthroline monohydrate, based on both experimental and computational research, with the main goal of evaluating the thermodynamic effects for the hydrate formation.

The experimental techniques used were the Calvet microcalorimetry and static bomb combustion calorimetry aiming, respectively, the determination of the enthalpy of sublimation and of the massic energy of combustion of the title compounds. These quantities were used to derive its enthalpy of formation in crystal and gas phases, at T=298.15 K.

The computational calculations performed with the composite G3(MP2)//B3LYP approach, based on the Gaussian-N theory, enabled the optimization of the structures, computation of their vibrational frequencies and of their energy at 0 K and their absolute enthalpies at 298.15 K. The previous quantities were combined with the calculated absolute enthalpies of the compounds in hypothetical reactions in the gas-phase, allowing the computation of the gas-phase standard molar enthalpy of formation, at 298.15 K, of the title compounds.

The experimental and computational enthalpies of formation will be discussed and compared. The thermodynamic effects for the hydrate formation of *o*-phenanthroline will be also performed.



(a) (b)

Figure 1. Molecular diagram of *o*-phenanthroline (a) and *o*-phenanthroline monohydrate (b).

Acknowledgements: This research was developed within the scope of the projects UID/QUI/00081/2013, POCI-01-0145-FEDER-006980, and NORTE-01-0145-FEDER-000028, awarded to CIQUP, financed by FCT, Lisbon, Portugal, and co-financed in the framework of COMPETE, with community funds (FEDER) and national funds of MEC. Vera Freitas is financed by national funds through the FCT - I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

Molecular structure and plastic crystal formation ability of 1,2-dichlorocyclohexane isomers

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Plastic crystals, first recognized by Timmermans [1], are mesophases displaying positional order but having orientational disorder. This mesophase has small melting entropies (less than 2.5R) and transitions from/to other crystalline phases with high enthalpies [1].

In our research group, research has been carried out concerning the relationship of molecular and crystalline structures and the ability to give rise to plastic crystal mesophases. Di-substituted hydroxylated cyclohexane derivatives have been the object of study [2-6].

In this communication, the investigation was extended to two dichloro substituted cyclohexane derivatives, *cis* and *trans* 1,2-dichlorocyclohexane. A combined approach using differential scanning calorimetry, polarized light thermomicroscopy and X-ray powder diffraction has been employed in the results interpretation.

The results confirm the plastic crystal forming tendency observed for cyclohexanediol isomers: the co-existence of axial and equatorial substituents in the same molecule favours the formation of plastic crystal phases. In fact, for *cis*-1,2-dichlorocyclohexane, with one chlorine atom in axial position being the other one equatorial, a plastic crystal mesophase was identified, as for *cis*-1,2, *trans*-1,3 and *cis*-1,4 cyclohexanediols [2-5]. For *trans*-1,2-dichlorocyclohexane, whose substituents must be both either equatorial or axial, three polymorphic forms were found, but no mesophase was identified. This was also observed for *trans*-1,2, *cis*-1,3 and *trans*-1,4 cyclohexanediols, which share the same substituent orientation [2-4,6].

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Novel solid forms of a recent anti-rheumatic drug: solid state characterization and intrinsic dissolution rate evaluation

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Pharmaceutical co-crystals, combining an API and an acceptable co-former [1], have the potential for enhancing the physical properties of the API by impacting its solubility, stability, oral bioavailability and processability, without compromising its biological function [1,2]. Thus, co-crystal formation research has special interest for the pharmaceutical industry, especially for those APIs whose oral bioavailability is solubility-limited.

In this work the co-crystallization of iguratimod (IGU), an API with poor aqueous solubility, approved in Japan and China [3] for treatment of rheumatoid arthritis, with pyridinecarboxamide isomers and benzamide was investigated. Co-crystallization was successfully undertaken with nicotinamide (NIC), picolinamide and benzamide but not with isonicotinamide, which is not typical. Co-crystal synthesis was achieved by liquid assisted grinding and the solids obtained were characterized by differential scanning calorimetry, polarized light thermomicroscopy, infrared spectroscopy, powder X-ray diffraction and single crystal X-ray diffraction.

The crystalline structure of the iguratimod:nicotinamide (1:1) co-crystal was solved. Iguratimod dimers linked by the sulfonamide groups are present in the structure, as well as nicotinamide amide-amide centrosymmetric dimers. Both dimers are linked together by $\text{N-H}_{\text{NIC}}\cdots\text{O=C}_{\text{IGU}}$ and by $\text{N-H}_{\text{IGU}}\cdots\text{N}_{\text{aromatic,NIC}}$ hydrogen bonds. This co-crystal can be of particular relevance because nicotinamide, a water-soluble vitamin and a member of the vitamin B group, is a Generally Regarded as Safe Substance, GRAS. The intrinsic dissolution rates of both iguratimod and IGU-NIC co-crystal were evaluated.

An investigation on the polymorphism of iguratimod was also carried out and shows its propensity to crystallize in different crystal packing arrangements, being three polymorphic forms unquestionably identified.

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Thermochemical *vs* structural studies on hydroxyl-indanone derivatives

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Thermochemical processes for biomass conversion are used to convert biomass into "energy products", as heat and electricity, transport fuels, and other chemicals [1]. Specifically, concerning the chemicals, the knowledge of accurate thermochemical data for the chemical transformations constitutes a crucial contribution in guiding experimental investigations to produce valuable chemicals from biomass. In this context, our research group is involved in a broad experimental and theoretical study over key compounds that can be derived from biomass [2,3].

The present work involves an experimental and computational study of thermodynamic properties of hydroxyl-indanone derivatives, namely 6-hydroxy-1-indanone and 7-hydroxy-1-indanone. The standard molar enthalpies of formation in the gaseous state, at $T = 298.15$ K, for both compounds were derived from their standard molar energies of combustion and their standard molar enthalpies of vaporization, obtained from static-bomb combustion calorimetry and high-temperature Calvet microcalorimetry, respectively. High level ab initio calculations were also performed to obtain the gas-phase standard molar enthalpy of formation of these compounds. The results are compared and discussed.

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PS2.077

Contribution for the thermodynamic study of anthranilate derivatives

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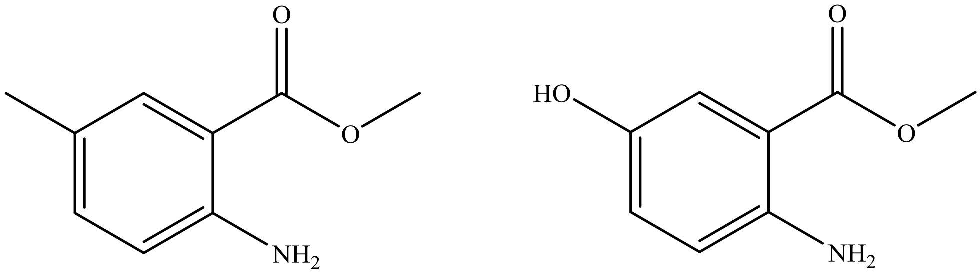
The olfactory properties of fragrances make them desirable ingredients for products like perfumes, essential oils, shampoos and cosmetics, among many others. However, the everyday use of fragrance products as well as their presence in various environments constitute a concern in understanding their reactivity [1-3].

The aim of this work is to evaluate and discuss the energetic properties of methyl 2-amino-5-methylbenzoate and methyl 5-hydroxyanthranilate (Figure 1), performing experimental and computational studies.

This communication reports the massic energies of combustion of methyl 2-amino-5-methylbenzoate and methyl 5-hydroxyanthranilate, measured by static bomb combustion calorimetry. The corresponding enthalpies of sublimation were measured by both Calvet microcalorimetry and Knudsen effusion techniques. These results are used to derive the enthalpy of formation of the anthranilate derivatives, in the solid and gaseous phases, at $T = 298.15$ K.

The values derived from the experimental measurements and computational studies of methyl 2-amino-5-methylbenzoate and methyl 5-hydroxyanthranilate, will be analysed.



a) b)

Figure 1. Structural formula for a) methyl 2-amino-5-methylbenzoate and b) methyl 5-hydroxyanthranilate.

Acknowledgements: Thanks are due to Fundação para a Ciência e Tecnologia (FCT) of Portugal, Project UID/QUI/UI0081/2013 and FEDER Projects POCI-01-0145-FEDER-006980. C.A.O.S. thanks FCT for the doctoral grant SFRH/BD/137672/2018.

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Thermal analysis of Ga and In acetylacetonate powders

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Additives as metal-acetylacetonate can provide elements to substitute in the crystal lattice of MgB_2 or they can generate specific composite microstructures with formation of nano precipitates. Both situations will influence superconducting properties. Namely, substitutions will promote local lattice distortions acting as pinning centres, while composite microstructure will influence connectivity, on one hand, and grain boundaries, residual stresses, and nano-precipitates acting as effective pinning centers, on the other hand. High connectivity and introduction of pinning centres push the critical current density to higher values making possible fabrication of different superconducting applications based on MgB_2. Such positive effects were observed in our previous works in which we explored for samples produced by spark plasma sintering the influence of different additives [1]. Understanding of the additives behaviour versus temperature is important in selecting technological parameters for fabrication of an added MgB_2 bulk material with desired or improved properties.

In this work are presented results of differential thermal and thermo-gravimetric analysis (DSC-TG) in the temperature range 20 - 600 °C on the In and Ga acetylacetonate. The heating and cooling rates were of 10 °C/min. Experiments were performed in argon flow since a similar atmosphere is used in SPS fabrication of MgB_2. During heating, both investigated substances have shown a two-step transformation into a metallic residue. Curves shape is similar but endothermal peaks are at different temperatures of 193 and 313°C for the In and 202 and 311°C for the Ga acetylacetonate, respectively. Weight loss ends at 320-340°C for both materials.

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New nickel (II) complexes with mixed ligands as potential antimicrobial agents

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Coordination compounds with mixed ligands, carboxilato ions and pyrazole derivatives, are interesting due to different proprieties associated with each type of coordinated moieties. The presence of carboxylato ligands can lead to surprising structures because of their various bonding modes (unidentate, bridging bidentate, chelate) as well as their possibility to be involved in hydrogen bonds. Pyrazole derivatives, on the other hand, are known for their biological activities such as antitumor, antimicrobial, antiviral, anti-inflammatory, antipyretic, antihistaminic, anticonvulsant, antidepressant, insecticides and fungicides [1].

Transition metal complexes with pyrazole derivatives have been the subject of some recent reports having in view their potential application as anticancer agents, catalysts and metallomesogens [2,3]

Extending our interests in the coordination chemistry of transition metal complexes containing azole type ligands and acrylate ions, we report herein the results obtained in synthesis and characterisation of new nickel (II) complexes with the general $[Ni(RPz)_2(acr)_2(H_2O)_x]$ (RPz: pyrazole derivatives, x:1 or 2).

Their chemical formulation was achieved on results provided by chemical analysis, mass spectra and thermal analysis data. The coordination modes of the ligands were assigned by FTIR measurements while the octahedral geometry of Ni(II) in complexes were assigned on the basis of NIR-UV-Vis spectra. The biological assays were performed on several microbial strains.

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Structure and thermal behaviour of a new co-crystal containing melamine

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Melamine (MA) and triazine derivatives can lead to high molecular weight complexes by self-assembly due the intramolecular networks of hydrogen bonds and π-π stacking interactions. [1]

The supramolecular complexes resemble in many respects the natural ones, especially with melanin: similar dimensions, the coplanarity of the monomer units, the ability of the amino, carbonyl or hydroxyl groups to coordinate various transition metal ions. [2]

Despite the large number of nitrogen atoms that could form complex combinations in which melamine can act both as a monodentate, bidentate and polydentate ligand, studies on its coordination chemistry have proven to be very poor in terms of number and diversity of synthesized compounds.

Having in view the interesting structures of compounds containing melamine, we intended to synthesize coordination compounds of nickel (II) with 2,2'-bipyridine (bipy) and melamine as co-ligands, starting from nickel acrylate ($Ni(acr)_2$). The result, a co-crystal of the used species, $[Ni(acr)_2bipy(H_2O)]\cdot MA$, was characterized by using IR, UV-Vis, thermogravimetric analysis and single crystal X-ray diffraction (Fig. 1).

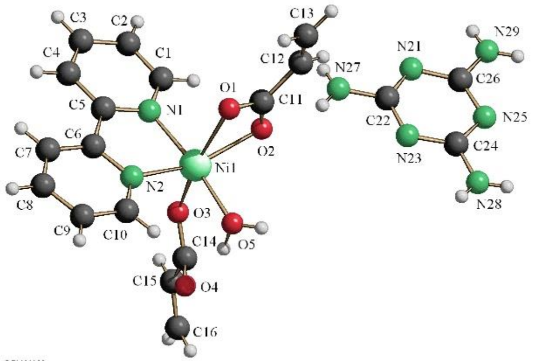

Fig. 1 Molecular structure of $[Ni(acr)_2bipy(H_2O)]\cdot MA$

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Thermal behavior of magnetorheological fluid, integrated within an innovative spherical joint system

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Smart fluids offer several additional degrees of freedom due to the change in viscosity by the action of the electromagnetic field. Stop-valves that are implemented at the sub-assembly permit, through continuous variation of energization, to control the relative movement of the components of a system; amongst them the smart fluid can provide a variable degree of compliance. The resultant structure is similar to a micro-clutch system with a continuous variation in the coupling degree, which allows for the development of innovative articulation systems. The realization of such a system by the authors of this paper requires a complex study not only of the proposed architecture, but also of the intelligent fluid stability that provides a complex joint control. Fig. 1 shows analysis curves of the MRF122 smart magnetic-rheologic fluid [1]. The fluid is thermally stable up to 180 ºC, and at higher temperatures it breaks down, losing the solvent initially, and then oxidizing the magnetic component.

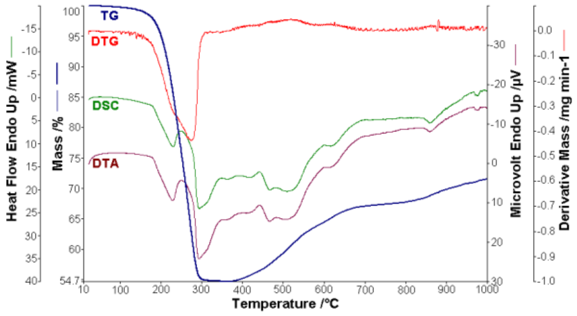

Fig. 1 Thermal analysis of MRF122

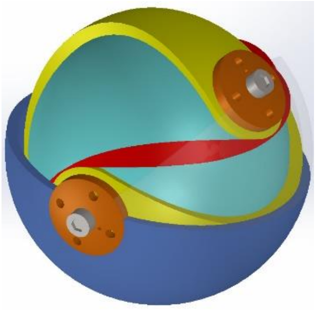

Fig. 2 Architecture of spherical joint based on MRF122

The joint shown in Fig. 2 is composed of two concentric spherical caps between which a movable element is immersed in a magnetorheological fluid for each axis of rotation. The displacement of the element through the fluid is possible due to its sieve structure. Each perforation of the sieve element constitutes a stop-valve. The stop-valve used is made up of two magnetic poles placed on the side of the fluid flow channel. By controlling the intensity of the generated magnetic field, one can control the flow rate of the fluid through the moving element and its dynamics respectively. Under exposure to the magnetic field, the fluid changes the flow rate inversely proportional to the field strength.

The smart fluid was analyzed in time, hitting the way it responds after a minimum of energization. This joint easily adapts to human orthoses or prostheses, hyper-redundant robots and any industrial application in high temperature environments.

[1] MRF-122EG Magneto-Rheological Fluid, Lord Technical Data

Preparation and characterization of stable colloidal suspensions based on magnetic iron oxide nanoparticles obtained by combustion synthesis

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The unique physical, chemical and mechanical properties of superparamagnetic iron oxide nanoparticles offer them a high potential for applications in multiple branches of medicine such as: cellular therapy, tissue repair, drug delivery, magnetic resonance imaging (MRI), hyperthermia etc. [1]. The stabilization of iron oxide nanoparticles is an essential factor to obtain colloidal suspensions, which should be stable against aggregation in both a biological medium and a magnetic field.

The aim of this work was to achieve stable colloidal suspensions of magnetic iron oxide nanoparticles dispersed in phosphate buffered saline (PBS) and in distilled water respectively.

The magnetic iron oxide nanoparticles were prepared via combustion synthesis [2], using iron nitrate (III) nonahydrate as oxidizer and citric acid as a fuel or a reducing agent. The redox reaction was ignited using a heating mantle and a microwave oven, respectively.

Iron nitrate was mixed in stoichiometric molar ratio with the fuel according to the reaction:

$6\ Fe(NO_3)_3 + 5\ C_6H_8O_7 \rightarrow 3\ Fe_2O_3 + 30\ CO_2 + 20\ H_2O + 9\ N_2$

The as obtained magnetic nanoparticles were coated with oleic acid and Tween 80, respectively and their stability was comparatively discussed. The phase composition of the magnetic nanoparticles was investigated by X-ray diffraction and FTIR spectroscopy and the thermal behaviour was studied by thermal analysis (TG/DSC). Specific surface area of the obtained powders was measured by nitrogen adsorption. The morphology and structure of both magnetic nanoparticles and colloidal suspensions were examined by SEM and TEM analyses. The hydrodynamic diameters of the colloidal suspensions were characterized by dynamic light scattering. The magnetic properties of both magnetic nanoparticles and colloidal suspensions were measured at room temperature.

Acknowledgments

This work was supported by a grant of Ministery of Research and Innovation, CNCS -UEFISCDI, project number PN-III-P4-ID-PCE-2016-0765, within PNCDI III.

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Thermal stability, physical properties and biological activity of bis [(phenyl azo) biphenyleneoxymethylene] anthracene

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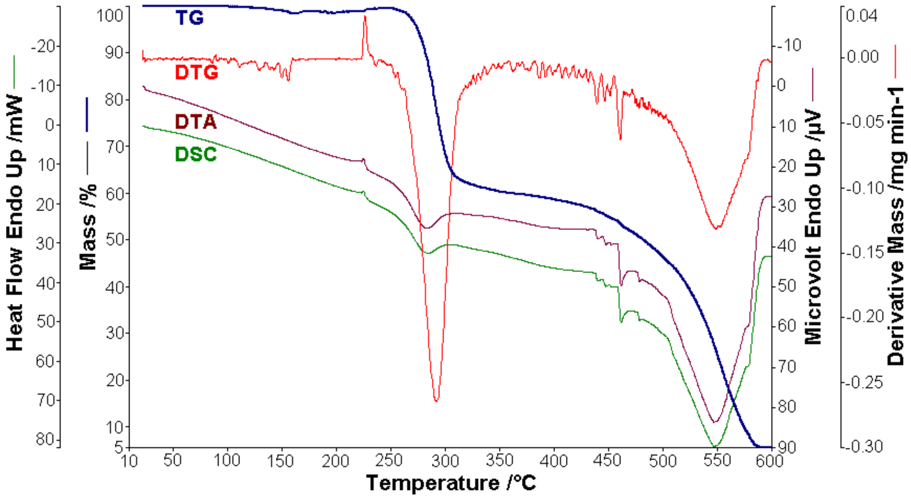
Bis (phenylazo) phenyleneoxymethylene] anthracene (BPBA) and its four derivatives were prepared by condensing of 9,10-bis (chloromethyl) anthracene with the sodium salts of 4-hydroxy-4’-(3,4-dichloro-phenylazo)-diphenyl, 4-hydroxy-4’-(4-chloro-phenylazo)-diphenyl, 4-hydroxy-4’-(4-methyl-phenylazo)-diphenyl, 4-hydroxy-4’-(2-chloro-phenylazo)-diphenyl and 4-hydroxy-4’-phenylazo-diphenyl [1].

Anhydrous sodium salts were prepared by reacting 4-hydroxy-4'-phenylazo-diphenyls with sodium hydroxide in an ethanol-benzene medium (1:1 by volume). In addition, the nucleophilic attack of the phenoxy anion on the bischloromethylate derivative results in the formation of the bisazobisester [2]. The results of spectral analyzes (in visible and IR) confirmed the composition and structure of the studied compounds [1].

This study extends the study of these compounds by determining the thermal stability, properties and biological activity of the compounds. Thus, measurements were made in UV, atomic fluorescence and refractive index. The existence of the birefringence property of the compounds, when illuminated by polarized light, was verified.

To determine the thermal stability of the compounds, their thermal analysis was performed on the RT-600 °C temperature range. Measurements were performed in air at a heating rate of 10 K/min with a PerkinElmer DIAMOND TG/DTA thermobalance.



All analyzed compounds are stable at temperatures above 250 °C. The antioxidant activity of the compounds as well as their interaction with some common proteins were determined.

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New biologically active Co(II), Ni(II) and Cu(II) complexes containing a tridentate ONN sulfathiazole-based Schiff base: Synthesis, spectral study and thermal behaviour

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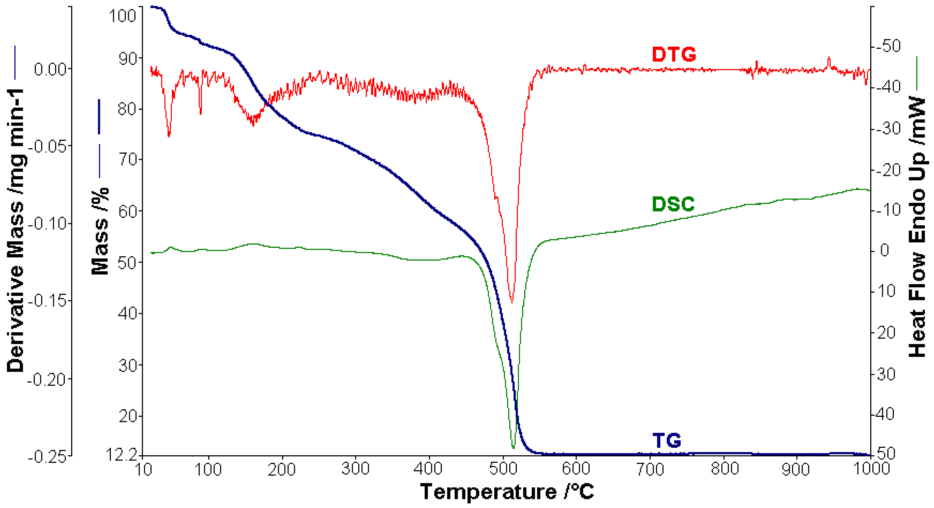
Schiff bases are a significant class of chelating agents in coordination chemistry because of their versatility and ability to form easy stable complexes with different transition metals. In the last years, interest in Schiff bases derived from sulfonamide antibiotics with transition metal complexes has increased due to their potential applications in chemistry, biology and medicine [1]. New Co(II), Ni(II) and Cu(II) complexes were synthesized with the Schiff base ligand obtained by the condensation of sulfathiazole with salicylaldehyde. They were characterized by elemental analysis, molar conductance, spectroscopic techniques (IR, DRUV), magnetic moments, thermal (TG/DTG/DSC) and powder X-ray diffraction data to explicate their structure. The results obtained showed that the complexes had composition of $[ML_2]\cdot nH_2O$ type being nonelectrolytes [2]. The IR data confirmed that the Schiff base ligand is tridentately coordinated to the metallic ions with two N atoms from azomethine group and thiazole ring and one O atom from phenolic group. An octahedral geometry was proposed for the three complexes. TG experiments revealed the thermal stability of metal complexes and confirmed their compositions suggested by the analytical data (Figure).



In addition to experimental data molecular modeling study has been made and present the optimized geometries of metal complexes. The powder XRD and SEM studies show that all the complexes are nanocrystalline.The Schiff base and its metal complexes were tested against various types of bacteria.

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Solid-state compatibility study between prednisone and pharmaceutical excipients

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Prednisone (PSONE) is a synthetic glucocorticoid first used in clinical trials in 1954. Its biological activity proved to be up to five times higher than the one obtained for this type of natural steroid hormones [1]. PSONE is a prodrug of prednisolone, the metabolic active compound with a wide range of therapeutic applications including autoimmune disorders, transplant rejection, chronic adrenal insufficiency, rheumatic or renal disorders, allergies, asthma, cataracts and many others [2]. Because of the poor solubility of the compound and its numerous clinical uses, new formulations are researched constantly in order to assure a high bioavailability upon administration and good patient compliance to the treatment [3].

The goal of the present study was represented by a compatibility evaluation between the active pharmaceutical ingredient (PSONE) and several excipients commonly used in various formulations, including Starch (Fig.1.). 1:1 mass ratio binary mixtures were prepared and investigated using thermal analysis (TG/DGT/HF) and FTIR spectroscopy in order to determine if any interactions occur when the compounds are used in the same formulation.

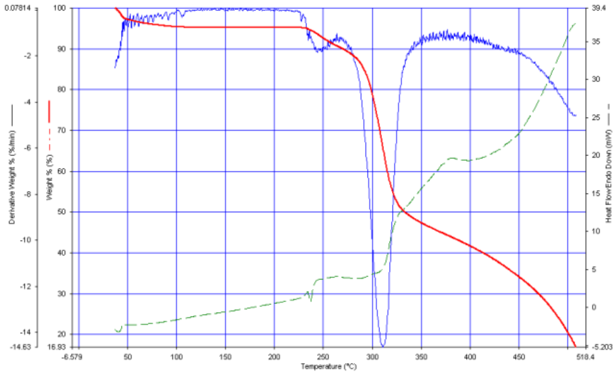

Fig.1. TG/DTG/HF curves obtained at $\beta = 10\ °C\cdot min^{-1}$ for binary mixture PSONE+Starch

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Thermal analysis and molecular modelling of inclusion complexes containing artesunate

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The formation of guest-host inclusion complexes containing cyclodextrins is a method that presents great interest in the pharmaceutical field since the obtained complexes are usually more soluble in water and present a higher stability, that in turn can determine a longer shelf life for the manufactured formulations [1]. Artesunate (ATS – fig.1.), a derivative of the antimalarial artemisinin, contains the main sesquiterpenic structure with the characteristic endoperoxide bridge of artemisinin, but the presence of the dicarboxylic external acid that forms an ester bond with the tetrahydropyran ring [2] confers the derivative a higher water solubility [3]. Utilizing this property, the use of ATS expanded beyond the initial antimalarial to the more recently researched anticancer properties [4]. Promising results regarding not only the improved solubility but also an increased cytotoxic effect on several cell lines were presented in literature for inclusion complexes [5].

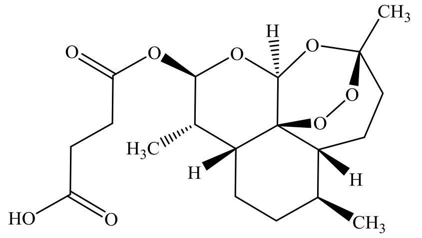

Figure 1. The chemical structure of ATS

Because of these aspects, the present study aims to evaluate the formation and thermal stability of five guest-host inclusion complexes obtained between ATS and different cyclodextrins, namely α-cyclodextrin (CD_1), β-cyclodextrin (CD_2), γ-cyclodextrin (CD_3), (2-hydroxypropyl)-β-cyclodextrin (CD_4) and (2-hydroxypropyl)-γ-cyclodextrin (CD_5).

The complex formation was evaluated using FTIR spectroscopy and thermal analysis (TG/DTG/HF) using a heating rate of 10 $°C \cdot min^{-1}$ and the determination of the most suitable arrangement of the active substance (ATS) in the cavity of each cyclodextrin was realized employing molecular modelling.

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Dynamic mechanical properties of polyhdroxybutirate reinforced with cellulose microfibrils

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Short-chain length polyhydroxyalkanoates such as poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) are fabricated on the industrial scale and are already used for some biomedical and packaging applications [1]. PHB is obtained from renewable resources, is biodegradable and biocompatible and exhibits some mechanical properties similar to that of common synthetic polymers. However, PHB is brittle and difficult to melt process. Plasticizers, elastomeric polymers, organic or inorganic fillers were used to correct the properties of PHB [2,3]. Among fillers, cellulose nanofibers or nanocrystals have been mostly tested to improve the properties of PHB [2,3]. However, both PHB and nanocelluloses are expensive and the use of cheaper fillers is demanded in most packaging or wound dressing applications.

Wood waste such as sawdust or wood chips may be a valuable source for cellulose microfibrils. In this study, cellulose microfibrils (CM) were obtained from sawdust using mechanical treatments (milling in a colloid mill and in a ball mill). PHB was plasticized with acetyl tributyl citrate (ABC) and reinforced with cellulose microfibrils in different concentration. PHB/CM composites were obtained by melt compounding and the influence of CM concentration and plasticizer addition on the thermal and mechanical properties of PHB was studied. The addition of cellulose microfibrils increased the storage modulus and the thermal stability of PHB and shifted the glass transition to a higher temperature at 10% CM concentration. Increased amount of plasticizer has as result an important decrease of the mechanical properties. Biodegradable composites with good mechanical properties and competitive price may be obtained starting from PHB by optimizing the concentration of plasticizer and cellulose reinforcement.

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Thermal and morphological characteristics of poly(l-lactic acid)/organic–inorganic hybrid nanocomposites

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Poly(lactic acid) (PLA), one of the most popular biodegradable polymers, is a linear aliphatic thermoplastic polyester that has been intensively studied and widely used for biomedical applications because of its high biocompatibility and biodegradability [1,2]. Despite the extensive research, the wider application of PLA in biomaterials has been limited by its slow crystallization, low thermal stability and excessive brittleness [1,2]. An efficient way to improve PLA properties is the addition of nanofillers. Among them, three-dimensional polyhedral oligomeric silsesquioxanes (POSS) nanofillers could be a promising choice. POSS derivatives are organic–inorganic hybrid materials characterized by the general formula $(RSiO1.5)_n$, where n is an integer number and R is an organic group. Besides their nanoscale dimensions, POSS fillers are biocompatible and recyclable, non-flammable, non-abrasive and non-migrating [3]. In this work, three types of POSSs with different structure were incorporated into a poly(l-lactic acid) matrix (PLLA) by a melt mixing method: trisilanol-isooctyl polyhedral oligomeric silsesquioxanes (TSio-POSS) with an open cage structure, allyl-heptaisobutyl (ALib-POSS) and aminopropyl-heptaisobutyl (APib-POSS) polyhedral oligomeric silsesquioxanes with a close cage structure. The effect of POSSs on the morphological, thermal mechanical and surface properties of PLLA/POSSs nanocomposites were evaluated by atomic force microscopy (AFM), thermogravimetric analysis, differential scanninig calorimetry (DSC), dynamic mechanical analysis (DMA) and water contact angle measurements. AFM showed a good distribution of self-assembled POSS molecules in the polymer matrix. The addition of POSSs had a positive effect on the thermal stability of PLLA matrix, both T_{on} and $T_{5\%}$ being enhanced depending on the POSSs structure. POSS acted as plasticizers lowering the E' of PLLA matrix in the glassy region and increased the E' above the glass transition temperature (T_g) except for TSio-POSS. In summary, the use of POSS proved to be efficient in overcoming PLA drawbacks.

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Thermal and mechanical properties of TiMnAlSnZrC alloy obtained from nanopowders

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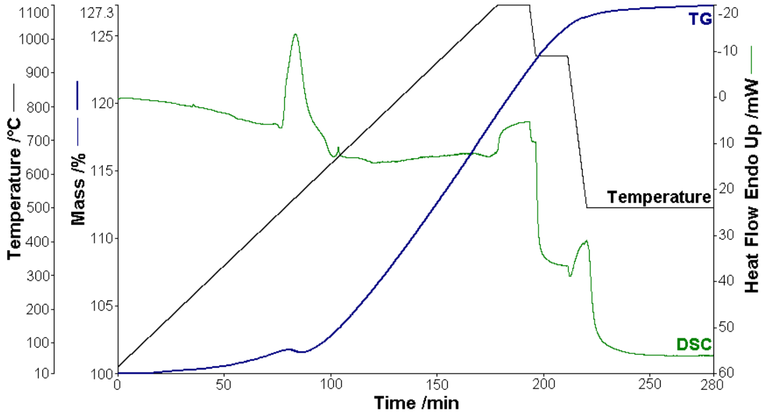
The alloy studied in this paper is obtained by powder metallurgy technology using a nanometric powder. The manufacturing technology starts from elemental powders of TiH2, Mn, Al, Sn, Zr and graphite that are mixed in a ball mill for 60 minutes [1]. This time is enough for the mixture to go from micrometric to nanometric dimensions. From the obtained mixture, the unilateral samples were compacted in a steel die and then sintered in four different ways, the maximum temperature being 1050° C [2]. Common to the four cycles is the fact that the heating rate was the same, the sintering time the cumulative was 90 minutes and argon was the atmosphere used in all cases. All the thermally analysed samples were heated under the same technical conditions as the sintered samples. The paper presents morphological analyses, SEM analyses, thermal analysis, as well as analysis of wear behaviour. The alloy studied can be used in the manufacture of aerospace and automotive components [3].

The Figure is the representation of the last heat treatment, the sample suffering more gravimetric and caloric effects.



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Thermal investigation of zeolitic materials synthesized from fly ash

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In this paper, is present the innovative procedure to compare different activation methods of fly ash by thermal analysis. For obtaining zeolitic materials from power plant fly ash are used different methods: direct activation, fusion and ultrasound [1, 2]. In this study, we present the samples synthesised in conditions: 20°C time 7 days, direct activation at 70°C, 90 and 125°C, 4, 8 and 12 h and ultrasound method at 70°C, 1 h respectively 2 hours [3, 4]. After modification the samples were cooled and crystallized at 20°C for 24 h. Fly ash and synthetized materials were characterised by: SEM/EDAX (Quanta 3D - AL99/D8229), XRD (X'Pert PRO MRD X-ray diffractometer), BET (Quanta-chrome Instruments), FT-IR (DIGILAB FTS 2000), thermal analysis (METTLER TOLEDO TGA/SDTA 851, the temperature 20 to 1000 °C, 10°C/60s).

According to the experimental results the synthesised materials have a BET surface between 21-122 m^2/g, bigger than fly ash 7 m^2/g [4]. The FT-IR and XRD analysis demonstrated that the ash contains: quartz, kaolinite, mullite, hematite and vitreous phase. In synthetized materials were found phases: quartz, analcime, sodalite, chabazite, faujasite, Na-Y, tobermorite etc. For fly ash thermal analysis demonstrated that the weight loss have three-stages and total weight loss was 6.52%. Experimental data demonstrated that the weight losses are higher for samples obtained by direct activation, that corroborate with other experiments demonstrated that the zeolite synthesis is more efficient in direct activation method. In this case were found four stages of weight losses, and total loses was up to 23.84%, function of activation conditions. The materials obtained by ultrasound method have two stages weight losses. The DTG/DTA curves permit to determine the amount and nature of zeolite. The endothermic and exothermic peaks, offer information regarding: the dehydration, amorphization/ recrystallization process. For all samples were observed an endothermic peak in the range 300–475°C due to loss of zeolitic water, and small exothermic peaks at higher temperatures due to zeolite destruction and crystallization of new phases. Thermal analysis permits fast identification of the synthetized zeolites and elucidation of the processes occurs during the thermal heating, for establishing of the better fly ash activation method. All experimental investigation enabled the clarification of the physicochemical process occurring during zeolites heating and the determination of the thermal stability of the synthesized materials.

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Bismuth-doped hydroxyapatite coatings on titanium implants

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The hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, a calcium phosphate ceramic, is the most important inorganic component of human hard tissues such as bone, dentine and enamel [1]. Synthetic hydroxyapatite is used in reconstruction and repair surgery, conservative dentistry and dental implantology. Hydroxyapatite is widely used as a coating of metallic implants for bones and teeth in order to improve and accelerate the osseointegration process. An important feature of the hydroxyapatite is that its structure allows the incorporation of a wide range of different foreign ions [2]. The introduction of even small quantities of some ions (Na^+, Zn^{2+}, Mg^{2+}, Ce^{3+}, Y^{3+}, Ti^{4+}, etc.) in the hydroxyapatite structure may increase the osteoblast adhesion and enhance properties of the hydroxyapatite pertinent to the orthopedic and dental applications [3-5].

This study makes evident the possibility of the Bi-doped hydroxyapatite to be deposited on the titanium implant surface by a solution-derived process according to an established biomimetic methodology. In order to increase the bioactivity of the titanium surface an alkali ÷ thermal oxidation treatment has been applied. Titanium implants were then coated with a Bi-doped hydroxyapatite layer under biomimetic conditions by using a supersaturated calcification solution (SCS) modified by adding a bismuth salt. The apatite deposits were investigated by means of scanning electron microscopy coupled with X-ray analysis (SEM-EDX), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and digital X-rays radiography method. The obtained results confirmed that the hydroxyapatite coatings on titanium surface were produced and bismuth ions incorporated into hydroxyapatite lattice. The Bi-doped hydroxyapatite coatings exhibit radiopacity, enhancing thus their applications in dental and orthopedic fields. These coatings show antimicrobial activity against Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* bacteria.

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Thermal/spectral analysis of archaeological objects

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Modern analytical methods play an important role in archaeological objects, and for their characterization different analytical techniques have been used in time. The thermal analysis methods (TG, DTA, DSC) help at heritage materials characterization and for qualitative distinction between heritage materials and heritage items, as well as for assessing the deterioration degree of them as a result of natural aging, since buildings and monuments act as repositories of airborne pollutants, the chemical composition of black crusts directly reflects the surrounding atmospheric environment [1]. Thermal analysis techniques provide a wealth of compositional information and thermal behaviour. Thermogravimetry (TG), Derivative Thermogravimetry (DTG) and Differential Scanning Calorimetry (DSC) are examples of the analytical methods that find application in the field of art and archaeology.

This paper focuses on the use of analytical methods such as: Fourier transform infrared spectroscopy, powder X-ray diffraction with thermal analysis to study the chemical and mineralogical composition of archaeological samples and organic residues preserved inside. In this paper, special attention was paid to the TG/TGA/DSC method, which allows the determination of characteristic of the surface of some ceramic samples from Hunedoara area [2]. The settlement from the Hunedoara – the Court area was discovered in the 70s and a series of ceramic fragments discovered in this area is mostly coarse and belong to the same the cultural horizon, with colors ranging from brick or orange to brown and black. Sporadically, ceramic fragments were burnt in the black-topped technique. The study is intended to identify the firing temperature, firing conditions and morphology of the ancient pottery samples. TG-DTA is considered the complementary technique to elucidate the firing temperature from the thermal characteristic reactions such as dehydration, decomposition and transformations of minerals in the course of controlled firing of the samples. The results showed that all the samples fired in a oxidizing condition and firing temperature also inferred.

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Thermal analysis and kinetic degradation study for corticosteroid drug fludrocortisone

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Fludrocortisone (FCSONE – Figure 1) is a synthetic fluorinated derivative of cortisol used for its mineralocorticoid activity in the treatment of Addison’s disease, orthostatic hypotension and salt-losing adrenogenital syndrome [1]. It is administered orally, formulated mostly as tablets containing the acetate salt [2]. Because of its beneficial effects, other formulations such as orally administered solutions and ointments are being researched [3,4] and a complex evaluation on the stability and behaviour under various thermal conditions of FCSONE is necessary.

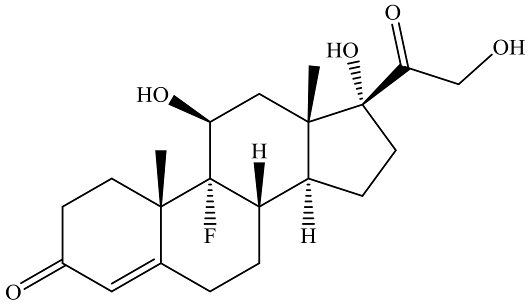

Figure 1. Chemical structure of FCSONE

The solid-state stability of fludrocortisone was evaluated using thermal analysis. The obtained data was collected using five different heating rates β = 5, 7, 10, 12 and 15 $°C\cdot min^{-1}$ and was later analyzed as to determine the values of the activation energies. Three isoconversional methods were used for this purpose, namely Kissinger–Akahira–Sunose, Flynn-Wall-Ozawa and Friedman, while the NPK method was afterwards employed to differentiate the chemical and physical processes that occur during thermal treatment.

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Thermal stability and kinetic degradation study for dihydroartemisinin

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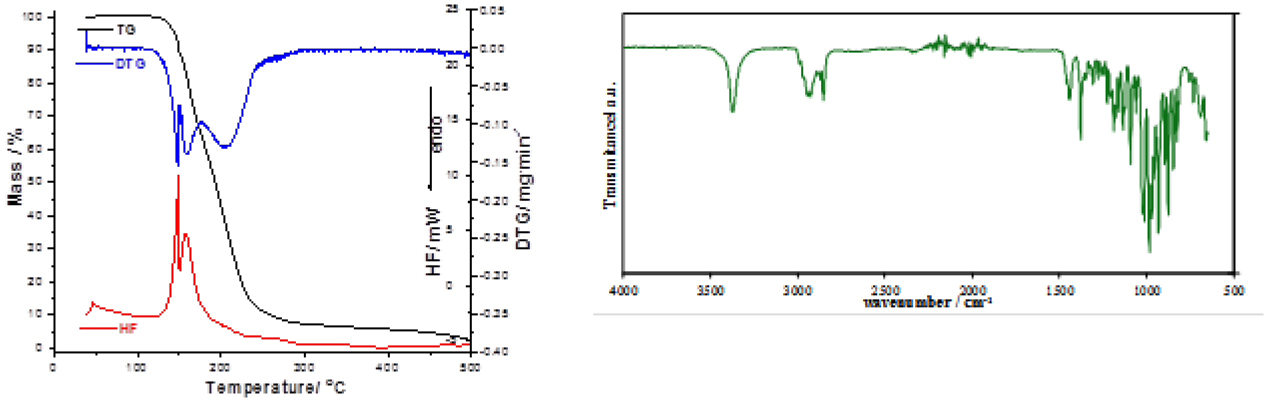
Dihydroartemisinin (DHA) or artenimol is the hydrogenated derivative of artemisinin used in the treatment of *Plasmodium falciparum* infections [1] and researched for its cytotoxicity, alone or in combination with ferrous salts or holotransferrin, but also for its antiangiogenic effect [2].



a. ***b.***

Thermoanalytical curves TG/DTG/HF at β = 10 °C·min^{-1} (a) and FTIR spectrum (b) for DHA

The present study presents the thermoanalytical determinations for DHA realized using five different heating rates, namely β = 5, 7, 10, 12 and 15 °C·min^{-1} in synthetic air atmosphere.

The activation energy values were obtained using the beforementioned data by employing three different isoconversional methods, namely Kissinger–Akahira–Sunose, Flynn-Wall-Ozawa and Friedman. For the identification of the different physical and chemical processes that take place during thermal treatment, the NPK method was used [3].

The identity and purity of the analysed compound was evaluated using FTIR spectroscopy.

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Search of interaction between prednisolone and pharmaceutical excipients in solid binary mixtures

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Prednisolone (PSOLONE, structure presented in Fig.1.) is a steroid hormone therapeutically used for its intense anti-inflammatory and immunosuppressive effects [1]. Several pharmaceutical formulations, such as tablets, capsules, inhalers, intranasal sprays, syrups, creams, ointments or injections are currently used [2]. Because of its extensive use and the numerous formulations, the evaluation of the possible interactions occurring between the active substance and the most commonly used pharmaceutical excipients is highly important [3].

As such, the present study aims to realize a comprehensive physico-chemical screening regarding the compatibility of PSOLONE with sodium carboxymethylcellulose, tylose, methyl cellulose, talc, magnesium citrate, mannitol, starch, calcium lactate, magnesium stearate, silica and polyvinylpyrrolidone K30.

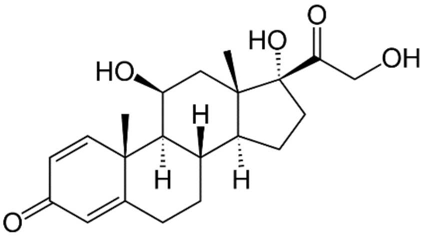

Fig.1. Structural formula of PSOLONE

For the formation of the binary mixture, each excipient was used in a 1:1 mass ratio with the active compound, PSOLONE, and the behaviour of the resulting samples was analysed under thermal treatment. Alongside thermal analysis (TG/DGT/HF), FTIR spectroscopy was used as to evaluate the interactions' possibility of occurrence.

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Aripiprazole - heptakis(2,6-di-O-methyl)-β-cyclodextrin inclusion complex. Compatibility studies with pharmaceutical excipients

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Aripiprazole (ARP) is an atypical antipsychotic drug with a unique mechanism of action used for the treatment of schizophrenia and mania associated with bipolar disorder [1]. It is characterised by very low aqueous solubility and high lipophilicity and undergoes extensive hepatic metabolism that leads to low bioavailability [2]. In order to enhance the bioavailability of ARP, inclusion complexes with different cyclodextrins have been obtained and characterized in our previous studies; the highest increase in ARP solubility was recorded with heptakis(2,6-di-O-methyl)-β-cyclodextrin (DIMEB).

Compatibility and stability studies play an important role in the drug development process. Physical and chemical interactions between an active pharmaceutical ingredient and excipients have to be assessed because the incompatibilities between the components of a dosage form can affect the stability, bioavailability, potency and safety of drug products. The data of the compatibility studies are used to determine the appropriate formulation of a drug product [3]. Thermal analysis is an analytical technique frequently used for drug substance characterization and for studying and predicting the stability of pharmaceuticals [3.4].

In this study the thermal properties of ARP, ARP/DIMEB inclusion complexes and its physical mixture with some common pharmaceutical excipients (starch, magnesium stearate, lactose monohydrate, microcrystalline cellulose and methylcellulose) have been evaluated. The behaviour of the binary system ARP/DIMEB in the presence of excipients had been studied using thermal methods of analysis (TG/DTG/HF) and ATR-FTIR spectroscopy.

The compatibility studies of the inclusion complex ARP/DIMEB with excipients present important data and can be a starting point for further research in the development of new formulations containing ARP, with enhanced bioavailability.

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Investigation of physical-chemical and antimicrobial properties of Ni(II), Co(II), Cu(II) and Zn(II) complexes with 3-amino-1,2,4-triazolium ion

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The design of new antimicrobials represents an important target in order to find a cure either for infections produced by multi-resistant strains or associated with their incorporation in microbial biofilm. One of the strategies used in this regard is to enhance the organic component activity by complexation. Such studies indicated an enhanced antimicrobial activity for complexes bearing a bioactive scaffold such as 1,2,4-triazole ring [1]. The complexes with essential metallic ions are preferred having in view their potential low toxicity associated with human body ability to manage

As result, a series of $[M_2(Hatr)_4Cl_6]Cl_2$ complexes (atr: 3-amino-1,2,4-triazole, M: Ni(II), Co(II), Cu(II) and Zn(II)) were synthesised. The compounds were characterised by microanalytical, IR, UV-Vis-NIR and thermogravimetric data. All complexes adopt an octahedral stereochemistry resulted from chloride coordination as bridge.

The $[Co_2(Hatr)_4Cl_6]Cl_2$ complex crystallize in triclinic system *P*-1 space group.

The thermal decomposition pattern in air comprises processes as ammonium chloride elimination, 1,2,4-triazole ring fragmentation and oxidative transformation of these fragments. The identified residues were the most stable metallic oxides.

The *in vitro* antimicrobial assays performed against Gram positive (*Staphilococcus aureus*, *Enterococcus faecalis*), Gram negative (*Escherichia coli*, *Pseudomonas aeruginosa*) and fungal (*Candida albicans*) strains showed that all complexes exhibited an enhanced antimicrobial activity in comparison with the ligand, both on planktonic and biofilm embedded microbial cells. The Co(II) and Ni(II) complexes exhibited the best antimicrobial activity.

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Preliminary study for preparation of transdermal patch with tramadol and acyclovir

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The importance of transdermal patches have been shown over the years into handling and administration of drug, also these proves the overcome of certain barriers as low solubility, etc[1]. Transdermal patches offer many advantages compared to conventional pharmaceutical formulations, the most important advantages are maintaining a constant and prolonged plasma level of the drug, reducing side effects, and consistent drug release profile, etc[2].

Tramadol $C_{16}H_{25}NO_2$ ((±)cis-2-[(dimethylamino)methyl]-1-(3-methoxyphenyl)-cyclohexanol hydrochloride); is a solid white substance with a good solubility in water. Pharmaceutical formulations with tramadol are present on the market as tramadol Hydrochloride[3].

Tramadol is used in pharmaceutical dosage form due to binding μ- opioid receptor. The second reason for usage is inhibition of reuptake of serotonin and norepinephrine[4].

Acyclovir is being used in the treatment of infections as cutaneous herpes, genital herpes, varicella, zoster infections, etc[5].

For the current study, we consider important to study the interactions between alginate, polyvinylpyrrolidone, glycerol, Polyacrylic acid, polilactic acid, Hydroxy Propyl Methyl Cellulose, Tween 20 and tramadol and acyclovir.

Thermal induces interaction for binary mixture between all these materials were studied using a TG/DTG/HF and FTIR analysis.

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Preparative study for preparation and analysis of medicated jelly with Ibuprofen and Ambroxol

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Medicated jellies are usually used in formulation of different paediatrics forms [1].

Last decades placed on the market different types of medicated jelly with different active substance, like Doxycycline hydrochloride, diflunisal, fenoprofen, etc[2].

Ibuprofen is the most used NSAIDs, also this is used as a potent inhibitor of prostaglandin synthesis, it is recognise with actions in various pain types[3]. Ibuprofen is used as an analgesic, anti-inflammatory agent and anti-pyretic agent[4].

Ambroxol (Trans- 4- [(2- amino- 3, 5- dibromobenzyl) amino] - cyclohexanolis) is a metabolite of bromhexine with similar actions and uses[5].

For the current study, we consider important to study the interactions between the most used materials in medicated jelly formulation (pectin, gelatine, etc) with ibuprofen and ambroxol.

Thermal induces interaction for binary for all mixture between the most used materials in medicated jelly preparation, ibuprofen and ambroxol was studied using a TG/DTG/HF and FTIR analysis.

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The influence of composition (Arabica and Robusta) on the thermal behaviour of some types of commercial coffee and resulting coffee grounds

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The increase of purchasing power and certain tax reliefs, namely, excise duty relief from 2016, contributed to a significant growth in coffee consumption in Romania over recent years. Further to the growth in coffee consumption, there also results an increasing coffee grounds quantity, which could be exploited [1-2]. This paper aims at analysing the thermal behaviour of six types of commercial coffee and the coffee grounds resulting from their use in a professional DeLonghi coffee machine. The influence of composition (Arabica and Robusta) on the thermal behaviour was thus highlighted for the first time. The analysed coffee contains Arabica (W_A%) and Robusta (W_B%) composition in different proportions: W_A/W_B=100/0, 70/30, 50/50, 35/65, 20/80 and 0/100. The analysis of thermal behaviour was carried out by recording the TG, DTG and DTA curves with a Mettler 851 derivatograph, in nitrogen, at a heating rate of 10ºC/min, within the temperature range of 25-700ºC. The DSC curves were recorded with a Mettler Toledo DSC1 in an inert atmosphere, at a heating speed of 10°C/min. Scanning within the temperature range -60-150ºC was carried out, with two heating runs and one cooling run. The coffee ground was dried in a Mettler Toledo HG63 at a temperature of 105°C. The obtained results indicate that the degradation is done in three or four stages, based on the composition. The first stage consists of water removal, which can be found in a percentage of 1 up to 5%. The thermal decomposition of samples starts at temperatures higher than 230°C, both in the case of different coffee types and coffee grounds. By comparatively analysing the temperature values at which the degradation starts, there can be noticed that in all cases there is an increase in the thermal stability of the coffee grounds with approximately 20 degrees compared to the coffee that is comes from. When the coffee grounds comes from coffee which contains 35% Arabica and 65% Robusta, the degradation mechanisms change at temperatures higher than 320°C, as confirmed by the occurrence of an additional degradation stage compared to the case of other samples. This can be explained by a different content of polysaccharides which can be found in coffee grounds [3]. The obtained DSC curves emphasized the presence of two melting peaks and one crystallization peak, which according to specialty literature [4] indicates the presence of coffee oil.

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Metamaterials for biodegradable metallic implants synthesized by laser techniques

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Nowadays, intense research is focused on the development of *"smart implants"* based on biodegradable metallic materials. Corrosion of metallic materials is critical because it can affect the bioactivity, biocompatibility and the mechanical integrity. Corrosion and surface film dissolution are the responsible mechanisms for introducing unwanted ions in the body from implants. Extensive release in the body of metal ions from implants can cause adverse biological reactions and lead to mechanical failure of the device[1]. Moreover, imperfect shielding can cause supplementary tensions which may lead to major difficulties such as implant loosening, delay in the healing process and consequently damaged bone growth. Bioactive materials play an increasingly important role in the biomaterials industry, and are extensively used in a range of applications, including biodegradable metallic implants.

We report on thin films deposition of Bioactive Glass by Pulsed Laser technique onto biodegradable metallic substrates pure Mg and Mg–Ca–Zn–Zr alloys. The coatings were obtained using a KrF* excimer laser source ($\lambda = 248$ nm, $\tau_{FWHM} \leq 25$ ns). The obtained coatings preserved their initial composition, as demonstrated by physical-chemical analyses: Infrared Spectroscopy, Scanning Electron Microscopy, and Energy Dispersive X-ray Spectroscopy. The results of Electrochemical measurements and Impedance Spectroscopy showed that the best corrosion rate has been registered for the coating using as a substrate Mg alloy. Once we have a slow corrosion rate, we have proposed to enhance the osseointegration and antimicobial properties. Based on this, we applied C-MAPLE method to fabricate in a single step process thin libraries of Lignin/Chitosan on Bioactive Glass/Mg alloys substrate. *In vitro* assays showed good attachment of MG-63 human osteoblast-like. The antimicrobial effect was demonstrated against *Gram negative* and *Gram positive* bacterial species, *Escherichia coli* and *Staphylococcus aureus* mainly involved in implant and nosocomial infections. A stronger inhibitory effect after 24 h on both tested microbial strains was showed. The assembled nanostructures possess variable biocompatibilty and anti-biofilm activity along the compositional gradient of Lignin/Chitosan metametarials deposited on Bioactive Glass/Mg–Ca–Zn–Zr alloy. The obtained results proved that the applied method allow for the fabrication of efficient shield barriers against corrosion on Mg/Mg alloys to be used as biodegradable metalic implants.

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Tuning functional properties of transition metal doped zinc oxide by the conditions of thermal decomposition of precursors: from DMS to oxide nanocomposites

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Transition metal, TM, doped ZnO nanostructures with multiple (e.g. magnetic, optical) properties combined with enhanced adsorption capacity are of great interest for applications in various multifunctional (photocatalytic, sensing, spintronic, magnetooptic, etc.) devices. Within this work the same preparation method (thermal decomposition of propionates) was used for fabrication of ZnO-TM (TM = Fe, Co and Ni) nanostructures by varying the heating (precursor decomposition) conditions. Structural, vibrational, optical and magnetic properties of the obtained nanostructures were investigated. Thermal analysis of the un-doped and TM-doped precursors was used to find the optimum synthesis conditions. The powders consist of nanocrystals of 6-20 nm. Un-doped ZnO shows room temperature ferromagnetism (RTFM) with saturation magnetization, *Ms,* and coercivity, *Hc,* dependent on the heating conditions – *Ms* varies between 10^{-5} and 5×10^{-3} emu/g and coercively takes values of up to 100 Oe. Co and Fe doping suppress the ferromagnetism and the doped systems show paramagnetic-like behaviour due to very fine clusters governed by the antiferromagnetic exchange interaction between TM ions. In the Fe doped ZnO a superparamagnetic component is detected; it becomes well pronounced above 2 at.% Fe exhibiting a blocking temperature, $T_{b,}$ at about 20K. The magnetization in the Co and Fe doped ZnO are sensitive to heating conditions. Ni-ZnO nanostructures exhibit DMS- like (dilute magnetic semiconductor) behavior [1] with improved coercively as compared to un-doped ZnO; they are less susceptible to the heating conditions. The EDX and XPS analysis on the synthesised samples indicate a higher concentration of TM as compared to initial stoichiometry and that the excess of TM is most probably located on the (particle, agglomerate) surface. X-ray diffraction show that for higher level of doping, above 2 at.% (nominal), the samples presents ZnO - TM oxide nanocomposites, e.g ZnO-$ZnFe_2O_4$, ZnO-Co_3O_4, ZnO-NiO. Temperature dependent Mössbauer spectroscopy investigation indicates the formation of superparamagnetic $ZnFe_2O_4$ clusters. Un-doped ZnO exhibit a broad defect-related photoluminescence, PL, emission in the visible range. TM doping suppresses the green PL emission (or enhances the blue emission). The investigated properties of TM-ZnO were explained in terms of: (i) the specific peculiarities of synthesis method (e.g. type and concentration of native defects), (ii) the thermal decomposition conditions of initial precursor and (iii) the propensity for the formation of (specific for each type of dopant) ZnO-TM oxide nanocomposites.

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Thermal analysis and properties of ball-milled and spark plasma sintered iron nanostructures - comparison with Fe-Cr (oxide dispersion strengthened) alloys

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Mechanical milling in combination with spark plasma sintering, SPS, is regarded as an efficient route for the production of nanostructured materials (fine grained structures in metals, alloys, composites, etc.). An advantage of SPS method is the shorter time of exposure under high thermal - high pressure conditions which hinders grain coarsening of the as-milled powders preserving their intrinsic properties; it also makes possible to produce highly dense compacts at lower (nominal) temperatures. The nanostructured Fe powders and compacts produced by ball-milling and SPS-consolidation were thoroughly investigated by structural, magnetic and thermal analysis. In the Fe powders the grain size decreases and the lattice constant increases with the increase of milling time. Thermal analysis shows that with advanced milling the Curie temperature, T_c, decreases and the temperature of $\alpha\rightarrow\gamma$ transition, $T_{\alpha\rightarrow\gamma}$, increases enlarging the stability region of the paramagnetic bcc-α Fe. *TG* mass loss region broadens towards higher temperatures with the increase of the milling time. The magnetization measurements of the furnace-heated as-milled Fe powders show a minimum in the saturation magnetisation, σ_s, vs temperature which correlates with a maximum in the rate of mass loss in TG. The powder milled for 170 h was SPS-consolidated at different temperatures between 850 °C and 1100 °C. The relative density of compacts increases with the increase of the consolidation temperature achieving near theoretical value for the Fe compact consolidated at 1100 °C. The SPS - consolidated Fe largely preserved the fine microstructure of the as-milled powder. The temperature dependence of magnetization of Fe SPS – consolidated at 1100 °C reveals a magnetic response specific for the nanostructured iron and iron-based alloys. Hc vs. T and zero-field-cooled, ZFC, and field-cooled, FC, curves for Fe compact exhibit a spin-glass-like behavior. The properties of nanostructured Fe were explained in terms of structure disordering and introduction of defects, and were compared with Fe-Cr based alloys reported in our previous papers [1-4].

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Comparative Analysis on AlSi12-SiC Composites Processed by Powder Metallurgy and Centrifugal Casting

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The paper present a comparative analysis of AlSi12-SiC composites, with different silicon carbide contents, processed by powder metallurgy (mixing-pressing-sintering) and by centrifugal casting (SiC-alloy melting-centrifugal casting) [1-2].

The casting process of the composite tubular form was done in refractory shell molding.

In the castings, the centrifugal force determined the appearance of a structural gradient both by the SiC particle separation and the matrix structure, influencing the variation of the properties of the composite on the radius.

The composites were made by mixing the powdered components and compaction-reinforcing them by further pressing and sintering.

The comparative analysis is based on the study of structure by optical microscopy and XRD; on the study of the phase transformations by thermal analysis (DIL, DSC) and on the determination of the mechanical properties (microharness) [3-5].

The manufacturing of materials and all the tests were made at the C08 Research Centre – Advanced Metal, Ceramic and Composite Materials and Technologies – within the Research and Development Institute of Transilvania University of Brasov.

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Thermal behaviour, spectral properties, optical anisotropy and biological activity of Azorubine

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Azorubine (E 122) is an azoic dye synthetized from aromatic hydrocarbons, which is used in food products. Its chemical formula is $C_{20}H_{12}N_2Na_2O_7S_2$ [1]. Five spectral techniques were used to identify azoic food dye azorubine in powder and solution form: FTIR, UV-Vis, Raman, laser fluorescence and Terahertz spectroscopy (Fig. 1). The Azorubine's morphology and his chemical composition were studied with a SEM (SU8010 from Hitachi) equipped with an EDXS unit from Oxford Instruments. The biological activity of azorubine was observed through its antioxidant activity and its phytotoxicity.

Thermal analysis [2] were efectuated in air with DIAMOND TG/DTA thermobalance from PerkinElmer indicates the elimination of four crystallization water molecules up to 199 °C, after which the compound has a thermal stability up to 310 ºC. Oxidative decomposition takes place in three exothermic stages of which the strongest between 395-687 °C develops a heat of 6087.0812 J/g. At 955 ºC the 30.50 % residue is obtained (Fig. 2).

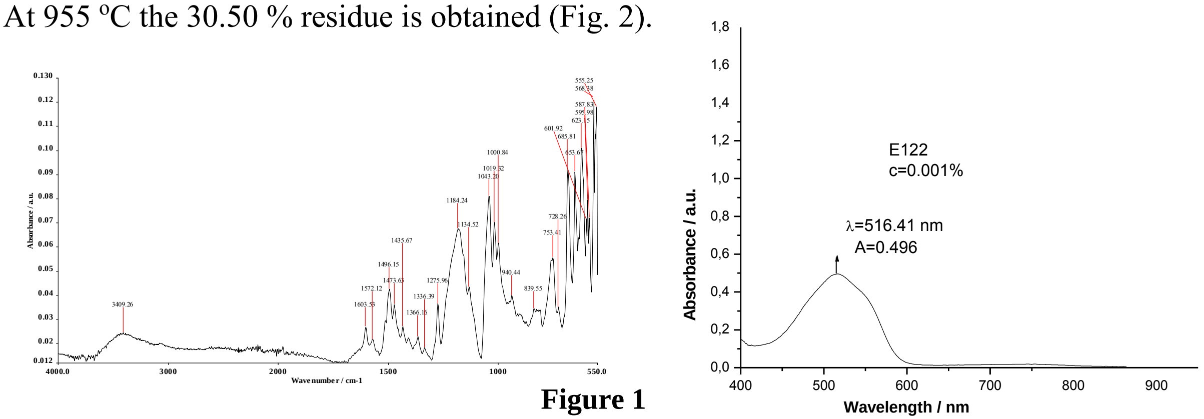

Figure 1

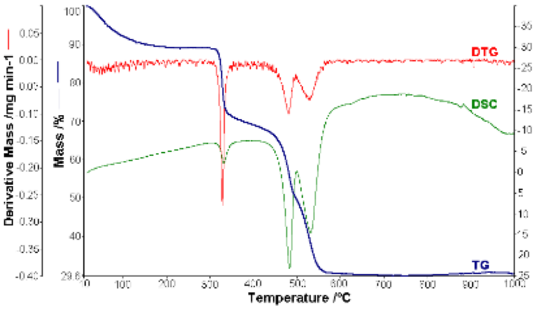

Figure 2

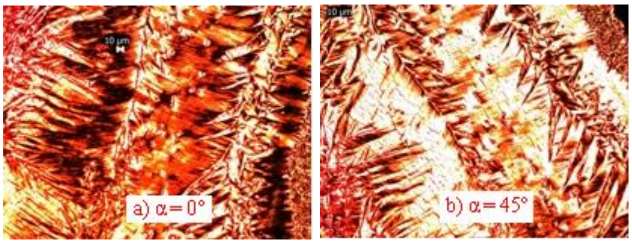

Figure 3

The optical anisotropy of azorubine was studied with the polarized light microscope LEICA DM 2500 P equipped with a video-recorder camera (Linkam Scientific Instruments Ltd.) at RT conditions. Azorubine exhibits the phenomenon of birefringence obtained in results crystallites by drying at RT of he`s aqueous solutions with concentration of c = 5 % (Fig. 3) [3].

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The thermal analysis and calorimetry - as a group of methods for developing modern competences of research for students

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In the current context of integrating training with research, it is important to induce research-like behaviour and research skills to/for students and ultimately to ensure professional development. Physical research methods must be involved through concrete examples in the educational process to provide those who study training through research, based on in-depth studies of materials and phenomena. The research of materials & phenomena, based on these methods, allows the integration of the disciplines within the Natural Sciences segment (chemistry, physics, biology, environmental) and the creation of a personal style of approaching of the scientific problems in the field. The study of the efficient mechanisms of integrating the physical methods of analysis of the chemical compounds in the process of training-research-elaboration of the new innovative solutions allows to highlight the particularities, advantages and disadvantages due to which it can be elaborated proposals for rationalization and implementation of the new methods in the process of formation of the future specialists. The thermal analysis can be successfully used in research training due to the interdisciplinary character based on the diversity of materials and their characteristic phenomena. Researching the behavior of materials at different temperatures, allows us to study both the composition and the properties, thus determining different fields of employment. The diversity of the fields & directions of application, allows the multilateral evolution of the research method, registering an increase in the number of publications and scientific events in the given field.

CEEC-TAC (Central and Eastern European Conference on Thermal Analysis and Calorimetry) is one of the major international events, being a very efficient forum for disseminating the results of research in different fields, based on the integrated method of thermal analysis. An analysis of the abstracts published and in the process of publication of the 5 international CEEC-TAC conferences, held between 2011-2019, highlighted a wide applicability of the thermal analysis and calorimetry methods, both in terms of thematic diversity (if to mention the present joint conference CEEC-TAC5 & Medicta2019 only: physical chemistry - 105, organic chemistry - 27, food chemistry - 5, analytical chemistry - 8, coordinative chemistry - 8, ecological chemistry - 6, chemical engineering - 3, materials technology - 103, pharmacology - 20, biochemistry - 44, biotechnology - 7, physiology human - 6, microbiology - 12, agriculture - 4, phytotechnology - 3, energy technology - 9, pedagogy – 2; the last 8 fields representing somehow a novelty and a progressive evolution in the last conferences) as well as the categories of researchers involved (professors, researchers, PhD-, MSc- and BSc-students). Out of the 371 participants registered at CEEC-TAC5 Conference – about 80 are students at different stages of study, in diverse areas of study programs. This number is constantly increasing, which denotes the opportunity of integrated application of the thermal analysis method at different levels of study. However, this application requires a suitable adaptation by developing a specific methodology, an interdisciplinary apical model, its implementation and evaluation of its impact in the formation of the competence of research in students.

Approaching some issues in an inter- and transdisciplinary context by using the integrated method of thermal analysis will allow to elucidate new aspects of the field with the development and application of the methodology in different usual situations, as well as specific conditions – which will create premises for the training of competent specialists in identifying solutions for various conditions of activity.

Poster Session 3

Thermal properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) nanocomposites with controlled degradability

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The environmental impact of plastic wastes, especially those coming from short term packaging, is huge and the accumulation of plastic fragments on the soil, in rivers and oceans is alarming. The high durability and inertness of petroleum based polymers makes them difficult to biodegrade and, therefore, the accumulation of environmentally polluting packaging waste is one of the major issues of this century. The development of bio-based polymers for packaging is an important research topic in the last decades [1-3]. Polyhydroxyalkanoates (PHAs) are seen as a viable alternative to synthetic polymers in packaging industry [1,2]. Among PHAs, Poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are commercially produced by microorganisms through fermentation. They are biodegradable and exhibit acceptable mechanical and barrier properties [2]. However, they do not show antimicrobial activity and their degradation rate is rather low for some packaging applications.

The hypothesis of this work was that nano-titania, alone or with other fillers, could be used to improve some properties of PHBV, to increase its antibacterial activity and to adjust its degradation rate. For this purpose, PHBV was blended with nano-titania and nanocellulose. The nanocomposite films were characterized by thermogravimetry, differential calorimetry and dynamic mechanical analysis. Nano-titania and nanocellulose had different effect on the thermal and mechanical properties of PHBV, an improvement of these properties being observed in nanocomposites containing nano-titania. The behaviour of nanocomposites after aging was also evaluated. The results showed that hybrid nanocomposites based on PHBV are interesting alternatives to commonly used polymers in packaging applications.

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Biocomposite foams based on polyhydroxyalkanoates: morphological and thermo-mechanical characterization

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Polyhydroxyalkanoates (PHAs) are synthesised by some bacterial strains and are intensively studied to substitute synthetic polymers in applications generating large amounts of plastic waste. PHAs are biodegradable and biocompatible, resistant to water or moisture and to ultraviolet radiation and they are good barrier to some gases [1]. However, the large application of PHAs in industrial or medical fields is hampered by their high brittleness. Copolymerization and incorporation of rubber particles or other toughening agents, plasticizers or fillers were tried to overcome this drawback [2]. Nevertheless, these treatments are usually accompanied by a reduction of stiffness and strength. Among PHAs, poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) copolymer are commercially available. PHBV is characterized by a lower processing temperature, increased ductility and decreased strength compared to PHB, however both are very brittle.

Another approach to obtain a large improvement of ductility and toughness in polymers consists of creating a foamed structure. Different methods can be used to obtain polymer foams, by using physical or chemical blowing agents, supercritical fluids, salt leaching, or freeze drying [3].

In this work, PHBV was modified using a foaming agent and nanocellulose (NC). NC was added in PHBV as reinforcement to balance strength and toughness. The composites were characterized by static and dynamic mechanical analysis, thermogravimetry, differential calorimetry and porosity. No important change of the thermal stability was observed after the addition of the foaming agent and NC. However, an increase of the compression strain and ductility was noticed in the foamed composites. The results have shown that balanced strength and ductility and low density may be obtained with PHBV/NC foams.

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The influence of hyaluronic acid on the phase transitions in Pluronic systems

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Pluronics are linear copolymers formed by three different blocks: two outer hydrophilic polyethylene oxide (PEO) blocks of the same length and an inner hydrophobic polypropylene oxide (PPO) block. Reverse Pluronics are also PEO/PPO linear block copolymers, but with a changed configuration (PPO-PEO-PPO) that leads to a different behaviour in water. While the regular type Pluronics form micelles in aqueous solutions under certain conditions, the reverse Pluronics can form different types of aggregates: flower type micelles, a micellar network or a random network. Pluronics are used as non-ionic surfactants in cosmetics, pharmaceutical formulation, in the optimization of drug delivery systems and food industry.

The aggregation behaviour of one regular (F127) and two reverse (10R5 and 17R4) type block copolymers in water and the influence of hyaluronic acid (HA), a naturally polysaccharide on the micelle formation have been investigated using micro-DSC, EPR, Rheology and DLS methods.

The thermodynamic parameters of the micellisation and gelation processes have been calculated via processing of the micro-DSC thermograms.

The DSC evidenced phase transitions were correlated with the EPR parameters of spin probes (TEMPO derivatives) at variable temperatures.

DLS measurements provided information about the particle size distribution of the various populations present in the analyzed samples as a function of temperature.

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On the thermal behavior of an epoxidized castor oil coating

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Epoxy resins are one of the most worldwide used thermosetting polymers, due to their low cost, high fabrication yield, superior physico–chemical, thermo–mechanical and electrical properties. Epoxy resins cover a wide range of applications from adhesives to insulating materials [1-4]. The final properties of an epoxy resin are dictated by the chemical structure and comprising components from the mixture (fillers, dyes, curing agents, reactive diluents, plasticizers). The study focuses on the obtaining and characterization of a flexible epoxy resin based on castor oil maleate and diglycidyl ether of bisphenol A (DGEBA). The epoxy system was synthesized through esterification with maleic anhydride. Its structural characterization was done with FTIR and ^{1}H–NMR spectroscopy. Thermal decomposition was undertaken by dynamic thermogravimetry in nitrogen atmosphere up to 600 ^{o}C. The global kinetic parameters were determined with the Friedman isoconversional method. The kinetic data showed a three stage thermal decomposition mechanism, characterized by diffusion, n^{th} order and Avrami–Erofeev reaction models. Kinetic parameters values per each stage were obtained via a multivariate non–linear regression method. A simultaneous TG/DTA–FTIR–MS coupling was used for the identification of the gaseous fragments evolved during thermal degradation.

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PS3.005

Kinetics of the thermal decomposition of magnesium hydroxide: Mechanistic features and impact of water vapor

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Understanding of physico-geometrical characteristics of the reactions in solid–gas systems is a continuous challenge. One current topic is the kinetic description for the overlapping multistep reactions constrained by physico-geometrical features. The other is the impact of atmospheric gas that has on the kinetics of the reactions in solid–gas systems. This study focused on the mutual correlation between the physico-geometrical reaction mechanism and impact of the atmospheric gas as exemplified by the thermal decomposition of $Mg(OH)_2$.

The physico-geometrical characteristics of the thermal decomposition of $Mg(OH)_2$ were investigated by analysing TG–DTG curves recorded in flowing N_2, as well as using the other physico-chemical techniques and microscopic observations. The thermal decomposition exhibited smooth mass-loss curves irrespective of heating program. However, the apparent activation energy E_a indicated detectable variations during the initial ($\alpha \leq 0.20$) and final ($\alpha \geq 0.85$) stages of the reaction, while maintained approximately constant value in the major reaction stage with the average value of 160±3 kJ mol^{-1}. Two different methods for analyzing the multistep reaction were applied to account for this kinetic behavior: one is the kinetic deconvolution analysis (KDA) [1] and the other is based on a consecutive surface reaction (SR) and phase-boundary controlled reaction (PBR) [2]. The results of KDA indicated two-step reaction with the contributions of each step, i.e., approximately (c_1, c_2) = (0.33, 0.67). No difference in E_a value was found between two reaction steps, i.e., approximately 130 kJ mol^{-1}. From the analysis based on the SR–PBR model, 3-D shrinkage of the reaction interface was expected for PBR. The E_a value for the SR was in close agreement with that obtained from the KDA; however, a significantly larger value of 247 ± 8 kJ mol^{-1} was estimated for PBR(3).

TG–DTG measurements were also carried out under various temperature and water vapor pressure conditions. These data were universally analysed by introducing an accommodation function into the fundamental kinetic equation [3]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(-\frac{E_\mathrm{a}}{RT}\right)f(\alpha)\left(\frac{P_0}{p(\mathrm{H_2O})}\right)^a\left[1-\left(\frac{p(\mathrm{H_2O})}{P_\mathrm{eq}(T)}\right)^b\right] \tag{1}$$

The universal Friedman plot based on Eq. (1) exhibited a systematic decrease in E_a value during the early stage of the reaction ($\alpha \leq 0.40$), followed by nearly constant value of 240 kJ mol^{-1}. Therefore, the mass-loss curves were reanalyzed based on SR–PBR(3) model, and subsequently the SR and PBR steps were analyzed separately using Eq. (1). As the results, the universal kinetic description was realized by the effect of the first part of the accommodation function, $(P_0/p(H_2O))^a$ with a = 0.64 and 1.98 for the SR and PBR, respectively. The apparent E_a values for the SR and PBR steps were estimated to be 204 ± 5 kJ mol^{-1} and 361 ± 15 kJ mol^{-1}, respectively. Details of the correlation between the physico-geometrical mechanism and impact of water vapor pressure is discussed in this presentation.

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Investigation of thermal behaviour for materials based on lanthanum manganite with nitrogen addition

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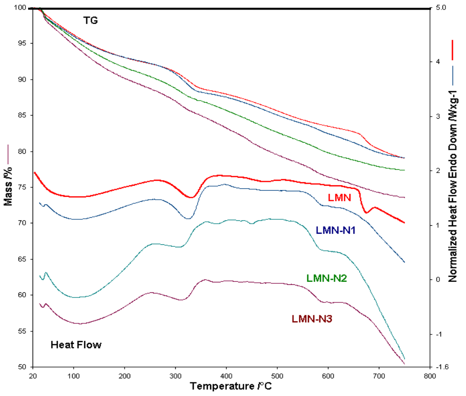
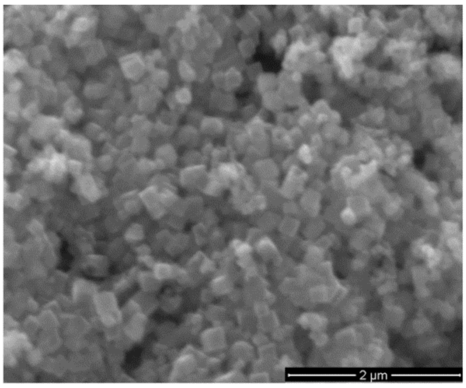
Despite a large number of materials with unique physicochemical properties, the perovskite-type oxides discovered in the previous century attract the attention of researchers because of such characteristics as ionic conductivity, superconductivity, catalytic and photocatalytic activity, and possibility of the modification of materials with new properties [1, 2]. By doping with metallic or nonmetallic ions, the physicochemical properties of materials with perovskitic structure are enhanced. In this work, we report the synthesis of lanthanum manganite with nitrogen addition (at different N concentrations: 1%, 2%, 3%) via sol–gel mehod followed by heat treatment at low temperature. The crystallinity and microstructure of the powders were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM/EDX) and Fourier Transform Infrared Spectroscopy (FTIR). The thermal behavior of the obtained materials was studied by TG/DTA analysis in air atmosphere. After achievement of investigations above mentioned, the morphology, particle size, structure and crystallization degree of obtained samples were analysed and compared.



Thermoanalytical curves (TG/HF) of lanthanum manganite with nitrogen addition



SEM iamge for 0.1% N doped $LaMnO_3$

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Phase transitions in perovskite-type manganites and effect of Ag-doping on its physico-chemical properties

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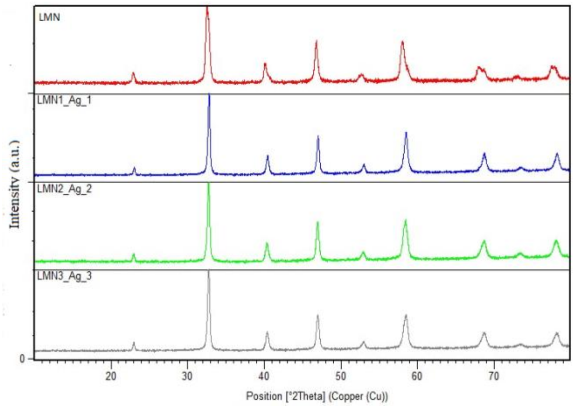
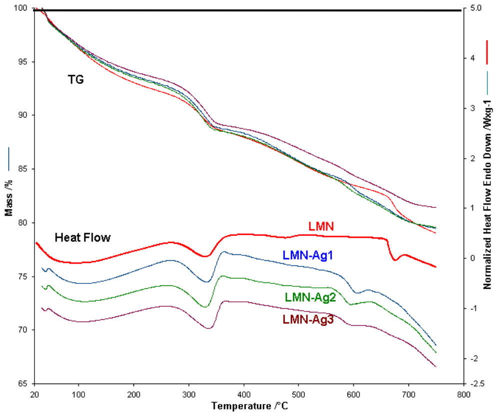
The perovskite manganites are strongly correlated systems in which competing interactions give rise to a variety of interesting phenomena including colossal magnetoresistance and magnetocaloric effect. Physical properties in these systems come from the interplay between the charge, orbital, spin and lattice degrees of freedom. These factors can be modified by calcination temperature, pressure, impurities, and particle size [1]. The aim of this study is to obtain undoped and silver-doped $LaMNO_3$, which present the perovskitic structure, in order to improve the photocatalytic properties. Therefore, a systematic investigation of $LaMnO_3$:Ag nanomaterials as a function of dopant concentration has been carried out and the results of these investigation are present here. Characterizations of the resulting powders were carried out by means of X-ray diffraction (XRD), thermogravimetric and differential thermal analysis (TG/DTA), N_2 adsorption–desorption (BET), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and diffuse reflectance spectroscopy (DRS).



X-ray diffraction patterns of undoped and silver doped $LaMnO_3$



Thermoanalytical curves (TG/HF) of undoped and silver doped $LaMnO_3$

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Defect chemistry and thermodynamics of proton-conducting perovskites $BaCa_{(1+y)/3}Nb_{(2-y)/3}O_{3-\delta}$

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The oxygen nonstoichiometry index δ, i.e. number of oxygen vacancies per formula unit, in perovskite-type $BaCa_{(1+y)/3}Nb_{(2-y)/3}O_{3-\delta}$ (BCNy) oxides can be tailored by varying the Ca–Nb ratio *y*, which equals $y = 2\delta$. These oxygen vacancies can be hydrated under humid atmosphere, providing nonstoichiometric BCNy oxides with good proton conductivity. It makes them promising materials for proton-conducting solid oxide fuel cell (SOFC) electrolytes and high-temperature humidity sensors. The present work aimed to partly address the lack of fundamental thermodynamic studies on BCNy by investigating their enthalpies of formation, hydration heats and related defect chemistry.

$BaCa_{(1+y)/3}Nb_{(2-y)/3}O_{3-\delta}$ oxides with $y = 0$, 0.18, 0.5 (BCN0, BCN18 and BCN50, respectively) were prepared via the standard ceramic technique from the high-purity $BaCO_3$, $CaCO_3$ and Nb_2O_5. Phase-purity of the as-obtained powders was confirmed by means of X-ray diffraction (XRD) with 7000S diffractometer (Shimadzu, Japan) using Cu Kα radiation Calorimetric measurements were performed with an original heat-flux differential scanning calorimeter (DSC). Temperature-dependent equilibrium water content in BCNy samples in dry and wet air was measured by thermogravimetry (TG) using CI Precision (UK) microbalances. Enthalpies of formation and enthalpy increments of BCNy samples were investigated using MHTC 96 (Setaram, France) drop calorimeter.

The defect structure models based on the single reaction of water uptake were discussed and successfully verified using the proton content dependencies, $x(T, p_{H_2O})$, in BCN50 [1] and BCN18 [2]. The values of the hydration enthalpy of cubic ($Fm\bar{3}m$) BCN50 and BCN18, either measured directly or evaluated using the equilibrium $p_{H_2O} - T - x$ data [1,2], were shown to be close to each other. In addition, the enthalpy of the cubic→monoclinic phase transition for BCN50 was calculated using calorimetrically measured low-temperature heat of hydration. The knowledge of the hydration and formation enthalpies along with the enthalpy increments allows calculating temperature- and water-content-dependent thermodynamic functions of BCNy.

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Split Anode Calorimetry for Plasma Arc Energy Density Measurement with Laser Calibration

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A split anode calorimeter has been developed for the measurement of plasma arc energy densities. The calorimetry device consists of two copper plates and a polyamide base [1]. Slots were machined into both the copper plates and the polyamide base to form two separated cooling channels. Several brass screws were fixed within the copper slots to create turbulent water flow. This improved the heat transfer efficiency enabling a more stable temperature reading. A laser beam with a diameter of 6.2 mm was used to calibrate the effectiveness of this calorimeter without complications of arc instability or oxidation effects. The laser beam profile was previously measured using an optical laser beam profiling system. The measurement with the split anode calorimeter showed the same symmetric bell-shaped energy distribution of the laser beam with a smooth symmetric curve. This demonstrated that split anode calorimeter has the capability of generating a clear and detailed profile of the welding arc. Measurement of a 130A plasma arc energy density was then carried out, using both the current and temperature data. Compared to the laser profile, the plasma arc profile showed a slight axial asymmetry. Images of the plasma arc were captured during the measurement process. Analysis of these images revealed distortion of the arc when traveling across the gap of the copper plates. The effect of the earth wire connecting position was investigated. It was shown that this position had a significant influence on the arc position leading to the asymmetric profile and erroneous energy density profiles. The earth wire connected point was then modified so that much less distortion of the plasma energy density profile occurred.

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Insight on thermal behavior and biomolecular interaction of Ru(II) and Ru(III) complexes with diaminodicarboxylate ligands

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Several ruthenium complexes with multidentate ligands were proved over the last years as anticancer, antiparasitic, anti-inflammatory and antimicrobial species [1]. These studies have also identified several biological targets involved in their transport, metabolization and mechanism of action such as nitric oxide, DNA, transferrin, human serum albumin and other proteins. Moreover, in the human body, either Ru(II) or Ru(III) species can be found, depending on the cellular compartment and the concentration of other redox species [2].

Having in view these aspects, new Ru(II) and Ru(III) complexes of the type $[RuLCl]\cdot H_2O$ and $[RuL]\cdot H_2O$ (where H_2L is N,N-ethylenediaminebispropionic acid or N,N'-ethylenediaminebispropionic acid) were synthesized and characterized by proper physico-chemical methods. Complexes were formulated as octahedral species with diaminodicarboxylate moieties acting as chelate and/or as bridged ligands.

Several transformations such as water and chloride evolving, diaminodicarboxylate moiety pyrolysis and oxidative degradation were identified by both TG and DTA curve profile. All these modifications at heating ended with RuO_2 stabilization in air flow.

Mechanistic aspects regarding the interaction with biomolecular targets (nitric oxide, calf thymus DNA, human serum albumin and transferrin) were investigated by several spectral techniques, namely UV–Vis absorption binding studies and fluorescence titration. The spectrophotometric study indicates that the complexes interact with calf thymus DNA via a groove binding mechanism and exert rather weak interactions with transferrin and human serum albumin. Furthermore, the results indicate the existence of a single binding site in both proteins. The values calculated for the quenching rate constant, Kq, indicate the existence of a static quenching mechanism. The interaction with nitrous oxide was evidenced via EPR technique.

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Physical-chemical characterization, thermal behaviour investigation and antimicrobial activity studies of some oxovanadium(IV) complexes with quinolone antibiotics

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In the context of growing bacterial resistance, in the last years many studies were focused on the capacity of quinolones to form metal chelates exerting better antimicrobial properties than the free molecules [1-3]. The increased biological activity of metal chelates is explained based on Overtone's concept of cell permeability and Tweedy's chelation theory [4].

In this study, the interaction of the quinolone antibacterial agents norfloxacin and ofloxacin with VO^{2+} has been initiated in order to examine the mode of ligand coordination and the effect of complexation on biological activity. Five new metal complexes have been synthesized in different conditions (weakly acidic and weakly basic medium) and characterized with physicochemical techniques (elemental analysis, conductivity measurements, IR, UV-Vis spectroscopy) and thermal analysis (TG, DTG, DTA).

The obtained complexes were formulated as $[VO(H\text{-}Nf)_2]SO_4{\cdot}3H_2O$ (**1**), $[VO(H\text{-}Nf)(H_2O)_2]SO_4{\cdot}3H_2O$ (**2**), $[VO(Of)(H_2O)_2](SO_4)_{0.5}{\cdot}2H_2O$ (**3**), $VO(OH)(Nf){\cdot}5H_2O$ (**4**), $VO(OH)(Of){\cdot}3H_2O$ (**5**) (were H-Nf – norfloxacin molecule in the zwitterionic form, Nf, Of – deprotonated norfloxacin and ofloxacin, respectively).

Thermal analysis of these complexes confirms their composition and allows the number and the nature or the water molecules determination. It was also evidenced intermediate steps corresponding to the quinolone moiety oxidative degradation. The final product of thermal decomposition was in all cases V_2O_5 as powder X-ray diffraction indicated.

The antimicrobial activity of the complexes against various microorganisms was similar or better than that of the free quinolone drugs.

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Thermal and physical-chemical characterization of new complexes with cyanoguanidine derivatives

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Dicyanamide or cyanoguanidine (cnge) is an organic compound which contain four nitrogen atoms as potential donors in interaction with metallic ions. Due to the large number of potential nitrogen donors, cyanoguanidine is expected to act as a versatile ligand. In most cases, cyanoguanidine is coordinated as a neutral unidentate ligand, through nitrogen atom from nitrile group [1-3]. There is few complexes with cyanoguanidine acting as bridging bidentate via the nitrile group and the adjacent imino nitrogen atom [4].

Transitional metals can catalyze some cyanoguanidine reactions such as the addition of water, alcohols and amines.

Having in view the versatility of cyanoguanidine as ligand, our efforts to synthesize complexes of copper with cyanoguanidine as ligand lead to new compounds, $[Cu(cnge\text{-}OCH_3)_2](acr)_2\cdot 0.5H_2O$ (**1**) and $[Cu(cnge\text{-}OCH_3)_2](Macr)_2\cdot 2H_2O$ (**2**) (where ($cnge\text{-}OCH_3$) is the compound resulted from methanol adition to cyanoguanidine, and acr/Macr are acrylate/metacrylate anions). The compounds were characterised by using IR, UV-Vis, thermogravimetric analysis and single crystal X-ray diffraction.

The thermal behaviour provided confirmation of the complexes composition as well as the number and the nature of water molecules and the intervals of thermal stability. The thermal transformations are complex according to TG and DTG curves including dehydration, acrylic/metacrylic acid release and $cnge\text{-}OCH_3$ oxidative degradation. The final product of decomposition was copper (II) oxide as powder X-ray diffraction indicated.

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Acknowledgment: This research was financially supported by “Carol Davila” University of Medicine and Pharmacy through Contract no. 23PFE/17.10.2018 funded by the Ministry of Research and Innovation within PNCDI III, Program 1 – Development of the National RD system, Subprogram 1.2 – Institutional Performance – RDI excellence funding projects.

Physical-chemical characterization of Pt(II) and Pt(IV) complexes with a ligand bearing triazolopyrimidine pharmacophore

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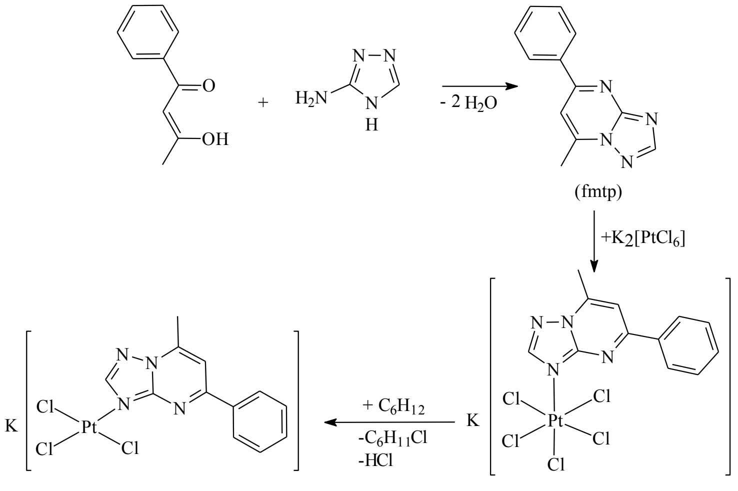
Several platinum complexes with amine ligands having both structure and action mechanism like cisplatin were proved very good anticancer properties. The clinical use of this species evidenced severe side effects and resistance acquire. As result many studies are focused on synthesis of new types of both Pt(II) and Pt(IV) complexes with different structures one of approach being directed on complexes with bulky amine derivatives. Among these, the triazolopyrimidine derivatives attract attention having in view their resemblance with purine bases.

Having in view these aspects, new Pt(IV) and Pt(II) complexes with 5-phenyl-7-methyl-1,2,4-triazolo[1,5-*a*]pyrimidine (fmtp) were obtained and characterized by proper physical-chemical methods. Complexes were formulated as octahedral K[Pt(fmtp)Cl_5] (**1**) and square-planar K[Pt(fmtp)Cl_3] (**2**) species with triazolopyrimidine acting as unidentate.



(2)

(1)

Several transformations such as stepwise chloride evolving, triazolopyrimidine moiety pyrolysis and oxidative degradation as well as PtO decomposition were identified by both TG and DTA curve profile. All these modifications of anhydrous complexes ended with a mixture of Pt and KCl in air flow.

Acknowledgment: This research was financially supported by “Carol Davila” University of Medicine and Pharmacy through Contract no. 23PFE/17.10.2018 funded by the Ministry of Research and Innovation within PNCDI III, Program 1 – Development of the National RD system, Subprogram 1.2 – Institutional Performance – RDI excellence funding projects.

Influence of the nature of phosphates on the properties and thermal behaviour of hydroxyapatite bioceramic precursors

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In order to study the influence of the nature of phosphates on the thermal behavior of hydroxyapatite precursors, different samples was studied using thermal analysis (see an example in Fig. 1) and UATR-FTIR spectra (see Fig.2 and 3), SEM, EDAX, EGA and XRD. Precursors was prepared therefore: to a solution of $Ca(CH_3COO)_2\cdot H_2O$ in distilled water was added drop-wise in 30 minutes and at room temperature, under sonication a solution of phosphates (see Table 1). Molar ratio Ca/P was in all cases 1.67. After sonication, the mixture was dried.

Table 1. Precursors obtained from different phosphates

a	$Ca(CH_3COO)_2\cdot H_2O$ in distilled water	trimethyl phosphate in distilled water
b	$Ca(CH_3COO)_2\cdot H_2O$ in distilled water	triethyl phosphate in distilled water
c	$Ca(CH_3COO)_2\cdot H_2O$ in distilled water	tributyl phosphate in ethanol
d	$Ca(CH_3COO)_2\cdot H_2O$ in distilled water	triallyl phosphate in ethanol

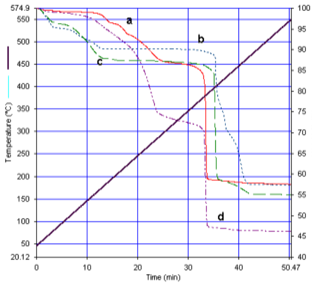

Fig.1 TG curves for prepared samples

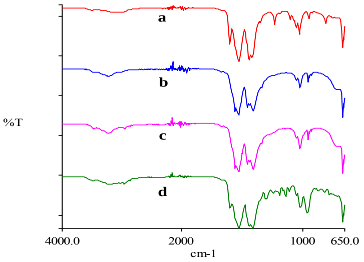

Fig.2. FT-IR spectra of initial samples

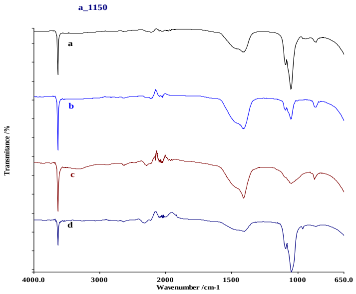

Fig.3. FT-IR spectra of treated samples 15 minutes at 1150°C

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Study for formulation of medicated vehicle with different antibiotics with application in stomatology

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Absorbable gelatine sponge is a fast haemostatic agent that performs effective haemostasis, it is a non-toxic, non-allergenic, non-immunogenic, non-pyrogenic and biocompatible material used usually after dental extraction.

Clarithromycin is a macrolide with a large spectrum[1], this present a good solubility in acetone, slightly solubility in ethanol and acetonitrile and practically is insoluble in water[2].

Oxacillin and ampicillin are the most used penicillin in dentistry. The activities of these is based on the inhibition of the wall bacteria cell synthesis by inactivation of transpeptidase enzyme[3].

For the current study, we consider important to study the interactions between sponge gelatine and antibiotics (ampicillin, oxacillin and clarithromycin).

Thermal induces interaction for binary mixture between absorbable gelatine sponge and ampicillin, oxacyclin and chlarithromycin (obtaining after impregnation) were studied using a TG/DTG/HF and FTIR (see Fig1-3) analysis.

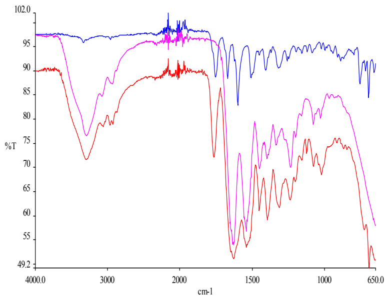

Fig. 1. FT-IR spectra: Amp, gelat, binary mixture

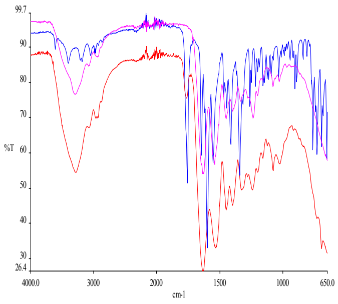

Fig. 2. FT-IR spectra: Oxa, gelat, binary mixture

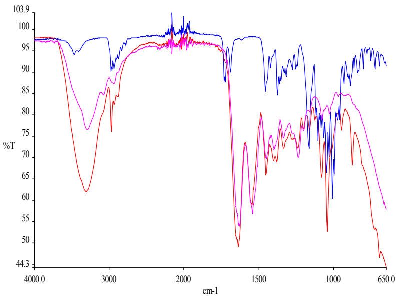

Fig. 2. FT-IR spectra: Claritr, gelat, binary mixture

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Nickel cobaltite modified glassy carbon for enhanced voltammetric detection of diclofenac

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Pure nickel cobaltite ($NiCo_2O_4$) was successfully obtained through the thermolysis of new Co(II)-Ni(II) oxalate coordination compound after the calcination at 400 °C for 1 h. The synthesis method of the oxalate coordination compound is based on the redox reaction between 1,2-ethanediol and nitrate ion. The synthesized precursor was characterized by chemical analysis, infrared spectroscopy and thermal analysis. The $NiCo_2O_4$ compound was investigated by X-ray diffraction, infrared spectroscopy and SEM microscopy.

The nickel cobaltite (NiCo) obtained was used to modify the glassy carbon (GC) electrode as NiCo/GC electrode to be tested for enhanced diclofenac (DCF) voltammetric detection. NiCo exhibited excellent electrocatalytic effect towards diclofenac oxidation and detection over a wide range of DCF concentrations in 0.1 M NaOH supporting electrolyte. The influence of the scan rate allowed to elucidate some mechanistic aspects related to electrochemical behavior of NiCo/GC electrode in NaOH supporting electrolyte and DCF using cyclic voltammetry (CV) technique. Two pairs of anodic peaks at ca. 0.15 V and 0.4 V /SCE and their corresponding cathodic peaks characteristic to the reversible redox reactions of Ni^{2+}/Ni^{3+} and Co^{3+}/Co^{4+} were observed, which are involved in DCF oxidation and implicit, in its detection. The electroanalytical parameters obtained for DCF voltammetric detection depended on the voltammetry technique type and the operating conditions. The best sensitivity of 188 $\mu A\ \mu M^{-1}$ was achieved at CoNi/GC electrode using differential pulsed-voltammetry (DPV) operated at modulation amplitude (MA) of 0.1 V and step potential (SP) of 0.05 V, which is much better than for other electrodes reported in the literature.

Nickel cobaltite synthesised through this new method exhibited excellent properties for voltammetric detection of diclofenac even at trace levels in aqueous solution.

Acknowledgement: This work was supported partially by research grant GNaC2018 - ARUT, no. 1350/01.02.2019, financed by Politehnica University of Timisoara and partially by a grant of the Romanian Ministry of Research and Innovation, project number PN-III-P1-1.2-PCCDI-2017-0245/26 PCCDI/2018 (SUSTENVPRO), within PNCDI III.

Use of MgFe-LDH obtained from secondary source as heterogeneous catalyst for advanced oxidation process of CR

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Dyes used in a lot of industries such as: textile, coating, plastic, and paper industries are discharged in water sources causing severe issue regarding the environmental pollution [1, 2]. The removal of dyes from wastewater before discharge is very import due to their inert and non-biodegradable properties [3, 4].

In the present paper the degradation process of Congo Red (CR) by using LDH/H_2O_2 oxidation, have been studied. The novelty of the paper consists in the obtaining of a catalyst MgFe-layered double hydroxide (LDH) starting from secondary sources. As secondary source of iron ions for the LDH synthesis was used residual solution resulted from the pickling step in the hot dip galvanizing industry.

Two types of MgFe-LDH (varying the molar ratio between Mg^{2+} and Fe^{3+} ions: Mg/Fe=2, 3) have been synthesized. The synthesized LDHs have been calcinated at 450 and 900 °C. The synthesized LDHs and the calcinated samples were subjected to XRD, TG, SEM-EDX, and FTIR analysis. The results showed that the LDHs obtained from secondary sources have similar characteristics with the synthesized LDHs from reagents.

The studied materials have been used as catalyst in the advanced oxidation process (AOP) of CR from aqueous solutions in the presence of H_2O_2. The dependence of the degradation degree of CR function of the H_2O_2 concentration, CR concentration, solid:liquid ratio, contact time and catalyst nature, has been established. It was observed that the Mg/Fe – LDH could be efficiently used as catalyst in the AOP of CR from aqueous solutions, obtaining degradation degree higher than 90%.

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Calorimetric Study of the $ZrMo_{1.5}V_{0.5}$ - H_2 system

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In the present work we studied the hydrogen absorption and desorption reaction processes for the $ZrMo_{1.5}V_{0.5}$ - H_2 system at 45, 65 and 95 °C and hydrogen pressure up to 50 atm by the calorimetric method applying the calorimeter Tian-Calvet type connected with the conventional Sievert's-type volumetric apparatus. Such installation permitted us to measure simultaneously P-C isotherms (P- equilibrium hydrogen pressure, C=H/ $ZrMo_{1.5}V_{0.5}$). The apparatus scheme, the experimental procedure and the treatment of obtained results were described elsewhere [1].

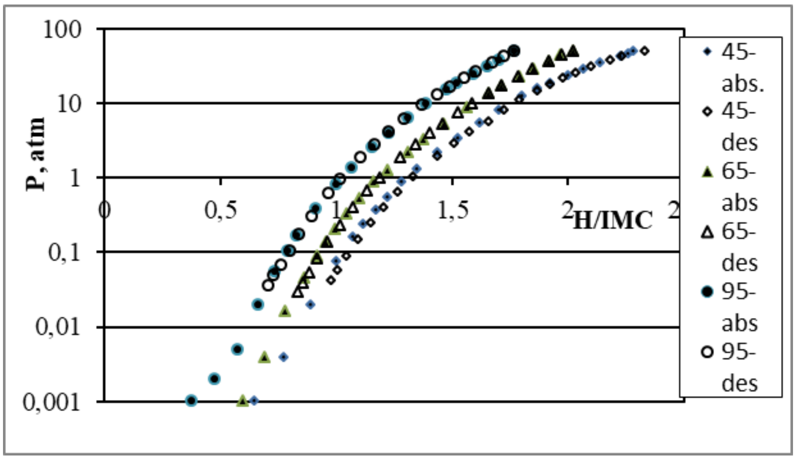

Fig.1. Absorption and desorption isotherms for the $ZrMo_{1.5}V_{0.5}$ - H_2 system at 45, 65 and 95 °C.

As one can see from the figure 1 in the P – C isotherms there are no plateau. The plots of the P=f(C) dependences coincide for both absorption and desorption processes in the other words there is not hysteresis in the $ZrMo_{1.5}V_{0.5}$ - H_2 system as well the molar partial enthalpy values for the desorption and desorption processes coincide in absolute values within the limits of experimental error too (see Table 1).

Table 1. Temperature dependence of reaction enthalpy for the $ZrMo_{1.5}V_{0.5}$-H_2 system

Temperature, °C	Range, H/IMC (absorption)	ΔH_{abs}, kJ/molH$_2$	Range, H/IMC (desorption)	ΔH_{des}, kJ/molH$_2$
45	1.3-1.9	-32.3±0.8	1.3-1.8	32.6±0.7
65	1.9-2.2	-34.4±1.3	1.8-2.2	35.7±0.7
95	1.4-1.9	-31.5±0.5	1.4-1.9	30.9±0.3

It should be noted from the data presented in Table 1 that at 45°C in the $ZrMo_{1.5}V_{0.5}$ - H_2 system there are two regions with constant enthalpy values for the hydrogenation and dehydrogenation processes whereas at 65°C there is only one region with the constant enthalpy values. Moreover the enthalpy values increase with the increasing of hydrogen concentration in the IMC at 45°C. We assume that it is probably connected with some minor structural distortions of the metallic matrix. To confirm this assumption it is necessary to carry out in situ neutron powder diffraction study at 45°C. At 95°C in the $ZrMo_{1.5}V_{0.5}$ - H_2 system there was no region where the enthalpy took on constant values.

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Thermomagnetometric analysis of nickel-zinc ferrites

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Soft magnetic materials, such as nickel-zinc ferrites, are widely used in electronics and radio engineering. The magnetic characteristics of nickel-zinc ferrites largely depend both on the chemical and phase composition, as well as on the technological conditions for their preparation [1, 2]. In the $Ni_xZn_{1-x}Fe_2O_3$ system, it is possible to obtain a large number of nickel-zinc ferrites of various compositions. X-ray diffraction (XRD) analysis in the context of nickel-zinc ferrites does not allow separating phases with close lattice parameter, which reflections merge into single peaks on the diffraction pattern. In our past works was shown possibility of applying thermomagnetometric method (TGM) of determination phase composition of lithium substituted ferrites [3, 4], but applying TGM to nickel-zinc ferrite is not studied.

In this work, nickel-zinc ferrites obtained in accordance with the chemical formula $Ni_xZn_{1-x}Fe_2O_3$ with $x = 0 \div 0.7$ from chemically pure oxides Fe_2O_3, NiO, ZnO. Obtaining a homogeneous mixture was achieved by repeatedly rubbing the mixture through a metal sieve with a mesh size of 0.5 mm in an agate mortar. Increasing of reactive activity was reached by mechanical activation in a Retsch ball mill with 2 mm steel balls at 1000 rpm during 10 min. The synthesis of nickel-zinc ferrites was carried out by solid-phase synthesis with isothermal exposure in an air atmosphere for 240 min at 900 ° C.

The resulting nickel-zinc ferrites were investigated by thermogravimetric analysis in air using a STA 449C Jupiter thermal analyzer. Magnetic phase transitions were detected using two permanent magnets applied to the outside of the measuring cell of the thermal analyzer and created a magnetic field of ~ 5 Oe. The saturation magnetization (Ms) of ferrites samples was measured at room temperature with the vibrating sample magnetometer with the maximum field of 10 kOe.

As a result of the studies, an experimental dependence of the weight change (Δm) during the magnetic transition of Nickel-Zinc ferrites was obtained. The applicability of the thermomagnetometric method for determining the phase composition of nickel-zinc ferrites is shown.

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Influence of ball milling conditions on the reactivity lithium ferrite powder

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Lithium ferrites with spinel structure are of particular interest for science and technology as they have a number of unique properties. Such ferrites actively interact with electromagnetic waves of the low-frequency microwave range, so they are widely used in various devices of modern microwave technology, for example, as discrete high-speed phase shifters. In addition, lithium ferrites can be used as the active phase of composite products for radar absorbing coatings.

The conventional way to synthesize lithium ferrites involves the use of high-temperature solid-state reaction including the mixing of oxide/carbonate and then mixtures annealing at high temperatures [11, 12]. As shown earlier for the formation of ferrite, the reaction between initial reagents proceeds from the temperature of 500 °C and comprises two steps, which correspond to the interaction between reagents with the Li_2CO_3 decomposition in the temperature range 500–650 °C and the melting of lithium carbonate residues at ca. 724 °C. The complete formation of the ferrite phase ends at temperatures of 900–1000 °C. Such synthesis method has some disadvantages which include chemical inhomogeneity, coarser particle size and volatility of Li_2O from ferrites during synthesis.

One of the methods that allow to reduce the synthesis temperature is preliminary ball milling of initial reagents in high energy ball mills. Such reagent powders are highly reactive, which makes it possible to obtain reaction products at lower temperatures and shorter thermal treatment period. According to earlier our investigations [1,2], the ball milling of initial reagents at 60 min with using 2220 rpm rotation speed for vial and 5 mm diameter of balls leads to an increase in the reactivity of powders and thus can be used to produce lithium ferrites at lower temperature than in conventional ceramic processing. However, during ball milling, a violation of the phase composition of powders was observed so that the Fe_3O_4 spinel phase was formed due to the reduction of α-Fe_2O_3 iron oxide.

In this work, the influence of ball milling conditions including energy intensity and diameter of balls on the reactivity lithium ferrite powder was studied by X-ray diffraction (ARL X'TRA) and TG/DSC analysis (STA 449 C Jupiter). The ball milling of Li_2CO_3-Fe_2O_3 mixture was carried out in a planetary mills (RETSCH) at room temperature using steel grinding bowls and balls.

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Hydration and properties of fly ash based geopolymers: effects of calcite addition and mechanical activation

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Geopolymers, also referred to as inorganic polymers, are a subclass of alkali activated materials prepared by the reaction of aluminosilicates with an alkaline agent (e.g. sodium hydroxide solution or liquid glass) at near ambient temperatures. Because of easy, energy-efficient and eco-friendly processing, and high performance, geopolymers have received attracting attentions in civil, material and environmental research fields for such applications as a promising partial substitute to traditional Portland cement, matrices for immobilizing the toxic wastes etc. [1,2]. Alongside with calcined clays and natural pozzolans, coal fly ash has been widely used as the solid precursor for production of geopolymers.

The goal of this research is to investigate the hydration and mechanical properties of geopolymers based on mechanically activated fly ash blended with natural calcite from carbonatite (igneous rock composed mainly of CaCO3). The content of calcite mixed with fly ash ranged from 1 to 10%. To alter the reactivity of the raw materials mechanical activation using a planetary mill AGO-2 was carried out. NaOH solution was used as the alkaline agent. The prepared specimens were cured at 22±2oC in tightly closed container. The specimens were tested for compressive strength after curing for 7 d and 28 d. It has been revealed that both mechanical activation and addition of calcite to fly ash improve compressive strength of the resulting geopolymer. The improvement in strength properties is found to be related to the higher reactivity of fly ash.

Isothermal calorimetry measurements were provided in calorimeter TAM III TA Instruments (closed glass ampule, 25°C 1 month) along with thermal analysis (TG and DSC coupled with MS) using STA 449 F1 Jupiter with QMS 403C Aeolos Netzsch (50-1450°C, HR 20K/min, Al2O3 crucible, Ar 150ml/min) have been carried out to elucidate the beneficial effects of calcite addition and improved reactivity during geopolymerisation.

The calorimetric experiments and thermal analysis have been performed at the Centre for Thermal Analysis and Calorimetry of the Research Park of St. Petersburg State University.

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The $Gd_2SrFe_2O_7$ complex oxide: mechanism of synthesis and antibacterial activity

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The complex oxides with perovskite-like structure are well known ceramic materials for industrial applications but their antibacterial activity investigation has started less then 10 years ago. The promising results obtained shows great potential of using oxides with perovskite-like structure as bactericides for different applications.

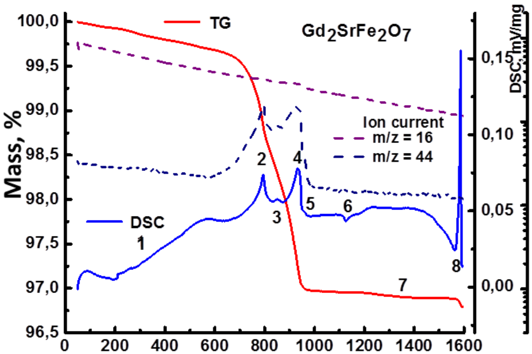
The mechanism of complex ferrites synthesis remains insufficiently studied. Information on the kinetics and synthesis mechanism is necessary for the development of optimal synthesis methods and also could help to answer a number of questions related to the determination of their chemical and thermal stability.

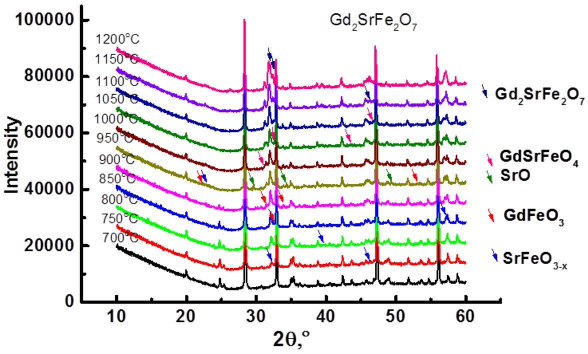
The study of the synthesis of complex oxide $Gd_2SrFe_2O_7$ was carried out by conducting the data obtained by simultaneous thermal analysis coupled with a quadrupole mass spectrometer for evolved gases determination and the high-temperature X-ray phase analysis results. It can be stated that reaction (1) is a complex multistage process.

$$Gd_2O_3 + SrCO_3 + Fe_2O_3 \rightarrow Gd_2SrFe_2O_7 + CO_2 \qquad (1)$$

The limiting stage of the formation of the $Gd_2SrFe_2O_7$ composite oxide is the interaction of the perovskite $SrFeO_{3-x}$ and Gd_2O_3 with the formation of the $GdSrFeO_4$ complex oxide with the K_2NiF_4 type structure. The mechanism of formation by the sol – gel method at the calcination stage remains the same as in the synthesis by ceramic technology. With the help of sol-gel synthesis, it is mainly possible to lower the temperature of the limiting stage and thereby reduce the synthesis temperature of the complex oxide $Gd_2SrFe_2O_7$.

Evaluation of the antibacterial activity of complex oxide $Gd_2SrFe_2O_7$ was performed using gram-negative bacteria - Eschrichia coli by two methods diffusion method for agar (inhibition zone test) and broth-dilution method. The minimum bactericidal concentration (MBC) was determined.





Acknowledgement. This work was supported by the RFBR grant №18-33-01209.

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Thermodynamics of sulfonated cobalt pthalocyanine derivatives interaction with pyridine and piperidine in aqueous media

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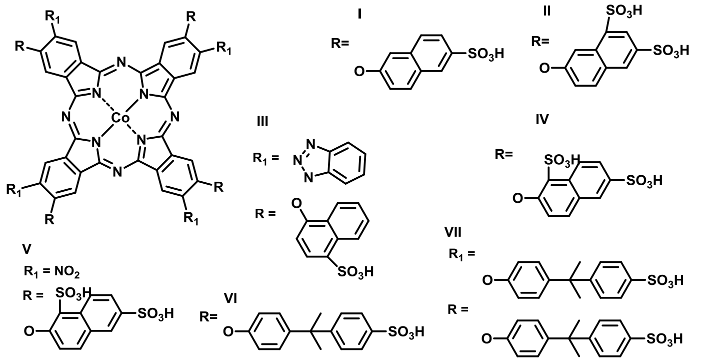
Unsubstituted metal phthalocyanines are known to be hydrophobic molecules, which makes it difficult to find their uses. This problem can be solved by introducing substituents, for example, sulfo-groups on the periphery of phthalocyanine macro ring. Such complexes are promising compounds for the production of new materials that can be used as catalysts, photosensitizers, dyes and solar energy converters. It should also be noted that, for example, the molecular complexation of metal phthalocyanines is a specific feature determining their biological, catalytic, photovoltaic and photocatalytic activity.

Therefore, in this paper, the processes of molecular complexation of water-soluble sulfonated cobalt phthalocyanines (Fig. 1. A) with pyridine (Py) and piperidine (Pip) as organic ligands (L) in aqueous media are considered. The coordination processes of small organic ligands were investigated by the spectrophotometric method. To calculate the stability constants (K_y) of molecular complexes (Fig. 1. B) from the data of electronic absorption spectra, analytical wavelengths were used. The composition of the resulting complex (Fig. 1. B) was calculated using the Bent-French semi-logarithmic method.



A

MPc	Pip CoPc:L, lg (K_y)	Py CoPc:L, lg (K_y)
I	1:2 (3.74)	1:1 (3.20)
II	1:2 (3.79)	1:1 (3.40)
III	1:2 (3.69)	1:1 (3.97)
IV	1:3 (3.66)	1:2 (4.04)
V	2:3 (3.88)	2:3 (3.78)
VI	1:2 (3.77)	1:1 (3.73)
VII	1:2 (3.84)	2:3 (3.73)

B

Fig. 1: A – the objects researched scheme; B – the composition and stability constants of molecular complexes

It is shown in the transition from pyridine to piperidine, an increase in the stability of molecular complexes is observed, which agrees with the quantum-chemical ideas about the structure of ligands. However, the benzotriazole fragment in III and IV in the composition of macrocycles contributes to the opposite effect.

The work was supported by State Assignment of The Ministry of Education and Science of the Russian Federation, Agreement No. 4.1929.2017/4.6 and by Grant of President of the Russian Federation (№ MK-204.2019.3).

Calorimetric study of fullerene-containing polymers

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Fullerenes, the new molecular allotrope of carbon, were discovered in 1985 by H.W. Kroto, R.F. Curl and R.E. Smalley, who were awarded the Nobel Prize in Chemistry in 1996 due to this seminal scientific finding [1]. Since then, the development of chemical reactions able to modify the chemical structure of fullerenes C_{60} and C_{70} led to new fullerene derivatives with outstanding structural, magnetic, superconducting, electrochemical and photophysical properties. Soon after the discovery of fullerenes, the first fullerene-containing polymer was synthesized in 1991. These compounds are formed by the polymerization of neighboring C_{60} and C_{70} molecules and different modifications of vinyl, cyclic and organosilicon polymers, which are represent a new fairly promising class of high-molecular compounds. It was found that the fullerene-containing polymers are able not only to preserve a lot of useful properties of the polymer but to noticeably enhance them that allow the expansion of areas of their practical application (e.g., electroluminescent devices, non-volatile flash devices, photovoltaic solar cells) [2].

The fundamental thermodynamic study of fullerene-containing polymers is a promising direction in the field of chemistry of nanostructures. In the present work, the heat capacities of several covalently linked C_{60}- and C_{70}-containing polymers were studied in a wide temperature range by precise adiabatic vacuum calorimetry and differential scanning calorimetry (DSC). The low-temperature heat capacities were analyzed on the basis of the Debye heat capacity theory of solids and the multifractal model. As a result, some conclusions on the structure topologies of fullerene-containing polymers were made. The obtained experimental data were used to calculate the standard thermodynamic functions of the investigated compounds. A comparative physicochemical analysis of thermodynamic characteristics of C_{60}- and C_{70}-containing polymers and the original polymers were made. As a result, a significant effect of fullerenes C_{60} and C_{70} in the polymer composition on its thermophysical properties was established.

This work was performed with the financial support of the Russian Foundation for Basic Research (Project No. 18-03-01090).

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Calorimetric and spectroscopic studies of DNA aptamers for mutant Huntingtin targeting

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Huntington's disease (HD) is a dominantly inherited neurodegenerative disorder with motor, cognitive, and psychiatric features caused by expanded HTT CAG trinucleotide repeats that extend a polyglutamine tract in the amino-terminus of huntingtin. HD results in severe movement and thinking disorders, which can eventually lead to death as no effective therapy exists. As for genetics, HD hinges on the CAG triplet expansion within the first exon of the HTT gene, which then encodes for a mutant, polyglutamine-expanded (polyQ) protein (mHTT).

Several recent reviews have described the mHTT biology, the related pathogenesis mechanisms, and the roles of polyQ and N17 in HD onset. We discussed the HTT biophysics and the perspective, innovative aptamer-based approach for its targeting in a recent review [1]. To date, most molecular approaches (e.g. antibodies, intrabodies) failed because of inadequate selectivity, toxicity, poor delivery, and system complexity. Aptamers promise to override these limits thanks to their unmatched specificity, easy selection, very low immunogenicity, and broad stability. In a recent study, four G-rich DNA aptamers were identified, able to selectively bind the mHTT, discriminating the wtHTT, and to ameliorate at least one of the aberrant effects of mHTT [2]. These aptamers fold into G-quadruplex structures and do not bind to the N-terminal end of the protein, but no data on their thermodynamic stability have been provided thus far.

We here present a biophysical characterization of these aptamers. Circular dichroism (CD) has been used to assess aptamers secondary structure and thermal stability. Differential Scanning Calorimetry (DSC) provided all thermodynamic parameters on the folding/unfolding equilibrium of aptamers.

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Solvation thermochemistry of aromatic hydrocarbons and their halogen derivatives in imidazolium-based ionic liquids

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In the last decade, ionic liquids (IL) became known as new and promising solvents for the pharmaceutical industry. The great interest of ionic liquids is primarily related to their physical properties: negligible vapor pressure and a wide temperature range of liquid state. An important aspect of ionic liquids is that their properties vary significantly depending on the combination of cation and anion.

In the present work, we quantitatively analyzed the effect of the polarizability of solute molecules (aromatic hydrocarbons and their halogen derivatives) on their solvation enthalpy in imidazolium-based ionic liquids.

Recently ionic liquids were found to be solvophobic solvents. Therefore, the solvophobic effect contribution to the solvation enthalpy of the studied compounds was estimated. Also, a comparison of the data obtained in ionic liquids with similar results in molecular solvents was made.

The solution enthalpies of aromatic compounds and their halogen derivatives are measured by using the solution calorimetry method. Solvation enthalpies in ionic liquids were calculated based on the data on the vaporization and sublimation enthalpies of these compounds. Although ILs are solvophobic solvents, based on the proposed method, it has been shown that solvation enthalpy of compounds studied does not contain a solvophobic effect contribution. This result is very important for the analysis of intermolecular interactions in IL solutions. The correlations between the solvation enthalpy of aromatic compounds and their halogen derivatives and the polarizability parameter are obtained. The results are similar to those for molecular solvents. Differences are observed only in the numerical values of the correlation parameters. The correlations obtained in this study can be used to calculate the solvation enthalpy of aromatic hydrocarbons and their halogen derivatives in ionic liquids.

Acknowledgements

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Redox-behaviour of novel $CrO_x/Pd/SiO_2$ catalytic nanomaterials

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Modifying the Pd nanoparticles in the catalytic materials is currently considered as promising way to improve the catalytic properties. Introduction of both Cr^{6+} by impregnation and Cr^0 by vapor deposition on to the Pd/SiO_2 catalysts was shown to decrease the activity in hydrogenation of double C-C bond thus improving selectivity in the partial hydrogenation of butadiene [1]. In these catalysts Pd^0 facilitates reduction of the CrO_x nanoparticles to Cr^0 at 600 ºC. Deposition-precipitation of Pd^0 nanoparticles on TiO_2 support in presence of CrO_4^{2-} ions resulted in changes of redox and catalytic properties of the materials [2].

The goal of the present work is to reveal the conditions of redox-depositing of CrO_x species on the surface of the silica-supported Pd nanoparticles, as well as to study the reducibility of thus synthesized materials and their catalytic activity in the hydrogenation of phenylacetylene and other aromatics with molecular H_2.

In this work the novel $CrO_x/Pd/SiO_2$ materials have been first synthesized by the redox-method via reduction with adsorbed H_2 or via the catalytic reduction with H_2. The method of temperature programmed reduction with hydrogen (TPR-H_2) proved deposition of CrO_x species on the surface of the Pd nanoparticles. Phase composition, the particle size and morphology have been characterized with XRD, SEM, TEM.

The TPR-H_2 method was applied to study the influence of preparation conditions on the reducibility of supported CrO_x species and stability of the reduced moieties to oxygen at ambient conditions. Decrease in the decomposition temperature of β-PdH from -11 – 80 ºC to -60 – 40 ºC, as well as the intensive hydrogen consumption at -50 – 40 ºC due to reduction of CrO_x, which commonly proceeds at 250 – 900 ºC, have been first shown.

The initial and reduced $CrO_x/Pd/SiO_2$ materials exhibited the decreased catalytic activity in hydrogenation of (i) triple C-C bond to double bond in phenylacetylene, (ii) carbonyl group in aldehyde to OH group at 22-45 ºC and atmospheric H_2 pressure.

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Facile synthesis of hierarchical trimodal micro-mesoporous Cu hydrosilicate material and its catalytic application for hydrogenation of nitro-group in aromatic compounds

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Aromatic amines, which are intermediates of various industrial reactions, are commonly synthesized by the reduction of aromatic nitro compounds that is catalyzed by noble metals [1]. In the last years, the use of transition 3d-metals has become one of the frontiers, and Cu-based materials are found to be efficient catalysts for the reduction of nitrobenzene to aniline with molecular hydrogen [2]. Recently we reported for the first time that the Cu/SiO_2 materials catalyze hydrogenation of *p*-dinitrobenzene to phenylenediamine, and the formation of Cu phyllosilicate seems to play an important role [3, 4].

In the present work the methods of thermal analysis (TG-DTA, TPR-H_2) were applied to study the formation of Cu phyllosilicate inside the pores of commercial meso-macroporous silica support. The methods of thermal analysis, texture characterization via N_2 adsorption-desorption (surface area, pore width and volume), XRD analysis, SEM and TEM microscopy were used in order to clarify the genesis of material during preparation by deposition-precipitation using urea hydrolysis. The preparation conditions of chrysocolla-like structure have been revealed (92ºC, 8-11 h, urea : Cu = 10).

The prepared materials have been tested in the reduction of nitro aromatics with molecular hydrogen in a batch system. Complete conversion of substrate with high yield of amines has been achieved in relatively short time at the mild conditions (130-170ºC, 1.3 MPa H_2).

The work was carried out with a financial support from Russian Science Foundation, grant no. 17-73-20282.

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The identification and stabilization of new phases in Ga – S and Ga – Se systems

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Recently [1] we argued that, in contrast to traditional views on the Ga – S systems, the phase diagram of this system is sophisticated in the region of pre-melting temperatures and concentrations between 50 and 60 mol.% of sulfur. Now we can make similar conclusion concerning the Ga – Se diagram.

With respect to the Ga – S system, using two independent methods of thermal analysis (DTA and ChTA [1, 2]), it was argued that in a narrow temperature range (877 – 922°C) exists a new phase (σ-phase) with a sulfur content of ~59.0 mol % [1]. In this work we provide the direct evidences that the high-temperature phase in the Ga - S system (σ-phase) really exists. For that purpose we involved the high-speed quenching procedure and further structural analysis with the use of XRD and transmission electron microscopy (TEM). It was found that the σ-phase has the defect zinc-blende structure ($F\bar{4}3m$, $a = 5.210$ Å). Out of the range of stability this phase simultaneously easily decomposes to the heterogeneous composite of monoclinic Ga_2S_3 (Cc , $a = 11.14$, $b = 6.41$, $c = 7.04$ Å, $\beta = 121.2°$) and layered hexagonal β-GaS ($P6_3/mmc$, $a = 3.59(1)$, $c = 15.47$ Å).

Also we made an effort to stabilize this metastable (at room temperature) phase by some impurities. In case of the iron dopant we expanded the temperature range, where the σ-phase exists as stable solid. Due to the introducing of iron into this sulfide we can prepare the phase type as zinc-blende without quenching.

Concerning the Ga – Se system we have also found new compound type as a σ-phase (which was found in the Ga – S system). The phase of zinc blende structure manifests itself in TEM studies of the annealed and quenched Ga – Se alloys, having the 59.0 mol % selenium content. The temperature of annealing was 900 °C with the duration of 36 h. Obviously this phase exists in a narrow temperature range and decomposes when slowly cooling as a σ-phase in the Ga – S system. However, this data has not been confirmed by DTA, probably, by the reason of very low thermal effect of the phase formation/decomposition.

Next we discussed the similarity between the Ga – S and Ga – Se systems and phase diagrams. These systems include well-known phases of Ga_1Ch_1 and Ga_2Ch_3 stoichiometry (Ch = S, Se). Both the sulfide and selenide Ga_1Ch_1-phases have the layered structure with Ga-Ga bonds and van der Vaals gaps. Both the sulfide and selenide the Ga_2Ch_3–compounds are famous for their “defect” structures where $^1/_3$ of the positions in the metallic sublattice are vacant. Finally, the high-temperature zinc-blende-type phases of ~59 mol.% S, which exist in a narrow temperature range is a distinctive feature of the both systems.

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On the In – S system: the results of thermal analysis and vapor pressure measurements

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In – S system is known as a well-researched system [1, 2]. Indium sulfides are important for new technologies, mainly as fluorescent materials and transient formations in the synthesis of ternary compounds which are considered to be very promising for solar energy. However some details concerning this system were not clear up to now. For example, recently we found a phase, which is similar in composition to In_1S_1 stoichiometry: this phase exists in a narrow temperature range (~665 – 690°C) [2]. This phase cannot be quenched and decomposes while cooling. Next, the concentration region near the 60 mol. % - content of sulfur is complicated for this diagram too: three phases manifest themselves near the A_2B_3 stoichiometry (spinel-type $In_{3-x}S_4$, tetragonal In_2S_3 and high-temperature modification In_2S_3' [2]).

To investigate the dubious regions of the phase diagram we applied both thermal analysis (DTA, ChTA [2]) and vapor pressure technique with the use of auxiliary component [3]. The instrument base included the high-temperature spectrophotometric method. The gaseous of hydrogen sulfide H_2S or indium chloride $InCl_3$ were used as the auxiliary components.

The temperature in these experiments falls within the range between 300 and 870°C.

Hydrogen sulfide has the absorption peak near the wavelength of 198 nm. The UV-spectra of indium chlorides vapor have maxima at the wavelength of 215 nm ($InCl_3$), 240 nm (In_2Cl_4), 262 – 280 and 337 – 362 nm (InCl). In this work the extinction coefficients for the characteristic peaks for hydrogen sulfide and indium chlorides were found. Moreover, for indium chlorides the temperature dependences of the extinction coefficients were also calculated.

The spectrophotometric quantitative analysis of the hydrogen or chloride-containing vapor phase allows to obtain the phase composition and principal thermodynamic properties of the equilibrium indium sulfides, which are equilibrium with the vapor phase. In this work we discuss the nonstoichiometry of $In_{3-x}S_4$-phase, the existence of a narrow two-phase region between $In_{3-x}S_4$ and low-temperature phase of In_2S_3'. Also we show the ways of the investigation of InS high-temperature modification.

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Light Scattering Study of Phase Transitions for n-Alkane in Water Nanoemulsions

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Paraffin waxes are important for the industries of food, paper, cosmetics, household chemicals, fossil fuels, and alternative energy. Static and Dynamic Light scattering are commonly adopted to measure the size of emulsions and suspensions as well as the polymer molecular weight in solution.

We used Light Scattering to obtain information about dynamics and the thermodynamics of phase transitions in paraffin nano-emulsions (~100 nm) [1-3].

In particular, we investigated the phase transition temperature range for several n-alkanes nano-emulsions without surfactant and compared the results with the literature data for bulk systems and with measurements on DSC, finding solid agreements.

The hysteresis of the light scattered intensity in the presence of a phase transition, upon heating and cooling, is studied and discussed in details.

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Phase Transition Determinations in n-Alkane Paraffin Wax via Light Scattering Data Analysis Techniques

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We are interested to the phase transition determinations of paraffin nano-emulsions via Light-Scattering measurements.

The crystallization and deposition of paraffin waxes is a crucial problem in the Oil and Gas field which involves massive economic investments every year. Paraffin waxes and their emulsions, moreover, represent a main interest in numerous industries and particularly since Phase-change materials.

Modern commercial Light-Scattering equipments allow to change and adequately control the sample temperature during the measurements.

In this work we show how Light-Scattering techniques, more commonly adopted to measure the emulsion/solution size and the polymer molecular weight in solution, can be also suitable to investigate their phase transitions in absence of surfactants [1-3].

Furthermore, we offer a study on the differences, when present, in determining the phase transition temperature using several data processing methods.

We investigate how the data samples quality may influence the different technique determinations, comparing the obtained results among them along with the literature and different instrument available ones.

We are confident that those findings may induce a wider use of the instrument and a further technique enhancements able in future to accomplish even more precise determinations.

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Influence of heating on the solid acidity of Gd_2O_3

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Currently, the search for new functional catalytic materials based on rare earth metal oxides remains one of the urgent tasks [1]. Compounds based on gadolinium oxide are widely used in medicine, in the production of ceramics, glasses, catalysts. Nanostructured gadolinium oxide was synthesized from $Gd((NO)_3)_3 \cdot 6H_2O$. Gadolinium hydroxide was precipitated with an ammonia solution in the presence of agar-agar, an organic stabilizer that formed a protective film on the surface of the particles preventing their aggregation. The resulting gel was frozen, dried by sublimation drying at 200 °C, calcined at a temperature of 700 ° C. We used Hammett indicators (methyl purple, fuchsin basic, methyl orange, methyl red, bromothymol blue) for the determination of the total amount and strength of solid acid sites. Adsorption of indicators on the surface of the oxide allows determine the qualitative composition and concentration of active centers on the surface of the oxide, as well as the distribution of active centers by force [2].

The specific adsorption of the indicator, and hence the number of adsorption centers (Brønsted acids and bases), decreases with increasing annealing temperature. The number of Brønsted acid sites with pK_α =3.46 on the surface of gadolinium oxide remains unchanged. Oxide catalysts with an acidic surface catalyze many industrially important reactions (dehydration of alcohols, polymerization of olefins, cracking). Gadolinium oxide, dried at 200 °C, can be used as an acid catalyst.

To assess the catalytic properties of the obtained gadolinium oxide, differential scanning calorimetry of two model samples was performed: the first-activated carbon; the second – containing activated carbon and gadolinium oxide in a mass ratio of 9:1. Thermal analysis was performed on a NETZSCH STA 449C instrument from 25 to 350 °C at a heating rate of 10 °C/min (platinum crucible, nitrogen atmosphere).

In the process of heating activated carbon, carbon is destroyed and oxidized by oxygen contained in the pores. This process is accompanied by the release of heat. When the catalyst Gd_2O_3 is added to the activated carbon, the reaction start temperature decreases from 206.95 to 203.85 °C, the thermal effect increases from 397.7 to 563.9 J/g, the mass loss increases from 10.42 to 20.38%. Activation energy is reduced from 1.67 to 0.01 kJ / mol.

It can be concluded that the synthesized gadolinium oxide, dried at 200 °C, has Brønsted acid sites on the surface. It can serve as an acid catalyst in the processes of restructuring of the carbon skeleton and for carbon oxidation in carbonaceous materials.

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Determination of water activity in frozen salmon by DSC

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Food safety and quality of frozen fish is reduced in the process of multiple frosts at different stages of fish movement to the consumer.

The method of differential scanning calorimetry (DSC) can simulate multiple processes of freezing and cooling of food. Analysis of the salmon sample was carried out in a synchronous thermal analysis device STA 449 F3, Jupter, NETZSCH company with the connection of a Dewar vessel. In the helium atmosphere fish samples were continuously cooled three times to -30 °C and heated at a speed of 5 K/min to 25 °C.

In the process, a monotonous decrease in the peak area (heat) with an increase in the number of frosts from -190.5 to -110.1 J/g was observed, this is due to a decrease in the amount of free water in the sample. Ice crystallization temperatures in fish (-10.43; -10.89; -11.54 °C) are below the crystallization temperature of pure water (0 °C).

Table. The process of crystallization

Experience	Crystallization peak temperature, °C	Exotherm heat, J / g	Activity of water
First freeze	**-10,43**	**-190,5**	**0,931**
Second freeze	**-10,89**	**-171,4**	**0,915**
Third freeze	**-11,54**	**-110,1**	**0,899**

The value of cryoscopic temperature (crystallization temperature) can be used to determine the value of water activity in fish [1].

It is now firmly established that the level of water activity affects the intensity of oxidative, enzymatic, microbiological and other processes occurring in the product. Thus, for most pathogenic microorganisms, the minimum levels of water activity are determined, below which they can not develop, which is very important for predicting food safety. For example, in the area of activity 1,00 - 0,95 in fish can grow the following microorganisms: Pseudomonas; Escherichia; Proteus; Shigella, Klebsiella; Bacillus; Clostridium perfingens; some yeast.

The method used by the authors [2], based on the results of scanning calorimetry and the consequence of Raul's law, was used to calculate the activity of water. As is known, the freezing temperature of solutions decreases in proportion to their concentrations: $\Delta t_{\text{зам.}} = K \cdot b$, where K=1.86 is the cryoscopic constant of water, b - is the molar concentration of the solution.

With an increase in the number of frosts and a decrease in the cryoscopic temperature, a decrease in water activity from 0.931 to 0.899 is observed. On the one hand, the decrease in water activity leads to inhibition of microbial growth - this is a positive process, but the decrease in water activity as a result of multiple frosts and defrost will worsen the organoleptic and physico-chemical properties of the product, it will adversely affect its quality.

A new temperature program for complex heating and cooling of fish samples in the furnace of the synchronous thermal analysis device has been worked out. Water activity in the frozen fish with the increase in the number of freezing is reduced. This technique can be used to determine the quality of frozen products and the optimal conditions for their storage.

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Finite element modelling of high temperature pressureless sintering of silicon nitride

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Silicon nitride ceramics has been studied extensively and widely used for high temperature applications due to its superior thermomechanical and tribological properties, namely, high-temperature strength, good oxidation resistance and low thermal expansion coefficient. Pressureless sintering of silicon nitride ceramics is a complex multistage process. Understanding of the sintering staging is an extremely important issue in terms of silicon nitride production [1-3]. Much of the research and development has been focused on the fabrication of ceramic while lack of research is devoted to sintering modelling. The aim of the current study is to investigate processes occurring during the high-temperature sintering of silicon nitride ceramics.

The simulation was performed using finite element method. The modeling sample represents a longitudinal section of the cylinder of silicon nitride with a corundum shell. It was subjected to thermal treatment representing sintering process. Structural parameters, such as Young's modulus, Poisson's ratio and mass density, as well as thermal ones, such as thermal expansion coefficient, thermal conductivity and specific heat were used as the input parameters.

Temperature distribution in the simulated sample has been clearly described during heating and cooling, respectively. Simulation results demonstrate the correct temperature gradient distribution around the sample perimeter is seen. Relative deformation does not exceed 10^{-8}. Moreover, the sample showed no signs of irreversible destruction indicating stability of the material, as well as consistence of the model input parameters. The proposed model can be used further to study the shrinkage of ceramics based on silicon nitride in the process of liquid-phase sintering.

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Transport properties and current characteristics of silicon nitride

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Silicon nitride is one of the most extremely promising ceramics. Silicon nitride is characterized by high strength at room and elevated temperatures, excellent oxidation and thermal shock resistance, as well as a low coefficient of friction and resistance. In addition to its high mechanical properties, silicon nitride exhibits unique functional properties. Despite the fact that a large number of studies devoted to the study of the microstructure and mechanical properties of silicon nitride, there are not so much studies devoted to investigation of the charge transport. Such widely used methods as pressureless sintering and spark plasma sintering and most common used additives as Al_2O_3-Y_2O_3 and Al_2O_3-MgO have been used. The features of the transport properties of silicon nitride have been analyzed in detail in this study.

Calculated concentration of acceptor impurity was equal to is $4.5 \cdot 10^{21}$ cm^{-3}. For Al_2O_3-Y_2O_3 doped presureless sintered silicon nitride while for silicon nitride with Al_2O_3-MgO was equal to-$3.2 \cdot 10^{21}$ cm^{-3}. Oxygen impurities (Si-O bonds) create hole traps, while electron traps occur in pure silicon nitride due to the strong Si-N bonds, making this material characterized by a very high concentration of deep electron traps. Obtained values of the intrinsic concentration of charge carriers and their mobility, diffusion constants and acceptor concentrations. The oxygen impurity concentration can be estimated at 6.75 10^{21} cm^{-3} and 4.3 10^{21} cm^{-3} for Al_2O_3-Y_2O_3 and Al_2O_3-MgO, respectively.

Influence of mechanochemical treatment at thermal decomposition and adsorption of brown coals

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One of main components of brown coals and peat – the humic acids (HA). Thermal stability of the called objects defines overall stability of these natural materials. Application of the mechanochemical activation (MA) to peat and brown coals treatment for improvement of selection, combustible properties and stability of storage is known. Earlier [1] was shown influence of MA on thermal decomposition of humic acids and brown coals.

The aim of the work is to research the thermal decomposition of brown coal at the level of finding separate stages and determination of thermochemical parameters, a research of the adsorption capacity and studying of influence of mechanochemical activation on these phenomena.

The thermal analysis was carried out on the Netzsch thermoanalyzer, in the atmosphere of air, heating rate 10 K/min. At TG-curve next peaks are found: 524, 663, 772, 868 and 1004K. The technique of processing of results came down to the analysis of curve DTG with definition of number and position of peaks (thermolysis stages) with the subsequent synthesis of each peak. For each of stages at the maximum reaction rate activation energy was calculated.

As a result of mechanochemical treatment the noticeable decrease of activation energy of processes of the considered peaks is observed. So, the initial sample has an energy range 76-952, the activated – 49-620 kJ/mol. Presumably, a mechanochemical treatment leads to an increasing of decarboxylation of acid groups processes in peripheral and the condensed parts of HA macromolecules.

For the studied samples of brown coal the specific surface area determined by nitrogen adsorption was investigated. It consists of interblock and pores components, about 1.23 and 0.33 m^2/g, respectively. Studying of other adsorptive characteristics of coals, such as pore size distribution was carried out. Influence of MA on these characteristics was studied.

The interblock component of a surface isn't responsible for change of activation energy of a thermolysis. Changes of the pores surface (under MA) can define the other physical and chemical processes (for example, formation and stability of radicals) both the direction and rate of thermolysis reactions.

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Synthesis and thermal study of intercalated and grafted organic-inorganic hybrids based on $H_2K_{0.5}Bi_{2.5}Ti_4O_{13}$

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Hybrid organic-inorganic compounds based on layered perovskite-like oxides is a new promising class of materials which properties could be tailored by targeted modification of both organic and inorganic parts. Preparation of such materials is recently focused on a stepwise approaches including subsequent intercalation and grafting reactions that lead to formation of bulk hybrid compounds followed by their exfoliation into 2D organically modified nanosheets. Such hybrid compounds and nanosheets are considered as perspective materials exhibiting photocatalytic, catalytic, ferroelectric, and luminescent properties that could be used as polymer filling agents, building blocks for thin films preparation, components of Li-ion batteries and fuel cells electrodes and etc. Although, application of such materials might be limited and strongly dependent on their stability, in particular, thermal stability, such investigations have not been yet widely performed. On the other hand, thermal analysis, including thermogravimetric analysis (TG) and simultaneous thermal analysis coupled with mass-spectrometry (STA-MS) are powerful methods, which could provide the information for both quantitative composition of such hybrids and their thermal stability.

In the present work we report the results on the synthesis, thermal stability and composition of organic-inorganic hybrids based on layered perovskite-like bismuth titanate $H_2K_{0.5}Bi_{2.5}Ti_4O_{13}\cdot H_2O$, which could be prepared by simple ion exchange reaction from Ruddlesden-Popper phase $K_{2.5}Bi_{2.5}Ti_4O_{13}$. Organic-inorganic hybrids have been prepared by intercalation and grafting reactions. Intercalation reactions imply acid-base interaction between solid acid and organic bases (usually *n*-amines). Then, the preliminarily intercalated by amines compounds are used as starting materials for grafting reactions, which imply the covalent bonding between the grafting agents (usually alcohols) and inorganic matrix. In this work, we applied *n*-amines intercalated derivatives for reactions with *n*-alcohols. In particular, methylamine, *n*-ethylamine, *n*-propylamine, *n*-butylamine, *n*-hexylamine and *n*-octylamine-intercalated hybrids were used for reactions with methanol, *n*-propanol, *n*-butanol, *n*-hexanol and *n*-decanol. Characterization of the obtained samples have been carried out by XRD, C/H/N analysis, FTIR and Raman spectroscopies, 13C and 1H MAS-NMR spectroscopy and SEM. Thermal stability of the intercalated and grafted hybrids and their quantitative composition (in respect to water and organic molecules contents) have been studied by TG analysis. The mechanism of thermal degradation of selected samples was performed using STA-MS and XRD analyses.

Scientific research was performed at the Research Park of St. Petersburg State University: Center for Thermal Analysis and Calorimetry, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Magnetic Resonance Research Centre, Center for Optical and Laser Research and Interdisciplinary Center for Nanotechnology.

Thermal analysis and ^{1}H and ^{13}C NMR study of layered perovskite type $H_2La_3Ti_3O_{10}$ with intercalated or grafted organic molecules

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Organic-inorganic layered perovskites due to their remarkable properties are considered as promising photocatalytic materials [1]. For the successful development of these composite hybrid nanomaterials, knowledge on their thermal stability as well as structure and dynamics of both structural parts are highly required. Here, we report on the results of our complimentary study by thermal analysis (TG, DSC) and nuclear magnetic resonance (NMR) technique of the structure, stability and dynamics of $H_2La_2Ti_3O_{10}$ Ruddlesden-Popper layered perovskites with organic molecules (methanol, methylamine, n-butylamine, ethanolamine) introduced into the interlayer space. In our previous study we applied ^{1}H NMR to probe proton dynamics in $H_2La_2Ti_3O_{10}$ [2]. In the present study ^{1}H magic angle spinning (MAS) NMR and ^{13}C-^{1}H cross-polarisation (CP) MAS NMR were applied to study structure and mobility of organic parts of the hybrid materials.

The comprehensive NMR analysis reveals that the formation of hybrids materials with methylamine and n-butylamine is carried out according to the type of intercalation: the organic components are inside the interlayer space as organic cations with the protonated NH_3^+ group, forming non-covalent bonds with the perovskite frame. Ethanolamine is partially intercalated into the oxide structure, one third of molecules forms graft-derivatives, it means, it forms strong Ti-O-C covalent bonds with the perovskite framework. The remaining ethanolamine molecules electrostatically are bounded to perovskite blocks by NH_3^+ groups. When methanol enters the interlayer space of $H_2La_2Ti_3O_{10}$, a covalent hybrid is formed.

These results are in good agreement with thermal investigation data (TG and DSC in complex with MS of gases evolved): the methanol and ethanolamine derivatives exhibit higher thermal stability compared to those of methylamine and n-butylamine.

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Calorimetric and spectroscopic investigation of irreversible denaturation of lysozyme in water-DMSO mixtures

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Lysozyme is a small globular protein with applications in the medical and food industries [1]. Thermal denaturation of lysozyme is largely reversible; however, aggregation was noted at high protein concentrations [2].

We have used a combination of differential scanning calorimetry and spectroscopic methods to study the irreversible denaturation of lysozyme at relatively low concentration (5 mg/ml) in water and water-DMSO solutions. On the repeated heating and cooling DSC scans of the lysozyme solution in water, the area of the endothermic peak of lysozyme unfolding decreases and a lower temperature peak develops, indicating an irreversible denaturation, in agreement with the observations made by Wu *et al.* [3]. To investigate the kinetics of this process, we have incubated lysozyme water and water-DMSO solutions at the elevated temperatures and studied the effect of temperature and duration of the incubation on thermodymamic and structural properties of lysozyme.

As evident from the IR spectra of the protein, the irreversible denaturation is related to the deamidation process. However, at partial deamidation lysozyme is still able to maintain the native structure, as seen from CD and IR spectroscopy results. The thermal stability of the deamidated lysozyme is reduced, which results in the appearance of the low-temperature endothermic peak noted above. The addition of DMSO does not affect deamidation, although, with the increase of the concentration of the organic cosolvent, the difference between the stabilities of the native and deamidated protein forms is reduced.

The kinetic parameters of the deamidation process were calculated from the DSC scans at different incubation temperatures and times. The apparent activation energy of the irreversible denaturation does not show a dependence on the composition of the water-DMSO mixture. It was found that the deamidation is slowed down when the protein is in the native state.

The obtained results should be considered in the processes involving thermal treatment of lysozyme.

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Dilatometric analysis of sintering lithium-zinc ferrite ceramics

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Ferrites are widely used as magnetic materials and are a key element of most modern radio engineering, electronic and computing devices, including lithium ferrites, which are widely used in microwave technology, and also as cathodes of lithium batteries. Substituted lithium-zinc (Li-Zn) ferrites with the chemical composition of $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ are characterized by high values of saturation magnetization and Curie temperature and, thereby, provide active interaction with electromagnetic waves at the low frequency band of the microwave range. The ceramic technology is conventional way to produce ferrites, which involves both the synthesis of ferrites with the formation of single-phase ferrite compositions (via solid-state reaction with oxides/carbonate) and further sintering at high temperatures to produce high-density ferrite ceramics. Because of complex composition of reaction mixtures, repeated alternation of grinding and thermal treatment operations is often performed for completeness of solid-phase reactions, thereby significantly increasing the time of synthesis. A mechanical activation procedure, that is milling the reagent mixture in a high energy ball mill, is widely used to increase the reactivity of reagents and reduce the sintering temperature and annealing time.

In this study, the one-stage production of high-density $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ ferrite ceramics was investigated by heating of mechanically milled mixture (Fe_2O_3-Li_2CO_3-ZnO) in order to exclude the stage of preliminary synthesis procedure. The initial mixture was milled in the AGO-2C planetary ball mill for 60 minutes at a drum rotation speed of 2200 rpm. The samples from milled mixture were compacted by cold pressing in the form of pellets in a PGr-10 hydraulic press at 200 MPa for 3 min. The sintering of powder compacts was conducted in a DIL 402 C (Netzsch-Gerätebau GmbH, Germany) dilatometer using different heating rates of 2, 5, 10 °C/min and an isothermal aging at 1050 °C for 1 h . XRD analysis of the powder mixtures was performed using POWDER CELL 2.5 software. An ARL X'TRA powder diffractometer (Switzerland) was used for the analysis. Phase identification was performed using the PDF-4 powder database of the International Center for Diffraction Data (ICDD). The model-fitting kinetic analyses of ferrite densification were performed by using full DIL data and Netzsch Thermokinetics software. The electrical and magnetic parameters of ferrite ceramics were estimated. It was established that preliminary ball milling the initial reagent mixture in the planetary mill allows not only to accelerate the solid-phase reactions, but also to combine the both technological stages of synthesis and sintering in one stage of thermal treatment. $Li_{0.4}Fe_{2.4}Zn_{0.2}O_4$ ferrite ceramics obtained is characterized by high density and low porosity as well as high values of the specific magnetization and the Curie temperature.

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Control of magnetite phase formation in milled Fe_2O_3 powder by XRD and thermal analysis

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Nanoparticles of iron oxides, in particular magnetite (Fe_3O_4), are widely used in practice, for example, in magnetic systems of recording and storage information, as pigments and effective catalysts in various chemical transformations, in obtaining separation materials and magnetic fluids for various purposes, in creating composite materials, including radar absorbing coatings, and others. In recent years, one of the most promising and actively developed areas of their application is biomedicine. Their magnetic properties change significantly when particles transition from a micro - to a nanoscale state. Recently, many approaches to the synthesis of magnetic nanoparticles of various elemental and phase compositions have been developed, including nanoparticles of iron oxides: magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3). In this work, the effect of mechanical milling of hematite powder on phase formation of magnetite was investigated by TG and XRD analysis.

Hematite powder was mechanically milled in the Emax (Retsch) ball mill at a drum rotation speed of 2000 rpm. Vials and balls with a diameter of 5 mm were made of stainless steel. The ball mass-to-powder ratio was 1:10. XRD analysis of the powder mixtures was performed using POWDER CELL 2.5 software. The ARL X'TRA powder diffractometer (Switzerland) was used for the analysis. X-ray tube with a copper anode was used as an X-ray source, and a semiconductor detector with a Peltier cooler (Peltier detector) with a resolution of 250 eV was used as a receiver of non-elastically scattered radiation. Phase identification was performed using the PDF-4 powder database of the International Center for Diffraction Data (ICDD). Thermal analysis of the testing samples was carried out using a synchronous thermal analyzer STA 449C Jupiter (Netzsch, Germany) with a weight sensitivity of ~ 0.1 μg in corundum crucibles (Al_2O_3). The studies were conducted in air. Heating was carried out to 800 °C with the speed of the dynamic stage in the range of (2.5–20) °C/min. Proteus Analysis software was used to process thermal analysis data.

According to XRD data, the formation of a magnetite phase as a result of the mechanical activation of hematite powder within 30 minutes was established. The formation of 100% phase magnetite occurs with an increase in the time of mechanical milling up to 60 minutes. The results of XRD analysis are well correlate with the data from thermal analysis. An increase in the weight of milled hematite powder was shown. It is associated with the oxidation process of magnetite phase as the result of heating in a furnace of analyzer furnace.

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Design of bioavailable antifungal drugs

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Transition to personalized medicine, high-tech public health and health saving technologies through the rational use of drugs is not possible without the development of the medical materials and medicines of new generation. One of the key problems in the development of such compounds is their poor solubility and membrane permeability. This leads to low bioavailability, effects and low therapeutic effectiveness of drugs. Analysis of the databases of drug compounds developed in recent decades has shown that being highly selective to biological receptors, they are practically insoluble in aqueous media. This circumstance is one of the main reasons why candidates do not pass biological and clinical trials and do not enter the market. Therefore, much attention is now being paid to solving poor solubility problems by creating soluble forms on the basis of new pharmaceutical cocrystals. The most promising systems which significantly improve the solubility and bioavailability of active pharmaceutical ingredients (API) are multicomponent crystals (cocrystals). Adjustment of the solubility and permeability properties can be carried out using the fundamentally new approaches based on the aimed regulation of the properties of multicomponent crystals (cocrystals).

In this work, a screening experiment of multicomponent molecular crystals was conducted for an antifungal drug by the DSC method. Analysis of the obtained data allowed to select 14 promising binary systems with highest probability of forming a multicomponent crystal. All selected systems were examined by powder X-Ray diffraction. The comparison of PXRD data have proven that each of studied samples has a unique diffraction pattern clearly different from a superposition of that of initial compounds, which clearly indicates the formation of the new crystalline phases in corresponding systems.

A preliminary estimation of aqueous solubility of all discovered crystalline forms was carried out with the aim to select the optimal systems for further biological studies. Out of five candidates with highest solubility values, one sample was shown to improve the solubility of the API by 2.3 times compared to the reference form.

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Solvation thermochemistry of organic molecules in binary solvents

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The solvent often has a decisive effect on the course of various chemical, physical, chemical and biological processes in the condensed phase. The solvent in particular its properties, determine the rate of chemical reactions, equilibrium constants of chemical reactions and electronic transition energies. In this study, solvation phenomena in binary solvents significant theoretical and practical interest, since the use of binary solvent increases ability, to change the properties of the medium for the detailed study of the mechanism of the phenomenon and to select the optimal solvent for any problems of chemical processes, including the pure solvents.

The intermolecular interactions of organic molecules (aprotic and proton donor compounds) in binary solvents has been studied. We used approach the solvation thermodynamic for solvation effects study . This method allow us to estimate the contributions of intermolecular interactions. The work evaluated the specific relative cavity formation enthalpy in binary solvents at different ratios of components. The influence of the nature and type of the intermolecular interactions of compounds on value specific relative cavity formation enthalpy of binary solvents were shown. The approach based on separation of intermolecular interactions on the contributions of specific and non-specific interactions for solute - binary solvent systems. The enthalpies of hydrogen bonds of proton donors (methanol, pyrrole, chloroform) in binary solvents at different ratios were calculated. It was defined that enthalpies of hydrogen bonding depend on the mole fraction of the proton acceptor in the binary mixture. This result is related to the degree of the complexation of proton donors in binary solvents. It was found that for all proton donors, a linear relationship between the degree of complexing and the mole fraction of proton acceptors. The degree of complexing decreases in the series pyrrole, methanol, chloroform.

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Group contribution scheme for bromo-substituted compounds

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Bromoalkanes are used as solvents, insecticides and fungicides, as reagents to manufacture pharmaceuticals and organic chemicals. Bromoalkanes are of great importance for chemical synthesis (e.g. Grignard reagent).

In our previous work [1] we have proposed the group additive scheme for solvation enthalpies calculation of linear, branched alkanes, alkenes, alkines, cyclic alkanes and alkenes, linear nitriles, alcohols, ketones and aldehydes. In the present work we expand this additive scheme for halogen-substituted compounds.

Thereby, in order to develop an additive calculation scheme, it is necessary to have a reliable set of experimental values. First of all we collected available literature data on vaporization enthalpies and determined vaporization enthalpies of 1-bromoalkanes by using solution calorimetry method. In our previous works [2-3] solution calorimetry method was successfully applied for determination of vaporization/sublimation enthalpies of aromatic and aliphatic compounds. In work [3] linear relationship between enthalpies of solvation of aromatic and linear aliphatic compounds in *n*-heptane and molar refraction of solute was developed:

$$-\Delta_{\mathrm{solv}}H^{\mathrm{A/n\text{-}hept}}=(1.017\pm0.009)\cdot MR^{\mathrm{A}} + (5.81\pm0.37) \qquad (1),$$

where, $\Delta_{\mathrm{solv}}H^{\mathrm{A/n\text{-}hept}}$ — is the enthalpy of solvation of compound A in n-heptane; MR^{A} – is the molar refraction of A.

However, Eq. (1) can be used only for 1-bromoalkanes. In case of dibromoalkanes (1,5-dibromopentane, 1,6-dibromohexane, 1,8-dibromoctane and 1,9-dibromononane) vaporization enthalpies were measured by using transpiration method. Obtained values were used as a standard compounds for correlation gas chromatography to derive vaporization enthalpies of other bromoalkanes.

As a result we have measured vaporization enthalpies of 1-bromoalkanes by three experimental methods with excellent agreement at 298.15 K. Validated vaporization enthalpies and measured solution enthalpies at 298.15K were used for estimating solvation enthalpies of bromoalkanes and developing the group contribution scheme of bromo-substituted compounds. It was shown that bromo-group contribution depends on the nature of neighbouring atoms.

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Thermal characterization of bimetallic Ag-Fe ion exchangeable mordenite

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Silver-based materials have been attracting great interest due to their effectiveness in various catalytic processes in the chemical industry. An ideal catalyst must meet a number of requirements; in the case of supported catalysts, this is a good and controlled dispersion of the active phase over the surface of the support. Monovalent Ag^+ cations are stable in aqueous solution, so ion exchange can be easily carried out in zeolites. Likewise, the reversible oxidation-reduction of silver provides a usable system for studying the mechanisms of the formation of ensembles of spatially well-defined metal clusters. Ag-catalysts modified with transition metals, such as iron, are of great interest due to the influence of the promoter element on the process of formation of clusters and nanoparticles on zeolites. In this contribution, we report on the results of the analysis of Ag-Fe mordenite, performed using thermogravimetry, differential scanning calorimetry and temperature programmed reduction. The latter provides access to the charge state of cations and their local environment [1].

The main goal of the study is to follow up how the preparation method, namely, the temperature of the ion-exchange procedure and the order of introduction of cations impact on the state, localization and morphology of silver- and iron-containing species.

Ag-Fe zeolites were prepared from Na^+-mordenite supplied by Zeolist Int. (Product CBV10A) with a nominal Si/Al atomic ratio equal to 6.5. Studies of the elemental composition by inductively coupled plasma optical emission spectroscopy (ICP-OES) and X-ray photoelectron spectroscopy (XPS) have shown that the amount of exchanged silver and iron is sensitive to the processing method (more to the processing sequence and less to the temperature). For all the silver-containing samples studied, a significant portion of silver is on the surface, forming nanoparticles of 4-9 nm in size, located on the surface of the zeolite [2]. TPR curves indicate the presence of Ag^+ and charged silver clusters. No trace of Fe^{2+} was found in the iron-containing samples that is in fair agreement with our Mössbauer studies. TPR analysis of dehydrated samples (annealed at a temperature corresponding to complete water release) allowed us to identify transition metal ions coordinated by water molecules.

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Effect of thermal treatment of Cu-exchanged mordenites on Cu^{2+} localization studied by thermal analysis and EPR

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Copper-exchange zeolites are highly promising materials for heterogeneous catalysis, especially for reduction of NOx. The multiple researches revealed that their catalytic properties are governed by both the valence state of copper ions and their location and coordination in the zeolite lattice, as well as by copper content. In our previous study of copper-exchanged mordenites obtained from Na+, NH_4^+ and H^+ forms, we have shown that the preparation method (conventional or microwave (MW) assisted) influences copper and water content, copper surrounding, while does not change the electronic state of copper ions [1]. Moreover, it has been found that the MW procedure leads to deeper ion-exchange, especially for samples obtained from sodium form [2]. Applying complementary methods, including temperature programmed reduction, we have proposed a mechanism of thermal decomposition of complex copper-containing species in Cu-mordenites with over-exchange [3].

In this contribution we focus on the effect of thermal treatment of Cu-exchanged mordenites obtained from ammonium and protonated forms with Si/Al = 10. The study was carried out by applying various comprehensive methods including thermogravimetry, differential scanning calorimetry, mass-spectrometry and electron paramagnetic resonance. The sample treatment pathways were following:

(1) NH4-MOR → (heating) → H-MOR
(2) NH4-MOR → (Cu-exchange) → Cu-NH4-MOR
(3) H-MOR → (Cu-exchange) → Cu-H-MOR
(4) Cu-NH4-MOR → (heating) → Cu-H-MOR-1
(5) Cu-H-MOR → (heating) → Cu-H-MOR-2

The main subject of the study was to reveal how the order of heat treatment and ion exchange affects the copper state and its localization in the mordenite framework.

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Investigation of the thermal and combustion properties of energetic materials based on nanoscale Al, Ni and FeO_x powder materials

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The development of technologies for production of nanoscale powder materials opens new areas of application for a large number of classical energetic materials. For example, thermite materials, which have been used for several decades for welding rails and as a solid rocket fuel, in nanoscale form can work as local heat sources or improve the quality of soldering of heat-sensitive microelectronic components. However, the influence of the composition of nanoscale powder materials on the thermal properties, energy and combustion characteristics is not clearly understood. Previously, we investigated the aluminum-nickel bimetallic system [1], which was later used as heat sources for thermoelectric batteries [2]. However, these materials are characterized by a moderate combustion rate and a satisfactory amount of generated heat. In this work, we studied the thermal properties, kinetic parameters of reaction, and combustion characteristics of the thermite mixtures based on the nanoscale Al, Ni and FeO_x powder materials.

Particle sizes, morphology and compositions of the investigated materials were controlled by scanning electron microscopy (Jeol JSM-6010 Plus/LA with energy-dispersive detector). An average particle size of less than 100 nm was determined.

Phase transformations in materials during heating were examined by X-ray diffraction analysis (PANalytical XPert Pro).

Thermal properties and kinetic parameters were studied by differential scanning calorimetry (Shimadzu, DSC-50), simultaneous DSC and TGA measurements (Netzsch, STA 449 F3 Jupiter) and bomb calorimetry (IKA, C 2000). Kinetic triplet (the activation energy, reaction model and pre-exponential factor) of the reaction was determined with using model-free (Flynn–Wall–Ozawa) and model fitting (Coats–Redfern) methods.

High-speed video recording (10000 fps) allowed to determine combustion front propagation velocity after the electrical initiation in the samples.

So, the effect of the iron oxide addition to the nanoscale powder mixture of aluminum-nickel on the thermal properties, kinetic parameters of reaction, and energy and combustion characteristics was investigated. The optimal composition was determined taking into account gas evolution.

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Investigation of thermophysical parameters of effective thermoelectric materials on the basis of chalcogenides of bismuth and antimony

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Low temperature thermoelectric materials (TEM) are actively used in the thermoelectric devices working on the basis of Peltier effect. In addition, such materials are needed and intensively investigated now for multisectional thermoelements in thremoelectric generators (TEG). The quality of TEM is determined by their thermoelectric figure of merit, which in turn is highly dependent on thermophysical parameters. However, determination of these parameters is connected with the measurements of heat fluxes, and their precise definition is a complex experimental problem. So, the aim of this work was investigation of the temperature dependences of thermophysical parameters (heat capacity, thermal diffusivity, thermal conductivity) of effective low temperature TEMs, which we developed for practical uses in multisectional TEGs.

Developed low temperature TEMs were fabricated by different methods:

- $Bi_2Te_{2.8}Se_{0.2}$ (0.14 wt.% of $CdCl_2$) and $Bi_{0.5}Sb_{1.5}Te_3$ (2 wt.% of Te and 0.14 wt.% of TeI_4) obtained by the zone melting method with operating temperature range 200-500 K;
- $Bi_2Te_{2.4}Se_{0.6}$ (0.18 wt.% of CuBr) and $Bi_{0.4}Sb_{1.6}Te_3$ (0.12 wt.% of $PbCl_2$ and 1.50 wt.% of Te) obtained by extrusion with operating temperature range 300-600 K;
- $Bi_2Te_{2.76}Se_{0.24}$ (0.075 wt.% Te and 0.026 wt.% $CdCl_2$) and $Bi_{0.52}Sb_{1.48}Te_3$ (0.14 wt.% Pb) obtained by the ultrafast cooling of the melt with operating temperature range 300-600 K.

Time-of-flight secondary ion mass spectrometry (ToF.SIMS 5) was used for the investigation of material compositions. To study the heat capacity of TEMs in the temperature range from room temperature to 600 K, the calorimetric method was used (Netzsch Phoenix F1 and Shimadzu DSC-50 calorimeters). Al_2O_3 standards were used for the calibration of the calorimeters. The heat capacities of TEMs lies in the range from 0.15 to 0.25 J/(g·K) and practically does not change with temperature in the operating temperature ranges.

To obtain reliable results on the thermal conductivity of TEMs two experimental techniques were used. The first technique is based on the determination of thermal conductivity with using of the results of measurements of heat capacity and thermal diffusivity of TEMs. Laser-flash method was used for the investigation of the thermal diffusivity (Linseis XFA500). Measurements were carried out in the temperature range 300-600 K. The second technique developed by us includes a hardware-software measuring complex and is based on the use of a stationary absolute method. Measurements were carried out up to 600 K.

The values of thermal conductivities obtained by two methods correlate with each other and is equal to 1.4-2.0 W/(m·K) at temperatures of 300-600 K. Their difference does not exceed the measurement errors of techniques. The mechanisms of heat transfer were determined. The maximum values of the dimensionless thermoelectric figure of merit for the materials ivestigated are 1.0–1.2 in the operating temperature ranges.

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Thermal stability of thermoelectric materials on the basis of chalcogenides of bismuth and antimony obtained by different methods

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Multisectional thermoelements for thremoelectric generators (TEG) are actively developed now due to the perspectives of sufficient increasing the efficiency. In this case different thermoelectric materials (TEM) with maximum values of figure of merit (Z) in neighbor temperature ranges are needed. TEGs undergo multiple thermal cycling in the wide temperature range up to 1300 K. For this reason TEMs with not only high thermoelectric parameters but also stable thermal properties are required. However, the knowledge of the stability of thermoelectric materials is insufficient. So, the aim of this work was investigation of thermoelectric parameters, thermal properties and stability of low temperature TEMs, which we developed for practical uses in multisectional TEGs.

Developed low temperature TEMs were fabricated by different methods:

- $Bi_2Te_{2.8}Se_{0.2}$ (0.14 wt.% $CdCl_2$) obtained by zone melting has a maximum value of $Z = 2.89\cdot10^{-3}$ K^{-1} at 300 K in the operating temperature range 200-500 K;
- $Bi_{0.5}Sb_{1.5}Te_3$ (2 wt.% Te and 0.14 wt.% TeI_4) obtained by zone melting has a maximum value of $Z = 3.16\cdot10^{-3}$ K^{-1} at 300 K in the operating temperature range 200-500 K;
- $Bi_2Te_{2.4}Se_{0.6}$ (0.18 wt.% CuBr) obtained by extrusion has a maximum value of $Z = 2.30\cdot10^{-3}$ K^{-1} at 300 K in the operating temperature range 300-600 K;
- $Bi_{0.4}Sb_{1.6}Te_3$ (0.12 wt.% $PbCl_2$ and 1.50 wt.% Te) obtained by extrusion has a maximum value of $Z = 2.35\cdot10^{-3}$ K^{-1} at 300 K in the operating temperature range 300-600 K;
- $Bi_2Te_{2.76}Se_{0.24}$ (0.075 wt.% Te and 0.026 wt.% $CdCl_2$) obtained by ultrafast cooling of the melt has a maximum value of Z = 2.4 at 350 K in the temperature range 300-600 K;
- $Bi_{0.52}Sb_{1.48}Te_3$ (0.14 wt.% Pb) obtained by the method of ultrafast cooling of the melt has a maximum value of Z = 2.5 at 350 K in the operating temperature range 300-600 K;

Time-of-flight secondary ion mass spectrometry (ToF.SIMS 5) was used to study material compositions. Temperature dependences of thermoelectric, electrophysical and thermophysical parameters (Seebeck coefficient, conductivity and thermal conductivity) were investigated in the temperature range of 200-600 K, and showed that TEMs have high ZT, corresponding to the best materials used in the production of thermoelectric devices.

Investigation of the thermal properties and thermal stability of TEMs were carried out in the temperature range from room temperature to 600 K with using of differential scanning calorimetry (Shimadzu DSC-50) and thermogravimetry (Netzsch STA 449 F3 Jupiter). Multiple measurements were performed at a heating rate of 10 °C/min in an inert atmosphere. It was established that TEMs have high stability in the operating temperature ranges, during thermal cycling there were no obvious thermal effects and mass losses.

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Thermogravimetric study on protonation and hydration of perovskite type layered oxide $KCa_2Nb_3O_{10}$

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A series of layered perovskites with general formula $A'[A_{n-1}B_nO_{3n+1}]$, are members of the Dion-Jacobson type oxides. They have been actively studied since the $A'Ca_2Nb_3O10$ (A' = Li, Na, K) was prepared by Dion et al.[1]. The most well studied among them is $KCa_2Nb_3O_{10}$. It consists of two-dimensional perovskite layers interleaved with K^+ ions with a cubic arrangement of corner-shared NbO_6 octahedra and Ca^{2+} ion occupying 12-coordinated sites in the center of each cube. $KCa_2Nb_3O_{10}$ oxide can be transformed to its protonated and hydrated form known as $HCa_2Nb_3O_{10}\cdot1.5H_2O$ by ion-exchange in acid[2]. $HCa_2Nb_3O_{10}\cdot1.5H_2O$ intercalate organic amines and can be exfoliated onto nanolayers by intercalation of bulky organic bases usually with subsequent physical influence (shaking or ultrasonic treatment). $KCa_2Nb_3O_{10}$ and $HCa_2Nb_3O_{10}\cdot1.5H_2O$ as well as their exfoliated and restacked forms are known to be promising photocatalytic materials.

Despite the fact that $KCa_2Nb_3O_{10}$ and its protonated form have been known for a long time, the number of articles devoted to the creation of materials based on them, as well as the improvement of synthesis methods is growing. We present here the results of the investigation on the process of obtaining protonated and hydrated forms of $KCa_2Nb_3O_{10}$ in various conditions studied by means of TG, XRD, EDX and ICP methods.

Scientific research was performed at the Research Park of St.Petersburg State University: Center for Thermal Analysis and Calorimetry, Center for X-ray Diffraction Studies, Center for Chemical Analysis and Materials Research, Center for Optical and Laser Research and Interdisciplinary Center for Nanotechnology.

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Calorimetric study of siloxane dendrimers from the first to the fourth generations with trimethylsilyl terminal groups

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Dendrimers are a special class of hyperbranched polymers with perfect tree architecture. The combination of controlled size and surface functionality allows the use of dendrimers to create nanomaterials with unique electronic, optical, magnetic and chemical properties. Recently, Si-based dendrimers, for example carbosilane and siloxane dendrimers have attracted much attention of researchers [1]. Organosilicon dendrimers are characterized by thermodynamic stability, low characteristic viscosity and high flexibility compared with linear polymers. These properties are caused by the low polarity and high strength of the Si–C bond and the flexibility of the Si–O bond [2].

The aim of this work was to study the standard thermodynamic properties of siloxane dendrimers from the first to the fourth generations with trimethylsilyl terminal groups in a wide temperature range by precise adiabatic calorimetry and differential scanning calorimetry (DSC). The temperature dependences of the heat capacities of the studied compounds were determined for the first time. For all dendrimers, the glass transition and the low-temperature structural anomaly were detected, and the thermodynamic characteristics of these transformations were calculated and analyzed. The standard thermodynamic functions, namely, the heat capacity $C_p°(T)$, the enthalpy $[H°(T)-H°(0)]$, the entropy $[S°(T)-S°(0)]$, and the Gibbs energy $[G°(T)-H°(0)]$ were determined for different physical states of the investigated dendrimers. As a result, the physicochemical discussion and comparison of thermodynamic properties of siloxane dendrimers under study and the literature data for carbosilane dendrimers with different functional terminal groups was performed. This allows us to establish and analyze the practically important dependences "thermodynamic property – structure" for the studied compounds.

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Studies of the thermodynamic properties of betamethasone valerate and mometasone furoate in the range of temperature from T→0 to 350 K

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This work is a continuation of systematic studies of bioactive compounds – glucocorticoids [1-3]. The betamethasone valerate and mometasone furoate are the known glucocorticoids which are used by production and development of medicines for treat many different inflammatory conditions like arthritis, lupus, psoriasis, ulcerative colitis, allergic disorders, gland (endocrine) disorders, and conditions that affect the skin, eyes, lungs, stomach, nervous system, or blood cells [4].

The goals of this work include calorimetric determination of the standard thermodynamic functions of betamethasone valerate and mometasone furoate with the purpose of describing biochemical and industrial processes with their participation.

The temperature dependences of heat capacity of betamethasone valerate (CAS: 2152-44-5) and mometasone furoate (CAS: 83919-23-7) were determined in the first time by precision adiabatic vacuum calorimetry in the range from 6 to 350 K. In the above temperature range the standard thermodynamic characteristics $C_p^o(T)$, $H^o(T) - H^o(0)$, $S^o(T)$, $G^o(T) - H^o(0)$ were estimated. By the experimental data were calculated the standard thermodynamic functions for the range from T → 0 to 350 K. The standard entropy of formations of betamethasone valerate and mometasone furoate from simple substances were calculated at temperature T = 298.15 K.

As a result, some conclusions were made. The obtained experimental results were used for determining the standard thermodynamic functions.

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A study of chloro-*p*-xylylenes polymerization kinetics using high-vacuum *in-situ* differential scanning calorimetry

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Poly(*p*-xylylenes), also known by their trade name as Parylenes, are a class of polymers traditionally synthesized by vapor deposition polymerization technique enabling preparation of thin pinhole-free conformal coatings of controlled thickness without solvents or catalysts. Although over twenty types of Parylenes have been developed, only a few of them are commonly available, i.e. Parylenes N, C, D (unsubstituted poly(*p*-xylylene), poly(chloro-*p*-xylylene), and poly(dichloro-*p*-xylylene), correspondingly), as well as recently commercialized Parylene HT (a fluorinated version of the polymer), and Parylenes A and AM, having amino groups attached to the benzene rings.

The high reactivity of *p*-xylylenes and low polymerization temperatures make a study of the polymerization mechanism a nontrivial problem. In this work the polymerization kinetics of *p*-xylylene (PXN), chloro-*p*-xylylene (PXC) and dichloro-*p*-xylylene (PXD) in condensed state was studied by in-situ non-isothermal DSC measurements, using a custom-made heat-flux calorimeter integrated into a vacuum vapor deposition polymerization reactor. The total exothermal effect of polymerization reactions (86 ± 8 kJ/mol for PXN, 71 ± 9 kJ/mol for PXC, and 57 ± 6 kJ/mol for PXD) and its temperature range (-110 to – 75 °C for PXN, -140 to -80 °C for PXC, and -150 to -80 °C for PXD) were determined. The differential isoconversional method by Friedman was applied for the kinetics analysis. The variation of the effective activation energy with conversion degree reveals a transition from reaction-controlled to diffusion-controlled regime of the polymerization reaction. The reaction model was evaluated using a model-free method based on the use of the compensation effect. The calculated reaction model values were independent on the heating rate and correspond to the Avrami-Erofeev A2 model for PXN polymerization in the conversion degrees interval α of 20 – 80 %, the second-order reaction model for PXC polymerization for $\alpha = 30 – 90$ %, and a linear combination of the first-order and the second-order reaction models for PXD polymerization for $\alpha > 20\%$. One can suggest that this discrepancy can be related to heterogeneous kinetics of the *p*-xylylenes polymerization reaction in solid state, and difference in nucleation and growth kinetics.

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Excess heat capacities for the acetic acid + water mixture in the temperature range 278 – 358 K

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Excess heat capacities are one of the important properties that characterized both pure substances and multicomponent systems. The study of these thermodynamic properties is an actual basic and applied task. However, experimental data on the heat capacities of liquid mixtures are very limited, despite their practical significance. For example, using values on excess heat capacities it is possible to predict other thermodynamic properties, such as excess enthalpies, Gibbs free energy, activity coefficients in a wide temperature range. Moreover, these values give the opportunities to estimate parameters of various Gibbs free energy models (UNIFAC, NRTL etc.) more correctly. In our work a new set of experimental data on excess heat capacities of acetic acid + water binary system were obtained.

Binary mixtures of acetic acid and water were prepared by gravimetric method for the whole range of concentrations with a step of 0.1 mol. fractions. Preliminary densities of each binary system were measured using laboratory densitometer DMA 5000 M (Anton Paar) at temperatures from 278 to 358. The experimental determination of heat capacities was carried out using microDSC III Evo calorimeter (Setaram) in the temperature scale 278 – 358 K. The cells for Cp were prepared according to Setaram recommendation. Experimental procedure was tested by measuring of excess heat capacities for the standard substances: water and n-heptane. According to tests the deviation of experimental data (ARD) was less than 2 %.

We also applied the new data on excess heat capacities for calculation of heats of mixing (excess enthalpies, H^E) in binary system acetic acid + water at few temperatures. The calculated results are in good accordance with experimental data on H^E and reflect the necessity of consideration of temperature dependence of thermal effects of mixing. The new data set is useful both for the calculation of temperature dependence of other fundamental thermodynamic properties, especially when rigorous data is necessary for the industrial process design.

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Dynamics of thermal decomposition of the double complex salt $[Cr(ur)_6][Co(CN)_6]\cdot4H_2O$ and its constituent parts

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The destruction of double complex compounds (DCS) is a promising way of creating nanoscale metal and oxide functional materials. For example, an alloy of five platinum metals can be obtained by thermolysis of DCS.

$[Cr(ur)_6]Cl_3\cdot3H_2O$, $K_3[Co(CN)_6]$ and $[Cr(ur)_6][Co(CN)_6]\cdot4H_2O$ were synthesized and characterized by XRD, IR and elemental analysis. DCS was obtained by stoichiometric mixing $[Cr(ur)_6]Cl_3\cdot3H_2O$ and $K_3[Co(CN)_6]$. The thermolysis of complex compounds was carried out on the equipment STA 409 PC Luxx (NETZSCH) in an argon atmosphere at heating rates of 5, 10, 20 °C/ min in the temperature range of 30–1000 °C. The temperature decomposition interval narrows when the heating rate increases from 5 to 20 °C/ min, which reaches 30-40 °C for $[Cr(ur)_6]Cl_3\cdot3H_2O$ and DX and 150° C for $K_3[Co(CN)_6]$. Similar shifts are observed on the DSC curves for these compounds. The mass of the final calcination residue increases by 5-16 wt.% with increasing heating rate. This may be due to the fact that the ligands do not have time to completely retire to the gas phase at a higher heating rate to the same final temperature.

Curves TG and DSC $[Cr(ur)_6][Co(CN)_6]\cdot4H_2O$ are not a superposition of such curves for monocomplexes. The latter begin to decompose at higher temperatures (180 and 600 °C, respectively) than DCS (70 °C) (Fig. 1). The cationic and anionic components simultaneously affect to the thermal stability of $[Cr(ur)_6][Co(CN)_6]\cdot4H_2O$. $[Cr(ur)_6]Cl_3\cdot3H_2O$ and $K_3[Co(CN)_6]$ are more thermally stable than $[Cr(ur)_6]^{3+}$ and $[Co(CN)_6]^{3-}$ as part of the DCS. Sharp mass losses at 620 and 800 °C are observed when the DCS is heated; they refer to the decomposition of $[Co(CN)_6]^{3-}$. Similar peaks at $K_3[Co(CN)_6]$ are observed at 740 & 900 °C. It was also previously determined that the cationic and anionic parts of DCS begin to decompose simultaneously when heated to 200 °C.

The results obtained allow us to expand the database on the thermolysis of DCSs for 3d-metals, in particular, $[Cr(ur)_6][Co(CN)_6]\cdot4H_2O$. They can also be used to refine the mechanism of decomposition of DCS and determine the kinetic parameters of the reactions occurring in this process.

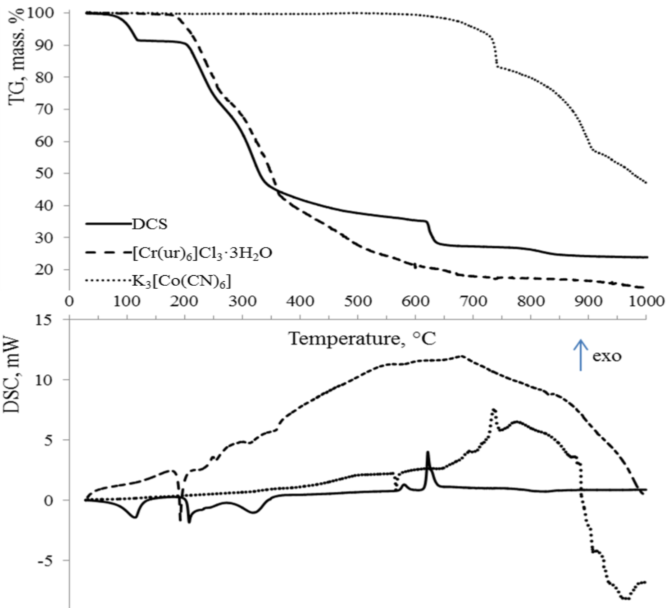

Fig. 1. Experimental data of the studied compounds

Host-guest inclusion complex of β-cyclodextrin and benzoic acid in water-ethanol solvents: spectroscopic and thermodynamic characterization of complex formation

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Benzoic acid (BA) is the simplest aromatic carboxylic acid that inhibits the growth of mold, yeast and some bacteria. Thus, benzoic acid and its salts are used as food preservatives, beverages and cosmetics. It is a constituent of some pharmaceutical formulations and independently displays a therapeutic effect in treatment of skin diseases. To improve bioavailability, ensure maximum effectiveness of the treatment, reduce toxicity, the solubility of drugs have to be increased. One of simple and effective ways is an encapsulation by cyclodextrins. In this study, an inclusion complex of benzoic acid with β-cyclodextrin ([BAβCD]) was obtained in water-ethanol solvents. The yield of complex synthesis in binary mixtures is greater than in water and reached maximum value at 0.10 mole fraction of ethanol. Results of FTIR spectroscopy analysis showed that the main difference in the spectra of the acid and inclusion complex was observed in the frequency range from 2500 to 3100 cm^{-1}, corresponding to aromatic hydrogen vibrations. These vibrations are highly attenuated in the complex. Phase solubility and differential scanning calorimetry studies revealed that in water the complex was obtained with 1:1 stoichiometric ratio and on increasing the solubility of benzoic acid. The logarithm of stability constant in water was found to be 1.99.

The thermodynamic parameters for [BAβCD] complex formation in H_2O-EtOH solvents were determined from calorimetric experiments carried out by means of the calorimetric titration system TAM III (TA Instruments) at T=25°C in water-ethanol mixed solvents containing X(EtOH)= (0.00, 0.10, 0.20 and 0.30) mole fraction at pH = 3.6 and T=25°C. However, at X(EtOH)= 0.30 mole fraction, according to the calorimetric titration data, no complex formation occurs. When transferring from H_2O to H_2O-EtOH solvents complex stability decreases from lg$K$ = 2.4 to lg$K$ = 0.7, whereas exothermicity increases from -12.2 kJ mol^{-1} to -44.3 kJ mol^{-1}.

In conclusion, addition of small amounts of ethanol to water impact on the complex formation and therefore thermodynamic studies are important for improving bioavailability of drugs in non-aqueous media.

Funding: This work was funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) [grant number 104.06-2017.329], Russian Foundation for Basic Research (RFBR) [project №19-53-54004] and Ministry of Foreign Affairs and International Cooperation of Italy [grants in favor of foreign citizens not residing in Italy and Italian citizens living abroad, № 946-22/10/2018].

The stability of aryloxy-substituted phthalonitriles towards thermo-oxidative destruction

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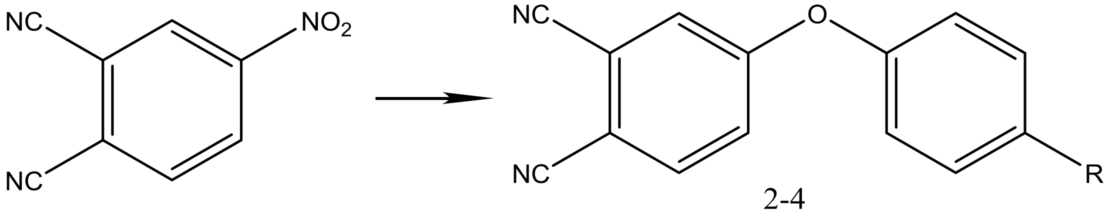
Substituted phthalonitriles are known to be precursors for the synthesis of macrocyclic compounds (MHC), which in turn are promising for usage in many fields of science and technology. Since MHC production is often carried out by template condensation at a high temperature in the presence of oxygen, it is important to know about the stability of the starting compounds to heat. In connection with this nucleophilic substitution, 4-aryloxy-substituted phthalonitriles (**2-5**) were obtained and their resistance to heating in air was evaluated.



R = OC_2H_4 (2), OC_4H_9 (3), OC_8H_{17} (4), $OCH_2C_6H_5$ (5)

Based on the DSC data analysis of the phthalonitriles synthesized (**2–5**), it can be seen when samples are heated to 240–260 °C, the mass of the sample decreases by approximately 3–5%, associated with the removal of the occluded solvent.

With further increase in temperature, processes associated with the destruction of the compounds under study are observed. Thermal-oxidative destruction of phthalonitriles (**2-5**) proceeds in two stages. The first exo-peak on the DSC curves appears in the limit of 278-360°C, and the *exo*-effect corresponding to the maximum at 496-581 °C. In addition, on the DSC curves at 59-116 °C, there was an *endo*-effect corresponding to the melting points of the nitriles synthesized. It was shown compound **4**, which has the longest substituent, melts at the lowest temperature of 59 °C, and the highest melting point (116 °C) is correspond to nitrile **5**, which includes a terminal benzyl fragment. Thus, the phthalonitriles synthesized are thermally stable compounds, the destruction of which begins at temperatures above 260 °C, and their resistance to thermal-oxidative degradation increases in the following row: **4** < **2** < **3** < **5**.

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On the ways of the fusion enthalpy determination below the melting temperature

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Fusion enthalpy is one of the key values in thermal analysis. Both fusion enthalpy values at the melting temperature and below this are of interest in chemical thermodynamics. However, its temperature dependence, which is related to the difference of the heat capacities of the liquid and crystal, is generally unavailable due to fast crystallization of liquids below the melting point.

Solution calorimetry can be used as an indirect source of information about the fusion enthalpy value at 298.15 K. In the present work the relationship between the fusion enthalpies of aromatic compounds at the melting temperature and the solution enthalpies in benzene at 298.15 K was studied according to Eq. (1):

$$\begin{aligned}\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}(\mathrm{cr},\ 298.15\ \mathrm{K}) - \Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}(\mathrm{l},\ 298.15\ \mathrm{K}) = \\ = \Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}}) + \int_{T_{\mathrm{m}}}^{298.15} [C_{\mathrm{p}}^{\mathrm{A_i}}(\mathrm{l}, T) - C_{\mathrm{p}}^{\mathrm{A_i}}(\mathrm{cr}, T)]dT\end{aligned} \tag{1}$$

Where $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ is the enthalpy of solution of compound $\mathrm{A_i}$ in benzene, $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ is the enthalpy of fusion at the melting temperature and $\int_{T_{\mathrm{m}}}^{298.15} [C_{\mathrm{p}}^{\mathrm{A_i}}(\mathrm{l}, T) - C_{\mathrm{p}}^{\mathrm{A_i}}(\mathrm{cr}, T)]dT$ is a thermal adjustment of the fusion enthalpy to 298.15 K calculated according to Kirchhoff's law.

Analysis of Eq. (1) allowed estimating the heat capacity integral values for the compounds which cannot be supercooled without crystallization at the currently available cooling rates. It was found that the linear extrapolation of the liquid state heat capacity temperature dependence between 298.15 K and T_{m} led to the heat capacity integral agreeing with the difference between $\Delta_{\mathrm{cr}}^{\mathrm{l}}H^{\mathrm{A_i}}(T_{\mathrm{m}})$ and $\Delta_{\mathrm{soln}}H^{\mathrm{A_i/C_6H_6}}$ for 30 compounds. Further this approach was extended to self-associated aromatic compounds (phenols, anilines) by replacing benzene with a solvent in which solution enthalpy of hypothetically liquid solute is close to zero.

A direct way to overcome crystallization of liquids below T_{m} while measuring the heat capacity is increasing the scanning rates. In the present work the methodology for determination of the heat capacity of deeply supercooled low-molecular-weight organic compounds by fast scanning calorimetry was developed. Direct study of the heat capacity of 8 organic compounds by fast scanning calorimetry confirmed the validity of the solution calorimetry approach.

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Thermal investigation of *α*-, *β*-, *γ*-cyclodextrin hydrates dehydration processes

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α-, *β*- and *γ*-cyclodextrins (CDs) are cyclic macromolecules consisting of 6, 7, or 8 glucopyranose units, respectively. These units form hollow truncated cone cavity with hydrophilic exterior and hydrophobic interior. A wide range of guest molecules can be included in the CD cavities, forming host-guest inclusion complexes. These inclusions may lead to beneficial changes of CD physicochemical characteristics such as solubility, thermal stability, volatility, resistance to oxidation, visible and UV light, etc. Due to these properties CDs are widely used in analytical chemistry, catalysis and also in pharmaceutical, food and cosmetic industries. Water plays an important role in formation of the CDs inclusion complexes because the process of complex formation is essentially a replacement reaction of water molecules located in CD cavities by hydrophobic guest molecules. Meanwhile, quantitative data on equilibria between CDs and H_2O are very scant and contradictory [1–3], which makes it difficult to produce high-quality materials.

The purpose of this work is a comprehensive study of the *α*-, *β*- and *γ*-CD hydrates dehydration processes by static method with quartz membrane-spoon manometers. The uncertainties in measurement of pressure, temperature and water content in CDs were 0.5 Torr, 0.5 K and 0.01 formula units, accordingly [4]. The measurements have been realized in the wide intervals of temperature ($313 \leq T/\mathrm{K} \leq 506$), pressure ($0.5 \leq p/\mathrm{Torr} \leq 760$) and composition ($\mathrm{CD}{*}x\ H_2O$, $2.6 \leq x \leq 15.9$).

As a result of this study thermal stability of investigated compounds was established, temperature dependences of pressure for dehydration processes were obtained (four types of dehydration processes were studied), enthalpies and entropies of dehydration were determined and Gibbs energy of bonding water with CDs was calculated. On the base of information obtained the conclusions about the nature of the interactions between host and guest molecules (water) were drown.

Accumulation of quantitative information on dehydration processes of *α*-, *β*-, *γ*-CDs hydrates will allow one to synthesize functional materials with desired properties in future.

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Thermal study of Bi(III) polybromides

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Bismuth halide complexes are of interest due to the variety of attractive physical properties of these compounds: luminescence, photochromism, semiconductor properties, etc. Recently, a family of polybromide complexes containing $\{Br\}^{n-}$ units was introduced [1-2]. Among them, there are compounds containing pyridinium-type cations and anions of the same structural type (Fig. 1): $(N\text{-}MePy)_3[Bi_2Br_9]Br_2$ and $(PyH)_3[Bi_2Br_9]Br_2$ (**1** and **2**). Preliminary studies (TG data) reveal [1] that these complexes demonstrate remarkable thermal stability. However thermal properties of Bi(III) polybromides are weakly studied: the only thermal study carried out by the DTA/TG method [1] provides only a qualitative estimation of the thermal behaviour of $(N\text{-}MePy)_3[Bi_2Br_9(Br_2)]$. So the aim of this work is to obtain quantitative data on the process of bromine evaporation from the studied complexes.

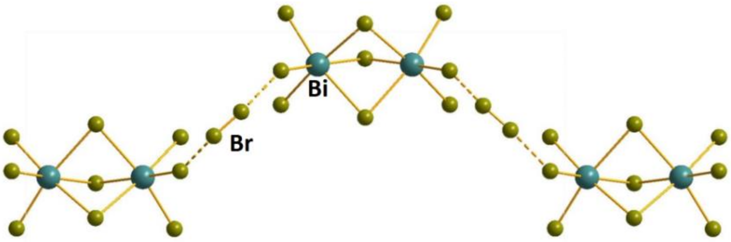

***Figure 1**. Structure of the anionic part in **1** and **2**.*

Thermal behaviour of $(N\text{-}MePy)_3[Bi_2Br_9]Br_2$ and $(PyH)_3[Bi_2Br_9]Br_2$ has been investigated by static method with glass (pyrex) membrane-gauge manometers [3]. The limiting uncertainties in measurement of pressure, temperature and solid phase composition on this set-up were 0.5 Torr, 0.5 K and 0.01 formula units, accordingly. The experiments have been carried out in the wide intervals of temperature ($313 \leq T/\text{K} \leq 533$) and pressure ($0.1 \leq p/\text{Torr} \leq 760$).

As a result of thermodynamic study of these complexes the fields of their thermal stability were established, the temperature dependences of bromine vapor pressure were obtained, the thermodynamic characteristics of evaporation processes ($\Delta_r H_T$, $\Delta_r S_T$) were calculated and the conclusions about the nature of interaction between bromine molecules and a matrix are made.

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Thermal analysis and porosimetry of natural zeolites from deposits in Cuba

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The main applications of natural zeolites are in the environmental field, particularly for catalytic processes, soil amendment, cement manufacture, energy recovery technologies, pharmaceutical, oilsands bitumen cracking, wastewater purification, decontamination of radioactive elements, for the immobilization of microorganisms and environmental remediation. Significant zeolite deposits are widespread in the Cuba area and are of great interest because of their abundance and potential economic value. Among sedimentary natural zeolite, the more important structures, as regarding their occurrence and practical applications, are clinoptilolite and mordenite. They were selected for study in this present work.

The aim of the present study is to investigate the thermal behaviour and the porosity of natural zeolites from different deposits of Cuba. Such materials as the clinoptilolite (Tasajeras) and mordenite (Santiago de Cuba) were investigated. Simultaneous thermal analysis (TG + DSC) coupled with mass spectrometry of evolved gas, porosity measurements by standard porosimetry and XRD analysis were applied.

The thermo-chemical parameters, such as the thermal effects of degradation processes of zeolites, mass loss of samples in the temperature range of 40 - 750 ˚C, and distribution of pore diameters including the average pore size were identified. Similarities and differences in the characteristics of the studied natural zeolites with zeolites of Mexico were analysed. Some similarity in the thermochemical properties of the samples by geographic location of deposits (one endothermic effect for samples from Cuba and two endothermic thermal effects for samples from Mexico) was shown. The highest values of surface area and largest average pore diameter corresponding to clinoptilolite samples from Tehuacan deposit allow us to suggest that these natural zeolites can be successfully used for catalytic performances. The data that was obtained in this study can represent great interest for geological researches of the regularities of formation of island and mainland deposits of natural zeolites in Latin America.

Scientific research was performed at the Research Park of St.Petersburg State University: Center for Thermal Analysis and Calorimetry and Center for X-ray Diffraction.

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Thermal properties of the low-melting Bi-Sn-Zn eutectic alloy

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Beside their large importance in lead-free soldering, low-melting eutectic alloys based on Sn, Bi, and Zn are among the most promising candidates for middle operating temperature phase change materials (PCMs) [1]. PCMs are widely used in the field of thermal energy storage (TES) [2]. PCMs store the thermal energy of a phase change (typically fusion), called the “latent” heat of phase change, on heating, and then when cooled, they give off the stored heat by reversing the phase change. Low-melting metals and eutectic alloys are relatively new class of PCMs. The main advantages of the low-melting metallic materials usage as PCMs are their high volumetric latent heat and high thermal conductivity. However, numerous important thermo-physical properties such as melting point, latent heat of fusion, specific heat capacity, thermal conductivity and surface tension for many low-melting eutectic alloys are still unknown [3].

In this study, melting temperature, latent heat of melting and thermal conductivity of the Bi-Sn-Zn eutectic alloy were experimentally investigated. Melting temperature and latent heat of melting were determined by using differential scanning calorimetry (DSC). Thermal diffusivity of the investigated eutectic alloy at 25 °C was measured by using xenon flash method on a Discovery Xenon Flash DXF 500 device. Based on the experimentally determined values of thermal diffusivity and the specific heat capacity values obtained by thermodynamic calculation, thermal conductivity of the investigated eutectic alloy was determined. In addition, microstructure of the investigated eutectic alloy was examined by means of **scanning electron microscopy** (**SEM**) with energy dispersive X-ray spectrometry (**EDS**).

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Acknowledgements

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The effect of drying mode on the kinetics of thermal degradation of graphene oxide/OH-functionalised poly (butylacrylate-co-methylmethacrylate) composite

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Nano-composite materials based on acrylate latexes and graphene oxide, i.e., reduced graphene oxide are novel class of materials that exhibits extraordinary properties [1]. A sample of composite by combination of graphene oxide and polymer latex of OH functionalized polymer latex made of methyl methacrylate and butyl acrylate (1:1) using 2wt% of hydroxyethyl methacrylate was synthesized [2]. The effect of drying mode, conventional (oven - drying at 70 ºC, 72 h) and lyophilisation (using lyophilisator Telstar LyoQuest-85 at -60ºC, 24 h) on the thermal stability and the kinetics of thermal degradation of the synthesized composite was investigated.

The thermogravimetric (TG) curves were recorded at Thermo gravimetric Analyser model Q500 (TA Instruments). The thermal stability is higher for the oven-dried sample then for the lyophilized one and that the degradation processes for both drying modes were complex. The degradation process of the oven-dried sample occurs through two clearly separated processes ($\alpha 1$: 623-772K, $\alpha 2$: 799- 933K) while the lyophilized sample reveals the three distinguishing degradation processes ($\alpha 1$: 530-586 K, $\alpha 2$: 558-671K, $\alpha 3$: 741- 891K).

With the aim to determine kinetics parameters of every single degradation process, their conversion curves were fitted by using the Weibull's function of reaction time distribution. The values of the Weibull's function parameters β and η of the kinetics function of degradation for the lyophilized sample are the highest for the third component of degradation ($\beta=4.2$ and $\eta=9.9$), whereas in the case of oven-dried sample the values of the β and η are higher for the second degradation process $\beta=3.8$ and $\eta=8.9$). Based on knowing values of parameters of Weibull's function, the values of temperature dependencies of specific rate of degradation, and kinetic parameters: activation energy (Ea) and pre-exponential (lnA) of the degradation were determined. The mechanism of thermal degradation of graphene oxide/OH-functionalized poly(butylacrylate-co-methylmethacrylate) composite was suggested and discussed.

Acknowledgement: The presented investigations were supported by The Ministry of Education, Science and Technological Development of the Republic of Serbia, through the Project 172015 and Cost Action CA15107.

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The kinetics of non-isothermal dehydration of equilibrium swollen Ca-alginate hydrogel

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High biocompatibility, biodegradability and low toxicity of calcium alginate hydrogel (CAH) enable its wide application in a range of industries, in particular in the pharmaceutical and food industries. Knowledge of CAH dehydration kinetics is of utmost importance for the design, optimization and development of new CAH applications. In this paper, the non-isothermal kinetics of the dehydration of equilibrium swollen CAH at different heating rates (5-20 K / min) were examined.

The CAH was prepared following the procedure of Rassis [1]. The basic primary structural properties of the synthesized CAH were determined.

The thermogravimetric (TG) curves were recorded at Thermo gravimetric Analyser model Q500 (TA Instruments). Based on the determined shapes of the dependencies of the rate of dehydration and the values of activation energies (Ea,α) from the degree of dehydration (α).

it was concluded that dehydration is a kinetically complex reaction that cannot be mathematically described by ordinary used kinetics models. However, using the statistical model of dehydration of a hydrogel based on Weibull's function [2], the kinetics of NIT dehydration CAH were successfully mathematically described. The values of the parameters of the Weibull function (β and η) at different heating rate were calculated. It was found that the values of the parameters β increase with the increase in the value of heating rate (from 1.50 to 1.93) while the values of the parameter η decrease (from 6.21 to 3.20).

Based on the knowledge of the Weibull function for different heating rates, the dependencies of the specific dehydration rate (k) from the temperature were calculated. It was found that the values of the k at a certain heating rate increase with increasing temperature in accordance with Arrhenius' equation. On the basis of this, the changes of the activation energy (Ea) and pre-exponential (lnA), of dehydration with temperature were calculated. A model of the CAH non-isothermal dehydration was suggested and discussed.

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Potentials and Development of Wind Energy in the Republic of Serbia

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The authors analyze the legal and political framework that is significant for the use of wind energy in the Republic of Serbia. In addition, the paper examines the compliance of Serbian legislation with the world trends in this area, as well as obligations from ratified international documents, the process of European integration and the Energy Community. Ratification of the Energy Community Treaty by which Serbia became a part of a connected European energy market. Besides, the authors discuss the potential and development of wind energy in the Republic of Serbia, as well as the reasons for further intensification of development. Research shows that the potentials for producing from wind energy in the Republic of Serbia are favorable [1, 2, 3]. Wind strength in the windiest area of the Republic of Serbia is comparable to the wind strength in windiest areas of Europe [4]. Promoting innovative renewable applications and reinforcing the renewable energy market will contribute to the preservation of the ecosystem by reducing emissions on local and global levels [5]. Therefore, the exploitation and wider use of wind energy should greatly benefit the Republic of Serbia from attracting investments in this sector and local economic development, ensuring energy security to mitigating environmental problems.

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Thermal characterization of the In–Sn–Zn eutectic alloy

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This study presents results of thermal analysis and microstructure investigation of the low-melting In–Sn–Zn eutectic alloy with potential for application in the field of phase-change materials (PCMs) [1-3]. The In–Sn–Zn eutectic alloy with nominal composition 52.7In-44.9Sn-2.4Zn (at. %) was prepared by melting of pure metals under an argon atmosphere Microstructure and composition of the ternary eutectic alloy were analyzed using scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS). Melting temperature and latent heat of melting were measured using differential scanning calorimetry (DSC). Experimentally obtained melting temperature and latent heat of melting for the In–Sn–Zn eutectic alloy are 106.5±0.1 °C and 28.3±0.1 Jg^{-1}, respectively. Thermal diffusivity and thermal conductivity of the In–Sn–Zn eutectic alloy have been determined using the xenon flash method. Thermal conductivity of the investigated eutectic alloy was determined to be 42.2±3.4 $Wm^{-1}K^{-1}$ at 25 °C. Experimental results were compared with the results of thermodynamic calculation according to the CALPHAD (calculation of phase diagram) method.

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Characterization of weld metal in welded microalloyed steel J55 made using a rutile electrode with a flux-cored wire core

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The development and production of welding electrodes with enhanced properties represents complex research that requires changes in certain technological phases of making the core and coating [1-3]. Improving the properties of the electrodes by changing the properties of the steel core is possible by replacing solid wire with alloyed flux-cored wire.

The possibility of use of flux-cored wire for making the electrode core requires primarily that the thickness of the steel shell is sufficient to enable the preparation of the rod of a required diameter and length with straight ends, to which the coating can evenly be applied by continuous pressing.

This paper presents the results of tests of mechanical properties (yield strength, tensile strength and toughness) at various temperatures and microstructure of welded joints of microalloyed high strength (HSLA) steels J55 (according to API Spec 5L) implemented using new quality coated electrodes.

The mastered quality of the coated rutile electrode has a core of flux-cored wire alloyed with Ni and Mo. The main objective of this research is to define the justification of replacing the solid wire electrode core with flux-cored wire.

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Influence of variation of pH and concentration on efficiency of naproxen removal from mixture of pharmaceuticals by advanced oxidation photocatalysis using ZnO/TiO_2

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Naproxen (NPX) is widely prescribed pharmaceutical for the skeleton-muscle pain or inflammatory rheumatic disorders due to its analgesic and antipyretic effects. It is one of the most frequently found persistent pharmaceutical pollutants in aquatic media and conventional treatment plants are inefficient for its removal. The use of catalysts for the efficient degradation of more than one category of pollutants is challenging and very important for the practical application perspectives. The efficiency of photocatalytic degradation of naproxen from a mixture of pharmaceuticals in the aqueous medium by advanced oxidation using nanoparticle photocatalysts powder ZnO/TiO2**,** activated by UV radiation, has been examined. The dependence of the change in values of pH and the different concentrations of naproxen on the degradation rate has been analyzed. With an increase in the initial concentration of naproxen from 2 mg L^{-1} to 10 mg L^{-1} in the aqueous medium, the efficiency drops about 6 times. Decomposition rate slightly increase with an increase in pH values from acidic to basic environment. The rate increases from 0.013 min^{-1} to 0.018 min^{-1}. The effect of mixture on efficiency was compared with the results of the decomposition of naproxen itself [1]. It has been shown that the decomposition of naproxen as the most persistent pharmaceutical in the mixture begins with a certain delay compared to the activation time of the photocatalyst, which is not observed when naproxen is separately degraded.

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Variation of the apparent activation energy throughout the glass transition process in chalcogenide system Cu-As-Se

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Variations of the apparent activation energy of glass transitions process E_g have been determined by applying an isoconversional method to differential scanning calorimetry data on the glass transition in chalcogenide glasses from the $Cu_x(As_2Se_3)_{100-x}$ system for x=1, 5, 10 and 15 at. %. The characteristic values of E_g have been calculated using the advanced isoconversional method developed by Vyazovkin [1-3] as well as isoconversional forms of relations of Kissinger [4] and Moynihan [5, 6]. According to temperature dependence on a heating rate apparent glass transition activation energies E_g were calculated for differently defined glass transition temperatures. The results showed the activation energy vary with the extent of transformation from the glassy to the supercooled phase, pointing out that it is a complicated process. The activation energy values are slightly changed with the change of copper content from 1 to 5 at. %, while larger changes are made by further increasing of copper content up to 15 at. %. The lowest value has a composition with 15 at. % of copper and this value is 231(13) kJ mol^{-1} at extent of conversion α of 0.5. A variability parameter Δ_E has been introduced to characterize the rate of decrease in E_g during the glass transition process. The highest absolute value for Δ_E has been detected in the composition with 15 at. % of Cu and was Δ_E = -6.1 kJ mol^{-1} K^{-1}. The observed changes have been related to changes in the structure of the glass with increasing copper content.

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The thermal properties of novel polyurethane hydrogels

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Due to the great similarity of hydrogels with soft tissues, they are the ideal material for use in regenerative medicine. One of the materials known for its compact structure, good mechanical properties and the ability to handle soft tissues is polyurethane. Polyurethanes (PU), known as hydrophobic or insoluble in water, can be modified by incorporating hydrophilic soft segments, e.g. poly (ethylene oxide) (PEO) to increase their hydrophilicity. In this paper, novel PU hydrogels are prepared by polymerization of aliphatic di-isocyanate and high molecular weight diols[1,2]. The goal was a preparation of hydrogel with a uniform structure, which is not porous. Two series of hydrogel were prepared, one at elevated temperature (60 °C) and second in vacuum at 25 °C. In synthesis, multifunctional isocyanates, poly (ethylene oxide) (with molecular weights 4000, 6000 and 10000 g / mol), with the corresponding initiator, are polymerized in tetrahydrofuran as a solvent, with stirring on a magnetic stirrer. The mixing was carried out at low speeds to avoid the formation of air bubbles. After synthesis, the samples were dried and then subjected to characterization by Fourier infrared spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG), and swelling ratio. The FTIR results show that the formation of the urethane group was completed and a quantity reaction was achieved[3], DSC results indicate that the melting temperature changes depending of used PEO[4]. Tg results show that, depending on the polyol, i.e. the length of its chain and the synthesis method, the thermal properties of polyurethane hydrogels can be significantly influenced. Swelling ratio of polyurethane hydrogels were 521% (with PEG 4000), 295% (with PEG6000) and 217% (with PEG 10000).

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Thermal properties of silicone nanocomposites

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Silicone elastomers are one of the most important class of polymer materials, because of their extraordinary properties. They are stable at high temperatures, as well as in oxidative environment, and understanding of the thermal stability of silicone elastomer is highly important in order to tune the properties of final materials for specific exploitations. The aim of this work was investigation of the influence of the silica nanofiller on thermal properties of silicone elastomers. Vinyl and hydrogen siloxanes (for polymer matrix synthesis), and hydrophilic or hydrophobic nanosilica (5, 10 and 20 wt%) were used for nanocomposite preparation. The influence of the nanofillers on the thermal properties of the silicone nanocomposites has been studied in detail. According to the TGA results clear trend of increasing of thermal stability of the silicone with the addition of nanofillers was observed. Thermal stability of the silicone elastomeric nanocomposites with hydrophilic silica was higher compared with hydrophobic ones. As it was expected the highest improvement of stability was registered for sample with 20 wt% of filler (for both types of used silica filler). DSC results has shown that with the addition of filler in the polymer matrix, phase separation and the appearance of melting of soft segments occur at temperatures around -50 °C. Namely, the addition of hydrophobic silica filler increasing Tm values, probably due to strong filler/polymer interaction. Lower compatibility of hydrophobic matrix and hydrophilic filler caused decreasing of Tm values. With the addition of both types of nanofiller slightly decreasing of melting enthalpy was observed for all samples.

Influence of thermally induced structural transformations on corrosion resistance of amorphous $Fe_{81}B_{13}Si_4C_2$ alloy

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Due to their isotropic structure lacking long-range atom arrangement and resulting isotropic physical and mechanical properties, amorphous alloys have been attracting a lot of scientific attention. They undergo microstructural transformations at increased temperatures or pressures or even during prolonged application under moderate conditions because of their thermodynamic and kinetic metastability. Since the microstructure is one of the determining factors for functional properties and practical application of these materials, understanding of thermal stability and thermally induced structural transformations of amorphous alloys is very important.

Thermal stability of the soft magnetic $Fe_{81}B_{13}Si_4C_2$ alloy was studied using differential scanning calorimetry (DSC) in the temperature range 25-650 °C. Thermally induced structural stabilization occurred as a stepwise process including a structural relaxation and crystallization. In order to find the crystallization products, X-ray diffraction (XRD) measurements were performed.

Amorphous structure contains no grain boundaries or crystalline defects which could induce localized corrosion and therefore is expected to be more corrosion resistant than its crystalline counterpart. Corrosion resistance of the $Fe_{81}B_{13}Si_4C_2$ alloy was examined by recording anodic polarization curves in three different media, 0.5M NaOH, NaCl and HCl, before and after thermal treatment at different temperatures. Significant dependence of the corrosion resistance on the corrosion media and alloy microstructure was observed. Alloy morphology was influenced by both the corrosion media and the temperature of thermal treatment.

Mechanical-acoustic study of electroporcelain made under different compression pressures

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The preparation technology has a remarkable impact on the physical properties of the final ceramic product. The technological process of traditional ceramics production consists of clay mining, purification, mixing with additives, shaping, drying, firing, and optionally glazing and grinding [1].

In this study the C 130 type electroporcelain (prepared according to the IEC 60672-3) is investigated by the mechanical-acoustic methods. The investigated material was prepared by PPC Čab, a.s. This material was chosen due to its wide range of application in the ceramic industry. Samples were prepared by cold isostatic pressing with different compression pressures from the interval 70 – 110 MPa. Prior to the pressing, the base materials were homogenised. Acoustic emission (AE), thermodilatometry (TDA), thermogravimetry (TGA) and Young modulus of elasticity (YM) were carried out during heating and cooling phase of the firing process in the temperature interval from 50 °C up to 1100 °C with a heating rate of 5 °C/min in static air atmosphere.

The AE activity was higher in the cooling phase, than during heating. This can be well explained by the different thermal expansion coefficients of various mineral phases. However, no dependence of the AE activity on the compression pressure was observed. No significant change by TGA and TDA were recorded. However, result of YM show that, with increasing compression pressure, values of YM are rising.

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Determination of the approximation for the temperature integral

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It is well known, that the Arrhenius temperature integral $p(y)$ does not have an analytical solution. For this reason, there is a variety of methods for the kinetic analysis which differ in their approximation [1]. These are proposed with different mathematical complexities and numerical precisions.

It was noted in reference [2], that one group of approximations can be described by the equation $p(y) \cong \exp(-ay + b)/y^k$. However, this term can be also used for the approximation of the Arrhenius temperature integral. This is demonstrated by the two-step linearly fitting process:

(i) the linear dependence of $(\partial p(y)/\partial y)$ vs $1/y$,
(ii) the linear dependence of ("ln" $p(y) + k \ln y$) vs y.

Using these steps, a more precise approximate formula for Arrhenius temperature integral is proposed.

Finally, the validity of this approximation is confirmed by using the data from the thermogravimetric analysis from 1°C min^{-1} to 10 °C min^{-1}. These experiments were performed on kaolin samples in a dynamic atmosphere of dry air.

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Structure and volume relaxation of selected BaO-P_2O_5 glasses

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The fundamental information that is inevitable for the evaluation of the relaxation process is obtained from experiments performed by thermal analysis methods such as DSC and TMA. In the glass transformation range, the relaxation kinetics is well described by the Tool–Narayanaswamy–Moynihan (TNMo) model with application of Tool’s fictive temperature, T_f, and the distribution of relaxation times expressed by the empirical Kohlrausch–Williams–Watts function (KWW) [1]. However, if structural relaxation and viscous flow proceed simultaneously, the Tool–Narayanaswamy–Mazurin (TNMa) model was proposed for the description of thermo-mechanical curves [2]. Structural relaxation of binary barium phosphate glasses containing (30, 35, 40, 45, 50, and 55) mol% of BaO was studied by non-isothermal thermo-mechanical analysis, and the relaxation process was described by TNMa and TNMo models. The model parameters and material constants were obtained by the nonlinear regression analysis of thermo-mechanical data by the own software written in FORTRAN [3]. The sum of squares of differences between the calculated and measured values of relative deformation was minimized by the regression analysis. For both models, the values of the exponent b of the KWW equation, and the modulus K were optimized. Moreover, the limit dynamic viscosity η_0, and B constant of the Andrade’s viscosity equation were optimized in case of the TNMa model. In case of the TNMo model, the additional optimized parameters were the viscous flow activation energy Δh^* and the dimensionless coefficient x. The match between model and experiment were quantified by values of Fisher’s F statistics and standard deviation of approximation s_{apr}. Based on a graphical comparison it can be stated that TNMa and TNMo models very well describes the experimental data.

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Crystallization kinetics of binary Yb_2O_3-Al_2O_3 glass

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The ytterbium aluminium garnet composition, YbA-G (62.5 mol.% Al_2O_3, 37.5 mol.% Yb_2O_3), was prepared in the form of glass microspheres by flame synthesis, using a methane-oxygen flame. To obtain a high homogeneity of glass microspheres, a modified sol-gel Pechini method was used to prepare the starting powder. Only the presence of a wider hump in the interval 23-40° in 2-theta range was observed in the XRD pattern of the prepared glass microspheres, which indicates the predominantly amorphous nature of the sample. However, the next detailed study on the morphology of the prepared system by scanning electron microscopy (SEM) showed the presence of a small portion of partially, or fully, crystallised microspheres (**Fig. 1**). The high-temperature X-ray powder diffraction analysis (HT XRD) was carried out in the temperature interval of 750-1450°C, and with a step size of 5°C, to determine the temperature influence on the phase composition. Only the crystallisation of $Yb_3Al_5O_{12}$, a ytterbium aluminium garnet phase (COD-04-001-9735), was observed throughout the temperature range. The DSC analyses, with heating rates of 2, 4, 6, 8, and 10°C/min, in the temperature interval of 25-1200°C, were performed in a N_2 atmosphere to better understand the temperature behaviour of the prepared glass microspheres. Two exothermic effects at 910°C and 933°C were observed, which can be attributed to the crystallisation of $Yb_3Al_5O_{12}$. The crystallization kinetics of the prepared sample were examined in terms of the JMAK model and the kinetic triplet (frequency factor $\underline{A}$, apparent activation energy $\underline{E_{app}}$, and the Avrami coefficient $\underline{m}$) was determined (**Tab. 1**) using RSS, R^2_{adj}, and AIC criteria.

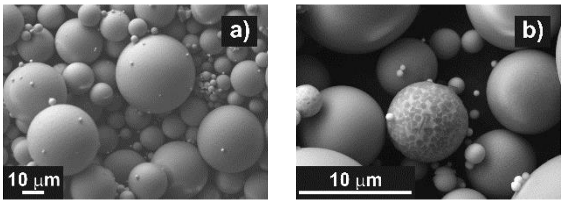

Fig. 1 SEM analysis a) prepared YbA-G sample, b) detail of crystalized microsphere

Tab. 1 The determined kinetic triplets

Peak	m	A ± sd [min^{-1}]	E_{app} ± sd [$kJ.mol^{-1}$]
1	3	$(1.76\pm2.0)10^{28}$	$(6.39\pm0.08)10^{5}$
2	2	$(1.28\pm1.6)10^{55}$	$(1.27\pm0.09)10^{6}$

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An on-line optical thermolysis of the graphene oxide (GO) thin films

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In our contribution to the previous CEEC TAC conference we presented our experience gained in a course of the thermal study performed on the 200-nm thick carbon films, obtained by the vacuum arch plasma deposition. In measurements we have monitored the film optical transparency (OT). The results have shown extremely high OT method sensitivity. In optical curves model fits with high values of the correlation coefficients were obtained [1]. In the present poster we summarize the main results obtained on thermal study of the graphene oxide (GO) thin films, employing the OT method. GO is an important graphene-derived carbon variety created by the graphite exfoliation in strongly oxidative water solutions, even to the individual graphene sheets [2]. In the process a number of individual oxygen groups are attached to the free bonds of the graphene planes and peripheral atoms, under formation of the hydrophilic GO flakes. The present GO thin films have been prepared out of the water dispersion of such flakes. However, with GO films it is necessary to remove the attached oxygen groups in order to restore, at least to some extent, the high electron conductivity of the native graphene sheets/flakes. To this purpose a number of the chemical and physical GO reduction methods had been designed. One of them resides in a low-temperature treatment of GO in air, bearing the close relationship to the ramp temperature of the films treatment in our experiments carried out in air atmosphere. Proceeding to the higher temperatures the optical curves provide us also information on the oxidation of the graphene by the gradual removal of the oxygen groups; the oxidation process ends up with a complete film gasification.

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Thermal and biological properties of Zn(II) 5-iodo- and 5-bromosalicylates with nicotinamide and caffeine

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New zinc(II) 5-halosalicylate complexes of general formula $[Zn(5\text{-}Xsal)_2L_2]$ (where X = Br, I; sal = salicylate; L = nicotinamide - nad, caffeine - caf, H_2O) were synthesized and their thermal, spectral, structural and biological properties were studied.

The thermal behavior of the complexes was studied by TG/DTG method in a nitrogen atmosphere and the decomposition reactions were proposed. It was found that the thermal decomposition of the prepared compounds is a multistep process. The thermal decomposition of hydrated compounds started with the release of water. During the thermal decomposition 4-iodophenol, 4-bromophenol, iodohydroxyphenylketone, 5-bromosalicylic acid, nicotinamide, caffeine and bromobenzene, CO_2, CO were evolved. The final solid product of thermal decomposition of all studied compounds was zinc oxide. The solid intermediates were determined by IR spectroscopy.

On the basis of measured IR spectra, the Δ values of prepared compounds were calculated. These values are higher than Δ value for sodium salt, so we propose the monodentate binding mode of carboxylate group.

Antimicrobial activity of the prepared compounds was tested against various strains of bacteria, yeasts and filamentous fungi (*S. aureus, E. coli, C. albicans, R. oryzae, A. alternata, M. gypseum*). Obtained results indicate that the studied zinc complexes are more effective against the tested microorganisms than the free acids or their sodium salts. In comparison with other studied compounds, the highest biological activity is exhibited by the complex containing 5-iodosalicylate. Our study confirmed the effect of the halogen substituent in the fifth position of the salicylato ligand on the antimicrobial activity against E. Coli, C. Albicans and R. Oryzae which increases in order Cl < Br < I.

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Thermodynamic model and Raman spectra of MgO-P_2O_5 glasses

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The structure of xMgO•(1-x)P_2O_5 ($x = 0.30, 0.35, 0.40, 0.45, 0.50, 0.55$) glasses was studied by Raman spectroscopy and thermodynamic model of Shakhmatkin and Vedishcheva (SVTDM) [1]. SVTDM was evaluated for each studied glass. Six following system components (defined as stable crystalline phases of the MgO – P_2O_5 binary phase diagram) were considered: MgO (M), P_2O_5 (P), MgO•2P_2O_5 (MP2), MgO•P_2O_5 (MP), 2MgO•P_2O_5 (M2P), 3MgO•P_2O_5 (M3P) [2]. The Principal Component Analysis (PCA) of experimental spectra resulted in three independent components. In the next step the Multivariate Curve Analysis (MCR) [3] of baseline subtracted and thermally corrected Raman spectra was performed for three components. MCR resulted in the Raman spectra (loadings) and relative abundances (scores) of each component. The MCR method reproduced 99.89% of spectral data variance. Correlation analysis attributed the MCR components to M2P, MP, and MP2 (Fig. 1).

Then the Malfait's decomposition was performed [4] based on the SVTDM equilibrium molar amounts of system components (MP2, MP and M2P), and resulting in Partial Raman Spectra (PRS) of M2P, MP, and MP2. Normalized MCR loadings coincide with a good accuracy with normalized PRS.

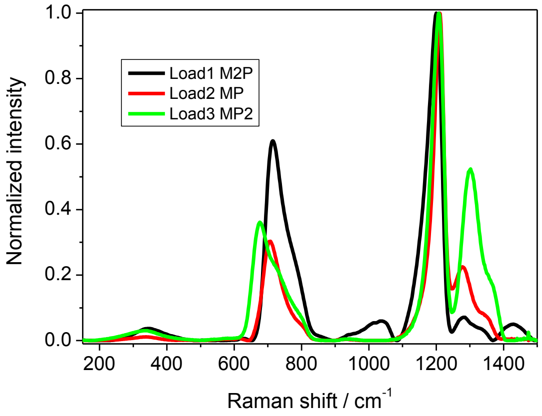

Figure 1:Normailzed loadings

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Crystallization kinetics of Ni-doped $Ca_2Al_2SiO_7$ glass microspheres

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The Ni-doped $Ca_2Al_2SiO_7$ (gehlenite) glass microspheres were prepared by flame synthesis from powder precursors [1]. The powder precursors were prepared by solid-state reaction from respective oxides/carbonates. The concentration of Ni was 0.5, 1 and 3 mol. %. All prepared systems were polydisperse with diameters between 5 and 140 μm. Detailed examination of morphology of the microspheres by SEM revealed no features (e.g. angular facets) indicating presence of crystalline phases. However, traces of crystalline gehlenite were detected in X-ray powder diffraction patterns of GNi0.5 (0.5 mol % of Ni) and GNi1.0 (1.0 mol. % of Ni). The HT-XRD measurements were carried out in the temperature interval 600-1100 °C and the temperature dependence of phase composition was determined. Formation of $Ca_2Al_2SiO_7$ as the main crystalline phase was observed for all prepared compositions and in the whole studied temperature range. DSC measurements in the temperature range 30-1200 °C at the heating rates 2, 4, 6, 8 and 10 °C/min were carried out to study the thermal behaviour of prepared glasses. The DSC records of all studied glasses contained one exothermic peak attributed to crystallization of the gehlenite phase. The peak maxima were shifted with increasing content of Ni in the samples from 998 to 980 °C. The kinetic parameters (frequency factor A, apparent activation energy $E_{app},$ and the Avrami coefficient m) of the crystallization were determined from the measured DSC records using the Johnson-Mehl-Avrami-Kolgomorov model [2] (Tab.1.). The linear temperature dependence of nucleation rate, diffusion-controlled crystal growth interface and 2 – D crystal growth were confirmed in case of GNi0.5 and GNi1.0 glasses. Constant nucleation rate, diffusion controlled crystal interface growth and 3 – D crystal growth prevails in crystallization of the GNi3.0 glass (3.0 mol. % of Ni).

Tab.1. Kinetic parameters of Ni-doped $Ca_2Al_2SiO_7$ glass microspheres

Sample	***m***	$A \pm SD$ **[min^{-1}]**	$E_{app} \pm SD$ **[kJ mol^{-1}]**
GNi0.5	2	$(3.68 \pm 0.66) \times 10^{29}$	723.0 ± 2.1
GNi1.0	2	$(1.5 \pm 0.4) \times 10^{28}$	683.9 ± 3.3
GNi3.0	1.5	$(7.25 \pm 0.99) \times 10^{29}$	721.1 ± 1.5

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Hydrothermal preparation and thermal stability of analcime

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Analcime ($NaAlSi_2O_6•H_2O$) belongs to the group of microporous natural zeolites with irregular channels that can possess various crystal structures. Because of its compact structure and resulting resistance to diffusion of either molecules or cations, applications of analcime as microporous material were delimited for a long time in comparison with other zeolites. Nowadays, its applications are expanding. Besides synthesis from chemical reagents, the successful preparations using other economic and locally available sources of aluminosilicate-rich materials were reported [1, 2]. In this work, analcime was prepared by the hydrothermal transformation of metakaolin based geopolymer activated by means of sodium water glass. There are two main reasons for the present research. At first, although the hydrothermal transformation of geopolymers into zeolites belongs to the most common methods of zeolite preparation, there is still a lack of information regarding the mechanism of this transformation. Secondly, despite the intensive study of analcime dehydration, some inconsistent findings regarding its structural transformations can be found in the literature [3-5].

The gradual transformation of geopolymer through primary and unstable zeolite phases up to final analcime was studied as a function of hydrothermal treatment duration (6 - 48 h) under the selected conditions (165 °C, 0.5 MPa). Composition and thermal stability of the prepared samples were assessed using simultaneous thermogravimetry and differential scanning calorimetry (TGA/DSC) and high-temperature X-ray diffraction (XRD).

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Crystallization of TiO_2 xerogel

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Nanomaterials based on titanium dioxide has a wide usage, mainly in the form of films in the solar systems and environmental applications [1,2]. TiO_2 in the form of anatase is required to be in these mentioned films [2]. This crystalline form is formed in the films during their thermal treatment. Sol-gel method represents advantageous method for preparation of TiO_2 materials [2,3]. In this method, the controlled reactions of hydrolysis and condensation of precursors (titanium isopropoxide) lead to preparation of TiO_2 sol which is transformed to gel and subsequently to xerogel after the sol is deposited on the substrate. Mentioned transformation is carried out by drying up to the temperatures of 100 °C. The subsequent thermal treatment at temperatures around the 400 °C causes the transformation of xerogel to anatase [2,4]. For achievement of the best properties of prepared films, the process of thermal treatment has to be controlled. For optimizing of thermal treatment process, it is needed to understand and observe which processes take place during the transformation from xerogel to crystalline form – anatase.

TiO_2 xerogel, dried at 80 °C, was prepared from sol in "titanium isopropoxide - isopropyl alcohol - nitric acid - distilled water" system. DTA/TG analysis at heating rates of 10 and 2 °C/min was used for study of processes which take place during the thermal treatment of xerogel. Besides assumed anatase crystallization, the processes connected with weight loss were observed and therefore, the process of thermal treatment of xerogel was observed using high-temperature Raman spectroscopy and high-temperature X-ray diffraction.

Based on the comparison of results of all analyses, it can be concluded that the anatase is formed from xerogel by the given reactions in the temperature range of (280-400) °C – the first reaction represents the decomposition of xerogel leading to the formation of amorphous TiO_2 and the second reaction represents the formation of anatase, respectively. The clear anatase occurs at 400 °C; the rutile occurs close to 600 °C and anatase to rutile transformation is complete at 900 °C.

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Use of methods of thermal analysis in study of metal-organic frameworks

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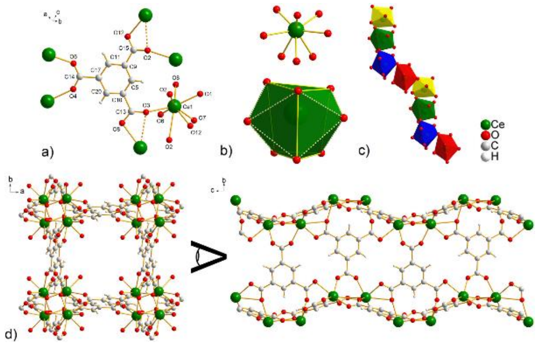
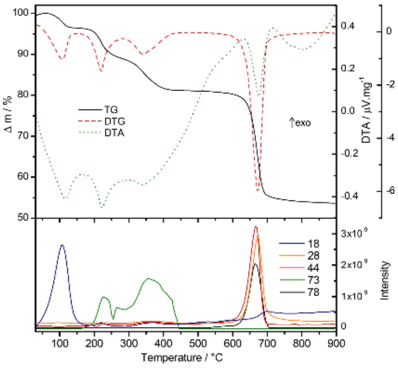
Topic of porous metal-organic frameworks (MOFs), has been one of the fastest growing fields in chemistry during the past decade. The driving force behind are superior characteristics and properties of porous MOFs compared to traditional inorganic porous materials as well as their applications in gas storage[1], catalysis[2], drug delivery[3] or other fields.

However, to prepare MOF with superior textural characteristics (large surface area, open and accessible porosity), the optimal conditions for sample activation have to be find. In our contribution we will show, how the methods of thermal analysis (TG/DTA-MS), can be used to optimise the textural properties of the MOFs. Thermal properties of novel MOFs were studied by simultaneous thermal analysis (TG-DTA) using Netzsch 409 PC apparatus, coupled with Aëolos Quadrupole Mass Spectrometer and powder XRD during *in-situ* heating.

In our contribution we will show, how the above-mentioned techniques were used to find optimal activation properties for MOFs, which touch the energy sector. The areas of our interest with MOFs and energetic applications concerned the magnetocaloric effect (MCE) and cryogenic magnetorefrigeration, where we studied three solvent (X) exchanged samples $[Gd(BTC)(H_2O)]\cdot X\}_n$. Another area, where MOFs touch the energy sector is gas adsorption and separation. From this point of view we will present the use of thermoanalytical methods in activation of several porous MOF, e.g. $\{[Pb_4(MTB)_2(H2O)_4]\cdot 5DMF\cdot H_2O\}_n$ or $[Ln(BTC)(H_2O)]\cdot DMF\}_n$ (Ln = Ho(III), Tm(III)), Ce(III), Lu(III)).





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Hydration of belite-calcium sulfoaluminate cements at different curing temperatures studied by isothermal calorimetry and thermal analysis

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In this study, the influence of different temperatures on the hydration of belite-calcium sulfoaluminate cements was investigated. These cements are promising low-energy and low-carbon cements with belite and calcium sulfoaluminate as main phases [1]. One of the main factors influencing the hydration of cement materials and consequently their mechanical and physical properties is temperature. Cements are exposed to different temperatures due to different climate conditions and also hydration heat which is produced during the setting of concrete. Temperature influences the kinetics of hydration, the composition of pore solution, precipitation, morphology and stability of hydrates [2, 3].

The cement clinker was synthesised from various natural (limestone, flysch, bauxite) and secondary raw materials (titanogypsum, bottom ash, mill scale). The targeted phase composition of cement clinker was 65 % belite (C_2S), 20 % calcium sulfoaluminate ($C_4A_3\acute{S}$) and 10 % ferrite (C_4AF). Furthermore, cement was prepared by adding to cement clinker 20.3 % of white titanogypsum and water to cement ratio 0.4 was used for cement pastes. Hydration kinetics and formation of phase assemblages were investigated at 20 °C, 40 °C and 60 °C. Cement reactivity and heat evolution were studied by isothermal calorimetry. The phase composition of cement pastes at 28 days of hydration was determined by X-ray powder diffraction and quantitatively with the Rietveld method. Differential thermal analysis and thermogravimetric analysis was carried out to support the identification of the hydration products with X-ray powder diffraction. The microstructure of hydrated pastes was observed with scanning electron microscopy with energy dispersive X-ray spectroscopy.

The results showed that increased curing temperature had a significant effect on the rate of the hydration process. Namely, the hydration kinetics was accelerated by elevated temperature (40 °C, 60 °C) in comparison to ambient temperature (20 °C). The results of isothermal calorimetry indicated that cement cured at higher temperature reacted earlier and released more heat during hydration. X-ray powder diffraction and thermal analysis showed that the main hydration product at 28 days of hydration was ettringite. There was no difference in the amount of non-reacted gypsum and ettringite at 20 °C and 40 °C, while at 60 °C the amount of gypsum increased and the amount of ettringite decreased, suggesting that at higher temperature hydration degree of the cement was lower. Microstructural investigations revealed the presence of clinker relicts and gypsum crystals, in addition to the formation of ettringite needles.

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Study of interaction between molten aluminium and hot-working tool steel using DSC and TG method

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Pressure die casting is one of the leading casting processes in the modern industry. In the case of pressure die casting, the melt is in contact with the tool, whereas the chemical interaction between the tool, made of hot-working tool steel and the melt occur. In addition, mechanical and heat wear of the tools also occur. For high productivity high resistance to these factors is required.
The interaction between molten aluminium alloys Al99.9, Al99.7 and AlSi12 and hot-working tool steel was investigated at various experimental temperatures, i.e. 670 °C and 700 °C, whereas the differential scanning calorimetry (DSC) and thermogravimetric (TG) methods were used. Optical and scanning electron microscopy were used in order to analyse interaction layer. The result of the interaction is the growth of a reaction layer, which is formed from intermetallic phases from Al-Fe system. Reaction layer varies regarding the aluminium alloy and the temperature, to which it is exposed, whereas it is compose from three or four different layers. The thickness of the interaction layer depends only from the temperature, but the number of different layers in the interaction layer depends from the type of the aluminium alloy.

Thermal decomposition kinetics of non-ideal high explosives for simulating slow & fast cook off test

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The thermal decomposition of metalized polymer-bonded explosives (PBXs) with the addition of ammonium perchlorate (AP) was characterized using slow and fast cook-off simulations, differential scanning calorimetry (DSC), and an isoconversional technique [1]. PBXs #1, #2, and #3 contain 95% cyclotetramethylene-tetranitramine (HMX) with binder; 66% HMX and 25% aluminum with binder; and 25% cyclotrimethylene-trinitramine (RDX), 35% aluminum (Al), 25% AP, and binder, respectively. The roles of Al and AP during thermal decomposition, distinct from the shock-to-detonation transition, were confirmed, indicating that Al does not contribute to the exothermic ignition process due to its higher reaction temperature compared to HMX; instead, Al leads to a higher explosion time and temperature for PBX #2 compared to PBX #1. We extract the kinetic scheme of PBXs based on the isoconversional technique [2]. In the slow cook-off test for PBX #3, a thermal runaway occurs at the RDX reaction temperature, which is lower than the AP reaction temperature, indicating that AP has a negligible effect. In the fast cook-off test, however, the reactions of RDX and AP occur simultaneously due to the higher heating rate, demonstrating the influence of AP on the explosion time and temperature.

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The experimental thermodynamic data for various liquid electrolyte solutions of Li-ion battery

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Lithium ion batteries(LIBs) have potential to give high energy density and high specific current capacity and therefore they are considered as most promising rechargeable battery. There are three basic parts of research subject for any LIBs: the anode, cathode and electrolyte. The energy stored in electrodes in LIBs however they should be work together with a lithium conducting liquid or solid electrolyte. Some characteristics of LIBs, such as life time, specific power and good performance at low and high temperature are largely dependent on the electrolyte, i.e., the combination of the electrolytes.

Liquid electrolyte is generally consist of a lithium salt, usually $LiPF_6$ or LiN $(CF_3SO_2)_2$ and organic solvent blend of linear and cyclic alkyl carbonates. The selection of the mixed solvents is therefore crucial part for enhancing the performance of LIBs. Practically, this mixed solvents are composed mainly ethylene carbonate (EC) and propylene carbonate (PC) with one or more co-solvents; dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), etc. In recent years, some co-solvent as additives that can increase the ionic conductivity have been used to supplement the deficiency. γ-Butyrolactone (GBL) is one of the best co-solvent for LiBs because it has excellent physical properties, a low melting point for low temperature application but high boiling point [1,2].

The purpose of this study is therefore to show the thermodynamic modeling for the optimized conditions by knowing some physical properties of the binary mixture of electrolyte solvent. The melting point data from solid-liquid equilibrium(SLE) could also be used to aid in the basic data for the separation process, *i.e.* crystallization. The following figures are example for the determined thermo-physical properties (density & viscosity) of the electrolyte solution.

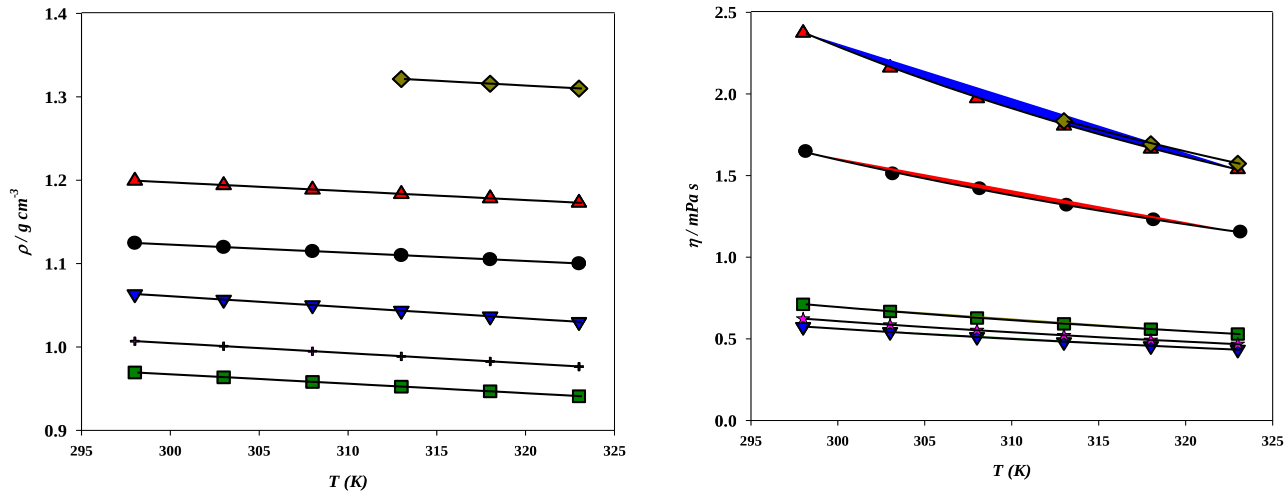

Fig. 1. Densities ρ ($g \cdot cm^{-3}$) and kinematic viscosities ν ($mm^2 \cdot s^{-1}$) for 298.2 – 323.2 K; (●), GBL; (▼), DMC; (■), DEC; (★), EMC; (◆), EC; (▲), PC;

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Phase equilibria and thermodynamic properties for the reaction products of biofuel manufacturing processes

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Biofuel, such as bio-butanol and biodiesel (Fatty acid alkyl ester), a biodegradable, sustainable and clean energy has worldwide attracted and it has some advantages compared to petroleum based transport fuel like as domestically produced from renewable resources, emit less air pollutants and greenhouse gas, can be directly use in most gasoline and diesel engines, less-toxic and safer to handle, etc. Biobutanol is conventionally fermented with ABE process from biomass, while biodiesel is a renewable, biodegradable fuel manufactured from vegetable oils, animal fats, or recycled restaurant grease [1]. However, separation of biobutanol from the fermented broth has still economical separation problem and the direct use of vegetable oils as biodiesel in compression ignition engines is also problematic due to their high viscosity and low volatility. Transesterification reaction of vegetable oil make lowering viscosity and enhancing other physicochemical properties. This reaction has several drawback and the major limiting factor to biomass use is the technology development for the separation, purification, and transformation of it into biochemicals and biofuels. Ineffective biodiesel separation and purification causes severe diesel engines problems such as plugging of filters, coking on injectors, more carbon deposits, excessive engine wear, oil ring sticking [2].

As a systematic study for a development of economical separation process of biofuel reaction products, solid-liquid equilibrium(SLE), liquid-liquid equilibrium (LLE) under atmospheric pressure for alkyl acetate mixtures among the bio-butanol fermented products and also fatty acid alkyl ester binary mixtures were determined. Thermo-physical data, density, viscosity and refractive indices for the same systems were directly measured and excess and deviation properties were calculated. The equilibrium data were correlated with common activity coefficient model and excess and deviation properties were correlated with Redlich-Kister polynomial. Followings are example of determined thermo-physical properties and LLE.

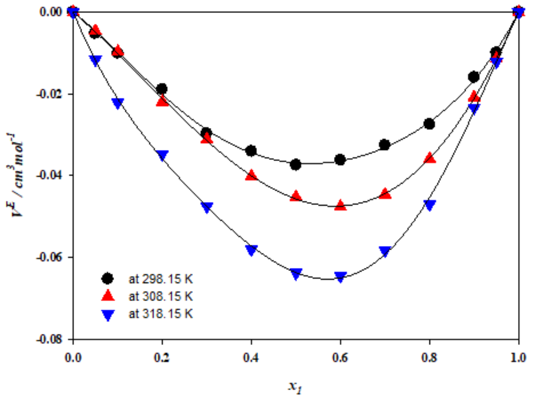

Fig. 1. Excess volume for system DMC+DES.

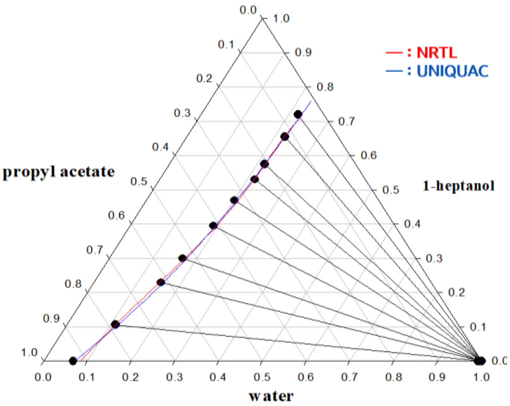

Fig. 2. LLE for system H_2O+heptanol+PA.

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Mechanisms and kinetics of the thermal decontamination of tritium and radiocarbon in spent activated carbon

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The nuclear industry generates spent GACs (granular-type activated carbons) to be disposed of in a radioactive waste repository. Owing to the high disposal cost and the shortage of available land, developing a thermal decontamination process to convert radioactive spent GACs into free-releasable waste is an attractive goal from an economic perspective. The major radioactive contaminants in GACs are tritium (^{3}H) and radiocarbon (^{14}C), which are adsorbed mostly in the form of H_2O and CO_2, respectively. This study investigated the mechanisms and kinetics of the thermal decontamination of ^{3}H and ^{14}C species in spent GACs.

The results of a non-isothermal TG analysis with a FTIR gas analysis showed three weight loss steps. The first weight-loss step started at 60 °C. The first and the second reaction steps overlapped at temperatures between 170 °C and 220 °C. The second weight-loss step finished at approximately 530 °C. Most adsorbed H_2O and CO_2 species were removed during the first and the second weight-loss steps. A further weight-loss step, the third, during only CO_2 species were emitted, started at 530 °C and continued to 1200 °C, showing a very slow and nearly linear weight loss rate with the temperature. This indicated that the third weight-loss step occurred due to the outgassing of adsorbed species existing in the microspores of GACs and that its rate was therefore much slower and did not significantly increase with the temperature..

Vacuum thermal desorption processing at 1200 °C and approximately 10^{-7} bar could reduce the outgassing time of adsorbed species in the microspores. However, the level of ^{14}C in GACs after this vacuum thermal desorption process still slightly exceeded the free release criterion of ^{14}C. This suggests that a small fraction of ^{14}C existed in the form of thermally stable carbon elements in the graphite structure of GACs. There may be an exchange reaction between ^{14}C in the adsorbed gaseous species, such as $^{14}CO_2$ and $^{14}CH_4$, and a stable carbon element in the graphite structure of spent GACs during the course of heating to 1200 °C.

Partial oxidation tests for the peeling of vacuum treated GACs were conducted to assess the potential to remove thermally stable ^{14}C species in the graphite structure of GACs. The peeling process was found to be effective for reducing the level of ^{14}C to a level below the established free-release criterion. A non-isothermal kinetic analysis and a prediction of the oxidative peeling process were also conducted to establish the optimum process condition without the need to use unnecessary energy or time.

Direct measurements and interpolation techniques in magnetocaloric materials for cooling applications

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Two important parameters determine the applicability of magnetic materials for caloric applications, the adiabatic temperature change, ΔT_{ad}, and the isothermal entropy change, ΔS_T, upon application of a magnetic field change.

In systems in which the activation of the magnetocaloric effect happens under rapid step changes of the magnetic field, the heating or cooling occurs also in sudden steps ΔT_{ad}. The values of ΔT_{ad} and ΔS_T under different field changes can be obtained with direct measurements, or with magnetization data using one of the Maxwell relations. But, in order to reach higher frequencies in the working thermodynamic cycles, rotary systems with a continuously cycling field are preferred. Also, materials with first-order transitions having a giant magnetocaloric effect are being used in practical prototypes for cooling.

The governing equation giving the temperature change of the cooling material contains a term with the ratio $(\partial S/\partial B)_T/c_B$. In first-order transitions, both, numerator and denominator, are diverging quantities, giving a large imprecision in the ratio and, consequently, in the solution of the dynamic system. This ratio can be transformed in an expression proportional to $(\partial T/\partial B)_S$. [1] Direct measurements of this term through thermograms of the temperature change under an adiabatic field change can be made, avoiding the problem of diverging variables.

Adiabatic measurements of thermodynamic variables require slow techniques that make very hard collecting comprehensive data to complete experimental values in the required temperature and field ranges. Very often, experimental devices use families of materials with giant magnetocaloric effect that allow a continuous change of transition temperatures through small stoichiometric changes. A series of these materials with gradually spaced transition temperatures are necessary to be present in an active system. Using measurements in a few number of members of the continuous family, interpolation techniques for the heat capacity $C(T,B)$ [2] and for the new named variable, $(\partial T/\partial B)_S$, give, with a high precision, the corresponding values for other members with different temperature range of optimal effect.

Direct thermodynamic measurements of these magnetocaloric parameters are presented and interpolation techniques to obtain continuous functions or indexed tables of the corresponding parameters.

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Thermal behaviour of the different parts of almond shells as waste biomass

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The use of biomass to generate heat and electricity energy has increased substantially in the European Community, becoming the highest-growth renewable energy, which is expected to grow and increase next years. Some authors distinguish between natural biomass and products derived from natural materials [1, 2, 3]. The almond industry generates large quantities of waste products that need to be recycled or processed. World production of almonds was 3.21 million tonnes in 2016, with the United States as the larger producer with 1.8 million tonnes. The Spanish production, in second place, accounts for 202.339 tonnes with a total of harvested area of 544.518 Ha in 2016. The production of Almería province (SE Spain) was 44.256 tonnes. Thus, it is generated a large amount of waste biomass, being of interest for several applications, such as pyrolytic liquid fuels, fuel gas, chemicals and active carbon.

The objective of this study is to know the thermal behaviour of the different parts of almond shells produced in an industry as a waste biomass (almond shells, variety marcona). For this purpose, several experiments have been conducted under laboratory conditions. Preliminary results are presented in this communication.

The waste raw materials after cleaning the almonds was washed with distilled water and separated in several parts taking into account their physical characteristics, as follows: a) complete shells: exocarp, mesocarp and endocarp without grinding (Sample C); b) ground samples of complete shells sieved under 0.2 mm, resulted a sample similar to industrial conditions (Sample M); c) hard layers of the endocarp (Sample E); d) internal layers of the endocarp (Sample I), and e) mature drupes (Sample P), being constituted by the flexible part of green colour (fresh form) or yellow (after drying). Lignine, cellulose and hemicellulose of these samples have been determined. The pyrolysis has been studied using a laboratory furnace with determination of weight loss, ashes and volatile matter. Elemental and DTA-TG analyses of selected samples have been performed.

The results have demonstrated the influence of several parameters, such as the particle size and previous treatments, in the thermal behaviour of the different parts of the almond shells as studied in this investigation. Taking into account these results and the content of lignine, cellulose and hemicellulose, the prediction of the higher heating value of these wastes can be proposed. Preliminary results on thermal decomposition of these biomass wastes are presented and discussed. A complete kinetic study, using different kinetic models, will be the next step in this investigation.

Characterization, thermal and ceramic properties of phyllite clays from SE Spain

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Phyllite clays or phyllites are finely divided metamorphic rocks predominantly comprised of clay minerals such as chlorite and muscovite (illite) [1]. The presence of phyllite clays has been reported in several countries [1-2]. Phyllites belong to the foliated and platy group composed of tabular and elongated minerals. For instance, three varieties of a regionally metamorphosed argillaceous rock, quartzitic, carbonaceous and micaceous phyllites, have been reported [1]. In general, the most weathered phyllite clays were found near the surface and / or surrounding faults with laminar appearance. The existence of preferential cleavage in phyllite clays gives them the property of being easily breakable in thin sheets [1-3]. Phyllite clays are abundant in the Betic Cordilleras (Andalusia, SE Spain), e.g. in the provinces of Almería and Granada [2, 3]. These phyllite clays have traditionally been used as sealing material to impermeabilize roofs, embankments and the central area of ponds, as core material in zoned dam/reservoir construction, waste landfill applications and preparation of mortars. However, the studies on thermal and ceramic properties of phyllite clays have been scarce.

The objectives of the present research are to study a set of phyllite clays from SW Spain. The thickness of phyllite clay deposits was variable, but after removing the first surface layer (1-30 cm), the thicknesses were 1-2 m. Representative samples were obtained. The results are presented for the mineralogical, chemical and textural characterization of 53 raw samples using XRD, XRF, SEM-EDS and TEM. Thermal analysis methods (ATD-TG and Dilatometry) have been applied to a more complete characterization of these samples and to know their thermal properties. From these results, samples have been selected for a ceramic study by firing pressed powdered samples up to 1300 ºC. Sintered materials with porosities almost zero can be obtained after firing at 1100-1200 ºC with apparent densities between 2.1-2.4 g/cm^3 and good mechanical strengths, with application as ceramic materials. Higher firing temperatures (> 1250 ºC) produced deformation and expansion of the ceramic bodies.

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The effect of particle shape on the thermal conductivity of epoxy-boron nitride composites

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Boron nitride (BN) is widely used as a filler in epoxy resin systems in order to achieve high thermal conductivity while maintaining electrical insulation. The BN filler particles, as well as being of various sizes, may be in different forms, principally either as platelets or as agglomerates. There is little information in the literature about the effect on the thermal conductivity of adding BN particles of different shapes. Here we investigate this effect of BN particle shape on the cure kinetics and thermal conductivity of epoxy-BN composites.

The epoxy system is based on a DGEBA epoxy crosslinked with a thiol. The BN filler is in various forms: platelets with sizes of 2, 30 and 180 µm, and spherical agglomerates of size 120 µm. The epoxy and thiol are mixed in a stoichiometric ratio and the BN filler is added in a proportion to give volume percentages of 3.7, 12.9, 25.7, 34.2 and 44.4%, the highest value being achieved only for the 30 and 180 µm platelets. The cure kinetics was studied by both non-isothermal differential scanning calorimetry (DSC), at rates of 2, 5 and 10 K/min, and isothermal DSC at cure temperatures of 60, 70 and 80 ºC. The same epoxy-thiol-BN mixtures were also cast into silicone moulds and cured isothermally in an oven to provide samples for the measurement of the thermal conductivity by the Transient Hot Bridge method.

In the non-isothermal cure of composites with 120 µm agglomerates, the peak exotherm temperature increases on the addition of the BN particles, and increasingly so as the BN content increases. This behaviour lies intermediate between the much greater shift for the 2 µm particles and a smaller shift for the 30 and 180 µm platelets. The isothermal DSC results show an initial decrease in the time to the peak exotherm as the BN content increases, followed by an increasingly rapid increase. Similar to the non-isothermal cure, the composites with the 120 µm agglomerates lie intermediate between the rather dramatic increase for the 2 µm composites and the much smaller increase for the 30 and 180 µm composites.

The thermal conductivity of all the composites increases with BN content, but there is a significant effect of particle size, larger particles giving a higher thermal conductivity [1]. For the platelets and 34.2 vol% of BN, for example, the values are: 1.28, 2.36 and 3.02 W/mK for the 2, 30 and 180 µm particles. This dependence mirrors the effect of the filler on the cure kinetics. The 120 µm agglomerates composites give a value of 3.08 W/mK for the same BN content, essentially the same as that for the 180 µm platelets. Comparison with earlier results [1] shows that composites with 120 µm agglomerates have a thermal conductivity which depends on BN content in a very similar way to that for 80 µm agglomerates, suggesting that agglomerates are more effective than platelets. The most noticeable effect, though, is for the smallest platelets, with a size of 2 µm, for which the cure kinetics is distinctly different from that for the other particle sizes and for which the thermal conductivity is significantly lower.

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Thermal energy storage using low-cost natural compounds for concentrated solar power plants

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There is an enormous interest in increasing dispatchability in concentrated solar power plants (CSP). In fact, one of the main disadvantages of these power plants is its intermittency. Unlike conventional fuel power plants, that could be turn on and off when needed, solar power plants depend on the sun and it does not shine at all times. Therefore, there is a high need for energy storage. Available technology based on batteries is still an expensive solution, while storing thermal energy seems to be a more affordable option. The state of the art technology for storage in CSP plants is based on molten salts. Nevertheless, the high cost of this technology is a significant limitation. The use of thermochemical energy storage systems is a very promising technology for CSP. In particular, the system based on the calcination-carbonation reaction of $CaCO_3$/CaO (also known as Calcium Looping (CaL) process) have a great potential. This process is based on limestone, which is a low-cost, abundant and environmentally friendly material. The process is straightforward, the endothermic calcination reaction is induced by the concentrated solar power releasing CO_2 and CaO that are stored in separated containers (they could be stored for as long as needed). Then, when there is energy demand, CO_2 and CaO are mixed to promote the exothermic carbonation reaction that releases the thermal energy. This thermal energy is used to produce electrical power. This idea set the bases of the SOCRATCES project (grant agreement No 727348, Horizon 2020 research and innovation programme, European Union) that explores the feasibility of the CSP-CaL integration by constructing a pilot-scale plant to prove this technology and improve the understanding in the process integration

Study of kinetics and thermal conductivity of epoxy-thiol composites filled with boron nitride of different size and shape, and hydrides

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The objective of the present work is to investigate the influence of boron nitride (BN) particles, with respect to size, geometry and hybrid mixture, in epoxy composites. The composites are based on an epoxy matrix, of diglycidyl ether of bisphenol-A (DGEBA), cured with either a diamine or a thiol. For cross-linking with the thiol, an encapsulated imidazole latent initiator was use. The filler particles are BN platelets, with nominal sizes of 2 and 6 μm, BN agglomerates with nominal sizes of 80 and 120 μm, and hybrids which are mixtures of particles with different size and geometry, 80/2 and 80/6. Filler loadings up to approximately 40 vol% have been used, which is limited by the ability to mix the resin and particles in a simple way. The effect of the different filler particles on the cure kinetics has been investigated by DSC, and the thermal conductivity has been measured by the Transient Hot Bridge method.

The results of the cure kinetics study showed that in both epoxy-thiol and epoxy-diamine systems the glass transition temperature of the fully cured system and the heat of reaction are independent of the cure conditions and filler type and content. On the other hand, for the epoxy-thiol system the peak temperature in non-isothermal cure generally increases with increasing BN content, indicating an influence of BN content on the cure kinetics. Likewise, there is an influence of BN content on the iso-conversional activation energy for the epoxy-thiol composites. For example, for 13 vol% BN it decreases from about 70 kJ/mol to 50 kJ/mol when the degree of conversion increases from 10% to 40% and then increases to 67.5 kJ/mol at 90% conversion, whereas the unfilled system shows a similar trend but with higher values, between 80 and 70 kJ/mol. In contrast, for composites based on the epoxy-amine system, the peak temperature during non-isothermal cure is not affected by the filler content.

This difference in the cure kinetics between the epoxy-thiol and epoxy amine systems is believed to result from an improved interface between filler and matrix in the epoxy-thiol system, and thermal conductivity measurements confirm this. For the same 34 vol% of BN, 6 μm, the epoxy-thiol composites display a higher value of thermal conductivity, 2.3 W/mK, compared with 1.7 W/mK for the epoxy-diamine system, though both represent a significant increase from the value of 0.2 W/mK for the unfilled system. It has been found also that the size and geometry of the particles have an important influence: the thermal conductivity increases with particle size, while agglomerates have a better performance than platelets. For example, a value of 3.72 W/mK has been achieved with 34 vol% agglomerates of 120 μm. The hybrids, 80/2 and 80/6, give intermediate thermal conductivity values compared to composites prepared with the same single size particles, but allow a higher BN content to be reached. For example, hybrids of 80/6 with 40 vol% content give a thermal conductivity of 4.17 W/mK.

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Thermal cycling influence on the martensitic transformation of Ni-Mn-Sn based magnetic shape memory alloys

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In this work we analyze the influence of thermal cycling on the thermal behavior and microstructure of several magnetic shape memory alloys (off stoichiometry Heusler Ni-Mn-Sn alloys with minor additions of Ti, Cu or Pd). The shape memory effect can be not only controlled by changing the temperature and/or the pressure, as it occurs in traditional shape memory alloys, but also by varying the magnetic field up to moderate field values [1].

These alloys have a martensitic structural transformation. The hysteretic process is usually analyzed in the literature during the first cycle. The same for the thermomagnetic and magnetic analysis [2]. Nevertheless, the applicability of these materials in magnetic refrigeration (due to the magnetocaloric effect) is based on the maintenance of this effect after cycling. Alloys with good thermal and structural stability are candidates for cycling applications.

We have performed one hundred cooling-heating thermal cycles on several Ni-Mn-Sn based alloys doped with a fourth element. After cycling, both the microstructure (as determined by analysis of X-Ray diffraction patterns) and the thermal behavior (by differential scanning calorimetry) is found to be stable in all samples with one exception. In this case, after cycling it appears a pre-martensitic phase. Thus, there are two transformations on cooling. First from the austenite parent phase to the pre-martensitic phase and second (at low temperature) from the intermediate phase to the stable at low temperature martensite.

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Phase diagrams of Heusler magnetic shape memory alloys

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In this work we review different phase diagrams involved in the characterization of magnetic shape memory alloys. These alloys can have so many transformations. There are structural transformations as the reversible and hysteretic austenite to martensite. Likewise, it is possible to obtain different austenite or martensite phases by modifying the composition and/or the temperature. There are also magnetic transformations (from ferromagnetism to paramagnetism, superparamagnetism and so on). Thus, traditional phase diagrams are complex in these systems.

It is usual to represent some characteristic temperatures (the martensite start temperature and the Curie temperature) as a function of the composition or as a function of the e/a parameter (average of the electrons by atom in the outer shells) [1,2]. A linear trend is usually found. Nevertheless, if we compare characteristic temperatures obtained for alloys with the same composition produced by different techniques and conditions (bulk alloys by arc melting, ribbons by melt-spinning, microwires by Taylor-Ulitovski method or powders by mechanical alloying or crushing) the phase diagram differs. As decreasing the dimensionality two effects were found: a diminution of the temperatures of the martensitic transformation and sometimes the inhibition of the martensite formation. We show phase diagrams comparing our results with those found in the literature. A way for modifying phase diagram is the annealing of samples that has an opposite effect to the lowering of dimensionality. Complementary phase diagrams are the transformation temperatures as a function of the applied: a) magnetic field or b) pressure.

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Biomolecular interactions of selected buffers with haemoglobin

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In the present study, we attempt to find the experimental evidences for the stability of globular protein hemoglobin (Hb) in biological buffers and to explore the interactions between the buffers and Hb. Since pH value control is a key factor in handling proteins, the selection of buffers is important [1]. Among several others, tris (hydroxymethyl) aminomethane (TRIS), N-[tris (hydroxymethyl) methyl]-3-aminopropanesulfonic acid (TAPS) and N-[tris (hydroxymethyl) methyl]-2-aminoethane-sulfonic-acid (TES) buffers are commonly used to maintain the pH of the biological medium in the physiological pH range of 6 to 11, which allow them to be used in biological, biochemical or environmental studies. The biological buffers investigated in this work are structurally related and all contain TRIS group. These TRIS family compounds are probably the most frequently used buffers in biological experiments. Due to their well-reckoned characteristics such as biocompatibility, high stability, and non-toxicity, they are widely used for various biochemical purposes [2]. As buffers are always presented in biological media as a buffering agent, using them as a protective agent could also overcome the problems of finding a suitable external protective agent and thus may help in the enhancement of the applications of proteins in the biological fields [3].

To elucidate the influence of commonly used biological buffers on the hemoglobin (Hb) structure, the biomolecular interactions between Hb and the selected buffers, including TRIS, TAPS and TES, are investigated by using various spectroscopic and other techniques. The instruments used in this study are ultraviolet-visible (UV-Vis), fluorescence, dynamic light scattering (DLS), Fourier transform infrared spectroscopy (FTIR) and circular dichroism (CD). Fluorescence results reveal that the addition of biological buffers increases the hydrophobicity around the tryptophan environment in Hb. Evidently, the alpha-helix structure of Hb was slightly destroyed at higher concentrations of the buffer detected by CD spectroscopy. However, the thermal stability of the protein transition temperature (T_m) gradually increases with an increase of the concentration of the biological buffers. The results also show that generally the biological buffers are able to enhance the stability of Hb.

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Inhibition effects analysis on ammonium nitrate mixed with dry extinguishing agent

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There are many accidents induced by ammonium nitrate (AN) in manufacturing process, which have caused the serious loss of property and human being. Therefore, we used AN as our main topic material for discussing its thermal characteristics, such as kinetic parameters by DSC. Beside, Dry extinguishing agents also was applied in this study for deeply evaluating the inhibition effectiveness and inhibition reaction mechanism. Meanwhile, safety parameters will also be researched for these complex reactions. Results by this study will benefit to the process of AN and the relevant staff, which also have the safety protection in the working environment.

Microstructure properties of aluminium alloy and zinc coated steels combined with cold metal transfer welding

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In this study, aluminium alloys (AA 6063) and zinc-coated steel (EN 10346) materials were combined with cold metal transfer (CMT) welding using Al-Si alloy (Er4043) welding wire. The thickness of the aluminium and steel materials used in the experimental studies is 2 mm and the diameter of the welding wire is 1.2 mm. Microstructures were characterized by microscopy of the optical and scanning electron. In general, the lack of fusion zone was observed in the joining area of metals. The lack of fusion can be explained by the inability of the unstable zinc vapour formed during the welding of aluminium and steel sheets. The fact that zinc vapour cannot move away from the weld metal during cooling causes large gaps in the weld metal [1-4].

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Effect of aspect ratio on mechanical properties of glass fibre reinforced polypropylene composite materials

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In this study, the mechanical properties of glass fibre powder reinforced polypropylene matrix composite materials produced by extrusion method were investigated. The aspect ratio sizes of the glass fibre powders were measured with an optical microscope and were determined. E glass fibre was used in experimental studies and fibre diameter 11 μm. Five different glass fibre aspect ratios (13: 1 - 23: 1 -45: 1- 65: 1 82: 1) were reinforced to the polypropylene matrix. Polypropylene matrix was added 1% maleic anhydride as initiator. The mechanically stirred solution was added as a cobalt octoate accelerator at 0.035%. Tensile and impact test specimens were prepared according to ASTM D790M-92 and ASTM D638M-91 standards to examine the mechanical properties of glass fibre reinforced polypropylene matrix composites. When the general results were examined, the tensile and impact strength of the compote material increased with the increase of the glass fibre aspect ratio.

The use of DSC in the analysis of topical formulation - skin interactions

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The transdermal route has a number of benefits over other more traditional routes, such as oral delivery and intravenous injection. The avoidance of hepatic “first-pass” metabolism is often seen as the most significant benefit [1]. Unfortunately, the transdermal route is frequently looked at as an alternative route, rather than a primary target [2]. Differential scanning calorimetry (DSC) has been used previously in the analysis of human skin [3-5]. The stratum corneum is often the primary focus of research into skin barrier function and this is no different for DSC analysis. The aim of this research is to provide information on all layers of the skin, not just the stratum corneum, and to identify differences caused by the application of topical formulations. Individual layers of epidermis and dermis were separated after submersion in 0.32 M ammonium hydroxide (NH OH) for 45 seconds at 60°C. Stratum corneum sheets were obtained by trypsin digestion for 12 hours at 32°C. Lipid extraction was performed using chloroform and methanol (2:1) for 48 hrs. Ibuleve (DR1) and Voltarol (DR2) were applied to individual skin layers after separation and left for 24 hours. Following this, the formulations were removed and samples were freeze-dried. DSC experiments were conducted using a TA Instruments Q2000 DSC. Samples were run in hermetically sealed Tzero aluminium pans. Heating and cooling were conducted at 2°C min with sample mass of 0.5 – 15 mg. Dermal tissue shows a single endothermic transition at 61ºC, within the temperature range used, although there is evidence to suggest another transition occurs near 120ºC. It has been seen that the application of the formulations to dermis tissue did not yield any change in DSC signals when compared to the control. The epidermis shows endothermic transitions at -9ºC, 5ºC, 55ºC, 73ºC and 89ºC, with the peak at -9ºC having a shoulder at -15ºC. On second heating the transitions below 10ºC remain the same however, the transitions at 55ºC and 91ºC are removed, leaving a single transition at 70ºC. Both formulations (DR1 and DR2) have had the significant effect of lowering the lipid-related transitions at 73°C and 89°C by 10°C and 15°C respectively. The formulations can also be seen to have lowered the intensity of the signals at -10°C and 5°C, suggesting some lipid has been extracted by the formulation. During the second heating cycle, the transition seen at 70°C in the untreated sample is also seen 15°C lower in the samples treated with formulations. DSC has be used to show that the application of two topical formulations have significantly modified the endothermic transitions present within the epidermis and stratum corneum near 70°C and 90°C. These transitions are known to be related to skin lipids and so this suggests that these higher temperature lipid transitions have a more significant role in drug delivery than those seen at -15°C and 5°C. It is thought that the ability to modify these transitions and the extent of this modification could be used to predict whether a formulation will penetrate the skin successfully.

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The influence of chocolate coating on glass transition temperature of freeze-dried strawberries

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Edible coatings have been used for centuries to protect foods and prevent moisture loss. These practices were accepted long before their associated chemistries were understood. In the early to mid-twentieth century, coatings were used to prevent water loss and add shine to fruits and vegetables, as casings for sausages, and as some sort of sugary coating on confectionaries, including chocolate. When a packaging material such as a film, a thin layer or a coating, is an integral part of a food and may be eaten with the food, it is qualified as ‘edible’ packaging. Coatings are either applied to or formed directly on foods, while films are self-supporting structures that can be used to wrap food products [1].

Gounga et al. [2008] applied the double coating with chocolate was shown to be satisfactory in improving the quality and increasing the shelf life of chestnut, hence providing a wider range of choices of new products at the consumer’s disposal. However, consumers expect food to be safe and more nutritious. Chocolate is a highly nutritious energy source, with a fast metabolism and good digestibility. The presence of cocoa, milk and sugar in its composition can be the warrant for an appropriate ingestion of proteins, carbohydrates, fats, minerals and vitamins [2].

The aim of this work was to analyse the influence of different chocolate coating of freeze-dried strawberries on glass transition temperature. Modulated differential scanning calorimetry (MDSC) was used to determine the glass transition temperature of freeze-dried strawberries (obtained by different wetting liquid) at low water activity. The thermal transition experiments in freeze dried strawberries were conducted with a differential scanning calorimeter (DSC Q200; TA Instruments). The cell was purged dry nitrogen and calibrated for baseline on an empty oven and for temperature using standard pure indium. Specific heat capacity (C_p) was calibrated using a sapphire. An empty sealed aluminium pan was used as a reference in each test. Freeze dried strawberries (10–15 mg) were hermetically sealed in aluminium pans and cooled from room temperature to - 80°C at 5°C per min. Samples were scanned from - 80°C to 300°C at a heating rate of 5°C per min, which is commonly used to determine the glass transition temperature. In the case of MDSC, samples were scanned at a constant heating rate of 2°C per min. with an amplitude of ±1°C and 60 s period of modulation. DSC curves were analysed with respect to the total, reversible and non-reversible heat flow. Glass transition (T_g) was determined as the mid-point of a vertical shift in the reversing transition curve of the diagrams. The measurements of T_g were done in three replicates for each sample [3]. The different compositions of chocolate coating had an influence to the glass transition temperature. The shape of DSC curves differed depending on whether or not the coating incorporated was dark or milk chocolate.

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Thermal analysis - an effective characterization method of polymer films formed by poly(vinyl acetate)

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Poly(vinyl acetate), further named as PAcV, is a non-toxic polymer with many industrial and medical applications, that can be synthesized by vinyl acetate radical polymerization/electropolymerization in alcoholic solution [1] or in aqueous phase containing an emulsifier known as emulsion/miniemulsion polymerization [2, 3]. To prepare a control agent for metal corrosion, PAcV was synthesized, under our laboratory conditions, by emulsion polymerization of vinyl acetate using poly(vinyl alcohol) as emulsifier, Fenton reagent as reaction initiator, and acid acetic as aqueous phase pH-regulator. A white and viscous emulsion containing 31% solid substance was obtained. PAcV synthesized film was comparatively characterized by thermal analysis with a polymer film obtained from standard Sigma Aldrich product, simultaneously recording TG, DTG and DSC curves (Fig.1), with temperature scan rate of 10 °C/min using a Perkin Elmer thermal analyzer with Pyris software.

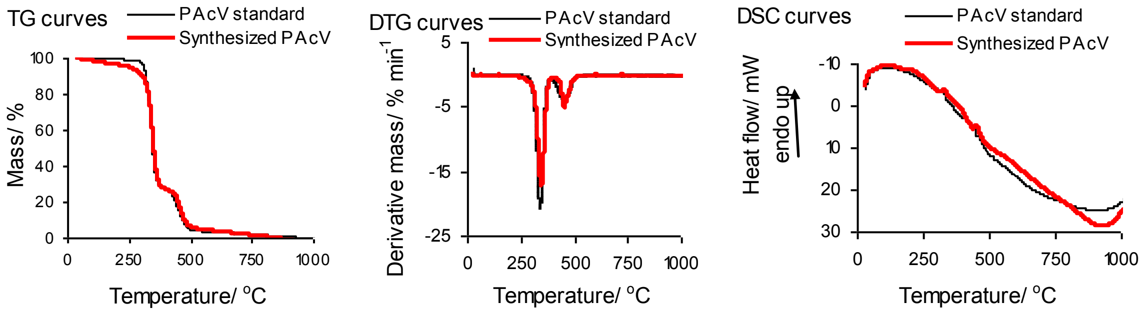

Fig. 1 Thermoanalytical curves recorded for PAcV standard film and PAcV film synthesized.

As Fig. 1 (TG curves) shows, for both the standard film and the synthesized film the highest mass loss is observed in temperature range between 295° C and 375 °C, where the macromolecular chain is cleaved and acetic acid is released, resulting unsaturated compounds. The mass loss notified values of the standard (68.75%) and synthesized film (66.93%) are close to that expected (69.76 %) confirming the previously assumed ones. The maximum mass loss is highlighted at 340 °C for the standard and 353 °C for the synthesized film, respectively (DTG curves), being followed by the endothermic peaks on the DSC curves around 340 °C. The similarities between processes suggest that the values of polymerization degree and average molecular mass of synthesized polymer are close to those of the standard compound.

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Thermal characterization of metal/polymer system based on silver nanoparticles/poly(vinyl alcohol)

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Poly(vinyl alcohol), further referred to as PVA, and silver nanoparticles (nAg) were used to prepare a corrosion inhibitor based on nAg/PVA for different substrates in acidic environment [1-3]. The composite films was prepared as shown in our previous study [4] and was characterized by SEM/EDS [4], Raman spectroscopy and thermal analysis comparatively with PVA film. The TG and DSC curves (Fig.1) were recorded between *RT* and 1000 °C with the temperature scan rate of 10 °C/min using a Perkin Elmer analyzer with Pyris software.

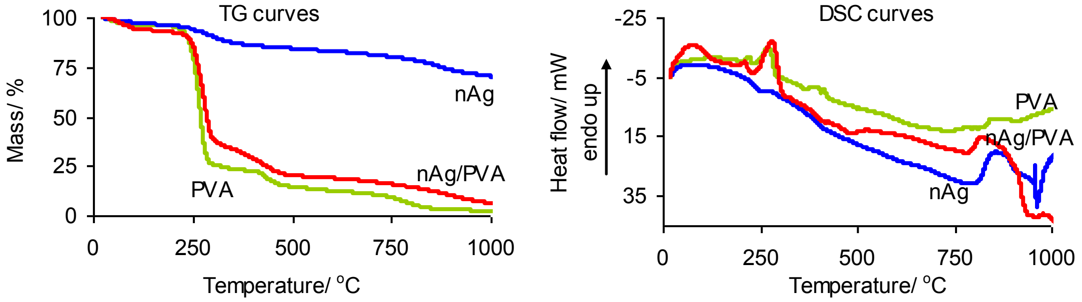

Fig. 1 Thermoanalytical curves recorded for PVA, nAg/PVA and silver nanoparticles

The main stage of decomposition of PVA and nAg/PVA takes place in temperature range between 220 °C and 325 °C, when simultaneous processes such as macromolecular chain cleavage, dehydroxilation or oxidation reactions can occur. These are marked on DSC curves by endothermic peaks at 220 °C and 286 °C highlighting water release and other small-molecule compounds, e.g. acetaldehyde elimination. At temperature values higher than 325 °C, the composite degradation follows another trend compared to PVA indicating the presence of silver nanoparticles inserted into polymer matrix. Moreover, at 1000 °C, the final residue percentage increased from 1.98%, recorded in the absence of silver nanoparticles, to 6.02%, in their presence due to the occurrence, in addition, of Ag or some Ag compounds. Consequently, thermal analysis has proven to be very effective method to detection o the metal particles inserted into a polymeric chain. According to the revealed data, a nAg concentration of 4 % was found in the poly(vinyl alcohol) matrix.

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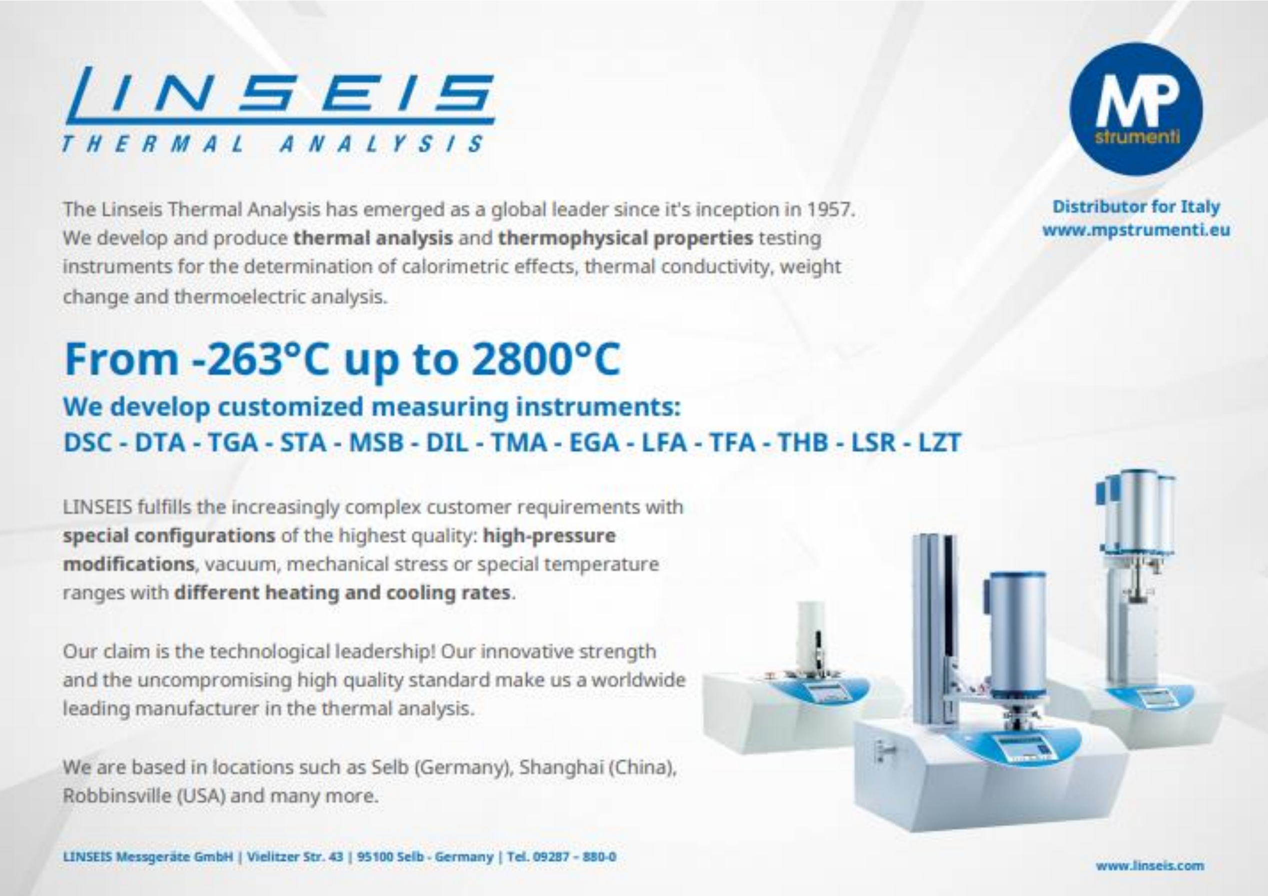

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