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CLUSTERS – MODELS FOR THE DEVELOPMENT AND IMPROVEMENT OF FIRM COMPETITIVENESS – TEXTILE CLUSTERS IN SERBIA

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Key words: cluster, economic development, regional development, Serbia’s textile and clothing industry

Abstract: *Scientific literature explained from both theoretical and practical aspects, the phenomenon of clustering encouraged its development. A cluster represents “geographical concentration of inter-connected enterprises, providers and institutions in certain fields in order to attain common aims.” The reasons to found a cluster are numerous and their importance for productivity, innovation and development of new firms is generally known. Clusters are based on systemic connections between enterprises; they are usually geographically limited and determined by natural, demographical, culturological, economic and other regional features. Joining in clusters allows enterprises an easier access to specialized suppliers, lower costs to develop new products and services, to exchange technical and technological knowledge and information and common coming-out to new, domestic and foreign markets. In this work we will show the importance of clustering, the way clusters operate and a review of active clusters in the domain of textile industry in Serbia as one of possible ways to increase its competitiveness.*

1. INTRODUCTION

Clustering phenomenon in scientific literature is explained from theoretical and practical aspect. Clusters were very well described by Professor Michael Porter, by experts from OECD and many others. Porter presented the clusters as the base of “new competitive economy”. He defines them as “geographical concentration of inter-connected companies, specialized suppliers, service providers, akin enterprises activity, and with them associated relevant institutions (Universities, standardization agencies and professional associations) that in certain fields compete with one another, but also collaborate“. In economically developed countries, cluster as a concentration of “critical mass” has great competitive success in certain fields; it represents an important feature of every country, regional and municipal economy. [3]
In practice, clusters are made of a group of inter-connected enterprises, companies and associated institutions, found on different levels of agglomeration, that deal with certain activity or vertically linked activities which connect common feature and complementarity.[1]

2. CLUSTER CATEGORIZATION

Clusters are determined by natural, demographic, culturological, economic and other regional features. Depending on the regional features and enterprise participants, clusters put their priorities and they establish systemic relations between enterprises that make possible the realization of common aims, using the resources of their region. The relations can be built on common or complementary products, production processes, basic technologies, needs for natural resources, requests for certain qualifications or distribution channels. Founding clusters usually goes following the line "from bottom to top". Clusters made in industry represent complex organizational models, geographically networked akin enterprises from one or several industries, and also enterprises from complementary and different activities. When founding and developing industry clusters different participators have different functions.

Duality as cluster feature is represented through:

- Functionally defined systems of inter-connected activities, known as *industry clusters*, and
- Spatially defined systems - aggrupation of similar and related activities known as *regional* or *local clusters*.

Industry clusters mainly consist of participants, activities and resources joined for the products and services development, production and sale and aren't limited to urban zones. The focus of these clusters is to strengthen competitiveness within different sectors. Regional or local clusters represent spatial agglomeration of enterprises and other subjects that perform same or similar economic activities, making a base that efficiently encourages the effect of knowledge expansion and creates different forms of studying and adjustment. These clusters are mainly made by small and medium sized enterprises, and their success is primarily conditioned by geographical vicinity. [2]

Cluster categorization can be based on the level of invested knowledge. Clusters based on knowledge are spatially limited but, unlike regional, with more accent on innovations and technical progress.

Besides industrial and regional clusters, there also are *innovative clusters*. Combining interior strength, flexibility, stability and sense for administration these clusters research the possibilities for creating new enterprises and technological diversification, for creating nets between participants within a cluster and for forming clusters. [2]

Hopkinson gave the simplest classification of industrial clusters and it is: [1]

- Horizontal clusters - they consist of partners of the same level that use the same market, technology, natural resources and work force.
- Vertical clusters - connect enterprises from industry and other activities in chain of making additional value
- Regional clusters - consist of partners from regional, industry sector;
- Clusters in a branch – consist of partners in a specific action field;
- Entrepreneurial clusters – consist of partners of small and medium-sized enterprises and entrepreneurships, and
- International clusters - that form overlapping industrial cluster nets

The connection between firms is vertical, through chains of buying and selling, and horizontal through complementary products and services, usage of similar raw material, technologies and institutions and other connections that imply social relations with the environment too. Clusters can be differentiated one from another by their size, depth, width and development.

Clusters have life cycles that begin with embryonic stage, which can be generated by innovations, inventions or interior investments, go on to growth stage – established cluster, when the markets are developed enough to make secondary products and to attract imitations and competitors in order to stimulate entrepreneurial relations, mature stage when the processes and services become a routine, there are more imitators on the market and the expenses became key competitive advantage, till the decline stage – weak cluster, when the products become completely replaceable with lower expenses or more efficient substituents. Establishing and developing a cluster is burdened by many problems, but they vary according to their life cycle stage, compared with establishment reasons, previous experiences, region mentality, etc. [6]

At the base of the process of cluster establishment there is the dominance of economic relation, i.e. prevalence of economy factor. Permanent mutual intertwining of economic and social appeared through cluster operation influences the competitiveness augmentation of all cluster participants, confidence increase, enabling more effective common treatment on development and progress projects.

3. TEXTILE SECTOR - CLUSTERS IN SERBIA

Cluster development is one of basic tools of European Union for regional competitiveness improvement and for encouraging innovations in European enterprises. Enterprise groups that are concentrated in European regions get support for collaboration in resolving common issues, through idea and resources distribution and through participation in common projects co-financed by EU. These projects help companies to connect to academic institutions and institutes for research and development, and also to get engaged in innovations and introduce new ideas to the market.

In this context, policy of cluster development ought to have special role in restructuring Serbian industry and in improving its productivity and international competitiveness, in production, export and employment increasing and life standard growth of the population. Their development has scarcely started in 2005, within the "Strategies for development of Innovative and Competitive small and medium-sized enterprises in the period of 2008-1013". This strategy and measures of economic policy of the Government of the Republic of Serbia are compatible with The European Charter for Small Enterprises and with the Small Business Act. The charter points out the importance of small enterprises and the entrepreneurs for the growth, competitiveness and employment increase in EU and it defines what the countries EU members and European Commission should do to improve the business environment for this enterprises.

Although the sector of small and middle-sized enterprises is the most competitive part of the economy of the Republic of Serbia, the participation of this sector in overall number of enterprises and employment in Serbia is on the average level of EU. Greater participation that this sector has in overall traffic BDV and profit, from EU average, is mainly a consequence of logging of big enterprises in Serbia in comparison with big enterprises in EU and to a lesser extents the consequence of the development of this sector.

Textile industry of Serbia is considered one of the most important branches of Serbian processing industry. It disposes of great production capacity when it comes to production programmes –textile, garments, leather and leather objects:

- Heavy and easy, male, female and children's garments
- Knitwear garments
- Cotton textiles
- Sports cotton garments

- Primary textile products
- Home and technical textiles
- Leather products and clothing

The treaty of free textile market with EU was the first bilateral treaty which Serbia had with the Community and the obtained results in this economy branch are obvious.

According to the data of Community of textile, clothing, leather and shoes industry in 2012, the production of clothing objects realized a growth of 10, 4% and the realization was bigger 6, 8%. In December 2012, the production had a growth of 18, 7% compared to the same month in 2011. In period January-December 2012, as it was observed in overall textile industry in Serbia, it realized the export worth 662, 8 million dollars, which is 6% more compared to the same period in 2011.

Table 1: List of mapped clusters in Serbia

	Name of the cluster	**City**	**Sector**	**Source**
1.	TEKSTILNI START UP KLASTER	Nis	textile	LEDIB Cluster house
2.	TEKSTILNI KLASTER NIŠAVSKOG OKRUGA	Nis	textile	LEDIB Cluster house
3.	Klaster za revitalizaciju starih zanata- CRAFTS	Belgrade	textile	Ministry of Economy
4.	Klaster modne i odevne industrije Srbije- FACTS	Belgrade	textile	Ministry of Economy
5.	Klaster tekstilaca ZLOTEKS	Loznica	textile	Ministry of Economy
6.	Asocijacija tekstilaca – ASSTEX	Novi Pazar	textile	Ministry of Economy
7.	Klaster umetničkih zanata	Sombor	handcrafts	LEDIB Cluster house
8.	Klaster kreativne industrije Vojvodine KVIK	Novi Sad	creative industries	LEDIB Cluster house
9.	Klaster dizajnera i štampara	Nis	creative industries	LEDIB Cluster house

Remark: this information if from September 2012. (www.pks.rs)

The program of economic development on Balkans LEDIB, financed by Neighbour program of Foreign affairs of Denmark represents quinquennial program for the support of local economy development with a focus on the development of sectors of small and medium-sized enterprises that comprehend two components:

- *Creating favourable business environment* is a component that supports local governments in making favourable business environment, promotes the dialog between public and private sector and supports business organisations that plead for small and medium-sized enterprises.
- *The development of small and medium-sized enterprises* (SME) is a component that supports SME through cluster development, backup giving to the services of business development and gives backup to SME financing.

CLUSTER HOUSE is a unique developmental business organization for cluster supporting, to small and medium-sized enterprises and associations. It is in Nis and it was founded on the initiative of seven clusters from southeast Serbia and with the technical backup of LEDIB program in January 2011.

Its aim is a support to cluster initiatives, to inform clusters and their members, to encourage their development, to create a net of clusters in Serbia and on Balkans and to promote cluster development on national and international level. As the coordinator of Balkans cluster net, in partnership with the experts for cluster development from Denmark, CLUSTER HOUSE founded the first Training Centre for cluster development on Balkans.

Cluster of fashion and clothing industry of Serbia – FACTS (cluster I stage) was formally registered in 2010 in Belgrade and at the moment its members are 14 private firms of textile clothing industry with 2500 employed in total and 3 academic institutions. Association of textile men ASSTEX (cluster I stage) was founded in 2009 in Novi Pazar as an association of textile producers with the aim to build capacity and to increase competitiveness of cluster members, and they are 14 enterprises and 3 scientific and research and supporting institutions. Textile men cluster ZLOTEKS represents a cluster with 13 private firms, working and protective clothing producers and 3 academic institutions. Start up textile cluster -TEKSTILNI START UP CLASTER was founded at the end of 2009 by nine inter-connected subjects, textile enterprises and 3 supporting industries in charge of work (research, education, design) support and for cluster development. The membership of this cluster now is formed by 27 textile enterprises and 244 staff members.

Cluster for old crafts revitalization in Serbia CRAFTS was founded in 2010 in Belgrade as a non-profit business association of nine entrepreneurial shops in the sector of traditional crafts. The mission of clusters is to reinforce entrepreneurship by pointing out sustainable development, natural and human resources that exist in Serbia, to make redesigned traditional products which will be innovative and competitive on European market, and also to educate about the importance of cultural heritage through workshop work methods.

Creative Industries Cluster of Vojvodina - KVIK was founded in 2010 to support the development of the creative industries in Novi Sad and beyond. Cluster members are public and national culture institutions, education and research institutions and vast range of entrepreneur studios, leaders and prestigious companies in the field of creative industries. Key cluster initiatives are: support, networking and cooperation among key segments of the creative industries: Culture, Art, Design and Media; expansion of cooperation established between creative industries with other industry sectors by raising awareness of the possibility of itself synergy in order to create new values, products and services; International cooperation and networking in joint projects.

4. CONCLUSION

It is obvious that without economy development there isn’t regional or country development. But the possibilities of investment in development are limited, so the enterprises mainly have to find the ways of their development by themselves. Economic progress and sustainable development of Serbia will depend to a large degree on the success of restructuration, how efficient is the economic development and of increment of competitiveness of industry that can’t be provided without industry clusters development. They stimulate private property and entrepreneurial skills, they are flexible and they can be rapidly adjusted to oscillatory changes on selling and purchasing markets, they generate employment, help the diversification of economic activity and make important contribution to export and traffic and also have an important role in innovations and high technology business.

Every region has its features and specificities. Without access to practice and to other's experience, without a comparative analysis and research and without exit to developed markets clusters and member enterprises, focused exclusively on interior relations, which represent a limiting factor, they have difficult access to new knowledge sources and technology, they are limited to learning just within their limits and have difficulties in attaining competitive positions. One of the ways to overcome the isolation is, besides using modern media for communication and establishing collaboration with scientific and research institution abroad, to organise visits to clusters and enterprises in other countries, to establish collaboration between domestic and foreign clusters, to organize visits to fairs from different domains, etc. cluster value can be its contribution to the maintenance of regional economic stability. Economy clustering in Serbia is on its beginnings and the cluster contribution, that is, competitiveness development through augmentation of productivity and creating innovative strategies, can’t be forgotten in the period to come when we should expect more intensive processes of cluster making and operating.

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PROPERTIES OF COMPOSITES BASED ON HEMP AND NATURAL RUBBER CROSSLINKED IN PRESENCE OF BENZOYL PEROXIDE

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Keywords: polymeric composites, natural rubber, hemp, physical–mechanical characteristics, crosslink density, swelling parameters

Abstract. *In this paper, obtaining and characterization of polymer composites based on natural rubber and hemp, in which the elastomer crosslinking has been achieved with benzoyl peroxide, are presented. Besides the elastomer crosslinking, benzoyl peroxide may cause the chemical modification of hemp fibers surface. The mechanical characteristics, gel fraction, crosslink density, water uptake and swelling parameters of natural rubber /hemp fibre composites vulcanized by dibenzoyl peroxide have been investigated as a function of the hemp content. The hardness, modulus at 100% elongation, tearing strength, tensile strength and elongation at break have been improving with increasing fiber content in composites materials due to the better interaction of fiber in NR composites. These results indicate that hemp has a reinforcing effect on natural rubber. Gel fraction value is over 95% for all blends and varies irregularly depending on the amount of hemp in the composites. The crosslinking density (ν) of samples increases as the amount of hemp in blends increases because hemp acts as a filler in natural rubber blends and leads to reinforcement of blends. The water uptake and swelling parameters also increased with increasing amount of fiber content due to the hydrophilic characteristics of hemp.*

1. Introduction

Rubber fibre composites are used in rubber industry due to the advantages they impart in processing and low cost coupled with high strength. Normally a rubber fibre composite can offer a set of properties that may give it the potential of entering application areas not possible with either of the components in the composite [1]. These composites combine the elastic behaviour of rubber with the strength and stiffness of fibre. The aim of the present work is to study the potential of using hemp fibre as reinforcement in natural rubber**.** Hemp fibre is obtained from the bast of the plant *Cannabis sativa* L. It grows easily - to a height of 4 m - without agrochemicals and captures large quantities of carbon. Long, strong and durable, hemp fibres are about 70% cellulose and contain low levels of lignin (around 8-10%). The fibre diameter ranges from 16 to 50 microns. Shorter, woody core fibres ("tow") contain higher levels of lignin. Hemp has been used for centuries to make rope, canvas and paper. Long hemp fibres can be spun and woven to make crisp, linen-like fabric used in clothing, home furnishing textiles and floor coverings. Hemp fibres are also used to reinforce moulded thermoplastics in the automobile industry. The short core fibres go into insulation products, fibreboard and erosion control mats, while the fibrous core can be blended with lime to make strong, lightweight concrete [2]. There are few studies regarding the use and applications of hemp fibers in the development of composites rubber / hemp. E. Osabohien and S. H. O. Egboh [3] performed a study regarding the utilization of bowstring hemp fiber as a filler in natural rubber compounds, but elastomer crosslinking was carred out using the classical method based on sulphur and vulcanization accelerators. In this paper, some composites based on natural rubber and hemp, in which the elastomer crosslinking was carried out using benzoyl peroxide were analyzed. This method of crosslinking results in a better composite resistance to aging those obtained by the classical method of crosslinking (with sulfur and vulcanization accelerators) [4]. In addition to the elastomer curing, benzoyl peroxide can produce the chemical modification of hemp fibres surface. Mechanism of NR crosslinking by peroxide is described in Scheme 1. Peroxide (ROOR) thermally decomposes to alkoxy pre-radicals (RO*) at the vulcanization temperature due their low thermal stability (*reaction 1*). The formed alkoxy pre-radicals abstract hydrogen atom from the NR structure producing site for cross-linking in NR (NR*) (*reaction 2*). NR molecules combine through crosslinking sites to form vulcanized rubber, NR-NR (*reaction 3*). During this process some unwanted reactions may also occur (*reactions 4 and 5*).

$$(1)\quad \mathrm{ROOR} \longrightarrow 2\,\mathrm{RO}^{*}$$

$$(2)\quad \mathrm{RO}^{*} + \mathrm{NR} \longrightarrow \mathrm{NR}^{*} + \mathrm{ROH}$$

$$(3)\quad \mathrm{NR}^{*} + \mathrm{NR}^{*} \longrightarrow \mathrm{NR{-}NR}$$

$$(4)\quad \mathrm{NR}^{*} + \mathrm{RO}^{*} \longrightarrow \mathrm{NR{-}OR}$$

$$(5)\quad \mathrm{NR}^{*} \longrightarrow \mathrm{NR}_1^{*} + \mathrm{NR}_2$$

Scheme 1. Mechanism of NR crosslinking by peroxide.

Simultaneously with natural rubber crosslinking, the chemical modification of hemp fibers may also occur (Scheme 2). Therefore, free radicals may react with the hydrogen group of cellulose or lignin fibers of hemp. For example [5-6]:

$$(6)\quad \mathrm{RO}^{*} + \mathrm{Cellulose{-}H} \longrightarrow \mathrm{ROH} + \mathrm{Cellulose}^{*}$$

$$(7)\quad \mathrm{NR}^{*} + \mathrm{Cellulose{-}H} \longrightarrow \mathrm{NR{-}H} + \mathrm{Cellulose}^{*}$$

$$(8)\quad \mathrm{NR}^{*} + \mathrm{Cellulose}^{*} \longrightarrow \mathrm{NR{-}Cellulose}$$

Scheme 2. Chemical modification of hemp fibers.

Benzoyl peroxide (BP) and dicumyl peroxide (DCP) are chemicals in the organic peroxide family that are used in natural fiber surface modifications. In peroxide treatment, fibers are coated with BP or DCP in acetone solution for about 30 min after alkali pre-treatment [5-7]. As a result of peroxide treatment, the hydrophilicity of the fibers decreased [5] and the tensile properties increased [6].

2. Experimental

2.1. Materials

In preparing the above polymer composites the following materials were used: natural rubber

(NR) Crep 1X (Mooney viscosity is 74 ML_{1+4} at 100ºC, 0.32% volatile materials, 0.38% nitrogen, 0.22% ash, 0.021% impurities), antioxidant pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate Irganox 1010, polyethylene glycol PEG 4000 (1,128 g/cm^3 density, 4-8°C melting point range), ground hemp (thread length of max 3 mm) and dibenzoyl peroxide Perkadox 14-40B (1,60 g/cm^3 density, 3,8% active oxygen, 40% peroxide, pH 7) as vulcanizing agent for vulcanization.

2.2 Sample preparation

Blends were prepared on an electrically heated laboratory roller. For preparation of polymeric composites, the blend constituents were added in the following sequence and amounts: 100 parts natural rubber (NR) roll binding (2'), embedding 3 phr (parts to 100 parts rubber) PEG 4000 and 1 phr Irganox 1010 antioxidant (2'), adding 5, 10, 15 and 20 phr ground hemp (2-4'), respectively 8 phr of dibenzoyl peroxide Perkadox 14-4B (2') as vulcanizing agent was added, homogenisation of blends and removing from the roll in the form of sheet (4'). Process variables: temperature 25-50 ±5^{o}C, friction 1:1.1, and total blending time 8-14'. Plates required for physico-mechanical tests with sizes of 150x150x2 mm^3 were obtained by pressing in a hydraulic press at 160^{o}C and 150 MPa; the curing time was 19'.

2.4. Laboratory tests

Mechanical characteristics: Tensile strength tests were carried out with a Schopper strength tester with testing speed 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2012. *Hardness* was measured by using a hardener tester according to ISO 7619-1/2011 using 6 mm thick samples. *Elasticity* was evaluated with a test machine of type Schob using 6 mm thick samples, according to ISO 4662/2009.

The sol-gel analysis was performed on crosslinked NR rubber (with and without hemp) to determine the mass fraction of insoluble NR (the network material resulting from network-forming crosslinking process) samples (*gel fraction*). The samples were swollen in toluene and extracted after 72 h in order to remove any scissioned fragments and unreacted materials. The networks were then dried in air for 6 days, and in an oven at 80°C for 3 hours, and reweighed. The gel fraction was calculated as:

$$Gelfraction = \frac{m_s}{m_i} x\, 100 \tag{1}$$

where m_s and m_i are the weight of the dried sample after extraction and the weight of the sample before extraction, respectively [8-9].

The crosslink density ($\underline{\nu}$) of the samples was determined on the basis of equilibrium solvent-swelling measurements (in toluene at 23-25°C) by application of the well-known modified Flory-Rehner equation for tetra functional networks. The samples (2 mm thick) were initially weighed (m_i) and immersed in toluene for 72 h. The swollen samples were removed and cautiously dried to remove excess solvent before being weighed (m_g) and, during this operation, the samples being covered to avoid toluene evaporation during weighing. Traces of solvent and other small molecules were then eliminated by drying in air for 6 days and in an oven at 80°C for 3 hours. Finally, the samples were weighed for the last time (m_s), and volume fractions of polymer in the samples at equilibrium swelling ν_{2m} were determined from swelling ratio G as follows:

$$\nu_{2m} = \frac{1}{1+G} \tag{2}$$

where:

$$G = \frac{m_g - m_s}{m_s} \times \frac{\rho_e}{\rho_s} \; ; \tag{3}$$

ρ_e and ρ_s are the densities of elastomer samples and solvent (0.866 g/cm^3 for toluene), respectively.

The densities of elastomer samples were determinate by hydrostatic weighing method, according to the SR ISO 2781/2010. By this method, the volume of a solid sample is determined by comparing the weight of the sample in air to the weight of the sample immersed in a liquid of known density. The volume of the sample is equal to the difference in the two weights divided by the density of the liquid.

The samples crosslink densities, ν, were determined from measurements in a solvent, using the Flory–Rehner relationship:

$$\nu = -\frac{Ln\left(1-\nu_{2m}\right)+\nu_{2m}+\chi_{12}\nu_{2m}^{2}}{V_1\left(\nu_{2m}^{1/3}-\frac{\nu_{2m}}{2}\right)} \tag{4}$$

where V_1 is the molar volume of solvent (106.5 cm^3/mol for toluene), ν_{2m} is the volume fraction of polymer in the sample at equilibrium swelling, and χ_{12} is the Flory-Huggins polymer-solvent interaction term (the values of and χ_{12} are 0.393 for toluene **[8-9].**

Water uptake test - the effect of water absorption on fiber reinforced natural rubber composites are investigated in accordance with SR EN ISO 20344/2004. The samples were dried in an oven at 80°C for 2 hours and then are allowed to cool to room temperature in desiccators before weighing. Water absorption tests were conducted by immersing the samples in distilled water in bottles and kept at room temperature (23±2^{o}C). Samples were removed from the bottles at periodic intervals and the wet surfaces were quickly wiped using a clean dry cloth or tissue paper and weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. The moisture absorption was calculated by the weight difference. The percentage weight gain of the samples was measured at different time intervals. The water uptake was calculated as:

$$\text{Water uptake}(\%) = \frac{m_S - m_1}{m_1} \times 100 \tag{5}$$

where, m_S is the weight of the water saturated specimen at periodic intervals and m_1 is the initial weight of the oven-dried specimen.

Swelling Parameters - Swelling studies provide information on the strength of interface, degree of dispersion of fibres, and their alignment in the elastomer matrix. Swelling behavior was determined by the change in mass using the following method. For cured rubber blends vulcanized the test pieces of known weight (m_1) were immersed in water in diffusion test bottles and kept at room temperature for 49 days (until no further increase in water uptake was detected). After immersion the samples were taken out from the solvents and the wet surfaces were quickly dried using a tissue paper and re-weighted (m_2). The test samples of the blends were further dried in air for 6 days and in an oven at 100°C for 6 hours cooled in a desiccator and immediately weighed (m_3). The swelling parameters [10] of blends were calculated by the following swelling data:

(a) Calculation of Qt (mol % uptake of the solvent): The mol % uptake of the solvent, **Qt,** for the composite samples was determined using the equation:

$$Q_t = \frac{(m_2 - m_1)/M_S}{m_1} x100 \tag{6}$$

(b) Swelling index (SI %) was calculated by the equation:

$$SI(\%) = \frac{m_2 - m_1}{m_1} x100 \tag{7}$$

(c) Soluble fraction (SF %) was determined by the following relation:

$$SF(\%) = \frac{m_1 - m_3}{m_1} x100 \tag{8}$$

3. Results and Discussion

3.1. Physical–mechanical characteristics

Variations in mechanical properties with the amount of fiber increasing in NR/fiber composites are provided in Figures 1-5. The hardness (Figure 1) and modulus at 100% elongation (Figure 2) increased with increasing of fiber amount in blends. The hardness shows an increase of about 27% with 5 phr hemp and 60% with 20 phr hemp, while modulus at 100% elongation exhibited an increase of 5.5% and 105% with the same fiber loading.

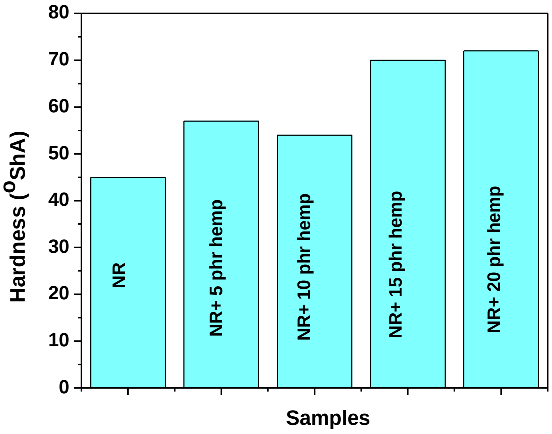

Figure 1. Hardness according to the amount of hemp in composites.

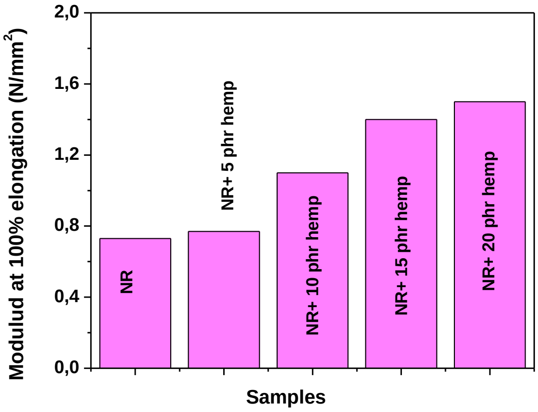

Figure 2. Modulus at 100% elongation according to the amount of hemp in composites.

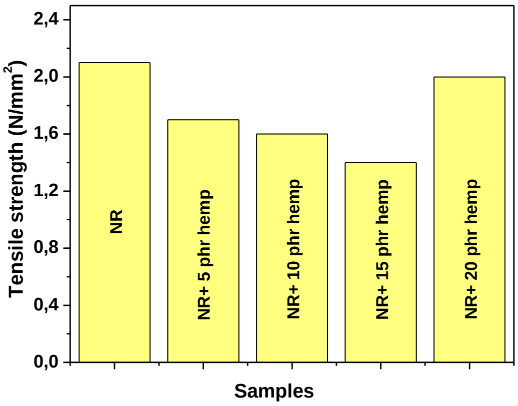

Figure 3. Tensile strength according to the amount of hemp in composites.

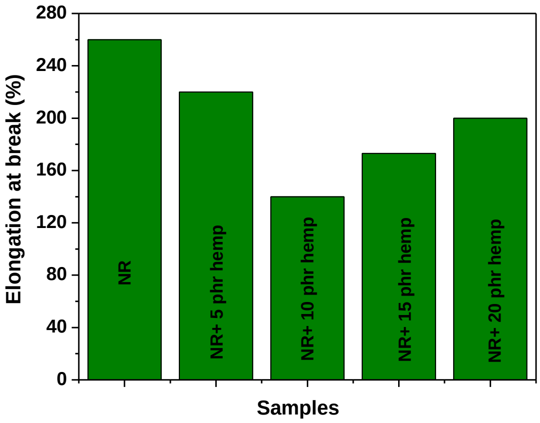

Figure 4. Elongation at break according to the amount of hemp in composites.

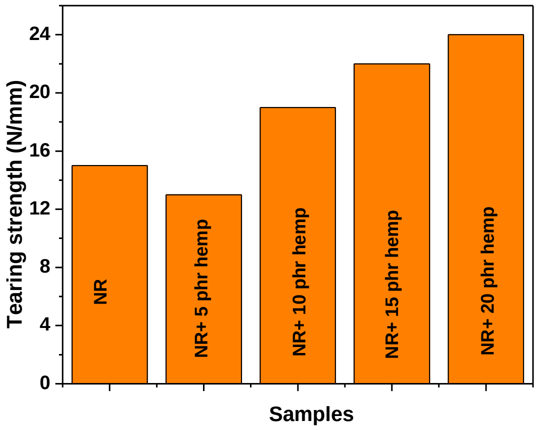

Figure 5. Tearing strength according to the amount of hemp in composites.

It can be seen from the Figure 3 that the tensile strength decreased with increasing filler (hemp) loading. According to Salmah et al. **[11],** the decrease intensile strength is due to the poor adhesion of the filler-matrix and the agglomeration of filler particles. But we have improved adherence filler-matrix by introducting peroxide. It has been shown that for irregularly-shaped fillers, the strength of the composites can decrease due to the inability of the filler to support stresses transferred from polymer matrix [12]. On the other hand, poor interfacial bonding causes partially separated micro-spaces between the filler particles and the polymer matrix [13]. The elongation at break (Figure 4) decreased with increasing of fiber content in composites blends. The decresing of elongation at break with the fiber content increasing in the composites is the result of higher crosslinking. The elongation at break show a decrease of 16% with 5 phr hemp and of 33.4% for blend with 15 phr fiber content. The tearing strength (Figure 5) follows the same trends as hardness and modulus at 100% elongation: increased with increasing of fiber content in composites. The tearing strength shows an increasing of about 26% with 10 phr hemp and with 60% for 20 phr hemp content in composites. The hardness and modulus at 100% elongation values increased due to the better interaction of fiber in NR composites. These results indicate that hemp has a reinforcing effect on natural rubber.

3.2. Gel fraction and crosslink density of the blends

Table 1 shows the gel fraction (mass fraction of the network material resulting from a network-forming polymerization or crosslinking process; the gel fraction comprises a single molecule spanning the entire volume of the material sample) and cross-link density (number of crosslinks per unit volume in a polymer network) of the samples vulcanized by dibenzoyl peroxide as a function of the hamp content. Gel fraction value is over 95% for all blends and varies irregularly depending on the amount of hemp in the composites. The crosslinking density (ν) of samples increases as the amount of hemp in blends increases because hemp acts as a filler in natural rubber blends and leads to reinforcement of blends.

Table 1. Gel fraction and crosslink density of samples

Sample	**Gel fraction (%)**	***ν (10^{-4} mol/cm^3)***
NR	95,17	2,3458
NR / 5 phr hemp	96,62	3,0240
NR / 10 phr hemp	96,68	3,2264
NR / 15 phr hemp	96,19	3,5515
NR / 20 phr hemp	96,65	4,0724

The experimental results confirmed by other works [9, 14] showed that with the increasing in crosslink density, hardness and modulus at 100% elongation increased, whereas the elongation at break decreased. Analysing the results of physical-mechanical properties presented in Figures 1-5, it is noticed that hardness and modulus at 100% elongation of blends have higher values, and elongation at break has lower values compared to the control sample, which is in accordance with values of crosslink density in Table 1 and literature data.

3.3. Swelling parameters

The swelling parameters (Tables 2-5) and water uptake (Figure 6) of samples significantly depend on the amount of hemp in blends, because the latter have hydrophilic characteristics.

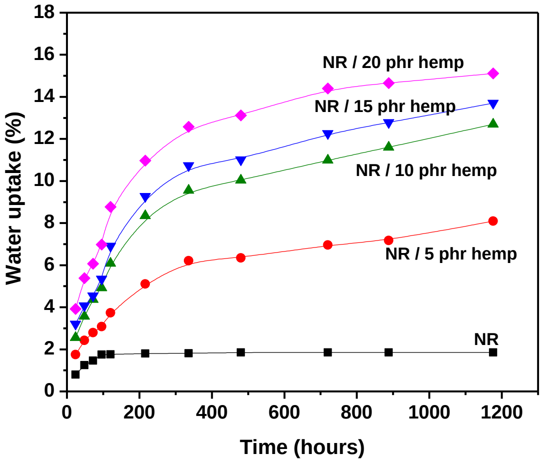

Figure 6. Water uptake according to the amount of hemp in composites.

Table 2. Qt (mol % uptake of the solvent):

	Qt (%)										
Time (hours)	24	48	72	96	120	216	336	480	720	888	1.176
NR	0.04	0.07	0.08	0.09	0.09	0.09	0.11	0.11	0.11	0.11	0.11
NR / 5 phr hemp	0.09	0.14	0.16	0.17	0.21	0.28	0.35	0.35	0.39	0.39	0.50
NR / 10 phr hemp	0.14	0.19	0.24	0.27	0.34	0.46	0.53	0.56	0.61	0.64	0.70
NR / 15 phr hemp	0.18	0.23	0.25	0.29	0.38	0.51	0.59	0.61	0.68	0.71	0.76
NR / 20 phr hemp	0.22	0.30	0.34	0.39	0.49	0.61	0.69	0.73	0.80	0.81	0.84

Table 3. Swelling index of samples

	Swelling index **(%)**										
Time (hours)	24	48	72	96	120	216	336	480	720	888	1.176
NR	0.79	1.25	1.43	1.75	1.76	1.80	1.81	1.85	1.85	1.85	1.85
NR / 5 phr hemp	1.75	2.43	2.79	3.08	3.72	5.11	6.21	6.34	6.96	7.17	8.08
NR / 10 phr hemp	2.56	3.57	4.37	4.92	6.09	8.35	9.56	10.04	10.99	11.59	12.70
NR / 15 phr hemp	3.20	4.07	4.54	5.34	6.91	9.27	10.72	11.01	12.26	12.78	13.70
NR / 20 phr hemp	3.92	5.38	6.07	6.98	8.77	10.97	12.58	13.12	14.40	14.65	15.11

Table 4. Swelling coefficient of samples

	Swelling coefficient										
Time (hours)	24	48	72	96	120	216	336	480	720	888	1.176
NR	0.008	0.012	0.014	0.017	0.0176	0.018	0.018	0.018	0.018	0.018	0.018
NR / 5 phr hemp	0.018	0.024	0.028	0.031	0.037	0.051	0.062	0.063	0.069	0.072	0.081
NR / 10 phr hemp	0.025	0.035	0.043	0.049	0.061	0.083	0.095	0.101	0.101	0.116	0.127
NR / 15 phr hemp	0.032	0.041	0.045	0.053	0.069	0.092	0.107	0.110	0.123	0.127	0.137
NR / 20 phr hemp	0.039	0.054	0.061	0.069	0.087	0.109	0.126	0.131	0.144	0.146	0.151

Table 5. Solubility (soluble fraction) % of samples

	Solubility %
NR	1.0674
NR / 5 phr hemp	0.6903
NR / 10 phr hemp	0.7479
NR / 15 phr hemp	0.9718
NR / 20 phr hemp	1.4689

It may be observed that the water uptake and swelling parameters increased with the increasing of fiber content amount in composites. The water absorption becomes constant after 1176 hours. In these composites the water is absorbed mainly by the hemp. The maximum percentage of water uptake for NR with 5, 10, 15 and 20 phr hemp fiber immersed at room temperature for 1176 h is 8.09, 12.70, 13.70 and 15.11% respectively. The water uptake for all blends, except NR (which absorbed a low percentage of water, 1.85% after 1176 h), is linear at the beginning, then slows and approaches saturation after prolonged time. Both the initial rate of water absorption and the maximum water uptake increase for all composites samples as the fiber volume fraction increases. This phenomenon can be explained by considering the water uptake characteristics of hemp fibre. When the NR/hemp composite is exposed to moisture the hydrophilic hemp fiber swells. The high cellulose content in hemp fibre (approximately 75%) further contributes to more water penetrating into the interface of composites materials [15]. The natural rubber is a hydrophobic material and its water absorbability can be neglected [16]. At a similar absorption time, composites with higher fiber content exhibit higher water absorption because one of the properties of these natural fiber (hemp) is the hydrophilic characteristics.

The obtained composites can be used in manufacturing products with applications in the automotive industry, in the furniture industry etc.

4. CONCLUSIONS

The mechanical characteristics, gel fraction, crosslink density, water uptake and swelling parameters of natural rubber /hemp fibre composites vulcanized by dibenzoyl peroxide have been investigated as a function of the hemp content. The mechanical characteristics (hardness, modulus at 100% elongation, tearing strength, tensile strength and elongation at break) have been improving with fiber content increasing in composites materials due to the better interaction of fiber in NR composites. These results indicate that hemp has a reinforcing effect on natural rubber. Gel fraction value is over 95% for all blends and varies irregularly depending on the amount of hemp in the composites. The crosslinking density (ν) of samples increases as the amount of hemp in blends increases because hemp acts as a filler in natural rubber blends and leads to reinforcement of blends. The water uptake and swelling parameters also increased with increasing amount of fiber content due to the hydrophilic characteristics of hemp. The water absorption becomes constant after 1176 hours. In these composites the water is absorbed mainly by the hemp.

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Technical textiles - solutions for sustainable development of the environment

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Abstract. *Technical textiles are advanced materials engineered for many functions. Textile materials are used in construction in ground and building structures, agrotextiles and geotech: geotextiles and civil engineering. Agrotextiles offer a very attractive market and the geosynthetics market has grown massively over the past few decades.*

1 INTRODUCTION

Whilst the traditional European textile industry has experienced increasing competition from low-cost manufacturing countries, a new prosperous technical textile industry has grown, representing high value, technological manufacturers and producers. These companies remain economically viable because of the significant inputs of technical and quality elements that are more readily absorbed by the high-end applications in which their products and processes are used. Furthermore, technical textiles constitute an enabling technology for other important industries: light weight construction, automotive and medical technology. [1]

The primarily reason for the success of technical textiles is the innovativeness of woven, knitted and nonwoven fabrics, especially in combination with each other because around 70 percent of all technical innovations are dependent on the qualities of the materials used (Allianz Faserbasierte Werkstoffe Baden Württemberg, AFBW, 2010). Another very important aspect for the huge economic potential offered by functional textiles is the great importance given to diversification in research to promote the discovery and implementation of these innovations. [8]

Yet in this high end market, industries face a permanent pressure to remain competitive. Evidently, continuous advancement of products alone may be not sufficient but industries must also refocus by developing new, highly flexible production technologies and integrating fast feedback strategies along the production line to rapidly respond to market demand. Such flexible production technologies must overcome the economic dilemmas between efficient large scale production and customer oriented product diversification on one side and minimum complexity versus elaborate optimisation of production processes on the other side. [3]

The leading international trade exhibition for technical textiles, Techtextil (organised biennially since the late 1980s by Messe Frankfurt in Germany and also in Osaka, Japan), defines 12 main application areas (of which textiles for industrial applications represent only one group):

- agrotech: agriculture, aquaculture, horticulture and forestry
- buildtech: building and construction
- clothtech: technical components of footwear and clothing
- geotech: geotextiles and civil engineering
- hometech: technical components of furniture, household textiles and floorcoverings
- indutech: filtration, conveying, cleaning and other industrial uses
- medtech: hygiene and medical
- mobiltech: automobiles, shipping, railways and aerospace
- oekotech: environmental protection

- packtech: packaging
- protech: personal and property protection
- sporttech: sport and leisure. [7]

The technical textile firms produce a wide range of complex fabrics for use in air, gas and water filtration which reduce greenhouse gas emissions and prevent groundwater contamination by toxic chemicals, eg: gas collector systems in coal fired power stations and landfill, mining and industrial leachate filtration and collection systems. Once used, filtration media is destined to landfill, inclusive of the noxious chemicals it has filtered/and captured – an increasingly unacceptable practice. Knowledge and thus solutions to the decontamination and calorific separation of noxious chemicals that may be imbedded in textiles used for industrial applications will only be achieved through research and collaboration between industry and research agencies. [3]

Technical textiles are advanced materials engineered for many functions. They make an important contribution to the protection of our environment. Examples include:

- textile filtration media plays a key role in our daily lives through the purification of drinking water and industrial and domestic effluent. The technical textile firms produce a wide range of complex fabrics for use in air, gas and water filtration which reduce greenhouse gas emissions and prevent groundwater contamination by toxic chemicals, eg: gas collector systems in coal fired power stations and landfill, mining and industrial leachate filtration and collection systems.
- geotextiles are engineered permeable fabrics which play an invaluable role in improving the durability of the civil engineering infrastructure through improving the stabilisation of road and highway systems, reducing the erosion alongcoastline; providing drainage and lining layers in a waste containment structure; and promoting revegetation by stabilising the soil to allow a root system to develop.
- reduced water evaporation through the use of pool covers and antievaporation/shade cover systems on potable water storages and irrigation channels. Evaporation is a major cause of reduced water resources but that can be reduced to less than 97% through the use of advanced materials supplied by the technical textiles industry.
- the reduction of fuel consumption and greenhouse gas emissions is a primary focus of the automotive industry. Advanced materials produced by the technical textile industry play a key role in gas emission control systems and a reduction in the weight of materials used in a vehicle, with the added benefits of lower noise pollution and the opportunity for improved recycling of a vehicle’s components at the end of its life.
- latest generation nets that negate the use of chemical contaminants in the aquaculture industry (anti-fouling treatments) which pollute oceans. This improves fish health and increases yield in this growth industry. [3]

2. TECHNICAL TEXTILE – A SOLUTION TO THE ENVIRONMENT

Technical textiles are nowadays used for a broad spectrum of applications, from protective clothing to insulation material for buildings. The technical-textiles sector is one of the most innovative branches of industry in the world and, according to analysts, ranks as one of the five high-tech sectors with the greatest potential for development. At present, the global market for technical textiles is worth around US $ 127 billion (approx. € 97 billion) whereby Asia leads the world in terms of textile consumption with 8.5 million tonnes followed by the USA and Europe with 5.8 and 4.8 million tonnes respectively. [8]

It Companies involved in technical textiles invest a far higher proportion of turn-over in R&D (8-10 %), compared with a textile industry average (3-5 %) in order to remain competitive and such investment must increasingly be focussed on highly targeted R&D, working in close collaboration with EU universities and research centres to retain the technical lead that Europe presently enjoys over its competitors. [1]

In Germany – in this field, the world's leading nation alongside the USA – the share of technical textiles in total textiles sales currently amounts to approx. 52 percent. Technical textiles are primarily made and processed for the 'Mobiltech' (22 percent), 'Indutech' (18 percent), 'Buildtech' (10 percent) and 'Protech' (10 percent) areas of application. This weighting is valid for the whole world except that, according to the Association of the Yarns, Woven Fabrics and Technical Textiles Industry, the share held by the 'Mobiletech' area of application rises to no less than 28 percent. [8]

What is relatively new is a growing recognition of the economic and strategic potential of such textiles to the fibre and fabric manufacturing and processing industries of industrial and industrialising countries alike. In some of the most developed markets, technical products (broadly defined) already account for as much as 50% of all textile manufacturing activity and output. The technical textiles supply chain is a long and complex one, stretching from the manufacturers of polymers for technical fibres, coating and speciality membranes through to the converters and fabricators who incorporate technical textiles into finished products or use them as an essential part of their industrial operations.The economic scope and importance of technical textiles extends far beyond the textile industry itself and has an impact upon just about every sphere of human economic and social activity. [7]

Textile filtration media plays a key role in our daily lives through the purification of drinking water and industrial and domestic effluent.[3]

The existence of human beings on earth is the result of a fortuitous set of circumstances in which conditions for development of the species were present so that evolution could take place allowing us to reach our present state of being. Our tenuous continuation could be jeopardized at any time by changes in these conditions, and this far-reaching effect could result from shifts which might be totally insignificant by cosmic standards. They could bring about, for example, our inability to breathe, or stay warm or cool enough, or grow the food we need. Thus, we are only able to survive because our planet provides all the sustenance we need without major effort on our part.We can broadly define this set of conditions to which we are exposed as our environment. [7]

The line between a traditional textile and a technical textile may seem unclear to an outsider as many products could arguably fall into either division often depending on their end use or functional qualities. Of course, the broad range of products described as technical textiles adds to the complexity of defining exactly what an technical textile is, and thus individual firms identify themselves by their products' end use applications.

The process by which technical textiles are manufactured identifies the products further. For instance a technical textile could be nonwoven or the result of more traditional textile making technologies such as knitted or woven. More traditional fabrics, such as knits, can also be considered a technical textile if, for instance, they have some advanced characteristic or quality (i.e. UV resistance or reduced flammability) due to added chemicals or synthetic fibres used in the making of the fabric for a specific end use or application. By way of example, the raschelle knitting technique which was traditionally used for making shawls, scarves and babies' blankets is now used for making shade-cloth and fabric used to reinforce embankments. [3]

2.1 Technical textiles application - building and construction (Buildtech)

Textile materials are used in construction in both ground and building structures. The retrofitting of existing masonry walls and soil structures is particularly important for earthquake protection of historic buildings and protection of earthworks against landslides. Unreinforced masonry structures are highly vulnerable because being originally designed mainly for gravity loads they often cannot withstand the dynamic horizontal loads in case of strong earthquakes. In masonry applications, textiles are growing in importance as they provide a non-intrusive technique to provide reinforcing strength to a structure (damaged or undamaged). Soil structures, such as embankments, are subjected to landslides after heavy rainfalls or during earthquakes.

Hence the necessity to develop efficient methods for the retrofitting of existing masonry buildings and earthworks and of related monitoring systems to possibly prevent the structural damage.

Embedding sensors of different types into textile materials enables several important advantages. Structural health monitoring (SHM) can be conducted during construction, under in-service conditions, and post tragedy (i.e. after an earthquake). Such measurements can be used before or after an event to take preventive measures (before) or to assess the state of the structure (after). Measurements over time can be used to track changes in structural performance allowing for maintenance and repair actions when appropriate. In the case of chemical sensing, sensor embedded textiles can be used to detect environmental contamination.

The aim is to provide reinforcing strength and monitoring capability for geotechnical and masonry applications through the industrial production of multifunctional technical textiles and includes the following activities:

- The development of new and novel sensors. These sensors include fiber optic sensors, piezoelectric sensors, chemical sensors, and sensitive textile fibers (coatings)
- The development of new and novel sensor interrogation systems and data processing techniques
- The development of nanoparticle-based mortars and adhesives
- The integration of sensors into warp-knitted textiles for geotechnical and masonry applications (two dimensional and rope like structures)
- The evaluation of these products in a laboratory environment
- The development of numerical models for the employment of these materials
- The field testing of project products in real world, tough, and rugged environments

The different functions the textile structures are:

- to increase ductility and structural strength;
- to monitor strains, deformations, and acceleration;
- to detect presence of fluids and chemicals;
- to measure structural health.

Enabling technologies include the combination of warp-knitted grid-like reinforcing basic structure and rope-like reinforcement, the incorporation of optical fibres into textiles as well as the incorporation of sensing fibres - coating fibres with nanocrystalline piezoceramic materials or conductive polymers\alloys.

The use of textile material as load-bearing part of the building; use of multifunctional textiles for stabilisation and monitoring; use of nanostructured materials to tailor the interface properties; incorporation of sensors based on nanocrystalline piezoceramics and optical fibres, development of an impedance-based health monitoring technique [4]

2.2 Technical textiles application - agriculture (Agrotech)

Textiles and especially agrotextiles offer a very attractive market. Volumes in this market area are high and fast growing. At present, products are mainly based on Polyolefin’s (greater than 200 Ktonnes/annum in Europe) and to a lesser extent other petrochemical polymers such as PA and PET are used. In most cases these agrotextiles are at the end-of-life difficult to recover from the fields and will be polluted by a vast amount of organic material and sand, making efficient recycling and even combustion with energy recovery extremely costly and not attractive.

A number of agrotextiles are based on natural fibres, but in general these products are degrading that fast in the natural environment that there lifetime is usually limited to one or maximum two years and textiles with a relatively high weight per m² are required in order to compensate a bit for the fast degradation.

Bio-based polymers in combination with natural fibres and side products can offer a good alternative, if biodegradation can be modelled and adapted according the specific end applications. Intrinsic positive properties of the bio-based polymers such as low flammability, light fastness or intrinsic preservation properties can boost technological advantages, leading to major economic and technologic benefits in industrial implementation. [9]

But seaweed biomass remains a good alternative as a source of non-oil based materials such as biofuels, biopolymers, pigments, anti-oxidants and other chemical compounds that can be derived from seaweed. The future of terrestrial biomaterial and biofuel crops is in doubt: they take up valuable land for food production and consume large amounts of water.

With almost 71% of our planet covered by oceans that are bounded by extensive coastlines, growing biocompounds at sea bypasses the environmental and economic problems associated with their production on land. Why algae many macroalgae naturally grow very quickly, from single microscopic cells to 2m-long adults in six to eight months. [10]

It makes recyclability and zero-landfill affordable for farmers, greenhouse owners and horticulturists on any scale:

- Ideal for blocking moisture and repelling weeds
- Plant protection fabrics used in the early spring and late fall to extend the growing season in slightly inclement weather.
- Erosion control fabrics provide soil stabilization and protection in a multitude of diverse environments
- Protects plants, annuals, and vegetables from severe cold, frost & freezing temperatures.
- Developed specifically for large-scale greenhouse operations in automated planting/germination systems.

All of the above products are completely recyclable. [11]

Bio-based softeners are now fashionable: Environmentally friendly, bio-based softeners can lower CO2 emissions in the manufacture of PVC products up to 40 %. Since they are completely biodegradable and largely made from plants, they are also at risk of microbial infestation.

A new, pioneering solution for extending the useful life while retaining biodegradability of the protective foil made from renewable or biodegradable raw materials widely used in agriculture. In particular, PLA foil (polylactic acid) can be individually ‘tuned’ for a desired service life with specific performance characteristics. Seedlings and young plants are effectively protected. This individualization of the finishing makes a concrete contribution to improved quality and greater earnings for farmers. [12]

The Japanese plan will see a satellite attached to a thin metal net spanning several kilometres launched into space. The net is then detached, and begins to orbit earth, sweeping up space waste in its path.

During its rubbish collecting journey, the net will become charged with electricity and eventually be drawn back towards earth by magnetic fields – before both the net and its contents burn upon entering the atmosphere.

It is thought that the net will remain in orbit for several weeks, collecting enough rubbish to make the trip financially worthwhile, before sending another net into space. [13]

2.3 Technical textiles application - geotech: geotextiles and civil engineering

The geosynthetics market has grown massively over the past few decades - even during periods of uncertainty such as the recent global economic downturn - and industry analysts and manufacturers of geosynthetics expect growth to continue.

Growth in demand will be driven primarily by large-scale construction projects in developing countries.

The use of geosynthetic products in transportation infrastructure is also likely to grow rapidly in developing countries due to the large number of highways and railway lines which are being built in these countries.

Significant amounts of geosynthetics are also used in landfill - and the landfill market is likely to grow at a fast pace due to environmental concerns and a desire among authorities in developing countries to adopt modern landfill designs.

Large scale infrastructure developments are taking place in China, India and Russia, and environmental protection regulations and building construction codes are evolving in these countries. As a result, these markets are expected to be where the strongest gains will occur in the near future.

China will be the dominant market because of the amount of available land in the country, the size of its population and the number of large scale infrastructure projects which are under way and planned for the future. In fact the increase in demand in the Chinese market is expected to account for almost half of the increase in global demand. [15]

According to a new market report "Geotextiles Market by Product Type (Woven, Non-woven, Knitted) for Roadways, Erosion Control and Drainage – Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2012 - 2018, "the global market for geotextiles was valued at USD 3.2 billion in 2011 and is expected to reach USD 6.4 billion in 2018, growing at a CAGR of 10.3% from 2012 to 2018.

In terms of volume, the demand for geotextiles was 1,904.0 million square meters in 2011 and is expected to reach 3,398.4 million square meters in 2018, growing at a CAGR of 8.6% from 2012 to 2018.

Increasing demand from roadway construction, especially from BRIC countries, is expected to drive geotextile demand over the next five years. Special focus on the use of geotextiles in infrastructural activities coupled with favorable regulatory support is also expected to have a positive impact on global demand.

However, the fluctuating cost of commonly used raw materials such as polypropylene and polyester is expected to have an adverse effect on the market over the forecast period. In addition, the absence of defined standards across the countries has also emerged as a key challenge for market participants.

Among the product types, non-woven geotextiles was the largest consumed segment, accounting for over 60% of the overall demand in 2011. However, woven fabrics are expected to show substantial growth over the forecast period. Road construction was the largest application segment for geotextiles, and was valued at USD 1,502.8 million in 2011. [14]

The use of geotextiles in the construction of wind farms results in savings on materials and reduces the carbon footprint.

The market for renewable energy is growing. Since 1995 for example the number of wind farms has increased at an unprecedented rate and the International Energy Agency (IEA) expects an upsurge in numbers in the years ahead. Geosynthetics can play an important supporting role in the construction of wind farms. Their use in this application has produced savings on materials and reduced the carbon footprint, resulting in cost savings. [16]

Non-woven geosynthetics are inserted between the pavement and the road-bed in the process of repaving roads. They prevent the intrusion of precipitation and mitigate crack formation by reducing the stress between the upper layers of the pavement and the road-bed.

The chips serve to store information about the strengths and structures of the various road layers and materials plus road construction data and additional quality characteristics. To read and edit the data, vehicles are equipped with write/read units allowing the information to be read, changed and stored again onboard the moving vehicle. [17]

Increased local authority investment is required to improve water courses and surface drainage for water control and flood alleviation. As an alternative to hard stone and concrete finishes, geotextiles proven erosion control technology is creating flow resistant vegetated banks on projects around the UK and in Europe.

These geotextiles are based on a permanent high strength three dimensional matting structure with an internal fibre matrix, which incorporates soil and vegetation. This technology delivers proven erosion resistance to specified maximum water velocity and permissible shear stress; up to 50% reduction of costs compared to hard engineered solutions has been achieved. [18]

Geotextile positioned vertically in a dike can stop piping. That has been proven by an experiment with the textile on IJkdijk in Bellingwolde (Netherlands). Geotextile has been used in hydraulic engineering for some time now but using it for piping is new. The experiment has shown for the first time in the field that geotextile can actually stop piping. [19]

3. SOLUTIONS FOR SUSTAINABLE DEVELOPMENT OF THE ENVIRONMENT

Along with the rest of the world, the textile industry is rapidly heading toward a precipice: an environmental, social, and political disaster that we can all see coming all too well.

According to Steven A. Jesseph, president and CEO for Worldwide Responsible Accredited Production (WRAP): “By the year 2050, we will have almost 10 billion people competing for limited clean water, non-renewable and renewable resources, land to grow food, and energy to sustain their businesses, families, and lifestyles.”

It’s the textile industry’s responsibility as much as anyone else’s. “In terms of its scale of production and employment, the textile industry is one of the largest industries in the world, so its impact is significant,” notes Andrew Xin, vice-president of global business management for BASF Textile Chemicals.

The modern world needs textiles for a vast array of applications and textiles are completely ubiquitous. The immovable object of the need for textiles will soon meet the unstoppable forces of population pressure and resource depletion.

Experts are increasingly concerned with the growing scarcity of fresh water, especially with the great amounts of good-quality fresh water needed to dye fabrics. In addition, Chris Parkes, national sales manager for Concept III Textiles, notes that approximately 30-35% of the chemicals in the world go through the textile industry, and “the effluent problem hasn’t gone away.”

According to “Eric” Shengfeng Wu, of Oriental Giant Dyes & Chemical Ind. Corp. Taiwan, the sustainability concept of the “three Rs” (reduce, reuse, recycle) is still valid for the textile industry, and “the most important of those is ‘reduce’,” he says.

Everyone knows that for the textile industry, as for many industries, cost is critical. And thus, some textile mills use the excuse that sustainable production practices are “expensive” to keep from starting a sustainability program.

Kanti Jasani, president of Performance & Technical Textile Consulting, consider a sustainability program as another quality program: sustainable fabrics must necessarily be quality fabrics. He says that “these concepts are integral to the concept of sustainability” .

“That’s what sustainability means,” says Jasani. “It’s reducing costs in every single way while increasing quality. If you’re truly being sustainable, your costs will go down and profits go up.” The original definition of sustainability did not just mean ecologically sustainable, although that is often the part of sustainability that’s focused on today. Sustainability means social and economic sustainability as well.

Waste (such as effluents and emissions) and dealing with that waste “is an expense factor that has to be included in the production calculation worldwide,” says Anton Schumann of Rudolf Chemie GmbH.

Too often in the past, emissions were not calculated as part of the costs of products, but instead pushed off onto the environment for people living near the textile mills to pay, in terms of increased health risks and polluted air and water.

Thus sustainability is also an accounting issue—and for too long, environmental costs haven't been "accounted for."

Then there is the issue of toxicity. How to get color into textile materials without water is the big issue the textile industry is facing." Michael S. Brown, principal of Brown & Wilmanns Environmental LLC, says that current water-based dyeing is "fundamentally flawed technology that we're stuck with at the moment." In the short to medium term, the industry has to keep working on ways to use less water. But in the medium to long term, Brown believes that developing a sustainable technology that can replace water as a primary medium to color fabric is a priority for our industry. "The issue of the last decade has been carbon," says Brown. "The major issue of the coming decade will be water."

Schrott says that ozone has begun to be used for non-chemical bleaching of textile fabrics in some applications—especially denim washing. Ozone can be used to help clean up dye effluent in textile wastewater as well.

"Wastewater recycling, capture and reuse of chemicals, better use of heat exchangers, and more can all help a facility move toward the goal of becoming sustainable," says Jesseph. Moving further along the sustainability path, Jesseph says some mills are moving toward partial or full use of biomass as fuel to run their facilities. "A few enterprising textiles facilities have created biological wastewater treatment systems with virtually zero energy use and amazing results," he says.

The textile industry hasn't been sitting idle with regards to sustainability all these years. Jasani says that, according to a study by Cotton Incorporated, from late 1990 to late 2009, overall, the textile industry reduced the water, energy, and chemicals used in processing cotton by 50%. "On average, the 130 to 200 liters of water per kilogram of fabric were reduced to 65 to 70 liters of water per kilogram of fabric processed," says Jasani. "Chemical use was reduced about 40%, and energy consumption was reduced as much as 50%."[6]

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STUDY ON THE WINDING STRUCTURE OF BEAM

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Key words: Yarn ring, filling coefficient, winding layer, layer height

ABSTRACT. *One of the important factors that impact productivity and the quality of the goods in weaving, knitting and yarn dyeing processes is the quality of the winding structure of the beams used. Winding structure of the beam is characterized by winding density, density distribution, the length of the yarn winded and the shape of the beam's cover. These factors affect the winding tension of the yarn that is loosened during the use of the beam and the breakage of the yarn significantly. In this study, the formation of beam structure is examined in geometric and technological terms and methods and equations for determining such technological parameters as filling coefficient, winding density, winding layer number and the height of the layer are developed. Besides, theoretical and practical methods to identify the distance between the yarn rounds through the width and diameter of the beam are suggested.*

1. Introduction

There are many studies carried out on the formation of beam and on researching its winding structure. In the research in the [1] resource, the structure parameters of the winding structure of the beam is examined geometrically.

In this study, the researcher develops the concept of filling coefficient in winding structure for the first time and shows that yarn rounds have 3 different placements (Figure 1) during parallel winding. Besides, the researcher suggests theoretical formulas for identifying filling coefficient, winding density and the length of the yarn winded in first and second placement.

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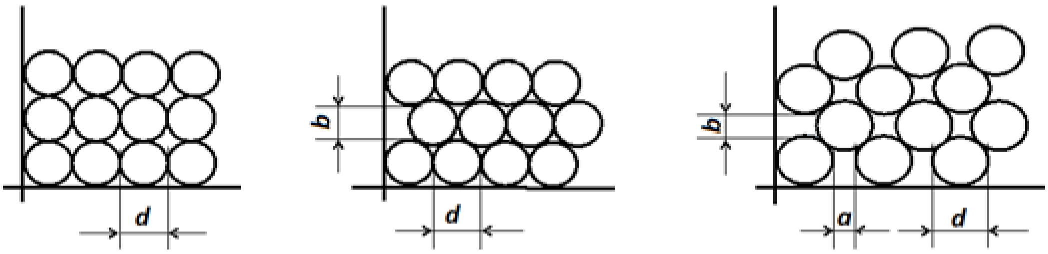


a) b) c)
$a = 0; b = 0;$ $a = 0; b = 0{,}732\,d;$ $0<a<b; 0<b<d$

Figure 1. The placement of yarn rounds in the width section of parallel winding structure

Information on the theoretical examination of winding structures in this scope is given in resources [2-4]. Considering the effect of changes and deformations in the width section of the yarn because of crushing, this issue was further improved with study [5] and proper formula was obtained. In the studies [2-5], *a)* and *b)* placements, which are valid for winding structures obtained by precision winding method, are discussed. In the beams obtained by winding multiple yarns, yarn rounds have *c)* placement. This is the general state of a) and b) and rounds are placed at *a* and *b* distances from each other in line with the width and diameter of beam (Figure *1c*). Geometric examination method of winding structure for this placement was first developed in [6,7] studies. In addition, theoretical equations that identify the filling coefficient and other winding structure parameters for all kind of placement of the rounds were suggested.

In this study, beam formation is examined in geometric and technological terms and methods to determine such parameters as winding frequency, filling coefficient, winding density, winding coefficient numbers and winding height. Besides, in order to determine *a and b* distances between the yarn rounds through the width and diameter of beam, a practical method is suggested. According to the data from the beams produced by implementing these methods, important winding structure parameters can be determined or the technological parameters of beam formation for producing beams of desired structure can be arranged.

2. Parallel Winded Beam Formation

All other beams except the ones prepared for dyeing are obtained by parallel winding method. In producing beams for dyeing, winding process is done via cross-winding method in order to decrease density. Both types of beams' bottom is formed by irregular winding environment and with the start of all yarns parallel to each other (regular winding), normal beam starts to be formed [8]. During regular winding, yarn that passes through the tread of the distributor comber of the machine winds around the beam and forms parallel positioned rounds. In case that the yarn is threaded through the comber equally, the distance between the rounds through the width of the beam is equal in all locations and it remains unchanged from the start of winding till the end. Depending on the number of yarn winded *(M)* and the width of beam *(H),* this distance is found by the following equation:

$$A = H/M \;\ldots\ldots\ldots(1) \text{ or } A = 1/P_T \;\ldots\ldots(2)$$

Here P_T – is technological frequency or winding frequency and it is the number of yarn winded on 1 cm beam and it is calculated by the $P_T = M/H$ equation.

A distance also means the space between the rounds as well. This space is calculated depending on the diameter of the yarn and on the value of *A* distance;

$$\Delta = A - d = H/M - d \;\ldots\ldots\; (3)$$

Here Δ –represents the space between the rounds;
d– represents diameter of the yarn

Since this space is many times larger than the diameter of the winded yarn, M number of helix winded in every round will be enough to cover the surface of the beam. Therefore, Δ

space should be filled with yarn rounds. Formation of a full winding later and structure is as follows:

At the start of regular winding, 1st rounds are winded at M number and A distance on the beam at the first winding (Figure 1*a*). In the second winding, while the 2nd ring is supposed to wind around the first one, it cannot hold there and thus, winds either on the right or left without a space. In the 3rd winding, the ring to be winded cannot hold on the 1st one again and has to locate itself either by the side of the 1st or 2nd ring. However, the 4th ring is winded on one of the rounds winded before and thus, the second layer starts to be formed. In the 5th cycle of the beam, the 5th ring locates itself by the side of the 4th ring. While the 6th ring should be over 4th or 5th rounds, it locates itself in between the two rounds. Therefore, after the winding of 7th and 8th and finally 11th rounds, the filling of *A* space with rounds ends and the first full winding layer on the body of the beam is formed (Figure 2b). (The full winding layer is given in color in the figure). Meanwhile, triangle-shaped hills are formed through the width of beam and in the number of the M yarns on the layer. Later, during the winding, with the pressure of the printing roller of the machine and with the effect of the own tension of the yarn, these triangle hills are turned into oval shapes.

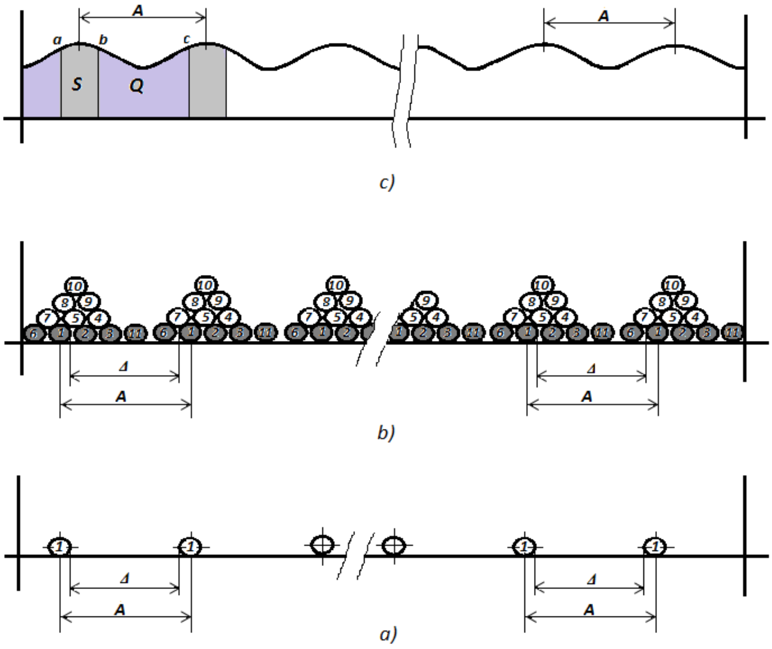


Figure 2. The positioning of yarn rounds during the formation of a layer in a beam
a) – at the start of winding, *b*) – at the end of layer formation, *c*) – the form of beam surface

Thus, the layer formation repeats periodically and the desired yarn length and beam structure with a wavy surface is obtained. The length of the wave that is formed on the surface of the beam (amplitude) is equal to *A* distance and depends on *H* width and *M* yarn number.

In the obtained beam, yarn rounds are mostly in the II and III position. In the S area under the *ab* top of the wave, the positioning of the rounds is almost at position II while in the Q area under *bc* curve of the wave is at position III. Besides, the *a* distance between the rounds located under the bc curve is changeable and it increases towards the center of the hollow section. Here the distance between the rounds is maximum. Thus, the winding density through the width of the beam changes wavily. Winding density is higher at areas under the hills compared to other areas. In the experimental studies we did on sizing beam, the winding density at areas under the hills is 25-30% higher compared to the areas under the hollow section. Besides, with the decrease of wave length, or in other words with the increase of wire number, it is seen that the density difference decreased.

As a result of the examination, it is found that the wavy structure on the surface of the beam does not cause to a tension difference in yarn during unwinding. Because all yarn unwinded from each hill are located on the same diameter of the beam. Because the tension in yarn under the same condition and unwinded from the same diameter is at the same size [2].

3. The winding structure parameters of the beam

3.1 Winding Layer and parameters

One of the important elements of winding structure is the layer that is formed of the rounds. Many studies have been carried out on the formation of layer on bobbin and other weft bobbins and on identifying the layer's parameters; and many researchers set forth different opinions [9,10]. Besides, there have been different explanations on the concept of layer and different equations have been suggested to identify the thickness of the layer. However, this issue has not been studied enough for the parallel winded beam structure.

Beam's winding structure is formed of horizontal and vertical layers. The horizontal layer can be defined as an area formed by two planes (*P-P*) threaded from the bottom of (*M*) width sections of two yarns located one over the other and an area filled with yarn rounds. The height of the area (h_E) has a value below the diameter of the yarn. The width of the area is equal to the width of the beam. The vertical layer, on the other hand, is an area formed by two planes (*Q-Q)* threaded in parallel to one another from the edge *(N)* of the width sections of two yarns located one over the other; whose height ($h_Ç$) does not exceed the diameter of the yarn and whose width is equal to the winding height in line with the diameter of the beam (Figure 3*a*).

Depending on the positioning of yarns in the winding structure, one layer could be formed of the yarn rounds in one or two layers. In the first type of placement, the layer is only formed of rounds placed at one layer. In this case, both the horizontal and vertical height of the layer is equal to the diameter of the yarn (Figure 4a). (In Figure 4, horizontal and vertical layers are shown in different colors). In all other placements, however, one layer covers one part of both rounds winded on each other (Figure 4 *b,c*). (Except the first layer). The main parameters of the layer are its height and the frequency of the layer. As we stated, the height of the layer (thickness) has a value below the diameter of the yarn and changes according to the placement of rounds and the size of *a* and *b* distances.

The height of the layer (thickness) changes according to the size of *a and b* distances according to the placement of the rounds. In the first placement, the rounds are placed uninterruptedly both horizontally and vertically.

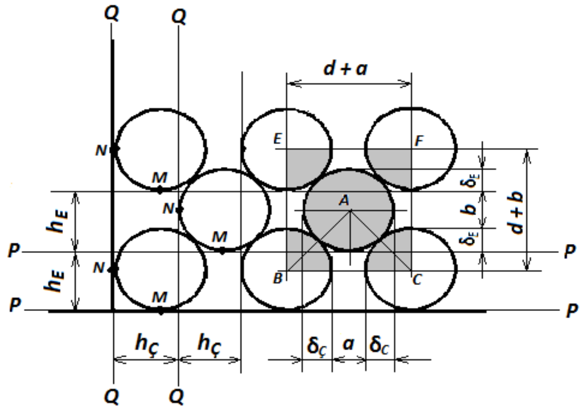
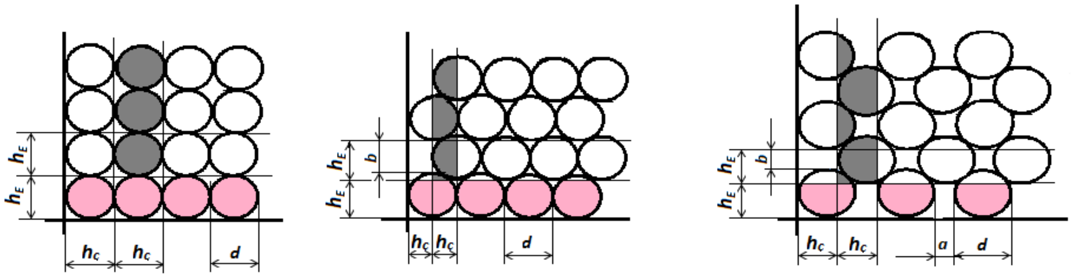


Figure 3. The diagram for calculating the winding structure parameters of beam

In this case, layer height has the maximum value and is equal to the diameter of the yarn, in other words $h_E = h_{\text{Ç}} = d$ (Figure 4*a*).



a) *b)* *c)*

$h_E = h_{\text{Ç}} = d$ $h_E = 0{,}866d$; $h_{\text{Ç}} = 0{,}5\,d$; $h_E = 0{,}5(d+b)$; $h_{\text{Ç}} = 0{,}5(d+a)$

Figure 4. The change of layer height in beam structure according to the placement of the rounds

In other cases, the height of the layer is calculated with the below given equation obtained from Figure 3.

$$h_E = 0{,}5\sqrt{4d^2 - (d+b)^2} \ \ldots\ldots\ldots.(3) \quad h_{\text{Ç}} = 0{,}5\sqrt{4d^2 - (d+a)^2} \ \ldots\ldots\ldots.(4)$$

Here h_E – represents the height of the horizontal layer;

$h_{\text{Ç}}$ – represents the height of vertical layer

d – represents the diameter of the yarn.

Height of the Layer in Figure 3 can be expressed with a simpler equation:

$$h_E = 0{,}5(d+b)\ldots\ldots.(5) \quad h_{\text{Ç}} = 0{,}5(d+a)\ldots\ldots.(6)$$

And the distances *a and b* are found with the below given equation formed according to Figure 3.

$$a = \sqrt{4d^2 - (d+b)^2} - d \ \ldots\ldots.(7) \quad b = \sqrt{4d^2 - (d+a)^2} - d \ \ldots\ldots.(8)$$

In the placement II, the rounds in the vertical layer are located in b distance to each other (Figure 1*b*). In this case, since $a = 0$ the height of horizontal layer according to the equation (3) is $h_E = 0{,}866d$. In $a = 0$ condition, $b = 0{,}732\ d$ according to the equation (6). The value of b when calculated according to equation (6) is $h_Ç = 0{,}5d$.

In placement III of the rounds, the height of the layers is calculated using either the equations (3), (4) or (7), (8). Therefore, it is necessary to know the *a and b* distances between the rounds. Since these distances are related to one another, it is enough to know the value of just one of them. Following that, the value of the remaining one can be found using either equations (6) or (7).

In general in order to examine the winding structure practically, the height of the horizontal layer of the beam is considered important. Therefore, based on such information as the practical data of the beam, the type and number of the winded yarn, such important parameters as the height of horizontal layer and later the filling coefficient of the winding structure and the real winding frequency are calculated. Another important parameter of layer is the layer frequency. The frequency of layers is the number of rounds in 1 cm in line with the width and diameter of the beam and is calculated as follows:

$$P_H = m_H/H \ldots\ldots\ldots\ldots.(9) \quad P_Ç = m_Ç/(R–r) \ldots\ldots\ldots..(10)$$

Here P_H –represents the frequency of layer in line with the width of the beam, ring/cm

$P_Ç$ – represents the frequency of layer in line with the diameter of the beam, ring/cm

m_H – represents the number rounds in the layer in line with the width of the beam,

$m_Ç$ – represents the number of rounds in the layer in line with the diameter of the beam,

R – represents the outer diameter of the beam, cm

r – represents the inner (body) diameter of the beam, cm

Depending on the value of *a* and *b* distances, it is possible to calculate the frequency of the layers using the following equations:

$$P_H = 1/(d+a) \ldots\ldots\ldots\ldots.(11) \quad P_Ç = 1/(d+b) \ldots\ldots\ldots..(12)$$

As seen in Figure 3, since $d+a = 2h_Ç$ and $d+b = 2h_H$ layer frequency can be calculated with the following equations:

$$P_H = 1/(2h_Ç) \ldots\ldots\ldots\ldots.(13) \quad P_Ç = 1/(2h_H) \ldots\ldots\ldots..(14)$$

In practical calculations, it is mainly the frequency of horizontal layer that is used. Knowing the frequency of layers, it is possible to calculate the winding density of the beam (μ) using the following equation [7].

$$\mu = TP_H/(10^5 h_E) \ldots\ldots\ldots(15)$$

From $P_H = 1/(d+a)$ and $d = C\sqrt{T}$, we can obtain the $T = d^2/C^2$ values by putting them in their place in the equation (13);

$$\mu = \frac{d^2}{10^3 C^2 h_E (d+a)} \ldots\ldots\ldots. \quad (16)$$

Here C- represents the fixed coefficient characterizing the type of the yarn.

This equation is the general equation identifying the winding density of parallel winding structure and is also valid for special cases.

In the first placement, in other words when $a = 0; b = 0$ (Figure *1a*)

$$\mu = \frac{1}{10^3 C^2} \text{ ....(17)}$$

In the second placement; when $a = 0$ (Figure *1b*), $b = d\sqrt{3}$; and $h = (d+b)/2 = 0{,}933d$ *(14)* equation becomes the following;

$$\mu = \frac{1}{0{,}933\ 10^3 C^2} \text{ ....(18)}$$

3.2 Filling coefficient

Filling coefficient is the coefficient which shows how much yarn and how much spaces the winding structure includes. This coefficient is expressed as the ratio of the area that the yarn covers in the width section of the beam to the area of the beam. Filling coefficient is also mentioned as density coefficient in the resources [4] and [10]. The general equation that identified this coefficient was first obtained in the study [6] indirectly for the first time. However, it is possible to obtain that result via a very short way using the Figure 3. In Figure 3, inside the *BEFC* square, the area of the width section of the quarter part of four yarns and full width section of one yarn is shown (colored areas). This area is equal to the area of two yarns' width section, which is $2Si$ and is inside the BEFC square. In this case, filling coefficient is determined using the $Kd = 2Si/S$ rate. If the area of the width section of the yarn is $S_i = \pi d^2/4$ and the area of the square is $S = (d+a)(d+b\ )$, the equation of the filling coefficient is as below:

$$K_d = 0{,}5\pi d^2/[(d+a)(d+b)] \text{ …………..(19)}$$

Using the equations (13) and (14), the relationship between layer height and filling coefficient can be found by putting the values in their place in $d+a$ and $d+b$.

$$K_d = \pi d^2/(8h_E h_Ç) \text{ ………………….(20)}$$

This equation can be used for finding the layer height in cases where filling coefficient is known. According to practical data, in order to find out the layer parameters and filling coefficient in examining winding structure, $Kd = 785\ C^2\mu$ equation given in the resources (15) and [7] can be utilized.

3.4 Results and Discussion

1. Parallel winded beam formation is researched in technological and geometric terms and the formation of waves on the surface of beam is explained. It is found that wave formation on the surface of the beam is inevitable. The number and wavelength of the occurring waves changes according to the frequency of wires. As the wire frequency increases, so does the number of waves; however the wavelength decreases as the wire frequency increases.

2. The wavy structure on the surface of the beam does not cause to a tension difference in the yarns during the unwinding later. Because each yarn ring that is unwinded is located to almost same diameter of the beam.
3. One of the important parameters of the beam's winding structure is the height and frequency of the layers. Theoretical formulas are made to determine these parameters and their implementation is shown in practical calculations.

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AUTOMATIC TENSIONER MECHANISM FOR A SINGLE YARN

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Keywords: Yarn, yarn tension, tensioner assembly, tension control.

ABSTRACT. *To produce with high efficiency and high-quality of technological processes in textile machines, to give the required tension for yarn and value of the tension must be kept constant as far as possible. For this purpose a wide variety of yarn tensioner assembly and devices are used. Adjusting the tension in currently used yarn tensioner maintained the signal coming from one side of depending on the value of output tension. Fluctuations occur in input tension cannot be used in adjusting. Therefore in most of the currently tensioner devices, sensitivity in adjusting of tension is low. Also all yarn tensioners used for the single yarn in textile machines give the required tension to only yarn and makes the adjustment of this tension.*

In this study, a high performance yarn tensioner assembly whose sensitivity of adjusting the tension is high, control the change of the tension during the operation and can measure the tension was developed and experiments were carried out. Developed assembly has features of bobbin can be used like a single yarn and can be used in similar machines.

1. Introduction

Tension of yarn is the most important technological parameter during the process of yarn formation, yarn winding and warping in textile industry. The tension of yarn that is lower or higher than the normal level, leads to inefficient performance of these processes and low quality semi-finished product. Having a high yarn tension during these processes causes increase in yarn break which results in decrease in efficiency of the machine. The tension of the yarn which is lower than the normal level affects the working mechanism of the machine and the productivity is negatively influenced by the high downtimes of the machine. The finished and semi-finished products that are produced using a low yarn tension are considered as defective. Therefore, applying the proper yarn tension and keeping it at this constant level are essential requirements in order to produce high quality products and perform technological processes with high efficiency [1].

A variety of mechanic, automatic and semi-automatic yarn tensioning devices and units with different working principles are utilized to obtain normal yarn tension [2,3,4,5]. In single yarn applied modern textile machines, yarn tension is adjusted automatically via mechanic, pneumatic, magnetic and electromagnetic yarn tensioning mechanisms. Sensor which monitors the variation of yarn tension is only placed before or after the tensioner device in these mechanisms. Yarn tension is regulated based on the region up to the tensioner device if the sensor is placed before it. In the latter case, yarn tension adjustment is carried out according to the change in yarn tension after tensioner device [2,3]. Generally, automatic yarn tensioner devices in which the sensor is positioned after the tensioner device are widely used in the industry [4].

The drawback of this system is that yarn tension adjustment is performed based on the data acquired from one side of the tensioner device. However, the tension of the yarn may vary on both sides of the tensioner device. Therefore, the sensitivity of the tensioner device is low in this type of machines. Moreover, the tension is only applied to the yarn and yarn tension is adjusted up to a certain level.

Фатдахов and Гордеев (1989) recommended a high-efficient modern device to automatically determine and control yarn tension in yarn production process. In their proposed approach, the yarn tension is controlled according to the tension on both sides of the tensioner device in contrast the other devices, which enables to adjust small and largely changing tension levels. Furthermore, this device can control by measuring the entry and exit values of tension thought the whole process.

The device is equipped with tensioner and the front and rear controlling systems. The tensioner device is placed at the middle of these regions. The yarn tension values from spool (F_0 input) and tensioner (F output) are controlled and sent signal to tensioner to adjust the tension level. In addition to the controlling system in the device, small tension variations around controlling region are also automatically regulated. If the fluctuations in yarn tension reach a certain limit, controlling units send signals to tensioner to restore yarn tension which is carried out immediately. Thus, this device allows high-precise adjustment of yarn tension unlike the other devices.

However, this apparatus has the following disadvantages:

- Tensioner may receive signals from both controlling units at the same time, which results in overflow or insufficient adjustment. If front and rear controlling units send tension increase and decrease signal, respectively, tensioner cannot adjust the yarn tension. On the other side, if both units send information to increase or decrease yarn tension, tensioner can only consider and process one of the signals.

- Tensioner cannot apply high differential tension between two sides of the yarn.

- Since the needle of the tensioner system is fixed to the controlling unit shaft, the measurement accuracy of tensioner is low. This disadvantage results from the fact that total rotational displacement of the needle on the scale is equal to the travel distance of the vertical shaft in control unit.

2. New Yarn Tensioner

A new tensioner with the same working principle was developed in order to eliminate signal conflict on tensioner, to increase the width of tension applied on yarn and to improve the sensitivity of measurement and yarn tension. Two tensioners with different pressure forces (1 and 2) were applied to increase the range of the tension in the proposed tensioner (Figure 1). First and second tensioners have 10 -15 sN and 20-30 sN tension application capacity, respectively.

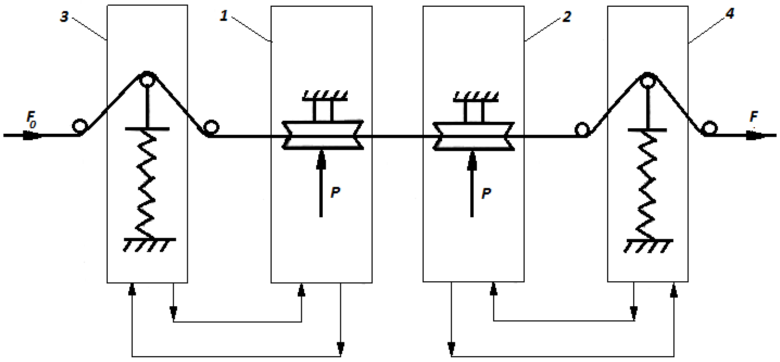


Figure 1. The scheme of the tension adjustment system in the developed yarn tensioner

The output yarn tension can be up to 50-60 cN. Each tensioner independently regulates the tension level based on the signal send by its control unit. Therefore, the signal conflict problems in tensioners are not emerged during the production process.

The general structure and working mechanism of the tensioner are illustrated in Figure 3.

The yarn tensioner mechanism comprises two tensioners placed facing one another in the mounting plate (1) and having the same technical structure; two controllers each connected to the tensioner and two tension measuring mechanisms. The tensioner comprises a hard disk (4) fixed to the shaft (3) which is attached to upper support plate (2), free thrust disk (5), pressure spring (6), pressure adjustment spring (7), adjusting spindle(9) having a centering bush (8) on the upper edge and adjusting nut (10). Adjusting spindle (9) is slipped through the spindle (12) placed to the lower support plate (11). By providing free connection of controllers and tensioners in the yarn tensioner, the locking issue, which occurs because of the simultaneous signals sent from the controllers, is solved and the adequate tension is automatically adjusted.

In order to provide tension to the yarn at different ratios isolable tensioners are prepared. Therefore, the thrust disk (5) is fastened to the pin (38) which is attached to the shaft by itself (3) and which has a screw (39) on its surface. With the pressure of the spring (7) the pin (38) tightens disk (5) to the hard disk (4) and provides the required tension for the yarn. Under this circumstance, the screw (39) is open (Figure 6). When it is necessary to isolate the tensioner, the disk (5) is pulled down and the screw (39) is tightened to the shaft (3) (Figure 7). As a result, thrust disk (5) locks at a distance from the hard disk (4) and tensioner stops working.

The controller comprises a shaft (16), which has a yarn guide pin (13) on its upper edge and which is placed on upper (14) and lower (15) support plates; control spring, whose one edge rests on centering pin (17) while the other rests on lower support plate (15); and yarn routers (34, 35).

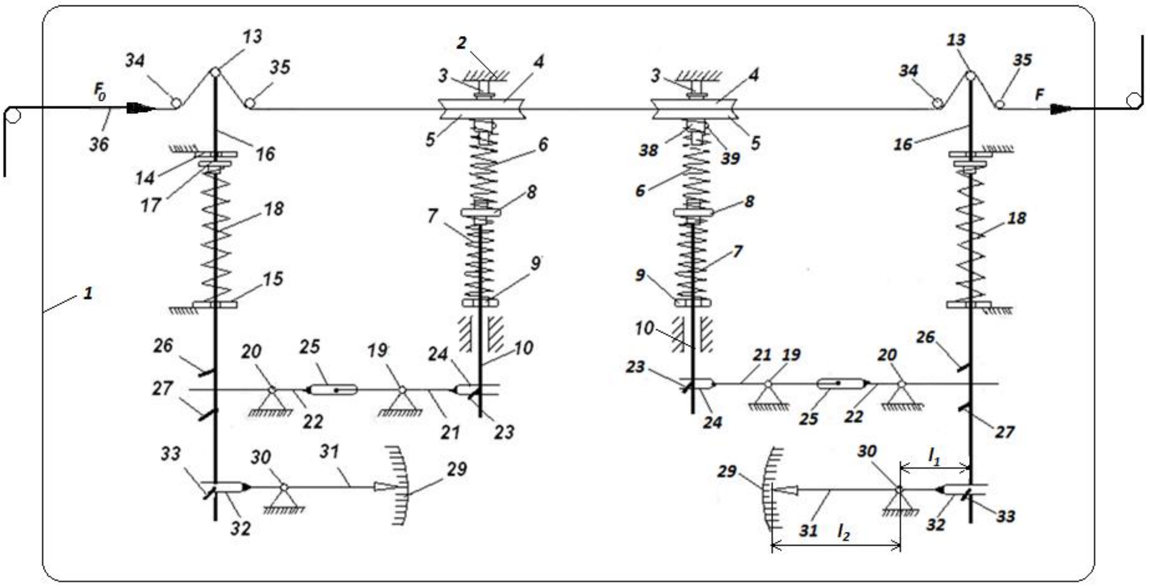


Figure 2. The scheme improved yarn tensioner mechanism and working principle

The connection of the tensioners with the controllers is provided via the arm of the tensioner (21) and arm of the controller (22) placed on the joints (19,20). The fork (23) on the right edge of the arm (21) is connected to finger (24) fixed below the tensioner shaft (10) while the left edge is connected to the slider (25) located on the right edge of the arm. The other edge of the arm (22) is placed by itself in between the upper (26) and lower (27) adjusting bars fixed below the shaft of the controller (16).

Tensioner measuring mechanism is comprised of a scale on the scale stand (28) fixed to mounting plate (1) and an indicator placed on joint (30). Using the rod (33) screwed below the shaft (16) moving up and down via the fork (32), the indicator moves.

If the normal level of the yarn tension F_n slightly fluctuates, the adjustment is achieved by control units without the involvement of tensioner region. The width of the tensions in control units are $\pm \Delta F_0$ in front control unit and, $\pm \Delta F$ back control unit. The value of the tension in the prescribed range is the tension corresponding to the displacement which is equal to the distance between the adjustment bars (26,27) of the control unit shaft (16). If the displacement of the control unit shafts is bigger than the half of the distance between adjustment bars, then tension adjustment is applied by tensioner. In this case, the adjustment of the tension is performed as follows:

If the output tension of the yarn F is higher than normal level, back control unit (4) sends signal to tensioner (2) to decrease the tension (Fig. 2). Yarn lowers down the shaft of the rear control (16) unit in case of high tension in the yarn. In this case, the top adjustment bar of the shaft (26) pushes the right edge of the arm (22) and rotates the arm in clockwise direction around the support. Then, arm 21 connected to this arm with slider (25) rotates in counter-clockwise direction and pulls the shaft (23) downward by pushing the rod fixed at the shaft of the tensioner (10) through the fork at left end (24). With the withdrawal of shaft the washer at its top end (8) squeezes the bottom spring of the tensioner (7). Consequently, spring length decreases and the length of spring above it (6) increases. This configuration leads to relaxation of spring and compression force in the disc (5) and yarn tension decrease as a result.

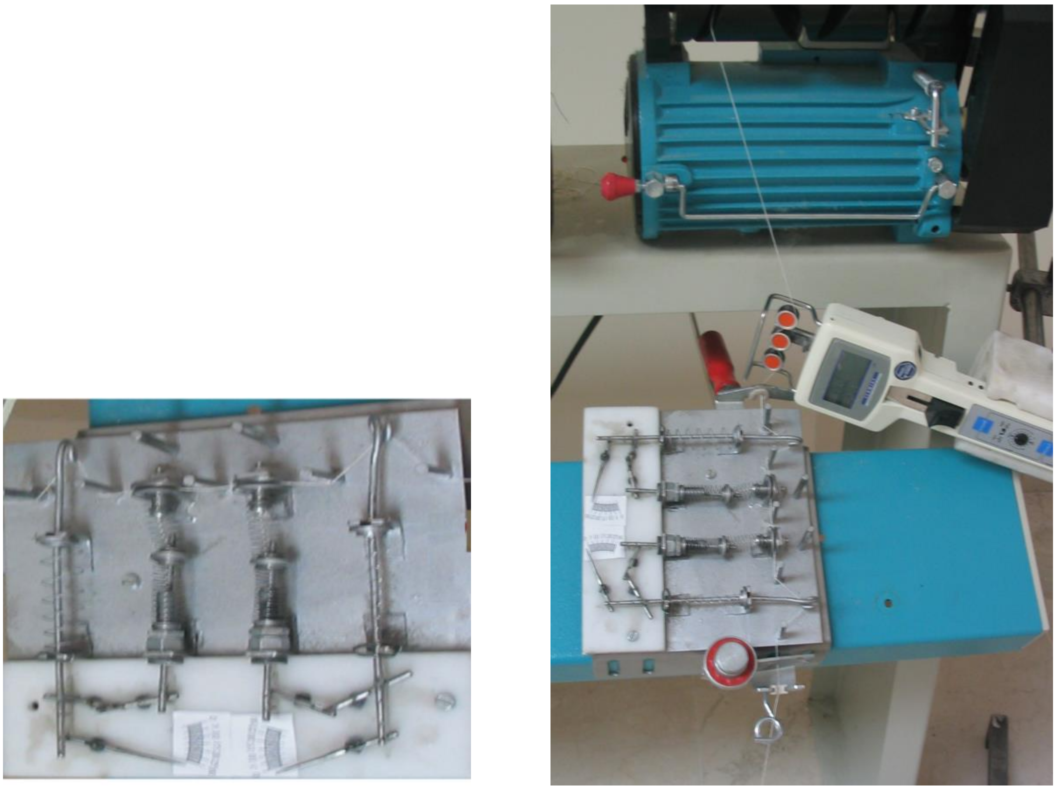
Decrease in tension level leads to the relief of compressed spring (18) in control unit shaft which pushes the shaft upward. The adjustment bar at the bottom end of the shaft (27) pulls the right end arm (22) to upward, which rotates the left end of arm (21) to upward. In this case, shaft (10) is pushed upward; the pressure applied on disc (5) by springs (7,6) rises and consequently tension on yarn increases. Thus, the adjustment of the yarn tension is achieved at the rear tensioner. Input tension adjustment is also carried out with the same mechanism applied on the rear tensioner.

The measurement of the input and output tensions during the production process is conducted through a tension checking system composed of indicator (31) and scale (29) excited by controlling shafts (Fig. 3).

As shown in Figure 3, the indicator (31) actuated by control unit shaft (16) is designed as an arm placed on the support in the new machine. The length of the movement path of the indicator on the scale L_1 and the length of the movement path of the haft (L_2) are related to each other with the following equation:

$$L_1 = \frac{L_2 l_2}{l_1}$$

(l_1–the length of the indicator from support to the shaft of the control unit, l_2 – the length of the indicator from support to the edge indicator on the scale)



a) *b)*

Figure 3. a)Tensioner trial sample, b)The location of the tensioner in the bobbin machine

needle l_2 length segment l_1 part of the 2,0 - 2,5 floor is designed as a great way to move the needle L_2 den 2,0 -2,5 large floor. Since l_2 is 2.0 – 2.5 times longer than l_1, the movement path of the indicator is 2.0 – 2,5 times longer than L_2. Adopting a rotational indicator in the new design make the sensitivity of the new machine 2.0-2.5 times higher than the old machine.

On the other hand, the indicator of the tensioner presented by (Фатдахов and Гордеев 1989) is fixed to tensioner shaft, which makes the length of the movement path of the indicator on scale equal to the length of the movement path of the shaft.

A trial experiment was performed in the designed yarn tensioner machine and it was also compared with different yarn tensioners in the bobbin machine (Figure 3). Experiments were conducted on different yarn at various winding speeds in the conical bobbin machine. 10 Ne, 20/2 Ne cotton and 50 denier polyester yarns were used in the trial experiment. The tension was measured with SCHMIDT DTMX-200 electronic digital tension measuring device. Tension measurements were made in different winding speeds.

To assess the extent of the fluctuations in tension statistical parameters including average deviation, standard deviation, variance and coefficient of variation were utilized in data analysis.

3. Conclusions and Discussions

Experimental results indicated that the yarn tension exhibited similar in all three tensioners. This conclusion means that increase in winding speed causes an increase in yarn tension. Moreover, the increase in tension occurred at a lower rate compared to the device with rondelle.

The variation of the tension of cotton in the new machine was found to be less than the machine with rondelle. Especially, the difference in tension variation increases as the winding speed increases. The coefficient of variation of 10 Ne yarn at 740 m/min is 10.98 and 21.4 in the new machine and in the machine with rondelle. The difference in coefficient of variation is higher for polyester yarn. The coefficient of variations in the new machine are 0.83 and 3.5 at 540m/min and 740 m/min, correspondingly, which are 7.85 and 8.46 in the machine with rondelle. This statistical comparison shows that the new machine decreases the tension variation 9.2 and 2.7 times. This conclusion demonstrated that the adjustment feature of the new machine is better than the machine with rondelle.

The change of the coefficient of variation of tension depending on the winding speed is almost same in both tensioners (except the polyester yarn). The coefficient of variation reaches minimum and maximum values at 380 m/min and 540 m/min winding speeds, respectively. This coefficient decreases gradually for additional speed increase. In contrast, the change of coefficient of variation for polyester yarn is different in the new machine. For polyester yarn, the coefficient of variation starts to rise when the winding speed is more than 540 m/min.

The main advantage of the new designed device is that it has capability to control the tension level continuously and can apply a wide range of yarn tension in contrast to other yarn tensioner devices.

Vibration-relieving devices should be used to improve the sensitivity and adjustment capabilities of the proposed device.

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EFFECT OF ULTRASONIC ENERGY ON REDUCTIVE CLEANING PROCESS OF DYED POLYESTER FABRICS

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Keywords: disperse dyed polyester fabric, reductive cleaning, ultrasonic methods, conventional method

Abstract. *After dyeing of polyester with disperse dyes, reductive cleaning processes were applied by using dextrose mono hydrate and commercial alkaline-dispersant reductive substance (Cyclanon ARC–BASF) with sodium dithionite-sodium hydroxide. In this study effects of ultrasonic and conventional methods on reductive cleaning processes were investigated in terms of ΔE*, ΔL*, Δa*, Δb*, *ΔC* and ΔH* colour values, K/S values and fastness properties.*

After conventional (Temperature 70°C, Duration 20 minutes) and ultrasonic (Temperature 70°C, Duration 10 minutes) reductive cleaning processes, the values were compared. Total colour differences of ultrasonic reductive cleaned samples with all reductive cleaning agents were in acceptable range. K/S values were higher for ultrasonic sodium dithionite and sodium hydroxide reductive cleaning processes depending on the sodium hydroxide concentration. K/S values were generally higher for ultrasonic dextrose mono hydrate and sodium hydroxide reductive cleaning process. Higher K/S values were obtained by conventional reductive cleaning process by using Cyclanon ARC. Using of ultrasonic energy for reductive cleaning did not have any negative effects on fastness properties of reductive cleaned samples.

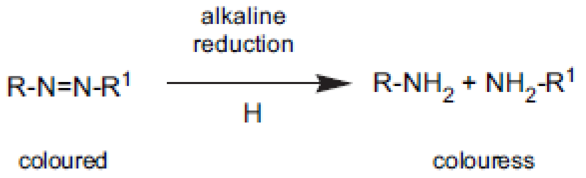
1. Introduction

Washing process is applied to dyed textile material to remove the unfixed dyestuffs and chemicals of dyeing processes to obtain optimum fastness properties and colour values. Reductive cleaning substances are widely used for reductive washing processes. These substances are conductive inorganic chemicals contain reductive groups. Sodium dithionite is the widely used reductive cleaning agent applied in alkaline condition. (Formula 1)[1].

$$3\ Na_2S_2O_4 + 6\ NaOH \rightarrow 5\ Na_2SO_3 + Na_2S + 3\ H_2O \qquad (1)$$

In this application, dyed textile material is processed at 50-70°C for 20-30 minutes with NaOH, $Na_2S_2O_4$ and surfactants afterwards asidic / acidic neutralization process is applied if necessary.
Polyester is a hydrophobic material, when the reductive cleaning is performed under the T_g of polyester only dye chromophores which are on the surface of the material are decomposed. So, unused dyestuffs and substances are removed without changing the colour [2].

It is supposed that chromophore of the azo structured disperse dyes decompose and form to colourless amino compounds by process of alkaline solution of reductive substance (Formula 2).



(2)

It is not possible to obtain good fastness properties and colour saturation without reductive cleaning process. The purpose of the reductive cleaning for light colour dyeing is to decrease the oligomer forming. Neutralization processes after reductive cleaning and setting the pH of alkaline dyeing baths for alkaline reductive cleaning are increased the cost of dyeing. To prevent these problems some commercial supporter substance blends can be provided to increase the cleaning and conductive substance effect without changing the pH and can be added directly to the acidic baths [3].

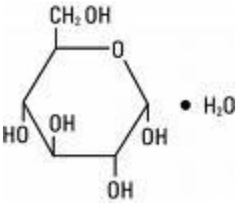
Ecology is an important factor for reductive washing. Reductive substances such as sodium dithionite which contains sulphur are hazardous for biologic purifying plants because of consuming too much oxygen and show toxic effect. Sodium dithionite has some disadvantages such as contains aromatic amines in disperse dyes. Sodium dithionite is an alternative to boron contain products for continue reductive washing and has advantages to package dyeing and stability control of stock tanks[4].

Detergent based chemicals are suggested instead of sodium dithionite based reductive cleaning substances for final process of disperse dyed polyesters. It is indicated that no difference are observed at λ_{max} values and hue – chroma values, but low decrease is observed at colour strength when washed at 98°C for 15 minutes, also washing fastness at a temperature of 60°C is higher and obtained high decrease in terms of BOD, COD and TOC [3].

Good washing fastness results without colour damage are obtained by 1 minute ozone process of disperse dyed polyethylene terephthalate fibres. But more than 1 minute ozone process is decreased the tenacity of fabrics without any colour damage. It is indicated that by ozone process which is applied at room temperature in 1 minute is decreased the cost of energy and also chemicals which are used in conventional reductive cleaning are not used in this process [4].

Ecology and environmentally friendly production concepts are forced companies for cleaner production. In this study colour and washing fastness properties of the conventional reductive cleaning agents and dextrose mono hydrate and commercial alkaline – dispersant agent reductive substance (Cyclanon ARC–BASF) were investigated.

Sodium sulphur which provides dissolution of sulphur dyestuffs by reduction is harmful for the environment. Carbon hydrates which have reductive potential, non-toxic and biodegradable are used for dissolution of sulphur dyestuffs instead of sodium sulphur [5]. Dextrose mono hydrate is a purified and α-D-glucose structured monosaccharide which contains one molecule crystal water and six carbons (Formula 3). Dextrose mono hydrate is the crystal form of glucose and basic energy source of live metabolism. Dextrose mono hydrate is reductive and has two types as mono hydrate and dry dextrose.



(3)

Cyclanon ARC is a commercial reductive, alkaline and dispersant agent blend. It is used after disperse dyeing process of polyester and polyester blends to improve the fastness properties. Reductive cleaning process can be applied without using alkaline by using this product.

Ultrasonic sound waves have frequencies that human cannot hear. The chemical effect of the power of ultrasonic energy is emerged by cavitation. Ultrasonic energy is conveyed by waves. These waves create compression and relaxation in molecular structures of the environment pass. Liquid is decomposed and cavitation bubbles are occurred when negative pressure is applied to the liquid. These bubbles are crashed to each other and caused to come out an energy after consecutive compression periods [6].

The use of ultrasonic energy in textile wet processes has some advantages such as short processing time, low energy and chemical consumption and improved product quality. As a result of the cavitation at solid/liquid interface an increase in mass transfer is obtained from liquid to solid [7].

High amount of water, electricity and thermal energy are used in textile wet processes. Also chemical substances are used to accelerate or decelerate the process time in some wet processes. High temperatures are required to transfer the mass from liquid condition to textile material. This transferring process is dependant to temperature and time. Radiofrequency, microwave and IR heating techniques are used to decrease process time and energy consumption. Ultrasonic energy is an important alternative technique for textile processes however it is not used for industrial processes. In order to use ultrasonic energy in industrial processes some problems such as machine design, homogeneity in baths, ultrasonic pressure distribution, position of the transducers, fabric position in the machine and temperature of the bath should be solved [8].

Use of ultrasonic energy in sizing baths, preparation of emulsion paths, alkaline and bleaching processes, dyeing, final washings and enzymatic processes are carried out. Process time is decreased and whiteness index is increased even at low temperatures in hydrogen peroxide bleaching process by using ultrasonic energy [9]. After bio cleaning of raw cotton with pectinase by using ultrasonic energy, tenacity, wettability and whiteness index of the raw cotton textile material are increased [10]. Combination of conventional and ultrasonic processes is decreased enzyme consumption, process time and fibre damage. Ultrasonic energy improves the effect of enzyme without decreasing the fabric strength in cotton’s enzymatic pre-processes [11]. It is indicated that chemical consumption, fibre damage and waste bath amount are decreased by using ECE detergent instead of reductive substance in reductive cleaning of disperse dyed PLA fibres [12]. Better washing fastness properties are obtained by using ultrasonic probe at the final washing of reactive dyes [13].

2. Experimental

2.1. Materials

Woven polyester fabric was supplied from Sahinler Holding (170 g/m^2). Fabric was cleaned at

60 °C for 15 minutes with 1 g/l Sandozin NIN (surfactant; Clariant) and 2 g/l 1 Na_2CO_3 at bath ratio of 1:20. Cleaned samples were dried at open atmosphere after rinsed well. In this study Dianix Black CCR (DyStar) was used as disperse dye without purification.

2.2. Dyeing

Polyester fabric was dyed with alkaline polyglicoleter structured non-ionic egalation substance Lyogen DFT (Clariant) at 5% colour strength in Polimat HT sample dyeing machine (Type A11612N-Emsey) which has 300 ml stainless steel tubes. Dyeing recipe and temperature-time diagrams are shown in Table 1 and Figures 1.

Table 1. Dyeing Recipe

Lyocol WPN :1 %
Albegal FFA : 0.5 g/l
Lyogen DFT : 0.5 %
Sodium Acetate : 3 %
pH : 5.5 (acetic acid)

Material Amount : 5 g
Bath Ratio : 1:20
Dyeing Time : 110 min
Disperse Dyes : %5 o.w.f.

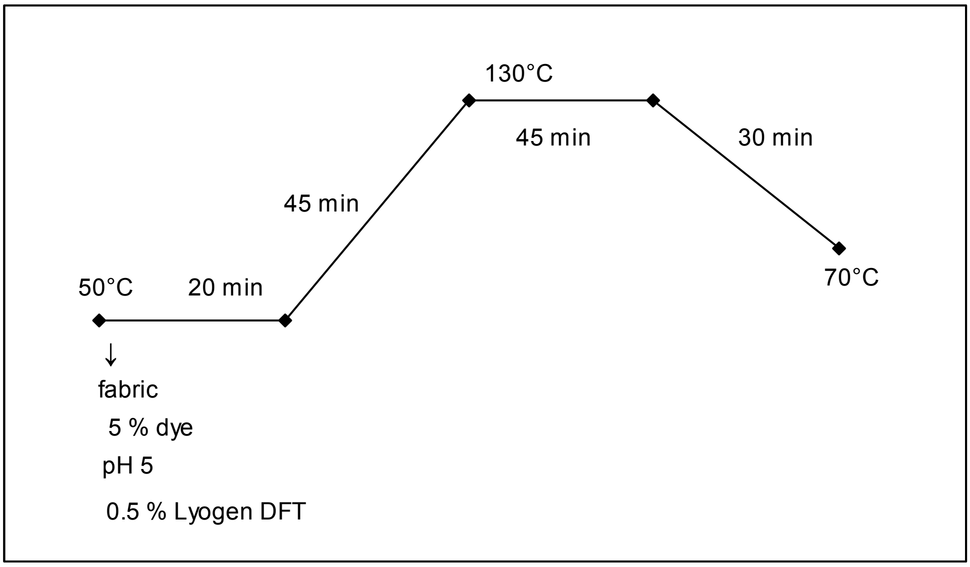


Figure 1. Temperature – Time Diagram

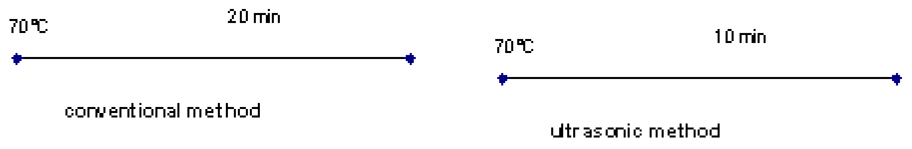


Figure 2. Temperature – Time Diagrams for Reductive Cleaning

2.3. Reductive Cleaning

Reductive cleaning conditions are given in Table 2.

Table 2. Conditions of Reductive Cleaning Process

Code	Conditions	Code	Conditions
	$Na_2S_2O_4$ - NaOH (38 ° Bé)		
1	2 g/L $Na_2S_2O_4$ -2 mL/L NaOH	3	2 g/L $Na_2S_2O_4$ - 4 mL/L NaOH
2	2 g/L $Na_2S_2O_4$ - 3 mL/L NaOH	4	2 g/L $Na_2S_2O_4$ - 5 mL/L NaOH
	Dextrse mono hydrate - NaOH (38 ° Bé)		
5	2 g/L DMH -2 mL/L NaOH	7	2 g/L DMH - 4 mL/L NaOH
6	2 g/L DMH - 3 mL/L NaOH	8	3 g/L DMH - 5 mL/L NaOH
	Cyclanon ARC		
9	1.5 g/L Cyclanon ARC	10	2.5 g/L Cyclanon ARC

2.3.1. Reductive Cleaning Process by Using Sodium Dithionite and Sodium Hydroxide

After dyeing process, fabric was rinsed with hot water and reductive cleaned by conventional method, bath ratio of 1:200, at 70° for 20 minutes. The reason of high bath ratio is to compare with ultrasonic process which needs high bath ratio for effective sonication. All reductive cleaned dyed fabrics were rinsed first in hot water then in running water, finally they were dried at room temperature. X brand ultrasonic bath was used as the sonication source for ultrasonic process and samples were reductive cleaned, at bath ratio of 1:200 at 70° C for 10 minutes. Properties of the ultrasonic bath were 220 volt and 205 watt, wave range 50-60 Hz, wave sensitivity 47Hz ± 6%. All methods were repeated 3 times.

2.3.2. Reductive Cleaning Process by Using Dextrose Mono Hydrate and Sodium Hydroxide

Samples were reductive cleaned by conventional process at bath ratio of 1:200 at 70°C for 20 minutes (Figure 2). Samples were reductive cleaned by ultrasonic process at bath ratio of 1:200 at 70°C for 10 minutes.

2.3.3. Reductive Cleaning Process by Using Cyclanon ARC

Samples were reductive cleaned by conventional process at bath ratio of 1:200 at 70°C for 20 minutes (Figure 2). Samples were reductive cleaned by ultrasonic process at bath ratio of 1:200 at 70°C for 10 minutes.

2.4. Colour Measurement

Colour values of dyed samples were measured by Datacolor Spectra Flash 600 plus reflectans spectrophotometer by using Datamaster software according to CMC 2:1 CIELab and CIELch

system. Colour measurements were performed by using 10° observer and D65 light source and conventionally reductive cleaned samples were accepted as standard.
Different tones of same colour are taken place on a line extending outward which is made up by a* and b* coordinates. The angle of rotation "h" which increases from red to yellow is a colour measure. For example h=0 ° corresponds to red colour tone, h=90° corresponds to yellow colour tone and h=270° corresponds to blue colour tone. A remote point from neutral point is expressed the chroma (C*) and this is the measure of the colour saturation at a defined L* value. Colour differences were calculated in CIELab units according to Formula 4, 5 and 6 [14].

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (4)$$

L*a*b* Cartesian coordinates can be converted to L*C*h* cylindrical coordinates by Formula 5 and 6.

$$C^* = [(a^*)^2 + (b^*)^2]^{1/2} \quad (5)$$

$$h = \arctan b^*/a^* \quad (6)$$

L^*_{numune} - $L^*_{standard}$ if it is positive sample is lighter than the standard, if it is negative sample is darker than the standard

.

C^*_{numune} - $C^*_{standard}$ if ΔC* is positive sample has higher chroma (saturation), if it is negative sample has lower chroma.

2.5. K/S Values

Colours of the dyed fabrics were evaluated by colour strengh (K/S) which is calculated by using Kubelka-Munk equality (Formula 7). % reflectance values of the samples were measured by Datacolor Spectra Flash 600 plus reflectans spectrophotometer by using Datamaster software according to CMC 2:1 CIELab and CIELch system. Colour measurements were performed by using 10° observer and D65 light source [14].

$$K/S = (1-R)^2/2R \quad (7)$$

R; reflectance value of the fibre at maximum absorption wavelength, K; absorption coefficient, S; scattering coefficient.

2.6. Fastness Determination

Washing fastness tests of the dyed fabrics were performed according to ISO 105-C06 standard[15] and Washing Fastness Test Machine (Gyrowash / James H. Heal Co. Ltd.) was used. Light fastness tests of the dyed fabrics were performed according to TS 1008 EN ISO 105 - B02[16] standard and Light Fastness Test Machine (James H. Heal) was used for the test.

3. Results

Reductive cleaned samples were accepted as standard for the colour measurement of dyed samples by Datacolor Spectra Flash 600 plus reflectance spectrophotometer. Results were given in Table 3.

Table 3. Values of Colour Measurement

Code	ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE*
			$Na_2S_2O_4$ - NaOH			
0 original	0.52	0.03	0.08	-0.07	0.05	0.47
1	-0.88	-0.01	0.41	-0.40	0.09	0.94
2	1.55	0.03	0.08	-0.08	0.04	1.45
3	-0.64	0.20	-0.15	0.18	0.18	0.65

4	-0.11	-0.12	-0.28	0.26	-0.17	0.44
			Dextrose mono hydrate - NaOH			
5	-0.20	0.01	0.04	-0.04	0.02	0,18
6	-0.29	0.08	0.10	-0.08	0.10	0,31
7	-0.66	0.17	0.14	-0.13	0.18	0,64
8	-0.38	0.01	0.20	-0.19	0.06	0,43
			Cyclanon ARC			
9	0.06	0.10	0.08	-0.03	0.12	0,18
10	0.11	-0.15	-0.17	0.08	-0.21	0,34

Colour differences of the conventionally reductive cleaned samples' colours and ultrasonic reductive cleaned sample's colours were acceptable when $Na_2S_2O_4$ and NaOH used in reductive cleaning ($\Delta E^* < 1$) (Figure 3). Saturation of the colour increased and the colour became darker and turned to red and blue by increasing the alkaline concentration (Table 3).

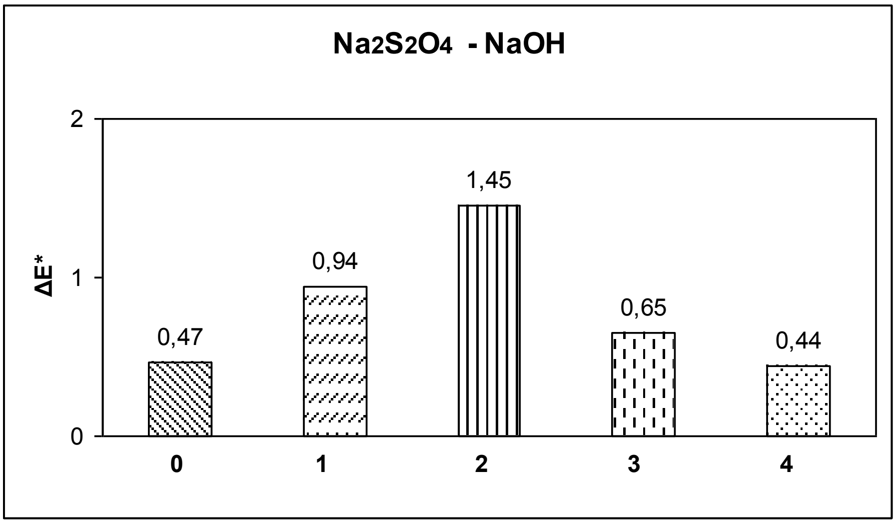


Figure 3. ΔE^* Values of $Na_2S_2O_4$ - NaOH Reductive Cleaned Dyed Samples

Total colour differences (ΔE^*) of the ultrasonic reductive cleaned samples were acceptable when dextrose mono hydrate and NaOH were used(Figure 4). But colours obtained from ultrasonic reductive cleaned samples were darker than standard sample. Colours of all samples were red and yellow tone according to the standard. But chroma (saturation) values of the samples were low and colour became dull (Table 3).

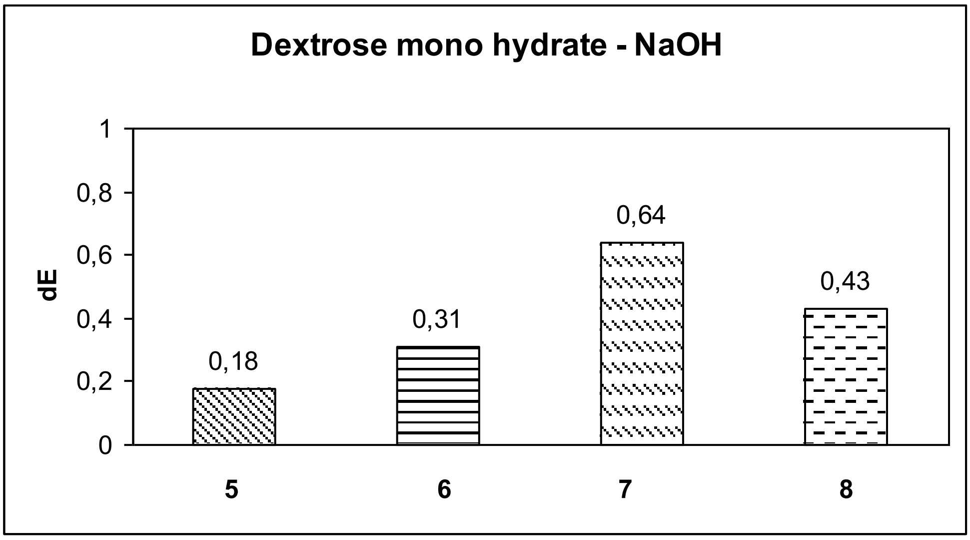


Figure 4. ΔE* Values of Dextrose mono hydrate - NaOH Reductive Cleaned Dyed Samples

Total colour differences (ΔE*) of the ultrasonic reductive cleaned samples were acceptable when commercial product Cyclanon ARC were used (Figure 5) and colour were lighter. Colour tone turned from red to green and yellow to blue. Colour saturation improved by increasing of concentration (Table 3).

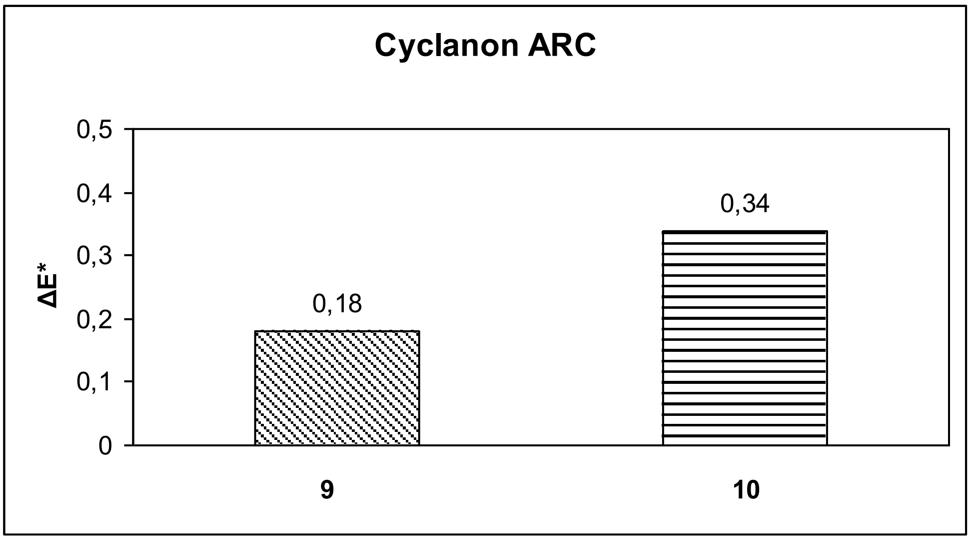


Figure 5. ΔE* Values of Cyclanon ARC Reductive Cleaned Dyed Samples

K/S values of reductive cleaned samples with sodium dithionite and sodium hydroxide at maximum absorption (520nm) were given in Figure 6. Higher K/S values were obtained with the increasing of sodium hydroxide concentration for ultrasonic reductive cleaned samples.

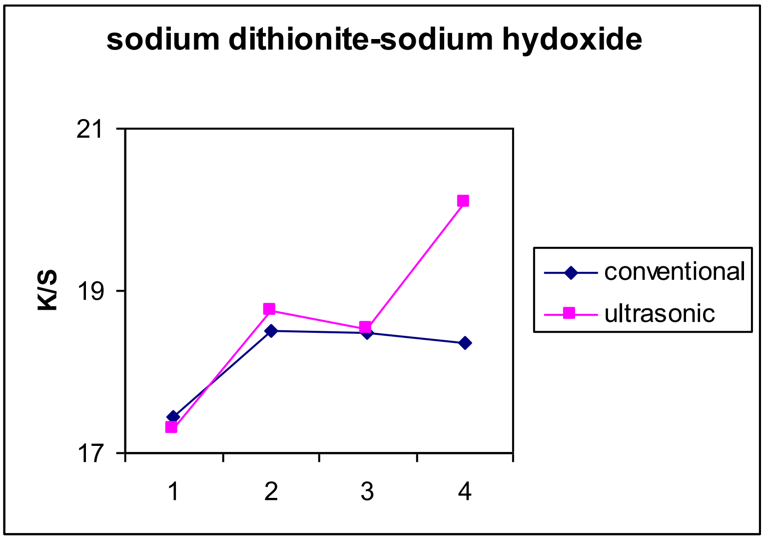


Figure 6. K/S Values of $Na_2S_2O_4$ - NaOH Reductive Cleaned Dyed Samples

K/S values of ultrasonic reductive cleaned samples with dextrose mono hydrate and sodium hydroxide were higher, and results were given in Figure 7.

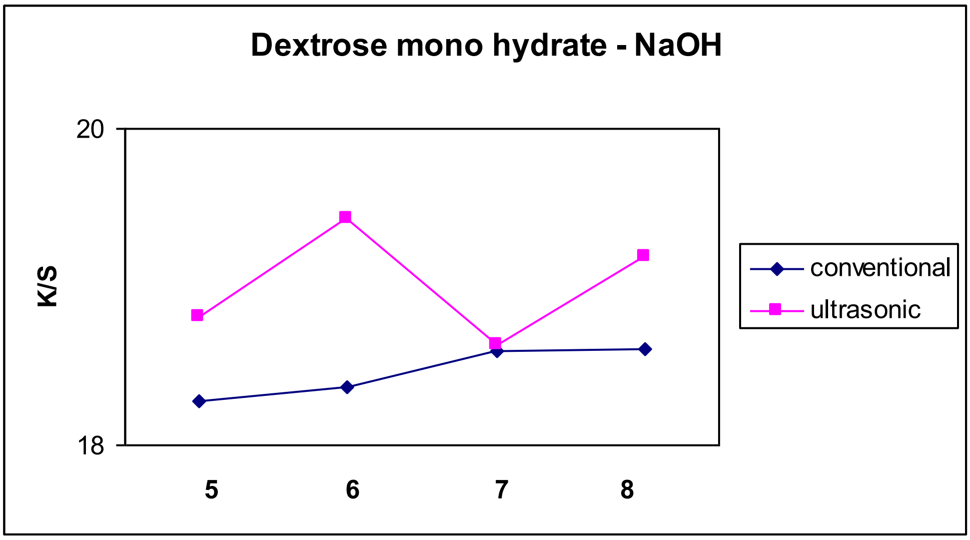


Figure 7. K/S Values of Dextrose mono Hydrate - NaOH Reductive Cleaned Dyed Samples

Higher K/S values were obtained by using Cyclanon ARC for conventional reductive cleaning of dyed samples and results were given in Figure 8.

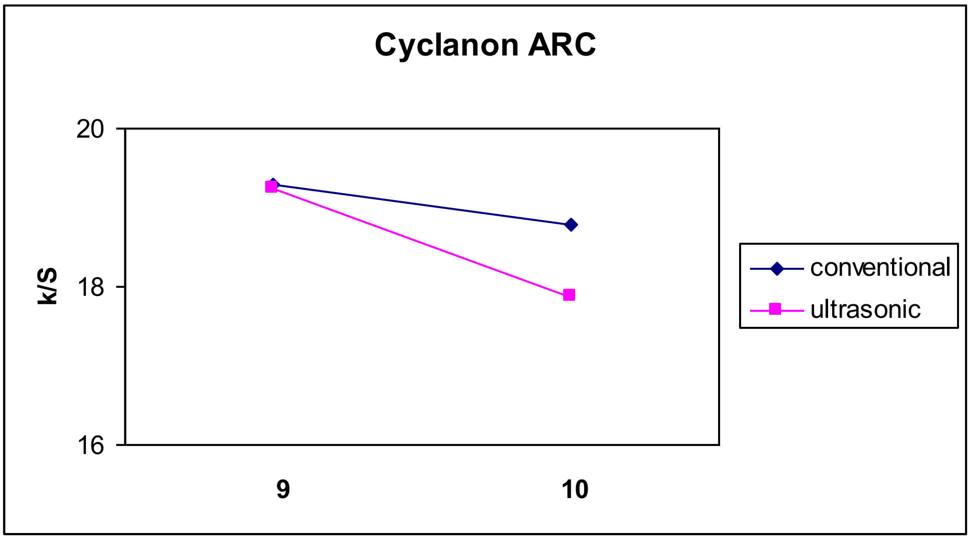


Figure 8. K/S Values of Cyclanon ARC Reductive Cleaned Dyed Samples

Disperse dyed polyester materials were reductive cleaned with environmentally friendly dextrose mono hydrate and Cyclanon ARC. Any decreasing wasn't observed at fade washing fastness values of reductive cleaned samples with dextrose mono hydrate and Cyclanon ARC when compared to conventional reductive cleaning substances (sodium dithionite and sodium hydroxide) (Table 4).

Slightly decrease was observed only on nylon part of multi fiber material after stain washing fastness test of reductive cleaned samples with sodium dithionite and sodium hydroxide (Table 4).

No stain was observed on any part of multi-fibre material after washing fastness test of reductive cleaned samples with dextrose mono hydrate and NaOH (Table 4). Decreases were observed on acetate, nylon and polyester parts of multi-fibre materials after washing fastness test of reductive cleaned samples with Cyclanon ARC which is blend of reductive-alkaline-dispersant substances. Washing fastness values on nylon and polyester parts were improved by using ultrasonic method.

(Table 4). Ultrasonic method and reductive cleaning substances have not affected the light fastness properties of the dyed samples negatively.

Table 4. Washing and Light Fastness Properties of the Reductive Cleaned Samples

	Washing Fastness (ISO 105 C06)														**Light**	
	Fade		Stain													
Experiment			***CA***		***Co***		**PA**		***PES***		***PAN***		***Wo***			
	k	*u*	*k*	*u*	*k*	*u*	*k*	*u*	*k*	*u*	*k*	*u*	*k*	*u*	*k*	*u*
$Na_2S_2O_4$ ve NaOH																
Original	5	5	4/5	5	5	5	4/5	5	4/5	5	5	5	5	5	5/6	5/6
1	5	5	5	5	5	5	4/5	5	5	5	5	5	5	5	5/6	5/6
2	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5/6	5/6
3	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5/6	5/6
4	5	5	5	5	5	5	4/5	5	4/5	5	5	5	5	5	5/6	5/6
Dextrose mono hydrate ve NaOH																
5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5/6	5/6
6	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5/6	5/6
7	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5/6	5/6
8	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5/6	5/6
Cyclanon ARC																
9	5	5	4/5	5	5	5	4/5	5	4/5	5	5	5	5	5	5/6	5/6
10	5	5	4/5	4/5	5	5	4/5	5	4/5	5	5	5	5	5	5/6	5/6

4. Conclusion

- By using environmentally friendly reductive cleaning substances instead of sodium dithionite which is widely used by the textile plants, it will be possible to decrease the environmental harmful substances in the waste water.
- Total colour differences of ultrasonic reductive cleaned samples in different concentrations were acceptable also washing and light fastness properties were not affected negatively so ultrasonic process can be applied by the industrial plants because of its short process time and low energy requirement.
- High K/S values were obtained at maximum absorption (520nm) with the increasing of sodium hydroxide concentration for the ultrasonic reductive cleaned samples. K/S values of ultrasonic reductive cleaned samples with dextrose mono hydrate and sodium hydroxide were higher. Higher K/S values were obtained with Cyclanon ARC by using conventional method.

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THE INVESTIGATION OF THE SOUND ABSORPTION PROPERTIES OF RICE HUSK/POLYURETHANE COMPOSITE MATERIALS

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Keywords: Sound absorption, waste rice/polyurethane composites, surface modifications

Abstract. *As known the sound absorption properties of natural materials are vitally important. The sound absorption properties of materials improve with the increasing the ratio of porosity. The surface modification of the waste rice was carried out by using sodium hydroxide via conventional method. Finally the sound absorption properties of the rice husk/polyurethane composite with low and high sound frequency were investigated.*

Introduction

Modern city life presents living condition for limited areas on daily and private lives to habitant. One of the most important disadvantages of coexistence is also sound pollution. Research on this issue has improved development of acoustic insolation on living area.

The sound absorption materials are classified as passive and active according to their nature. The active sound absorption materials need external energy to absorb sound, whereas passive sound absorption materials generally consist of porous material [1, 2]. The frictions occur due to the irregular located pores in the porous materials, after the friction heat in evaluated material is released. Elastic porous materials absorb the sound energy which is converted to heat energy at low frequency. Porous sound absorbing materials are used in order to control the acoustic of the building room, car interior, recording studio and industrial noise[3,4]. One of the most important problems faced by noise control engineers is how to design efficient sound absorbers and do~~es~~ not introduce any environmental hazards [5]. Many scholars investigated the using of lignocellulosic materials in the application of sound absorbing. The primary advantages of using resin reinforced lignocellulosic materials are high stiffness and tensile strength, easily recyclability, biodegradability, abundance in the entire world, and low cost [6].

Sound absorption properties of tea leaf fibers [7], jute fibers, rice straw and wood particles [8,9], corncob [10], flax, hemp, beech tree, pine, rape seed [11], corn stalk [12], kenaf and cotton [13] were investigated owing to these properties.

In this study, the sound absorption properties of polyurethane/ rice husk were undertaken. Firstly, the surface modification of the rice husk with sodium hydroxide via conventional and microwave methods were performed. Then the rice husk and polyurethane were mixed. The sound absorption properties of composite which consists of polyurethane/ rice husk were measured by using impedance tube.

2. EXPERIMENTAL

2.1. Materials

In this investigation, polyol, isocyanate, rice husk were used to obtain polyurethane / rice husk composite.

2.2. Surface Modification

Rice husks have been exposed to surface modification with sodium hydroxide by conventional method. The properties of surface modification are given in Table 1.

Table 1. The Properties of Surface Modification

Sample	**Method**	**Time, min**	**Temperature, °C**	**Surface Modification Agent**
1	Conventional	10	98	Sodium Hydroxide
2	Conventional	20	98	Sodium Hydroxide
3	Conventional	30	98	Sodium Hydroxide

2.3. Preparation of Polyurethane/Rice Husk Composite

In order to obtain polyurethane/ rice husk composite, firstly polyol and isocyanate were mixed according to weight ratio of 1:1. After rice husk added to the mixture, this composite was cured for one day at room temperature.

2.4. Measurement of the Sound Absorption Coefficient

The sound absorption coefficient of the prepared composite materials was measured in accordance with ISO 10534-2 standard by using as measuring device a Brüel & Kjear Impedance Tube based on two microphone transfer function method (Figure1).

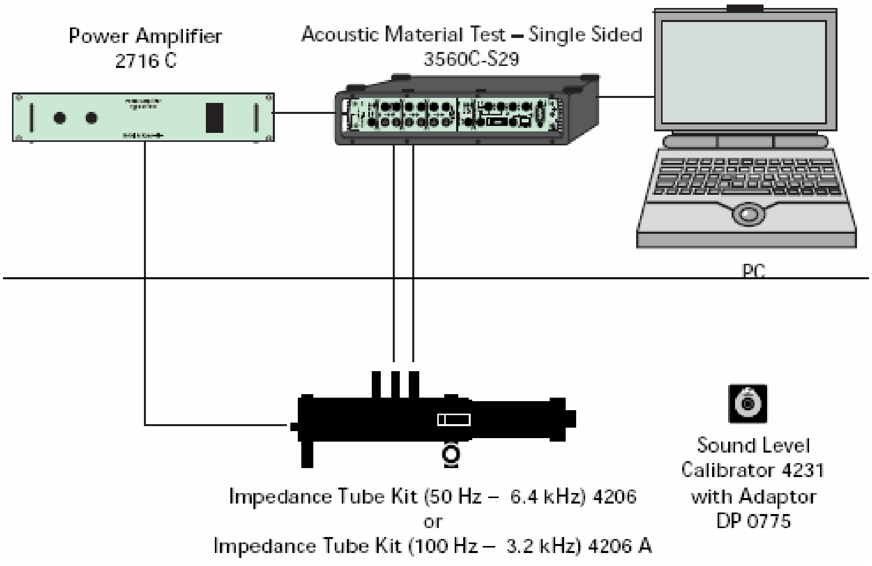

Figure 1. Impedance Tube Measuring Device

3. Results and Discussion

The sound absorption properties of the prepared composites shown in Figure 2, were measured on the 100-6300 Hz frequency range.

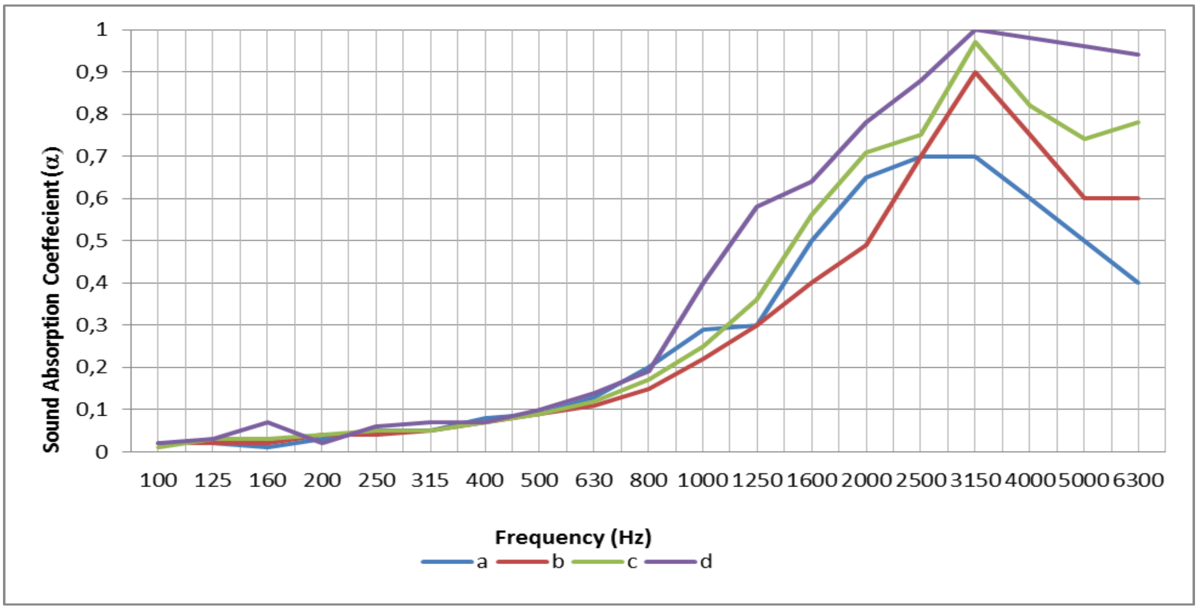

Figure 2. Rice husk / polyurethane composite sound absorption coefficient

(a. untreated rice husk/ polyurethane composite; b, c and d rice husk / polyurethane composite treated with sodium hydroxide for 10, 20 and 30 mins, respectively).

The sound absorption coefficients of the samples were between 0-0.1 at 100-630 Hz frequency. However, in the frequency range 800-3150 Hz, the absorption coefficient varies with time composite material surface modification. The sound absorption coefficient of the composites was 0.36 at 20 min whereas 0.58 at 30 min at 1250 Hz frequency. This means, the sound absorption coefficient was maximum at 3150 Hz frequency for all the samples, varying between 0.9-1 for the composites. At this maximum sound absorption coefficient, the difference between the untreated and 30 min treated samples was about 42.5%. The sound absorption coefficients of the composites were 0.4, 0.6, 0.78 when they are subjected to 10, 20 and 30 minutes sodium hydroxide treatment, and, 0.94 when the sample was treated with sodium hydroxide for 30 mins.

4. Conclusions

It can be clearly seen that the sound absorption was increased by use of rice husk/polyurethane composite. This increase can be explained by the effect of sodium hydroxide causing porosity on the surface of the sample.

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SUSTAINABLE DYEING PROCESS WITH AGRICULTURAL WASTES FOR TEXTILE PRODUCTS

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Keywords: Natural Dye, Olive mill waste water, mordant, sustainable dyeing, wool.

Abstract. *Olive mill waste water (OMW) appears as a waste product after the production of olive oil, and it was reported that the amount of released OMW is about 30 million tons for the Mediterranean countries annually [1]. The present study deals with the extraction of natural dye from this agricultural waste by using aqueous extraction method, and dyeing of wool fibres. Five different time intervals were used to determine the best extraction and dyeing time during the processes.* $CaCO_3$, *NaAlg, citric acid, tannic acid,* $AlCl_3$, $NaHCO_3$ *were used as mordant in the dyeing procedure. Studies of the wash, staining and rubbing fastness, and colour tone were practiced. At the end of the study, it was obtained brown and yellow colour tones on the wool fibres from dark to light shades. According to colour fastness results, dyed samples provide suitable fastness values to wash, staining and rubbing. Therefore, it is possible to say that olive mill waste-water can be used for carpet yarn dyeing.*

1. INTRODUCTION

Olive oil industries have gained fundamental economic importance in many Mediterranean countries. During olive oil extraction, the manufactures produce two effluents and they are residual solids (husk) and large quantities of liquid effluents which are called olive oil wastewaters. For the second effluent, it is estimated that around 30 million m^3 of OMW which are generated annually in the Mediterranean area during the seasonal extraction of olive oil. [2]

On the other hand, an interest in the use of natural dyes has been growing rapidly due to the result of stringent environmental standards imposed by many countries in response to toxic and allergic reactions associated with synthetic dyes [3]. Hence, natural dyeing of textile products is becoming more and more important for the sector. But, the high cost of natural dyes, their low-fastness properties and their narrow colour ranges have limited their usage in the textile sector. This situation has led researchers to find new sources of natural colouring agents which are cheaper than known sources of natural dyes. The beverage and food industry releases enormous-significant amounts of wastes which contain natural dyes and the wastes could used as a source for the extraction of natural dyes for textile dyeing processes [4-5].

Olive mill waste water contains a valuable potential of abundant natural colouring substances which are renewable, available with large quantities and free costs. Some study showed that this natural dye can be easily applied in the dyeing of textile materials [1].

The present study focused on the dyeing performance of the dye solution extracted from olive mill waste water for wool fibres. Water was used as the solvent in the extraction. Optimum extraction time, optimum dyeing time and the optimum amounts of mordants were investigated. At the same time, the fastness properties of the dyed samples were investigated. The colours were measured by means of the CIELab coordinates in all cases and fastness properties were also determined.

2. EXPERIMENTAL

2.1. Materials and chemicals used in The Dyeing Processes

Scoured wool yarn was used as a textile surface. $CaCO_3$ (Fluka, Germany), NaAlg(Fluka, Germany), citric acid (Fluka, Germany), tannic acid(Fluka, Germany), $AlCl_3$(Fluka, Germany), $NaHCO_3$(Fluka, Germany) were used as mordants. They were laboratory reagents grade and were used without further purification.

2.2. Preparation of Dyeing Bath From OWM

2g of olive mill waste-water was extracted with 20 ml water and then extract was filtrated and used as a dye bath. The liquor ratio was used as 1 to 10 because most of industrial dyeing machines work at this ratio. According to the employed method, extracted waste was boiled between 30 and 120 minutes with an interval of 15 minutes. The six aqueous solutions were obtained and they were used as dyeing baths for the coloration of woollen fabrics.

2.3. Determining optimum extraction time

As described in the section above, six dye bathes were prepared. Wool yarn was added to the dye bathes by using 1 to 1 waste water-wool ratio and boiled with the extracts for one hour. Afterward, the sample which was dyed was washed with olive oil soap and then rinsed. CIE lab values of the yarn were measured by Macbeth Color-Eye 7000 spectrophotometer and L*, a*, b* values were obtained. Deeper or in another words, lower L value was accepted as the optimum extraction time.

2.4. Determining optimum dyeing time

In this step, it was also followed similar way and the extract obtained in the first step was used. 2 g wool yarn was boiled with dye bath between 30 and 120 minutes with an interval of 15 minutes. After each dyeing, wool yarn was washed with olive oil soap and rinsed two times with cold water. CIE lab values of the yarn were measured with Macbeth Color-Eye 7000 spectrophotometer. Deeper or in another words, lower L value was accepted as the optimum dyeing time.

2.3. Mordants and optimum mordant amount

Mordants used in the experiments were directly added to the dye bath and stirred 5 minutes to dissolve. 2 grams of wool yarn was boiled with dye extract during the optimum dyeing time. Shade differences were analyzed with CIE lab values according to amount of mordant. Likewise, the lowest L values gave us the darkest colour tone. Hence the lowest values of L indicated the amount of optimum mordant.

2.4. Fastness properties of dyed samples

2.4.1. Washing fastness

Washing fastness of the dyed samples was performed in accordance with EN ISO 105-C01. After drying, the change in colour of the sample (wet-fastness colour) and the staining degree to white fabric (wool, wet-fastness bleeding) were evaluated by using the Grey Scale for Assessing Change in Colour (EN ISO 105-A02) and the Grey Scale for Assessing Staining (EN ISO 105-A03) (notes: 1–5; 1: a large visual change, worst rating, 5: no visual change, best rating).

2.4.2. Rubbing fastness

Dry and wet rubbing colour fastness of dyed samples was performed by using Crockmaster according to EN ISO 105 – X 12 standard method. The staining of the cotton rubbing cloths evaluated with the grey scale (ISO 105-A01:1994) for staining under suitable illumination.

3. RESULTS AND DISCUSSION

Optimum extraction time is clearly seen from the Figure 1. L^* axis values give us the darkness or brightness degree of the colour. When L^* values is 100, it means that the colour of the sample is white. On the other hand, L^* value is 0, it means that the colour of the sample is black. a^* and b^* axes in the graph have no numerical limits. Positive a^* means that colour tone goes to red while negative a^* means that colour goes to green side. Positive b^* means that colour goes to yellowish side while negative b^* means that colour goes to blue side.

According to Figure 1, L^* value has a minimum point at 45 minutes. So this point indicates the darkest colour tone on the dyed samples and hence optimum extraction time is 45 minutes. On the other hand, after the boiling process more than 45 minutes, the colour tone is fading. This result can be interpreted as some pigments decomposed with the effect of time and temperature.

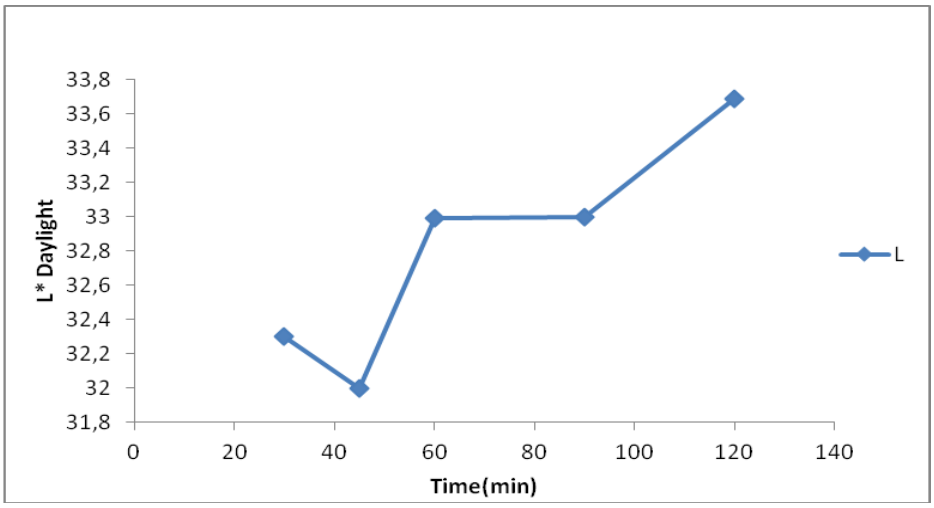

Figure 1. Optimum extraction time for the dye extract from olive mill waste-water

Optimum dyeing time is clearly seen from Figure 2. According to graph, L* value reaches the lowest degree at 60 minutes. This point indicates the deeper colour tone of the wool yarn dyed with the dye extract from olive mill waste-water.

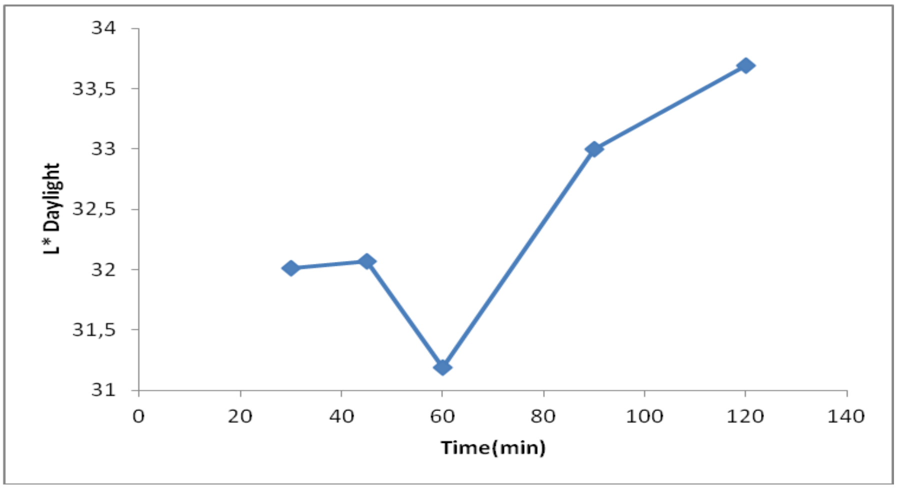

Figure 2. Optimum dyeing time for the dye extract from olive mill waste-water

For determining optimum mordant amount, several dyeing experiments were performed with different amount of mordants. In the following tables (Table 1-7), the CIE lab values of the dyed samples were showed for different amounts of $CaCO_3$, NaAlg, citric acid, tannic acid, $AlCl_3$, $NaHCO_3$ mordants. When the results are analysed, it is observed that there was not any change in the colour tone on the dyed samples by the increasing amount of the mordant. The lowest L* value measured for each mordant gives the optimum amount of mordant. Optimum values for each mordant were determined as, 1 g/L tannic acid, 1 g/L $CaCO_3$, 2 g/L NaAlg, 2 g/L $AlCl_3$, 4 g/L $NaCO_3$, 3 g/L $MnCl_2$ and 4 g/L citric acid. Over the optimum mordant amount, there is not any significant changes in L* values. Therefore, it is meaningless to increase the mordant amount beyond the optimum value.

the amount of the mordant (tannic acid) (g/lt)	L*	a*	b*
1	**33,82**	8,67	17,62
2	34,68	7,91	16,87
3	34,51	8,18	17,46
4	37,54	8,68	17,63
5	33,90	8,51	17,23

Table 1. Color difference with different amounts of tannic acid mordant

the amount of the mordant(CaCO3) (g/lt)	L*	a*	b*
1	33,45	7,91	16,55
2	**32,75**	9,75	19,21
3	33,94	9,49	19,44
4	33,67	9,8	18,98
5	32,83	10,00	19,47

Table 2. Color difference with different amounts of $CaCO_3$mordant

the amount of the mordant(citric acid)(g/lt)	L*	a*	b*
1	38,21	9,68	17,98
2	37,27	8,82	17,40
3	36,19	10,49	20,75
4	**35,32**	10,21	20,43
5	35,86	10,28	22,10

Table 3. Color difference with different amounts of citric acid mordant

the amount of the mordant(NaAlg)(g/lt)	L*	a*	b*
1	41,37	10,25	19,81
2	**36,34**	9,25	19,57
3	39,98	9,23	19,67
4	37,99	8,84	18,75
5	37,99	8,37	18,82

Table 4. Color difference with different amounts of NaAlg mordant

the amount of the mordant($AlCl_3$)(g/lt)	L*	a*	b*
1	37,10	7,80	18,56
2	**32,55**	9,35	18,21
3	39,04	7,14	19,22
4	37,82	7,47	17,01
5	41,67	7,37	19,57

Table 5. Color difference with different amounts of $AlCl_3$ mordant

the amount of the mordant($NaCO_3$)(g/lt)	L*	a*	b*
1	39,26	7,21	16,71
2	39,48	7,50	16,48
3	42,30	7,41	16,45
4	**37,58**	5,81	16,48
5	44,01	8,02	16,74

Table 6. Color difference with different amounts of $NaCO_3$ mordant

the amount of the mordant(MnCl2)(g/lt)	L*	a*	b*
1	33,98	7,36	17,72
2	33,85	7,73	16,96
3	**33,28**	7,26	16,44
4	33,77	7,64	17,22
5	33,74	8,08	18,67

Table 7. Color difference with different amounts of $MnCl_2$ mordant

Mordant	Fading	Staining					
		Wool	Acrylic	Pes	PA 6.6	Cotton	Acetate
Tannic Acid	4	4/5	5	5	5	5	5
Acetic Acid	4	4/5	5	5	5	5	5
$CaCO_3$	4/5	4/5	5	5	5	5	5
NaAlg	4/5	4/5	5	5	5	5	5
$AlCl_3$	5	5	5	5	5	5	5
$NaCO_3$	5	5	5	5	5	5	5
$MnCl_2$	4/5	4/5	5	5	5	5	5

Table 8. Test results of colorfastness for washing test

Mordant	Rubbing Fastness		
	Dry	Wet	Fading
Tannic Acid	5	5	5
Citric Acid	4	3/4	4/5
$CaCO_3$	4/5	3/4	4/5
NaAlg	5	4/5	5
$AlCl_3$	5	5	5
$NaCO_3$	5	5	5
$MnCl_2$	5	5	5

Table 9. Test results of color fastness for rubbing test

It is clearly seen from the tables, the dye extract from olive mill waste-water gives higher washing fastness values.

3.1. The colour tones obtained from olive mill waste-water

Tannic acid

Citric acid

$CaCO_3$

NaAlg

$AlCl_2$

$MnCl_3$

$NaCO_3$

4. CONCLUSIONS

At the end of the study, optimum extraction time for the dye extract from olive mill waste-water was determined as 45 minutes and the optimum dyeing time was found as 60 minutes. When the wool yarns were dyed with the dye extract from olive mill waste-water, brown-green colour tones were obtained. According to colour fastness results, dyed samples provide very well fastness values to wash, staining and rubbing. Therefore, it is possible to say that the dye extract from olive mill waste-water can be used for carpet yarn dyeing.

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INNOVATIVE SOLUTIONS FOR MEDICAL TEXTILE VIRTUAL MODELING BASED ON GRID NETWORK

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Abstract. *In this paper is presented a new aspect of modeling the biofluid parameters. The parameters involved are characterizing phase bio-fluid flow into and through the three-dimensional structure type invasive medical devices obtained by mechanic-textile processing technologies. The goal presented in this paper is Linux console application type software for the calculation of the biofluid flow velocity value. To achieve this goal it was necessary to use computing power calculation gives by Grid Network usage and implicit the usage of the FORTRAN algorithms programming language. Also was realized a transition complex - real space obtained by approximating several parameters.*

1 INTRODUCTION

Most programs are written by using the algorithmic programming language FORTRAN because in this way can be solved the complex mathematical expression. The programs are containing a main program and some external subroutines and functions that can be called from main program. Also in the main program may be the list of instructions to execute by the computer. The program is based on an algorithm [1], by the organization, and can use also some external data in main program. It can consider that the program is a package of data and algorithm.

Based on complex mathematical models, previously performed, which highlights the flow parameters in terms of the movement bio-fluid - solid coupling for Y textile structures [2], subroutines were developed to calculate the flow velocity for bio-fluid, by using the programming language FORTRAN [1] and power of the GRID Network.

As in the areas of bio-fluid flow artery bifurcation becomes difficult to determine the numerical simulation is required that flow rates using appropriate calculation routines.

To achieve this goal were the following steps:

- obtaining the mathematical model for velocity;
- writing the velocity.f program, by designing the adequate routines in FORTRAN programming language, using network GRID infrastructure for the benefit of speed and massive computing power in the execution of arithmetic complex;
- writing job and the wrapper for the program velocity.f;
- receiving results through program run velocity.f.

2 MATHEMATICAL MODELING

Starting from complex mathematical modeling and using known parameters for biofluid flow in conditions of coupling motion biofluid - solid textile structure Y, it was developed subroutines for calculating the flow velocity of the biofluid, by using algorithmic programming Fortran language and the advantages of distributed computing and parallel computing gives by Grid Network System.

For modeling the biofluid flow on the tridimensional structures was required the study of the biofluid on the structures that are axial symmetrical elastic (elastic tube model) [3].

- For the elastic tube model it is attached the equation 1 :

$$u'_r = \frac{A}{r} e^{i\alpha(z-c't)};\ u_z = Be^{i\alpha(z-c''t)} \tag{1}$$

$$A = \frac{s(\lambda+\mu)}{\mu}; B = \frac{s(\lambda+\mu)}{\lambda+2\mu}; \qquad c' = \sqrt{\frac{\mu}{\rho}}\ ;\ c'' = \sqrt{\frac{\lambda+2\mu}{\rho}}$$

Where:

u$_r$, u$_z$ –Movement vector components;

R- Undeformed tube radius;

t – Time period.

- Interface conditions (2):

$$V_r = \frac{\partial u_r}{\partial t}\ \ for\ \ r = R + u_r(R,z,t)\ \ ,V_z = \frac{\partial u_z}{\partial t}\ \ for\ \ r = R + u_r(R,z,t) \tag{2}$$

$$-p + 2\nu\rho'\frac{\partial V_r}{\partial r} = \sigma_{rr} \quad for\ \ r = R + u_r(R,z,t)$$

Where:

$$\sigma_{rr} = \lambda\theta + 2\mu\frac{\partial u_r}{\partial r} = \left(\lambda Bi\alpha e^{-ic''t\alpha} - \frac{\partial\mu A}{r^z}e^{-i\alpha c't}\right)e^{i\alpha z}$$

$$\theta = \frac{\partial u_r}{\partial r} + \frac{u_r}{r} + \frac{\partial u_z}{\partial z}$$

$$\lambda\theta + 2\mu\frac{\partial u_r}{\partial r} = \lambda\frac{\partial u_r}{\partial r} + \frac{u_r}{r} + \frac{\partial u_z}{\partial z} + 2\mu\frac{\partial u_r}{\partial r} =$$

$$\frac{\partial u_r}{\partial r} = \frac{\partial}{\partial r}\left[\frac{A}{r}e^{i\alpha(z-c't)}\right] = -\frac{A}{r^z}e^{i\alpha(z-c't)}$$

$$\frac{u_r}{r} = \frac{1}{2}\cdot\left[\frac{A}{r}e^{i\alpha(z-c't)}\right] = \frac{A}{r^z}e^{i\alpha(z-c't)} \Rightarrow \lambda\frac{\partial u_r}{\partial r} + \lambda\frac{u_r}{r} = \lambda\left(\frac{\partial u_r}{\partial r} + \frac{u_r}{r}\right) = 0$$

$$\frac{\partial u_z}{\partial z} = \frac{\partial}{\partial z}\left[Be^{i\alpha(z-c''t)}\right] = Bi\lambda e^{i\alpha(z-c''t)}$$

$$2\mu\frac{\partial u_r}{\partial r} = 2\mu\frac{\partial}{\partial r}\left(\frac{A}{r^z}e^{i\alpha(z-c't)}\right) = -2\mu\frac{A}{r^z}e^{i\alpha(z-c't)}$$

$$p = \frac{p}{\rho'};\ \rho' - fluid\_density$$

- Initial conditions (3):

$V_r = V_r(r,z,0_+) = f_1(r,t), V_z = V_z(r,z,0_+) = f_2(r,t)$, particular it can be $f_1 = f_2 = 0$ (3)

- After Laplace transformation (4)

$$u(r,z,p)=\int_0^{\alpha} V_r(r,z,p)e^{-pt}dt, \quad si \ (r,z,p)=\int_0^{\alpha} V_z(r,z,p)e^{-pt}dt, \tag{4}$$

$$\pi(r,z,p)=\int_0^{\alpha} e^{-pt}dt$$

$$u=u(r,z,p)=h_1(r,z,p)=-\frac{i\alpha c'}{i\alpha c'+p}\cdot\frac{A}{r}e^{i\alpha z}=-\frac{i\alpha c'}{i\alpha c'+p}\cdot\frac{A}{r}e^{i\alpha z}$$

$$\omega(r,z,t)=-\frac{i\alpha c''}{i\alpha c''+p}\cdot Be^{i\alpha z}, \qquad -\pi+\nu\frac{\partial u}{\partial r}=T_1(r,z,p)$$

For calculating the expression for $T_1(r,z,p)$ it was starting from equation (5) and it was obtained the expression (6) for T_1:

$$-p+2\nu\rho'\frac{\partial V_r}{\partial r}=\sigma_{rr} \tag{5}$$

Where:

- p is the fluid pressure (blood);
- ν is the coefficient of the cinematic pressure;
- ρ Blood density.

$$T_1(r,z,t)=\int_0^{\alpha}\sigma_{rr}e^{-pt}dt=\frac{1}{\rho'}\int_0^{\alpha}\left(\lambda Bi\alpha e^{-i\alpha c''t}-\frac{2\mu A}{r^2}e^{-i\alpha c''t}\right)e^{i\alpha z-pt}dt=$$

$$=\frac{1}{\rho'}\int_0^{\alpha}\lambda Bi\alpha e^{-i\alpha c''t}\cdot e^{i\alpha z-pt}dt-\frac{2\mu A}{\rho' r^2}\int_0^{\alpha}e^{i\alpha z-i\alpha c't-pt}dt, \tag{6}$$

where :

ρ', λ, μ are material constants;

A, B -constants;

c’, c” propagation speed of the fluid (in the longitudinal direction and transverse).

The known values for c’ and c” are (7):

$$c'=\sqrt{\frac{\mu}{\rho}};\ c''=\sqrt{\frac{\lambda+2\mu}{\rho}} \tag{7}$$

After the application of the transformation Laplace the initial conditions become (8):

$$\omega(r,z,t)=\int_0^{\alpha}V_z(r,z,p)e^{-pt}dt\Rightarrow\omega(r,z,t)\big|_{z=0}=\omega(r,z,t)=$$

$$=a\int_0^{\alpha}(1-\cos\beta t)\left[\left(R+\frac{A}{R}e^{-i\alpha c't}\right)^2-r^2\right]e^{-ptdt}, \tag{8}$$

Where a, A, β are constants and a, β are experimental coefficients.

For forwarding the algorithmic steps it was necessary to known the functions expressions $f(z)si\,g(z)$ (9)

$$f(z)=sRJ_1'(Rs)u(R,z,p)-RJ_1(Rs)\frac{\partial u}{\partial r}\bigg|_{r=R}+\frac{1}{\nu}RJ_1(Rs)\pi(R,z,p)+\frac{1}{\nu}\int_0^R r\left[-\frac{g_1}{p}-f_1(r,t)\right]J_1(r,t)dr \tag{9}$$

Where:

- s is the $J_0(R,s)=0$ equation solution, where R is the undeformed tube radius and J_0 is Bessel function of the order 0 ;
- $J_1'(Rs)$ are derivates of the order 1 for Bessel function of the order 1;
- $u(R,z,p)$ is radial velocity on the contour, that is zero equal on this case;
- $\left.\frac{\partial u}{\partial r}\right| r=R$ is the derivate value in radial direction of the fluid velocity
- p is the variable result from Laplace transformation application;
- g_1 is weight component on radial direction
- $f_1(r, z)$ is distribution of velocity component at initial moment (from experimental dates). For preliminary calculation this can be zero equal;
- $\pi(R,z,p)$ is the value of Laplace transformation for blood pressure on the undeformed area of the tubular zone (from experimental dates).

For obtains the solution were calculated the values for $c_2(s, p)$, and $c_4(s, p)$ (10).

$$c_2(s,p)=\frac{sH(s,p)}{s-\omega} \text{ and } c_4(s,p)=\frac{sH(s,p)}{s-\omega}, \text{ where: } \omega=\sqrt{s^2+p_r} \tag{10}$$

Where:

- s is parameter resulted from Laplace transformation;
- p is the variable from Laplace transformation;
- v is the blood cinematic viscosity .

$H(s,p)=\frac{4Ra\beta^2}{ps^2(p^2+\beta^2)}J_1(Rs)$, where: a,β experimental coefficients;

s is a parameter resulted from Laplace transformation;
R is undeformed tube radius;
J_1 are Bessel functions of order I.
s_j a,j'' is root for equation $J_0(Rs)=0$

The obtained solution is (11):

$$v_z(r,z,t)=\frac{1}{\pi i R^2}\sum_j \frac{J_0(rs_j)}{[J_1(Rs_j)]^2}\int_{\gamma-i\infty}^{\gamma+i\infty}\left[C_1(s_j,p)e^{-\omega z}+C_2(s_j,p)e^{-s_j z}+T(s_j,z,p)\right]e^{pt}dp, \tag{11}$$

Where:

$$C_2=-\left\{\frac{\frac{2v\alpha c'' B\omega s}{i\alpha c''+p}-(2vs^2+p)\left[\frac{c'' Bs}{i\alpha c''+p}-\frac{\alpha\beta^2}{vsp(p^2+\beta^2)}\right]}{\Delta}\right\}RsJ_1(Rs), \tag{12}$$

With notation: $\Delta=4v\omega s^3-\frac{1}{v}\left(2vs^2+p^2\right)$

3 VELOCITY MODEL PROGRAMMING

In FORTRAN it was created a main program that calls some subroutines and an external function [4] for integral calculation (figure 1):

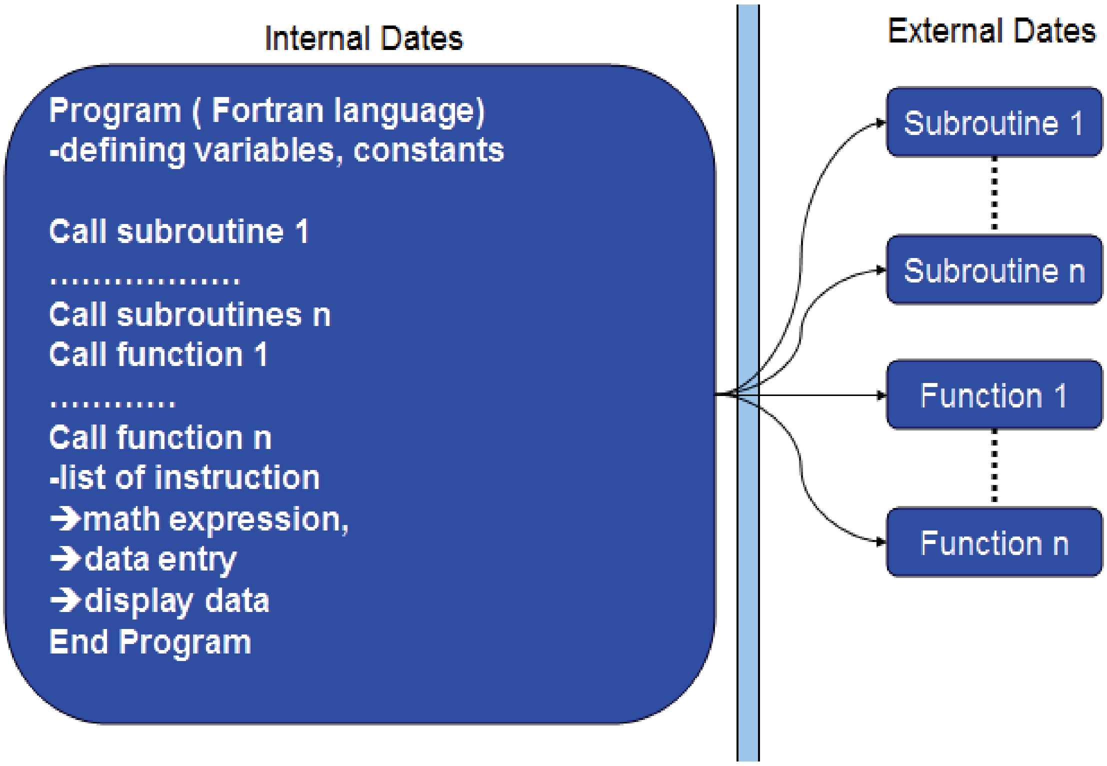


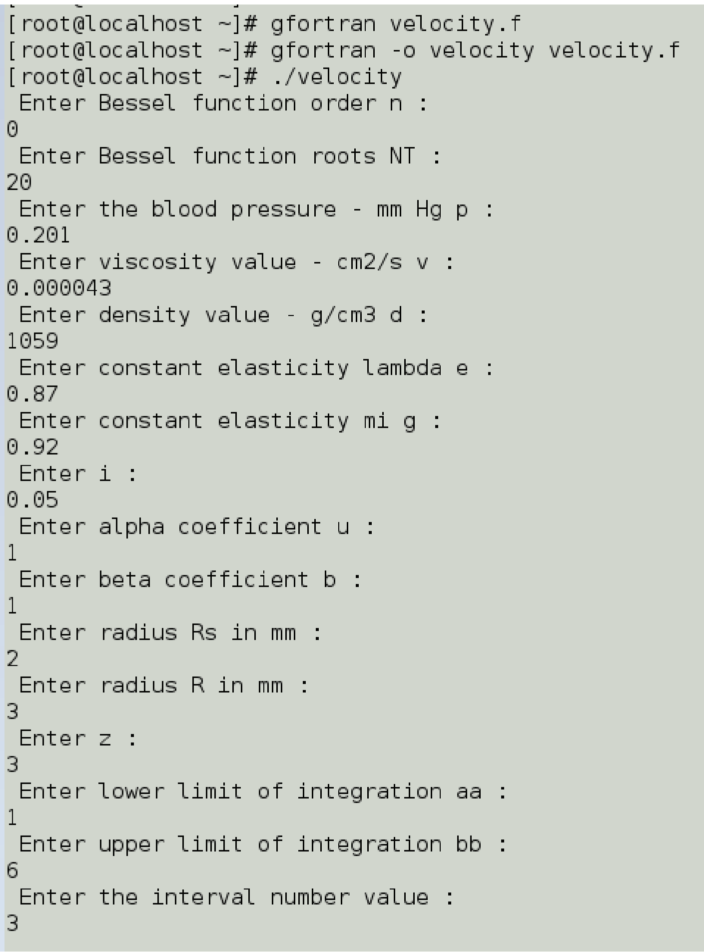
Figure 1: FORTRAN program structure

-SUBROUTINE MembriIntegrala (N,NT,RJ0,RJ1,RY0,RY1,RY2,RY3, RY4,RY5,RY6, RY7,RY8,RY9,RI1,RI2,RI6,RI7)

-SUBROUTINE FUNCTII(N,X,BJN,DJN,FJN,BYN,DYN,FYN,GYN,OYN, PYN,RYN,QYN, VYN,YYN,IYN,ZYN,ZY1,ZYP, ZY5,ZY6)

-function: REAL Function FF(y), for integral expression calculation by using the call of the external function FF,

When the velocity.f it was running we obtained the permission to input the parameters values from keyboard (figure 2):



```
[root@localhost ~]# gfortran velocity.f
[root@localhost ~]# gfortran -o velocity velocity.f
[root@localhost ~]# ./velocity
 Enter Bessel function order n :
0
 Enter Bessel function roots NT :
20
 Enter the blood pressure - mm Hg p :
0.201
 Enter viscosity value - cm2/s v :
0.000043
 Enter density value - g/cm3 d :
1059
 Enter constant elasticity lambda e :
0.87
 Enter constant elasticity mi g :
0.92
 Enter i :
0.05
 Enter alpha coefficient u :
1
 Enter beta coefficient b :
1
 Enter radius Rs in mm :
2
 Enter radius R in mm :
3
 Enter z :
3
 Enter lower limit of integration aa :
1
 Enter upper limit of integration bb :
6
 Enter the interval number value :
3
```

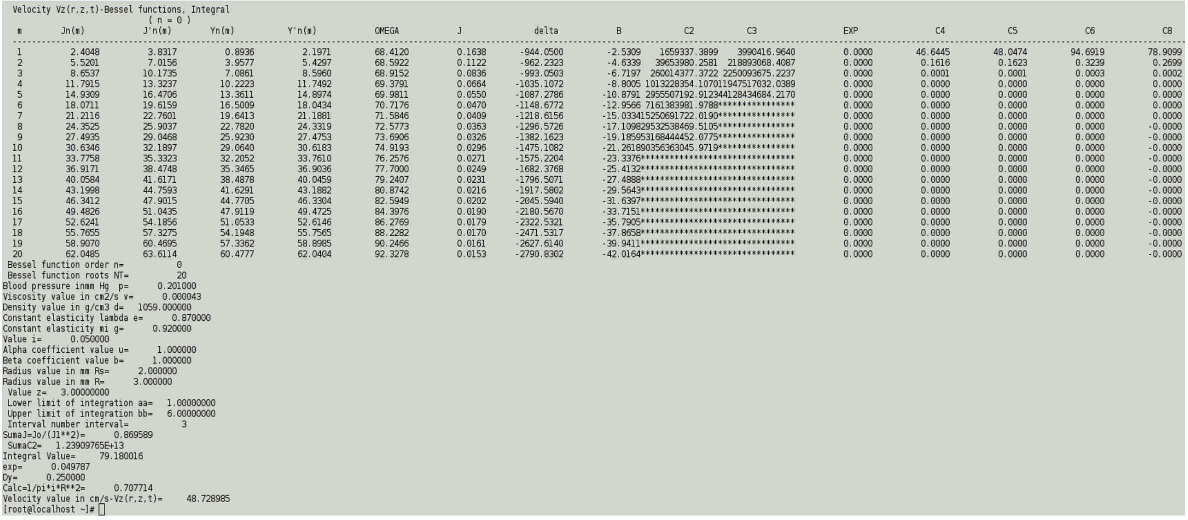
Figure 2: Program parameters input

-the obtained results highlights (figure 3):

-numerical value for math members expression, necessary for velocity v_z calculation

-series value: Jo/J1**2

-Integral value - for the integration interval introduced by user.



```
 Velocity Vz(r,z,t)-Bessel functions, Integral
                         ( n = 0 )
  m       Jn(m)          J'n(m)        Yn(m)          Y'n(m)          OMEGA          J            delta           B          C2           C3                EXP           C4           C5           C6           C8
 -------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------
  1        2.4048         3.8317        0.8936         2.1971         68.4120       0.1638       -944.0500      -2.5309    1659337.3899    3990416.9640       0.0000       46.6445      48.0474      94.6919      78.9099
  2        5.5201         7.0156        3.9577         5.4297         68.5922       0.1122       -962.2323      -4.6339   39653980.2581  218893068.4087       0.0000        0.1616       0.1623       0.3239       0.2699
  3        8.6537        10.1735        7.0861         8.5960         68.9152       0.0836       -993.0503      -6.7197  260014377.3722 2250093675.2237       0.0000        0.0001       0.0001       0.0003       0.0002
  4       11.7915        13.3237       10.2223        11.7492         69.3791       0.0664      -1035.1072      -8.8005 1013228354.107011947517032.0389       0.0000        0.0000       0.0000       0.0000       0.0000
  5       14.9309        16.4706       13.3611        14.8974         69.9811       0.0550      -1087.2786     -10.8791 2955507192.912344128434684.2170       0.0000        0.0000       0.0000       0.0000       0.0000
  6       18.0711        19.6159       16.5009        18.0434         70.7176       0.0470      -1148.6772     -12.9566 7161383981.9788****************       0.0000        0.0000       0.0000       0.0000       0.0000
  7       21.2116        22.7601       19.6413        21.1881         71.5846       0.0409      -1218.6156     -15.033415250691722.0190****************       0.0000        0.0000       0.0000       0.0000       0.0000
  8       24.3525        25.9037       22.7820        24.3319         72.5773       0.0363      -1296.5726     -17.109829532538469.5105****************       0.0000        0.0000       0.0000       0.0000      -0.0000
  9       27.4935        29.0468       25.9230        27.4753         73.6906       0.0326      -1382.1623     -19.185953168444452.0775****************       0.0000        0.0000       0.0000       0.0000      -0.0000
 10       30.6346        32.1897       29.0640        30.6183         74.9193       0.0296      -1475.1082     -21.261890356363045.9719****************       0.0000        0.0000       0.0000       0.0000      -0.0000
 11       33.7758        35.3323       32.2052        33.7610         76.2576       0.0271      -1575.2204     -23.3376********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 12       36.9171        38.4748       35.3465        36.9036         77.7000       0.0249      -1682.3768     -25.4132********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 13       40.0584        41.6171       38.4878        40.0459         79.2407       0.0231      -1796.5071     -27.4888********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 14       43.1998        44.7593       41.6291        43.1882         80.8742       0.0216      -1917.5802     -29.5643********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 15       46.3412        47.9015       44.7705        46.3304         82.5949       0.0202      -2045.5940     -31.6397********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 16       49.4826        51.0435       47.9119        49.4725         84.3976       0.0190      -2180.5670     -33.7151********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 17       52.6241        54.1856       51.0533        52.6146         86.2769       0.0179      -2322.5321     -35.7905********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 18       55.7655        57.3275       54.1948        55.7565         88.2282       0.0170      -2471.5317     -37.8658********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 19       58.9070        60.4695       57.3362        58.8985         90.2466       0.0161      -2627.6140     -39.9411********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 20       62.0485        63.6114       60.4777        62.0404         92.3278       0.0153      -2790.8302     -42.0164********************************       0.0000        0.0000       0.0000       0.0000      -0.0000
 Bessel function order n=           0
 Bessel function roots NT=          20
Blood pressure inmm Hg  p=      0.201000
Viscosity value in cm2/s v=      0.000043
Density value in g/cm3 d=   1059.000000
Constant elasticity lambda e=      0.870000
Constant elasticity mi g=      0.920000
Value i=      0.050000
Alpha coefficient value u=      1.000000
Beta coefficient value b=      1.000000
Radius value in mm Rs=      2.000000
Radius value in mm R=      3.000000
 Value z=   3.00000000
 Lower limit of integration aa=   1.00000000
 Upper limit of integration bb=   6.00000000
 Interval number interval=           3
SumaJ=Jo/(J1**2)=      0.869589
 SumaC2=   1.23909765E+13
Integral Value=     79.180016
exp=      0.049787
Dy=      0.250000
Calc=1/pi*i*R**2=      0.707714
Velocity value in cm/s-Vz(r,z,t)=     48.728985
[root@localhost ~]# 
```

Figure 3: The results values of the program velocity.f

4 DISCUSSION

This numerical simulation of the velocity it was necessary because in the bifurcation area of blood vessels the flow of the fluid it is difficult to be estimated.

To achieve this goal it was necessary to use the inverse Laplace transformation and the transition from complex to real space.

This change was required by the fact that using the complex calculations in FORTRAN programming for solving integral improper [5, 6] type led us to the results of a - not a number (“NaN”).

For realization of Fortran subroutines it were considered: C1=0 and T(s,z,p)=0

Also the formula for tangential velocity computing becomes (13):

$$v_z(r,z,t)=\frac{1}{\pi i R^2}\sum_j \frac{J_0(rs_j)}{\left[J_1(Rs_j)\right]^2}\int_{\gamma-i\infty}^{\gamma+i\infty} C_2(s_j,p)e^{-s_j z}dp \tag{13}$$

The FORTRAN subroutines for velocity v_z computing it was the objective of a national research project – developed in our institute. In this project was used the resources optimization power, in the complex computing processes, of the Grid Network System existent in the INCDTP infrastructure.

For using the Grid network facilities it was necessary to:

- write the job for velocity.f program
- write the wrapper (the list of activities to execute for obtaining the results)

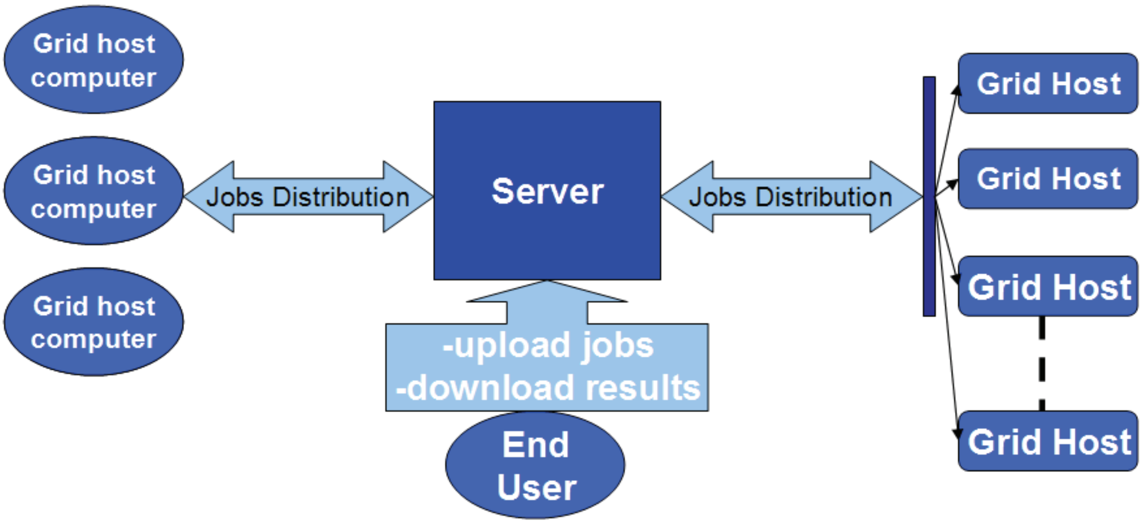


Figure 3: Grid Network - principles

5 CONCLUSIONS

By using the Grid Network power computing for parallel calculation [7] of the complex mathematical formula for the biofluid flow velocity it was obtained the velocity value very quick. The condition for using Grid Network it was to create the program by using the algorithmic programming language FORTRAN.

The advantages are:

- Distributed computing [7] ➔ parallel execution of the math calculations
- Time saving;
- Precision calculation;
- Logic programming execution based on modularization.

This software application can be used by researches and can be start-up for developing another complex software application.

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COMPRESSIBILITY OF FOLDABLE WEFT KNITTED STRUCTURES WITH AUXETIC POTENTIAL

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Keywords: knitting, auxetic potential, foldable structures, compressibility

Abstract. *Common materials have Poisson's ratio values ranging between 0.0 and 0.5. Auxetic materials exhibit the negative Poisson’s ratio. They expand laterally when stretched longitudinally and laterally contract when compressed. Auxetic effect of foldable structures is based on the structural disequilibrium of face and reverse loops, which causes the fabric to crease, contract, and form into 3-dimensional structure after the production process. Foldable structures shrink in both course and wale directions. Under applied strain in horizontal or vertical direction, 3-dimensional foldable structures smooth into flat fabric, creases unfold and the structure expands in both directions. Folding behaviour influences the thickness of the fabric, which increases with folding process. Higher thickness of the fabric means the more closely folded structure. Compressibility is an important mechanical property of textiles. It can be defined as a decrease of initial thickness due to appropriate increase of compressive force at measuring time. The compressibility behavior plays a significant role in the fabric structural stability. It is affected by different knitting parameters such as density, fabric thickness, texture, etc. The objective of research was to evaluate the compressibility of links-links weft knitted fabrics with zigzag structure which could potentially be used as packaging and mechanical damage protection material. The influence of yarn material composition, structural parameters of the foldable structures such as repeat size on the compression properties of foldable links-links knitted structures were examined in order to evaluate their adequacy for shock absorbing and compression resistant materials.*

1. INTRODUCTION

In the recent years the use of textile technology to fabricate auxetic materials attracts more and more attention. It is reflected in the extent of the research work exploring the auxetic potential of various textile structures and consequently in the number of the research papers published. Common materials have Poisson's ratio values ranging between 0.0 and 0.5. Auxetic materials exhibit the negative Poisson’s ratio. They expand laterally when stretched longitudinally and laterally contract when compressed [1]. This counterintuitive behaviour gives auxetic materials various beneficial effects compared to the conventional ones [2,3]. Therefore, auxetic materials can also be suitable for packaging, where synclastic curvature enables perfect fit of the textile wrap whereas indentation resistance and fracture toughness protect the content [3-5] or clothing, where the ability to improve the fit of the garment to the body enables greater comfort of the wearer [6].

Generally there are two approaches to produce auxetic textiles. First one includes the use of auxetic fibres to produce an auxetic textile structure, whereas the other comprises the use of conventional fibres to produce a textile structure with auxetic properties. As the knitting technology enables the design of various mesh planar structures and foldable 3D structures with auxetic potential, this research field has greatly expanded. 3D foldable weft knitted structures with auxetic potential exhibit extreme versatility and multi-functionality. They offer new, aesthetically intriguing relief surfaces, appropriate for the use for packaging and shock absorbing materials. The folding and auxetic potential enable good fit to the content and adequate protection of the goods from external damages.

Auxetic effect of foldable structures is based on the structural disequilibrium of face and reverse loops, which causes the fabric to crease, contract, and form into 3-dimensional structure after the production process. Foldable structures shrink in both course and wale directions. Under applied strain in horizontal or vertical direction, 3-dimensional foldable structures smooth into flat fabric, creases unfold and the structure expands in both directions. Liu et al. [7] determined that the fabric with more folded and more closed zigzag form also exhibits more significant auxetic effect. This behaviour influences the thickness of the fabric, which increases with folding process. Higher thickness of the fabric means the more closely folded structure.

The objective of research was to evaluate the compressibility of links-links weft knitted fabrics with zigzag structure which could potentially be used as packaging and mechanical damage protection material. The influence of yarn material composition, structural parameters of the foldable structures such as repeat size and width/height ratio on the compression properties of foldable links-links knitted structures were examined in order to evaluate their adequacy for shock absorbing and compression resistant materials.

2. THEORETICAL

Compression may be defined as a decrease in intrinsic thickness with an appropriate increase in pressure. Intrinsic thickness is the thickness of the space occupied by a fabric subjected to barely perceptible pressure. Compression is one of the important properties of fabric, in addition to friction, bending, tension and shear. The compressive force applied allows the yarn to undergo deformation non-linearly, resulting in a change in thickness of the fabric [8]. The compressibility behavior plays a significant role in the fabric structural stability. It is affected by different knitting parameters such as density, fabric thickness, texture, etc.

Fabric compression involves the movement of fibres and yarns within the diameter axis to which the fabric is oriented. This behaviour is accounted for by studying the fabric’s internal non-linear structure, the visco-elastic nature of the fibres themselves, and to some extent the friction between fibres and yarns [8].

Fabric compression behavior is generally described by the relationship between the applied force (normal to fabric plane) per unit area and the resulting fabric thickness. The relationship is obtained by a simple test, in which the fabric specimen being tested is placed horizontally on a platen, and subsequently loaded and unloaded by a presser foot. The thickness of the fabric, which is the distance between the presser foot and the platen, is recorded as a function of the applied pressure. This pressure-thickness relationship describes the compression characteristic of the fabric. The pressure-thickness curve of textile fabrics in lateral compression is highly nonlinear [9].

3. EXPERIMENTAL

3.1 Sample preparation

A study of the influence of the unit cell size as well as the zigzag rib width of knitted structures on their compression properties was performed.

First series of the zigzag knitted structures was produced in various unit cell sizes with the same number of courses and wales in a zigzag form from the biggest 24×24 to the smallest 4×4 repeat size (Figure 1), while the second series was produced with various widths of a zigzag line in a unit cell with a constant number of courses from the widest 24×24 to the narrowest 2×24 repeat size (Figure 2).

Both series of knitted structures were produced from two different yarns: 46,38 Wo/53,62 PAN, 70,54 tex and 86,38 CV/13,62 PA, 74,78 tex (experimentally determined), respectively. The samples were knitted on the Shima Seiki SES122RT knitting machine, gauge12E with cam position set to the value 35. After the removal from the knitting machine, specimens folded into 3-dimensional structures. The compression tests were performed after the samples were relaxed for several days.

In previous investigations, it was found [10] that with the second series of the samples, the width of zigzag lines distinctively influences the ability to fold; structures made of Wo/PAN fully fold for the unit cell repeats from 24×24 to 16×24 while structures made of CV/PA fully fold from the unit cell repeats 24×24 to 14×24. Therefore, only the compression properties of the fully folded knitted structures were examined due to their protective packaging potential.

3.2 Test method and procedure

The compression test was performed on the dynamometer INSTRON 5567. The speed of the movable pressure foot was 0.3 mm/s. The compression load was read when the distance between the movable pressure foot and the fixed flatten reached 1 mm. Circular pressure foot with the diameter 9 cm was used. Ten measurements of the maximum compressive load at the compressed thickness of the knitted structure t_{compr} = 1 mm for each sample were performed.

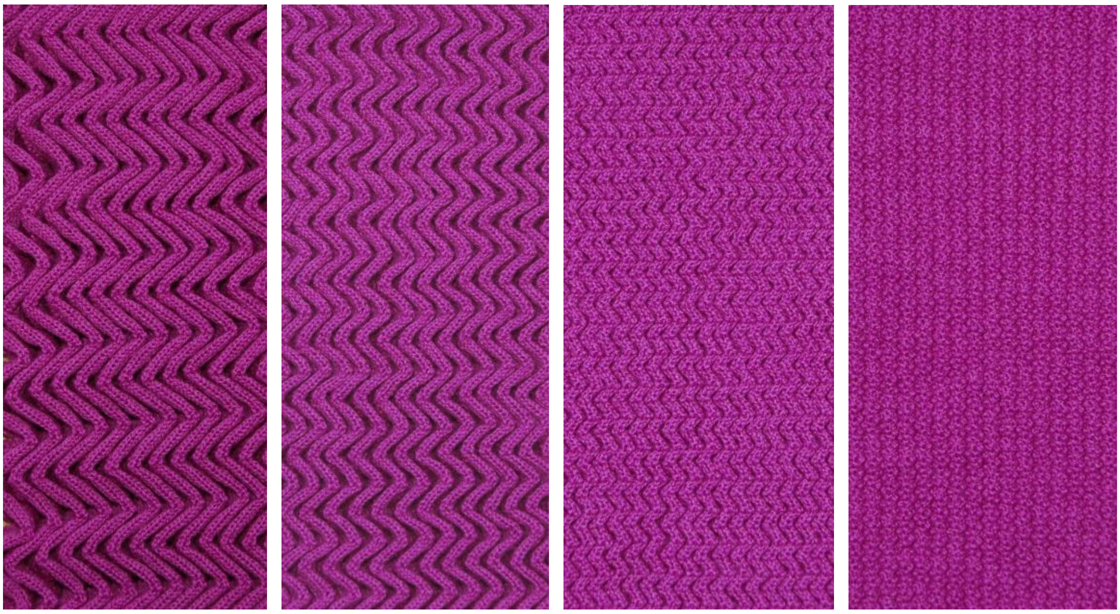

Figure 1: Zigzag knitted structures with different square repeating unit cell sizes

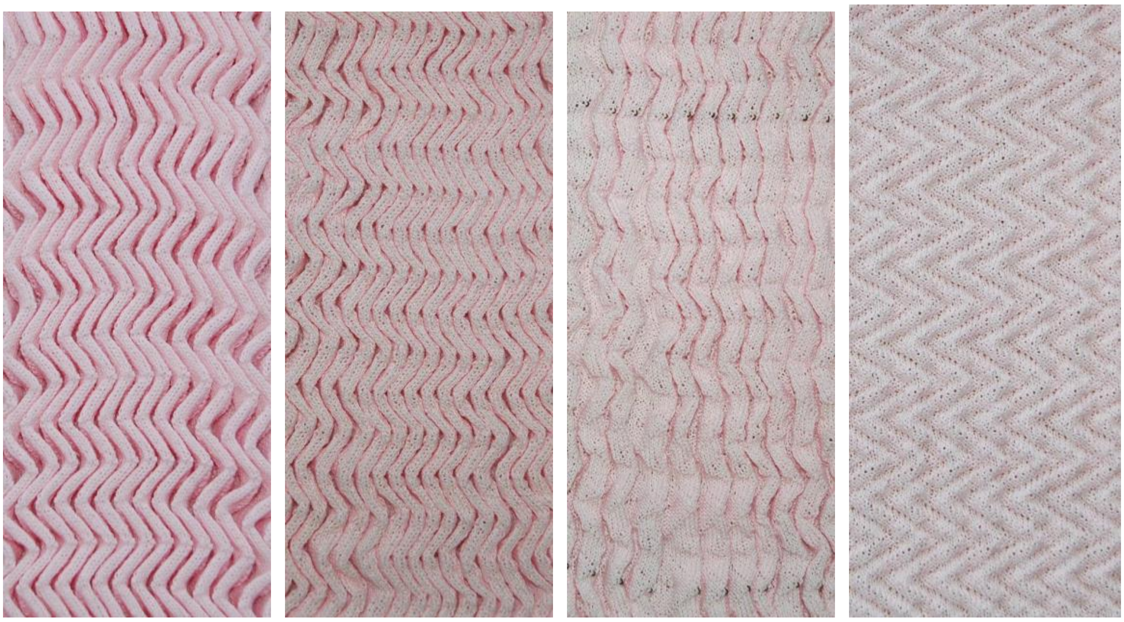

Figure 2: Zigzag knitted structures with different widths of a zigzag line

4. RESULTS AND DISCUSSION

The results of the maximum compression load measurements are presented in Tables 1 and 2.

The results of the compressive stress at the maximum compression load are presented in Figures 3, 4 and 5.

Table 1. Maximum compression load for the foldable zigzag knitted structures with the same number of courses and wales in a unit cell repeat

Pattern repeat	Maximum compression load (N)			
	CV/PA		WO/PAN	
	mean	cv	mean	cv
24 x 24	6526.36	12.48	4408.17	9.27
22 x 22	6005.64	9.23	3503.05	5.49
20 x 20	5807.19	8.89	2829.05	7.70
18 x 18	5144.61	11.57	2368.65	15.87
16 x 16	4911.03	6.81	1993.34	14.01
14 x 14	4553.02	6.48	1229.51	9.55
12 x 12	3573.88	7.28	1087.91	12.08
10 x 10	2732.81	6.78	806.15	8.04
8 x 8	1627.38	6.80	574.16	6.44
6 x 6	753.70	8.57	300.97	2.77
4 x 4	174.65	8.51	103.89	6.54

Table 2. Maximum compression load of the foldable zigzag knitted structures with different widths of a zigzag line and a constant number of courses in a unit cell repeat

Pattern repeat	Maximum compression load (N)			
	CV/PA		WO/PAN	
	mean	cv	mean	cv
24 x 24	6526.36	12.48	4408.17	9.27
22 x 24	6236.32	10.81	3888.23	9.87
20 x 24	5581.71	8.85	2815.86	7.46
18 x 24	5408.08	8.01	2176.13	8.18
16 x 24	3418.32	13.99	464.03	20.36
14 x 24	570.48	13.60	141.77	12.51

Previous investigations showed that knitted structures with the bigger repeat are thicker [11]. Furthermore, knitted structures made from Wo/PAN yarn are thicker than knitted structures made from CV/PA yarn [11]. The results of the previous investigations were considered in the analysis of the foldable structures compression properties.

Zigzag folded knitted structures with the square repeat comprising the same number of courses and wales (1st series of samples) fully fold in both course and wale direction (Figure 1). Full folding emerges for all the repeat sizes and for structures produced from both yarns. The structures designed with various widths of zigzag ribs (2nd series of samples) exhibit substantial deterioration for the smaller repeats (Figure 2); the structures with rib widths less than 7 loops are very poorly folded; their thickness is significantly decreased.

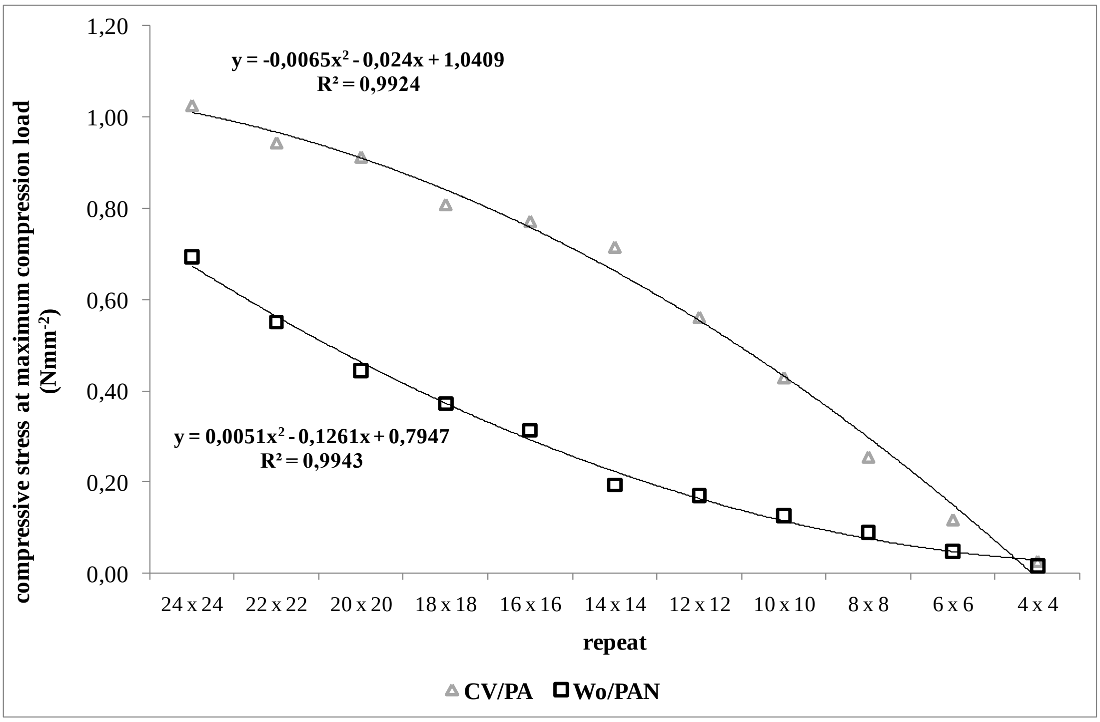

Figure 3. Compressive stress at maximum compression load for the foldable zigzag knitted structures with the same number of courses and wales in a unit cell repeat

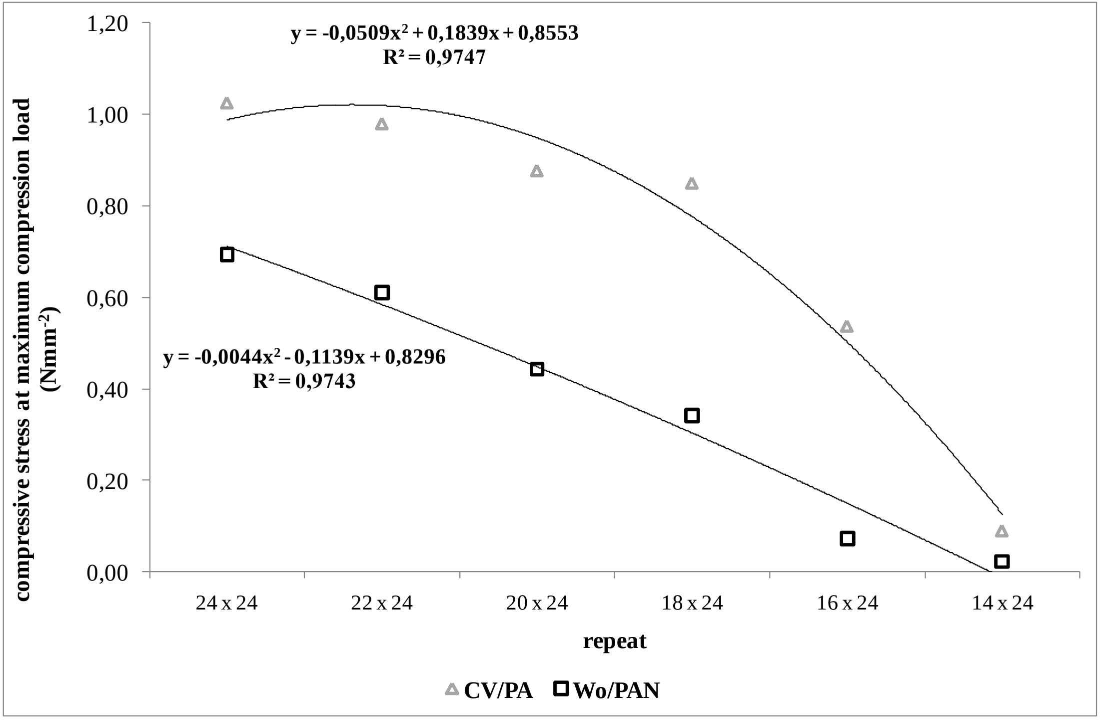

Figure 4. Compressive stress at maximum compression load for the foldable zigzag knitted structures with different widths of zigzag ribs and a constant number of courses in a unit cell repeat

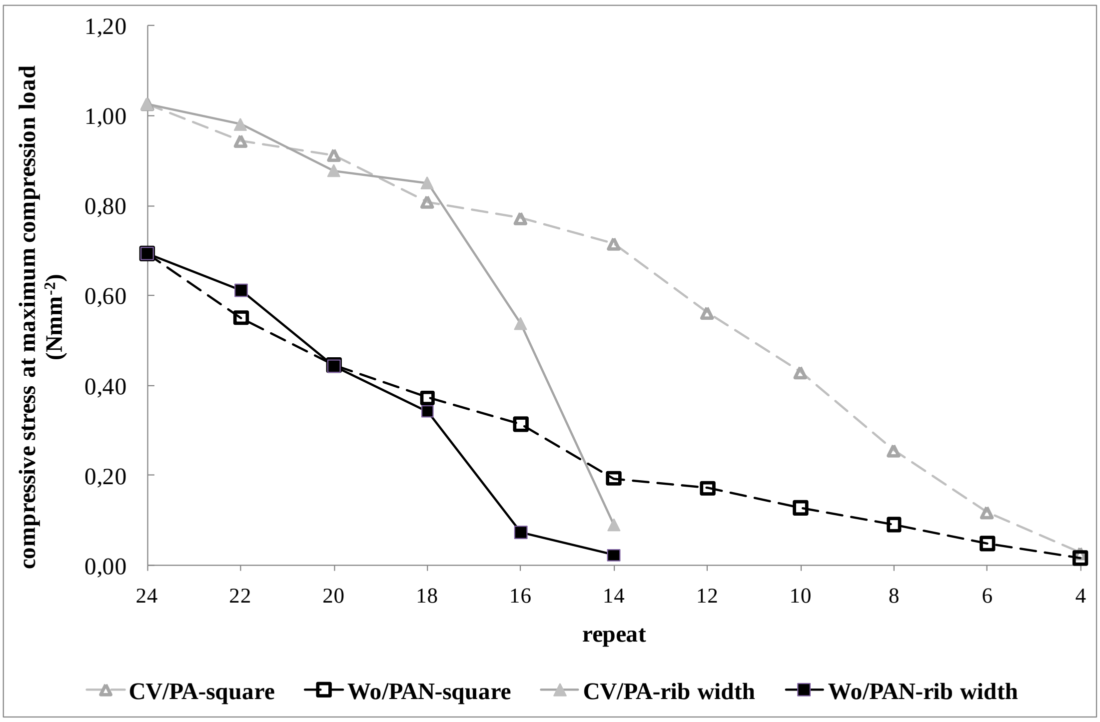

Figure 5. Comparison of compressive stress at maximum compression load for foldable zigzag knitted structures with various repeats: square - same number of courses and wales in repeat; rib width - different widths of zigzag ribs and a constant number of courses in a repeat

It can be seen from the Tables 1 and 2 that the maximum compression load of the CV/PA samples exceeds the maximum compression load of the Wo/PAN samples for the structures with comparable repeats; as mentioned above, knitted structures made from Wo/PAN yarn are thicker than knitted structures made from CV/PA yarn [11]. The maximum compression load decreases with the repeat reduction which can be explained by the fabric thickness decrease. For all the measured repeats and materials, the maximum compression load at the compressed thickness of the knitted structure t_{compr} = 1mm exceeds 100N.

From the Figures 3 and 4 it can be seen that the decrease of the compressive stress with the knitted structure repeat reduction is not linear. For the CV/PA knitted structures the decrease gets more distinctive with the smaller repeats while for the Wo/PAN knitted structures the compressive stress decreases more in the case of bigger repeats.

From the Figure 5, it can be seen that the compressive stress decreases similarly for the structures with the repeat widths from 24 loops to 18 loops. Foldable knitted structures with the repeat widths smaller than 18 loops differ substantially; structures with the square repeat which are all fully folded (1st series of samples) exhibit gradual compressive stress decrease while for the structures designed with various widths of zigzag ribs (2nd series of samples) instant drop of the compressive stress is evident. These structures do not fully fold when the rib width is smaller than approximately 7 loops.

Foldable knitted structures are compressible; their behavior is very important in terms of handle and comfort. For the folded knitted structure thickness reduction to 1mm, rather high loads are required.

Foldable links-links knitted structures offer new, aesthetically intriguing relief surfaces. They can be appropriate for the use in clothing sector, interior design, seat covers for the automotive industry, mattresses, and for packaging and mechanical damage protection material.

5. CONCLUSIONS

The maximum compression load of the CV/PA foldable knitted structures exceeds the maximum compression load of the Wo/PAN structures with comparable repeats although knitted structures made from Wo/PAN yarn are thicker than comparable knitted structures made from CV/PA yarn. The maximum compression load and fabric thickness decrease with the repeat reduction. For all the analyzed repeats and materials, the maximum compression load at the compressed thickness of the knitted structure t_{compr} = 1mm exceeds 100N.

The decrease of the compressive stress with the knitted structure repeat reduction is not linear. The compressive stress decreases similarly for the structures with the repeat widths from 24 loops to 18 loops. For the foldable knitted structures with the repeat widths smaller than 18 loops, the compressive stress differs substantially; structures with the square repeat exhibit gradual compressive stress decrease while for the structures designed with various widths of zigzag ribs instant drop of the compressive stress is evident.

Foldable knitted structures are compressible. They can be appropriate for the use in clothing sector, interior design, seat covers for the automotive industry, mattresses, and for packaging and mechanical damage protection material.

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THE APPLICATION POSSIBILITIES OF LIPOSOMES IN TEXTILE FINISHING PROCESS

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ABSTRACT: There is an increasing interest in using natural products such as phospholipids to create ecofriendly textile processes. Liposomes are the bilayers composed by phospholipids encapsulating an inner solution phase. Liposomes allowing transport of active agent to one end of cell membrane to the other one have potential application in numerous fields, such as pharmaceuticals, cosmetics, foods, detergents and textiles. Recently, liposomes have been investigating as carriers in transferring dye molecules on textile material at lower temperature and environmentally. Production of liposomes has been limited in laboratory environment in our country. This study provides information on general characteristics of liposomes and the studies on the use of liposomes in textile dyeing processes with other textile auxiliaries, especially wool dyeing, were examined[1].

Keywords: Liposome, encapsulation, dyeing, wool

1. GENERAL INFORMATION

Liposomes are closed vesicles with an aqueous interior of the region and they are spherical phospholipid bilayers with 10 nm diameters ranging from 10 mm. Liposomes are not a substance, they are carrier systems.

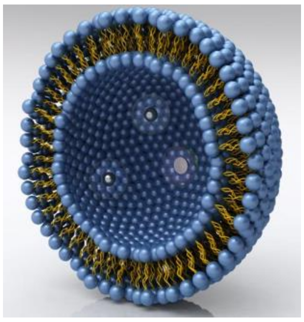


Figure 1: Monolayer Liposome

Liposomes consist of two parts which are hydrophobic and hydrophilic. The hydrophilic portion consists of phosphate groups and choline, hydrophobic parts consist two hydrocarbon chain[3]. Liposomes can be classified according to size which are small and large. Also they can be classified according to layers which are monolayer, bilayer and multilayer[4].

Application of this technology results in saving energy by reducing the time and reducing the temperature more than those needed in conventional wool-dyeing method, avoiding the use of any other synthetic auxiliaries. In addition, the fibers are protected by dyeing at low dyeing temperatures by use of liposomes. Liposomes are known to be easily biodegradable than those conventionally synthesized auxiliaries. Therefore, liposomes cause a distinct decrease in the contamination of dyebath. Using liposomes in dyeing process gives a more natural handle and improved quality properties to fibers with a lower temperature and lower environmental impact. The liposomes are also highly effective in bleaching of wool. The presence of liposomes in bleaching bath increases the quality of bleached wool by reducing significantly the concentration of basic component-hydrogen peroxide[3,5,6,7,8,9,10].

2. PREPARATION OF LIPOSOMES

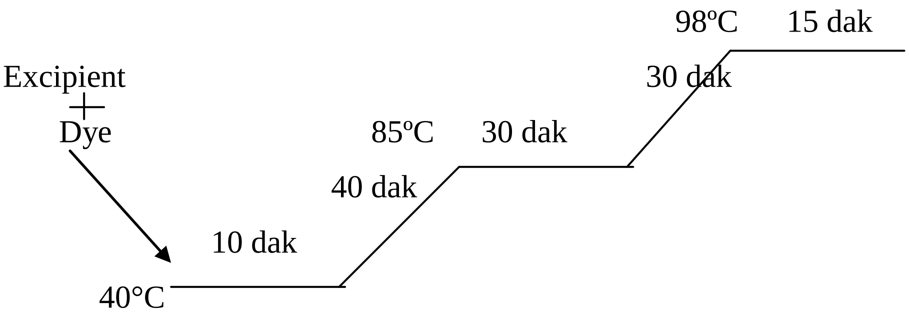
During the manufacture of the liposome we use soy lecithin and cholesterol to create liposome membrane structure and as the organic solvent used is a mixture of chloroform and methanol. Liposome manufacturing was performed according to the thin lipid layer (Bangham method) method. Six different lipid mixtures were produced in different lipids: cholesterol weight ratios. These rates are listed in the table below.

PC:CH w/w	PC (lesitin) (gr)	CH (Kolesterol) (gr)	Kloroform (ml)	Etanol (ml)
10.0-0.0	0,1	–	4 ml	2 ml
10.0-0.0	0,5	–	4 ml	2 ml
9.5-0.5	0,5	0,026	4 ml	2 ml
9.0-1.0	0,5	0,055	4 ml	2 ml
8.5-1.5	0,5	0,088	4 ml	2 ml
10.0-0.0	10	–	8 ml	4 ml

Table 1: Liposome Production Rates

3. DYEING WITH LIPOSOME

Nyloset Scarlet N-2G (1:2 metal complex dyestuff) was used in dyeing process. Then 2% dyestuff produced with liposomes prepared with the staining solution. The preparation of dye solution, sonicator was used for being a homogeneous mixture of pure water and the dye with a liposome and being distributed in full liposomes in the solution. The dyeing process was done within 15 minutes after solution preparation to constitute liposomes aggregate in HT steamer machine. Liquor ratio of 1:10 for 5 grams during the painting process and wool fiber used. 50 ml of liquor volume was calculated. Conventional dyeing processes with bunded albegat dyeing and conventional dyeing was also done. So we could ensured liposome and benchmarking of conventional dyeings.



The samples washed with water after was allowed to dry.

4. MEASUREMENTS AND ANALYSİS

4.1. COLOR MEASUREMENT

After complete drying dyed samples were measured color. Dyed fabrics and the maximum absorption at a wavelength of 400-700 nm spectral region, K / S values were calculated in order to be able to determine the efficiency of the dyed wool fabric dyeing. A value in the table redness, yellowness b value, the L value represents the lightness values.

			L*	a*	b*	K/S	ΔE
Conventional dyeing			41,889	41,920	20,939	9,6094	–
Conventional dyeing (% 1 Albegal set)			42,276	42,509	19,566	10,044	1,543
Dyeing with Liposomes							
PC:CH w/w	PC (lecithin) (gr)	CH (Kolesterol) (gr)					
10.0-0.0	0,1	–	40,330	43,968	21,954	11,939	2,767
10.0-0.0	0,5	–	41,055	42,861	20,760	10,694	1,259
9.5-0.5	0,5	0,026	41,196	43,340	21,448	10,850	1,66
9.0-1.0	0,5	0,055	40,678	42,141	20,554	10,712	1,29
8.5-1.5	0,5	0,088	38,641	42,939	21,768	13,128	3,504
10.0-0.0	10	–	40,970	39,460	21,842	10,027	2,777

Table 2: Color Measurement Results

When compared to the data, dyeings made with liposome dye in darker colors than conventional dyeing and conventional dyeing with 1% albegat set. However liposome dyeing made with 10 g of lecithin is used in the sixth example, the structure was observed undesirable deterioration. So it shows that, the process of dyeing was observed a negative effect on the use of very high amounts of lecithin.

4.2. WASHING FASTNESS

The washing fastness of dyed fibers to measure the dimensions of 4x10 related nodes the same size were planted and the washing process was done. Color changes were evaluated using the gray scale.

	Secondary Cellulose Acetate	Unmercerized Cotton	Nylon 6.6	Polyester	Acrylic	Wool
Conventional dyeing	4-5	4	4	5	4	4
Conventional dyeing (% 1 Albegal set)	4-5	5	4	4-5	4	4
1	4-5	5	4	5	4	4-5
2	4-5	5	4	4-5	4-5	4-5
3	4-5	5	4-5	4-5	4-5	5
4	4-5	5	4-5	4-5	5	5
5	4-5	5	4	4-5	5	5
6	4-5	4-5	4	4-5	4-5	4-5

Table 3: Washing Fastness Results

These results show that liposome-dyed fibers already have good wash values. Also the fourth liposome-dyed fiber shows the best result. So it can be used in future studies.

4.3. SWAET FASTNESS

The sweat fastness of dyed fibers to measure the dimensions of 4x10 related nodes the same size were planted and the sweat process was done. In this test we measured acidic and basic sweat fastness values. Sample contamination and discoloration and multi-fiber gland evaluated with gray scale in the D65 light.

	Acidic Sweat						Basic Sweat					
Conventional dyeing	4	4	4	3-4	4	3-4	4	4	4	3	3-4	4
Conventional dyeing (% 1 Albegal set)	4	4	4	3-4	4	4	4	4	4	3-4	4	4
1	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
2	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
3	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
4	4-5	4-5	4-5	5	5	5	4-5	4-5	4-5	4-5	4-5	5

5	4	4-5	4-5	5	4-5	5	4-5	4-5	4-5	4	4-5	5
6	4	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5	3-4	4	4

Table 4: Sweat Fastness Results

These results show that liposome-dyed fibers already have good sweat values. Also the fourth liposome-dyed fiber shows the best result. So it can be used in future studies.

5. CONCLUSION

These results show that liposomes will be used in textile dyeing especially in wool dyeing. In particular to the optimization of wool dyeing processes, dyeing dyestuff liposomes can be used as a carrier. However, in our country it is made in the laboratory production of liposomes and these products are supplied as ready from abroad. Therefore, we have to give importance to liposome technology which provides an efficient and versatile usage.

In our future work we will do liposome optimization. After deciding on the optimum liposome different rates and in different colors with different dyestuffs and after that dyed materials to be analyzed.

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A STUDY ON ILLUMINATING PROPERTY OF PHOTOLUMINESCENT FIBER

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Keywords: Photoluminescent material, afterglowing, illumination.

Abstract. *Photoluminescent materials generate illumination in darkness. They have the ability to absorb most types of light (sunlight, fluorescent, etc.) as energy and then to re-emit that energy which human eye perceives as light. When darkness occurs, the fibres become highly visible. Luminescent fibres have wide usage areas such as costuming, defence industry, decoration, transportation, night work, daily life, etc. In recent years, their importance increases with the safety benefits of photoluminescent materials in protective clothing, pathways, life-vests, carpets. In this study, illumination characteristics of photoluminescent fibres were analysed. Luminance intensity of photoluminescent fibres and duration of luminescence were measured on yarn and fabric samples. Knitted fabrics were exposed at different light sources and for different times. At the end of the study, it was shown that exposing and emitting time of photoluminescent fibre depends on type of the light source. Once the fibre absorbs the certain light for 5 minutes, the stored light energy in the fibre makes the sample luminous in darkness for more than 30 minutes.*

1. INTRODUCTION

People have difficulties to find our way when it is dark or electricity cut. In particular, older people, kids and the people with obstacles can be falling down or injured when they are moving. Photoluminescent materials increase visibility of any object or place with emitting a series of coloured lights in the darkness, such as yellow, blue and green. Photoluminescent materials can be incorporated into textile structures and they provide major advantages in many uses, especially safety equipment. In the past, photoluminescent products were used for marking the emergency pathways to provide visibility in power failure situations. Today, they have large usage areas such as protective clothing for fire-fighters and chemical workers, athletic and hunting gear, ropes and cords, life vests, carpets for theatres, airplane interiors etc. Photoluminescent materials can be added to textile products by painting, coating or laminating. However, at now, there have been attempts aimed to combine the fibre-forming polymer and rare-earth photoluminescent materials during fibre spinning process[1-2]. Direct incorporation of the photoluminescent materials into fibres overcomes many of the difficulties with coating methods and provides enough durability and good afterglow properties. Photoluminescent fibre absorbs any visible light and the light energy will be stored in the fibre. Hence, fibre luminous will be possible in darkness for a certain time. This cycle can be repeated limitlessly.

In literature, there are limited studies regarding with photoluminescent textile products. Ge et al. (2012) prepared rare-earth luminescent fibre by using rare-earth strontium aluminate as the rare-earth luminescent material, fibre-forming polymer PET as the matrix. The microstructure, composition and properties of rare-earth luminescent fibre were studied. In another work, Yan et al. (2012) prepared the luminous fibre by melt spinning mixturing complex strontium aluminate phosphor and polyethylene terephthalate. Bracko et al. (2011), impregnated photoluminescent pigments to the spun yarn and analysed the effect of washing process on luminance level. Shim et al. (2004), worked on incorporating photoluminescent pigments to the yarn by coating method.

Present study aimed to determine illumination characteristic polyester fibre having photoluminescent materials. In the study, it was studied the required exposing time and duration of luminescense. In addition, the effects of light source type and charging time, and also the changes in luminance with time were also analysed.

2. MATERIALS AND METHODS

In the study, polyester yarn, a mixture of curtisium photoluminous material and polymer, was used. Yarn fineness is 150 deniers*2 ply (15 filaments). At first, the yarn was knitted on sample knitting machine and knitted fabrics were obtained. The fabrics were cut and the weight of the fabric was measured. In the study, 15 g of knitted fabric was used. The fabric was fixed on white paper 2 x 2 cm in size without any crease. Three samples were prepared. And then the samples were charged for different times. The fabrics were exposed to the illumination sources. D65 and F illumination lights were used and the yarn was left under the light for 1, 5 and more minutes. The mechanism of photoluminescent sample is absorbing the light and storing during the charging process, and then illuminating. To measure the illumination property of the fabric, it was prepared a special box to provide the darkness. 4IN1 Multi-Function Environment Meter luxmeter was used to measure the intensity of the light. Following to charging process, the sample was taken from D65 and F lights and put into the box (Figure 1). Prior to the exposure to light or activation, respectively, the samples were kept in complete darkness. Intensity of the light emitting from the sample was reported. The distance between the sample and the measuring machine was 15 cm. Similar measurements were also done on the yarn. The yarn was evenly wound on a white cardboard carrier 2 x 2 cm in size and activated for 5 minutes with D65 light. Three measurements were done for each analysed parameters such as sample form type (yarn and fabric), light source and charging time.


(a) (b)

Figure 1: 4IN1 Multi-Function Environment Meter luxmeter (a) and measurement box (b)

3. RESULTS AND DISCUSSION

3.1 The effect of charging time

In this part of the study, the fabrics were waited under the D65 light at 1, 5 and more minutes. Luminance intensity of the fabrics was measured by luxmeter after the illumination. The measurements were done at certain intervals, starting from 10 seconds to 30 minutes. The decay characteristic of the luminescent fabric sample is given in Figure 2. In the graph, the axial axis shows decay time while the vertical axis demonstrates the luminance intensity.

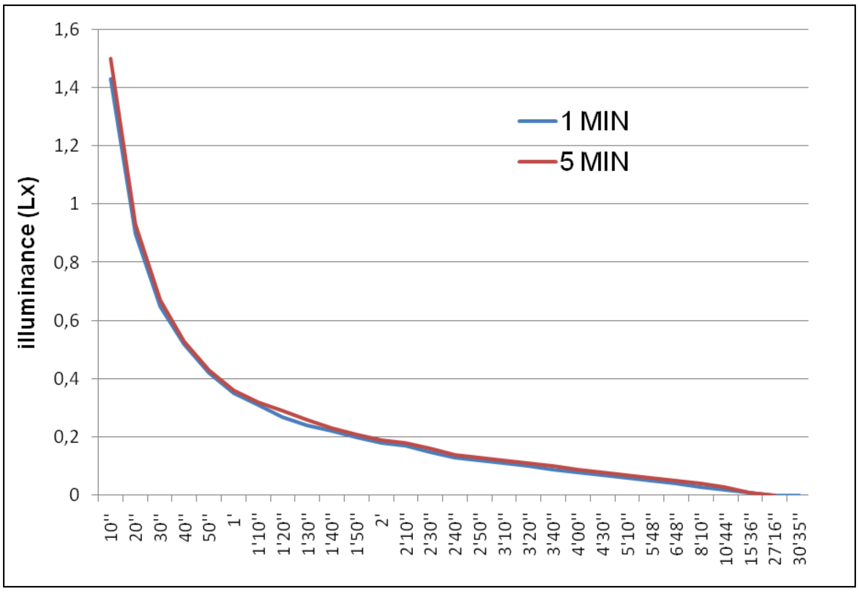

Figure 2: Decay curve of the afterglow for different charging times

As seen in Figure 2, luminance intensities after the excitation or the removal of the light source decrease rapidly at the start of luminescence. Afterglow undergoes a rapid large reduction during the first minute. Then it was observed long decay of the afterglow and the speed of this period is slower than initial afterglow. Therefore, as mentioned in literature[2-3], luminance intensity curves of the photoluminescent fabrics display three-region structure of fast, medium and slow decay. This trend was determined for both charging time and hence the characteristics of the curves are similar.

On the other hand, when the effect of exposing time on afterglow intensity was analysed, we did not determine any significant differences. Only, at 5 minute, luminous intensity became slightly higher than that of the 1 minute exposing. In addition, duration of illuminescense is longer for 5 minute exposing than that of the 1 minute exposing. Nevertheless, the difference was not considerably high. In particular, at the higher charging times than 5 minutes, we obtained similar illuminance intensity values and decaying time with that of the 5 minutes. These findings indicate that luminous intensity reaches saturation when the samples were exposed to illumination at a certain time. In present study, illumination intensity becomes more or less constant after 1 minute. Therefore, as the charging time increases, luminance intensity can not become more. After the certain time, the luminous intensity of the luminous sample was seen to change only slightly with time of excitation. Luminous intensity of the yarn or in other words, saturation may depend on luminous intensity of the photoluminescent material and photoluminescent material content in fibre structure[3].

3.2 The effect of light source type

The photoluminescent knitted fabrics were exposed under two different light sources for 5 minutes and luminous intensity of the fabrics was measured. D65 and F light types were used. D65 symbolizes the daylight while F is yellow light. Prior to the measurements, luminescent intensity of D65 and F lights were also determined by luxmeter and the intensity is 2600 cd/m^2 (lx) for D65 and 2700 cd/m^2 (lx) for F light.

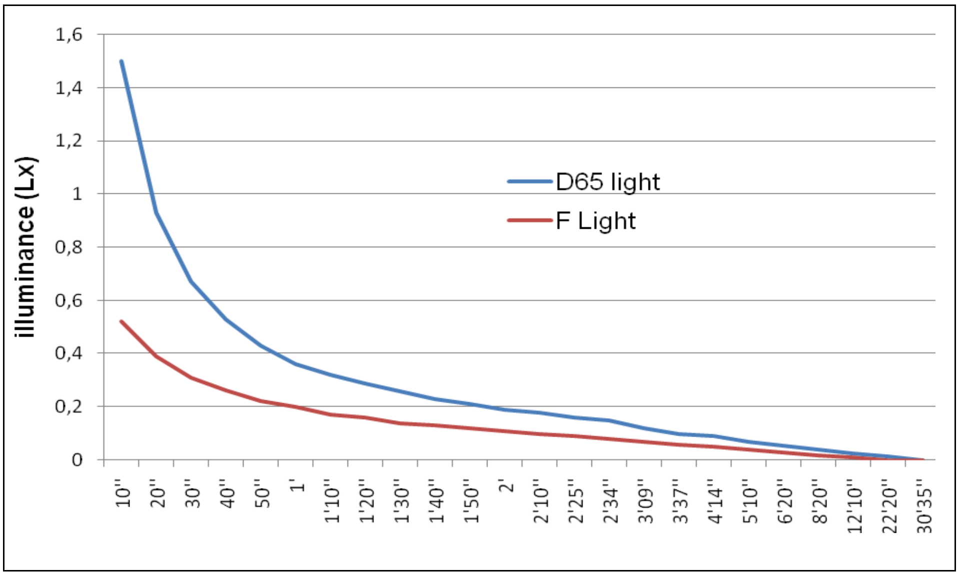

Figure 3: Decay curve of the afterglow for different light source

From Figure 3, it is seen that luminous intensity obtained by F light is lower than that of the D65. D65 light provides three times higher afterglow intensity in comparison to F light. Likewise to D65 light, luminance intensity curve of the F light displays three-region structure of fast, medium and slow decay. However, the curves do not overlap. Along the all decaying period, the samples charged with D65 light have higher illuminance. On the other hand, for F light, luminous intensity decreases to zero after 22 minutes. As to D65 light, luxmeter did not report any illumination value after the time reached 30 minutes. Therefore, D65 light enhances longer afterglowing duration than F light. It is also required to state that there is still slightly visible light after 22 minutes for F light and 30 minutes for D65 light. It is not observed a dying down of the light. The reason of this case may that intensity of the light is not in the measurement range of the luxmeter.

The difference in luminance intensity values could be due to the different colour temperatures and wavelengths of the lights. Colour temperature is 6500ºK for D65 light and 2300-2800ºK for F light[5]. Therefore, D65 light source provides more energy.

Luminescent fibre emits a series of coloured lights in the darkness, such as yellow, blue and green. Luminescent materials such as rare-earth materials used for the fibre have an unfilled and external shielded 4f5d electronic configuration[2,6]. Therefore, various energy levels, spectral terms and over 200,000 energy-level transition channels can be formed in the ion. The energy levels and spectral lines of the ions are far greater than common elements and can absorb or emit various wavelengths. After the excitation with the light, the electrons traverse from the excited into the ground state, whereby they emit visible light[4]. D65 light may lead to an effective excitation and more electron activity. Hence, more luminant intensity and long-lasting afterglowing can be obtained with D65 luminance. Photoluminant samples may be more sensitive to D65 light due to its wavelength than F light.

3.3 The effect of sample form

In the study, it was also analysed the effect of sample form on afterglowing characteristics. Illumination intensity measurements were done on photoluminescent yarns and knitted fabrics. Likewise to knitted fabrics, photoluminescent yarns were evenly wound on a white cardboard carrier and activated for 5 minutes with D65 light. Three measurements were done for each analysed parameters and the results were summarized in Table 1. As seen in Table 1, knitted fabrics provide higher luminous intensity compared to yarn form although both samples were wound on the same cardboard. However, samples have different weight and fabrics are 15 g while yarns are 2.5 g. Therefore, fabric form may store more energy and give higher exposing intensity and long-lasting afterglowing. In the yarn form, luminous intensity decreases to zero after 9 minutes. As to fabric form, luxmeter did not report any illumination value after the time reached 30 minutes. The differences in the intensity values and afterglowing period reach to three times.

Parameter	**Sample form**	
	Yarn	**Fabric**
Illuminance (Lx)	0.38	1.50
Afterglowing period (minute/second)	9'25"	30'35"

Table 1. Afterglowing characteristics

4. CONCLUSIONS

In this study, afterglowing properties of photoluminescent yarns and fabrics were studied and the effects of decaying time and luminance source were analysed. The knitted samples were exposed at 1 and 5 minutes and it was determined that they enhance an illuminance at about 30 minutes. Particularly, luminance intensity values were determined as similar for 1 and 5 minutes. Luminous intensity reaches saturation and becomes constant after the certain exposing time. Therefore, very low short time for exposing, such as 5 minutes enhances the illumination about 30 minutes. Luminous intensity and emitting time can be increased with luminous intensity of the photoluminescent material and photoluminescent material content in fibre structure. On the other hand, luminance intensity of photoluminescent materials changes depending on type of light source or wavelengths of the lights. D65 light type gives higher intensity values than that of the F light. Electrons in photoluminescent materials are excited according to energy levels of the light type. At the starting of exposing, luminance intensities are very high. However, there is a rapid reduction after the one minute. Following to initial afterglowing, illumination shows a slow period. Therefore, photoluminescent materials display three-region structure of fast, medium and slow decay. In any textile material, luminance intensity and luminescense are getting higher as the usage of photoluminescent fibres in fabric form increases.

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WET-LAID AS A TECHNIQUE TO BIOCOMPOSITES MANUFACTURING

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Keywords: wet-laid, composite, bio-based, mechanical properties, natural fibers

Abstract. *The main objective of this work is the mechanical characterization of biocomposites fabricated by wet-laid technology. These composites have been obtained from a thermoplastic matrix (PP and HDPE) reinforced with short flax fibers. Wet-Laid technology employs a modified papermaking process in which fibers and large water flows are used to create nonwovens. This technology is used for the development of compounds made from nonwoven fibers, which have the ability to disperse in liquids.*

1. INTRODUCTION

As a result of the growth interest regarding global environmental factors, the principles of sustainability and industrial ecology are being integrated into the development of the next generation of materials, products and processes. The depletion of oil resources and the increase of environmental regulations, are acting synergistically to upgrade new materials and products that are compatible with the environment and independent of fossil fuels. High ecological composites, known as "Green Composites" fit well within this new deals [1].

On the other hand, Wet-Laid technology is used for the development of compounds for all nonwoven fibers, which have the ability to disperse in liquids. In this regard, the main characteristics of Wet-Laid technology focus on obtaining a product with good homogeneity and high production levels. [2]

Regarding flax fiber, it is derived from a plant that grows in temperate and moderately humid as in Belgium, France, Ireland, Italy and Russia. Flax fiber with higher quality is obtained by manually processing of flax plant. Flax fiber is the strongest of the vegetable fibers, even more than cotton. These fibers are easy to fibrillate and are suitable for the production of nonwovens with resistant to wrinkling or composite materials for covering doors, car dashboards and spoilers [3].

2. EXPERIMENTAL

2.1 Materials

Flax fibers (F 513/6) used were supplied by STW Fibres (Schenkenzell, Germany). The fibers used are technical fibers (50-100 □m thickness) and elementary fibers (10 to 20 □m of thickness). High-density polyethylene (FPE 910 F) and polypropylene (PP 2.8/6) fibers used binder material in the nonwovens sheets production was also supplied by the company STW Fibres.

2.2 Fiber preparation

The fiber preparation includes a first step of separation of the fibers and a second step in which the fibers are well dispersed in the aqueous medium. This mixing is transported using hydraulic pumps to the hydroformer plant, which has been provided by the company Pill Nassvliestechnik GmbH (Reutlingen, Germany) to elaborate the nonwoven.

2.3 Non-woven processing

The nonwovens consolidation was carried in various steps as it is showed in Figure 1. First, insufflate hot air in the nonwoven, and after passing the material between two hot rollers (calender) that apply pressure and heat. Following, the materials place in a drying module to remove the moisture. The module for nonwoven drying has been provided by Talleres Tacome, S.A. (Onteniente, Spain).

The final step involves the winding to be stored until further use. The winding machine has been provided by the company Talleres Tacome, S.A.

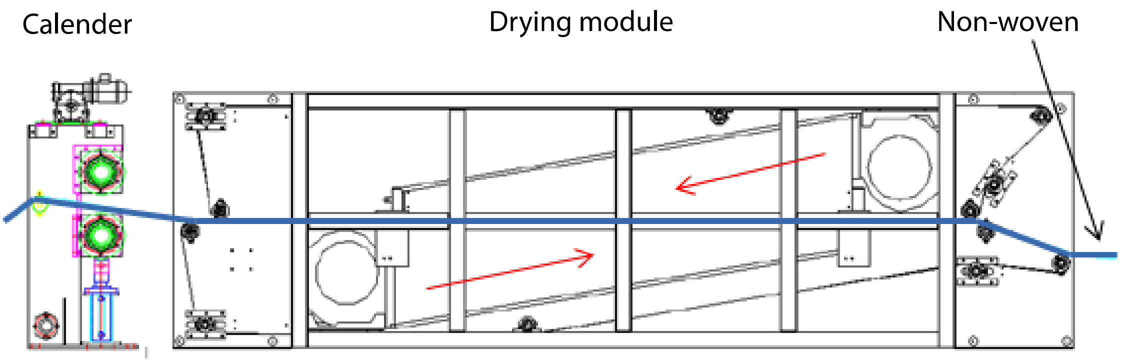


Figure 1: Scheme of thermal consolidation process of wet-laid nonwoven

2.4 Composite processing

The composite have been made by using a hot plate press applying a pressure of 1 bar for 10 min at 200 °C and 190 ° C for PP and for HDPE respectively.

2.5. Mechanical characterization

The tensile and flexure tests were carried out using a universal tensile test machine ELIB 30 (S.A.E. Ibertest, Madrid, Spain) following ISO 527 and ISO 178 respectively. A 10 mm/min crosshead speed was used to determine tensile strength. All specimens were tested at room temperature. A minimum of five samples was analyzed to obtain every result.

Impact strength was determined by using the Charpy impact machine (S.A.E. Ibertest, Madrid, Spain) according to ISO-179.

2.6. Scanning electron microscope (SEM) analysis

SEM photographs of different samples were carried out by a SEM JEOL 6300 (JEOL USA, Peabody, USA). Samples were previously coated with gold; the coating process was performed in vacuum conditions. The fracture surfaces observed were obtained in the different tensile tests at room temperature.

3. RESULTS AND DISCUSSION

3.1 Mechanical characterization

The results obtained from tensile test regarding tensile strength of the biocomposites of short flax fiber polypropylene fiber are shown in Figure 2. As it can be observed both tensile strength increases with increases in polypropylene content in the material, presenting the highest value (19.5 MPa) for 30 wt% of PP content.

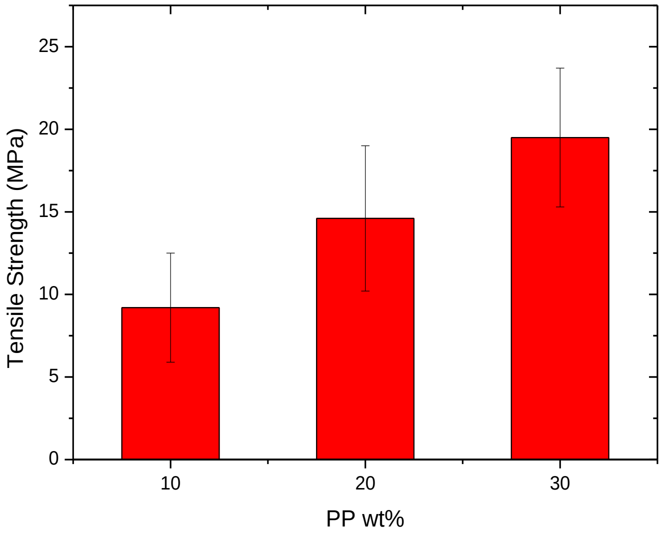


Figure 2: Variation of tensile strength of flax-PP biocomposites as a function of PP amount.

Regarding the elastic modulus, in Figure 3 it can be observed the values of these properties obtained for the different compositions of flax-PP biocomposites analyzed. Similar to tensile test, the elastic modulus increases with the PP content. So, the elastic modulus increases from 1532 MPa for biocomposites with 10 wt% of PP, to 1912 for biocomposites with 30 wt% of PP.

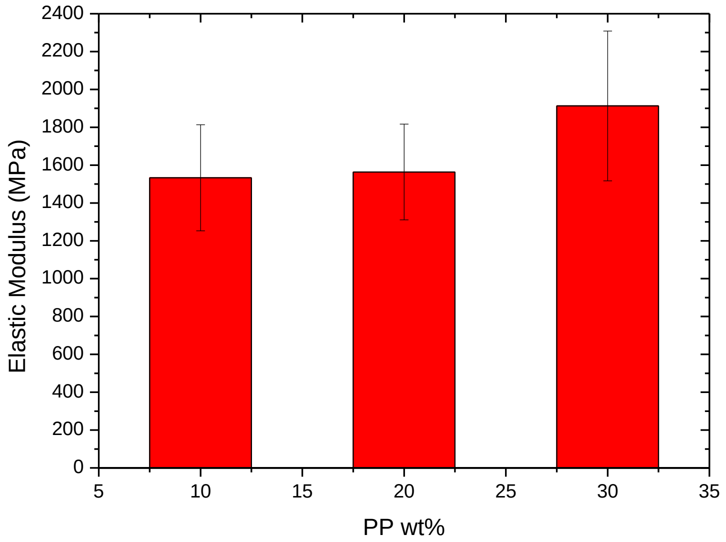


Figure 3: Variation of elastic modulus of flax-PP biocomposites as a function of PP amount.

Regarding the flexure test, the results obtained in terms of flexural strength and flexural modulus, are showed in Figure 4 and 5 respectively. The flexural strength increases as expected with the PP content, increasing from 2.1 to 3.6 MPa. However for flexural modulus, the results show a stability of this property for the different compositions of PP-biocomposite analyzed.

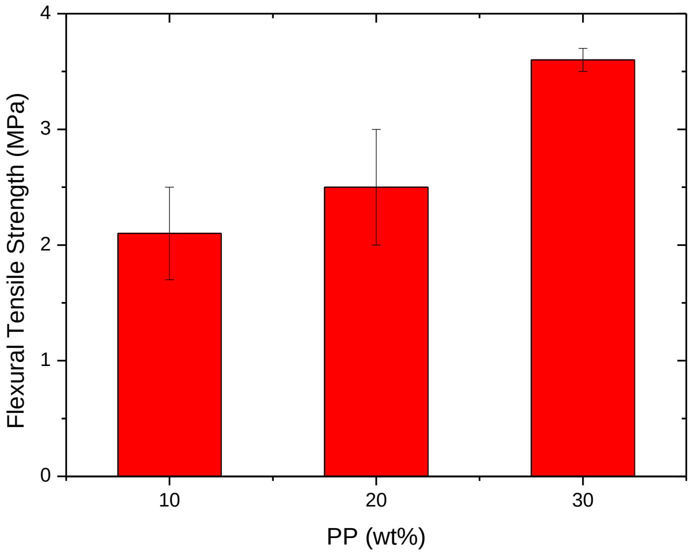


Figure 4: Variation of flexural tensile strength of flax-PP biocomposites as a function of PP amount.

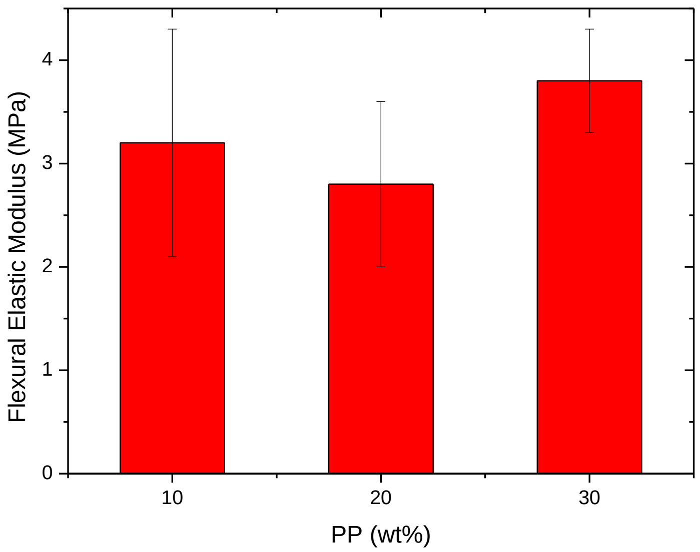


Figure 5: Variation of flexural elastic modulus of flax-PP biocomposites as a function of PP amount.

Regarding the impact behavior of biocomposite, Figure 6 shows the variation of impact strength of flax-PP biocomposites as a function of PP amount. As it can be observed, impact strength of biocomposites increases with the PP content, reaching values from 3.8 to 5 KJ/m^2. On the other hand, Figure 7 shows the variation of hardness Shore D of flax-PP biocomposites as a function of PP amount. In this case, the hardness Shore D remains practically constant from 10 to 30 wt% of PP content (Figure 7), in values in the range 60-75 shore D.

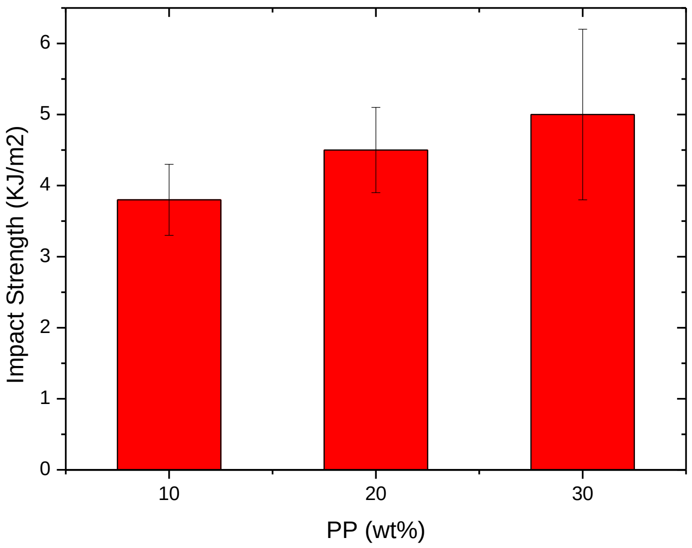


Figure 6: Variation of impact strength of flax-PP biocomposites as a function of PP amount.

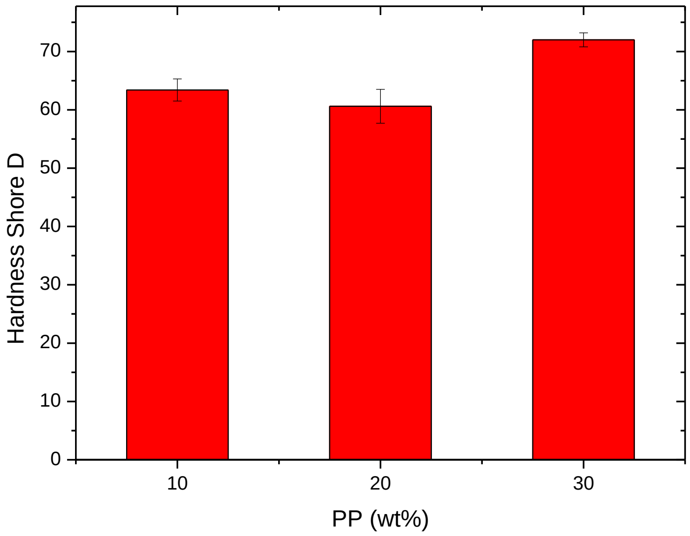


Figure 7: Variation of hardness Shore D of flax-PP biocomposites as a function of PP amount.

Regarding the mechanical characterization of composite materials with HDPE matrix and short flax fibers, Figure 8 and 9 show the variation of tensile strength and elastic modulus respectively for flax-HDPE biocomposites, as a function of HDPE content. The trend is similar to the PP-biocomposite, tensile strength and elastic modulus increase with the HDPE content, however the values obtained are higher than the previous composite. So for a 10 wt% of HDPE the tensile strength is 17.9 MPa instead of the 9.2 MPa of PP-biocomposites, and for 30 wt% of HDPE, the tensile strength reaches 27.1 MPa instead of the 19.5 MPa of PP-biocomposites. For elastic modulus the difference of values between the two types of biocomposites is lower. So for 30 wt% of HDPE, the tensile strength reaches 2439 MPa instead of the 1912 MPa of PP-biocomposites with similar PP content but for 10 wt% of HDPE, the elastic modulus is even lower than PP-biocomposites (1279 MPa and 1532 MPa respectively).

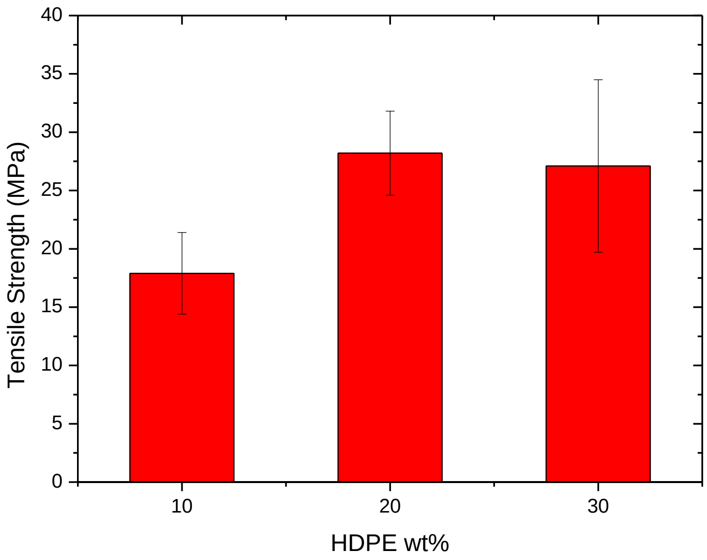


Figure 8: Variation of tensile strength of flax-HDPE biocomposites as a function of HDPE amount.

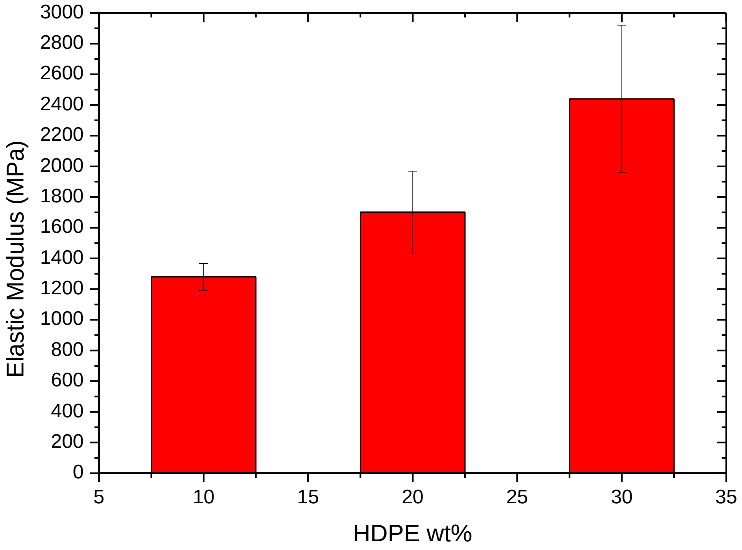


Figure 9: Variation of tensile strength of flax-HDPE biocomposites as a function of HDPE amount.

Meanwhile, the results obtained from flexure test indicate the same tendency that the obtained for PP-biocomposites (figure 8 and 9). The flexural strength increases with the HDPE content, with values from 2.4 MPa to 4.4 MPa from 10 and 30 wt% of HDPE respectively. However the flexural modulus increases for 20 wt%, but for 30 wt% decreases slowly. By this way it can be observed flexural modulus of 2.4, 5.0 and 4.6 for HDPE-biocomposites with 10, 20 and 30 wt% of HDPE respectively. In comparison with the PP-biocomposites the values obtained from flexure test show a better response to bending stresses for HDPE–biocomposites relating to PP-biocomposites.

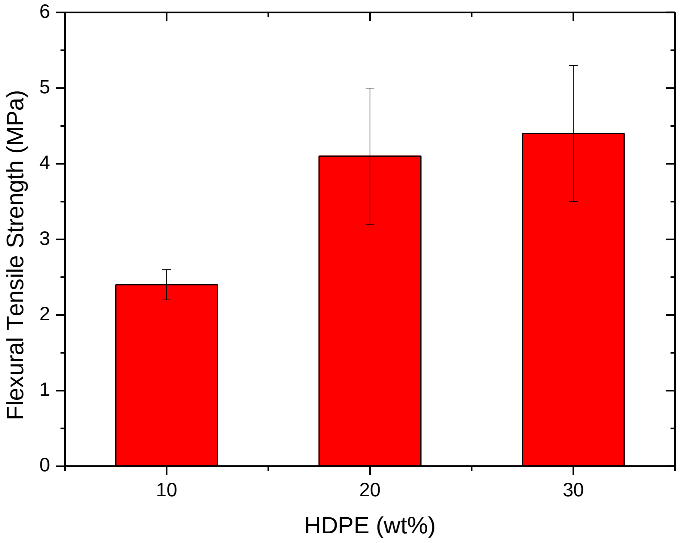


Figure 10: Variation of flexural tensile strength of flax-HDPE biocomposites as a function of HDPE amount.

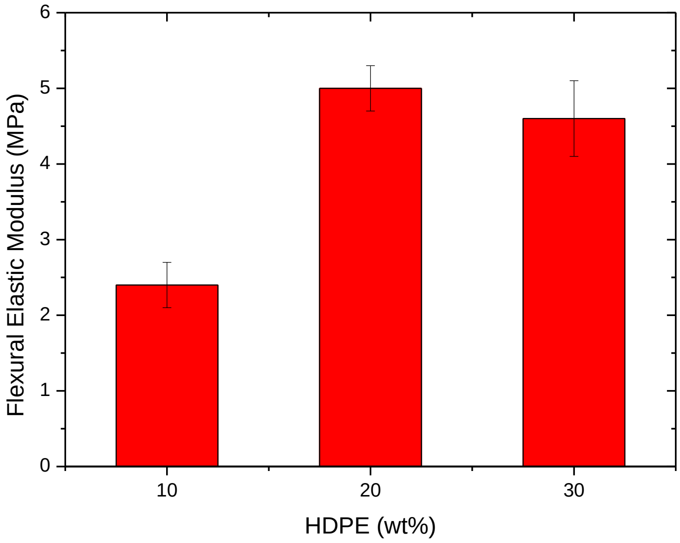


Figure 11: Variation of flexural elastic modulus of flax-HDPE biocomposites as a function of HDPE amount.

Regarding the impact behavior, Figure 12 shows the variation of impact strength of flax-HDPE biocomposites as a function of HDPE amount. As it can be observed, the impact strength decreases significantly with the HDPE content from 9.2 KJ/m^2 to 4.1 KJ/m^2 for 10 wt% and 30 wt% of HDPE respectively. In comparison with PP-biocomposites, tendency is reversed. However in all compositions, the impact strength in HDPE-biocomposites is higher than PP-biocomposites. On the other hand Figure 13 shows the variation of hardness Shore D of flax-HDPE biocomposites as a function of HDPE amount. As it can be observed, hardness Shore D remains practically constant from 10 to 30 wt% of HDPE content, in values in the range 60-70 shore D. These results are similar with the obtained for PP-biocomposites.

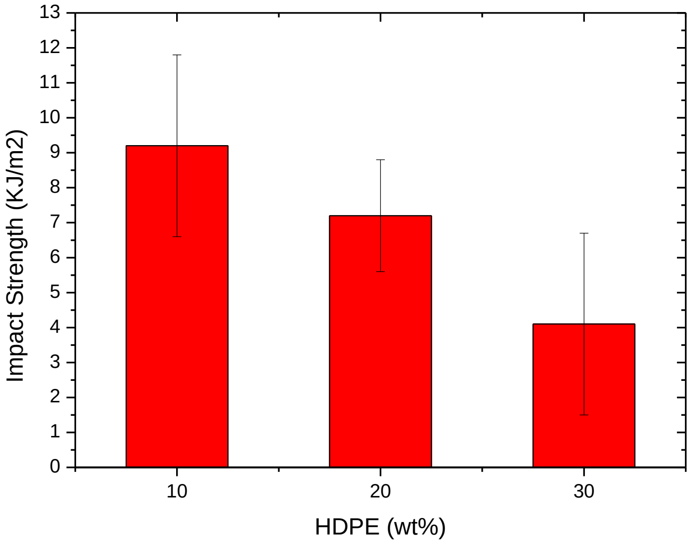


Figure 12: Variation of impact strength of flax-HDPE biocomposites as a function of HDPE amount.

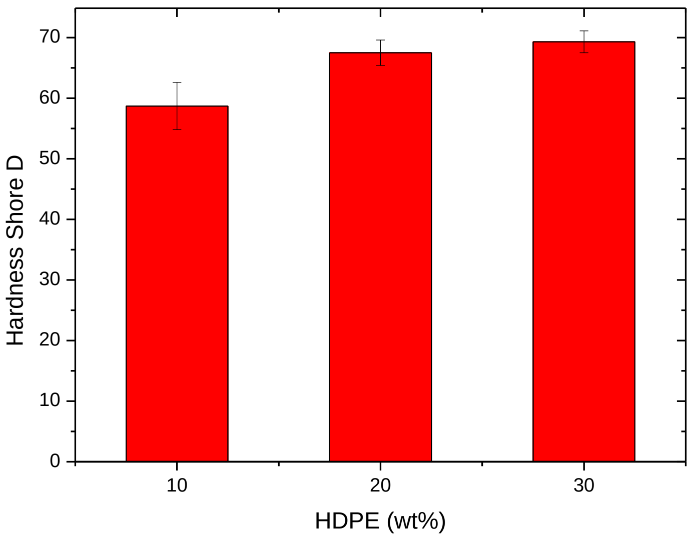
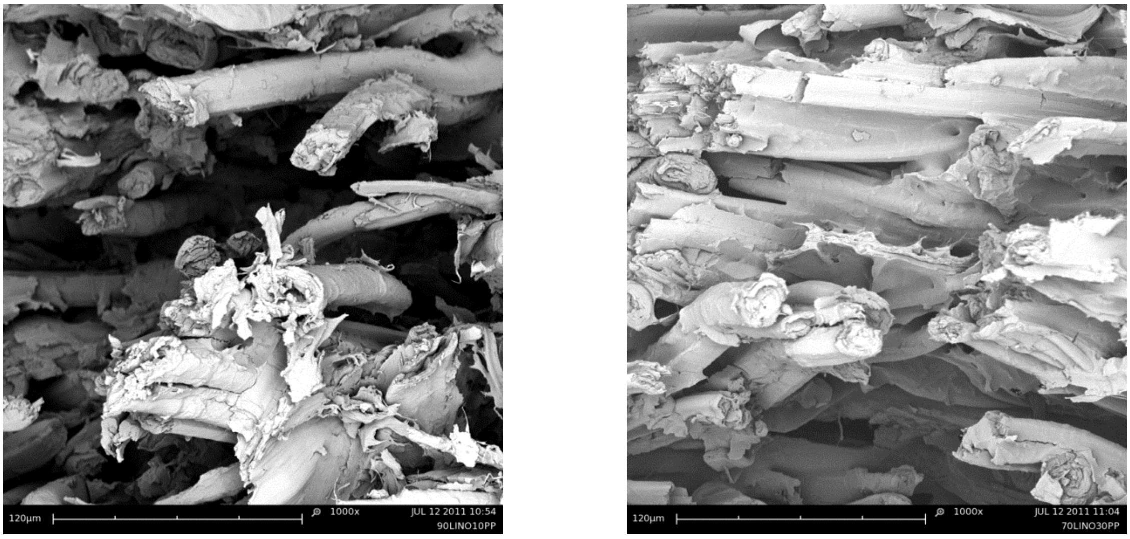


Figure 13: Variation of hardness Shore D of flax-HDPE biocomposites as a function of HDPE amount.

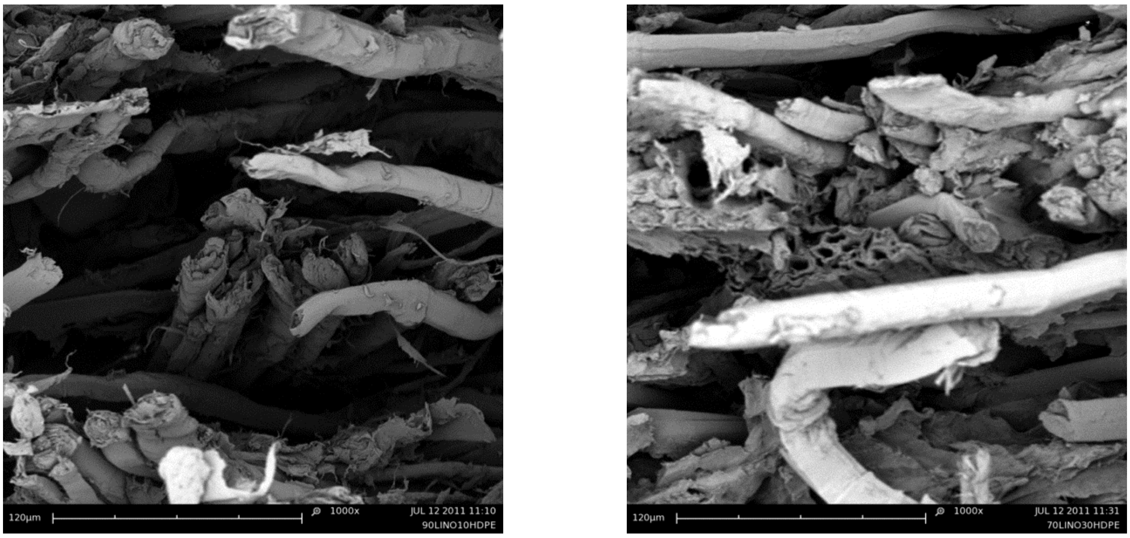
3.2 SEM analysis

Figure 14 shows the SEM micrographs of fractured surfaces of flax-PP biocomposites with different PP amount after tensile test. The images show a lack of adhesion between natural fibre and PP matrix is observed. This fact contributes in a decisive way to the fall in tensile strength and impact strength. The micrographs obtained form HDPE-biocomposites, an adhesion level matrix-fibre similar due to nature of polymers use as matrix in the biocomposites (HDPE and PP)



a)
b)

Figure 14: SEM micrographs of flax-PP biocomposites with different PP amount: a) 10 wt%; b) 30 wt%. (1000x)



a) b)

Figure 15: SEM micrographs of flax-HDPE biocomposites with different HDPE amount: a) 10 wt%; b) 30 wt%. (1000x)

4. CONCLUSIONS

It is viable to perform composites from nonwovens flax fibers with polyolefin thermoplastic as a matrix by using the wet-laid technique and subsequent thermocompression. By wet-laid technique it is possible to use waste or other material “biobased” in the form of short fibers or particles for processing biocomposites. The lack of adhesion between natural fibre and polymer matrix contributes in a decisive way to not achieve higher values of tensile strength and impact strength Although the mechanical properties of the biocomposites resulting are not excellent, they are sufficient for many applications such as thermal or acoustic insulation or as elements in furniture that do not need to support high loads as separators desks or shelves separators.

ACKNOWLEDGEMENTS

Authors thank to “Ministerio de Ciencia e Innovación” ref: IPT-310000-2010-037 “ECOTEXCOMP: Investigación y desarrollo de estructuras textiles aplicables como refuerzo de materiales compuestos de marcado carácter ecológico” for the financial support.

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DYEING OF WOOL WITH PEGANUM HARMALA SEED EXTRACT IMPROVED BY METAL MORDANTS AND PLASMA TREATMENT

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Keywords: Natural dye, Plasma, Harmala, Dyeability

Abstract. *In this study, the aqueous extract of* ***Peganum Harmala*** *seeds was used to dye wool fibers. To improve the dyeability of the fibers and reduce the dyeing temperature, low temperature plasma as an environmentally friendly pretreatment, was employed. Oxygen was used as plasma treatment gas. The effects of plasma treatment and several metal mordants including alum, copper sulfate and potassium dichromate on the dyeability of wool fibers were studied. Both pre-mordanting and plasma treatment improved the absorption of the dyes onto wool fibers. Compared to untreated and pre-mordanted samples, plasma treated wool showed better dyeability.*

1 INTRODUCTION

Since ancient times, natural dyes have been used for many purposes, such as the dyeing of textiles. The use of natural dyes to in textile industry declined rapidly after the discovery of synthetic dyes by Perkin in 1856. Synthetic dyes reign in the textile industry because of their low cost and brilliance while possessing excellent desirable properties, variety and ease of application. Recently, an international awareness of environment, ecology and pollution control created new interest in using natural dyes. Many researchers have studied various aspects of natural dyeing [1-4].

Generally, the number of suitable natural dyes is limited and the procedure of natural dyeing is complicated and the dyeing yield is low for most natural dyes. Nowadays, there is a need for discovering technically and commercially new processes and alternative natural dye sources. The new interest has highlighted a need for research to accommodate natural dyes in the present industrial scenario [2].

Usually, there are some problems in dyeing with natural dyes, such as low exhaustion of dyes and poor fastness of dyed fabrics. Attempts to overcome these problems have mainly focused on the use of metallic salts as mordants, which are traditionally used to improve fastness properties or exhaustion and to achieve different shades with the same dye [5].

Plasma technology is well known for imparting functional finishes to textile materials without the use of harmful and pollutant chemicals or water. Some of the functionalities achieved by plasma treatment of fibers include altered moisture relations (absorbance or repellence), anti-microbial, soil repellence, stain resistance, soft handle and improved dyeing properties. This variety is possible by altering process parameters such as supply frequency, discharge power, treatment time, type and pressure of the processing gas [2,6].

The surface of wool fiber plays a critical role in wool processing, particularly with respect to dye uptake. Removal of the surface lipid layer results in improvement of polymer adhesion and dye uptake [4].

Plasma treatment has been found to modify the lipid layer and surface cuticle of wool without affecting its bulk properties. The treatment improved wettability and increased dye uptake, leading to an enhancement in the depth of shade and evenness [4,6]. It has also been suggested that the dye hydrophilic nature is a deciding factor for this improvement [2].

Peganum Harmala is a wilding plant native from the eastern Iranian region. In this study, the aqueous extract of *Peganum Harmala* seeds was considered as a new source of low cost natural dye. The ability of this natural dye for coloration of wool fibers was studied. The effect of pre-mordanting with various metal mordants on the color strength of the dyed samples was investigated. Plasma treatment was applied as a preparation process and its effect on the exhaustion of the dye on wool fibers was studied.

2 EXPERIMENTAL

2.1 Materials

All chemicals used in this study were of analytical grade and purchased from Merck. Distilled water was used throughout the work. Woolen fabric (Plain weave, Area weight: 262 g/m^2, Warp density: 20 count/cm, Weft density: 17 count/cm, Yarn fineness (Nm): 48/2) was supplied by Iran Merinos Co. (Iran). In order to remove any impurities from the fabric, the samples were scoured in a solution containing 1 g/l of a nonionic detergent, Ultravon GPN (Ciba) for 30 min at 50 °C (L:G = 40:1), then rinsed with tap water and dried at 25 °C.

Peganum harmala seeds were grinded to a fine powder. To prepare the original solution of the dye, each 100 gram of powder was added to 1 liter of distilled water and boiled for 2 hours and then filtered. Before filtration, the volume of the solution was adjusted to the initial amount by adding distilled water. The concentration of the resultant solution is 10% W/V.

2.2. Methods

Plasma Treatment: The woolen fabric samples were pretreated using radio frequency (13.56 MHz) low pressure plasma equipment (model: Junior plasma, Europlasma, Belgium) with oxygen gas. The sample chamber was evacuated to 100 mTor and maintained at this pressure during process. Then, oxygen was introduced with a flow rate of 20 sccm (Standard Cubic Centimeters per Minute). Plasma was generated at 100 W for five minutes. After that, air was introduced into the chamber and the plasma treated sample was removed.

Mordanting: in case of samples which need to be mordanted, pre-mordanting was performed using the different metallic salts including alum, copper sulfate and potassium dichromate. The wool samples were mordanted at 80 °C, pH=5 and L:G= 40:1, for 45 minutes.

Dyeing: The appropriate volume of original dye solution was mixed with distilled water (if necessary) for dyeing of the samples (L:G= 40:1). The pH value of the dyebath was adjusted on 5 to 9 using small amounts of acetic acid or sodium carbonate 1% W/V solutions. The dyeing was started at 40°C and the temperature was raised to final temperature (60 or 100 °C) at the rate of 2°C per minute. Then the samples remained in that condition for 1 hour, then rinsed and air dried. All mordanting and dyeing processes were carried out using a laboratory dyeing machine made by Rissanj co.-Iran.

Color measurements: the reflectance of dyed samples were measured on a Color-eye 7000A spectrophotometer using illuminant D65 and 10°standard observer. Color strength (K/S) of each dyed sample was calculated using kubelka-munk equation:

$$K/S = (1-R)^2/2R \qquad (1)$$

Where R is the observed reflectance, K is the absorption coefficient and S is the light scattering coefficient.

3. RESULTS AND DISCUSSION

Five samples were dyed at pH=5 (as most of dyeing recipes for natural dyes) using different amounts of the dye without using any mordant.

Figure 1 shows the effect of initial dye concentration on the color strength of the dyed samples. It is evident that the color strength of dyed samples increased with the increase in the initial dye concentration and this natural dye showed a good dyeing build up.

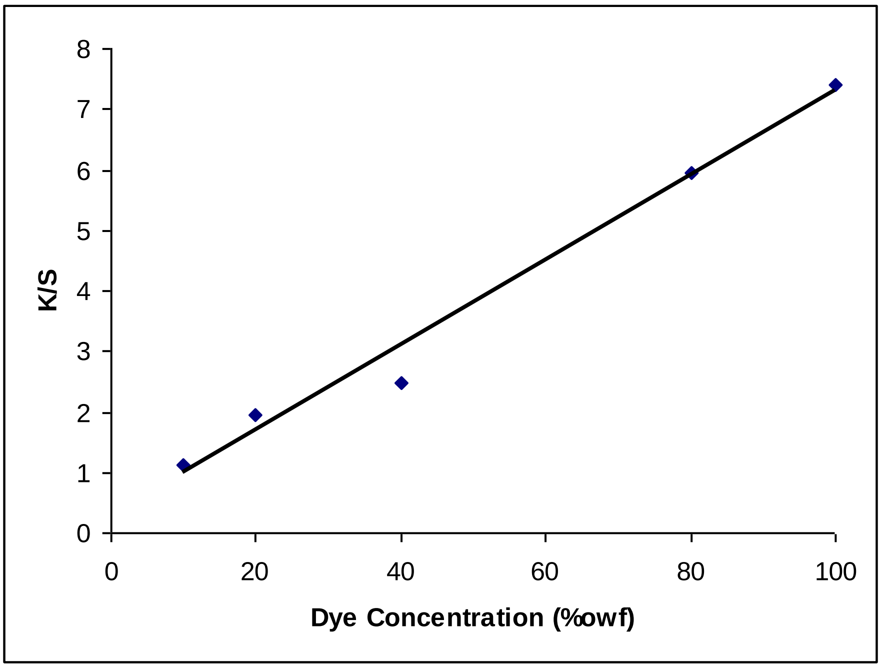

Figure 1: The effect of initial dye concentration on the color strength of the dyed samples (pH=5, L:G= 40:1, 1 hr at 100 °C)

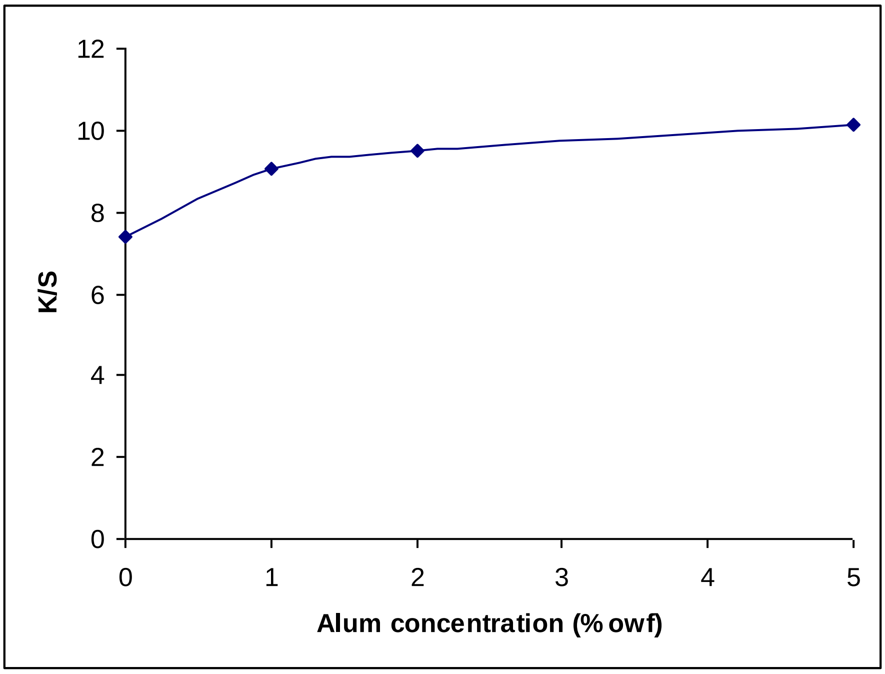

Figure 2: The effect of alum mordant on color strength of dyed samples (100 % owf dye, pH=5, L:G= 40:1, 1 hr at 100 °C)

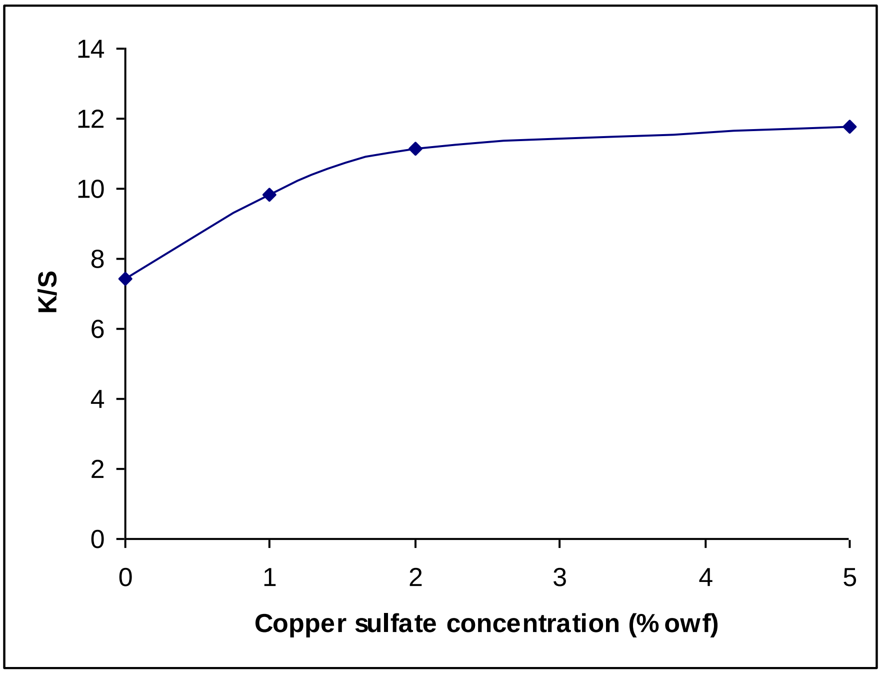

Figure 3: The effect of copper sulfate mordant on color strength of dyed samples (100 % owf dye, pH=5, L:G= 40:1, 1 hr at 100 °C)

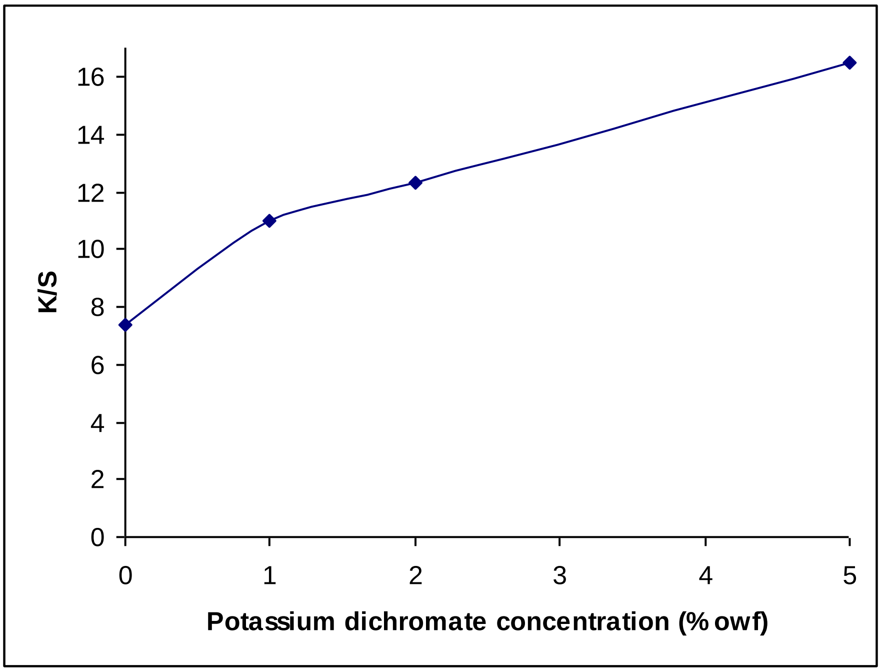

Figure 4: The effect of potassium dichromate mordant on color strength of dyed samples (100 % owf dye, pH=5, L:G= 40:1, 1 hr at 100 °C)

Three mordants were applied on woolen samples before dyeing and the effect of mordanting on the absorption of the dye was studied. As shown in figures 2, 3 and 4, pre-mordanting with all mordants increased the color strength of the dyed samples and the K/S values showed increasing trends with increasing the amount of the applied mordant. Because the graph of K/S against mordant concentration reached a plateau between 4-5 % owf for alum and copper sulfate mordants, the use of higher amounts of mordants is not necessary and the rest of the experiments are conducted using 5 % owf of alum mordant.

Figure 5 shows the effect of pH of the dyebath on the color strength of samples pre-mordanted with 5 % owf alum. The color strengths of the samples were higher at higher pH values. Figure 6 shows the chemical structures of the main alkaloids of *Peganum harmala* seeds. These alkaloids have N atoms in their structures which can gain positive charge in water. In alkaline conditions, wool fiber gains more negative charges (COO^-) and can absorb more positively charged alkaloids. So the color strength increased in alkali medium [7].

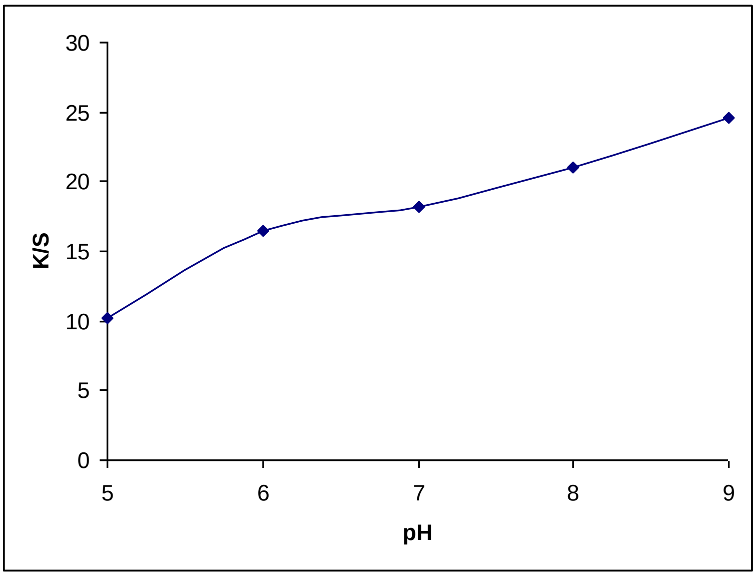

Figure 5: the effect of pH of dyeing bath on the color strength of samples pre-mordanted with 5 % owf alum (100 % owf dye, L:G= 40:1, 1 hr at 100 °C).

To find out the effect of plasma treatment of wool fibers on absorption of this dye, dyeings were performed at two different pH values (5 and 9) on alum mordanted and non-mordanted samples. Table 1 shows that pre-mordanting with alum has different effects on the color strength of samples at different pH values. As shown in figure 2, pre-mordanting with alum has positive effect on color strength of samples dyed at acidic condition (pH=5). When comparing samples A and D, B and C or G and H, it is found that, pre-mordanting with alum has inverse effect on the color strength of samples dyed at pH=9 (with or without plasma treatment).

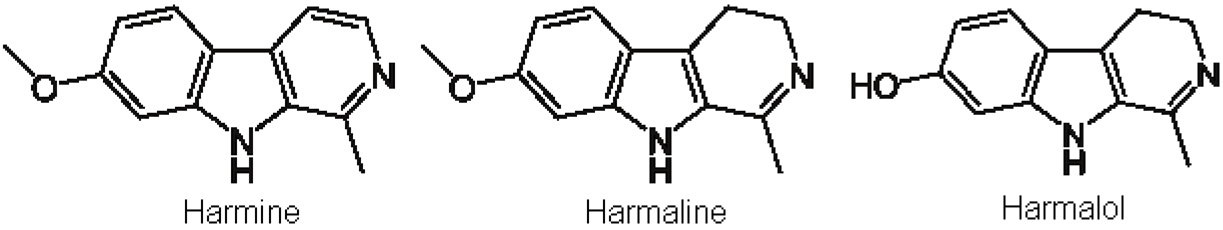

Figure 6: Chemical structure of main alkaloids present in *Peganum harmala* seeds

Comparing samples "A and B or C and D", "E and F" and "G and H", shows the effect of plasma treatment on color strengths of samples dyed with or without pre-mordanting, at alkaline or acidic pH and at 60 or 100 °C respectively. In all cases plasma treatment showed a remarkable increasing effect on the color strength of dyed samples.

Also when comparing the samples A and H it can be found that the sample plasma treated and dyed without mordanting at 60 °C showed higher color strength value than the sample dyed at 100 °C after mordanting but without plasma treatment.

Plasma treatment has destroyed the surface lipid layer (scales) of the wool fibers which acts as a barrier for penetration of dye molecules into the fibers. This can lead to increase the dye penetration into the fibers and lower the dyeing temperature compared to untreated samples [4].

Table 1: The effect of plasma treatment on dye absorption

Sample code	Temperature (°C)	Alum (5 % owf)	Plasma	pH	K/S
A	100	*	-	9	24.65
B	100	*	*	9	27.43
C	100	-	*	9	34.32
D	100	-	-	9	26.58
E	100	*	-	5	10.15
F	100	*	*	5	15.34
G	60	*	*	9	26.49
H	60	-	*	9	28.12

4. CONCLUSION

In this study, the aqueous extract of the seeds of *Peganum Harmala* was used as a natural dye for dyeing of wool. It showed good dyeing properties and build up on wool fiber. Pre-mordanting with alum, copper sulfate and potassium dichromate increased the K/S values of samples dyed at pH=5. Plasma treatment prior to dyeing was highly effective for increasing the penetration of the dye molecules into the fibers.

It can be concluded that plasma pre-treatment as mentioned in this paper can be a suitable alternative for the conventional mordanting process in natural dyeing, resulting in comparable K/S results at lower dyeing temperatures, without using toxic mordants.

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DETERMINING OF ENERGY CONSUMPTION PERFORMANCE OF EXPERIMENTAL OPEN LOOP ADSORPTION SYSTEM FOR TEXTILE DRYING PROCESSES

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Keywords: Textile drying, zeolite, energy.

Abstract. *Drying is a very broad subject and consists of an extremely energy-intensive process[1]. The results of conventional methods are not enough effective that increase energy efficiency. One of the biggest factors that increase the energy consumption of drying processes is latent heat [2]. The zeolite mineral used as natural and synthetic, has a very important role among industrial raw materials because of their crystal structure and chemical properties. Due to micro porous crystal structure of zeolites, they have a good adsorption characteristics enough not to compare with other adsorbent materials. Zeolites give adsorption heat while taking moisture in the air depend on temperature, and when they are heated they give the moisture back. We can benefit them as heat and moisture changer because of these characteristics. In this study, an experimental open loop adsorption system for textile drying processes were compared with the conventional drying system that used electric energy. The open-loop drying system was designed using synthetic zeolite (molecular sieve) bed. Adsorbent and adsorbate pair are synthetic zeolite and water. This system leads to the removes of moisture in humid air and adsorption energy warms up process air. [2,3,4]. For drying of a textile material, electric energy source and zeolite bed were separately and together used and energy consumption performances were measured.*

1. INTRODUCTION

Zeolites can perform adsorbtion/desorption thousands times [5]. High water uptake capacity, adsorption energy, long life and non-toxic properties of zeolites can be an alternative for textile drying systems [2,3]. For the heating application the sorption system is operated as a thermal driven heat pump. The desorption energy Q_{des} is the driving force, whereas condensation and adsorption energy Q_{cond} and Q_{ads} can be used for heating purposes. The energy of evaporation Q_{evap}, which could be waste heat at low temperature, is necessary if the humidity ratio of the air is too low for the adsorption process [see Fig 1.]. As an example, a gas fired adsorption heat pump in conjunction with solar collector for heating was developed [3,6]. At basically; the adsorption systems, provides dry and hot air and at same time gives thermal energy. Textile materials are dried with the conventional methods by using hot air. The hot air that used at during drying process are heated by electric or steam sources. By increasing of water content per mass of drying process air decreases drying capacity [2,3,4]. This problem is solved either taking the fresh air or condensing water vapor in the air. Experimental drying system was designed for this problem and the humidity of drying air was controlled by the zeolite bed [2,4].

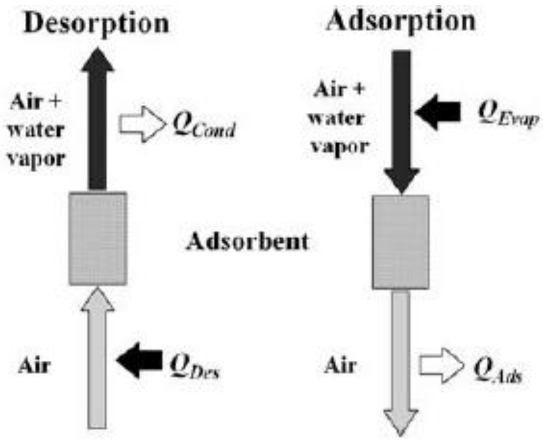
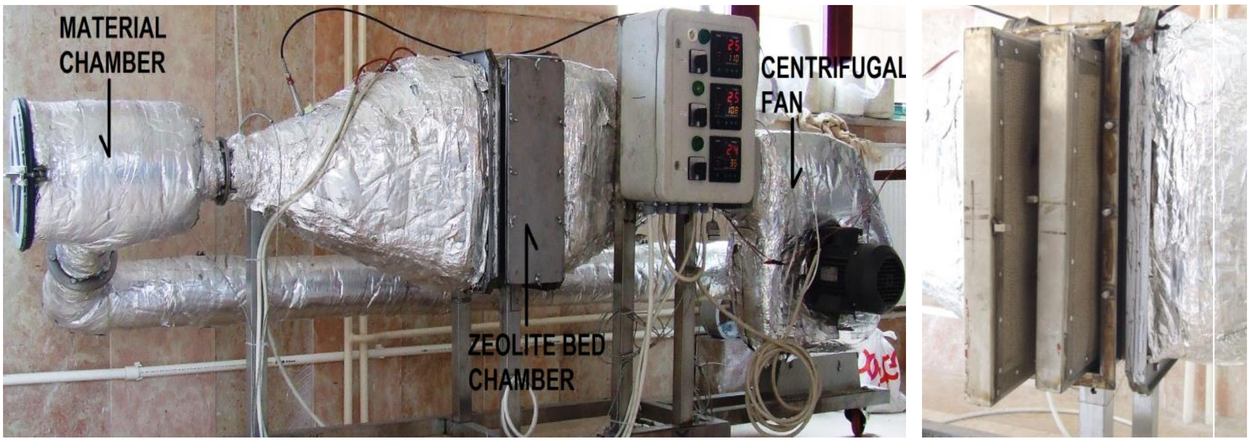


Figure 1. Adsorption-desorption system (heat and mass fluxes) [3]

Some previous studies similar to this study, the zeolite drying beds could be used in textile products. Unlike previous studies, this study examined the performance of open loop drying [2, 4].

2. MATERIAL AND METHODS

The experimental drying system was designed in open loop and was isolated for heat fluxes [see Fig 2a]. The adsorbent and adsorbate pair is water and synthetic zeolite granules (Z10-01) with 2.5-5 mm diameters. The zeolite granules of homogeneously mixed were placed inside of special bed. The centrifugal fan was used for circulation of the drying air in the open loop (by-pass ratio %20). [see Fig 1a]. The average velocity of drying air that perpendicular to the surface of the zeolite bed is 0.8 m/s. Mass of active zeolite for per bed is 4000 g. [see Fig 2b]. Zeolite granules (Z10-01) can absorb the water up to 30% by weight. Electrical heating elements for heating of the drying air were placed into the test system. The control of heating elements was done with a PI thermostat.



(a) (b)

Figure 2. Experimental adsorption system for drying of textile materials [1]

Two different experimental methods were applied in this study. The content of two methods; at first one, the fresh and waste air valves were opened fully, for the second one close loop circuit of experimental system was closed. Thus, %20 inner loop air and 80 % fresh air were circulated. The main parts and main measurement points of the experimental drying system were given below [see Fig 3].

At first method; only electrical heat source was used. The zeolite bed that saturated with water moist was mounted inside of open drying loop. So that the resistance of the air is equal to the second experimental conditions were provided.

At second method; a active zeolite bed that applied desorption process at oven was used. As external heat source, both of them electrical energy and adsorption energy of zeolite bed were used.

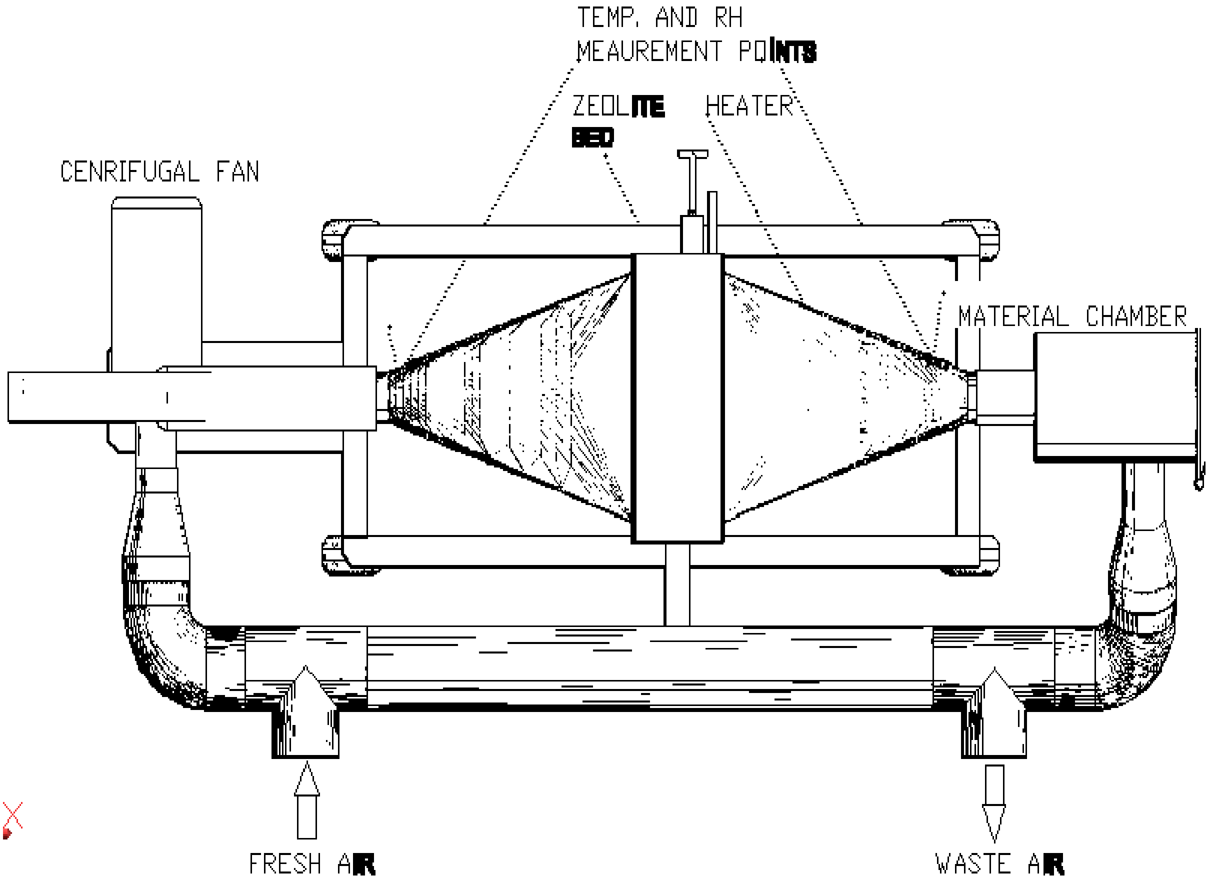


Figure 3. The main parts of experimental drying system

Inlet-outlet temperatures (wet bulb, dry bulb) and relative humidity of drying air and electrical power consumption of heaters were measured and data was transported to a computer by data-logger [see Fig 4].

Figure 4:Data acquisition and evaluation equipment

The USA cotton was chosen to be used for drying. The scouring of cotton and washing treatment procedure were performed. For drying test, 90 g of dry cotton moistened with 400 g of demineralized water and replaced material chamber [see Fig 5]. Both of them were lasted 30 min.

Figure 5. The moistened cotton in the material chamber

Zeolite beds in a furnace were used to perform the desorption process. The adsorbed zeolite bed was desorbed during 40 minutes in a drying oven at 300^{o}C for second experiment. The air in the oven was circulated with a fan for homogenous desorption. The desorption level of the zeolite bed was measured with bed weight by a load cell that mounted on the oven [see Fig 6].

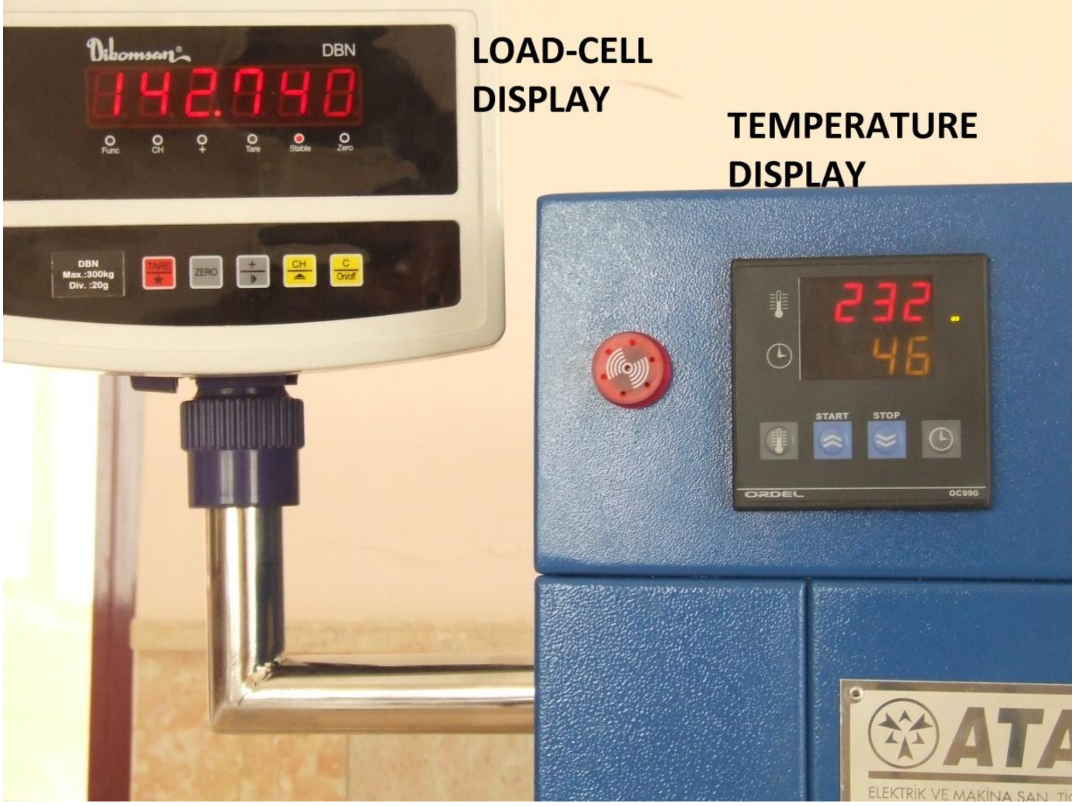


Figure 6. Desorption oven

3. RESULTS

Two different energy sources were used for the experiments. At the first method; electric heater was used as heat source. At the second method; zeolite bed and electrical heater were used. The bed provided more efficient drying performance and led to significant reduction in the energy consumption with energy. Each experiment was lasted for 30 minutes.

At the first experiment, electrical energy consumption of the heater was measured 0.950 kWh.

After drying, 26 g of water content were measured in the cotton fiber. The average input-output temperatures and the average input-output relative humidity of drying air were calculated 119.1 ^{o}C (T_{in1}) and 83.6 ^{o}C (T_{out1}), %4.1 (RH_{in1}) and %1.1 (RH_{out1}) as a result of experiment data [see Fig 7,8].

At the second method; Zeolite bed slowly adsorbed moisture from process air according to fully closed system [2] and released heat. After drying, 2 g of water was found in cotton. Electrical energy consumption of the heater was measured 0.845 kWh. The average input-output temperatures and the average input-output relative humidity of drying air were calculated 116.7^{o}C (T_{in2}) and 78.8 ^{o}C (T_{out2}), %3.5 (RH_{in2}) and 0.8 % (RH_{out2}) as a result of experiment data [see Fig 7, 8].

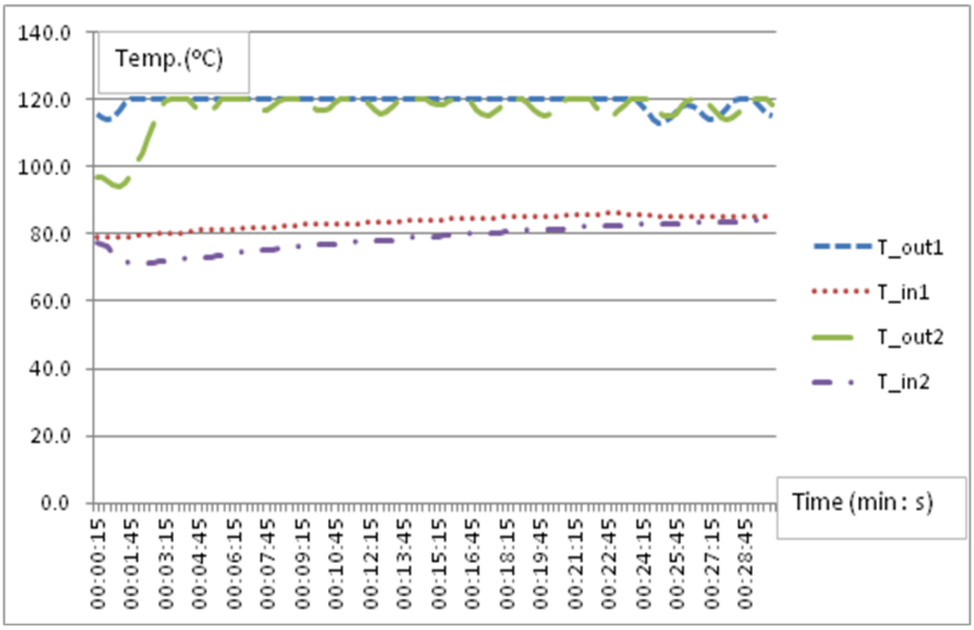


Figure 7. Results of temperature

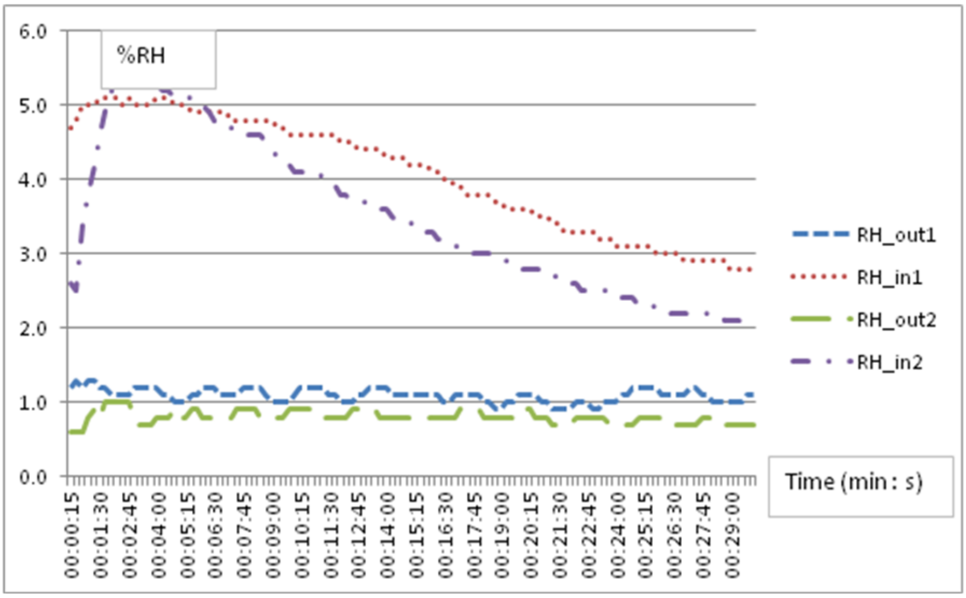


Figure 8. Results of relative humidity

4. CONCLUSIONS

The convective textile drying process for ideal drying conditions was examined with two different methods. The moistened textile material was used for drying at the first and the second methods. Both of them of two methods were used for removing the moisture from the drying air. The zeolite bed performed two functions as a result of dehumidification-heat source. The hot and moist air obtained as a result of desorption of the zeolite bed can be transferred to the wet textile processes for saving of energy.

According to the first test, energy was consumed less than %11 in the second test. In the second test, for every 90 g dry cotton, extra 24 g drying performance was obtained. Due to large amount of outdoor air in the system, the performance of the zeolite beds was decreased. The low relative humidity of the drying air was the result of this state.

In the second experiment, the average relative humidity of the resulting output was less than 15% when it was compared to the first experiment. This situation was due to the zeolite bed. However, the increase in the percentage of outside air has reduced the bed performance. This closed-loop experiment showed impact of the relative humidity on the performance of zeolite bed. When it is compared with previous study which has same experiment conditions (but different with used closed loop system), the zeolite beds showed better performance [see Fig 9].

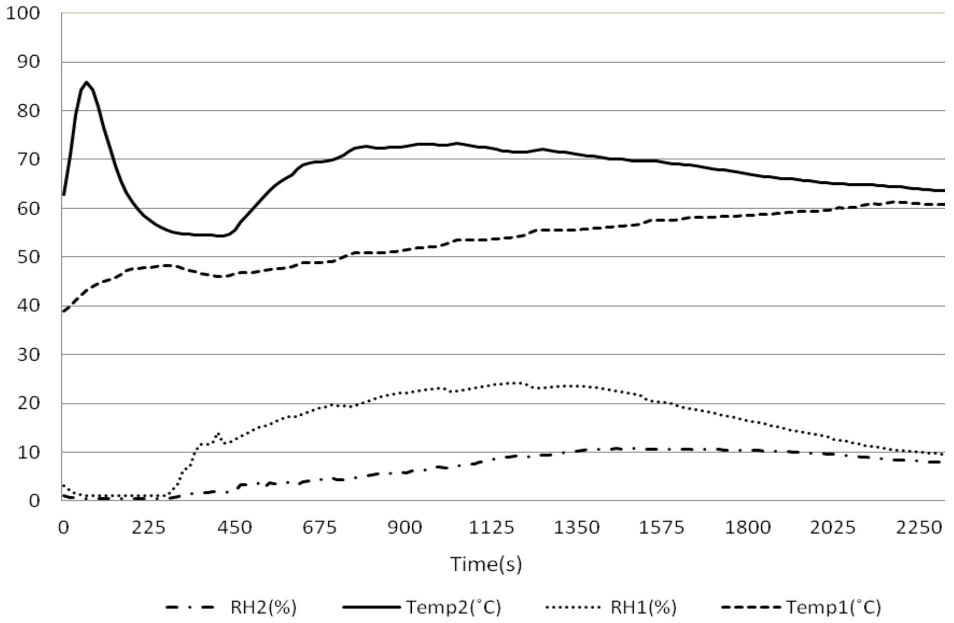


Figure 9. Results of temperature and relative humidity

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OVERTIME WORK CONCEPT IN THE READY TO WEAR INDUSTRY AND ANALYS OF COMPANY'S EFFECTS OF PRODUCTIVITY

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Keywords: Ready to Wear, Overtime, Business Productivity

Abstract. *In today's competitive environment, for garment companies, it is not possible to gain a competitive advantage with cheap labor. Companies thinks that an advantage can be gained by increasing working hours for closing the differences. In this article, the effects of overtime work are studied for efficiently.*

In this study, garments companies, which are operating in Bursa, was being analyzed. 300 employees, which work for five of these garments companies, were interviewed to determine the causes and the effects of overtime and impacts of overtime on operational efficiency by using a program named Microsoft Excel.

It should not be forgotten that, workers that have a job in the companies also a social being and they have own presence. Loophole in the law is exploited for this situation and it is seem that workers have not know their rights very well. It must be known that, the system with overtime work; unfavorable for productivity, increases faulty product rates and decreases the motion of dependence for the company.

If companies wants to improve potential of production and depending on that, wants to improve profit rates, they have not to decide working hours without workers want.

1. Introduction: Concept of Labour

The Labour is a set of actions that are inevitable and a recurring to individuals maintain their lives and individuals in essence benefit from that actions variety of way.
In modern societies, "labour" is one of the most basic and the most important activities for human beings. This concept has explained the meaning with the beginning of industrial revolution, the activity that slaves have to do until that day, has become an activity in order to sustain lives of people. The labour is a concept ranging the meaning from the various viewpoints. These meanings are as follows;

- The labour is a phase of the production process (Each labour creates tangible thing)
- The labour is a way to earn an income.
- Working is an element of prestige. (Anyone who works gets the prestige and status of to produce something.) [1]

2. Concept of Shift and Overtime

Shift means, that working, showing to effort or to perform an activity in a certain period of time. At the beginning of 20th century the workers have been achieved the limitation of working hours as 8 hours in a day in many civilized countries. [3]

On the contrary, overtime is increasing the duration of the normal working hours to fit urgent jobs. According to clause 63 of maximum working time is 45 hours per week and unless otherwise agreed this duration may be divided equally to working days of the week. Unlike the former provisions in the Turkish Labour Legislation number 1475, to apply as dividing equally the weekly working times to the days of the week removed from legislation, and bring flexibility to this rule, distribution of the normal weekly working time to the days of the week agreements in a different way has been recognized. [7]

The workers can be worked more for reasons such as the general benefits of the country, nature of the work or the increasing of production outside the daily work period provided by law. The protection of the health and safety of workers is closely related to public order, [2]

Overtime requires the presence of limited working hours. Developments have followed each other about limitation of working times and the recognition of resting rights of employees.

Approval of worker should be obtained for overtime and working extra hours. (Turkish Labour Legislation, clause 41/7). At the beginning of each year this approval of worker is received as written and stored in the employee personnel file by the employer need overtime and working extra hours. (Regulation of overtime and working extra hours on Turkish Labour Law, clause 9/2).

The sum of working extra time cannot exceed 270 hours in one year. (Turkish Labour Legislation, clause, 41/8,45; Regulation of overtime and working extra hours on Turkish Labour Law, clause 5). Worker's daily working time must not exceed 11 hours.

The wages for each overtime paid per hour by raising the amount of wages fifty percent of normal operation. (Turkish Labour Legislation, clause, 41/1). Working extra hours, wage will be paid for each working extra hours will be charged by increasing the amount of twenty-five percent normal working hours per hour. (Turkish Labour Legislation, clause, 41/3). [3]

2.1. Why overtime is required and is overtime efficient?

Low productivity, weakness of planning and insufficient time control requires overtime for enterprises. In addition to this enterprises which effective time management have not became a part of the corporate culture, unfortunately see the overtime as necessity.

Researches presents that if the quantity increases, quality decreases. When the working hours increases the worker performance decreases, finally the employer, employee and the client cannot satisfy.

Compelling degree of working times for employees causes such as problems:

- Performance decrease
- Distractibility
- Increasing the probability of failure

- Creativity decrease
- Alienation themselves, their colleagues, work and product that create
- Motivation reduction
- Unwillingness to work
- Disregard of private life and social life
- Prevention of personal development [6]

2.2. Productivity of Enterprises

One of the key concepts that will solve the economic problems of the contemporary world is “productivity”. Also the productivity is the driving force of the development. Increased productivity speeds up the development and takes it to more advanced dimensions under a rationalist and contemporary administration.

In technical terms, “productivity” is defined as the ratio between the amount of the goods & services produced and the input used for producing the said goods & services, and this measurement is generally formulized as output/input.

The productivity definition which is popularly accepted in recent years is considered together with increasing the quality of the goods and services produced, preservation of the environment and the natural structure, providing the best living and working conditions for employees, and the efforts to increase the amount of production per unit of input. [8]

The organization of working time have a great importance in terms of the enterprises. The impact of working time to cost and productivity necessitate workers have to worked with worker hours program that meet the needs of enterprises. Enterprises have to make production planning reacting to changes and development in time. Workers operate in accordance with this production plan. For this reason, need to change of working times from classic shift concept to "flexible" concept integrated have emerged. “Flexible working” concept has been established as a bit of necessity in the Turkish Labour Legislation with the effect of international developments. [4]

Increase of real productivity cannot be achieved more and harder working, because working harder does not benefit efficiency more than a very limited value depending on the physical limits of human beings.[5]

3. Research Methodology

3.1. Research Objective

This research in ready-to-wear companies to reveal the effects of the efficiency of the concept of overtime and apparel companies in order to provide recommendations were made.

For this research it has been contacted located within the city limits Bursa and Tekirdağ which are manufacturing firms engaged in exporting in garment industry and production personnel working directly with the questionnaire. Surveys’ education backgrounds are over secondary education and they work in production, model shop, storage, refectory and human research deparments.

3.2. Research Methods

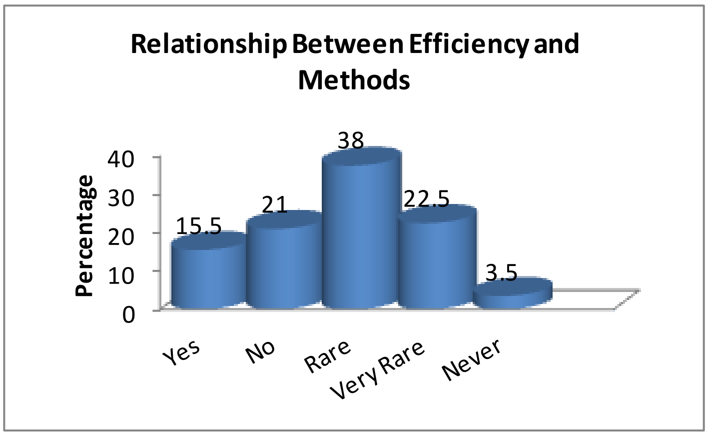
The survey consists of two parts. The first section to recognize the demographic characteristics of the participants and the second section for participants are asked to answer the questions. The questionnaire contains 20 questions and is answered by 200 participants. The survey results were evaluated in Microsoft Excel programme. In this study, regarding to the employees' answers to questionnaires we tried quantify the relationship between these major topics:

1. Activities and methods to increase the detection efficiency,
2. Working hours and preventive actions,
3. How often implemented in overtime,
4. Relationships with other components of working hours (Season, transporting, meal etc.),
5. Analysis of the causes and the need for overtime,
6. Whatever your working hours,
7. Efficiency effects of overtime.

3.3. Research Findings and Analysis Studies

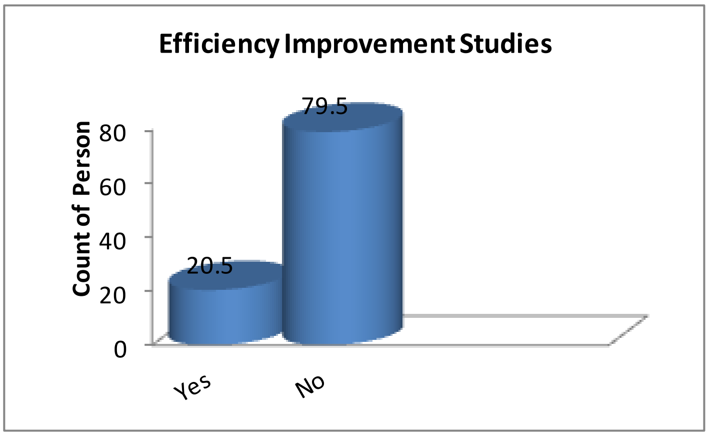
Applied to the interpretation of the findings of surveys are shown in the graphs below.

Graphic 1



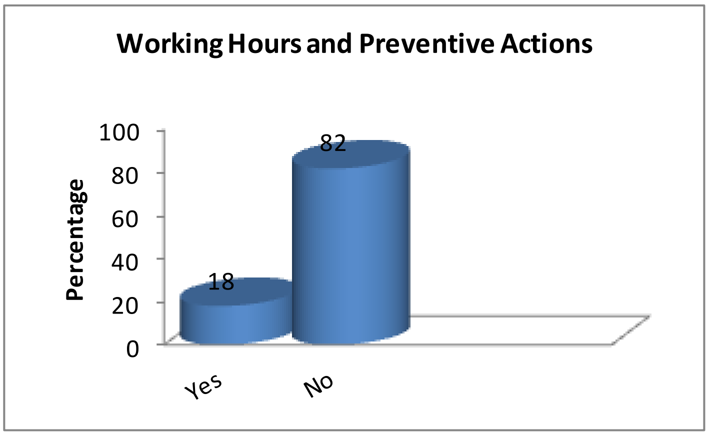
- In Graph 1, 38% of those surveyed are rarely used to increase the efficiency of workplace practices. %47 of those think that it is very rarely or not.

Graphic 2



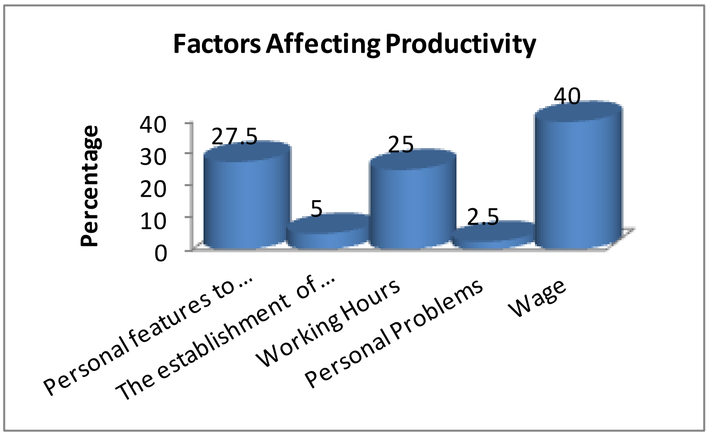
- In Graph 2, 79,5 % of participants are given thought to not applied efficiency improvement studies in the last six months.

Graphic 3



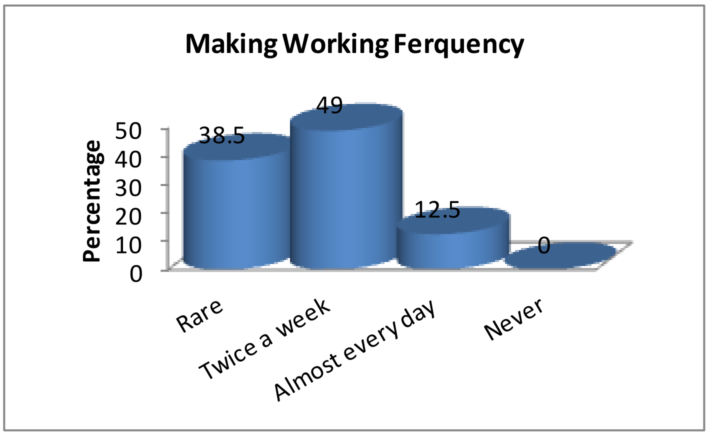
- In Graph 3, 82 % of participants claimed that managements are not do anything about fixing overtime and preventive actions.

Graphic 4



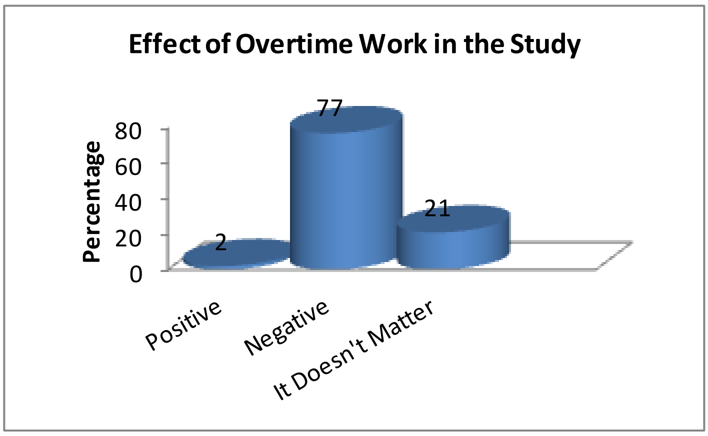
- In Graph 4, 40 % of participants claimed that wage is the first factor in working life of productivity affection.

Graphic 5



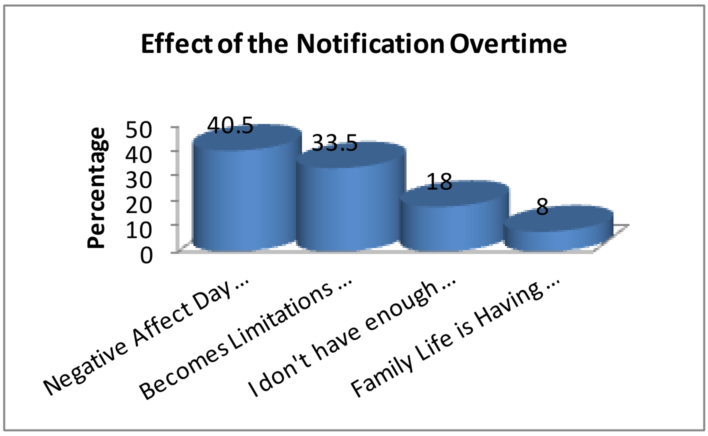
- In Graph 5, 49 % of participants claimed that they worked twice a week. Said that the staff does not have to.

Graphic 6



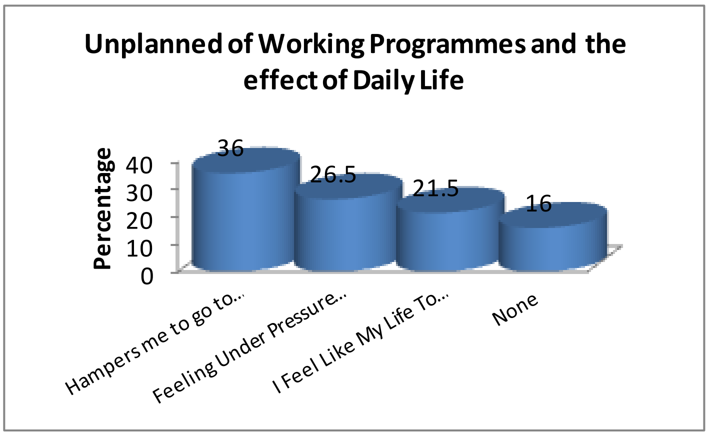
- In Graph 6, 77 % of participants claimed that overtime has a negative influence on the day after.

Graphic 7



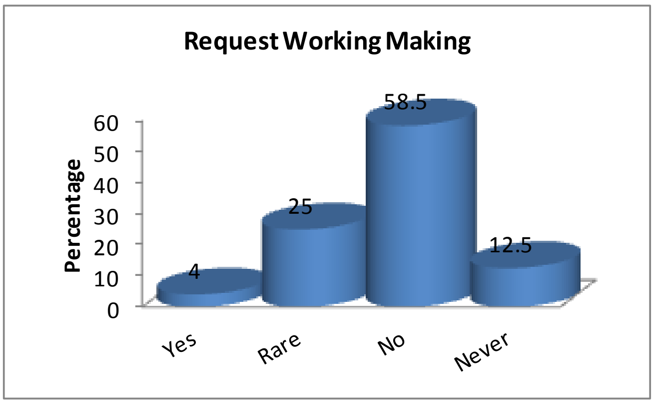
- In Graph 7, 40,5 % of participants claimed that saying overtime suddenly influence negative their daily programme.

Graphic 8



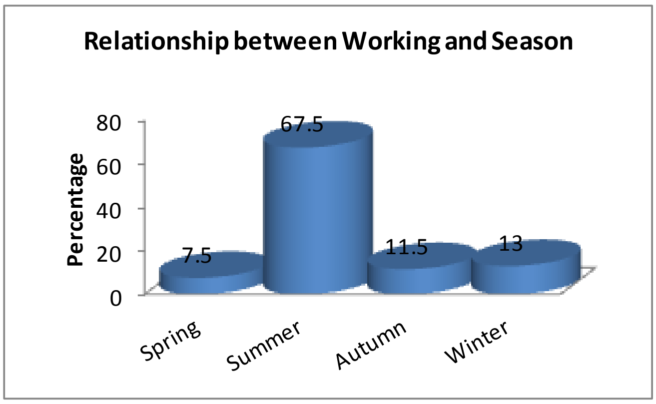
- In Graph 8, 36 % of participants claimed that unplanned overtime has effection daily life like " Hampers me to go to work willingly".

Graphic 9



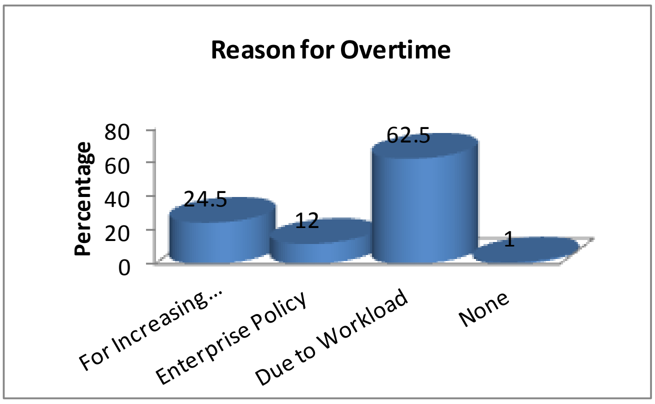
- In Graph 9, When doing overtime 58,5% participants have not give any consent.

Graphic 10



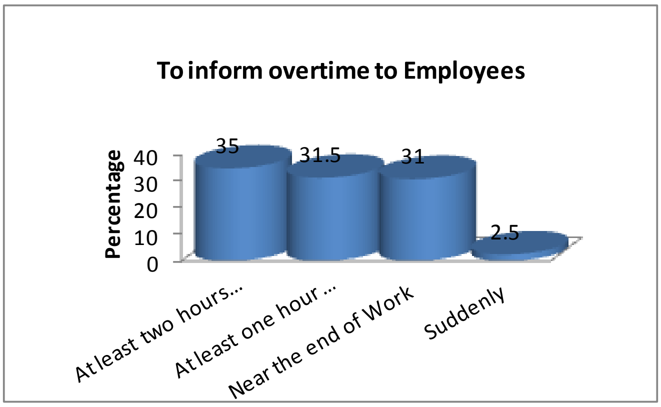
- In this graph 10 of working and season we can see that increased overtime in summer months according to 67,5 % participants.

Graphic 11



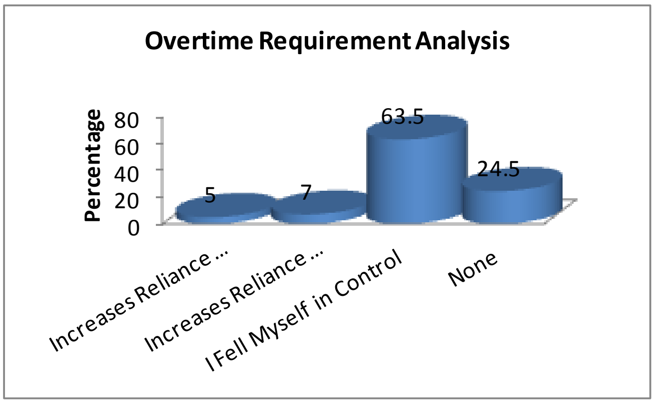
- In graph 11 we can say: 62,5% participants claimed that reason of doing overtime due to workload.

Graphic 12



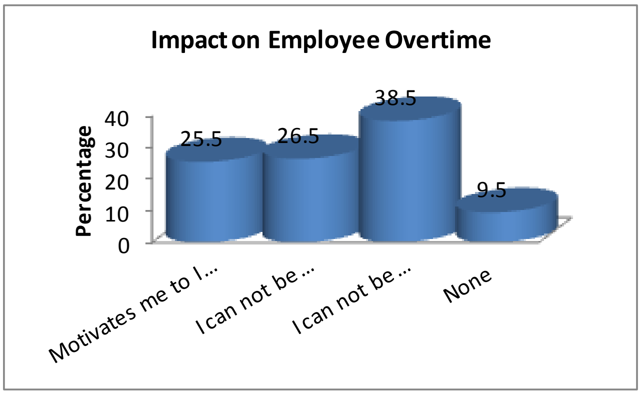
In Graph 12, 35 % of participants expressed an opinion that notify to workers overtime at least two hours before.

Graphic 13



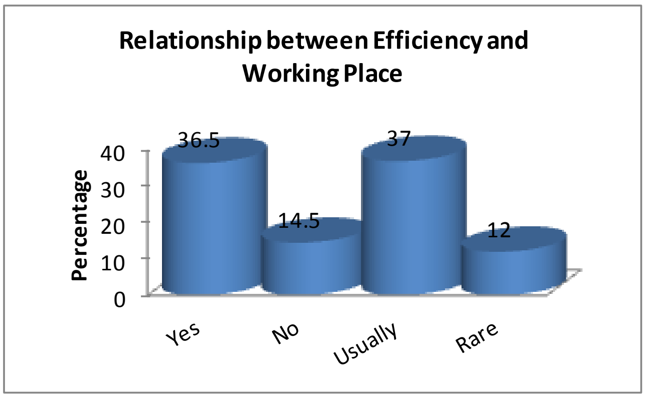
- In this case Graph 13, we can say: %63,5 participants think that they fell theirselves in control when they do overtime.

Graphic 14



- In this graph 14 of overtime, we can see that 38,5 % participants can not be motivated because of obstruction social life.

Graphic 15



- And in the Graph 15 we can say that 36,5% of participants who say “Yes” and 37% participants who say “Usually” declared working place is effective on overtime.

4. Results and Conclusions

Determination of the upper limit of working time has been one of the top priority issues since the dawn of labour law legislation. Determination of the upper limit of the day or week for working time is intended to the elimination of hazards that threaten the health of workers and to provide workers time required for the development of his personality. According to studies conducted in this regard it was seen that the most ideal total working time limit for the employees is 45 hours per week.

The main policies of enterprises are to provide the maximum output with the least cost. Workers perform the production. In this context, if the enterprises want to ensure the highest efficiency from workers on behalf of realize the targeted production standard; they should be sensitive about working time and wages. Understanding of the working time as “the duration that the worker has been at employer’s disposal" has not been deserved various rights to employer. It hasn’t seen daily working times over 12 hours in most of the factories in Turkey. However, according to the results of the research in the summer months that overtime is mostly applied; it was requested to work very long hours for days or even weeks from workers. As a result of this situation, it was concluded that workers feel themselves under pressure.

It should not be forgotten the idea that workers are social being and they have private lives when applying overtime. Overtime hours should be reported with pre-made calendars. Otherwise, if the worker has been informed about overtime during the day; the worker's social life and daily plans are hampered and it has been affected efficiency and motivation of workers negatively.

In addition, enterprises don’t implement corrective and preventive action in overtime and this is a problem for employees. This situation expands circulation of workers in enterprises so it prevents the institutionalization of enterprises and creation of corporate culture.

As a result, the efficiency of work has been adversely affected by overtime. It was observed that working hours passes eight hours in a day in the textile and garment industry which is a labour-intensive sector, causes an increase in the number of repair, more fatigue, more carelessness. This situation affects the quality of the business negatively.

If enterprises want to increase production potential and, accordingly, the profitability ratios, when determining overtime hours as well as the idea of employees should not be ignored. In this context, valuing and asking the idea of employee provides more motivation of employees, increase their commitment to the enterprise, reducing of circulation of employee. This is essential for the institutionalization of enterprises.

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β-cycodextrin/PVA nanofibrous membrane: Electrospinning and adsorption property for heavy metals

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Keywords: Nanofibers, Electrospinning, β-Cyclodextrin, Poly(vinyl alcohol), Heavy metal ions

Abstract: *In this study, β-CDs nanofibers were prepared by Electrospinning of β-CD mixed with poly(vinyl alcohol). β-CD /PVA nanofibers were characterized by Scanning Electron Microscopy (SEM). The viscosity of β-CD/PVA solution was increased with the concentration of β-CD and high viscosity of β-CD/PVA solution was beneficial to form more uniform nanofibers. Then the obtained nanofibers were used for efficient removal of heavy metal ions. The concentration of heavy metal ions were measured by atomic absorption spectroscopy before and after using adsorbent and the difference was referred as adsorbent capacity. Different parameters such as adsorbent dosage, contact time and pH were investigated. It has shown that the nanofibers have great potential for removal of heavy metal ions from waste water.*

1. INTRODUCTION

Cyclodextrins(CDs) are cyclic oligosaccharides consisting of D-glucopyranose units bonded through α-(1,4) glycosidic linkages. Six, seven or eight units bound into a ring are marked as cyclohexa-, cyclohepta- or cycloocta amylase, which are known as α-, β-, and γ-cyclodextrins, respectively. β- cyclodextrins are used most commonly[1]. The cyclodextrin consists of tours like macrocyclic ring. All hydroxyl groups are located at the top and bottom of the tours. Thus the hydrophobic cavity of cyclodextrins is capable of including a variety of hydrophobic compounds via host-guest complexation[2].

Since the distinct physical and chemical properties of inclusion complexes can be tailored by β-CD inclusion complexes, β-CD is used in many fields, such as pharmaceuticals, foodstuff, separate technique, environmental protection and genetic engineering.

Electrospinning is a versatile technique for producing multifunctional nanofibers from various polymers, polymer blends and composites[2]. Electrospinning applies high voltages to a capillary droplet of polymer solution or a melt to overcome liquid surface tension and thus enables the formation of much finer fibers than conventional fiber spinning methods[3]

Electrospinning nanofibers have many unique properties such as high surface area-to-volume, pore size within a nano range, high porosity and flexibility for chemical/physical functionalization [4]. Therefore, it has been shown that the very fascinating properties of these electrospun nanofibers make them applicable in numerous areas, including biotechnology, membranes/filters, electroanalysis, power source, and so on[5]. Poly (vinyl alcohol) (PVA) is a non-toxic, water-soluble, biocompatible and biodegradable synthetic polymer, which is widely used in biomedical field. PVA has better fiber forming and highly hydrophilic properties, and its fibers have been commercialized since the 1950s[6].

However, most of the electrospinning nanofibers cannot capture organic molecules or heavy metal ions. Simple nanofibers containing β-CD will, therefore, gain special characteristics, which outstandingly develop and extend the practical application areas of nanofibers. On the one hand, nanofibrous membranes consisting of β-CD can be used for the separation of industrial waste, since they have large surface area along with a nano-porous structure [4]. On the other hand, β-CD can capture molecules for removing the polluting substances from the environment by forming inclusion complexation.

In this study, β-CDs nanofibers were prepared by Electrospinning of β-CD mixed with poly(vinyl alcohol). β-CD /PVA nanofibers were characterized by Scanning Electron Microscopy (SEM).

SEM results showed that the electrospun nanofibers have the ability of capturing heavy metal ions such as Ni^{2+}. The molecular capture ability of nanofibers was increased with increasing the amount of β-CD.

2. MATERIALS AND METHODS

2.1 β-CD and Poly Vinyl Alcohol was purchased from Sigma Aldrich, Distilled water was used.

2.2. Electrospinning

First of all, β-CD was dissolved in distilled water to obtain β-CD 8% (w/w). The solution was stirred for 2 hour at room temperature. Poly Vinyl alcohol was dissolved in water and heated till 90 ^{0}C for 2h to obtain PVA 8% (w/w) and added to above solution to obtain β-CD /PVA in mass ratios of 30/70. The above solution was electrospun to obtain nanofibers.

2.3 Characterization of nanofibers

The morphology of electrospun β-CD/PVA bicomponent fibers was observed with a scanning electron microscope (SEM) (XL30 Philips) with gold coating. The average fiber diameter and diameter distribution were determined by randomly measuring the diameters of the nanofibers at 100 different points from SEM images.

2.4 Molecular recognition of β-CD/PVAnfm

The filtration performance of the β-CD/PVAnfm fibers were tested using Ni^{2+} as a model heavy metal ion. Uptake was determined by measuring the reductions in absorbance or depletion from solution using atomic absorption spectroscopy. The weight of fiber mass and the amount of Ni^{2+}used were calculated under the assumption that 30% β-CD (w/w) is present on the fiber surface. A 100 ppm of Ni^{2+} solution was prepared in water. The pH of the solution was adjusted to neutral (pH 7) by adding drops of pH buffer solution; the pH of the solutions was unchanged during the course of the atomic absorption experiments. 5mg of β-CD/PVA fibers were placed separately in the bottom of flask and was filled with 10 ml of Ni^{2+} solution. The absorption of the Ni^{2+} solutions were recorded initially (time = 0, right after adding the fibers) and every 1 h.

3. RESULTS AND DISCUSSION:

3.1 SEM images

The reported weight ratio was selected based on two factors including ease of electrospinnability and the nanofiber mechanical stability. It usually took 5 h to obtain a sufficiently thick membrane that could be detached from the collector.
Fig.1 shows the fabrication of fibres at nanolevel.

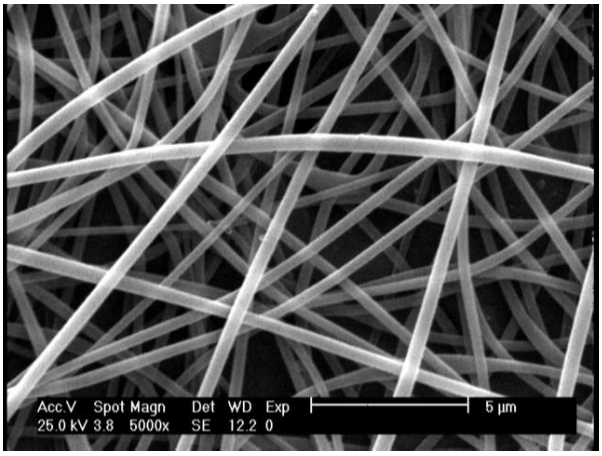

Fig. 1: SEM image of electrospun nanofibers prepared from 30/70solution of β-CD /PVA

3.2 Sorption of Ni^{2+}

The trapping ability of β-CD/PVA fibers was tested using Ni^{2+}as a model system. The β-CD/PVA fibers were immersed into a Ni^{2+} solution and the change in absorbance of Ni^{2+} was recorded as a function of β-CD/PVA mass ratio by atomic absorption spectroscopy. It was observed that the absorbance of Ni^{2+} solution decreased significantly by increasing the amount β-CD in the of β-CD/PVA fibers. The β-CD/PVA fibers function as a molecular filter through complexation of the Ni^{2+} molecules with the β-CD molecules on the surface of the PVA fibers. It was observed that the higher the content of β-CD on the fibers, the more rapidly the Ni^{2+} is removed from the solution. These findings are very promising and show the potential application for β-cyclodextrin functionalized electrospun fibers to be used in filters for the removal of heavy metal ions. β-CD molecules have the ability to trap polluting substances (organic waste, heavy metals, radioactive wastes, etc.) from the environment where the complexation is limited by the size of the waste molecules and β-CD cavity. We expect that such β-cyclodextrin functionalized electrospun nanofilters will be very applicable for waste treatments as long as the β-CD cavity can form complexation with the target molecules.

4. CONCLUSION

In this study nanofibers of β-CD blended with PVA were fabricated by electrospinning. Although electrospinning from aqueous solution of β-CD was unsuccessful, β-CD blended with a small amount of PVA could be electrospun into nanofibers without acids or organic solvents. According to spectroscopic methods, moreover, we demonstrated that the electrospinning uniform β-CD /PVAnfm could capture some heavy metal ions readily and effectively. Since the composite nanofibrous membrane could be used as the attractive host matrix for the available loading of guest molecules and result in the enhanced spectrophotometric response. Thus, the specific property of β-CD nanofibrous membrane, in the case of super molecule interactions, would be exploited and combined with spectrophotometric detections.

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APPLICATION OF CHITOSAN/PVA NANOFIBEROUS MEMBRANE FOR MOLECULAR CAPTURE

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Abstract. *Nanofibers with average diameters of 86 nm have been prepared by electrospinning of 72.5% deacetylated chitosan mixed with poly(vinyl alcohol) (PVA) in 2% (v/v) aqueous acetic acid. The formation of bicomponent fibers was feasible with 3% concentration of solution containing up to an equal mass of chitosan. Finer fibers, fewer beaded structures and more efficient fiber formation were observed with increasing PVA contents. The interaction between CS and PVA in the solution was studied FTIR spectra. The spectroscopic measurement showed that CS/PVAnfm could recognize some organic molecules such as Acid Blue 26 by electrostatic interactions. The molecular capturing ability of CS/PVAnfm was increased with the amount of CS in composite nanofibrous membrane. The results suggested that the composite nanofibrous membrane was potentially applied to purification/separation processes.*

1. INTRODUCTION

Chitosan is N-deacetylated form of chitin that is obtained by alkaline treatment of chitin (50% of aqueous NaOH) at high áter n ra[1]. Chitosan has a repeated structure of (1,4)-linked β-D-glucosamine and an apparent Pk of 6.5. Commercial products are traditionally composed of 80% β-D-glucosamine and 20% N-acetyl-β-D-glucosamine [2]. Chitosan is a cationic polymer. It's key properties are biocompatibility, non-toxicity (its degradation products are natural metabolites) and solubility in moderated acidic aqueous solutions. Chitosan has been widely used in food, cosmetic, biomedical, treatment of wastewater, chromatographic support and pharmaceutical applications[3, 4]. A large variety of useful forms, including beads, films, sponges, tubes, powders, and fibers, can be obtained from chitosan [5].

Electrospinning is a versatile technique for producing multifunctional nanofibers from various polymers, polymer blends and composites[6]. Electrospinning applies high áter n to a capillary droplet of polymer solution or a melt to overcome liquid surface áter n and thus enables the formation of much finer fibers át conventional fiber spinning methods[7]

Electrospinning nanofibers have many unique properties such as high surface áte-to-volume, pore size within a nano range, high porosity and flexibility for chemical/physical functionalization [8]. Therefore, it has been shown that the very fascinating properties of these electrospun nanofibers make them applicable in numerous áter, including biotechnology membranes/filters, electroanalysis, power source, and so on[9]. However, because of the strong molecular interaction, generating smooth and uniform electrospun chitosan nanofibers still remains a great challenge. Poly (vinyl alcohol) (PVA) is a non-toxic,

áter-soluble, biocompatible, and biodegradable synthetic polymer, which is widely used in biomedical field. PVA has better fiber forming and highly hydrophilic properties, and its fibers have been commercialized since the 1950s[10].
In current work nanofibers of CS/PVA were synthesized through Electrospinning method. Then the obtaind nanofibers were used for efficient removal of acid dyes. The concentration of dye molecules were measured by uv-visible spectroscopy before and after using adsorbent and the difference was refered as adsorbent capacity. Different parameters such as adsorbent dosage, contact time were investigated. It has shown that the nanofibers have great potential for removal of organic molecule. Acid Blue 26 was selected as a model organic molecule.

2. MATERIALS AND METHODS

Chitosan and PolyVnyl Alcohol were purchased from Sigma Aldrich, Acetic Acid and other solvents were from analytical grade. Distilled water was used.

2.1 Electrospinning procedure

First of all, chitosan was dissolved in acetic acid 2% (v/v), to obtain chitosan 3% (w/w). The solution was stirred overnight at room temperature. Poly Vinyl alcohol was dissolved in water and heated till 90 ^{0}C for 2h to obtain PVA 8% (w/w) and added to above solution to obtain chitosan/PVA in mass ratios of 20/80. The above solution was electrospun to obtain nanofibers.

2.2 Crosslinking of nanofibers

The electrospun PVA/CS nanofibrous mats were crosslinked via aGAvapor crosslinking method. Briefly, a Petri dish containing GA solution (20% aqueous solution, 10 mL) was placed at the bottom of a desiccator. Then the electrospun nanofibrous mats deposited onto the supporting aluminum foils were put onto the top ceramic plate of the desiccator. Vacuum was applied for 48 h. After that, the mats were exposed in a fume hood for 2 h, followed by a heating treatment at 100 ◦C in an electric oven for 1 h to remove the residual GA and to partially enhance the crosslinking. The nanofibrous mats were rinsed with water 3 times to remove the excess GA.

2.3 Molecular recognition of CS/PVAnfm

The filtration performance of the CS/PVAnfm fibers was tested using Acid Blue 26 as a model organic molecule. Uptake was determined by measuring the reductions in absorbance or depletion from solution using UV–vis spectrophotometry (JENWAY 6505) in the wavelength of 635 nm. The weight of fiber mass and the amount of Acid Blue 26 used were calculated under the assumption that 20% CS (w/w) is present on the fiber surface and thus available for complexation and 1:1 complexation between CS and Acid Blue 26 molecules occur. A 10 ppm of Acid Blue 26 solution was prepared in water. The pH of the solution was adjusted to neutral (pH 7) by adding drops of pH buffer solution. The pH of the solutions was measured with a pH meter (pH meter 827, Metrohm) before and after the UV–vis experiments; the pH of the solutions was unchanged during the course of the UV–vis experiments. 5mg of CS/PVA fibers were placed separately in the bottom of flask and were filled with 10 ml of Acid Blue 26 solution. The absorbance spectra of the Acid Blue 26 solutions were recorded initially (time = 0, right after adding the fibers) and every 1 h.

2.4 Viscosity measurements

All polymers increase the viscosity of the solvent in which they are dissolved. Several important viscosity functions are used in viscosity studies. The relative viscosity, ηr = η/η_0, is the dimensionless ratio of solution viscosity, η, to solvent viscosity, η_0. The specific viscosity, ηsp = $(\eta-\eta_0)/\eta_0$, is related to the fluid viscosity increase due to all polymer solute molecules. The reduced viscosity, ηred = ηsp/c, is the fluid viscosity increase per unit of polymer solute concentration, c, expressed in g/mL.
The intrinsic viscosity, [η] (in mL/g), is the limit of the reduced viscosity as the polymer solute concentration approaches zero following the Huggins relationship:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \quad (1)$$

The viscosity-average molecular weight (Mv) of chitosan was determined by dilute solution viscosity measurement using Ubbelohde capillary viscometer (Schott, Germany) at $25^{\circ}C$ A mixture of $0.1M$ HOAc- $0.2M$ NaCl was used as the solvent to prepare chitosan solutions with concentrations from 1×10^{-3} to 2×10^{-4} g/mL. The viscosity-average molecular weight (Mv, in Daltons or Da) was derived from the following Mark–Houwink equation:

$$[\eta] = 1.81\times10^{-3} M_v^{0.93} \qquad (2)$$

2.5 Characterization of nanofibers

The morphology of electrospun chitosan /PVA bicomponent fibers was observed with a scanning electron microscope (SEM) (XL30 Philips) with gold coating. The average fiber diameter and diameter distribution were determined by randomly measuring the diameters of the nanofibers at 100 different points from SEM images.
FT-IR spectra of chitosan, PVA, , chitosan/PVA were recorded by a Nicolet Nexus 670 USA. All samples were prepared as KBr pellets and scanned over the wave number range of 4000–650cm^{-1} at a resolution of 4.0cm^{-1}.

3. RESULTS AND DISCUSSION

3.1 FT-IR spectra

Fig. 1 gives FT-IR spectra of CS/ PVA nanocomposite fibers with different weight ratios. The PVA nanofibers exhibited a number of absorption peaks at 2940, 1448, 1333, 1248, 1095, and 847 cm^{-1}, which were attributed to the __ (CH$_2$), _ (CH–OH), _ (CH–OH), _ (CH), _ (C–O), and _ (C–C) resonance, respectively. CS membrane showed FT-IR absorption features around 898 and 1151cm^{-1} peaks assigned saccharine structure and a weaker amino characteristic peak at 1255cm^{-1} was the absorption of _ (O–H), and the peak at 1383 cm-1 was assigned to the CH3 symmetrical deformation mode. It was observed that the absorption peak at about 3441 cm^{-1} concerned with –OH and –NH stretching vibrations shifted to a lower wave number with the increase of PVA content in the blends. Moreover, compared with FT-IR spectra of pure CS membrane, the absorption peak of CS/PVA nanofibers at 1255 cm^{-1} disappeared. These results suggested the formation of hydrogen bond between CS and PVA molecule. Fourier Transform Infrared Spectroscopic measurement exhibited the existence of relevant functional groups of both PVA and CS in the composites.

The CS exhibited characteristic broad bands of OH group at 3400-3500 cm^{-1}.The bands of NH2 group and O-C-NH2 group can be observed at 1638 cm^{-1}. The broad bands of CH3 group and CH3-O group can be observed at 1000 – 1200 cm^{-1}. The FT-IR spectra of PVA showed the characteristic broad band at 2900-3000 cm^{-1} for CH2 group and CH3 group, respectively.

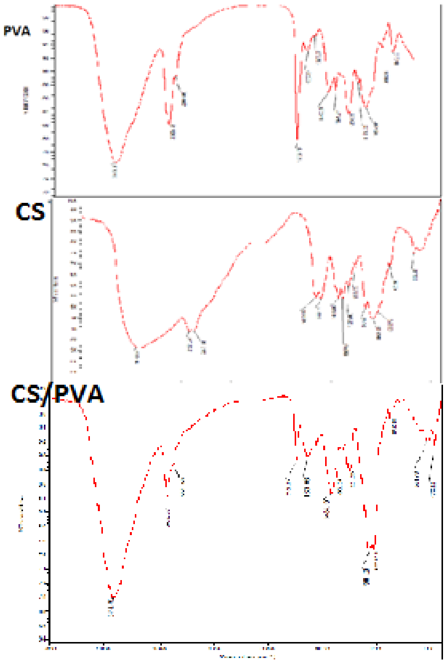

Fig.1. FTIR spectrum of CS, PVA, CS/PVA nanofibers.

3.2 SEM images

The reported weight ratio was selected based on two factors including ease of electrospinnability and the nanofiber mechanical stability during cell growth procedure.
It usually took 5 h to obtain a sufficiently thick membrane that could be detached from the collector.
Figure 2 shows the fabrication of nanofibres.

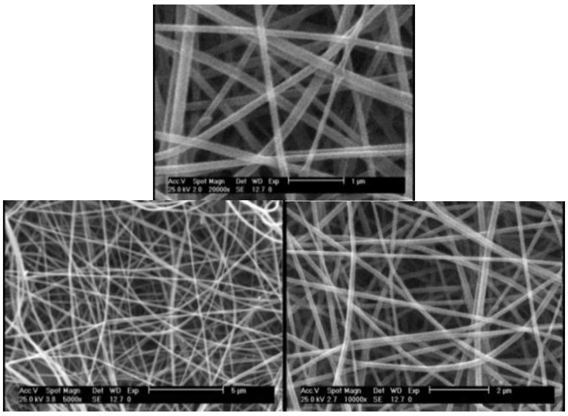

Fig.2. SEM images of electrospun nanofibers prepared from 20/80solution of chitosan/PVA

3.3 Uptake of Acid Blue 26

The trapping ability of CS/PVA fibers was tested using Acid Blue 26 as a model system. The CS/PVA fibers were immersed into a Acid Blue 26 solution and the change in absorbance of Acid Blue 26 was recorded as a function of CS/PVA mass ratio by UV–vis spectrometry (Fig. 3). It was observed that the absorbance of Acid Blue 26 solution decreased significantly by increasing the amount CS in the CS/PVA fibers and blue solution become colorless, due to the removal of Acid Blue 26 from solution by CS.

The CS/PVA fibers function as a molecular filter through electrostatic interaction of the Acid Blue 26 molecules with the CS molecules on the surface of the PVA fibers. It was observed that the higher the content of CS on the fibers, the more rapidly the Acid Blue 26 is removed from the solution. These findings are very promising and show the potential application for chitosan functionalized electrospun fibers to be used in filters for the removal of organic molecules.

We expect that such chitosan functionalized electrospun nanofilters will be very applicable for waste treatments as long as the CS ccan interact with the target molecules.

3.3.1 Effect of adsorbent dosage

CS/PVA$_{nfm}$ dosage is particularly important because it determines the extent of decolorization and may also be used to predict the cost of CS/PVA$_{nfm}$ per unit of solution to be treated. The effect of adsorbent dosage on the removal of Acid Blue 26 is presented in Fig. 3. It was observed that the adsorption efficiency of Acid Blue 26 by CS/PVA$_{nfm}$ increases from 85.61% to 86.66% mg/g with the increase in adsorbent dose from 5 to 10 mg in 10 mL of 10 mg/L Acid Blue 26 solution at 30 ◦C, 150 rpm, 4.5h at a pH of 7.8. As expected, the adsorption density increases significantly as adsorbent dosage decreases. This is explainable because at a higher adsorbent dose extra adsorption sites are available for the adsorption. Also, by increasing adsorbent dose, the quantity of Acid Blue 26 adsorbed onto the unit weight of the adsorbent gets reduced, thus causing a decrease in qe value with increasing adsorbent dose. The CS/PVA$_{nfm}$ mass of 5 mg was selected because an increase of the

CS/PVA_{nfm} mass to 10 mg did not provide significantly higher adsorption efficiencies (85.61%, 86.66%for 5 mg and 10mg of CS/PVA_{nfm}, respectively). Increasing CS/PVA_{nfm} dose had a dramatic positive impact on color removal and there was an approximately linear relationship between CS/PVA_{nfm} dose and color removal of the dye[11]. Increase in adsorption with adsorbent dosage can be attributed to increased adsorbent surface and availability of more adsorption sites. However, if the adsorption capacity was expressed in mg adsorbed per gram of material, the capacity decreased with the increasing amount of sorbent. This may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in total adsorbent surface area available to the dye and an increase in diffusion path length. It was also indicated that the time required to reach equilibrium decreased at higher doses of the adsorbent[12, 13].

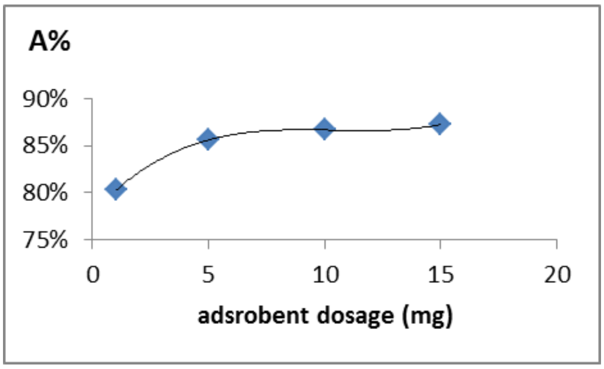

Fig.3. Effect of nanofiber dose on sorption of Acid Blue 26 on CS/PVA_{nfm}. Experimental conditions pH 7.8, Acid Bleu 26 concentration (10 mg/L), reaction volume 10 mL, contact time 4.5h , $T=30^0C$.

3.3.2 Sorption kinetics

In order to evaluate kinetic data, the agitation time was varied from 1 to 24 h and the kinetic studies were done at 10 mg/L dye concentration and 5mg adsorbent dose.

Dye removal was monitored with time. Kinetics of dye sorption governs the rate, which determines the residence time, and it is one of the important characteristics defining the efficiency of an adsorbent. Adsorption of dye by the polymer initially indicated rapid binding of dye and more than 50% adsorption takes place within 2 h, however with the passage of time adsorption rate slows down. Equilibrium at 4.5 h was reached and no change in the uptake capacity was observed up to 24 h. The initial rapid binding increase is due to greater number of vacant sites available initially, resulting in a high concentration gradient between adsorbate in solution and adsorbate in the adsorbent[14].

The rapid interaction between adsorbents and the dye molecule to be removed is desirable and beneficial for practical pollutant adsorption applications. During the process, the adsorbent surface is progressively blocked by the adsorbate molecules, becoming covered after some time. When this happens, the adsorbent cannot adsorb any more dye molecules. As each particle purifies a certain volume of liquid, increasing the dosages rapidly promotes equilibrium between adsorbate and adsorbent because the number of particles to treat the same volume of liquid is increased. In general, the adsorption capacity increases with time and, at some point in time, reaches a constant value where no more dye is removed from the solution. At this point, the amount of dye being adsorbed onto the material is in a state of dynamic equilibrium with the amount of dye desorbed from the adsorbent. The time required to attain this state of equilibrium was termed the equilibrium time (te) and the amount of dye adsorbed at te reflected the maximum dye adsorption capacity of the adsorbent under these conditions.

The process was initially very fast and then slowly reached equilibrium[15].

Maximum accumulation occurs within 4–5 h for Acid Blue 26 dye on CS/PVA$_{nfm}$ and adsorption kinetics were relatively fast. Adsorption of dyes is fast at the initial stages of the treatment time, and thereafter, becomes slower near the equilibrium. It is obvious that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, it is difficult to occupy the remaining vacant surface sites due to repulsive forces between dye molecules adsorbed on the solid and those in the solution phase.

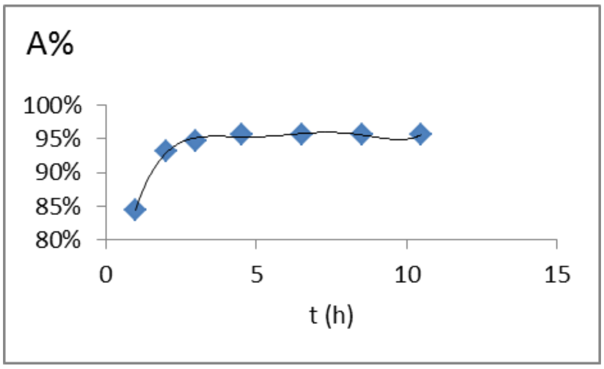

Fig.4. Kinetics of dye sorption on CS/PVAnfm. Experimental conditions pH 7.8, adsorbent dose (5,7,15 mg), Acid Bleu 26 concentration (10 mg/L), reaction volume 10 mL, T=30^{0}C.

3.3.3 Sorption capacity

The amount of dye sorbed per gram of the nanofiber was calculated by the difference between the initial and the final readings using the following equation:

$$q_e(mg/g) = \frac{C_o - Ce(V/1000)L}{W(g)} \qquad (3)$$

where qe is the amount of dye adsorbed on the CS, C$_o$, the initial dye concentration (mg/L), C$_e$, the equilibrium concentration of dye in solution (mg/L), V, the volume of dye solution used (L), and W is the weight of the CS used (g) as adsorbent.

Adsorption capacity is an important factor to evaluate, because it determines how much nanofiberous CS/PVA$_{nfm}$ is required to purify dye (analyte) from a given solution quantitatively[16]. The maximum capacity of CS/PVA$_{nfm}$ for Acid Blue 26 was determined. 5 mg of CS/PVA$_{nfm}$ nanofiberous membrane were contacted with 10 ml of dye solution containing 10 mgL^{-1} dye molecules at an optimum adsorption pH of 7.8 and contact time of 4.5 h. Then the concentration of the remaining dye in the solution was determined by UV-Vis spectroscopy at the wave length of 635 nm. The adsorption capacity (adsorption uptake rate) is then calculated and is usually expressed in milligrams of dye adsorbed per gram of the (dry) adsorbent. The amount of dye adsorbed at equilibrium, q$_e$, is calculated from the mass balance equation given by Eq. (3). According to these results, the maximum amount of dye that can be sorbed by CS/PVA$_{nfm}$ was found to be 392 mgg^{-1} at a pH of 7.8.

4. Conclusion

In this study nanofibers based on CS blended with PVA were fabricated by electrospinning.

Although electrospinning from aqueous solution of CS was unsuccessful, CS blended with a small amount of PVA could be electrospun into nanofibers without acids or organic solvents.. FTIR and results indicated the the formation of hydrogen bond between CS and PVA molecule. According to spectroscopic methods, moreover, we demonstrated that the electrospinning uniform CS/PVAnfm could capture some organic molecule readily and effectively. Since the composite nanofibrous membrane could be used as the attractive host matrix for the available loading of guest molecules and result in the enhanced spectrophotometric response. Thus, the specific property of CS functional nanofibrous membrane, in the case of super molecule interactions, would be exploited and combined with spectrophotometric detections.

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DESIGN APPROACH OF TOWER PARACHUTES

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Abstract. *This article describes the development and results of numerical models describing parachute inflation behavior. The model was developed using Fluid Structure Interaction (FSI) techniques. The modeling was performed in an infinite mass scenario, where the parachute does not influence the freestream air velocity. The results of the modeling, discussed herein, compare favorably with the indoor vertical parachute tests, with good prediction of both inflation force and post inflation breathing frequency. The necessity for this kind of system was necessary in a research institute with limited manufacturing capabilities and is best suited for rapid prototyping and small production series of parachutes that is often needed in the RnD activities.*

1 INTRODUCTION

Parachutes are used in a wide variety of applications, including sports activities, payload recovery, military applications and flood relief efforts. One particular type of parachute is the tower parachute that is a basic round parachute used for student training and it is dropped under controlled conditions from a parachute tower, thus the computation is very similar with that of ballistic parachutes.

The aerodynamics of parachutes is very complex. It involves three-dimensional unsteady turbulent flows past rapidly deforming boundaries. The aerodynamic design of parachutes is largely an empirical process and the database has mostly been generated via wind tunnel and drop tests. Recently, there have been some advances towards the numerical prediction of parachute aerodynamics and for institutions with limited live testing capabilities this solution become increasingly reliable and a viable alternative to live testing and empirical design.

Computer modeling of the Fluid–Structure Interactions (FSI) involved in parachute aerodynamics has always been challenging especially because a parachute is a light structure very sensitive to the unsteadiness of the aerodynamic forces. The FSI modeling techniques we developed to address those challenges are based on a stabilized space–time formulation. We have recently augmented these techniques with a number of enhancements to increase the robustness and scope of our FSI modeling. These enhancements include more sophisticated fluid–structure coupling techniques and improved mesh generation methods. With these enhancements, we are able to address more of the computational challenges involved in parachute FSI modeling. The challenges we can now address include the type of geometric complexities seen in some of the advanced parachute designs proposed and tested.

2 TECHNICAL APPROACH

The parachute in question and the objectives of the modeling will dictate which method is selected. The numerical approach discussed in this paper utilizes a first order Eulerian temporal solution with a second order accurate advection method[1]. An Eulerian formulation on a Cartesian mesh is used for the fluid, Lagrangian 4-noded membrane elements based on the Belytschko-Lin-Tsay formulation for the parachute structural mesh, and a quasi-penalty based coupling method to enable the two to interact. The use of an Eulerian-Lagrangian coupling algorithm permits the interaction of the fluid and structure to occur within the same computational solver and completely avoids the numerical problems associated with distortions of the fluid mesh. Unlike previous models that force air to flow through the spatially fixed Cartesian mesh, this model contains stationary fluid and the parachute and payload move through the fluid mesh. It is only within the last 4-5 years that this method of solving both the fluid and structure within the same code has emerged as a viable way of simulating parachute performance. The application of Eulerian formulations can lead to a propensity for energy dissipation and dispersion inaccuracies connected with the fluxing of mass across element boundaries. In addition, the Eulerian mesh is required to span the entire range of activity associated with the Lagrangian structure. In many applications, this can result in a large size mesh and hence a high computing cost. Ballistic parachutes are relatively unique aerodynamic devices that are designed to generate drag and as such their bluff body form is ideally suited to Euler based solutions.

Figure 1. Free-Hanging Parachute Configuration

The flat circular canopy used for testing was fabricated from 0.026 kg/m^2 fabric (PIA-C-7020 Type I)[2]. In order to predict the inflation force it was critical to replicate the initial parachute canopy shape before the release of the parachute. Figure 1 depicts a parachute in the free-hanging position prior to being raised to the ceiling. This required taking the known flat circular parachute planform and allowing it to deform appropriately into a representative free-hanging geometry. This had to be accomplished without inducing excessive stress and strain in the canopy that could artificially alter the canopy geometry, prior to the drop test simulation. The approach selected was to deform the parachute structure in a separate simulation and then use that geometry as the starting shape for the drop test simulation. To enhance the overall accuracy of this method for the 2 m flat circular canopy, the full parachute canopy was reduced to a single gore. By limiting the simulation to a single gore, the resulting parachute geometry was more symmetric and any induced fabric strains were minimized. The single parachute canopy gore was constructed flat where the geometry of the gore could be accurately

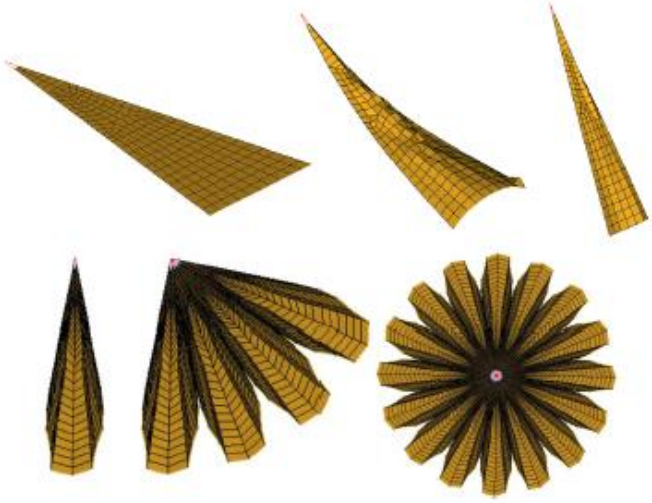

Figure 2. Flat Circular Canopy, Free Hanging Shape Generation

defined, as seen in Figure 2. The gore fabric was then allowed to fall under a simulated gravity loading, the radials were constrained to move only on their original plane and the apex was fully constrained. This caused the gore to fall slowly into a vertical folded shape. Several iterations of this approach, with various falling speeds, were used to ensure no permanent strains were induced in the fabric. A permanent strain would be carried forward into the finite mass simulation, and as the parachute inflated in the fluid the canopy would take an unrealistic deformed shape. Once the simulation was completed the single gore was then rotated 16 times to construct the full parachute, as illustrated in Figure 2.

Figure 3. 2m Flat Circular Parachute Inflation Time Lapse Images

Given the dynamic nature of the inflation process, it is not possible to suitably capture it in this paper with a single screen shot. Therefore, multiple time elapsed screen shots have been assembled in Figure 3 to illustrate the inflation process. The images are shown with a perspective view to aid the spatial observation of the canopy geometry during the inflation process. As illustrated in Figure 3, the parachute starts in its free hanging position and then rapidly inflates. It is shown to progress into an over inflation shape, almost flat, and then contract and once again over inflate. This phenomenon is often referred to as breathing or squidding. The breathing motion was most likely caused by the constraint on the motion of the parachute imposed by the guide-wire. The natural tendency of a flat circular parachute is to oscillate through a coning angle from side to side about its descent axis as it discards excess accumulated air. As this natural oscillation was restrained, the canopy appeared to expel the excess air by means of the breathing motion.

Figure 4 compares the predicted descent velocity as a function of time with the velocity measured during the drop test. The model under-predicts velocity by 3-8% throughout the simulation, this equates to an over-prediction of parachute drag. This difference is within the experimental variability and error bars supplied by the test team. The greatest difference in velocity is seen in the initial parachute over inflation following peak deceleration, which occurs at approximately 1.1 seconds. It is likely that this is related to the time of initial parachute operational performance (referenced as the time at which the velocity first deviates from freefall velocity). As can be seen in Figure 4, the model moves from the red line prior to the drop test data and this is likely caused by a different free hanging skirt geometry of the parachute and the parachute opening marginally earlier in the model than in the test. Also noteworthy is the accurate prediction of the more complex dynamics involved, specifically the breathing exhibited as the parachute descends along the guide wire. The breathing frequency of the model and the experiment are both approximately 2 Hz. This frequency can be identified in the velocity time history data by the small increases occurring every 0.5 seconds. Also observable in both sets of data is a smaller velocity reduction that precedes the more

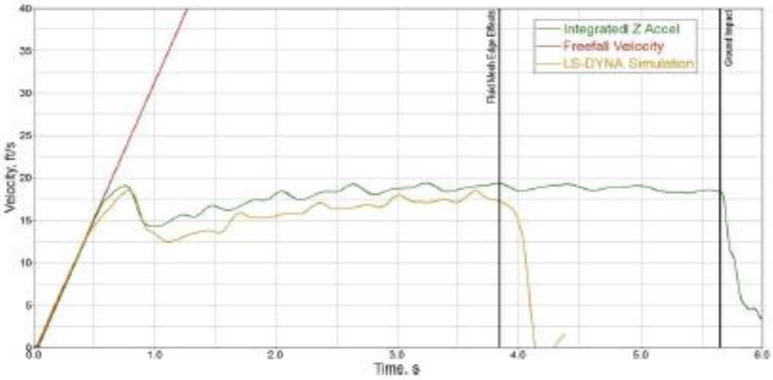

Figure 4. 2m Flat Circular, Descent Velocity

significant velocity increase. These velocity variations represent the different phases in the breathing cycle of the parachute. Also shown in Figure 4 is the ground impact of the payload during the test, at approximately 5.6 seconds, and the fluid mesh edge effects as the parachute reaches the bottom of the computational fluid mesh. Not visible in any of the data provided herein is the lateral motion of the parachute as it descends down the guide wire. This lateral motion is observed in both the test data and the numerical model. Due to computational resource restrictions the 2m diameter flat circular canopy finite mass drop test simulations were restricted to approximately 4.0s of simulation time. Capturing the parachute system performance over the entire length of the drop test was deemed less of a priority than capturing the parachute performance accurately over the inflation and primary breathing cycles.

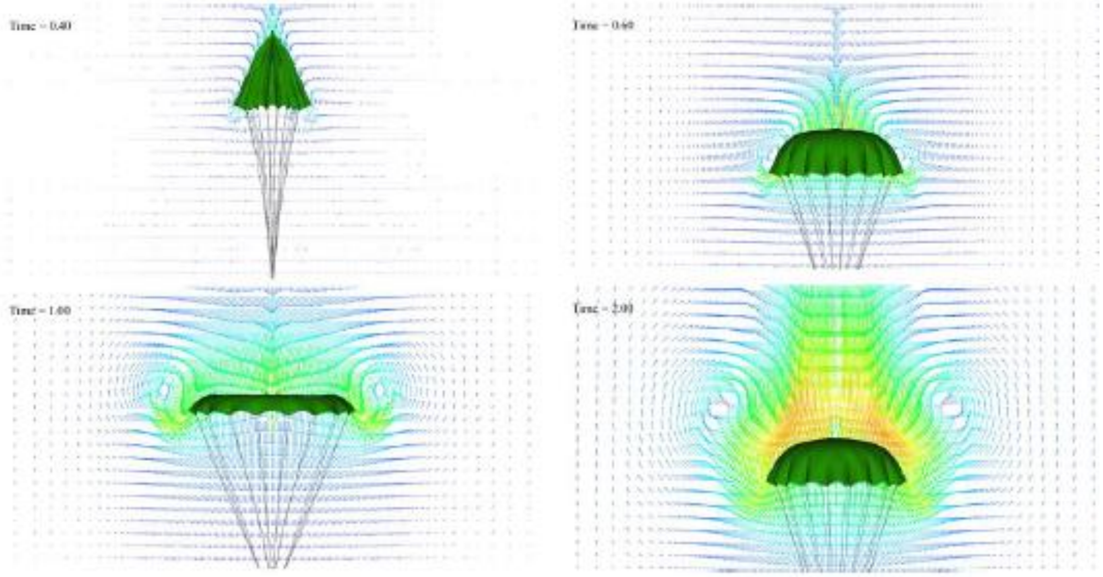

Figure 5. Flow Field Velocity Vectors

Figure 5 illustrates the fluid flow on a section through the flat circular parachute as it inflates and breathes. The time shown in the top left of each image correlates to the time scale shown in Figure 4. The top left image depicts the parachute beginning to inflate and the surrounding air remaining stationary. The nature of the inflation is interesting; it replicates the skirt first inflation observed during the drop test series. As the inflation progresses the parachute drag area increases and rapidly decelerates the payload. Throughout this time the surrounding air becomes increasingly more disturbed. As the parachute reaches its maximum projected diameter a large vortex ring is shed from the canopy skirt and the parachute then begins to contract.

3 CONCLUSIONS

The article has documented the preliminary stages of demonstrating the applicability of existing Fluid Structure Interaction numerical methods for predicting the inflation of flat circular tower parachutes. The comparisons with test data have highlighted the accuracy of the finite element analysis code for finite mass parachute applications. Direct quantitative comparisons have been made with descent velocity, breathing frequency, and inflation force. The model was developed after the testing had occurred but without prior knowledge of the results, as such the model outputs can be considered true predictions. It is fairly common to observe good FSI model results post testing, when the results are known and have been studied in detail. It is not as common to find a predictive FSI model, especially one that compares well with complex transient test data.

The analysis method described herein requires the computational fluid domain to encompass the entire inflationary spatial field. This generates a large model that needs to be solved at each time step. Current work is aimed at improving the parallelization of this specific solver with the objective of considerably reducing runtime.

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COATING OF POLYESTER FABRIC WITH CARBON NANOTUBES USING PLASMA TECHNOLOGY

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Keywords: Coating, Conductive Textile, CNT, Functionalization, Plasma

Abstract. *In this article, we report the durable coating of polyester fabric with carbon nano tubes. Four fabric samples were prepared with different treatments to obtain the fabric with the lowest electrical resistance. Plasma treatment was done to prepare the fabric surface for depositing amino functionalized carbon nano tubes (NH_2-MWCNT). Electrical resistance, FTIR analysis, surface morphology and color variation of the samples were assessed. The results showed that the attachment of NH_2-MWCNT onto polyester fabric was affected by fabric surface morphology. Electrical resistance of NH_2-MWCNT coated polyester fabric reduced substantially for pretreated fabric with plasma which is subsequently coated with NH_2-MWCNT in the presence of acrylic acid.*

1 INTRODUCTION

The demand for electrically conductive textiles is increasing greatly in recent years. Electro-Conductive textiles have many potential applications including sensors, static charge dissipation, filters, electro-magnetic interference shielding, data transfer in clothing, military applications like camouflage and stealth technology and special purpose clothing acting as protection or dust and germ free purposes [1,2].

Several methods have been used to produce electrically conductive fibers, yarns or fabrics including wet spinning, melt spinning or coating of fibers with electrically conductive materials such as metal powders, graphite, carbon black carbon nano tubes or intrinsically conductive polymers like polyaniline, thiophene and polypyrrole. Among these manufacturing processes, coating techniques have gain more attention due to simplicity of the process and ease of handling. The textiles produced not only gain controllable electrical properties, but also maintain the physical properties of the textiles such as mechanical strength and flexibility intact [1, 3, 4].

Carbon nano tubes (CNTs) have recently been applied as the electronic element to make wearable electronic textiles owing to their light weight, high surface area besides superior mechanical and electrical properties [5-7]. Carbon nano tubes have been proved to be an ideal reinforcement in macroscopic composites to improve electrical, mechanical, and physical properties of materials [1].

Polyethylene terephthalate (PET) fiber is elastic, tough and resistant to abrasion; implying PET clothes can last for a long time. In this aspect, it seems PET fiber may be an ideal candidate for the manufacturing of electronic textiles. Unfortunately, little information is available at this time on manufacturing of durable CNT coated PET textiles [8-10] and this is the impetus of this study.

PET fiber is highly crystalline and hydrophobic in nature and presents an inherent low reactivity toward chemicals [10-11] and this restricts the absorption of CNTs on its surface. Several physico-chemical and chemical processes have been investigated and adopted for the surface modification of these fibers. These processes include co-spinning, non-covalent physical coating, plasma discharge, alkaline treatment for partial surface ester hydrolysis, partial aminolysis of surface ester groups, glycolysis, and graft polymerization [10]. Certain improvements in surface and adsorption properties can be imparted to PET fibers using plasma treatment and grafting of monomers like acrylic acid [11-14].

In this study oxygen plasma treatment and acrylic acid grafting was employed as means to attach amino functionalized CNTs on the surface of PET fabric. The attachment of CNTs was confirmed by ATR-FTIR, color measurement, and SEM analysis. The electrical conductivity of the CNT coated sample was analyzed and showed great improvement compared to untreated samples.

2 EXPERIMENTAL

2.1 Materials

Polyethylene terephthalate (PET) fabric (130 g/m^2, plain weave) was obtained from a local mill. Amino functionalized carbon nano tubes (NH_2-MWCNT) (purity > 95%, -NH2 content: 0.45 wt%, diameter < 8-15 nm, length: 50µm) were supplied from Neutrino Company, Iran. Triton X100 and acrylic acid was purchased from Merck.

2.2 Methods

In order to obtain a uniform coat of NH_2-MWCNTs onto PET fabrics, it is necessary to prepare a well-dispersed colloidal solution. NH_2-MWCNT was dispersed in water containing 1 g/l Triton X100 by ultrasonication at power of 40 W for 1 hour. To treat some samples with acrylic acid, 10% V/V acrylic acid was added after the initial ultrasonication and the process was continued for another 5 minutes. Samples were soaked in the prepared dispersion for 1 minute in the presence of ultrasound. Then the samples were dried and plasma treatment was done for samples treated by acrylic acid in the previous step.

Plasma treatment of the samples (before and after soaking in NH_2-MWCNT dispersion, if needed) was done in a low pressure plasma equipment (Model: Junior Plasma, Europlasma, Belgium) working with oxygen gas (flow rate: 20 sccm) at the pressure of 100 mTorr and power of 150 W for 120 seconds.

To compare the amount of NH_2-MWCNTs adhered on the surface of the samples; color measurement was done on the treated samples. The reflectance of treated samples were measured on a Color-eye 7000A spectrophotometer using illuminant D65 and 10°standard observer. Color strength (K/S) of dyed samples was calculated using Kubelka-Munk equation:

$$K/S = (1-R)^2/2R \qquad (1)$$

where R is the observed reflectance, K is the absorption coefficient and S is the light scattering coefficient.

Fourier transform infrared measurements were carried out using a Nicolet 670 with a resolution of 4 cm^{-1}. An average of 40 scans was recorded in the ATR mode.

The surface morphology of raw and NH_2-MWCNT coated samples were studied using a KYKY-EM3200 digital scanning electron microscope (KYKY Technology, China) after coating the samples with gold.

Electrical resistance of the samples was measured with a static-voltmeter R-4021, Rothschild. In this test, the discharge time (t) from 150 V to 75 V was measured and then the resistance was calculated according the following formula:

$$\text{Resistance R (ohms)} = \text{t (seconds)} \times 10^{11} \qquad (2)$$

3. RESULTS AND DISCUSSION

To find the best process for coating of PET fabric with NH_2-MWCNT, four samples were treated with the following procedures:

Sample 4: raw PET was treated in 10 wt.% NH_2-MWCNT dispersion in the presence of ultrasound for 5 minutes.

Sample 3: Plasma treated PET sample was coated with 10 wt.% NH_2-MWCNT dispersion in the presence of ultrasound for 5 minutes.

Sample 2: Plasma treated PET sample was coated with 10 wt.% NH_2-MWCNT dispersion in the presence of ultrasound for 5 minutes. Then acrylic acid was added and the process was continued as explained earlier.

Sample 1: Plasma treated PET sample was coated with 5 wt.% NH_2-MWCNT dispersion in the presence of ultrasound for 5 minutes. Then acrylic acid was added and the process was continued as explained earlier.

For comparison, an untreated PET sample was used as blank (sample 5).

Figure 1 shows the K/S value for different samples. It can be seen that the samples prepared without acrylic acid did not show significant difference with the blank sample. It means that only ultrasound and plasma treatment alone or in conjunction cannot lead to a high amount of adsorption of NH_2-MWCNT on PET fabric. Only the samples prepared in the presence of acrylic acid showed high K/S value. The amount of NH_2-MWCNT coated on the PET fabric increased with increasing the amount of it in the soaking bath.

Figure 2 shows the ATR-FTIR spectra of the samples. The gradual appearance of a peak at 1560 cm^{-1} from sample 5 to 1, attributed to amine groups, confirms the presence of higher amounts of NH_2-MWCNTs on the surface of samples 1 and 2.

SEM images shown in figure 3, confirm the higher amount of NH_2-MWCNTs on the surfaces of samples 1 and 2 and the polymerization of acrylic acid to poly-acrylic acid on the surface of these samples in the final plasma treatment stage is evident.

The surface of sample 5 is rough as expected and no difference can be seen on the surface of sample 4 compared to sample 5. It is due to very little adsorption of NH_2-MWCNTs on this sample. The surface of sample 3 is rough due to the etching effect of the pretreatment of the sample with oxygen plasma. But this pretreatment didn't lead to a remarkable adsorption of NH_2-MWCNTs on sample 3 compared to samples 4 and 5. The surfaces of samples 1 and 2 show higher amounts of NH_2-MWCNTs and grafted poly-acrylic acid. The sample treated with higher amount of NH_2-MWCNTs (sample 2) showed the higher amount of deposition of the nanoparticles.

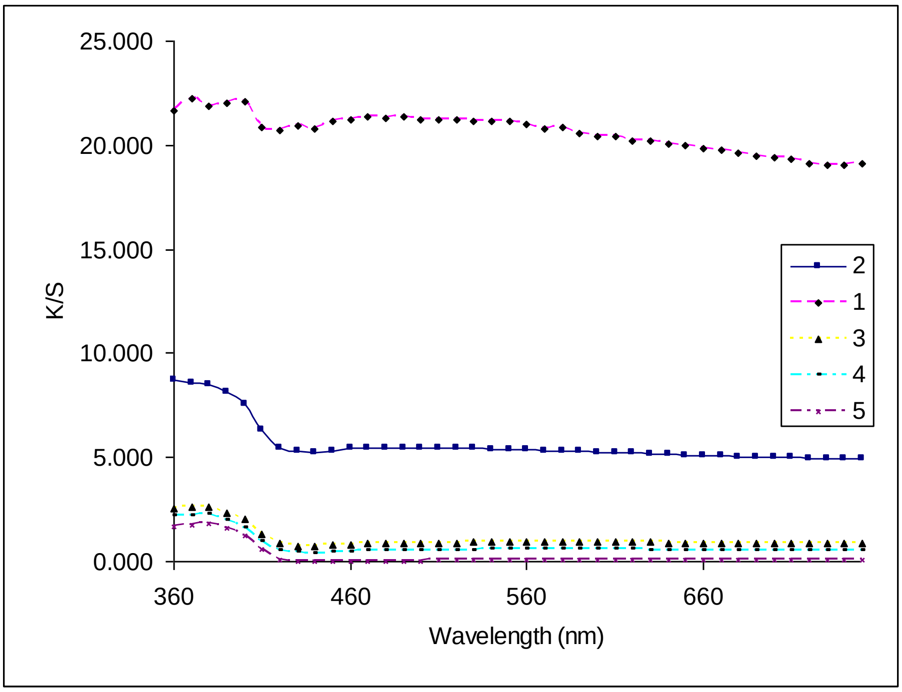

Figure 1: Color strengths of different samples

Electrical resistance of the samples was also determined. Because of the low amount of NH_2-MWCNTs coating onto samples 3, 4 and 1, only sample 2 was compared with the raw sample (sample 5). The discharge time for untreated sample was higher than 600 seconds while the much shorter time was found for sample 2 (around 2 seconds). So the electrical resistance for sample 2 was 2×10^{11} and the raw PET fabric can be considered as an electrical insulting sample. This shows that after plasma treatment, surface roughness of fabrics increased and thereby the large quantity of NH_2-MWCNTs was attached onto fiber surface. This gives rise to the development of electrically conductive networks in the PET fabrics and enhancing the electrical conductance.

4. CONCLUSION

In this study, amino-functionalized Carbon nano tubes were coated onto the polyester fabrics, leading to a highly electrically conductive fabric. Four procedures were conducted to load NH_2-MWCNTs on PET samples and the best procedure was selected. Plasma treated fabric which was subsequently coated with NH_2-MWCNTs in the presence of acrylic acid was chosen as the best sample for conducting static charge. FTIR analysis indicated the incorporation of amine functionalities on fabric surface after coating with NH_2-MWCNTs. The rough surface for plasma treated sample is responsible for more deposition of NH_2-MWCNTs on fabric surface and thereby the electrical resistance of NH_2-MWCNTs coated fabric decreased.

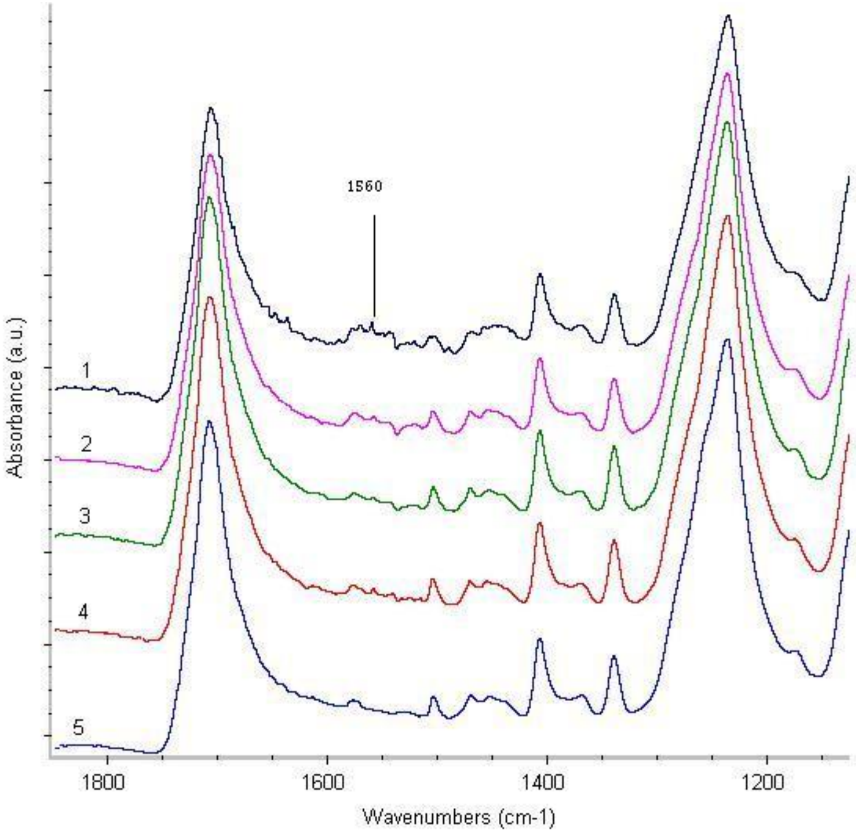

Figure 2: ATR-FTIR spectra of different samples

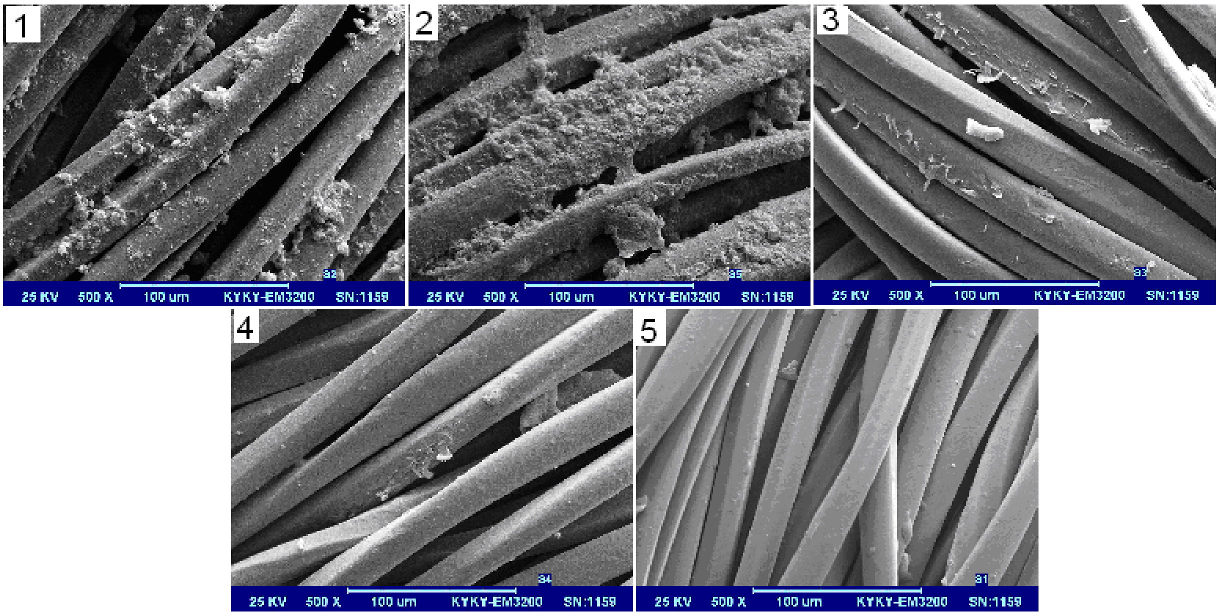

Figure 3: SEM images of different samples

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STUDY OF THE CURING PROCESS OF ELO AND ESBO RESINS FOR THE MANUFACTURE OF BIO-COMPOSITES

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Keywords: ELO, ESBO, curing process

Abstract. *The matrix of composite materials can be made of resin. This study analyzes the viability and obtains the optimal temperature for a proper infusion of ELO and ESBO bio resins. A complete analysis of the curing process has been done using gel time and plate-plate rheology.*

1. INTRODUCTION

Currently, several research groups are developing composites from renewable sources to achieve a more sustainable society. The composites are formed by two main components, matrix and reinforcement. There are numerous studies that use natural fibers as reinforcement as hemp, jute, sisal, coconut ... Most of these works with composite materials reinforced with natural fibers are made using conventional thermosetting resins or thermoplastic biopolymers.

Thermoset materials usually used for making the matrix of the composites are mainly produced from petroleum resources. Now there are on the market a few thermoset polymers that are produced from renewable resources. It is of great importance the development of thermoset resins exclusively from biological origin so it will be possible to manufacture composite materials entirely from natural origin. This work analyzes, compares and characterizes the curing process of two thermoset resins that can be used in the development of composite materials. Both studied resins came from the epoxidation of a natural oil, since this process transforms inexpensive and readily available vegetable oils into a product useful for making composites. The studied resins are Epoxidized Linseed Oil (ELO) and Epoxidized Soybean Oil (ESBO).

The main objective of this study is to analyze and understand the curing process of the two resins in order to determine their suitability to be used as matrix in the manufacture of bio-composite materials.

2. EXPERIMENTAL

2.1 Materials

Both studied resins are from natural origin. Epoxidized Linseed Oil (ELO) and Epoxidized SoyBean Oil (ESBO) have been studied in order to be applied in the infusion of a biocomposite.

These resins have been added in order to start the curing process, the components added to both resins are:

- Hardener: Epoxy embedding medium, hardener, Methyl nadic anhydride (MNA), supplied by Signa Aldrich (Barcelona, Spain).
- Starter: Propilenglicol E-1520 (PDO), supplied by Colarim Aditivos (Spain)
- Catalyzer: 1-Metilmidazol, 99% (1-MI), supplied by Signa Aldrich (Barcelona, Spain).

The different combinations and proportions of the various components for obtaining the end of the resins used for preparing the compounds are shown in the following tables (Table 1 and Table 2).

Component	Quantity
Resin (ELO, ESBO)	1 equivalent ratio
Hardener (MNA)	0,9 equivalent ratio
Starter (PDO)	1*% total* weight
Catalyzer (1-MI)	2*% total* weight
Resin (ELO, ESBO)	1 equivalent ratio

Table 1: Formulation of the components of ELO & ESBO resins.

Component	Equivalent Mass (g/equiv)
ELO	178
ESBO	238,1
Hardener (MNA)	178,2

Table 2: Formulation of the components of ELO & ESBO resins.

2.1 Techniques

The study of the curing process of the resins was performed using various techniques. It has been done in this way in order to contrast results and in order to obtain data from the different techniques used so, a more reliable conclusion of the curing of the two resins will be obtained. The study of the curing process was performed using the following techniques:

- The gel time has been determined using a Gelnorm-gel Timer (Gel Instrumentate AG, Germany). The gel time has been determined for isothermal analysis at 110, 120, 130 and 140ºC.
- Plate-plate rheology has also been applied in order to study the curing of the composite resin, the equipment used was an AR_G2 Rheometer (TA Instruments, USA).

3. RESULTS

As it was discussed in the previous section the objective of this study is to study and understand the curing process of the two analyzed resins, ELO and ESBO, with the aim of determining a suitable temperature for proper processing and preparation of composite blades. This study of resin curing process was performed using various techniques, so it is possible to contrast the different data. The different techniques are used in order to obtain a more reliable parameter suitable curing of the two resins.

3.1 Gel time using gel time technique

The gel time determination was performed using a specific equipment for that purpose. The time needed to reach the gel point with different temperatures for ELO and ESBO resin are shown in Table 3.

Temperature (ºC)	Gel time ELO	Gel time ESBO
110	27’ 31”	59’ 20”
120	15’	35’ 51”
130	9’ 9”	19’ 50”
140	5’ 51”	11’ 19”

Table 3: Gel time.

Gel times on the two resins are quite different. ESBO need more resin gel time. The results were plotted on a graph to more representatively observe the difference between both resins.

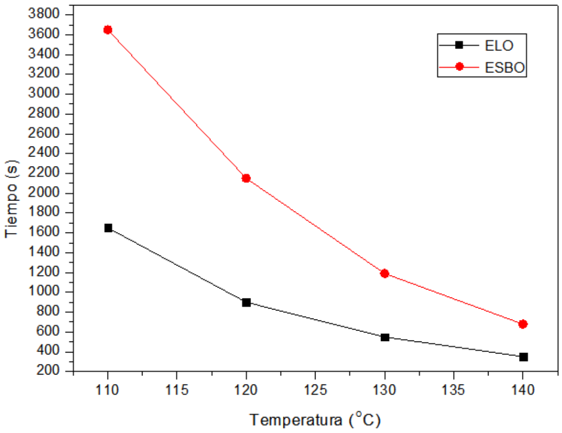

Figure 1: Gel time of ELO and ESBO resins

In addition to the gel time values determined, it is possible to calculate the activation energy necessary to activate the gelation process. The activation energy (E_a) has been calculated using kinetic models and the obtained gel time values. The representation of Ln (Tgel) versus 1/T for various values of temperature allows a linear fit from which it can be estimated the value of the activation energy. In order to do this it is necessary to apply a kinetic model.

$$t_{gel} = Cte \cdot \frac{1}{k} \tag{1}$$

$$k = A \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)} \tag{2}$$

After applying logarithms the next formula is obtained

$$t_{gel} = Cte \cdot \frac{1}{A \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)}} \tag{3}$$

$$t_{gel} = Cte'' \cdot \frac{1}{e^{\left(\frac{-E_a}{R \cdot T}\right)}} \tag{4}$$

$$Ln\, t_{gel} = Ln\, Cte''\cdot Ln\, e^{\left(\frac{-E_a}{R\cdot T}\right)} \qquad (5)$$

$$Ln\, t_{gel} = Ln\, Cte'' + \frac{-E_a}{R\cdot T} \longrightarrow y = ax + b \qquad (6)$$

Using formula 6 it is possible to approximate to a line with a linear regression. Performing this linear regression it is possible to obtain the graphs below, thus it is possible to calculate the activation energy of the gelling process.

In the graph corresponding to the ELO resin (Figure 2), Ln (T_{gel}) has been represented on the vertical axis as it was proposed on formula 6. In the x-axis it is shown the inverse of temperature, it has been multiplied by 1000 in order to present more representative results (Figure 2) and (Table 4).

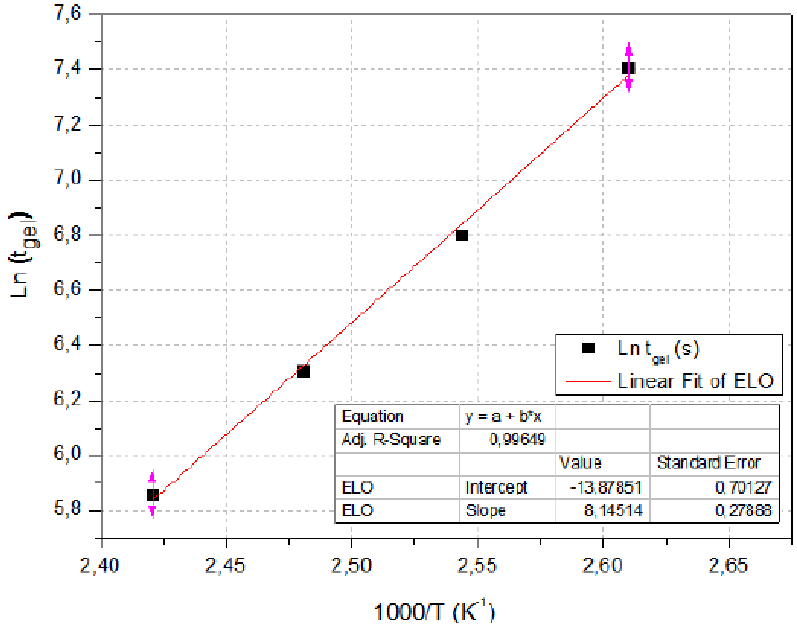

Figure 2: Linear regression of the gel time of ELO resin

Temp (ºC)	Temp (K)	t_{gel}(s)	Ln t_{gel}(s)	Gel time ESBO
110	383	1651	1.41	2.61
120	393	900	6.8	2.54
130	403	549	6.31	2.48
140	143	351	5.86	2.42

Table 4: Values of the lineal regression of the ELO resin.

It can be seen that the linear regression is closely matching 0.99649, so it can be considered a good approximation. Using these results it is possible to obtain the activation energy (Ea). Given that the gas constant equal to R = 8.314 (J/molk) and that b = 8.14514 corresponding to the linear regression, the formula 7 can be used to obtain the activation energy.

$$E_a = b\cdot R \longrightarrow E_a = 67.72 (kJ/molK) \qquad (7)$$

The procedure was the same with the ESBO resin.

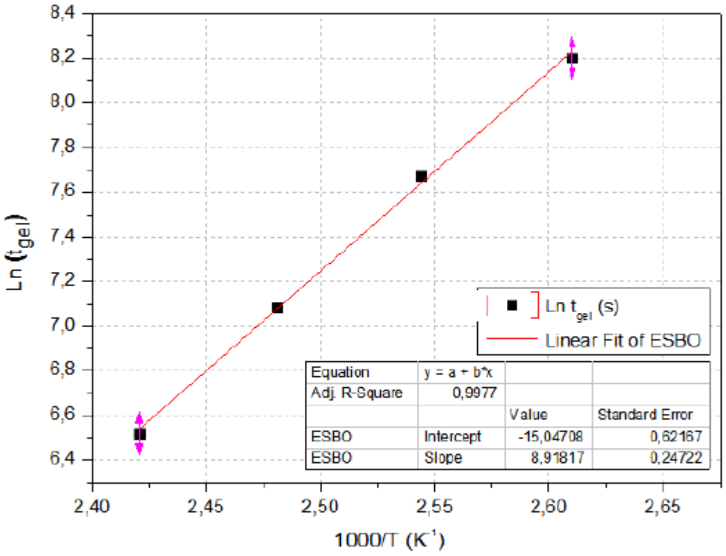

Figure 3: Linear regression of the gel time of ESBO resin

Temp (ºC)	Temp (K)	t_{gel}(s)	Ln t_{gel}(s)	Gel time ESBO
110	383	3650	8.2	2.61
120	393	2151	7.67	2.54
130	403	1190	7.08	2.48
140	143	679	6.52	2.42

Table 5: Values of the lineal regression of the ESBO resin.

Linear regression is considered correct because it has a correlation value of 0.9977. Given these results we can proceed to the calculation of the activation energy (Ea).

$$E_a = b \cdot R \longrightarrow E_a = 74.15 (kJ/molK) \qquad (7)$$

3.1 Gel time using rheology

Another way to obtain the gel time of the resin is with an isothermal curing study through plate-plate rheometry. This technique really evaluates the force required to rotate the plate to plate curing process under isothermal conditions wherein the resin changes from liquid to solid state, but it also can serve, as mentioned, to determine the gelation point. Rheometry has been used to contrast the results with the ones obtained with the gel time technique.

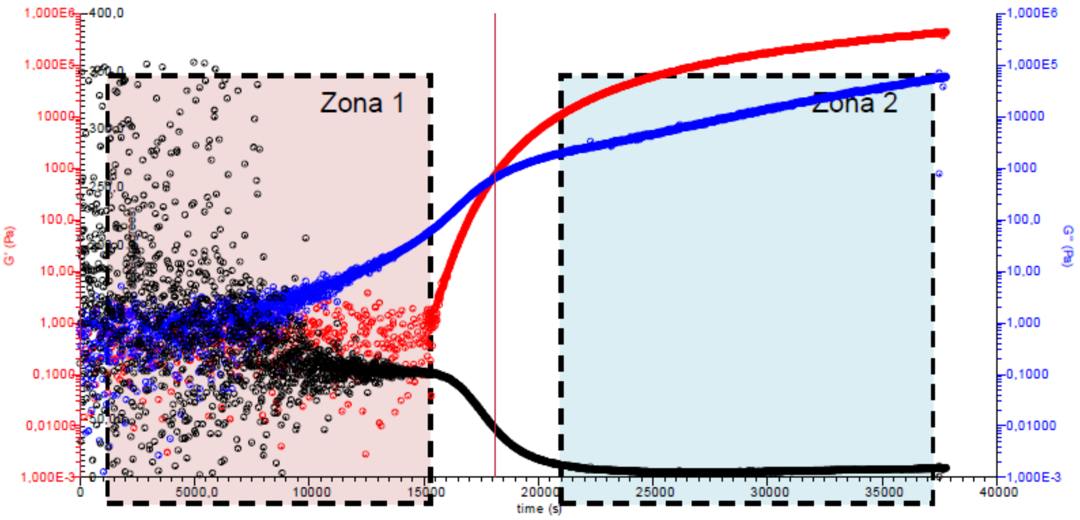

Figure 4: Curing of ESBO resin at 90ºC with plate-plate rheolometry

Figure 2 shows the results of the plate plate rheology of the ESBO resin at 90ºC. The figure plots the behavior of storage modulus (G'), loss modulus (G'') and the phase angle (δ). In the graph there are two main zones which are markedly identified. The zone 1 is where the phase angle between G 'and G" denotes a constant series of values around 90°, corresponding to the left side of the graph (red square), this behavior is characteristic of liquid resins. Zone 2 is the right side of the graph where the phase angle presents values around 0º which are characteristics of solid resins. These two zones are the both ends of the curing process of a resin. The curing process starts when the phase angle 90° begins to decrease until it reaches values of 0º. The vertical line shown in red coincides at the intersection of the two modules G 'and G", it also coincides with a value of the phase angle of 45°, this is the gel time point of the resin.

In the gel time technique it has been observed that at temperatures above 120ºC gelation time is very fast and it can prevent a proper resin infusion. In plate-plate rheometry it has been decided to analyze these resins at lower temperatures, in order to find the most suitable temperature for processing resins.

Temperature (ºC)	G'=G'' (Pa)	Time (s)
80	2607	18157
90	632	9305
100	195	4560
110	139	2787
120	171	800

Table 6: Isothermal curing of ELO resin using plate-plate rheometry.

Table 6 shows that an incresasement of the temperature reduces the gel time until a minimum at the temperature of 120ºC. At this temperature it is difficult to determine the gel time since it is achieved very fast.

Temperature (ºC)	G'=G'' (Pa)	Time (s)
80	-	-
90	565	16858
100	231	9008
110	414	4309
120	96	2748
140	72	807

Table 7: Isothermal curing of ESBO resin using plate-plate rheometry.

In the study of the resin it can be observed that there are no data for ESBO at 80°C since the curing process fails at that temperature (Table 7). So it was decided to consider curing at 140ºC. It can be clearly seen that as the temperature is increased until a limit of 140ºC, the gel time is reduced. 140ºC is the limit value acquisition which is critical because it is a very high temperature for this type of resin.

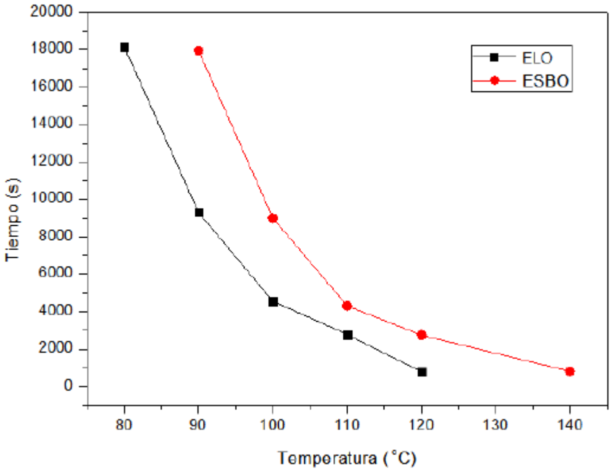

Figure 5: Curing of ESBO resin at 90ºC with plate-plate rheolometry

In Figure 5 shows the difference between the two resins. For these results, it can be said that for both resins, ESBO and ELO, as higher the curing temperature is, shorter gel time is obtained.

In plate-plate rheometry the activation energy (Ea) required to activate the gel can also be estimated, using the kinetic models already explained.

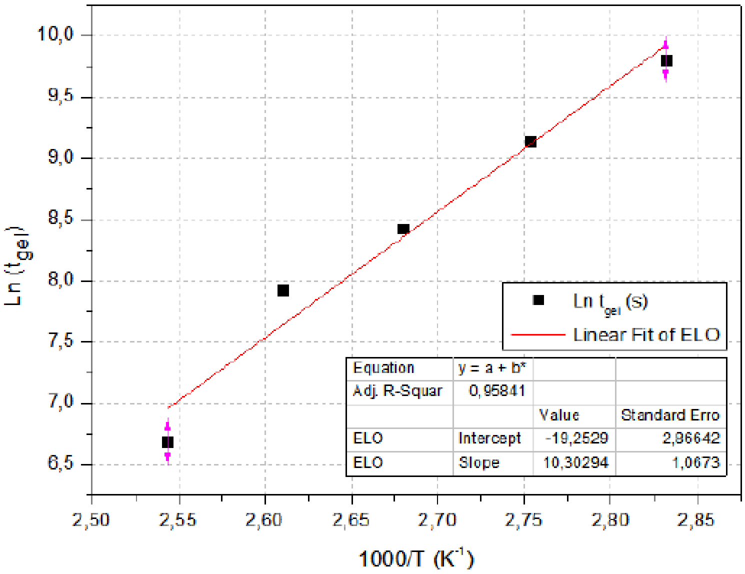

Figure 6: Linear regression of the gel time of ELO resin obtained with rheology

Temp (ºC)	Temp (K)	t_{gel}(s)	Ln t_{gel}(s)	Gel time ESBO
80	353	18157	9.81	2.83
90	363	9305	9.14	2.75
100	373	4560	8.42	2.68
110	383	2787	7.93	2.61
120	393	800	6.68	2.54

Table 8: Values of the lineal regression of the ELO resin.

Linear regression is considered correct because it has a correlation value of 0.95841. Given these results we can proceed to the calculation of the activation energy (Ea).

$$E_a = b \cdot R \longrightarrow E_a = 85.66(kJ/molK) \tag{8}$$

The same procedure is used for the ESBO resin.

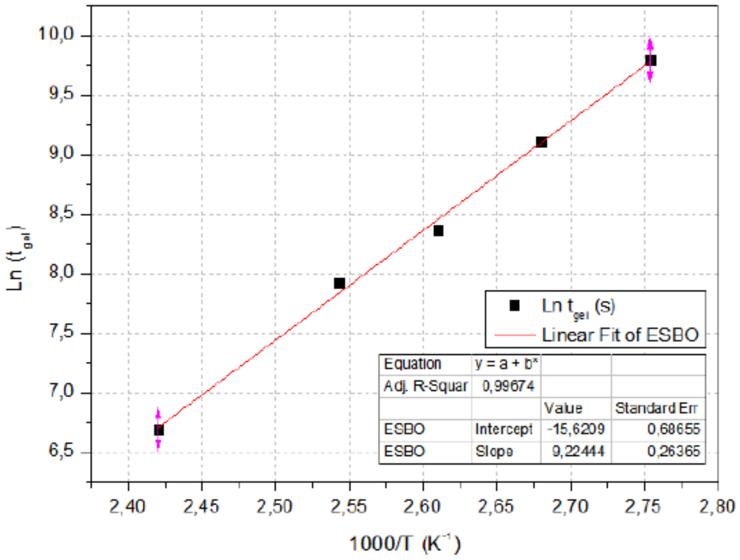

Figure 6: Linear regression of the gel time of ESBO resin obtained with rheology

Temp (ºC)	Temp (K)	t_{gel}(s)	Ln t_{gel}(s)	Gel time ESBO
90	353	17957	9.8	2.75
100	363	9008	9.11	2.38
110	373	4309	8.37	2.31
120	383	2748	7.92	2.54
140	413	807	6.7	2.42

Table 8: Values of the lineal regression of the ESBO resin.

Linear regression fit is more fiable for ESBO resin since it presents a correlation of 0.99674,. Given these results we can proceed to the calculation of the activation energy (Ea).

$$E_a = b \cdot R \longrightarrow E_a = 76.70(kJ/molK) \tag{9}$$

4 CONCLUSIONS

In conclusion we will then compare the results of two techniques for obtaining gel time of the resin ELO and ESBO. The results of the activation energy from the gel time and plate-plate rheometry are the following (Table 9).

Resin	E_a Gel Time (kJ/molK)	E_a Rhemetry (kJ/molK)
ELO	67.7	85.7
ESBO	74.2	76.7

Table 9: Activation energies.

As it can be seen in the table 9, the results obtained for ELO resin in both techniques are quite different, that is because the linear regression Gel Time is more accurate than the plate-plate rheometry. In ESBO resin occurs the same, although the difference between the two techniques is not so great. Therefore, due to a better fit of the regression line, the results obtained in the Gel Time are taken as correct. Thus, one can conclude that the activation energies of ELO and ESBO resins are very similar, may have the same consideration as the cured modeling processing on the resin infusion technique.

If the temperatures of the two techniques are compared, it can be said that the results of the two techniques complement the understanding of the curing process of the resins.

However, analyzing the obtained results it can be concluded that the most suitable processing temperatures of the resins are from 100 to 120ºC, being 100ºC the most suitable for the resin infusion technique. In the recommended temperature range the resin infusion technique can be done perfectly, there is enough processing time for a proper impregnation of the reinforcement fibers by the resin before gelation time.

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DEVELOPMENT OF ADVANCED COMPATIBLE MATERIALS FOR THE RESTORATION OF CULTURAL HERITAGE ASSETS (MYTHOS): FIRST RESULTS.

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Keywords: textile restoration; fibre analysis; genetic analysis; Fibreshape; Dia-Stron; scanning electron microscopy (SEM)

Abstract. *For the restoration and preservation of textile cultural heritage objects it is essential to use similar or identical materials for e.g. testing cleaning or restoration processes before treating the unique and irreplaceable originals. Main focus of the MYTHOS project is to develop such reference materials for enhanced restoration and conservation of hemp and linen based ancient arts. First issue is genetic analysis of original samples to identify actual hemp and flax species close to the ancient varieties. In parallel selected original samples are analysed in detail for damages and their mechanical and morphological characteristics. This information will be used as base for artificial ageing of actual fibres to achieve the desired restoration materials.*

Due to the nature of the samples analytical methods have to be either non-destructive or restricted to minimal sample amounts. Fibre tenacity and elongation have been analysed in a single-element test (Dia-Stron) on 90 single elements. The fibre width distribution is assessed by Fibreshape. Finally a part of these single elements is examined by SEM to identify degradation effects (e.g. fungal attack) and traces of the processing equipment used in spinning / weaving. The results are compared to data of actual hemp and flax fibres.

1 INTRODUCTION

The cultural heritage of each country includes the works of its artists, architects, musicians, writers and scholars as well as the anonymous artists, emerging from the soul of the people, and the set of values that give meaning to life, i.e., construction materials and no materials that express the creativity of the people, the language, rituals, beliefs, historical sites and monuments, literature, works of art, archives and libraries (UNESCO, 1982). For most European citizens, cultural heritage assets are unique and irreplaceable in their tangible form of historic buildings, collections, sites and movable objects as well as in their intangible value, which includes history, collective memory and identity. The combined effects of climate change, other environmental changes, human interventions and security risks threaten Europe's cultural heritage.

Textile based works of art restoration and conservation techniques applied today use ‘foreign’ materials (glues, additives, fibres etc.) that are incorporated directly in the works of art. There are no experimental materials appropriate to the different type of textiles in historical objects, in terms of technical and biological similarity that can supplement and enhance the restoration and conservation techniques directly on the work of art. MYTHOS project proposes to develop novel ways of treating and storage textile based European arts. The main objective of the project is to develop a set of reference materials, to be used by the cultural national and international organization (Museums, restoration Centres, Ministries of Culture, Education centres etc.). The reference materials will have similar biological and technical characteristics as the ancient textile arts which are on based hemp (*Cannabis* sp.) and flax (*Linum* sp.) fibres and will be dedicated to the restoration and conservation of the hemp and linen based arts. The cultural heritage textile objects are part of the National Peasant Museum collection that are in an advanced degradation state and in need of immediate action. The solution offered by MYTHOS will provide a long term conservation strategy preserving their originality and cultural identity.

Hemp (*Cannabis sativa* L.) and flax (*Linum usitatissimum* L..) plants represent one of the ancient culture that humans tried to domesticate since the early ages of civilizations and most likely the first plant cultivated by mankind for its textile use [1]. It is believed that the centre of origin of Cannabis is central Asia, from where it subsequently spread to Mediterranean countries as well as to Eastern and Central European countries [2].

Flax was subject of pioneer research from the area of plant tissue culture concerning indirect organogenesis, plant regeneration from adventitious shoots and pathogen development on leaves using *in vitro* cultures [3]. As a species easily regenerating in *in vitro* cultures, flax was readily employed in investigations of embryo cultures and transformation of other plant species, among others, rapeseed and cereals [4].

Due to the value of historical textiles for the cultural heritage and the necessity to preserve them for the future generations all the investigations will be micro-destructive or non-destructive. The analysis of such objects requires cooperation between researchers from different areas of science, i.e. archaeology, chemistry, history of art, textile technology, etc. In the frame of this project it is necessary to collect data about the tenacity of the original fibres to have initial target information for the new breed variants and the ageing processes in the later phases. This is normally not essential for the description of historical textiles and thus rarely reported in the literature (historical linen yarn tests [5]). In order to minimize the impact on the textiles only small subsamples can be taken to perform a micro-destructive analysis, e.g. yarn pieces from the hem. After the new cultivars with old genetic profiles are obtained they will be cultivated in specific greenhouses with controlled conditions until their vegetal maturity. The bast plants will be now used for obtaining the fibres, threads and new reference materials. Old processing techniques will be used for this, because all the physical and mechanical processes to which a fibre, thread or material is subjected, are fundamental for its final state.

This paper describes first results obtained from mechanical analysis of samples taken from historical textiles.

2 MATERIALS AND METHODS

2.1 Materials

Historical fabrics, yarns and fibres were supplied by the National Peasant Museum, Bucharest. For the first analytical approach samples were selected which could be supplied in larger amounts than usual: fibres from preserved complete bobbins / clews and material used as decorative fibres from historical objects. The samples analysed here are listed in table 1 and displayed in figure 1. For comparison two samples of technical flax and hemp fibres are added. Both are grown in Germany and were mechanically separated as raw material for the automotive industry. For this reason the fibres are in general less fine and have a broader property distribution than fibres for textile yarn production. Detailed data about the reference materials can be found in [6].

Sample name	Fibre type	Origin
M 3870	flax[1]	clew
M 3871	flax[1]	clew
Tech. Flax A	flax	Germany 2004
L 7024	hemp[1]	decorative fibres
GDE02	hemp	Germany 2001

[1] to be confirmed by genetical analysis (in progress)

Table 1: historical samples analysed.

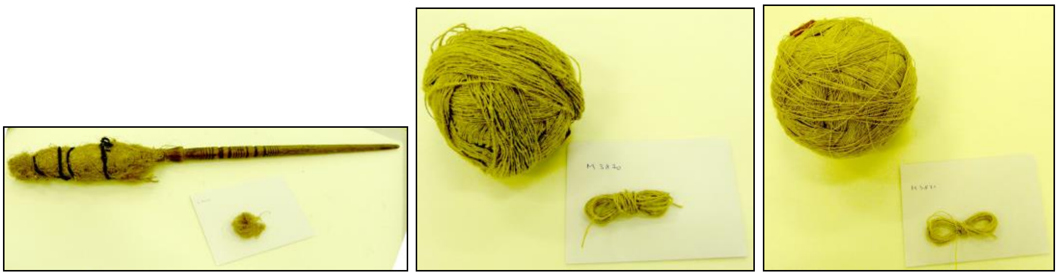

(a) (b) (c)

Figure 1: images of historical fibre samples (a) L 7024, (b) M 3870 and (c) 3871.

Actually a genetic analysis of the sample materials is in progress to prove the fibre type declaration and identify the varieties in detail. Up to now the mechanical and SEM analysis of the fibres have been performed as described below and will be reported here. Additional analysis on fibre fineness distribution is in progress and will be reported later.

2.2 Methods

To assess the mechanical and morphological properties of the fibres obtained from original historical textiles the use of destructive methods is unavoidable. To have minimised impact on the textiles only small subsamples are allowed to be taken, e.g. yarn pieces from the hem. For this reason fibre tenacity and elongation is analysed in a single-element test (Dia-Stron) on 90 single elements. This makes the analysis possible based on only 2 – 4 yarn snippets of approx. 2 cm length yielding approx. 200 single elements.

Preceding the analyses all samples have to be conditioned in standard climate at 20 °C and 65% relative humidity according to DIN EN ISO 139 [7] for at least 16 h. The mechanical characterisation is conducted on single elements based on DIN EN ISO 5079 [8] (1996), using a Dia-Stron System (Dia-Stron Ltd., Andover, UK) with clamping length 3.2 mm. Preceding the tensile test the cross-section of each single specimen is measured via laser beam. At least 90 specimens are measured to ensure statistically firm results [6].

A part of the remaining single elements was used for fineness analysis by the image processing system Fibreshape: fibres were cut into snippets of <5 mm length and prepared in glass slide-frames (GePe type 6004). These were analysed in a slide scanner (Minolta) at 4800 dpi (measuring mask 'ALFM48Z5'), using Fibreshape V4.2.

Finally a part of these single elements is examined by SEM to identify degradation effects (e.g. fungal attack) and to find characteristic traces of the processing equipment used in spinning / weaving. Prior to the measurement the fibres are sputtered 2 min. at 50 mA with gold dust (Edwards Sputter Coater S150B; Crawley, West Sussex, GB). SEM images of the fibres are recorded using a Cam Scan CS24 device (EO Elektronen-Optik-Service GmbH, Dortmund, Germany; acceleration voltage 20 kV; Software: analySIS 3.2, SIS Soft Imaging System GmbH, Münster, Germany).

3 RESULTS AND DISCUSSION

The results of tenacity measurement of the samples are displayed in figure 2 as *box-and-whisker* plots. The plots comprise the upper and lower deciles ($X_{0.90}$ and $X_{0.10}$) as outer dots, the upper and lower quartiles ($X_{0.75}$ and $X_{0.25}$) as box limits, and the median ($X_{0.50}$) denoted inside the box. In addition, the average values ±95% level of confidence are printed in the diagram. It is obvious that all historical samples are in the same range of tenacity, but the hemp sample is with median 258 N/mm² significantly below both flax samples with median 383 and 484 N/mm². Comparing this to the technical fibres from actual production there is an obvious difference: both of them display a higher tenacity of approx. 800 N/mm², combined with a much broader distribution, ranging to nearly 2000 N/mm² for the flax sample.

A similar tendency can be observed for the Young's moduli displayed in figure 3: all historical samples are in the same range of 10,000 – 13,000 N/mm² and display a similar width of distribution. Again the distribution of the reference samples is broader, but only for the flax reference it is significantly broader. It is only the flax reference sample, which has a slightly higher level of Young's modulus (19,000 N/mm²). All other samples including the hemp reference are in the same range.

In general most results presented here are in accordance with the literature [9]. Flax single element tenacity is reported to be in the range of 343 – 1500 N/mm² with mostly cited values around 700 N/mm². Both historical samples are at the lower end (383 and 484 N/mm²), but clearly inside the frame. The literature range for Young's modulus of flax is 8,000 – 100,000 N/mm² with mostly cited values around 70,000 N/mm². Again the samples are slightly above the lower end of the frame (10,700 and 13,300 N/mm²), i.e. clearly inside. The reference flax sample is in the mostly cited region of tenacity, but is at the lower end of the frame in Young's modulus.

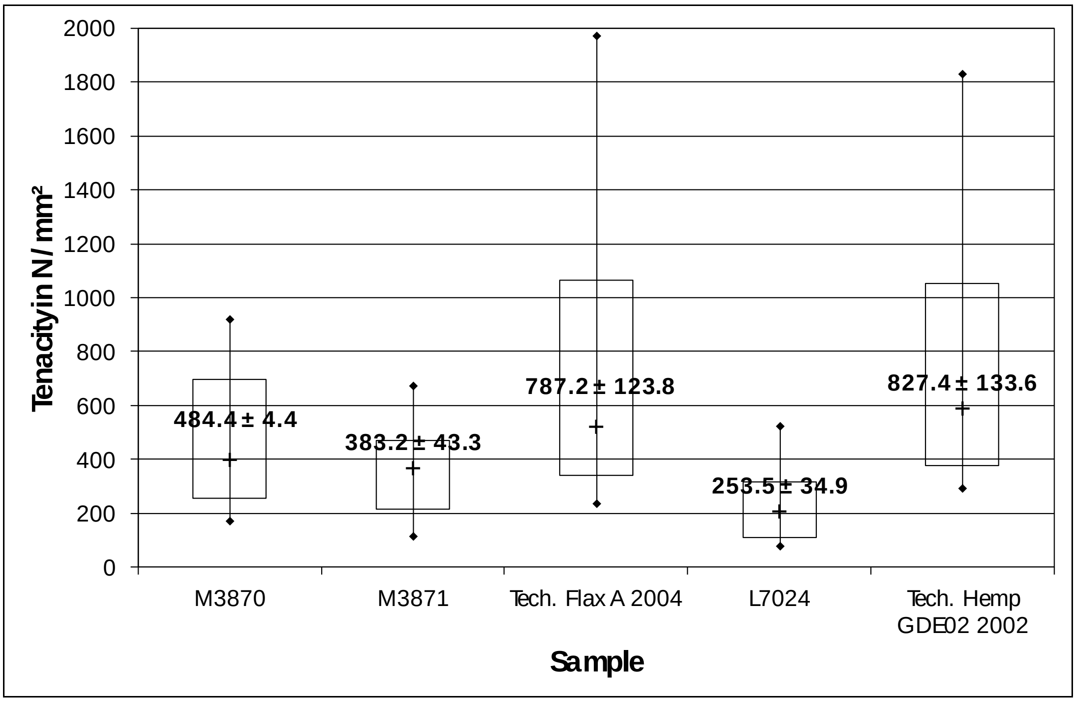


Figure 2: tenacity distributions of historical fibre samples compared to actual technical fibres with average values ±95% level of confidence.

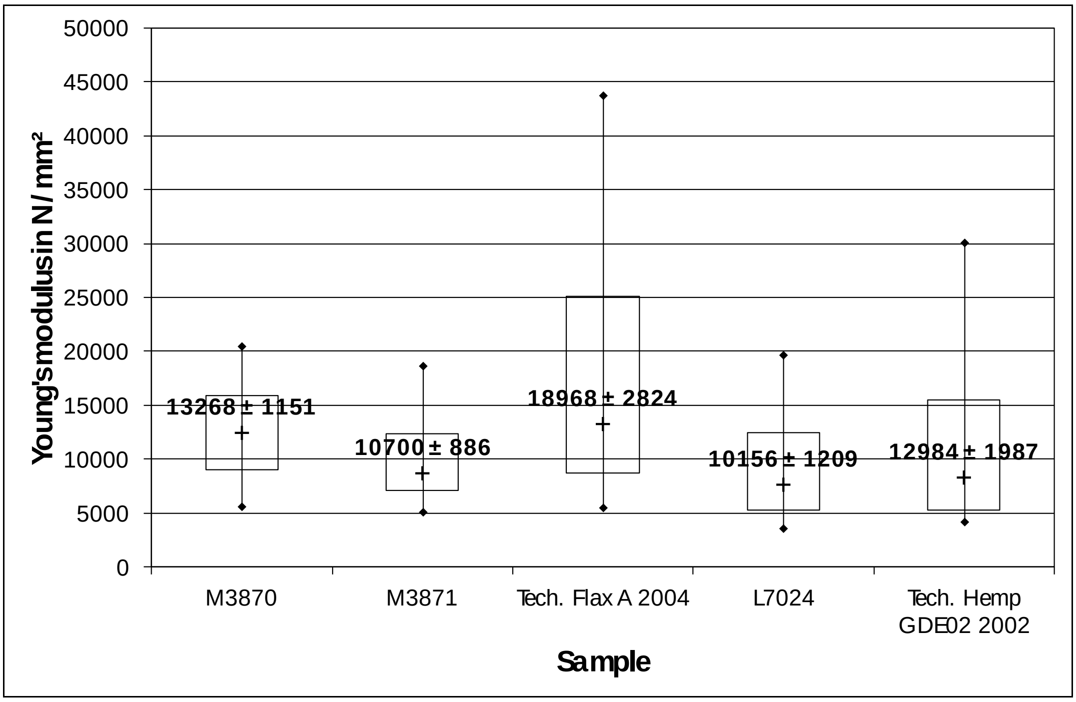


Figure 3: Young's modulus distributions of historical fibre samples compared to actual technical fibres with average values ±95% level of confidence.

Concerning the historical hemp and the hemp reference sample the situation is similar. Hemp single element tenacity is reported to be in the range of 310 – 1110 N/mm² with mostly cited values around 800 N/mm². The historic sample is slightly below this area

(258 N/mm²), and the reference (827 N/mm²) fits into the mostly cited region. Young's modulus is reported in the range of 3,000 – 90,000 N/mm² with mostly cited values around 65,000 N/mm². The historic (10,156 N/mm²) as well as the reference sample (12,984 N/mm²) are at the lower end but clearly inside the frame.

The fineness distributions of the historic and reference sample are displayed in figure 4. Due to the nature of these materials fibre bundle fineness or width are reported in very broad ranges in the literature [9]. Nevertheless the samples observed here are very fine for such materials. Flax fibre bundle width is reported in the range of 40 – 620 µm. Both the historic samples (27/35 µm) as well as the reference sample (20 µm) are clearly below this frame. This indicates the influence of the processing steps in spinning etc. for the historic samples as well as the coarse separation for the reference samples. The processing causes separation of the fibre bundles into finer elements. Similar observations were made for the historic and reference hemp. With 47 µm and 38 µm both are very similar to each other, indicating a similar intensity of processing. Compared to the literature range [9] of 25 – 500 µm, both are inside the frame, but clearly at the lower end.

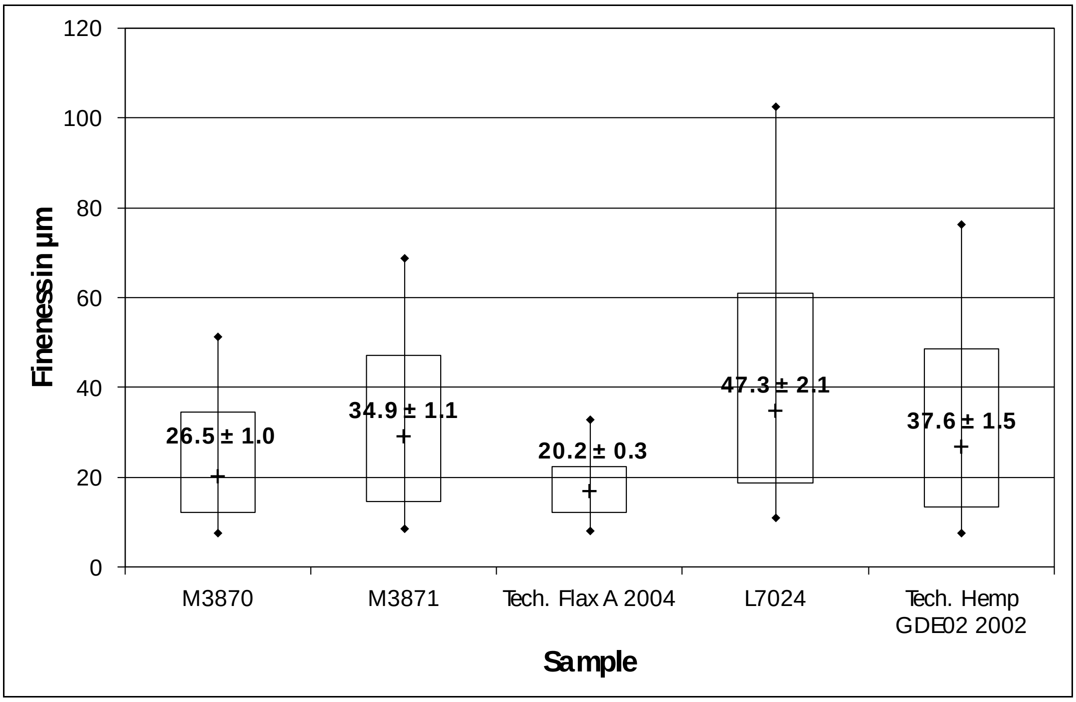
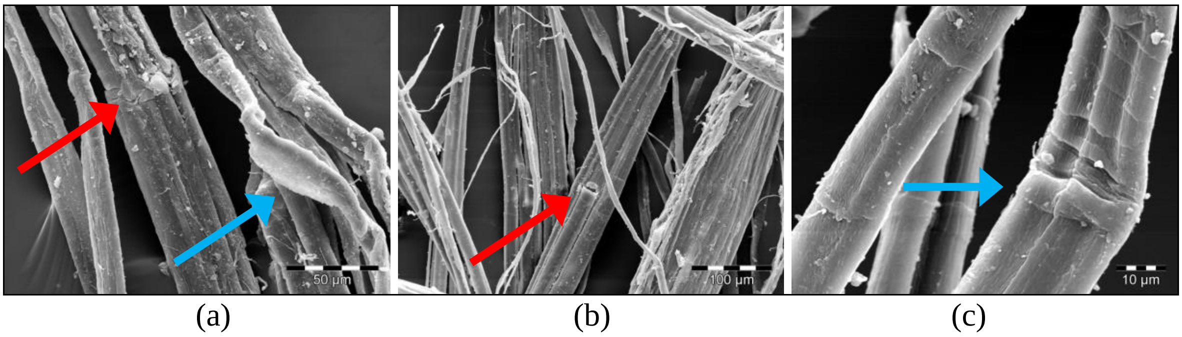


Figure 4: Fineness distributions of historical fibre samples compared to actual technical fibres with average values ±95% level of confidence.

The only difference between the materials observed here is, that both flax samples are very fine, whereas the hemp fibres are a little bit coarser. This corresponds to the former application of these fibres: for the flax fibres spun into a textile yarn such fineness has to be expected. The historic hemp fibre bundles were used for decorative purpose and thus less intensively separated. The selected reference materials correspond to the historic ones.

SEM analysis of the historic samples gave no hints on fungal damages. This must not be seen as general finding for historic textiles, but is valid for these analysed subsamples. Selected images of the three samples are displayed in figure 5. For all of them mechanical damages like cracks (marked by red arrows) or bucklings (marked by blue arrows) could be identified.



(a) (b) (c)

Figure 5: SEM images of (a) L 7024, (b) M 3870 and (c) 3871 with identified cracks (red arrows) and bucklings (blue arrows).

Such damages are well-known from new fibres which underwent erroneous processing [10]. Small cracks can also be caused by natural deterioration [11]. This indicates that the samples analysed here have been damaged more by processing than by degradation during storage.

4 CONCLUSIONS AND OUTLOOK

All historical samples assessed here are at the lower end of the literature range [9] in terms of tenacity Young's modulus. On the one hand this corresponds to the efforts of plant breeding during the last centuries, which led to actual bast fibres with higher tenacities and higher Young's moduli. On the other hand the selected reference samples represent varieties in actual use, whose mechanical fibre properties are only slightly above the level of the historical fibres. This indicates that these actual varieties used in mass production are not so far away from the historical ones (at least in terms of their mechanical properties).

This fact becomes more obvious looking deeper into details of the results: the main differences between historical and reference fibres have been found in terms of fibre tenacity, whereas all samples are in the same range of Young's modulus. Having in mind, that the tenacity is determined by the weakest point of the tested fibre (e.g. fungal or process-induced damages), but that Young's modulus represents the mechanical behaviour determined by the arrangement of the cellulose chains (crystallinity, fibril angle etc.) [12], it becomes obvious, that the difference between the material of historic and actual fibres is small.

As to be seen in the SEM images, the difference found in tenacity is presumably caused by processing damages, but this finding cannot exclude additional degradation effects during the centuries of storage (e.g. embrittlement) [11], but the fibres are still in a good state.

In addition, the historic and corresponding reference fibres were in the same range of fineness, indicating a similar intensity of processing. Based on these results it will be possible to set up a scheme for artificial ageing of new fibres to adapt them to the properties of the historic originals.

5 ACKNOWLEDGEMENTS

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PRETREATMENT OF POLYLACTIC ACID (PLA) FABRICS

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Keywords: PLA, Scouring, Bleaching, Degradation, FT-IR, XPS

Abstract: *Ingeo PLA (Polylactic acid) samples were subjected to scouring and bleaching processes. Scouring was carried out with sodium carbonate at various concentrations and process temperatures. Bleaching was carried out with hydrogen peroxide, sodium chlorite and sodium hypochlorite. Hydrogen peroxide was applied by exhaust and cold-pad-batch processes. The result showed that during scouring PLA samples were degraded at higher alkali concentrations and at higher process temperatures. Scouring temperatures higher than 60°C were deleterious because the scouring solution penetrated into the fibrous structure and damaged the fiber. Sodium chlorite and sodium hypochlorite caused little damage to the mechanical properties of PLA. Hydrogen peroxide when applied by the cold-pad-batch technique did not reduce strength appreciably but when applied by the exhaust technique decreased the strength significantly. The results showed that PLA could be scoured at 60°C, however, higher temperature led to degradations. Sodium chlorite and sodium hypochlorite could be used to bleach PLA and PLA-cotton blends on commercial scale.*

1. INTRODUCTION

PLA (Polylactic acid) is a new renewable and biodegradable material. Biodegradable materials are broken down into simpler and stable molecules, through macromolecular chain scission, in the presence of aerobic or anaerobic microorganisms [1, 2]. PLA is a synthetic thermoplastic material derived from natural resources [3]. PLA is a polyester manufactured from the condensation polymerization of lactic acid, the latter being produced by the enzymatic action on corn [3]. Cargill Dow LCC, established in 1997, is the largest manufacturer of PLA fibres marketed under the trade name of Ingeo® [4]. Unlike PET (polyethylene terephthalate), PLA does not depend on petroleum resources. PLA has some characteristics which are comparable to PET [5]. These characteristics include the moisture regain, tenacity, and crease resistance behaviour. PLA has some characteristics which are superior to PET. These include the specific gravity (PET 1.39, PLA 1.25) which make PLA a lightweight material, UV resistance (PET fair, PLA excellent) and refractive index (PET 1.54, PLA 1.4). Higher refractive index has been explained to cause deeper shades being produced on PLA than PET at the same dye concentrations [6]. The drawbacks of PLA are its poor thermal and hydrolytic stability. PLA has lower glass transition (T_g 55 – 65°C) and melting temperatures (T_m 130-175 °C) [3, 7]. Therefore, PLA cannot bear the harsh and severe process conditions as are employed for PET and blends of PET with natural fibres. Hydrolytic stability is of main concern in this work as most of the exhaust textile processes are carried out in aqueous medium. Previous work showed that hydrolytic stability of PLA depended on process temperature as well as time and pH of the medium. High temperatures, longer process times and neutral to alkaline pH medium caused excessive loss in mechanical properties of PLA samples. The results showed that acidic pH around 4.5~5 was the most suitable one for the integrity of PLA materials [8].

Textile fibres have various types of impurities, at different levels. These impurities could be natural, added or acquired. Synthetic fibres contain both added as well as acquired impurities. These impurities include the sizing chemicals, lubricants and waxes, anti-static agents, dirt and dust particles etc. These impurities have to be removed to insure uniform results in the post-treatment process e.g. dyeing and finishing. Pre-treatments are a series of processes aimed at removing these impurities. Scouring and bleaching are the two important pre-treatment processes considered in this work. Scouring is carried out in the presence of detergents and alkali(es) at different temperatures that may range from 60°C to 100°C. Synthetic fibres, generally, do not contain coloured impurities as do most of the natural fibres and hence do not require bleaching. However, in some cases where extra whiteness is required or where synthetic fibres are in blends with natural fibres, the formers have to bear the severe chemicals conditions required to bleach the later.

The present work was undertaken to study the pre-treatment of PLA fibres. Scouring was carried out at various temperatures and alkali concentrations, through an exhaust technique. Bleaching was carried out with various commercially important bleaching agents. Hydrogen peroxide, sodium chlorite and sodium hypochlorite were applied through exhaust technique to study their effects on tensile properties. Hydrogen peroxide bleaching was carried out at various H_2O_2 and alkali concentrations. SEM analysis was carried out to study the effects of various scouring and bleaching process conditions on the morphology of the fibres.

2. EXPERIMENTAL

2.1 Material & Machinery

Mathis Labomat IR dyeing machine was used to pretreat the PLA samples. Henna PH-210 digital pH meter was used to measure pH of the pretreatment bath before and after pretreatments. Knitted fabric constructed from 100% Ingeo spun yarn (30^s Ne) was used throughout the experimental work. Kieralon Jet B Conc. was obtained from BASF.

2.2 Scouring of PLA

The greige polylactic acid fabric was scoured in a bath containing 0-5 gm/L sodium carbonate and 0.5 gm/L Kieralon Jet B conc. (non-ionic surfactant, BASF) at 40-100°C for 20 minutes at liquor to materials ratio of 10:1. After scouring the fabric was rinsed with cold water and then dried at ambient conditions overnight. Figure 1 illustrates the processing profile of the alkaline scouring treatment.

2.3 Bleaching of PLA

2.3.1Hydrogen peroxide bleaching: The scoured Ingeo PLA fabric was subjected to typical “intense” bleaching conditions used for cotton in order to achieve “full bleach”. The fabric was treated with 1-5 ml/L hydrogen peroxide (35% w/w), 1-6 ml/L sodium hydroxide (50% w/w) and 0.5 gm/L Baystabil DB (H_2O_2 stabilizer; BASF) at 90°C for 45 minutes. The liquor to material ratio was 10:1. At the end of bleaching the fabrics were rinsed with hot water (60°C) for 15 minutes followed by cold rinsing and then treated with 1ml/L acetic acid solution to neutralize any residual alkali. Samples were dried at ambient conditions overnight prior to further testing.

2.3.2 Sodium chlorite bleaching: The scoured PLA samples were treated in a bath containing 1, 2, 3 and 5gm/l sodium chlorite (80% w/w), 3 gm/l sodium nitrate, 4 gm/l sodium di-hydrogen phosphate and 0.5 gm/l Kieralon Jet B conc. (non-ionic surfactant, BASF). The pH of the liquor was adjusted to ~4 with formic acid. Bleaching was carried out at 85°C for 45 minutes followed by hot washing (60°C) for 15 minutes and rinsing with cold water. The samples were dried at ambient conditions.

2.3.3 Sodium hypochlorite bleaching: The scoured PLA samples were treated in a bath containing 2, 4, 6 and 10 gm/l available chlorine (sodium hypochlorite, 14 % w/w), the pH being adjusted to 11 ~ 11.5 with sodium carbonate. The treatment was carried out at 40°C for 60 minutes followed by anti-chlor with 5 gm/l sodium bi-sulphite at 60°C for 15 minutes. Subsequently the samples were rinsed with cold water and left for drying at ambient conditions.

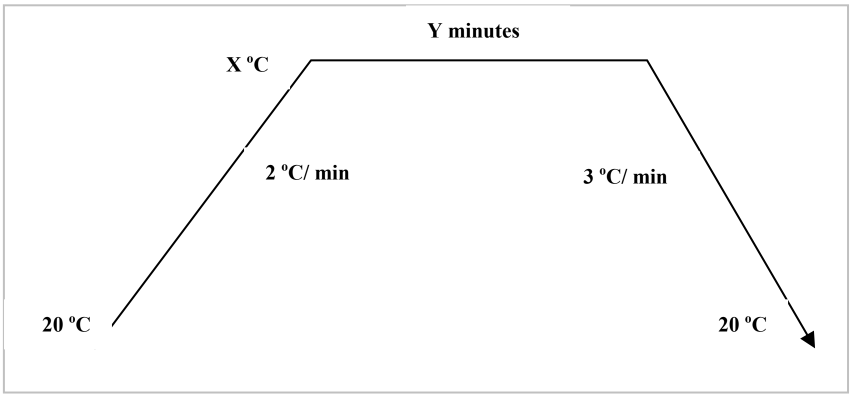


Figure 1: Pretreatment process profile

3. MEASUREMENTS

3.1 Measurement of Weight loss (%)

Samples were conditioned at standard conditions of 25°C and 65% R.H before testing. Following formula was used to calculate the weight loss of samples after dyeing, where W_1 and W_2 are the weights of the samples before and after dyeing dried at ambient conditions.

$$\text{Weight loss \%} = [W_1 - W_2] * 100 / W_1$$

3.2 Tensile Measurements

Yarns were taken out from control and each of the treated samples and conditioned at standards conditions of 25°C and 65% R.H before testing. Tests were performed according to BS EN ISO 2062:1995, using Instron Model 1122 tensile tester with a gauge length of 100 mm and at a strain rate of 1 min^{-1}. Ten tests were performed on each of the samples and the results acquired through desktop computer interfaced to the testing machine. The raw data was received and analyzed through computer software QT.

3.3 Measurement of Bursting Strength

Samples were conditioned at standard conditions of 25°C and 65% R.H before testing.

Jams H. Heal & Co. Ltd. digital bursting strength tester, TruBurst Model 610/02/1011, interfaced to a desktop computer was used to measure the bursting strength according to the ISO 13938-2 1999 standard test procedure. The samples were caught hold by a pneumatic cup, at a pressure of 6.3 bar, and pressure applied at a rate of 40 kPa/sec. Testing area and diaphragm were 7.3 cm^2 (30.5 mm diameter) and 1.0 mm Duraflex (JHH) respectively. Five tests were performed on each sample and the results acquired through James H. Heal software V1.04. All the necessary corrections and statistical calculations were performed automatically by the software.

3.4 SEM analysis

Surface morphology of the PLA samples was investigated using Scanning Electron Microscope. Samples were sputter-coated with Au in Polaron coating unit, model E5100 followed by loading sampler holder in the ZIESS SEM, model S-3000N. Gun-to-samples distance was 8-9 mm and voltage of 5kV was applied to accelerate electron toward the samples under high vacuum. Electron beam focusing, image magnification and brightness/ contrast were adjusted to take the photographs through SmatSEM software. The results are presented in figures 13a to g.

3.5 XPS analysis

XPS analysis of PLA samples was carried out with a Kratos Axis Ultra XPS instrument. The samples were irradiated with a monochromatic AlKα radiation source (1486.6 eV) operating at a base pressure of $3x10^{-9}$ Torr. Wide survey spectra were recorded at pass energy of 100 eV in order to determine the surface chemical composition. The oxidation states of elements were recorded at a pass energy of 20eV. The binding energy (B.E) values were calculated relative to C (1s) photoelectron peak at 285.0 eV.

4. RESULTS AND DISCUSSIONS

4.1 Effect of Pre-treatments on Weight Loss (%) of PLA

The effect of increasing the bath temperature of the sodium carbonate liquor was to increase the weight loss of the PLA fabric, Figure 2. The maximum weight loss was approximately 3% at a sodium carbonate concentration of 5 gm/L and a temperature of 100oC. Up to 60^oC there was a negligible weight loss, however, increasing temperature beyond this level caused a rapid increase in weight loss. Therefore it was concluded that a temperature up to 60^oC was acceptable for scouring of PLA fabric. The glass transition temperature (Tg) of PLA lies in the range of $55\text{-}65^oC$ and therefore scouring below T_g would restrict the scouring liquor from penetrating into the fibrous matrix and hence achieve less hydrolysis of the fibrous polymer, Figure 3a to 3f.

Figure 4 shows the weight loss of scoured PLA samples (scoured in 1gm/L sodium carbonate at 60^{oC}) treated with various bleaching agents. The results showed that hydrogen peroxide, applied by both the long liquor as well as cold-pad-batch, imparted more damage than any of the other bleaching agents due to the hydrogen peroxide bleaching treatments being either more alkaline or at higher temperature conditions. In the hot alkaline medium the PLA was degraded through hydrolysis, with the higher the alkalinity and process temperature, the more severe was the damage to the fibres. The Cold-Pad-Batch (CPB) hydrogen peroxide bleaching of PLA was performed at room temperature over 24 hours and although the hydrogen peroxide and sodium hydroxide concentrations were much higher as compared to those employed in exhaust application, the weight loss was comparatively less. Since the CPB process was carried out at room temperature, predominantly only the fibre surface was likely to get damaged and the fibre strength would be maintained. Although the sodium hypochlorite bleaching was also done in alkaline conditions, pH 11.0-11.5, the bleaching temperatures were relatively mild at 35-40°C and accordingly at these bleaching conditions there was little loss in weight, Figure 4.

The other chlorine-based bleaching system, sodium chlorite, was performed under acidic conditions and high temperatures and the results showed that sodium chlorite imparted the least damage to the fibres with the least loss in weight. At a pH of 4 and 85oC there was negligible increase in weight loss of the PLA samples when bleached with 2gm/L sodium chlorite. From these results it was concluded that all-PLA and PLA-cotton fabrics could be bleached "safely" with sodium chlorite and sodium hypochlorite bleaching systems. In contrast since wool is damaged by chlorine bleaches [43], PLA-wool blends can be bleached with hydrogen peroxide by the cold-pad-batch technique.

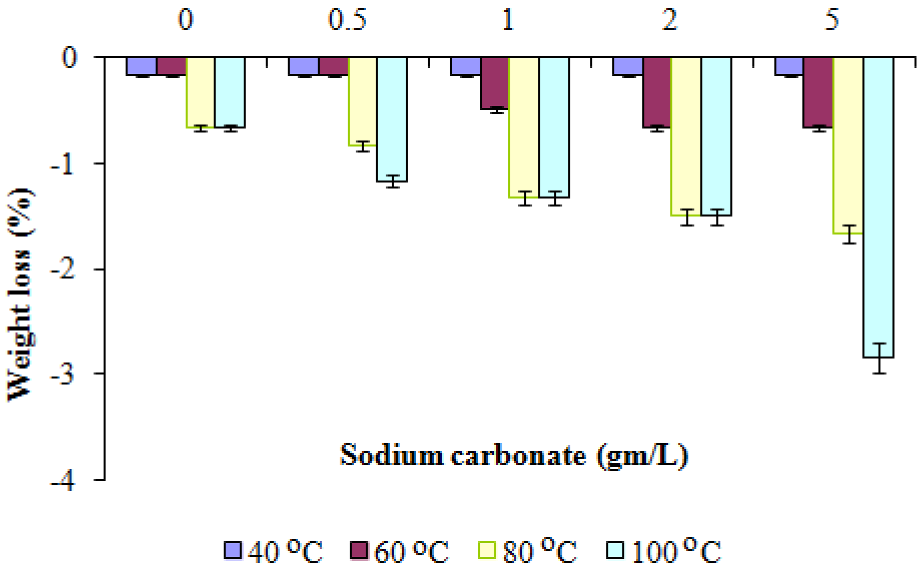
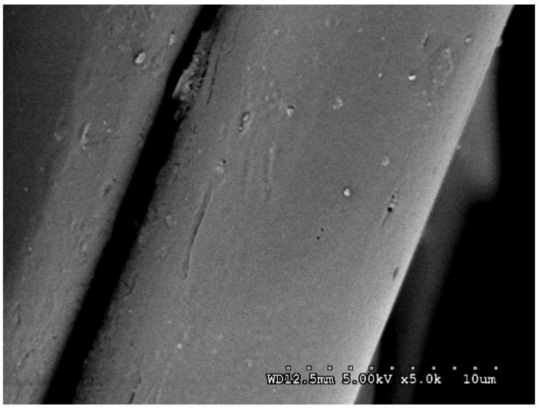
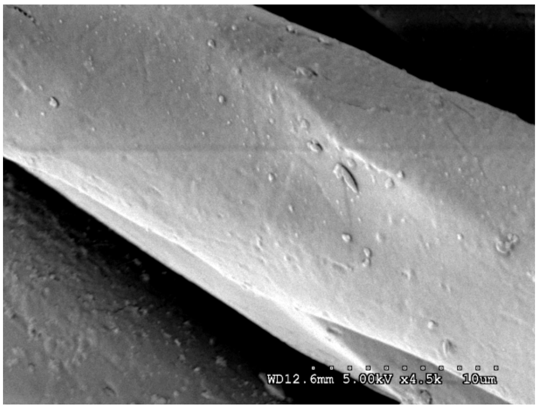


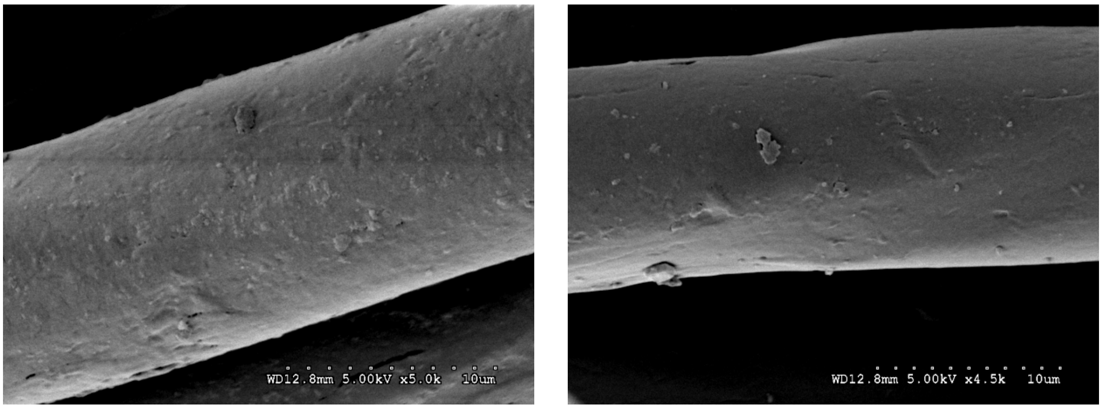
Figure 2. Effect of increasing scouring temperature and sodium carbonate concentration on the weight loss of PLA fabric (LMR 10:1, Time 20 min.).



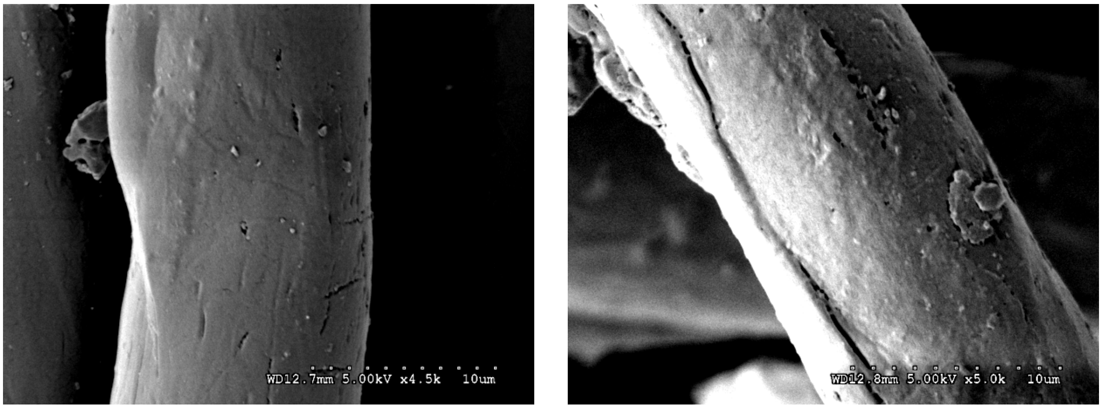
a – Na_2CO_3 0.5 gm/L, 40°C



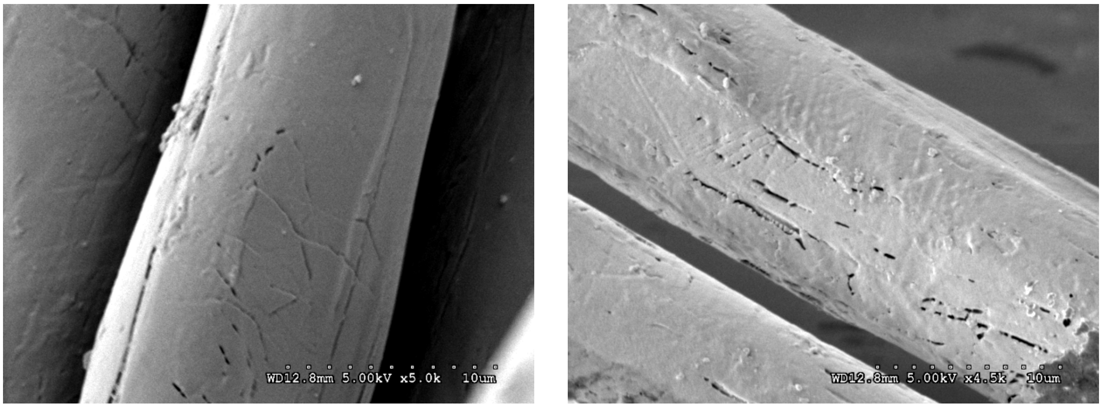
b - Na_2CO_3 5 gm/L, 40°C



c- Na_2CO_3 0.5 gm/L, 60°C **d** – Na_2CO_3 5 gm/L, 60°C



e - Na_2CO_3 0.5 gm/L, 80°C **f** – Na_2CO_3 5 gm/L, 80°C



g - Na_2CO_3 0.5 gm/L, 100°C **h** - Na_2CO_3 5 gm/L, 100°C

Figure 3: Scanning electron micrographs of scoured PLA fabrics.

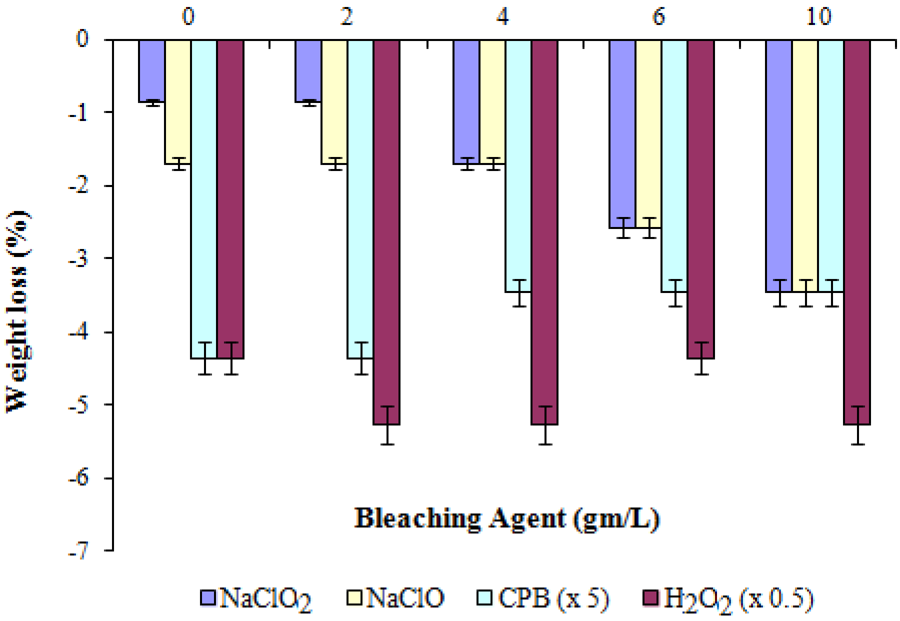


Figure 4. Weight loss of scoured PLA fabrics bleached with a range of oxidative bleaching agents (0.5 and 5 being the multiplication factors for H_2O_2 concentrations in the bleach bath).

4.2 Effect of Pre-treatments on Tensile Properties of PLA Yarns

PLA fabric was scoured at various alkali concentrations (0.5, 1.0, 2.0 and 5.0 gm/L) and processing temperatures (40°C, 60°C, 80°C and 100°C), Figure 5. The results showed that up to temperatures of 60°C, increasing alkali concentration had little effect on the overall tensile strength properties of the PLA yarns. In the temperature range of 80°C-100°C, an increase in alkali concentration caused ever higher losses in tensile strength. Therefore it can be concluded that scouring could be performed safely without appreciable loss in weight and tensile properties at 60°C even at a sodium carbonate concentration of 5gm/L which commercially would still be regarded as a relatively mild chemical process. However blends of synthetic and natural fibres may require more severe conditions due to the presence of natural impurities in the latter. Since scouring of cotton is carried out nearly at the boil, PLA may be damaged in PLA/cotton blends, as the results in Figure 5 predict. Therefore scouring of PLA/cotton blends should be carried out at lower temperatures, though it would take longer processing times.

SEM analysis of PLA fabric subjected to a range of scouring conditions indicated the scouring with sodium carbonate did not bring about any major changes in the smooth surface morphology of PLA fibres up to 60°C, Figure 3. However, scouring at temperatures above 60°C imparted damage to the fibres, in particular at 80°C where small localized holes appeared on the fibre surface. Further at 100°C there was more widespread severe damage to the fibrous structure observed. These observations correlated with the tensile data, Figure 5, where it was proposed that above the Tg hot and alkaline liquor penetrated into the polymer matrix and increased hydrolysis.

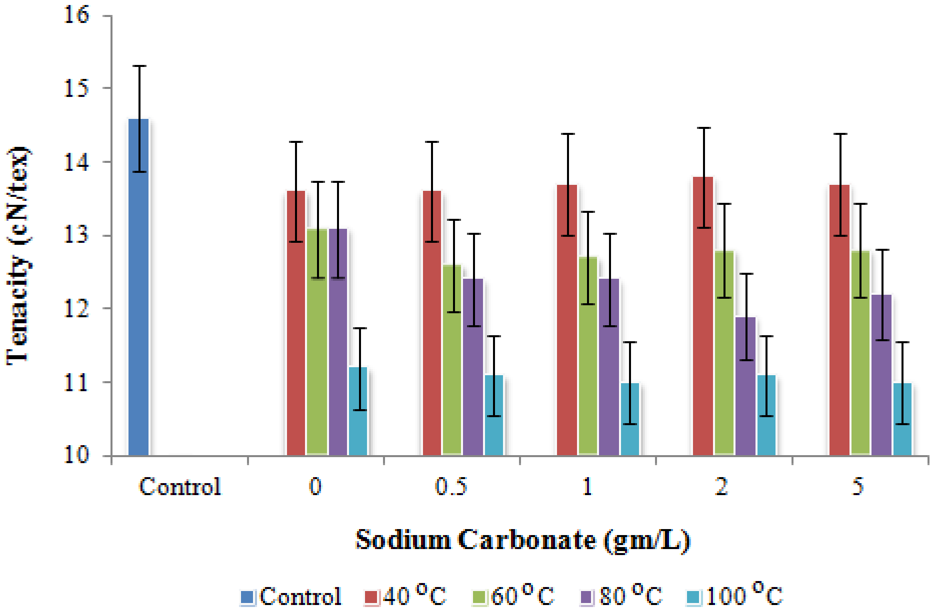


Figure 5. Effect of sodium carbonate concentration and temperature of scouring on the tensile strength of PLA yarns (Time 20 min., LMR of 10:1)

Bleaching agent	Bleach Concentration	Tenacity at Maximum (cN/tex)	%Strain at Maximum (%)	Modulus (N/tex)
Greige	---	14.7±1.0	61.5±3.2	0.83±0.01
Scoured	---	14.0±1.2	65.1±4.5	0.72±0.01
$NaClO_2^{*}$	0 % owf	13.2±1.1	63.4±6.2	0.61±0.02
	2	12.4±1.2	64.3±5.2	0.61±0.01
	4	12.4±1.3	63.5±3.5	0.62±0.01
	6	12.4±1.2	66.4±4.5	0.63±0.01
	10	12.2±1.2	65.0±4.2	0.62±0.03
$H_2O_2^{**}$ NaOH 0.5 gm/L	0 ml/L	11.1±1.0	65.3±5.2	0.61±0.01
	1	11.3±1.1	69.8±3.4	0.60±0.02
	2	12.0±1.0	68.9±3.6	0.53±0.01
	3	12.4±1.2	65.6±5.0	0.52±0.01
	5	12.9±1.1	70.9±5.2	0.55±0.01
NaOH 1gm/L	0 ml/L	9.2±1.2	53.5±6.0	0.55±0.01
	1	10.3±1.2	58.8±5.2	0.53±0.02
	2	11.3±1.0	59.2±4.8	0.52±0.01
	3	11.8±1.2	58.9±3.9	0.54±0.02
	5	12.3±1.1	60.2±4.0	0.50±0.01
NaOH 3gm/L	0 ml/L	6.2±1.0	20.1±4.1	0.51±0.01
	1	8.4±1.0	33.0±5.2	0.52±0.02
	2	10.8±1.1	57.0±2.8	0.56±0.01
	3	11.4±1.3	57.2±3.5	0.55±0.01
	5	11.9±1.1	59.6±4.2	0.54±0.03
$NaClO^{□}$	0 gm/L Cl_2	14.0±1.2	63.0±5.0	0.73±0.01
	2	13.7±1.1	60.1±6.1	0.78±0.02
	4	13.7±1.2	61.6±6.2	0.77±0.01
	6	13.7±1.1	63.0±4.5	0.75±0.01
	10	13.6±1.2	63.0±3.7	0.76±0.01
$H_2O_2^{***}$	0 ml/L	13.4±1.2	61.7±3.5	0.77±0.01
(Cold Pad Batch)	10	13.2±1.2	65.4±4.1	0.76±0.01
	20	13.3±1.1	64.5±5.2	0.74±0.02
	30	13.3±1.0	62.4±5.3	0.72±0.02
	50	13.3±1.1	65.2±4.8	0.72±0.02

Table 1**.** Effect of bleaching agents on the tensile properties of scoured PLA yarns (Na_2CO_3 2 gm/L, 60°C, LMR 10:1, 20 minutes), (pH ~ $11.5^{**,\,□}$, 4.5^{*}, Temperature $85^{o}C^{*}$, $90^{o}C^{**}$, $40^{o}C^{□}$, $25^{o}C^{***}$, LMR 10:1)

Table 1 shows the tensile properties of PLA yarns treated with a range of bleaching agents under various process conditions. The results indicate the long liquor hydrogen peroxide process, caused the greatest damage to yarns but it is evident that the alkaline conditions provided the greatest contribution to the deterioration of the fibres. Indeed since hydrogen peroxide is a weak acid, the alkali was consumed in the presence of hydrogen peroxide and produced the ionized perhydroxyl ions. Accordingly due to the lower amount of sodium hydroxide being present in the bleaching bath, there was better strength retention of PLA fibres. However, if the ratio of hydrogen peroxide and sodium hydroxide was maintained constant, there would be severe damage to the yarns. In the case of the other bleaching systems based on sodium hypochlorite, sodium chlorite or the hydrogen peroxide cold-pad-batch systems there were relatively smaller losses in strength. The results suggested that hydrogen peroxide could be used to produce mild whitening on PLA however if higher whiteness was required sodium chlorite would be a better option. Sodium hypochlorite was applied in the alkaline pH region at 40oC but since the treatment temperature was low, there were negligible changes in the tensile properties of PLA yarns. In contrast sodium chlorite was applied at 85oC and at pH 4.5 and despite the higher temperature; PLA retained its tensile strength at the elevated temperature when processed in the acidic pH region. Examination of Table 2 indicates that blends of PLA with cotton could be bleached safely with sodium hypochlorite or sodium chlorite. However if hydrogen peroxide is the preferred choice, the cold pad batch technique could be adopted because at lower temperature conditions hydrogen peroxide did not damage the PLA yarns.

Bleaching agent	Bleach Concentration	Tenacity (cN/tex)	
		PLA	Cotton
Greige	---	14.7±1.3	72.3±1.3
Scoured	---	13.5±1.2	69.1±1.2
$NaClO_2$ (% o.w.f)	1	12.8±1.2	64.1±1.2
	3	12.4±12	63.5±1.2
	5	12.0±10	61.0±1.0
	10	12.0±13	60.1±1.2
NaClO	2	14.3±1.2	62.8±1.2
(gm/L available Cl_2)	6	13.9±11	46.5±1.1
	10	13.0±12	41.0±1.2

Table 2. Tensile strength properties of PLA and Cotton yarns bleached with sodium chlorite (pH 4.5, 85°C, 45 min., LMR 10:1) and sodium hypochlorite (pH 11.5, 40°C, 60 min., LMR 10:1) bleaching agents

4.3 FT-IR Anylasis of PLA

The following figures show the Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FT-IR) Spectra of pretreated PLA samples. Figures 6.1a and 6.1b show IR spectra of scoured and bleached PLA samples, respectively. Since in attenuated total reflectance mode, infra red waves penetrated only a few nanometres into the sample, chemistry of surfaces could be studied [31, 32]. The objective of IR study was to investigate the changes in surface chemistry of PLA fibres that might have taken place during scouring and bleaching processes. However no new peaks were observed in IR spectra of the greige and pretreated PLA samples suggesting little changes in the surface chemistry of the material. The assignments used in this study were derived from the literature with the peak at 1746 cm-1 assigned to the asymmetric stretching of carbonyl bonds in ester groups (-COOC-) [33-37]. A pair of peaks at 2983 cm-1 and 2930 cm-1 was assigned to stretching vibration of –CH2 bonds, while the peak at 1179 cm-1 was assigned to -C-O-C- stretching of ester groups.

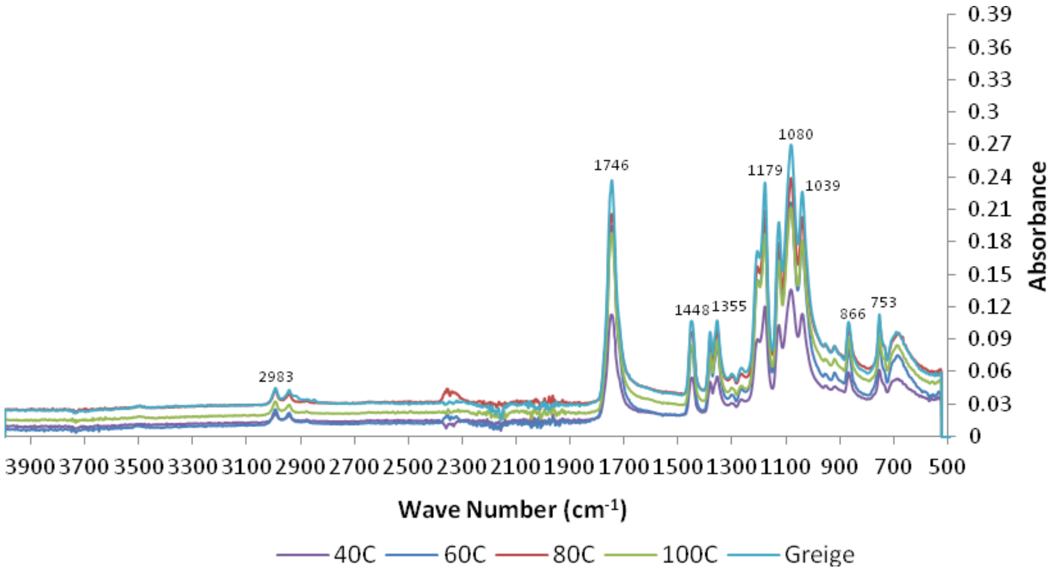


Figure: 6.1a – Fourier Transform Infra-red spectra of scoured PLA fabrics.

(Na_2CO_3 5.0 g/L)

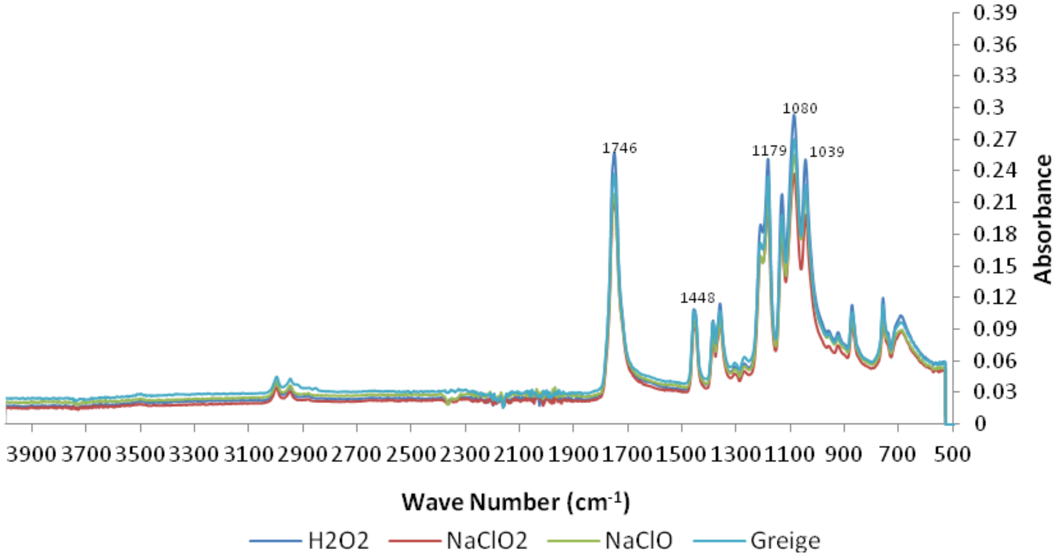


Figure: 6.1b – Fourier Transform Infra-red spectra of bleached PLA fabrics.

During scouring, hydrolysis of PLA occurred which resulted in the cleavage of ester bonds and the formation of carboxylic acid and hydroxyl groups at the polymer chain ends. The hydroxyl group (-OH) peaks in the IR spectra usually lie in the range of 2500 – 3300 cm-1 (carboxylic acid) and 3200 – 3600 cm-1. There were no peaks in the IR spectra of PLA in the region of 2500 – 3600 cm-1. Therefore, it was inferred that presence of hydroxyl groups in the processed PLA fabric was too little to be detected by ATR-IR set up. The Figure 3.17 b shows the FT-IR spectra of PLA bleached with hydrogen peroxide, sodium chlorite and sodium hypochlorite, respectively. Again like scoured samples no new absorption peaks were detected in IR spectra of bleached fabrics. It can therefore be concluded that no new functional groups were generated during bleaching of PLA samples. The intensity of various peaks in the IR spectra was found to be nearly the same. As a conclusion, there was little information gained about the changes in chemistry of PLA fabric due to scouring and bleaching processes using FTIR.

4.4 XPS Analysis of PLA

The literature indicates that previously various workers have fitted varying number of peak assignments to the C1(s) spectra [38 - 41]. Zhao et al. fitted four peaks of C1(s) of PLA, the peaks being –C-C-, -C-O-, -C=O and O=C-O [38]. Wardman et al. fitted five peaks to C 1(s) of PLA, the peaks being –C-C-/-C-H, -C(*)-COO-, -COOH, -C-O-C- and –(CO)-O-(CO)- [39]. Waliporn et al. fitted three peaks to C 1(s) spectra of PLA. In the present work only three peaks were fitted to the C 1(s) XPS spectra of PLA and were regarded as the most representative of the surface species present.

The C (1s) and O (1s) XPS spectra of greige PLA fabric exhibited a number of peaks, Figure 7. In addition to three major peaks characteristic of PLA, there were two minor peaks as well. The commercial textile fabrics contain some impurities both added as well as acquired. The minor peaks could be due to the presence of various sizing chemicals, oils, lubricants and waxes etc. The O (1s) XPS spectrum contained two peaks characteristics of PLA, these peaks being due to single and double bonded oxygen atoms to the carbon atoms, Figure 7. There were only three spectral peaks in the C(1s) XPS of scoured and bleached PLA fabric.

The peak at approximately 284.0 eV was attributed to the carbon-carbon/ carbon-hydrogen bonds in the PLA polymer. Since the electronegativity of carbon and hydrogen is nearly the same, the chemical shifts are not resolved. The other two peaks were attributed to the –C-O- and –C=O groups in the PLA polymer at the binding energies of approximately 286.0 and 288.0 eV, respectively.

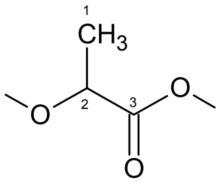


Figure 7: Chemical repeat unit of PLA

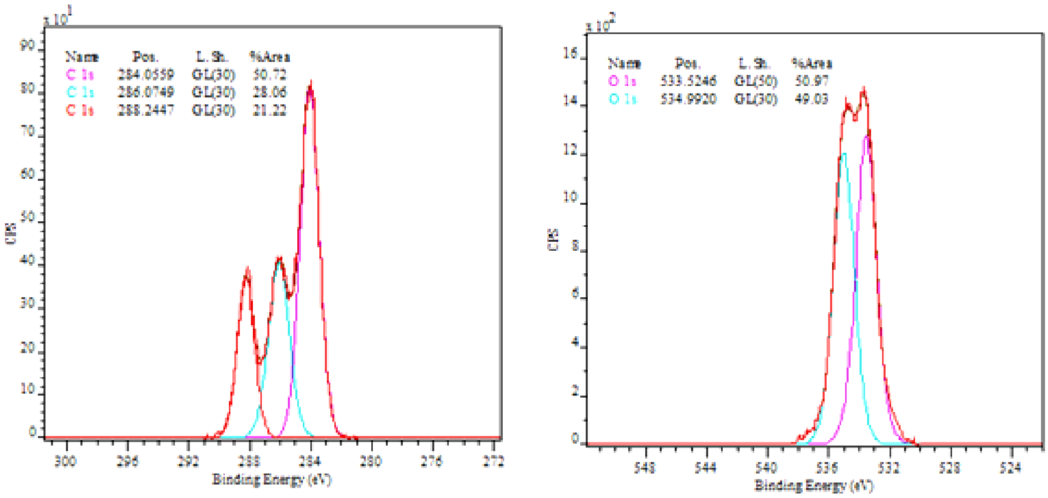


Figure 8a: C 1(s) and O(1s) of scoured PLA fabric (Na_2CO_3 5 gm/L, 40°C)

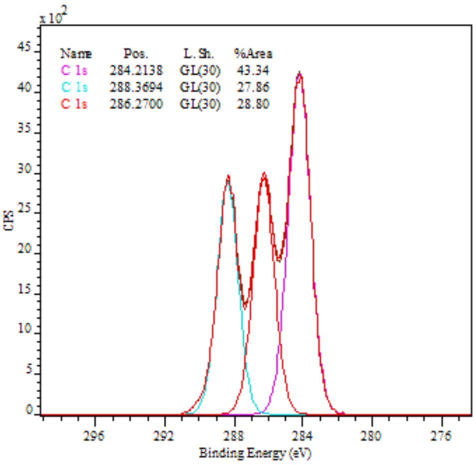


Figure 8b. C 1(s) Spectrum of H_2O_2 bleached PLA fabric (H_2O_2 5 ml/L, NaOH 1ml/L)

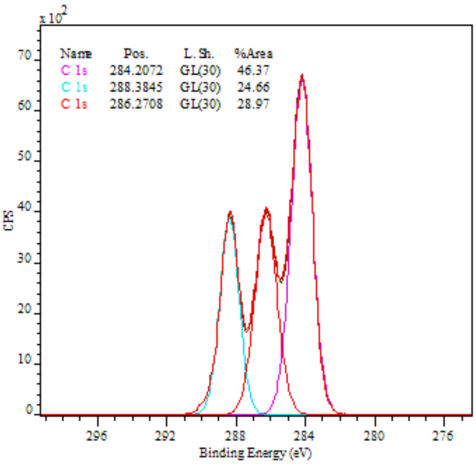


Figure 8b. C 1(s) spectrum of $NaClO_2$ bleached PLA fabric ($NaClO_2$ 5 % o.w.f)

Sample		C (1s) Components (%)		
		-C-C-/-C-H	-C-O-C-	>C=O
Greige		53.7	26.3	20.0
40°C	0.5 gm/L	50.8	27.4	21.8
	5.0 gm/L	44.8	29.8	25.4
60°C	0.5 gm/L	50.5	27.8	21.8
	5.0 gm/L	39.4	28.5	26.5
80°C	0.5 gm/L	50.7	28.0	21.2
	5.0 gm/L	40.7	30.8	28.5
100°C	0.5 gm/L	44.5	31.0	24.5
	5.0 gm/L	38.6	31.5	29.9

Table 3. 10. % C 1(s) Components of PLA fabrics after scouring.

Sample		C (1s) Components (%)		
		-C-C-/-C-H	-C-O-C-	>C=O
Greige		53.7	26.3	20.0
Scoured		50.5	27.8	21.7
H_2O_2 (ml/L)	1	46.5	27.8	25.7
	5	43.3	28.8	27.9
$NaClO_2$ (% owf)	1	46.5	29.1	24.4
	5	46.4	28.9	24.7
NaClO	1	47.3	28.5	24.3
(gm/L available Cl_2)	5	47.3	27.9	24.8

Table 3. 10. % C 1(s) Components of PLA following bleaching.

Figures 3.18a shows the C(1s) XPS spectrum of PLA fabric scoured with Na_2CO_3 at 5.0 gm/L and at 40°C. Figures 3.18b-3.18d show the C1(s) spectra of scoured PLA fabrics bleached with various bleaching agents. The XP C1(s) spectra of bleached PLA fabrics indicated that the least surface damage was done during sodium hypochlorite bleaching due to little change observed in the chemical composition of the PLA polymer i.e. the spectral percentage contribution of various C(1s) components was approximately unchanged. The results showed that the surface damage was higher due to hydrogen peroxide bleaching in comparison to sodium chlorite and sodium hypochlorite bleaching. When comparing the results of XPS and SEM it could be seen that hydrogen peroxide imparted greater bulk and surface damage/modification. The spectral contributions of the various C(1s) components of scoured PLA are presented in Table 3.10 and indicate that there was decrease in –C-C- species and increase in –C-O-C and >C=O spectral contributions. The increase of the latter two components might be due to the oxidation of PLA polymer and/or removal of surface contaminants. The spectral contributions of the various C(1s) components of bleached PLA are presented in Table 3.11 and the results indicated that sodium hypochlorite did not appreciably damage the PLA as the percentage of various C(1s) components remained the same even after treatment at 5 gm/L available chlorine. These results are in accordance with weight loss and tensile strength measurements where the bleaching was performed at low temperature and there were negligible changes in the structure of PLA fibres. The bleaching with sodium chlorite also did not greatly affect the tensile strength and the XPS results showed that during bleaching with sodium chlorite PLA did not undergo appreciable degradation due to little change in the chemical composition of the polymer. However, bleaching with hydrogen peroxide proved to be deleterious and evidenced by the higher levels of surface oxidation, Table 3.11.

5. CONCLUSIONS

PLA fabric was effectively scoured with a non-ionic detergent and sodium carbonate. Treatment temperature up to 60°C (T_g) should be used for 100% PLA fabrics and the pH conditions should not exceed 11. A concentration of up to 5 gm/L sodium carbonate at 60°C did not appear to have an appreciable effect on the PLA tensile strength. While in the case of PLA-cotton blends temperature up to 80°C was acceptable in the presence of 1 gm/L sodium carbonate. SEM analysis indicated that scouring above glass-transition temperature caused the formation of pin holes in the surface structure of the fibres. The formation of surface holes was higher at 100°C than at lower temperatures.

PLA fabrics withstood sodium hypochlorite and sodium chlorite bleaching conditions without appreciable weight and strength losses. Bleaching with sodium hypochlorite can be carried out at 40°C for 30 minutes in the presence of 10 gm/L available chlorine, however, maximum whiteness is achieved at 2 gm/L available Cl_2. With sodium chlorite bleaching treatment concentrations as high as 10% owf at 85°C was acceptable and maximum whiteness was obtained at 10% owf application levels. PLA-cotton blends should accordingly be preferably bleached with sodium hypochlorite and sodium chlorite, with the sodium hypochlorite concentration not exceeding more than 2 gm/L otherwise the cotton undergoes excessive strength losses. With sodium chlorite, Poly/Cotton blends can be bleached with up to 10% owf bleach. Cold-pad-batch bleaching with hydrogen peroxide at concentrations of 50ml/L at ambient conditions did not affect the PLA tensile strength. PLA-wool blends could be bleached with hydrogen peroxide by the exhaust technique, the maximum whiteness of 36 being obtained at 20 gm/L hydrogen peroxide (50% w/w). SEM results showed that hydrogen peroxide bleaching caused hole and slit formation in the PLA fibres and therefore resulted in strength losses. The presence of neutral protein hydrolysates exhibited some beneficial effects on the mechanical properties of PLA yarns during scouring, the maximum strength was obtained at 5 gm/L Byco C. The cationic protein hydrolysates caused clear strength losses. ATR-FT-IR spectroscopic analysis of scoured and bleach treated PLA indicated that little or no new functionalities were introduced into the polymer. XPS of pretreated samples showed that during scouring and bleaching newer surfaces were exposed and bleaching with sodium hypochlorite and sodium chlorite was less damaging than hydrogen peroxide processing of the PLA.

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THE EFFECT OF CLAY AMOUNT ON PET NANOCOMPOSITE PROPERTIES

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Keywords: Clay, nanocomposite, PET, melt blending.

Abstract. *In this study, it was researched the production of PET nanocomposites containing nano-clay particules. Nanocomposites were obtained by melt-spinning method. Cloisite 30B organoclay type was used and nanocomposite masterbatches were prepared by twin screw extruder containing different amounts of organoclay (1-3-5 wt%). SEM photographs, morphological structure and thermal properties of nanocomposites were analysed and compared with pure PET polymer.*

1 INTRODUCTION

Clay is one of the oldest materials used through the human history. It is a natural earthy, fine-grained material comprised largely of a group of crystalline minerals. The properties of clay are high modulus, flame and UV resistance, moisture absorbency, self-cleaning and low gas barrier. The importance of the clay results from its size and shape. The particles have extremely high aspect ratios (about 100-1500) and high surface area (750-800 m^2/g). Therefore, clay exhibits good harmony to nano-technology applications, particularly to polymer-clay nanocomposites. First research in clay/polymer nanocomposite production is made by Toyota in 1989[1-3]. They produced naylon 6/montmorillonite composites. Clay can be divided into natural clays (montmorillonite, hectorite and saponite) and synthesized clays (fluorohectorite, laponite, and hydrotalcite). Montmorillonite is the most widely used layered smectite clay type. It is composed of two silica tetrahedral sheets and a lumina octahedral sheet. Their physical and chemical properties depend on their structure and composition of hydrous phyllosilicates. The smectite clay possesses large surface area. In order to utilize their high surface area efficiently, the chemical modification of the clay is necessary. MMT clays are hydrophilic in nature and accessible to intercalation. Na^+ ions are displaced by quaternary-ammonium surfactants and the distance between silicate sheets are expanded. Owing to the organophilic nature, the modified clay is named organophilic clay or organoclay. In literature, many researchers worked on polyamide-clay and polypropylene-clay nanocomposite production. However, there are limited studies on PET-clay nanocomposite production. In polymer nanocomposite synthesis, the most common methods are intercalation of a suitable monomer and subsequent in situ polymerization, intercalation of polymer from solution, and polymer melt intercalation. In situ polymerization and solution intercalation methods, there are requirements of suitable monomer/solvent or polymer solvent pairs and the high costs associated with the solvents, their disposal, and their impact on the environment. On the contrary of these mentioned drawbacks, in melt intercalation, there is not a need of a compatible solvent or suitable monomer. Therefore, melt intercalation is the most common used method in polymer-clay nanocomposite production. In their study, Scaffaro et al. (2011), Frounchi et al. (2009), Litchfield et al. (2008), Kim (2007), Barber et al. (2005), Wang et al. (2005) and Solis et al. (2003) studied clay-PET nanocomposite production by melt intercalation method and they worked on the effect of clay amount on nanocomposite properties, particularly clay dispersion in PET polymer matrix and tensile properties. Gashti et al. (2012), researched the effect of clay type on dyeability of nanocomposites. Calcagno et al. (2009), determined that clay amount affects the crystallization degree of nanomposite. Kim (2007), also researched oxygen permeability of PET-clay nanocomposites. Ghasemi et al. (2011) and Scaffaro et al. (2011) worked on determination of proper clay type. Xiao et al. (2005), researched the effect of clay on thermal stability of nanocomposites.

In this study, it was aimed to produce clay-PET nanocomposites by melt intercalation method and to analyse the effect of clay on nanocomposite properties. Particularly, we focused on the changes in internal structure and thermal properties of PET polymer with clay addition.

2 MATERIAL AND METHOD

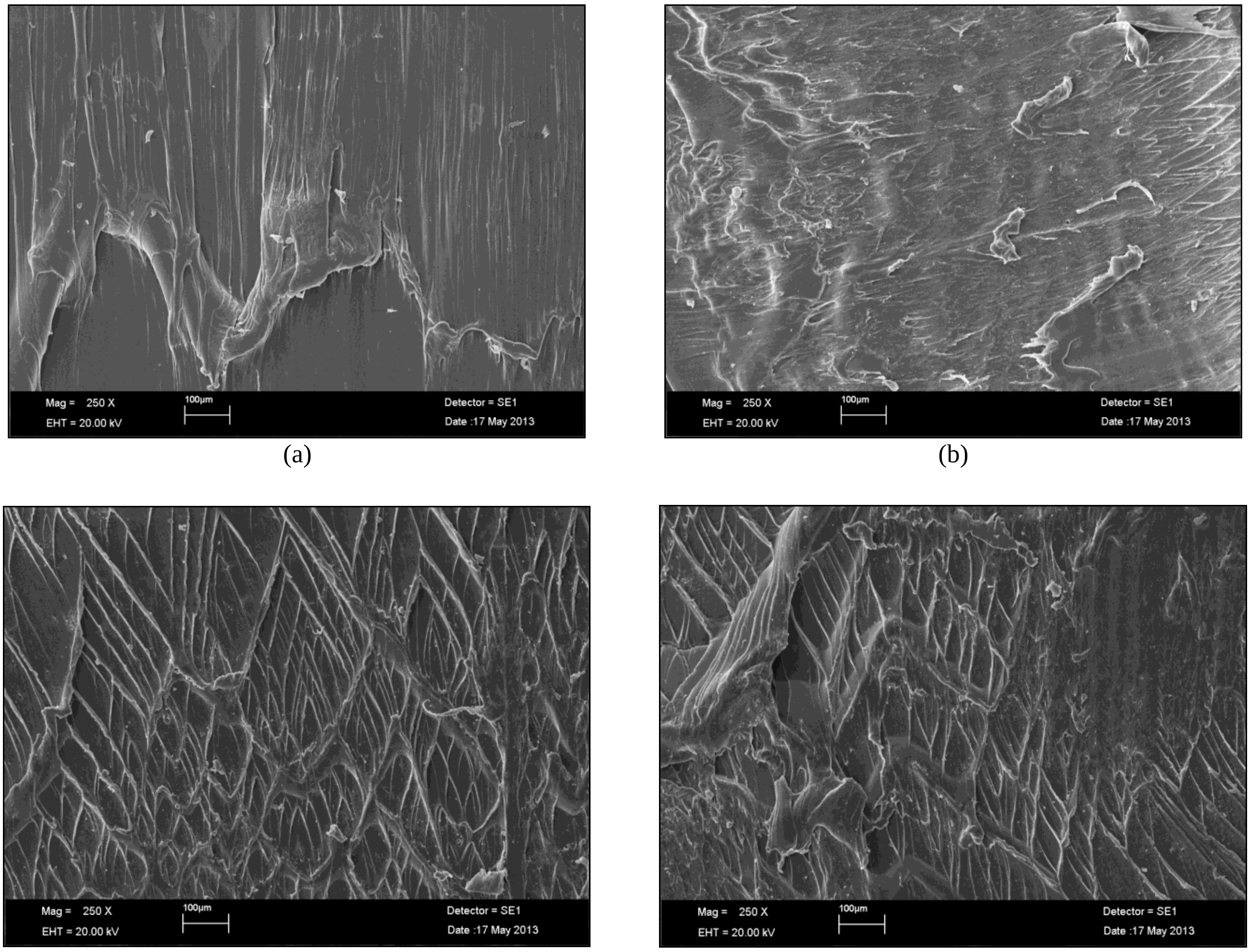
In the study, PET polymer was supplied from SASA Polyester San. A.Ş. Company of Turkey. Organically modified montmorillonite clay (Cloisite 30B) was used. Prior to melt processing, PET and nanoclays were dried up to 4 hour in vacuum oven. There are basically three different processes to make clay-based polymer nanocomposites. As mentioned, melt intercalation method was used for nanocomposite production due to its being eco-friendly and simple method. The contents of the montmorillonite in the nanocomposites were varied of 1, 3 and 5%. In the study, it was also analysed the effect of clay amount on nanocomposite properties. To provide uniform dispersion of clay pellets in polymer matrix, 30KW PTLE27 twin extruder was used. In extruder, the temperature was arranged at 250°C and the speed of extruder was arranged to 300 rpm.

After dried the pellets, in order to examine the clay distribution in polymer matrix, fracture surfaces of specimens were analyzed by Scanning Electron Microscopy (SEM). Wide angle XRD of the samples was performed to determine the clay pellets placement in polymer matrix. Thermal properties of nanocomposite were analysed. The findings were compared with PET polymer.

3 RESULTS AND DISCUSSION

3.1 SEM Images

To evaluate the phase morphology of the nanocomposites and the dispersion of the clay, SEM analysis was performed. In Figures 1-2, SEM images of the unprocessed PET polymer and nanocomposites are given.

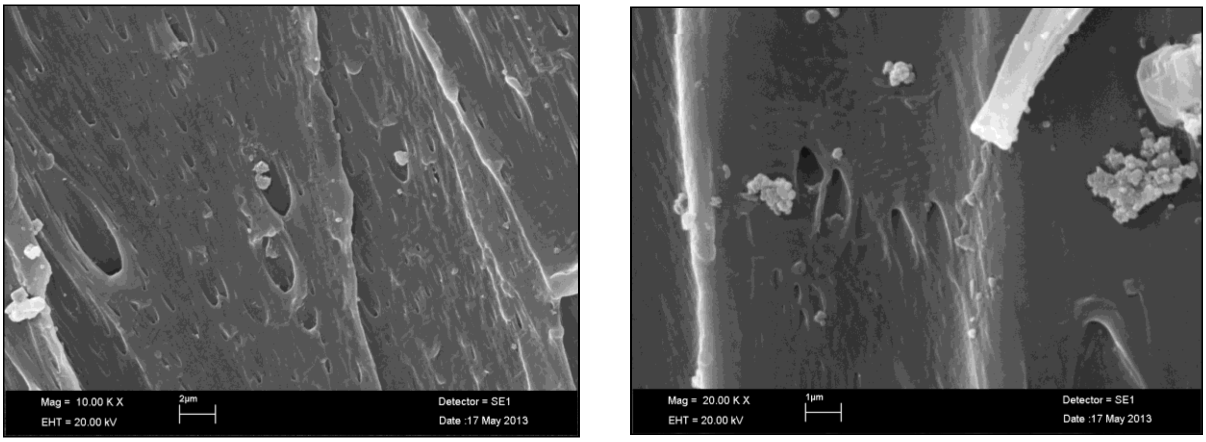


(a) (b)

(c) (d)

Figure 1: Fracture surfaces of PET (a) and PET-clay nanocomposites (b-c-d) (250 KX)

As seen in Figure 1, the surface of unprocessed PET is very smooth and the crack propagation lines can easily be seen on the photograph (a). In photograph (b-c-d), we see the fracture surface of samples including 1, 3 and 5% weight of clay. There is more tortuous path. Adding Cloisite 30B nanoclay particles to the PET composite leads to changes in the particle-particle and particle-PET chain interactions resulting in increased surface roughness. Clay pellets appear randomly dispersed in PET polymer matrix. According to Figure 2, when the clay amount increases in the polymer matrix, clay particles cause more agglomerates. In the images (a) and (b), the main difference is the dispersion the of clay platelets. Such agglomerations, unfortunately, cause localized stresses on the surface of the clay leading to worse impact strength[13].



(a) (b)

Figure 2: Fracture surfaces of PET-clay nanocomposites including 1% (a) and 5% clay (b) (20.00 KX)

3.2 Morphological Characterization

The structures of polymer nanocomposite samples were studied using XRD results. Figure 3 shows the XRD results for Cloisite 30B and 1-3-5% clay addition nanocomposites. The peaks in the graphs are attributed to the lamellar arrangement of clay platelets. This distance, corresponding to the d_{001} plane, is termed the gallery spacing of the clay and is dependant on the modification[6]. Generally, a peak broadening and a decrease of intensity in XRD pattern would be interpreted as a decrease in the degree of coherent layer stacking of the clay. The absence of the signal in XRD pattern would be an indication of clay exfoliation[14].

When the graphs are analysed, it was determined that Cloisite 30B clay displays a peak centred at $2\theta=20^{\circ}$ (4.39 A°). Actually, there are two peaks and another one was at $2\theta=61.8^{\circ}$ (1.36 A°). Nanocomposite sample containing 1 weight (wt) % clay shows a peak at approximately $2\theta=14.68^{\circ}$ corresponding to the basal interlayer spacing of 3.89 A°. Actually, the peak was indistinctive. Therefore, this might be an evidence for occurrence of effective intercalation and exfoliation processes. Nanocomposite master batch containing 3 wt % clay has an apparent peak located at $2\theta=19.44^{\circ}$ (4.53 A°) while nanocomposite containing 5 wt% clay showed only an indistinctive shoulder located nearly at $2\theta=12.98^{\circ}$ corresponding to a basal interlayer spacing of 6.78 A°. When considered the d-spacing of the Cloisite clay being 4.39 A°, the increases intergallery spacings of the nanocomposites containing 3 and 5 wt% clay indicates that intercalation occurred and that the interlayer space of the clay increased. On the other hand, d-spacing of 1.36 A° detected at Cloisite clay was not observed in the any nanocomposite samples containing clay. It can be suggested that clay platelets were present both stacked in small tactoids and exfoliated within the PET matrix polymer[14]. As a consequence, XRD results indicated that the nanocomposites provide better clay dispersion in polymer matrix. Therefore, there is an increase in the gallery spacing and hence some of the PET intercalated into the gallery space.

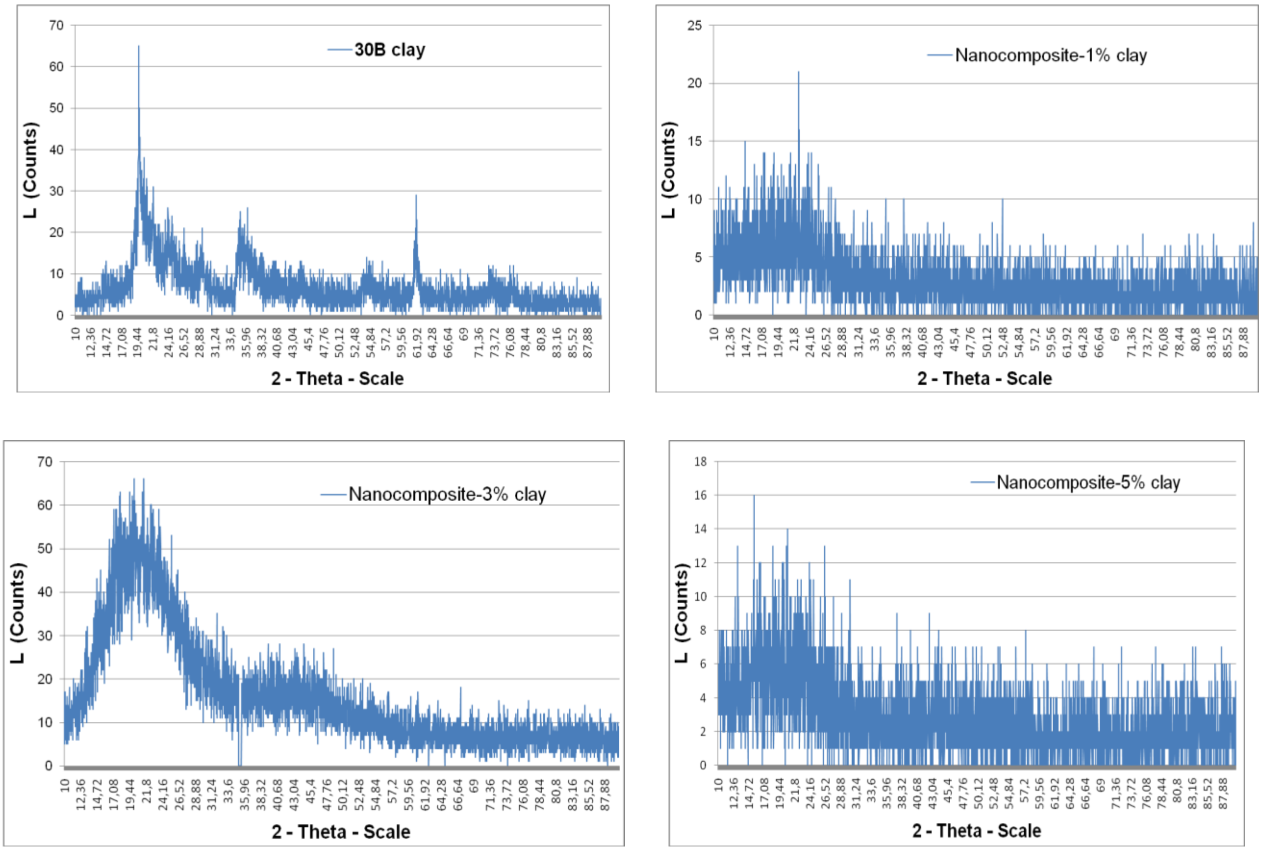


Figure 3: XRD results of Cloisite 30B clay and nanocomposites containing 1-3-5% weight clay

3.3 Thermal Properties

Thermal properties of the nanocomposites were investigated by DSC measurements. The first heating gives information about the behaviour of the materials.

Table 1. Thermal data collected from DSC thermographs of PET and PET-clay nanocomposite samples

	Tg (ºC)	-ΔHc (J/g)	Tc (ºC)	Tm (ºC)	ΔHf (J/g)
Pure PET	79.27	18.59	126.99	254.54	41.55
1% clay	81.51	24.09	120.69	258.22	47.67
3% clay	76.42	19.65	115.95	256.36	43.21
5% clay	77.44	22.71	118.65	255.24	41.34

When the thermal data are analysed (Table 1), it was determined that there are slight changes in the values. Glass transition temperature (Tg) is increased from 79.27 ºC to 81.51 ºC for nanocomposite containing 1 weight % clay. This increase can be attributed to higher interaction polymer chains and the layered silicate surfaces. However, in the samples containing 3 and 5 weight %, Tg decreased. On the other hand, there are significant changes in melting temperature. All nanocomposite samples display high melting temperatures. In particular, melting temperatures are increased from 254.54 ºC to 258.22 ºC with 1% clay addition.

4 CONCLUSIONS

In the study, it was produced nanocomposite materials from PET polymers as the matrix with the addition of organically modified montmorillonite clay as the filler. From SEM photographs, it was determined that clay particles were dispersed in polymer and this causes torturous structure in polymer surface. On the other hand, some of the PET was intercalated into the gallery space in the nanocomposite samples and an increase was occurred in gallery spacing of nanocomposite samples. With the clay addition, melting temperature was increased. Particularly, the sample containing 1 weight % clay leads to higher melting temperature.

ACKNOWLEDGEMENT

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THE INFLUENCE OF THE STRUCTURE AND CONSTRUCTION PARAMETERS ON THE DRAPING OF COTTON FABRICS

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Keywords: Draping, Fabric, Cotton, Construction characteristics

Abstract. *The ability of a material to become draped is a feature that defines the qualitative characteristics of fabrics as well as the design of clothing products. Generally speaking, draping can be defined as a phenomenon of crease-forming when the fabric is put under pressure of its own mass, but without the influence of external forces.*

Recent findings in the field indicate that researchers have mostly been defining the phenomenon of draping on the basis of the mechanical characteristics of textiles. However, the mechanical characteristics of fabrics are conditioned by the characteristics of fibers and the yarn, the type of interlacement and the thread density, but also on the conditions under which it is produced by the means of loom. Therefore, this paper presents the studies which draw attention to the connection between the parameters of the structure and construction of the woven cotton fabrics with the draping parameters. This paper focuses on linking the draping parameters with the characteristics defining the relative thread density in fabrics (linear density of the yarn, the volume of the fibers, the coefficient of fiber packing in the yarn, the interlacing pattern, the number of effect-changes of the threads in the pattern, the position of the binding nodes in the interlacing pattern and the coefficient of the flexibility of the applied yarns).

The results of this study will contribute to the development of the new method of analyzing the characteristics of draping of woven textiles.

1. INTRODUCTION

Draping is an important factor in presenting the aesthetics and functionality of woven fabric, as well as sewn garments. Generally speaking, draping can be defined as a phenomenon of crease-forming when the fabric is put under pressure of its own mass, but without the influence of external forces. Draping of fabric depends on mechanical and structural characteristics of fabric as well as on various external influences from the environment.

The ability of a material to become draped is a feature that defines the qualitative characteristics of fabrics as well as the design of clothing products. Modern fashion trends and modern technologies impose more requirements to textile industry. New and functional textile materials, modern methods of making clothes, competition in the fashion and clothing industry are factors that impose to textile industry constant changes and adjustments to the market. As a numerical indicator of drape ability of fabrics is used drape coefficient (DC), which can be defined as a ratio of ring area of fabric sample before draping and projected area of draped part of the fabric (Figure 1). Drape coefficient is expressed in percentage and has value from 0 to 100 %. In addition to drape coefficient, for describing the ability of fabric drape are used maximum (Amax) and minimum amplitude (Amin), which represents maximum and minimum distance from the center of the circle to the edge of draped part of fabric sample (Figure 1), and the number of folds (n) [1].

Extensive studies of fabric drape have brought some conclusions. The greatest impact on the drape coefficient has fabric stiffness. It was also revealed that the drape coefficient depends, besides of mechanical, on structural characteristics of fabric, such as: structure, type of yarn, raw material composition, applied interlacement, fabric density, etc. Draping can be classified into two categories: as two-dimensional and three-dimensional draping. Two-dimensional drape means that the fabric folds under the influence of gravity in one plane, and three-dimensional drape means that fabric deforms forming the folds in more than one plane, under pressure of its own mass.

A number of researchers involved in the analysis of the phenomenon of fabric drape. It is known Pierce's cantilever method and Cusick's drape meter for measuring fabric drape parameters [2]. Current studies of fabric drape are going in several directions, and researchers agree that draping is a very complex phenomenon and depends on many parameters.

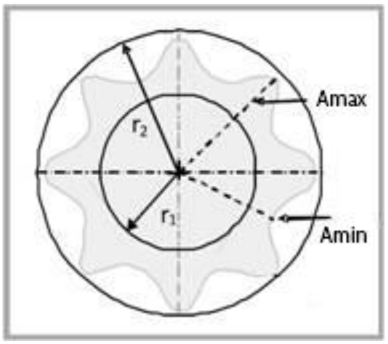

Figure 1: Projection of draped sample of the fabric

2. MATERIALS AND METHODS

For the purpose of this research 31 fabrics of the same fiber composition - 100% cotton were taken. For each analyzed fabric the following parameters are determined: weave, fabric weight (Q), warp density (d_{wa}), weft density (d_{we}), warp yarn count (Tt_{wa}), weft yarn count (Tt_{we}) and yarn twist (number of twist/meter) (table 1).

Determination of drape parameters was performed on a standard drape tester model 665 producer James H Heal & Co of England, according to British Standard BS 5058.

For all samples the drape coefficient (DC) maximum (Amax) and the minimum amplitude (Amin) and the number of folds (n) were determined. This experimental method means that circular fabric sample 30 cm in diameter hangs on a circular disk 18 cm in diameter. The sample with diameter of 36 cm can be used for rigid fabrics if their DC% s greater than 85% in fabric sample with a diameter of 30 cm, while in the case of soft fabric 24 cm diameter sample can be used, if their DC% in 30 cm diameter fabric sample is less than 30% [3].

However, if a different diameter of fabric samples would be used for this study, the obtained results of drape coefficient could not be in correlation with other parameters of the fabrics, because increasing of draped part of the sample reduces the drape coefficient, so all the fabric samples were tested with a diameter of 30 cm, regardless of the results of drape coefficient which were less than 30% or greater than 80%.

Sample	**Weave**	**Fabric weight Q (declared) (g/m^2)**	**Yarn density (d), (cm^{-1})**		**Yarn count (tex)**		**Yarn twist (m^{-1})**	
			Warp d_{wa}	**Weft** d_{we}	**Warp** $T_{t,wa}$	**Weft** $T_{t,we}$	**Warp**	**Weft**
1	Plain	143	27	18	30	30	846	846
2	Plain	220	22	22	50	48	586	586
3	Plain	150	40	25	20	25	826	748
4	Plain	200	30	22	30	34	846	590
5	Plain	155	28	22	30	30	708	708
6	Plain	315	16	15	64x2	64	330	570
7	Plain	150	24	24	30	30	842	842
8	Plain	200	37	20	17x2	17x2	680	680
9	Plain	117	43	28	7.6x2	17	1000	866
10	Plain	70	26	23	6x2	6x2	1200	1200
11	Plain	77,67	50	34	8,4	8,4	1048	1178
12	Plain	132,8	47	29	15	16	790	795
13	Twill 2/1	216,28	49	26	24	28	580	576
14	Twill 2/1	172	43	25	25	25	748	748
15	Twill 2/1	200	40	27	30	30	708	708
16	Twill 2/1	157	56	27	17	20	866	826
17	Twill 3/1	312	48	21	30	72	846	551
18	Twill 3/1	221	48	23	30	30	708	708
19	Twill 3/1	275	49	24	30	42	708	472
20	Twill 3/1	185	22	22	38	38	630	630
21	Twill 3/1	260	42	19	33	50	768	590
22	Twill 3/1	248	44	21	30	50	708	532
23	Twill 3/1	270	48	22	28	28	700	580
24	Twill 2/2	275	27	16	30x2	64	500	566
25	Twill 2/2 S	182,20	21	19	20x 2	19x 2	578	568

26	Twill 4/4 Z	302,21	27	19	30 x 2	30 x 2	366	373
27	Panama 2/2	196	37	22	17x2	17x2	680	680
28	Panama 2/2	324	43	23	34	72	708	394
29	Satin	330	44	22	34	34 x2	708	500
30	Satin	185	46	25	10x2	17x2	820	820
31	Satin	165	39	28	25	25	748	748

Table 1: Characteristics of the tested fabrics

Then there are calculated the parameters that define the relative density of the yarns in fabric (fiber volume mass, fiber packing coefficient (factor) in yarn, repetition unit of thread system analyzed, position of binding points in repetition unit, yarn flexibility coefficient) [4].

3. RESULTS AND DISCUSSION

The results are analyzed and in Figures 2, 3 and 4 the corresponding dependences are shown. Figure 2 shows the dependence of the drape coefficient and the product of number of folds and the quotient of the maximum and minimum amplitude. The results indicate that there is a correlation of these parameters analyzed.

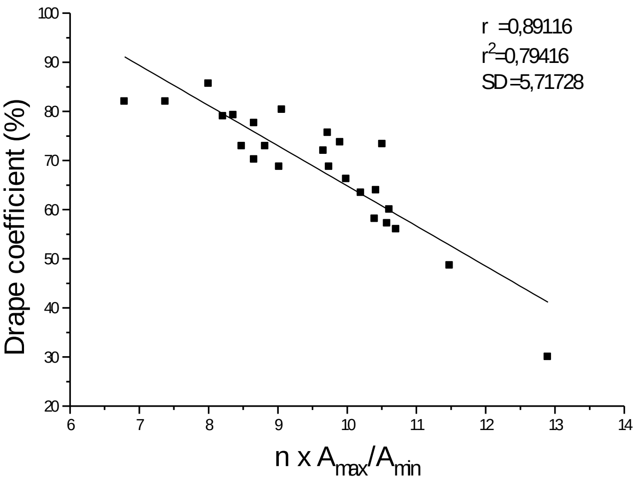

Figure 2: Dependence of drape coefficient and *n x Amax/Amin*

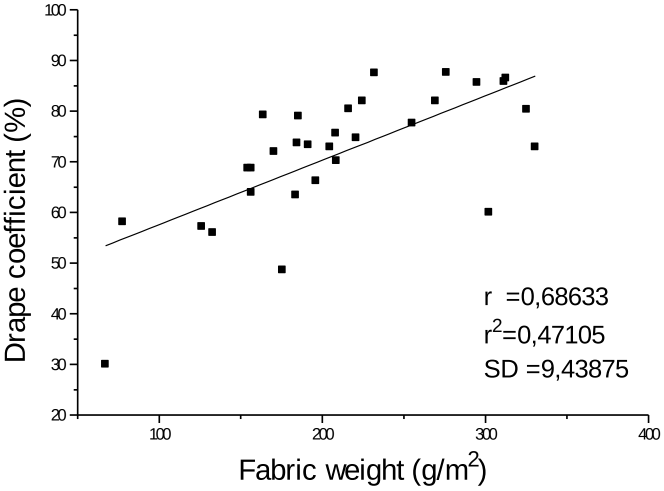

Figure 3: Dependence of drape coefficient and fabric weight

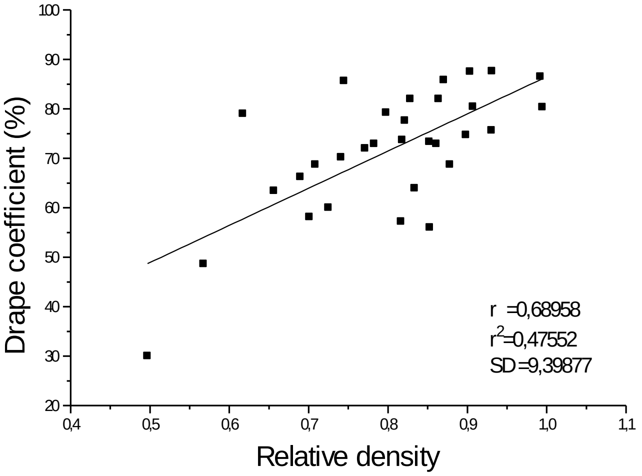

Figure 4: Dependence of drape coefficient and relative density of yarns in fabric

Figure 3 shows dependence of drape coefficient and fabric weight. The results show that the fabrics with higher fabric weight have higher drape coefficient. Fabric weight has a direct impact on the drape coefficient because fabric drape represents a folding of fabric under the influence of gravity, and that folding depends of mass of draped part of fabric. A prominent place in the process of projecting of elements of structure and construction of cotton fabric takes the relative density of the two yarn systems [5]. When projecting relative density of yarns in fabrics, special attention must be paid to: fibers characteristics (surface structure and shape of the cross section, length, crimp, fiber volume mass), yarn characteristics ((applied process of spinning and twisting, yarn count and yarn volume mass), characteristics of weaving process (the process of preparing warp for weaving, absolute yarn density in fabrics, construction, tightness of warp and weft systems etc.). Since the relative density includes of a number of parameters of woven fabrics, it is made an attempt to connect drape coefficient with characteristics that define the relative density and to create conditions for the proper prediction of woven fabrics drape for the clothing industry.

Figure 4 shows the correlation of relative density of fabric with drape coefficient. The results indicate that there is a connection of the given parameters.

With analysis of the parameters that define the relative density of the yarns and woven fabric drape coefficient, links that will be used for properly projecting the fabric according to the future purpose can be found. Further research will focus on the association of these parameters with the aim to develop a new method for predicting the drape of fabric.

4. CONCLUSION

Based on these results it can be concluded that for cotton fabrics drape ability depends on the structure parameters of fabric. The parameters of fabric structure can be used to determine the ability of fabric drape, and hence to predict appearance of finished garment. Previous studies in this direction were based on the mechanical properties of fabrics by which virtual models of garments were obtained. The results show a correct correlation between drape coefficient, the number of folds and maximum and minimum amplitude. In addition, good correlation was found between drape coefficient, relative density and fabric weight, which establishes a requirement for the development of new methods of projecting drape parameters, depending on the structure and construction of woven fabric for garment industry.

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IN-SITU GENERATION OF ZnO ON THE TEXTILE SURFACES BY HYDROTHERMAL METHOD

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Keywords: Antibacterial, Hydrothermal, In-Situ, Zinc oxide

Abstract. *Nowadays, the antibacterial products have great importance for different usage areas of textiles, and there is a wide range of process of giving antibacterial activity to the different kinds of textile materials. Several antibacterial agents are used to make the textile fabrics antibacterial such as colloidal* Ag^+*, Ag powder or ZnO particles. In this experimental study, it was investigated whether it was possible to combine producing the antibacterial ZnO particles by hydrothermal method and coating them with ZnO simultaneously on the textile fabrics (in-situ method) (%100 cotton and polyester). After in-situ coating process, the ZnO on the samples were characterized by SEM and XRD analyses, and the antibacterial activity of specimens was tested according to the ASTM E2149-1 (gram-negative Escherichia coli, gram positive-Staphylococcus aureus). In addition, the resistance opposite to the repeated washes of these antibacterial samples was investigated. The results showed that either cotton or polyester based samples had sufficient antibacterial activity and this activity did not reduce due to repeated washing treatments.*

1. INTRODUCTION

The researches on the new finishing methods and fabric-forming techniques have led to great advances in the medical and hygienic textiles. The hygienic and health textiles have been used in large quantities in places such as hospitals and theaters, etc., where contact with the skin of the users occurs repeatedly and frequently [1]. These textile materials are wanted to have a high antibacterial activity for the reason of health considerations [2-3].

Textile materials carry micro-organisms such as pathogenic bacteria and odor-generating bacteria [4-6]. The cotton fibers which have common usage provide an excellent environment for micro-organisms to grow, because of their large surface area and ability to retain moisture [7-9]. Most synthetic fibers, due to their high hydrophobicity, are more resistant to attacks by microorganisms than natural fibers [10]. Although textiles wholly made of natural fibers or synthetic fibers, neither natural nor synthetic fibers have resistance to bacteria or pathogenic fungi. Thus, various antibacterial finishes and disinfection techniques have been developed for all types of textiles [11, 12]. The antimicrobial finishing of textiles protects users from pathogenic or odor-generating micro-organisms, which can cause medical and hygienic problems, and protects textiles from undesirable aesthetic changes or damage caused by rotting, which can result in reduced functionality [13].

Controlling the growth of bacteria on the fibers or fabrics may be achieved by: a) a finishing process in which an antibacterial additive is fixed on the surface of the material by a resin, b) grafting of antibacterial agents on the cellulose chain, or c) incorporating agents into spinning solution of regenerated fibers. The finishing process is the technique most frequently employed to impart antibacterial activity to textiles [4].

Inorganic materials such as metal and metal oxides have attracted lots of attention over the past decade due to their ability to withstand harsh process conditions. Of the inorganic materials, metal oxides such as TiO_2, ZnO, MgO and CaO are of particular interest as they are not only stable under harsh process conditions but also generally regarded as safe materials to human beings and animals. The use of particles of silver and zinc oxide (ZnO) has been seen as a viable solution to stop infectious diseases due to the antimicrobial properties of these particles. The intrinsic properties of a metal particle are mainly determined by size, shape, composition, crystallinity and morphology [14]. In this sense, ZnO is a multifunctional material that has high luminous transmittance and piezoelectric properties, high chemical stability and suitability to doping, good electro-optical characteristics, excellent substrate adherence and hardness, non-toxicity and low cost [15]. In addition ZnO particles have been used for antibacterial and UV-blocking properties in textiles [16-18].

The ZnO particles on a material can be obtained by various methods such as thermal evaporation, chemical vapor deposition, sol-gel method, electrochemical deposition, ion beam assisted deposition, RF magnetron sputtering deposition, spray pyrolysis and hydrothermal deposition [19-23].

Among these methods, the hydrothermal method is promising for fabricating ideal material with special morphology because of the simple, fast, less expensive, low growth temperature, high yield and scalable process.

In general, the hydrothermal method refers to any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions in order to dissolve and recrystallize materials which are relatively insoluble under ordinary conditions [24].

In the textile applications, several methods were reported in order to obtain ZnO particles which give UV protection, antibacterial activity or antistatic properties etc. to the textile surfaces [25-31]. As it is reported in these literatures, the adhesion between the ZnO particles and polymer by a simple wet chemical method is rather poor and these particles may be removed from the surface easily. In terms of this explanation, it can be said that ZnO particles obtained by hydrothermal method has more satisfactory results for coating the textile surfaces because of its morphological properties and high purity [25].

Tanasa et. al. described the in-situ formation of ZnO on the cellulose fibre as shown in Figure 1 [25]. The ZnO particles grow in two steps on the fibre. In the last step, ZnO chelate complex forms under hydrothermal treatment and forms ZnO particles-coated cellulose based samples [25].

In this present paper, the zinc oxide (ZnO) particles were firstly growth and in-situ coated by hydrothermal method, and then these particles on the samples were characterized with XRD and SEM analyses. After in-situ coating and characterizing, the antibacterial activity of these samples was tested. In the experimental part, the antibacterial activity and durability of this activity against repeated washes of cotton and polyester samples coated with ZnO particles growth by hydrothermal method were investigated.

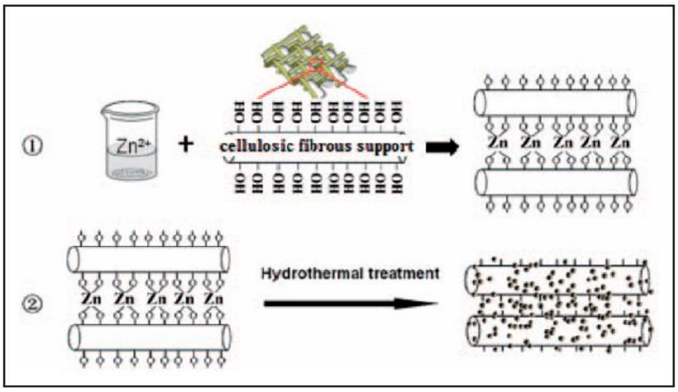

Figure 1 : In-situ formation of ZnO particles on the cellulose by hydrothermal method [25]

2. MATERIAL AND METHODS

In this experimental study, the zinc nitrate hexahydrate ($(Zn(NO_3)_2.6H_2O)$ and hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) were purchased from MERCK and used for synthesis of ZnO particles. All chemical products were used as received. The water was purified by reverse osmosis method.

Two kinds of pre-treated textile fabrics were used for in-situ coating process. The cotton sample with area mass of 175 g/m^2 was knitted with 100% cotton yarns, and it was single jersey plain knitted fabric. The polyester sample with area mass of 175 g/m^2 was woven with 100% multi filament polyester yarns, and it was 4/1 gabardine woven fabric. The desizing, scouring and bleaching processes were carried with bulk production in the textile mill.

The precursor solution was prepared by dissolving 0.01 M of zinc nitrate hexahydrate ($(Zn(NO_3)_2.6H_2O)$, 0.01 M of hexamethylenetetramine (HMTA, $C_6H_{12}N_4$) in 100 ml deionized water. Here, HMTA was used as complexing agent. The pH of prepared starting solution was measured and fixed to 6.5 value.

The samples (10x20 cm) were wrapped up around the glass plates and horizontally immersed in the prepared precursor solution. The hydrothermal growth was carried out at boiling temperature (≈ 98°C) in a sealed beaker placed on the hotplate during 2 hours for the cotton samples. The experiments were carried out at 200°C in an autoclave placed on the furnace during 2 hours for polyester samples. The working temperature was preferred above 75°C in this study for both cotton and polyester. In the hydrothermal method, the crucial stage is the hydrolysis of HMTA, and the working temperature is the most effective factor on this hydrolysis. Below 75°C, the rate of hydrolysis of HMTA slow down, and particles cannot grow on the fibre surface [31]. Therefore, the boiling temperature (approximately 98°C) and 200°C were chosen for cotton and polyester samples, respectively.

In addition, the cotton and polyester samples were studied at different temperatures because of their different morphological structures. As it is mentioned from the literature, cellulosic materials have ability of establishing chemical bonding with growth ZnO particles (Figure 1). However, polyester fiber probably showed chemically inert character because of its rigid structure. Therefore, we needed increasing the working temperature in order to reach and pass the T_g value of polyester fiber, increase the porosity of surface and ease the penetration of ZnO particles into these porous and surface. In addition, we thought that increase at the working temperature provided more homogenous surface character especially for polyester fibre.

After in-situ treatments, the process solutions were filtered and the samples were dried at room temperature.

Antibacterial Activity Tests. The antibacterial activity of the samples was tested according to the ASTM E2149-1 against gram-negative *Escherichia coli* bacteria and gram positive-

Staphylococcus aureus. In addition, five repeated washing treatments were applied to the samples in order to investigate durability of the antibacterial activity against wet processes at 40°C for 30 minutes followed by drying process.

X-ray Diffractometry. The crystal structures of ZnO rod arrays before and after washing treatments were investigated by Philips X'Pert Pro X-ray Diffractometer (XRD) with Cu Kα radiation (λ=1.54Å) source (applied voltage, 40 kV; current, 40 mA). About 0.6 g of dried samples with ZnO onto a sample container, and the XRD patterns were recorded at 2θ with a scan rate of 2 °/min.

Scanning Electron Microscopy. The surface morphologies before and after washing treatments were investigated using a scanning electron microscopy (SEM - JEOL, Tokyo, Japan) which was operated at 10 kV. The analyses have been performed by a high vacuum working mode.

3. RESULTS

Morphological Characterization

In order to characterize and show the ZnO particles on the fibre surfaces, the XRD and SEM analysis were carried out with untreated, coated and coated-washed cotton and polyester samples. The spectra of XRD analyses are given in Figure 2-3 for cotton and polyester, respectively. The XRD patterns of coated and coated-washed cotton samples compared with reference sample in Figure 2.

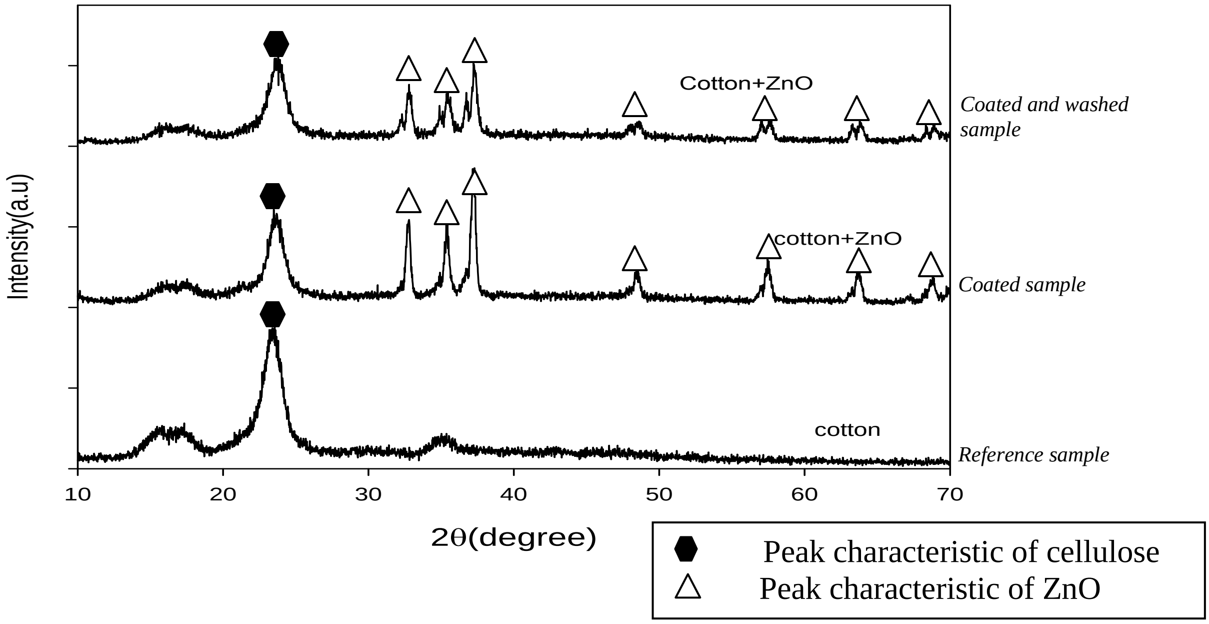

Figure 2: The XRD patterns of the cotton sample (a) untreated sample (b) coated sample (c) coated and washed sample

As shown Figure 2, we determined a dominant peak at 23.65 which characterised the cotton fibre for each sample [25, 34]. Figure 2 also showed the XRD spectra of the ZnO material on the fibre surface. The spectra showed well-defined peaks typical of ZnO in the crystal structure of ZnO, according to PDF-2, reference code: 01-079-2205. In addition, this characteristic peak could be the indexed the hexagonal wurtzite structure of the ZnO [26, 32].

According to Figure 2, the ZnO particles had peaks at 31.90, 34.49, 36.55, 47.44, 56.65, 62.85 and 67.95 correspond to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) planes, confirming the formation of hexagonal zinc oxide phase on the cotton fibre.

In Figure 2, we also compared the XRD pattern of unwashed and washed samples in order to determine the durability of ZnO particles on the fibre against repeated washes. The presence of peak at same position with XRD spectra of washed samples and unwashed samples can be seen in Figure 2. It meant that the XRD pattern of washed and unwashed samples matched well with each other. As could be seen from Figure 2, the intensities of the diffraction peaks decreased when the samples were washed.

The XRD patterns of coated and coated-washed polyester samples compared with reference sample in Figure 3. According to the Figure 3, the common diffraction peak of polyester was observed at 17.35, 22.90, 25.55 as mentioned in the literature [32]. In addition, similar peaks were measured for ZnO particles on the polyester that of cotton samples shown in Figure 2. According to the XRD spectra given in Figure 3, the typical peak of ZnO could be defined on either coated or coated-washed samples. This data was the signal of durability of ZnO on the polyester fibre against repeated washes.

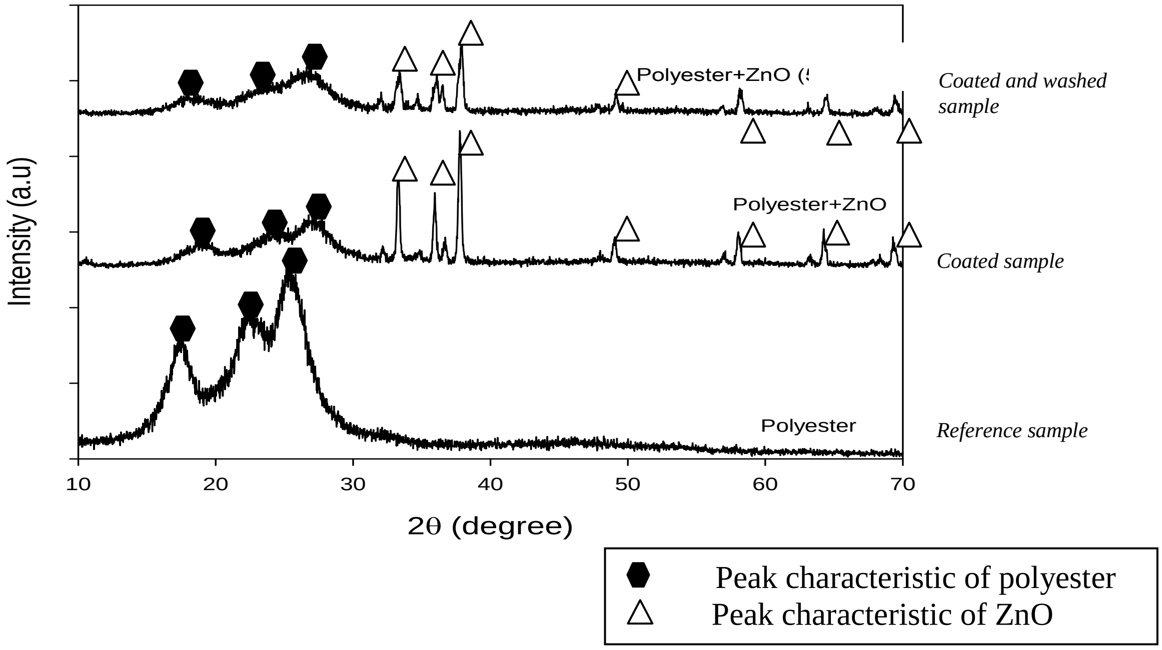

Figure 3: The XRD patterns of the polyester sample (a) untreated samples (b) coated samples (c) coated and washed samples

The surfaces of treated samples were observed by SEM microscopy. In Figure 4 and Figure 5, SEM micrographs show the ZnO particles on the cotton and polyester samples, respectively. According to both figures, particles placed to the fiber surface in both cases, although some aggregated particles were available. We could easily say that ZnO particles were better dispersed and placed more homogenous on the polyester surface than cotton sample, because in-situ synthesis temperature of the ZnO on the polyester was higher than cotton. The temperature has risen the hydrolysis of the HMTA in the precursor solutions, and this case improve the growing of ZnO on the surface.

As mentioned in the experimental part, the pre-solution was filtered after coating process of fabric. The nano ZnO powder got from the filtering stage was analyzed with SEM in order to make comment about morphological properties of material (Figure 4). According to Figure 4, it could be said that the particles had generally spherical character. In addition the size of the particles showed differences between 300 – 500 nm.

In addition, the SEM analysis showed that most of the ZnO particles remained bound to both cotton and polyester fiber surfaces after repeated washing applications. This case showed high correlation with the XRD spectra shown in Figure 5 and 6.

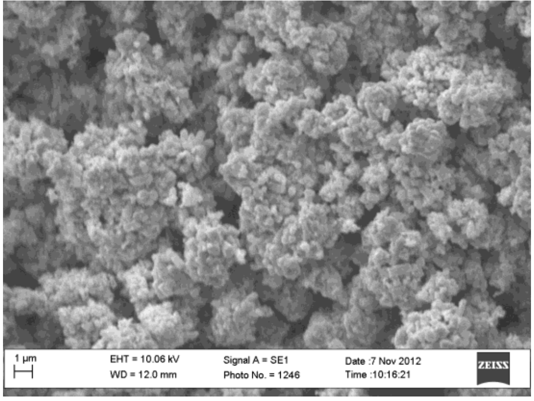

Figure 4 : The SEM images of filtered nano ZnO powder

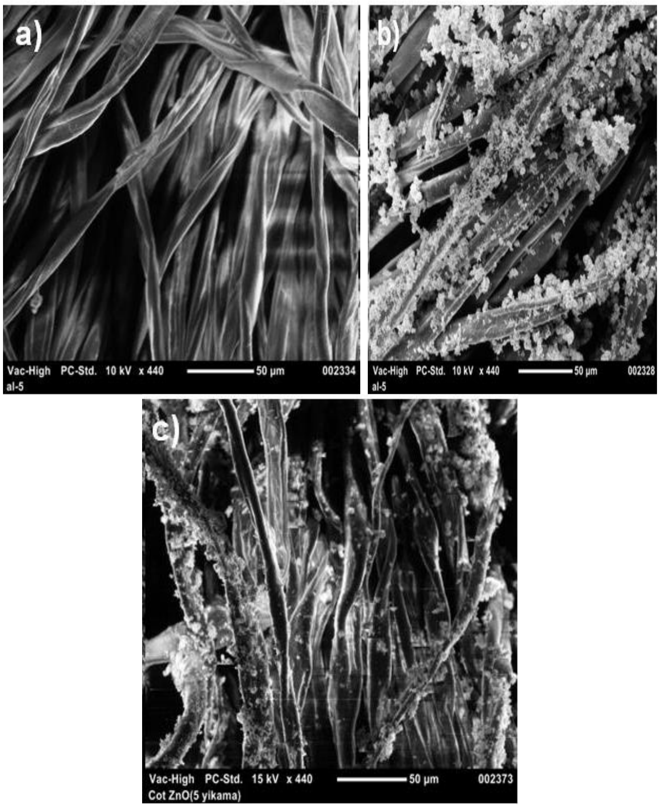

Figure 5: SEM images of cotton samples (a) untreated samples (b) coated samples (c) coated and washed samples

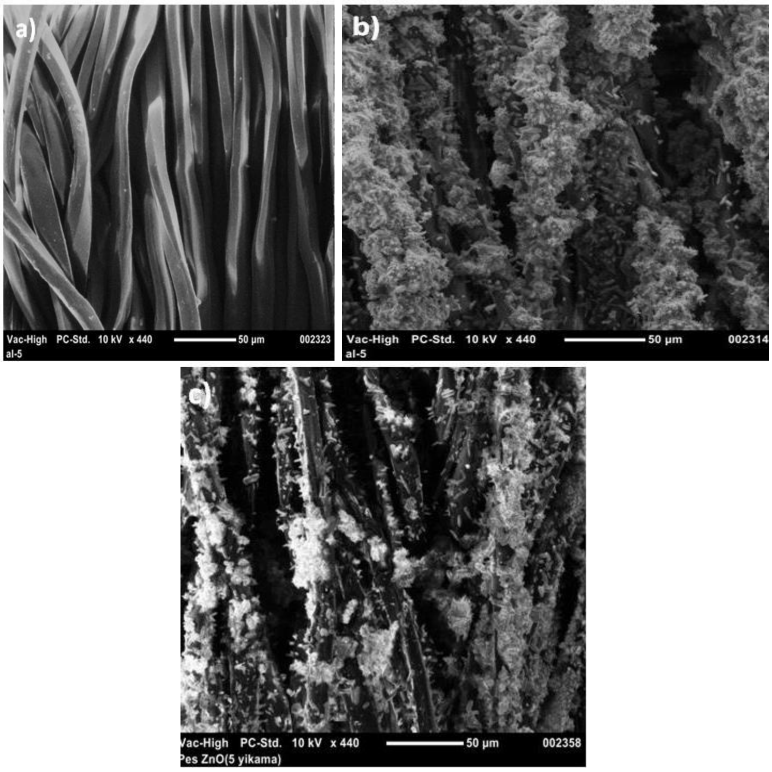

Figure 6: SEM images of polyester samples (a) untreated samples (b) coated samples (c) coated and washed samples

Type of samples	Reduction of the *E.Coli* bacteria number after an hour (%)	
	Cotton	Polyester
Untreated samples (reference)	26	15
Coated samples	99,9	99,6
Coated and 5 times washed samples	99.9	99,6

Table 1: The antibacterial activity of the samples (E.Coli)

According to Table 1, it could be said that cotton and polyester samples did not have exact antibacterial property before the coating process. We thought that the reason of little antibacterial activity (26% for cotton and 15% for polyester) of these untreated samples was the bleaching treatment and H_2O_2 used in this wet process.

The antibacterial activity of coated cotton samples can be seen from Table 1. The 99.9% antibacterial activity was observed after in-situ generation of ZnO on the surface. In addition, durability of antibacterial activity after repeated washings was another important result obtained in the study. The in-situ generated ZnO by hydrothermal method made solid bound with the surface of fiber. Similar activity results were measured for Staphylococcus aureus bacteria as shown from Table 2.

Type of samples	Reduction of the *Staphylococcus aureus* bacteria number after an hour (%)	
	Cotton	Polyester
Untreated samples (reference)	34	22
Coated samples	99.9	99.9
Coated and 5 times washed samples	99.9	99.9

Table 2: The antibacterial activity of the samples (S. Aureus)

Table 2 showed that the growing ZnO nano particles on the polyester samples made the fabrics antibacterial. Besides, it was clear that the antibacterial activity of samples after the washing treatments did not change.

4. CONCLUSIONS

In the study, in-situ generation of ZnO particles by hydrothermal method from the reaction of $Zn(NO_3)_2.6H_2O$ and $C_6H_{12}N_4$ was reported. The process chosen in the present study is cheap, efficient and consists of single application. We also aimed to investigate the antibacterial activity of ZnO on the surface.

The ZnO particles are uniformly placed onto the surface of cotton and polyester fibers. We also found out that the homogeneity of dispersion of ZnO on the surface was better for polyester than for cotton due to reaction temperature.

We succeeded to obtain durable antibacterial activity against two kinds of bacteria with in-situ coating of ZnO to the cotton and polyester textile surface. We also determined the in-situ generation of ZnO on the fibre with XRD and SEM analysis.

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THE RELATIONSHIP BETWEEN THE TEACHER AND THE STUDENT AS A WAY OF HUMANIZATION OF THE TECHNICAL HIGHER EDUCATION

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Abstract. *Teacher-student relationship is one of the major problems of contemporary education, about which is often concerned the global pedagogical thinking, like that of our country. From the historical point of view, both in literature and in educational practice were outlined two opposing views on teacher-student relationship: one characteristic to the traditional pedagogy based on a unilateral communication from teacher to student, the other modern, which considers the student exclusively as the subject of education, without any guidance from the teacher. Both points of view (the first emphasizing on the teacher as an authority, and the second on the full freedom of the student) are unilateral, however, rejecting the possibility of achieving real communication between the two poles of the educational act. The contemporary pedagogy sees the teacher-student relationship as a profound relationship in which both partners work together continuously and in which is well established the status of each one of them: the teacher as an educational factor and the student as an object and a subject of the education. Thus, the teacher, in order to meet his responsibilities as an organizer and a decision maker in establishing the educational strategies, as a mediator of the access to information and as an evaluator of the school performance, he has to know the psychology of the student, to transpose himself in the student's way of being, of feeling and acting. He must seek another place and role for the student in the educational act, to foster his activity and participation in the process of his own formation.*

1 THE CONCEPT OF „RELATED EDUCATION"

According to the „Pedagogical Dictionary" the pedagogical relationship refers to the specific education relationship between the adult and a child or a teenager in a systematic order „The construct contains descriptive and normative parts". Descriptive are the statements about the relationship between teacher and pupils/students in terms of understanding, anticipation, perspectives, knowledge, skills, judgments, actions and indications about the interim of the pedagogical relationship. The pedagogical relationships should, however, be understood as some normative categories, the teacher has to be distinguished by certain characteristics. Then from a primary perspective, a normative one, the pedagogical relationship must meet the following criteria: recognition of the child's personality/student and individuality, his comprehensive and formative education, to claim the responsibility of each party (H. Schanb, K.G. Zenke, 2001 p. 240). This definition of pedagogical relationship emphasizes the role of the personality of the one who teaches and the responsibility of each actor in maintaining the educational relationships in which the student is formed. In the pedagogical relationship the responsibility belongs to both subjects of the educational process. Teacher-student interaction requires active involvement of both parties in different proportions.

The relationship teacher – student impregnates and affects everything when it comes to teaching situations, especially as any relationship supposes the reciprocal control of behavior. At one extreme this relationship can be a battlefield, the teacher changing the „recipes” for forcing pupils/students to do what he wants, pupils/students changing "recipes" between them in order to escape. When this battle is won by the teacher, is said that he gets along well with pupils/students, and the losers are labeled as „good pupils / students”. When, on the contrary, the teacher loses, it's talked about a „weak class” and the „winners” are on the verge of repeating the year. When no one wins it is „a difficult class”. At stake is personal dignity of both sides.

At the other extreme of the teacher-student relationship is a totally identified with the class teacher, fighting for it with the officials of the school and the inspector (S. Marcus, 1999, p. 11).

These are the two theoretic extremes of a continuum. In reality, teachers and students should neither be in a face to face conflict, nor identified, which would cancel the purpose of the educational act. Desirable, but also the most difficult to reach and to maintain is the middle position, because it is not sufficient theoretical knowledge of teaching science or just understanding but also the love for the students.

As an interpersonal relationship in the pedagogical relationship there is a interdependence between the teacher’s and student’s behavior in the sense that the action from a side causes a change in the behavior of the other. But through his privileged position the teacher can take the initiative of the interaction which causes reactions from students. He can make so that the behavior of the students would be, more or less, dependent on him and from his behavior to result the atmosphere of a group within the class. It is therefore not an exaggeration to state that the construction of student autonomy depends heavily on pedagogical relationship, of the teacher’s behavior.

From a historical point of view, both in literature and in educational practice were outlined two opposing views on the relationship between the teacher and the student. Both points of view (the first puts emphasis on the teacher’s authority, and the second on the total freedom of the student) are, however, unilateral rejecting the possibility of achieving real communication between the two poles of the educational act.

For the purposes of contemporary pedagogy, the teacher-student relationship is seen as a profound relationship in which both partners work together continuously and in which it is well established the status of each side: the teacher as an educative factor and the student as object and a subject of education.

Thus, the teacher, in order to realize his duty as an organizer and as a decision maker in establishing the educative strategies, as a mediator of the access to information and as a school performance evaluator has to know the psychology of the student to translate himself in the way of being, of feeling and acting of the student. He has to have the purpose of changing the place and role of the student in the educational act, to stimulate the activity and the engagement of the student in the process of his own formation.

As for the student, in his position as an object of the educative influence and as the subject of his own formation, there should be a dialectical relationship, the efficiency of the educative action being dependent on its degree of engagement and participation in the instructiveeducative steps.

The approach of the teacher-student relationship within the requirements of the formative education is necessary especially since in the educational practice, still linger some attitudes characteristic to the traditional education, according to which the student is treated as a passive object of education involved only unilateral in the assimilation of the information provided by the teacher.

It can be said that the teacher-student interaction is influenced by existing relational systems in the group class. The socio-emotional climate existing here affects the students' behavior, their self-image. In this sense, the learning process, in addition to cognitive aspect involves cooperation and sociability. They are formed due to specific group class relations and may encourage and stimulate or on the contrary, to stop or inhibit the open and free communication between the teacher and the students.

In this paper we aim to highlight the following data:

- ✓ a few moments in the development of the teacher-student relationship in traditional and modern school;
- ✓ the types of teacher-student relationships in the contemporary society was another important point in our analysis;
- ✓ the realization of a study on the mutual perceptions of the relationship between the two partners in order to humanize the relationship between them.

Table 1 below shows the keywords that characterize traditional and humanized school.

Traditional school	**Umanized school**
Key-words	
Competition	Cooperation
Classifications, awards and penalties	Encouragements, self learning, tolerance, responsability
Listening	Participation, envolvement
Transmition, reception	Analisis, manifestation, conversation
Restraint	Liberty

Table 1: The key words that characterize the traditional and the humanized school.

There are no good or bad students – it is the teacher's problem to educate them, to refine them and bring to light the virtues of each one of them, helping them to discover their potential abilities, to give weight and value to their words, taking care always that this exercise is complete.

To provide a teacher-student relationship, based on cooperative relationships, on direct communication and guidance to encourage the individualization of the work, is a premise for productive after school work.

The modern didactics changes the vision of the student, putting him in the spotlight, aiming to make it interactive subject, co-participant and co-author of his own formation.

The teacher has to guide, mentor, and facilitate the instruction and the education.

G. Leroy says that **„the process of education starts when you teacher learn from the student, when you, translate yourself in his place, and you understand what he understood in the way he understood".**

The work of the teacher is primarily to ensure pupil/student with the resources, the key that will help him in his learning process (A. Sangra, 2001, p. 3).

2 TYPES OF TEACHER -STUDENT RELATIONSHIPS

The teacher – student relationship can be seen from many points of view (M. Zlate, 1972):

a) strict didactic(in the process of teaching and listening);
b) methodological-pedagogical (selection, organization and the prioritization of the teaching methods);
c) psychological (the two partners are regarded as some state ensembles, processes and their characteristic mental attributes).

A closer analysis of the interactions within the class/group revealed several types of relationships between teachers and students. Among them we can mention:

- ✓ communication relationships;
- ✓ management relationships;
- ✓ socio-affective relationships.

a) **Communication relationships** can also be of several types. Based on the teaching functions performed there are:

- of transmission, itself, the information (to explain new terminology, the statement of facts, interpretation of statements, expression of views, etc..)
- of structuring the information and concentration of the attention on the subject or on the work procedures;
- of requesting of some verbal or physical relationships from the students, stimulating their focus on issues etc.;
- of student's response to the teacher's requests;
- of reaction, acceptance, rejection, modification, extension, etc., of what has been said before;
- of assessment by the teacher of the student's answers etc.;
- of expression of some affective states (satisfaction, pleasure, annoyance, contentment, amazement, etc.).

b) **The relationships of management** of the class activity. They may establish limits of directing rigorously and the boundaries of the students' independence. Therefore, they can be:

- ***relations of domination by the teacher***, managed to create a „climate" of authority.

The emphasis in this case fall, on directing and order, on severe constraint and scolding of the students, on the stimulation of unconditional obedience, on the obedient acquiring knowledge, on their passive reception, on remembering and not thinking, on the suppression of the will of initiative, of independence, of creativity. Such relationships are unidirectional (the teacher decides, orders, gives commands - the student obeys, listens and executes) and conflicting, arousing feelings of aversion to the students by the teacher. The authoritarian professor is conservative, lack flexibility, is rigid, and does not take account of experience, interest and pupils judgment in realizing the pursued goals; the authoritative teacher appreciates the reproduction of the acquired knowledge without putting value on the originality or the authenticity of the students' thinking. Kenneth Moore, believes that authoritarian teacher's behavior can be described by the following verbs: to punish, to impose, to criticize, to use a sharp voice, to dominate, to inspire fear, to humiliate, to be harsh to require mandatory , to pressure.

- ***the democratic relationships*** - assume a new position towards the student, towards the ways of training and education and personality formation. Democratic teacher is essentially the empathetic type of teacher. The teacher's behavior is based on the tendency to integrate himself in the classroom's climate, to identify himself with the students' life and activity, his leading role is achieved through teaching methodology, such as to encourage the active participation of students, continuously enhance independence and their initiative, their spirit of responsibility, he suggests more than impose, stimulates more the interest and the curiosity, encourages the manifestation of spontaneity and creativity.

These are multi-directional relationships: of cooperation, of support to self-activity, of indirect influence, of cooperation, proving to be more effective and consistent with the principles of democratizing the school and our society. According to Kenneth Moore, democratic teacher's behavior can be described by the following verbs: to be friendly, to encourage, to help, to persuade, to be open to influence, to be firm, to stimulate, to direct, to be careful.

- ***indulgent relationships*** (laissez-faire - to let it be done) focus on the free development of the student, to leave the conduct of his work to the chance, considering that any intervention of a closed thinking is felt by the individual as a threat.

In this sense is denied any form of authoritarian intervention of the teacher, guidance or orientation to learning, training (pedagogical liberalism). But here the pedagogical liberalism misunderstood, pushed to anarchy and disorder because the teacher does not intervene lenient than only when the educational situation threatening to escalate into conflict, etc.).

c) **Socio-affective relationships** we point out that between teacher and pupils/students may experience spontaneous feelings of attraction or rejection, sympathy or antipathy, acceptance or non-acceptance, etc. In general, when the teacher comes to the class just as simple transmitter of information, concerned only with their reception, without any vibration emotional, affective - class relations become traumatic for the students and the more so, as the students are younger. Those mentioned here are intended to highlight the variety of types of relationships that can be establishes between teacher and pupils/students in the educational process and their implications many and what they may have on learning outcomes and school education.

3 HUMANIZING THE TEACHER-STUDENT RELATIONSHIP

The humanization and personalization of educational interaction involves substantial restructuring of the role of the teacher, the teacher „is the person who creates the conditions for the pupil/student to behave in a certain way, to put issues and tasks of knowledge, stimulate and maintain student activism investigator / student” (I. Neacsu, 2000):

- the teacher is not just the person who proposes content, gives lessons, make tasks but stimulate and maintain student activism investigator creates conditions for him to behave in a certain way, to discover and to put matters;
- to orient to specific student interests and capabilities is its attention to the achievements and creations. Teachers must possess the qualities necessary centering mainly on the expectations, demands, the needs and interests of students;
- the teacher must be able to be a double and work from his perspective and the group, be able to guess the order interpersonal characteristics of students collecting adequate capacity preferential relations between students, the anticipated social attitudes of students in relation to future learning situations.

In our era, deeply computerized, the man has found a new „partner” computer inter-human relationships has its specificity. A quality interpersonal relationship involves an attitude of mutually beneficial partnership in which partners give and receive what they are given alternative or what they lack and obvious that each man has „pluses” and „minuses”.

A prerequisite for effective teacher-student relationship is the manifestation of the sense of responsibility that must prove each role and its status (A. Pasca, 2012, p.8).

Investigations carried worldwide on the impact of education on social development come to show us that it is essential that the idea of forming man to inspire a philosophy of preparing him for a life in relation to complex modern cohabitation requirements or declare that thus fall outside reality. Both prospective education and its performance is emerging as ideas coming from their position and project requirement shall be based pedagogy to develop his own theory demanded an education intended to form man throughout his life size, and in accordance with the requirements of the third millennium, found a much greater extent in science and technology imperatives designed in indissoluble unit.

The questionnaire conducted in the educational institution were obtained following relevant data: the question which determinants that influence student success in school, 55.73% of respondents said that personal effort is the most important, 41.15% - teaching style, 32.81% - 30.73% and the quality of teaching - the relationship between teacher / student and only 2.08% thought otherwise.

So, the students realize that only through personal effort they can achieve perfection. But do not forget that for an incentive and motivate students to work is very important and attractive personality of the teacher by his attire, readability and style of teaching applied, the quality of teaching and not least the relationship between teacher and student, often regretfully longer Meet and currently being authoritative Teacher, which causes him to lose student interest and desire to do the book and taught himself matter.

Students

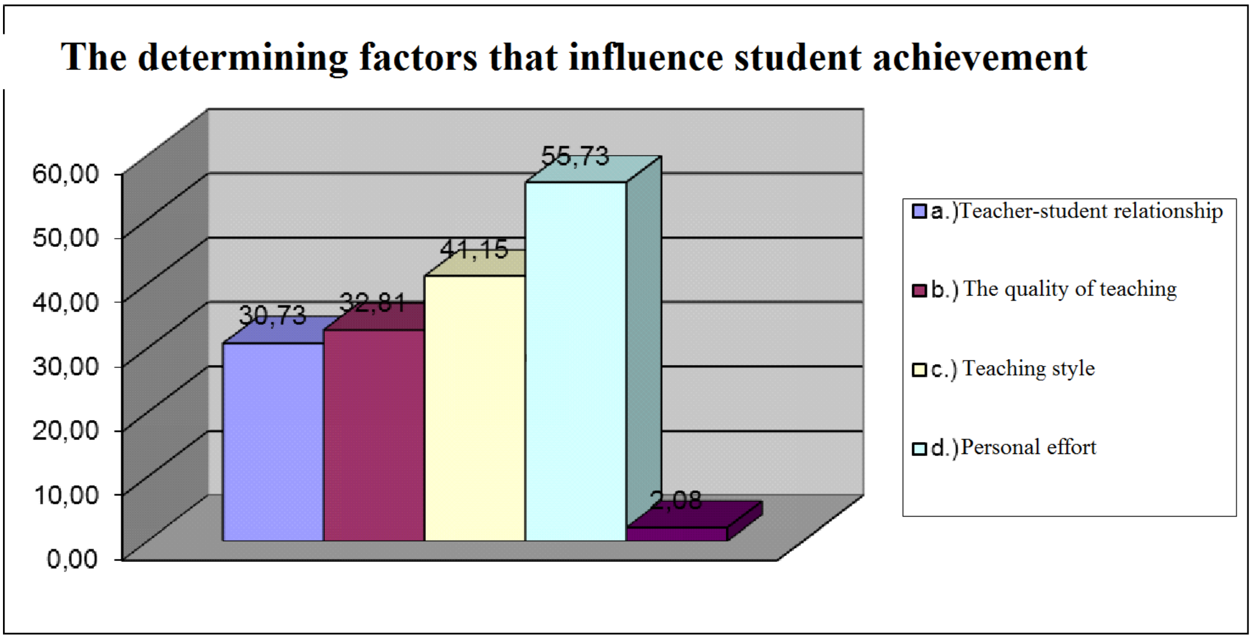

Figure 1: Diagram showing the share of determinants that influence student success in their view.

A style preference of students on the relationship between teacher and students was distributed as follows: for freestyle was delivered 46% of respondents to the Democrat - 43% for the authoritative - 9% and only - 2% of respondents wanted other styles than the above.

While the teachers believe that the relationships style encouraging/motivating the student to learn is: 55% Democrat, 20% liberal, authoritarian 21% and only 4% cited other styles. From the data presented it can be concluded that the preferential relations style both for students and for teachers is democratic style. Although now it tends to avoid the exercise of authority over the students, but from the data below shows that the authoritarian style is currently in the process of education, which gives department managers thought and institutions of higher education to train teachers and familiarize them with the new trends in science education in the country and worldwide.

Students

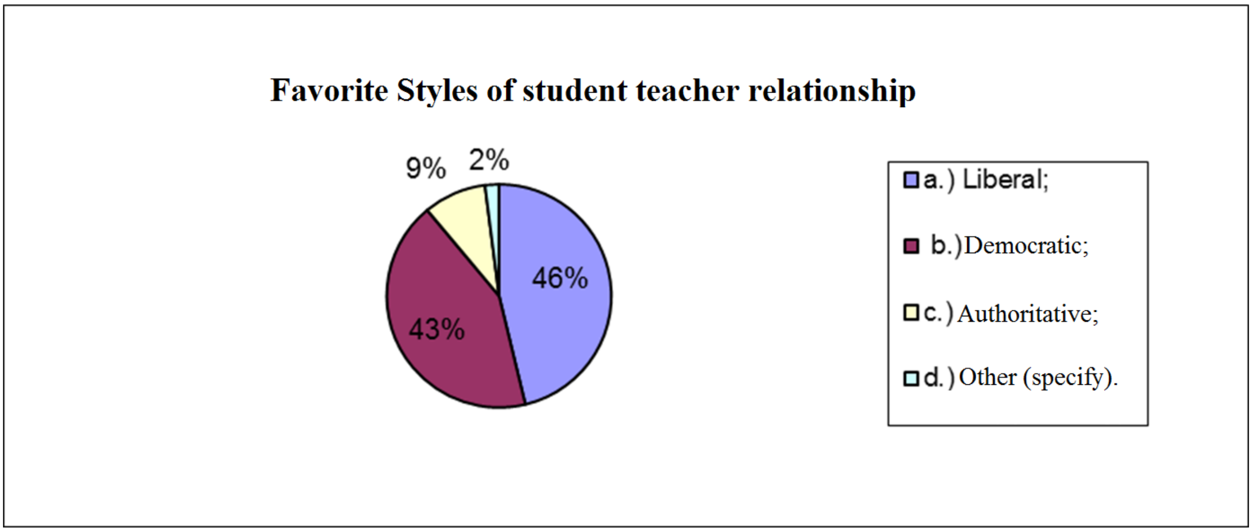

Figure 2: Diagram showing the style preferences of students on the relationship between teacher and students.

Teachers

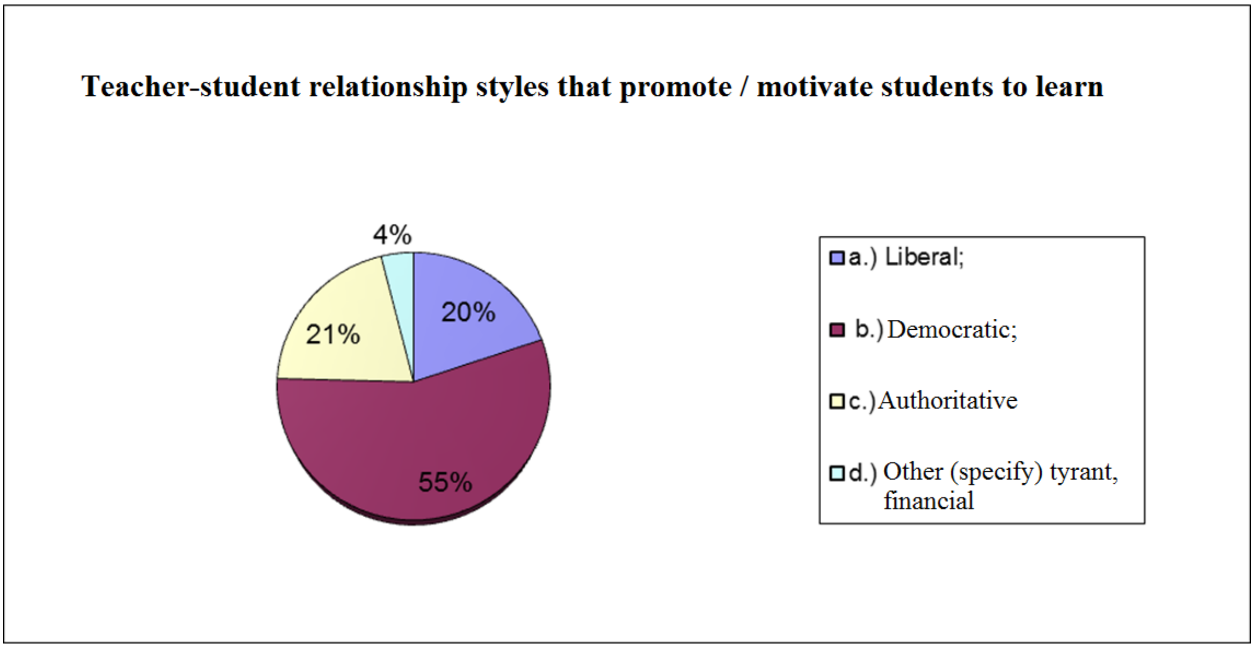

Figure 3: Diagram showing the teachers view the relationship between teacher and student style that motivates the student to learn.

In summarizing the above analysis we can say that the democrat style is that style that encourages/motivates the student to learn and be successful in school, but it is also the style that should prevail in the teacher-student relationship, which characterizes the relationship According teacher with student teachers.

4 CONCLUSIONS

The process of education is essentially a process of communication, it is important to acquire skills to communicate. Both teacher and student must be open to others and willingly to „give” and „receive”, abandoning the prejudice that „yes” is more valuable than „receive”.

The professor may be considered, metaphorically speaking, a well charged battery with expert information and some experience of life, and the student is a battery that is being „loaded” in school.

In such a possible applicative vision, the analysis that we realized can only be a starting point, a stimulus for future, research in the broad issues of human inter knowledge. From this point of view, we note that we do not claim to have exhausted the topic under discussion; this study can only be a reference point for certain theorizing concepts.

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THE PRODUCTION OF NATURAL BASED MICROCAPSULES HAVING ANTIBACTERIAL ACTIVITY

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Keywords: Chitosan/gum Arabic, PVA, complex coacervation, Rosemary oil and peppermint oil, antibacterial activity, microcapsules.

Abstract. *In this study, the preparation and characterization of microcapsules with antibacterial core and shell was carried out for textile applications. Rosemary oil and peppermint oil were used as antibacterial agents and microencapsulated by complex coacervation of polyvinyl alcohol (PVA), gum Arabic and chitosan polymers. Fourier transform infrared (FT-IR) spectroscopy analysis was performed to characterize the chemical structure of microcapsules. The morphology of microcapsules was analyzed with optical microscope and scanning electron microscopy (SEM). The antibacterial activity of wet slurry of microcapsules was investigated by using the disk diffusion method. According to the results of FT-IR and morphology analysis, peppermint oil and rosemary oil were encapsulated into chitosan/PVA and chitosan/gum Arabic shells successfully. Prepared microcapsules have smooth and compact surfaces, and have spherical profiles. According to the test results, the microcapsules produced have anti-bacterial activity only against gram positive bacteria.*

1 INTRODUCTION

Antimicrobial textiles find a variety of applications from clothing to medical applications such as health and hygiene, and infection control. For this reason, in the last few decades, a range of textile products based on synthetic antimicrobial agents such as triclosan, metal and their salts, organometallics, phenols and quaternary ammonium compounds, have been developed and quite a few are also available commercially [1]. In order to obtain the greatest benefit, an ideal antimicrobial treatment of textiles should satisfy a number of requirements. Firstly, they should be effective against a broad spectrum of bacterial and fungal species [2]. Recently, bio-compatibility of antimicrobial agent like other chemical finishes is one of the most important properties. Although synthetic antimicrobial agents are very effective, they have toxic effect on environment and also they can exhibit low toxicity to the consumers. The antimicrobial agent can cause toxicity, allergy or irritation to the user. In recent years, there is an increasing trend in textiles prepared with natural-based finishes to overcome these possible problems of synthetic antimicrobial agents. In this scope, naturally derived compounds and plant extracts with functional antimicrobial properties are being investigated and exploited in controlling pathogens in textiles [3].

In this study, peppermint and rosemary oils extracted from plants were used as natural antibacterial agent for textile applications. Peppermint and rosemary oils are used in food, cosmetics and medicines all over the world [4]. Anti-bacterial, anti-fungal and mosquito repellent properties of both of the essential oils have been reported in the literature [5,6]. But it is made use of from these features short-term because they are volatile. In this study, it is aimed to overcome this problem by microencapsulation of core materials into the polymer shell. Encapsulation of functional materials into polymeric shell structure is an attractive way of storing, as well as protecting, these from the environment until required for fulfilling appropriate applications. Recently, there has been growing interest in the microencapsulation of antimicrobial agents for textile applications [7,8]. In this study, it was aimed to microencapsulate the peppermint and rosemary oils as antibacterial core material for textile applications. In our previously studies, we have determined antibacterial activity of peppermint oil, rosemary oils and chitosan by using disk diffusion method [9,10].

In the study, preparation of microcapsules was carried out by complex coacervation. Microencapsulation by coacervation requires the use of two oppositely charged colloids [11,12]. In the literature, various core materials such as tamoxifen, n-Eicosane were encapsulated with variety of polymers such as silk fibroin, chitosan, gelatin B and acacia gum by using complex coacervation method[13,14]. In this study chitosan polymer solution in acetic acid and gum Arabic polymer and polyvinyl alcohol (PVA) polymer solutions in water were used as oppositely charged colloids. As is known, PVA is a synthetic polymer. But, it also has been employed in several biomedical applications and it is an FDA(*) approved material [15]. Due to these features, PVA was selected as a biocompatible polymer and used with other natural polymers in this study. Four different microcapsules were produced using combinations of different wall and core materials.

2 MATERIALS AND METHODS

2.1. Materials

Chitosan (Sigma Aldrich) as polycation and PVA and Arabic gum (Sigma Aldrich) as polianion were used to form the microcapsule wall polymer structure. Rosemary and peppermint oils were used as antibacterial agents (%100, Botalife). Span 20 as a surfactant (Sigma-Aldrich) and glutaraldehyde with concentration of 2.5 % (Sigma Aldrich) as a cross-linking agent were used. For adjusting pH, acetic acid (%100, Sigma Aldrich) and sodium bicarbonate (M=105,99 g/mol, SigmaAldrich) were used.

2.2.1. The Production and Characterization of Microcapsules

Complex coacervation metod was used for the production of natural based microcapsules. In the production of microcapsules, initially, rosemary oil and peppermint oil were dispersed in the PVA or Gum Arabic-water solution by adding surface active substance. Therefore oil-in-water emulsion was formed. In the second step, the chitosan polymer solution as polycation solution was added in the emulsion drop by drop. After the pH of the emulsion was adjusted to pH 4, polymer-polymer complex formation between cationic and anionic polymers was started and continued for 2 hours. Therefore polymer complex was deposited on the core material. In the last step of process, cross-linker was added for stabilization of microcapsules. Finally, microcapsules prepared were filtered and washed several times with deionized water and they were dried at room temperature. The process of the microcapsule synthesis was summarized in Chart 1. The amount of wall and the core material used in the preparation of microcapsules were given Table 1.

Chitosan was dissolved in 1,5% (w/v) acetic acid solution to prepare 1% (w/v) Chitosan solution

↓

PVA or Gum Arabic were dissolved in deionized water (100 ml) to prepare % 0.5 (w/v) PVA or Gum Arabic solutions

↓

Span 20 as a surfactant (1,5 g) and the core material (3 g rosemary oil or peppermint oil) were added in the anionic solutions and were mixed at the rate of 1000 rpm for 30 min.

↓

The solution of chitosan was added drop by drop in the emulsion for 15 min.

↓

pH were adjusted to pH 4 and the solution was mixed for 2 hours for the realization of phase separation.

↓

Cross-linked with a 1 mL (glutaraldehit) was added drop by drop.

↓

The system was stirred for 1 hour.
(The reaction medium was kept constant at 40 ºC at every stage of process)

↓

Microcapsules were washed several times with deionized water and were dried.

Chart 1. The Stages of the Microcapsule Synthesis

Sampels	**Rosemary oil (g)**	**Peppermint oil (g)**	**Chitosan (g)**	**PVA (g)**	**Gum Arabic (g)**	**Span20 (g)**	**Glutaraldehyde (ml)**
Microcapsules1	3	-	1	-	0,5	1,5	1
Microcapsules 2	-	3	1	-	0,5	1,5	1
Microcapsules 3	3		1	0,5	-	1,5	1
Microcapsules 4	-	3	1	0,5		1,5	1

Table 1. The Amount Of Wall And The Core Material Used In The Production Of Microcapsules

The morphology of microcapsules were analyzed by optical microscopy and Scanning Electron Microscopy (SEM), the chemical structures of microcapsules were investigated by Fourier transform infrared (FT-IR) spectroscopy and anti-bacterial activity of the slurry microcapsules was tested with the bacteria *Staphylococcus aureus* and *Escherichia coli* by using the disk diffusion method. In the method, antibiotic discs impregnated with 20 µl of slurry microcapsules and are left to dry in a laminar air flow. After this step, 100 µl 0.5 Mc Farland turbidity of Staphylococcus aureus and Escherichia coli bacterial suspension spread petri dishes and sterile disks impregnated with slurry microcapsule dried and placed in the cabin. Plates were incubated for 18-20 hours at 35 º C by inverting. After incubation, bacteria inhibition zone diameter was measured with a millimeter ruler. Different diameters of the zones around the discs have demonstrated the antimicrobial effects of these substances.

Dimethylsulfoxide (DMSO) which was used as the solvent-impregnated discs were used as negative control and Ciprofloxacin (Oxoid 5 µg) standard antibiotic disk was used as positive control for the detection of antibacterial activities of different concentrations of slurry microcapsules. The test results are evaluated according to the CLSI (Clinical and Laboratory Standards Institute), sensitive to strains, resistant to moderately and susceptible.

3 RESULTS AND DISCUSSION

3.1 The Optical Microscopy and SEM Images of Microcapsules

To investigate the morphology of the microcapsules optical microscopy and SEM images were used. The optical microscopy and SEM images of microcapsules with chitosan/gum arabic and chitosan/PVA shell were given Figure 1-7, respectively. As seen from the figures that microcapsules have relatively uniform spherical shape. According to the SEM images all microcapsules except microcapsule 4 have nano-sizes. The particle size of microcapsule 4 is bigger than 1 µm.

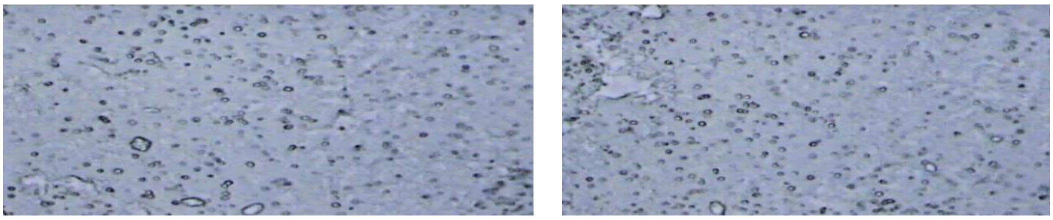

Figure 1. Optical Microscope Images of Microcapsules 1

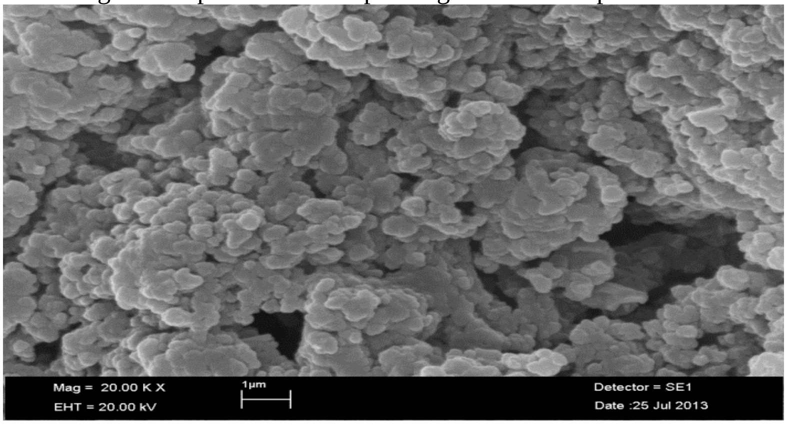

Figure 2. The SEM Imagines of Microcapsules 1

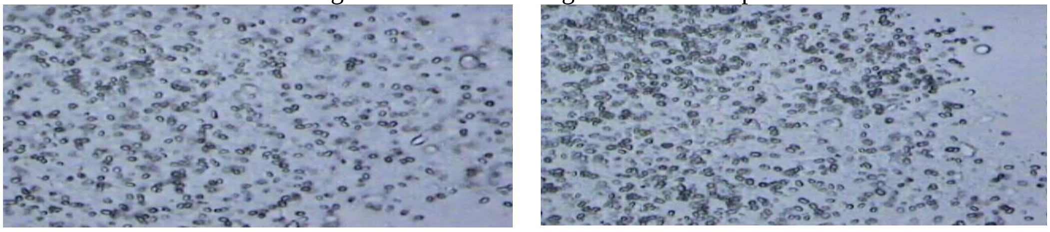

Figure 3. Optical Microscope Images of Microcapsules 2

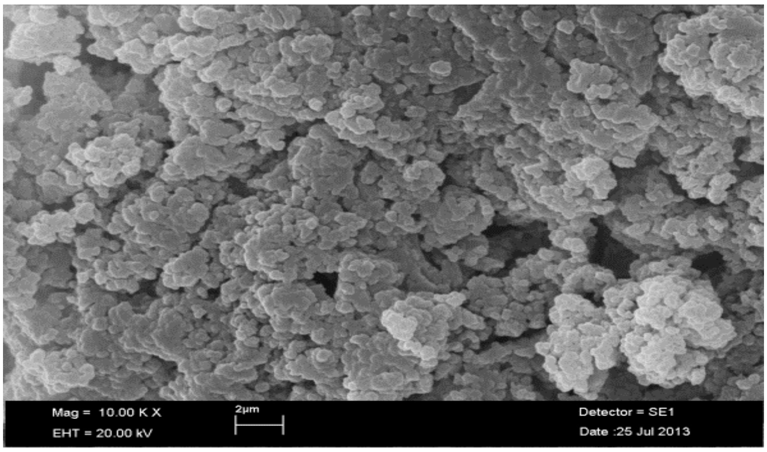

Figure 4. The SEM Imagines of Microcapsules 2

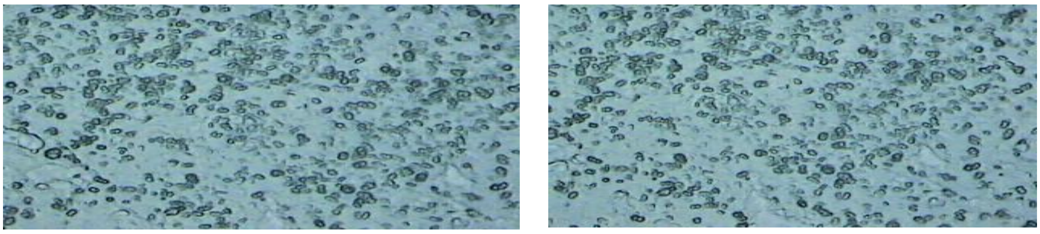

Figure 5. Optical Microscope Images of Microcapsules 3

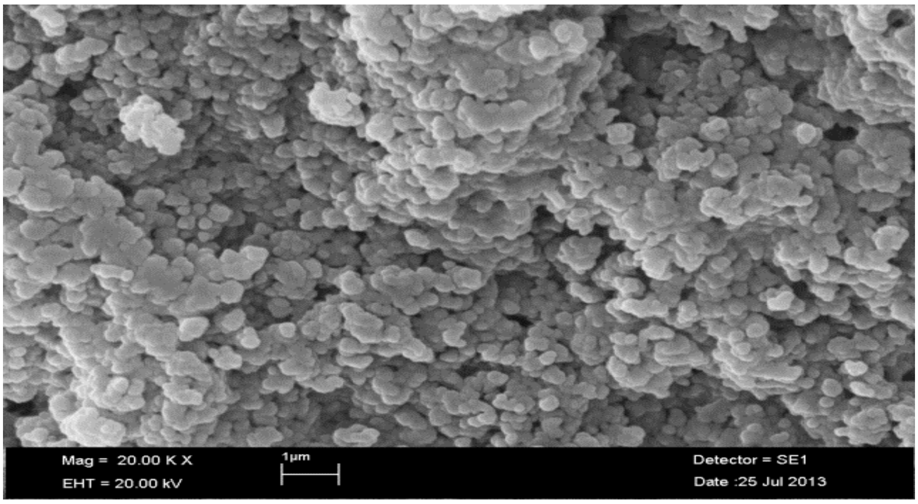

Figure 6. The SEM Imagines of Microcapsules 3

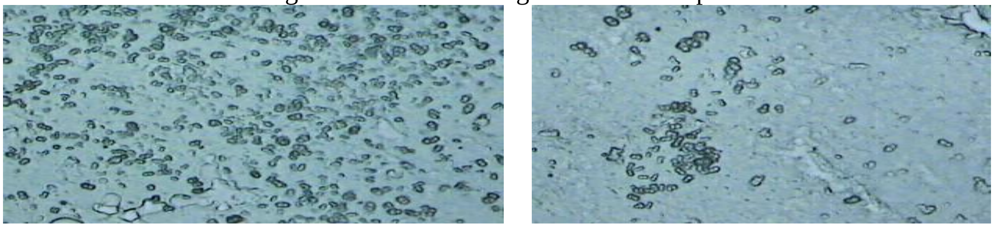

Figure 7. Optical Microscope Images Of Microcapsules 4

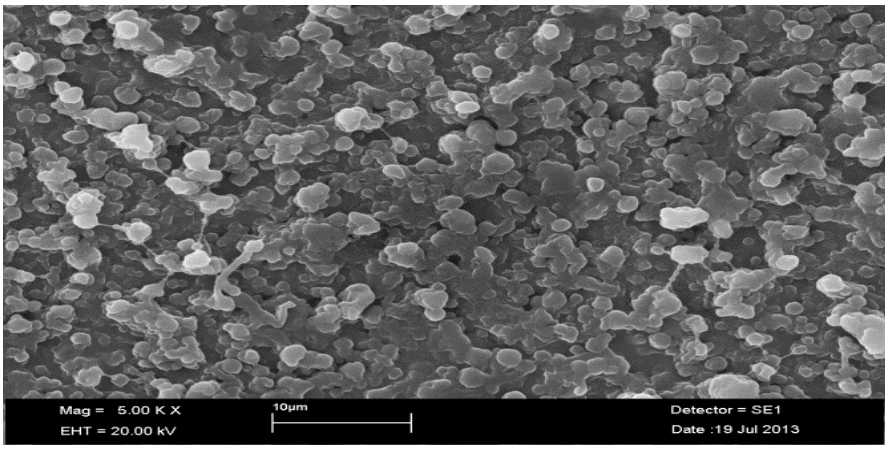

Figure 8. The SEM Imagines of Microcapsules 4

3.2 The FT-IR Spectra of Microcapsules

FT-IR spectroscopy analysis was performed to clarify the chemical structure of microcapsules. For this, IR spectra of microcapsules and core and shell materials used to prepare microcapsules were studied. Figure 9 shows FT-IR spectra of microcapsules 1, rosemary oil, chitosan and Arabic gum polymer. According to FT-IR spectra of rosemary oil, there are sharp two peaks at 2923 cm^{-1} and 2881 cm^{-1} that are C-H stretching peaks in structure of rosemary oil. These peaks arise at 2924 ve 2854 cm^{-1} in FT-IR spectrum of microcapsule. This is a proof of the presence of rosemary oil in microcapsule structure. FT-IR spectra of the peppermint oil, microcapsules 2, chitosan and gum Arabic were given in Fig. 10. The peaks at 2924 and 2867 cm^{-1} peaks in the FT-IR spectra of microcapsule-2 are characteristic C-H stretching peaks of peppermint oil that emerged at 2924 and 2871 cm^{-1} in the spectra of peppermint oil, proving the existence of peppermint oil in the microcapsule structure.

According to the spectra of Arabic gum given in Figure 9 and Figure 10, the peaks at 1600 and 1420 cm^{-1} are bending peaks of symmetric and asymmetric carboxylic groups of gum Arabic. The broad peaks at 3450-3448 $cm-^{1}$ in the FT-IR spectra of chitosan polymer belong to -OH stretching. The peak observed at 1740 $cm-^{1}$ in the FT-IR spectra of microcapsule 1 and microcapsule 2 is a stretching peak of carbonyl group (C=O). The carbonyl group can form via esterification reaction of OH group of chitosan and a symmetric and asymmetric carboxyl group of gum Arabic. In addition, the two peaks at 3295 cm^{-1} in IR spectra of chitosan and 3414 cm^{-1} in the spectra of gum Arabic were overlapped and emerged at 3430 cm^{-1} as a single peak in microcapsule spectra.

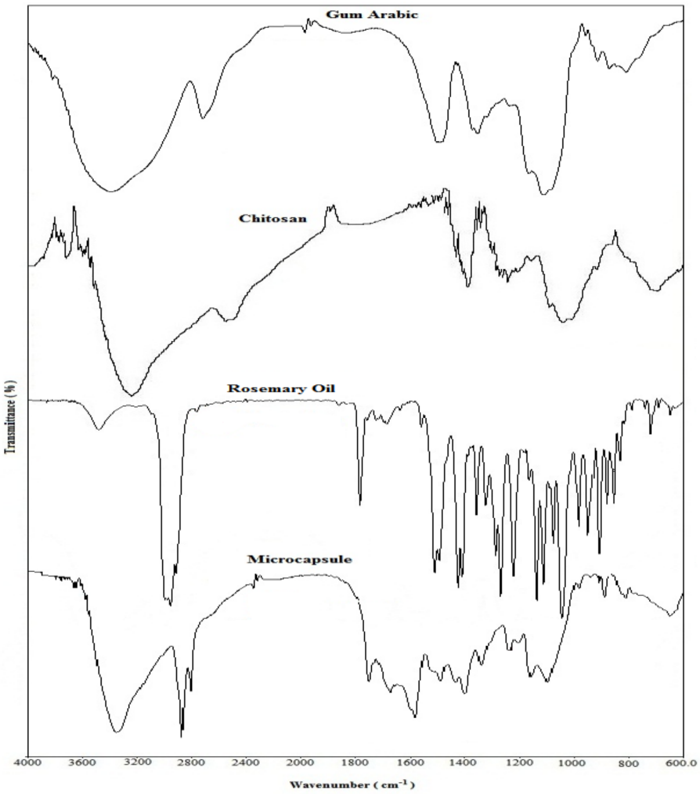

Figure 9. FT-IR spectra of microcapsules 1, rosemary oil, chitosan, Arabic gum

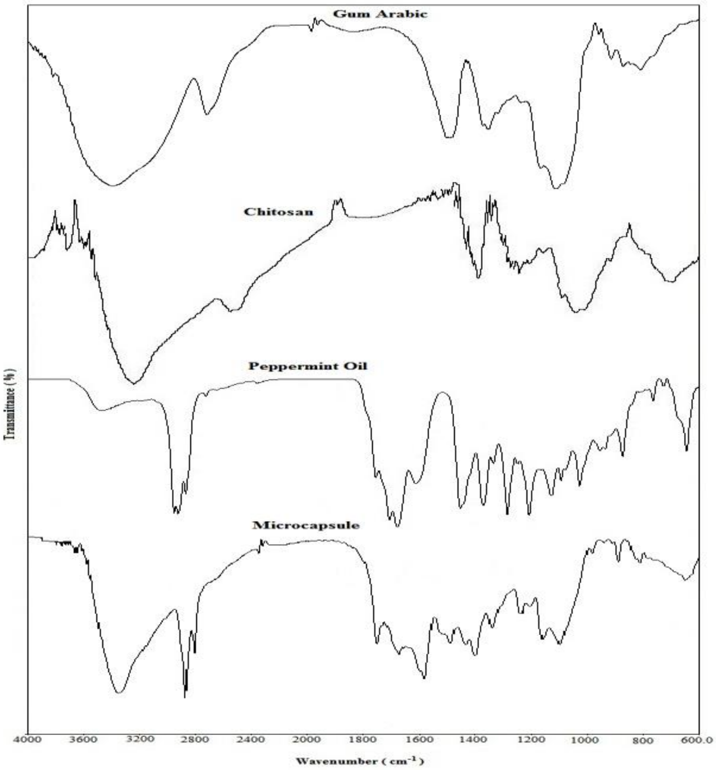

Figure 10. FT-IR spectra of microcapsules 2, peppermint oil, chitosan, Arabic gum

The FT-IR spectra of microcapsule 3, microcapsule 4, and the core and shell materials used to prepare microcapsules were given in Figure 11 and Figure 12, respectively. The peaks at

2920-2925 cm^{-1} ve 2867-2870 cm^{-1} in the spectra of microcapsules 3 and microcapsule 4 are C-H stretching peaks of rosemary oil and peppermint oil that arise at 2923- 2926 cm^{-1} and 2871-2881 cm^{-1} in the spectra of core materials. The presence of the characteristic C-H stretching peaks of core materials in microcapsules spectra prove the presence of core in microcapsule structure.

The broad peak at 3040 cm^{-1} wavenumber in FT-IR spectra of PVA and the broad peaks at 3450-3448 cm-^{1} in the FT-IR spectra of chitosan are belong to -OH stretching and hydrogen bonds. There is a peak at 1656 cm^{-1} in the spectra of microcapsules. This peak is a carbonyl (C=O) that is formed via cross-linking of -OH group of PVA and –NH_2 group of chitosan by glutaraldehyde cross-linker. This is a proof of formation of microcapsule shell structure.

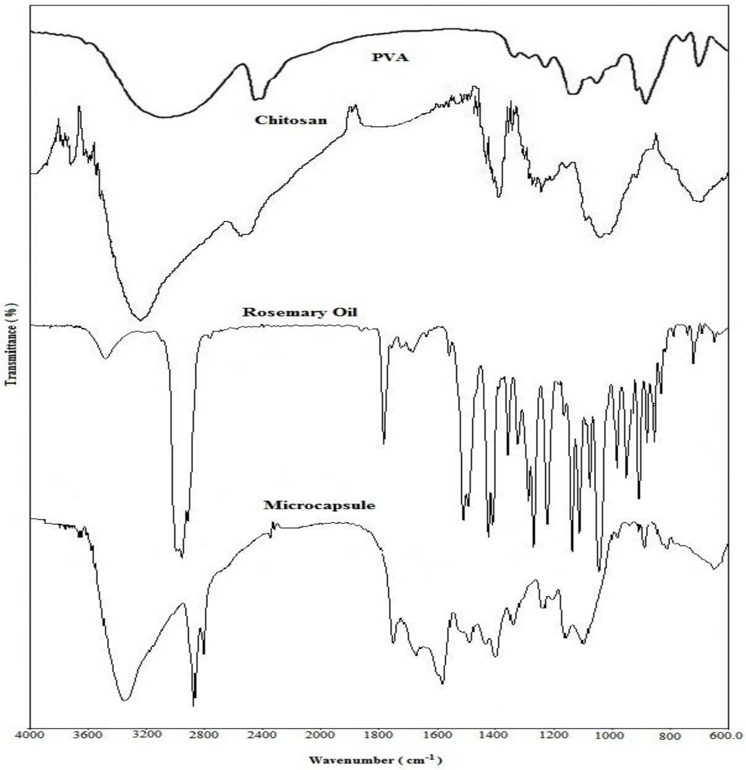

Figure 11. FT-IR spectra of microcapsules 3, rosemary oil, chitosan, PVA

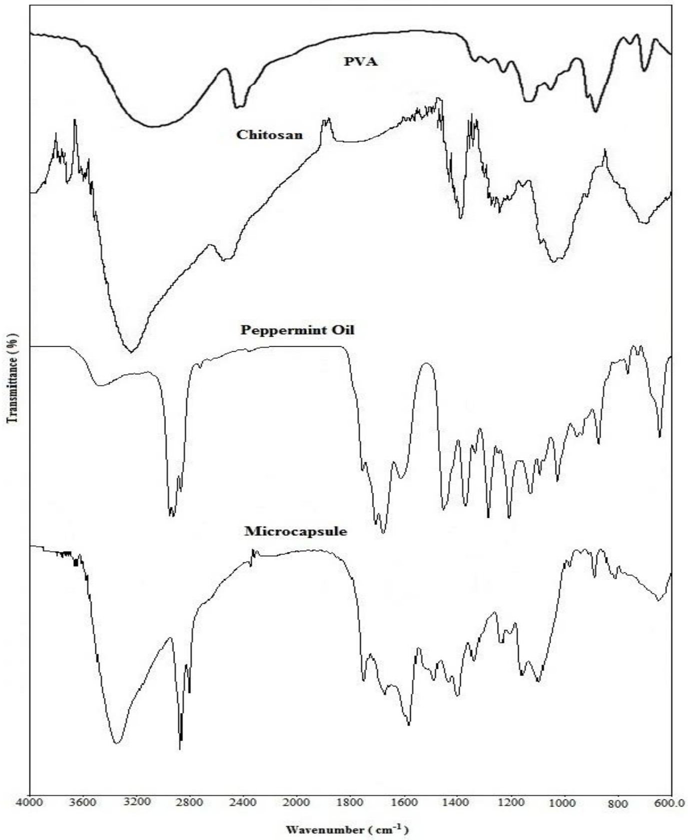

Figure 12. FT-IR spectra of microcapsules 4, peppermint oil, chitosan, PVA

3.3 The Results of Antibacterial Activity

Antibacterial test results of the wet slurry of microcapsules and the solvent used to prepare slurry microcapsules carried out by using *Escherichia coli* and *Staphylococcus Aureus* bacteria were given in Figure 13, 14, 15 and 16. It can be apparent from the sixth discs, the solvent used did not affect antibacterial activity test results. Additionally, according to the results, all of the slurry microcapsules (1,2,3,4) have shown antibacterial activity on *S. aureus(gram positive bacteria)* in two different concentration. But they haven't any antibacterial effect on *E. coli* strains. In previous studies, while rosemary and peppermint oils were used as core materials, chitosan and sodium alginate were used shell materials. The antibacterial activities of the chitosan/NaAlg microcapsules were proved against to gram positive and gram negative bacteria by using Agar Well Diffusion and Agar Disk Diffusion Methods [9,10].

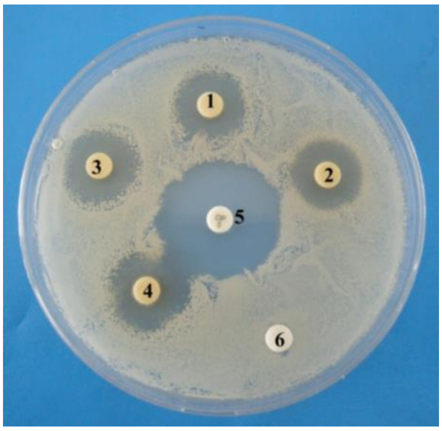

Figure 13. The antibacterial activities of microcapsules produced against to *Staphylococcus aureus*(gram-positive bacteria) in concentration of %100

1. Microcapsule **2**. Microcapsule 2, **3**. Microcapsule 3, **4**. Microcapsule 4, **5.** Ciprofiloksasin(Positive Control) **6.** the solvent(Dimethylsulfoxide)in *Staphylococcus Aureus(gram positive bacteria)*

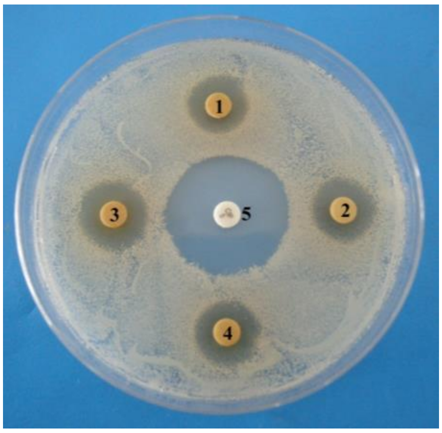

Figure 14. The antibacterial activities of microcapsules produced against to *staphylococcus aureus*(gram-positive bacteria) in concentration of %50

1. Microcapsule 1, 2. Microcapsule 2, 3. Microcapsule 3, 4. **4**. Microcapsule 4 **5.**Ciprofiloksasin(Positive Control) in *Staphylococcus Aureus(gram positive bacteria)*

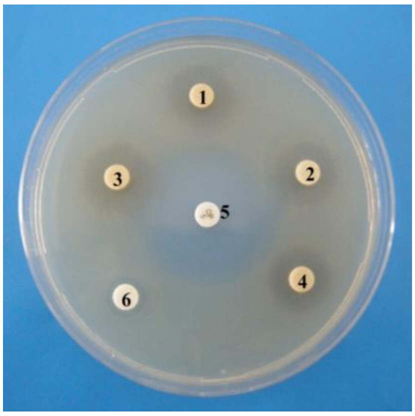

Figure 15. The antibacterial activities of microcapsules produced against in *Escherichia Coli (gram negative bacteria)* in concentration of %100

1.Microcapsule1, **2**. Microcapsule 2, **3**. Microcapsule 3, **4**. Microcapsule 4, **5.** Ciprofiloksasin(Positive Control) **6.** the solvent(Dimethylsulfoxide)

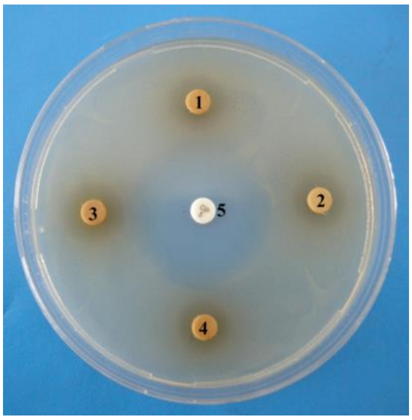

Figure 16. The antibacterial activities of microcapsules produced against *Escherichia Coli (gram negative bacteria* in concentration of %50

1. Microcapsule 1, **2**. Microcapsule 2, **3.** Microcapsule 3, **4**. Microcapsule 4, **5.**Ciprofiloksasin(Positive Control)

5 CONCLUSIONS

In this study, antibacterial microcapsules containing rosemary oil and peppermint oil were produced by using complex coacervation of chitosan/gum Arabic and chitosan/PVA polymer pair. According to the FT-IR spectroscopy analysis core materials were encapsulated in chitosan/PVA and chitosan/gum Arabic shell, successfully. Optical microscopy and SEM analysis indicated that microcapsules have uniform spherical shape and nano or micro sizes. The antibacterial activities of the slurry microcapsule were tested using agar disk diffusion method and antibacterial test results show that the microcapsules produced are only effective against to gram-positive bacteria.

(*)FDA: U.S. Food and Drug Administration.

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TEXTILES IN SPACE SUITS

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Keywords: EMU, Liquid cooling and ventilation, Dacron®, Mylar®, Teflon®, Gore-tex®

Abstract. *The feelings of discovery and curiosity are the most important reasons to have the human to observe and define environment first and later the space. While the first studies about space are on both understanding the structure of it and to sent a life form to space, today it is focused on establishments of new constructions and biological adaptation of a human being with the help of different disciplines such as physics, chemistry, material science, electronics, mechanics, biology, textiles etc. Therefore, especially high performance textiles are very important for space suits to be able to explore the new experiencing in planets and space in today's era. In space applications, materials are required to display specific features such as strength, lightness, high endurance, and resistance to erosion, corrosion, hard ignition and high dynamic deformation etc. It is rather difficult to obtain these features with only one material because of both technical and economic reasons. Hence, nowadays different structures made from different textile processes such as weaving, braiding, composites, covering and lamination are used in space suits. It satisfies the unique requirements of space especially the endurance and its flexibility. Various textile structures such as fibers, woven and knitted materials, nonwovens are used as a support and reinforcement component in every kind of composite laminated structures in space applications; one of which and the most important space textiles are the astronaut clothes called EMU (Extravehicular Mobility Unit). This paper explores the EMU and introduces some fibers such as Gore-tex®, Teflon®, Kevlar®, Nomex®, Dacron® and Mylar® which can be found in space suits.*

1 INTRODUCTION

The first space suits were introduced during 1950s when space exploration began and since then they have well progressed according to the technological improvements have been made in areas of materials, electronics and textiles. Overtime, they became more functional and complicated. Today, there are quite a lot completed space suits made by US, Russia and China. In this paper, an overview is carried out to study the space suit assembly that is employed in US and explore its part with some of the fibres that are used.

A space suit is designed to re-create the environmental conditions of Earth’s atmosphere during the space shuttle missions. Therefore, space suits have a vital role in protection of astronaut’s life during the tasks; they protect the astronauts from the harsh environment of space i.e. cold, heat, micrometeoroids, chemicals and pressure variations. As there is no atmospheric pressure or oxygen in space to sustain life, astronauts wear space suits assembly outside the space shuttle, in the vacuum. The space suit is also called Extravehicular Mobility Unit (EMU) where the materials are all white to reflect the sunlight as seen in Figure 1. EMU enables to protect astronauts at the outside of the space shuttle and it includes many individual components which later forms a single space suite as shown in Figure 2.

Figure 1: EMU space suit [1]

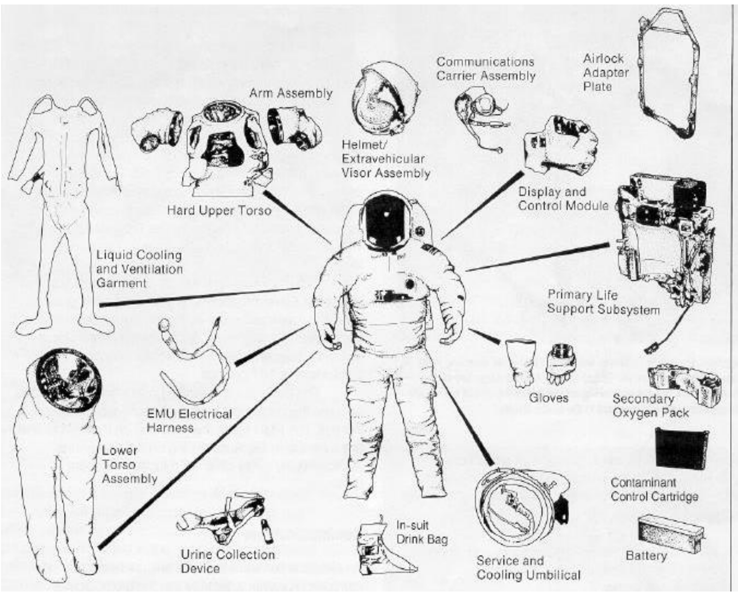

Figure 2: Space suit and its components [2]

EMU provides micrometeoroid protection, pressure and thermal, oxygen, cooling water, drinking water, food, waste collection, electrical power and communication[3]. Space suits for space shuttle missions are pressurized at 30 kPa and on Earth the pressure is 100 kPa; as it is noticed that the pressure provided is lower than that on Earth so the suit flexible and does not balloon[4]. Also on Earth all its parts weight about 112 kg. There are several layers of the space suit (EMU) which are mentioned below and Figure 3 also shows the layers of an EMU.

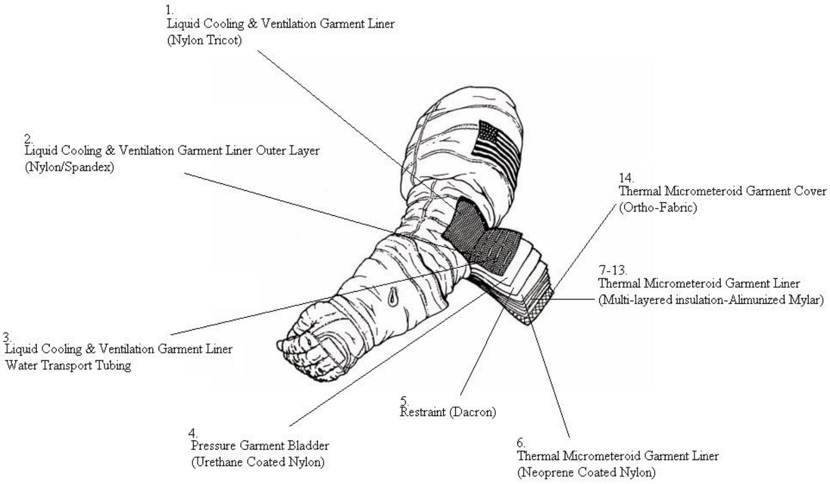

Figure 3: Cross-section of an EMU[2]

1.1 Micrometeoroid/tear protection layer

This layer is the outermost layer of a space suit and also protects from the micrometeoroids. The layer is known as Ortho Fabric® which is a blend of woven Nomex® and Teflon® with Kevlar® rip stops to be able to prevent the tear growth[5]. It mainly protects subsequent layers which are pressure restraint layer and the pressure bladder from abrasion and tears.

1.2 Super insulation layer

This layer provides thermal protection and therefore consists of aluminized Mylar® film which is reinforced with PET scrim. Super insulation layer protects the astronaut from outside temperatures ranging from -100 °C to 120 °C and inside the space suit assembly, the temperature may range from 10 °C to 45 °C [4].

1.3 Second micrometeoroid layer

This layer is the inner layer of the thermal micrometeoroid garment. It has a final barrier protection to the micrometeoroids with the help of Neoprene® coated nylon cloth[5].

1.4 Pressure restraint layer

This layer is made of PET fabric placed over the pressure bladder fabric to give it an additional support and shape[5].

1.5 Pressure bladder

This layer is composed of polyurethane coated Nylon®. For the pressure bladder in space suit, nylon is dipped in polyurethane more than six times to create an impervious barrier between the pressure of pure oxygen inside the space suit and the vacuum of space on the outside[5].

1.6 Liquid cooling and ventilation garment

This layer is a tube made of ethylene vinyl acetate. The garment covers the astronaut's upper and lower body to be able to control the temperature via the water circulation as seen in Figure 4. Water is pumped through the tubes near the spacewalker's skin to remove extra heat as it circulates entire the body. The garment is made out of combination of nylon, spandex and liquid cooling tubes. The nylon tricot is first cut into a long underwear-like shape. Meanwhile, the spandex fibres are woven into a sheet of fabric and cut into the same shape. The spandex is then fitted with a series of cooling tubes and then sewn together with nylon layer. A front zipper is then attached as well as connectors for attachment to the life support system[6].

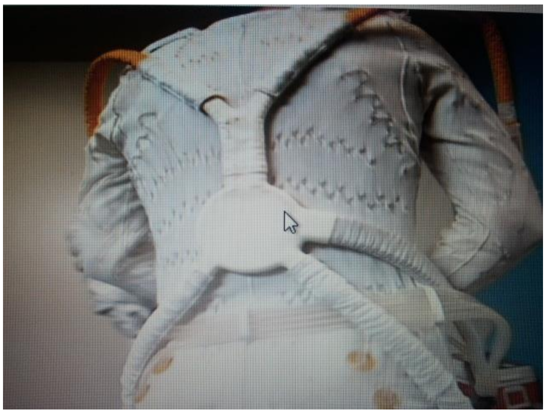

Figure 4: Liquid cooling ventilation garment[7]

1.7 Body comfort lining

This lightweight material is made of Nylon® chiffon and is the first layer of the fabric which touches the astronaut's skin. Therefore, it is positioned between the astronaut and the liquid cooling and ventilation garment.

1.8 Pressure restraint system

This layer is composed of items. Airtight linings with body comfort fabrics i.e. Dacron® cloth are the major parts of the component but on the other hand the suit must be flexible and keeps it shape along with inside pressure.

1.9 Gloves

The restraint layer of the EMU glove is positioned over bladder where is formed when a ceramic cast of a hand is dipped 7-8 times into a vat containing urethane and later hand-shaped bladder is uncovered from the ceramic cast and inflated to check if there are any leaks or defects. The fingertips of the glove are covered with silicone rubber to permit some sensitivity in handling tools and other objects, as seen in Figure 5. The rings, which give rotational mobility in the hand area of the gloves, snap into rings in the sleeves of the upper torso. Also, because of the fingers which are the part of the body that gets coldest in space, these gloves have heaters in the fingertips.

Figure 5: Gloves for space suit [7]

2. SOME FIBRES IN SPACE SUITS

The textiles that are used in space suits for EMU contain several parts[2] and these are: liquid cooling and ventilation garment (2 layers), pressure restraint garment (2 layers), thermal micrometeoroid garment (8 layers) and outer insulation garment (1 layer). The layers can be produced from many resilient textile materials i.e. Nylon® tricot, Teflon®, urethane coated Nylon®, Dacron®, Neoprene® coated Nylon®, Mylar®, Gore-tex®, Kevlar®, Nomex®. In below some of these fibres, which can be found in space suits, will be introduced.

2.1 Teflon® and Gore-tex®

The fluorocarbon, polytetrafluoro ethylene (PTFE) was introduced in 1954 by the Du Pont Company, and known by the trade name Teflon® (Figure 6) which is a chemically and environmentally resistant material. Teflon® is usually found in hollow woven, knitted, braided and felted forms of textile materials. PTFE is soft, very flexible and on the other hand has a high melting point. It has one of the best thermal stability of tough, flexible fibres and good at chemical resistant’s, it can be made as an expanded film for water and chemical barrier applications under the trade name Gore-tex®. Because of this, woven Teflon® and Nomex® with Kevlar® rip stop are used in ortho fabric in space suits for various functions of the cloth such as abrasion and tear protection for pressure restraint, bladder and for the thermal control against the micrometeoroid protection of the garment. On the other hand, Gore-tex® is a very fine barrier material which was first developed as a two layer laminated fabric by W.L.Gore & Associates Inc. The PTFE membranes are inherently hydrophobic and contain very small pores that resist the entry of liquid water even at extensive pressures or when rubbed or flexed, but easily allows flow gases or water vapour[8]. Besides its being breathable, allowing vapour transmission through the films (see Figure 7) but not water droplets, it is also light weighted and softness in touch. Moreover, the material has a very low coefficient of friction and is used to give nearly friction free surfaces and it has a high ignition resistance[9]. Consequently, Gore-tex® is also used with the combination of Kevlar® and Nomex® on the outer layer of the ortho fabric in space suits.

Figure 6: Cross-section of Teflon® fibre [10]

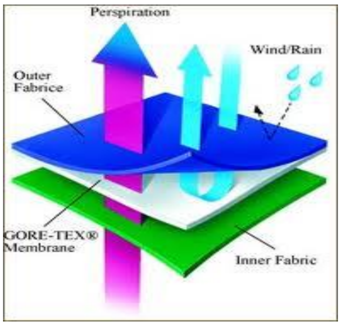

Figure 7: Gore-tex® layer system [11]

2.2 Nomex® and Kevlar®

Nomex® is the first meta-aromatic aramid fibre which was developed and introduced in 1963 by the Du Pont Company. Meta-aromatic aramid fibre has a high decomposition temperature and a high ignition temperature. It burns only with difficulty and little smoke generates. The force required breaking Nomex® fibres are at roughly 250 ^{o}C and it only loses its tenacity at 300-350 ^{o}C [12]. As it offers excellent flame resistance, Nomex® has a high level of thermal insulation, only starts to carbonise at around 380 ^{o}C and neither melts nor drips even at extreme temperatures, it has good textile properties, dimensional stability and resistance to degradation by a wide range of chemicals and industrial solvents[13]. Most varieties of Nomex® have an oval to dogbone fibre cross-section, as shown in Figure 8.

Kevlar® is a para-aromatic aramid fibre which was first manufactured in 1965 by the Du Pont Company and later was introduced to the consumers in 1973. Three types of Kevlar® aramid fibre are made; T-950 for use in tire reinforcement; T-29 for industrial ropes and woven fabrics; and T-49 which is a very high modulus fibre for the use of plastics reinforcement. To give an idea and on an equal-weight basis, Kevlar® aramid fibres are 2-3 times stronger than high-tenacity Nylon® and 5-8 times stronger than a steel wire[14]. More importantly and in contrast, para-aramid fibres have lower specific gravity than the steel. Their breaking elongation is roughly 4% and the modulus is around 4 times than that of Nylon® and 50 % higher than that of glass. If compared to other types of para-aromatic type aramid fibres, Kevlar T-49 has a slightly higher tenacity with more than twice the modulus.

As a result, meta-aramids are noted for their both heat and chemical resistance while para-aramids are noted for their high tenacity and high modulus, Kevlar® and Nomex® are widely used in EMU for micrometeoroid protection and for thermal protection purposes. The cross-section of Kevlar ® is given in Figure 9.

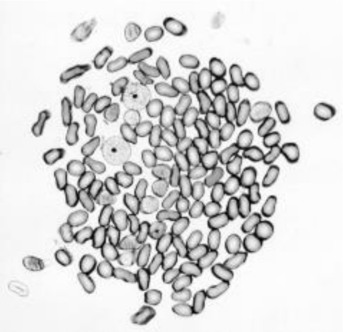

Figure 8: Nomex® [13]

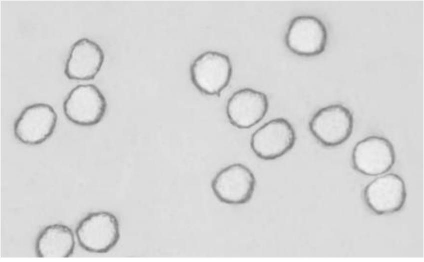

Figure 9: Kevlar® [15]

2.3 Dacron® and Mylar®

A polyester polymer was first formed by members of W. Carothers' research team at Du Pont Company. But later this development was set aside and the research was directed to polyamide, instead. Later in 1941, Dickson and Whinfield from Calico Printers' (England) commercialized the most well-known member of the polyester generic group of fibres which are known as polyethylene terephthalate (PET)[16]. Development of polyester was slowed by World War II, but the fibre had been well-studied by 1947 both ICI Fibers and Du Pont Company which both had the rights to manufacture. Dacron® was the first polyester fibre marketed in US and similarly Terylene® was the first polyester fibre commercialized in England[17]. Today, more than 95% of all polyester fibre produced from PET. Polyester fibre has a smooth surface and even in diameter with nearly circular cross-section and rod shape in lengthwise, as seen in Figure 10.

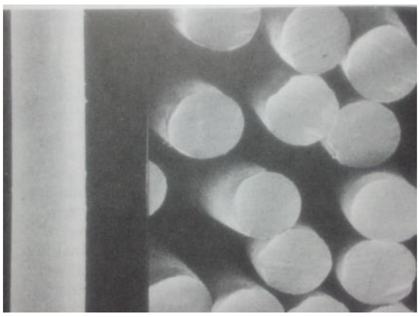

Figure 10: Longitudinal and cross-section of Polyester fibre [18]

Because of its versatility, polyester has the highest volume consumer usage of all man-made fibres and therefore finds application in many industrial textiles; Dacron® cloth is one of an EMU suit assembly material where also can be used in gloves and lower torso assembly of a space suits[6]. These fibres have high wet and dry tensile strengths as well as good chemical and microbial resistant properties; they also have been developed to enhance thermal insulation, water-vapour transport and wicking[19]. Polyester is a hydrophobic fibre and its moisture regain is very low (0.4%). This is because of the lack of polarity to attract water, the presence of benzene rings, and its fairly crystalline structure. Polyester fibre also has a medium specific gravity. Because of these adequate properties, Dacron® is used in super insulation layer of the EMU assembly.

Mylar® is a brand name for a special type of stretched PET film. It is generally known as BoPET (biaxially-oriented polyethylene terephthalate). There are two other well-known trade names for this material i.e. Melinex and Hostaphan. Mylar® has desirable properties for commercial applications such as electric insulator, transparent, high tensile strength, chemical stability, reflective, barriers for gas and odours [20]. BoPET film was developed in the 1950s initially by Du Pont Company, ICI and Hoechst. Later in 1964, NASA used it in one of its Echo Project[21] where a 40 m diameter balloon constructed from 9 µm thick Mylar® film which was sandwiched between two layers of thick aluminium foil and bonded. Since then, Mylar® has been used in different space missions and today this metallized BoPET film is being used in five layers reinforced with Dacron® scrim for the space suits to support resistance in radiation and to keep astronauts warm during their mission.

3. CONCLUSIONS

As it mentioned here that, the current space suit EMU (Extravehicular Mobility Unit) is the result of many years of research and progress in various industries such as materials, electronics, fibres, textiles and etc. While they remain a great tool for orbital operations, still, in the future, many advances are possible with the technological developments in all fields of industry to ease the tasks of astronauts in space.

Because of the technological developments in textiles and else, the space suits of the future may look dramatically different than the current ones. One can be suggested that space suits may operate at higher pressures than the current EMU which enables a reducing time currently required for pre-breathing prior to a spacewalk. Another can be considered to increase the manoeuvring capability of EMU by reducing its weight; although the suit has no weight on orbiting in space but it does retain its mass and this may affect the manoeuvring capability of the astronaut during his/her spacewalk and tasks out the spaceship. Additionally, for future long term and long range missions such as Mars transit, mission cost savings can be achieved by a reduction in the mass of liquid cooling ventilation garment. For this, new materials can be used for the heat removal capabilities i.e. carbon nanotubes which known to have a high thermal conductivity. Finally, the number of cooling tubes that are used in the liquid cooling ventilation garment may be reduced; with this achievement less water can be needed.

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FABRICATION OF ELECTROSPUN POLYACRYLONITRILE AND POLYURETHANE NANOFIBERS FOR SOUND ABSORPTION

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Keywords: Electrospinning, Nanofibers, Nonwoven, Transmission loss, Sound absorption

Abstract. *In recent years, due to numerous improvements in most of industries and the increase in the usage of enormous and powerful machines in every field, noise has become an unavoidable of mechanized life and has brought about serious hazards for human health. The main aim of this work is to examine the usability of polyurethane and polyacrylonitrile nanofibers for improving sound insulation properties of conventional polyester and wool nonwoven materials in a wide band of frequencies along with weight and thickness reduction. The effect of nanofiber layers number and its surface density on acoustic properties is investigated. Sound transmission loss and sound absorption analysis using impedance tube are carried out as the main factors affecting acoustic behavior of nanofiber samples. The results show that incorporation of nanofiber layers in nonwoven materials can improve both sound absorption and sound transmission loss simultaneously, especially in mid and lower frequencies, which are not easy to take by conventional materials.*

1 INTRODUCTION

The property of a material to oppose sound transfer through its thickness is called sound insulation. In practice, the efforts to reduce noise often involves identifying and analyzing the physical mechanisms involved in generation and transmission of sound and finally finding the possible means of noise reduction [1]. A variety of methods have been described for noise reduction, in which can be basically grouped as passive and active mediums. Active mediums differ from passive mediums in that it is necessary to apply external energy against incident sound waves in the noise reducing process. The absorbing materials and sound barriers are passive mediums. Sound absorbers lower noise by disseminating energy and turning it into heat. The amount of sound energy which is absorbed is described as the ratio of sound energy absorbed to the sound energy incident, and is termed the sound absorption coefficient (α). Sound barriers prevent sound from traveling from one place to another [2]. Nonwoven fabrics are extensively utilized in noise reduction where the sound absorption is important. Sound absorption and sound transmission are the main factors affecting acoustic properties and they depend on the interaction of sound wave with the fibers forming the nonwoven fabrics. While nonwoven fabrics are known as good sound absorbers at high frequency, they are less effective at low and middle frequencies because of their low density [3]. Various parameters can affect on acoustic behavior of fibrous materials: fiber denier [4,5], porosity [6], tortuosity

[7], fabric surface area [8], density [9], airflow resistance [10], thickness [11], fiber cross section [5,12]. In general, any acoustical treatment requires high performance in both absorption and transmission losses. High absorption can be achieved by using suitable absorbers while high transmission loss requires heavy barriers. An absorber needs to be porous and light, but a barrier needs to be impermeable and massive. How to best create a combination of these two contradictory properties in a multiple-layer is considered as a big challenge for all acoustic engineers [1].

Many new and light weight acoustical materials have been introduced in recent years. It has been claimed that active carbon fiber composite with a cotton base layer would be lighter in weight, higher in low frequency absorption and higher in transmission loss in both ranges of frequencies comparing to other fibrous composites. These simultaneous behaviors have been attributed to the very high specific surface area and high micro pore volume of the active carbon fibers [13,14]. In recent years innovative solutions have been derived from electrospun nanofibers. Electrospinning is an approach for providing fibers in nanometer scale, and it is based on applying an electric field between a needle and a collector for drawing a polymer droplet from tip of the needle toward the collector [15]. Special characteristics of these nanofibers such as high specific surface area, small fiber diameter and high porosity allow rapid interaction of materials with surrounding media [16]. The effect of nanofiber layers on sound transmission loss has not been discussed yet. However, there are a few studies on the effect of nanofiber layers on sound absorption properties [17].

The main aim in this work is to investigate the usability of polyurethane (PU) and polyacrylonitrile (PAN) nanofibers as improving sound insulation of conventional polyester and wool nonwoven materials in a wide band of frequencies. Composite samples consisting of nonwoven layers and nanofiber layers with different in number and its surface density is prepared and their effects on acoustic properties are studied.

2 EXPERIMENTAL

2.1 Materials

Polyacrylonitrile powder (PAN, MW=100000 g/mol) and polyurethane granule (commercial PU, MW=65000 g/mol) were supplied from Iran Polyacryl Co. and Bayer Co., respectively. N, N-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Merck as solvents. In order to prepare polymer solutions for electrospinning, PU was dissolved in DMF and THF in proportion of 40:60; and PAN was dissolved in DMF at the ambient temperature. Nonwovens were produced by carding machine, followed by needle punching. The properties of the used nonwoven layer were shown in Table 1.

Properties	Nonwoven	
	PET	Wool
Fiber length(cm)	6-8	12-10
Fiber fineness(µm)	19	33
Average Weight (g/m^2)	100	96
Average Thickness(mm)	2.53	3.01
Average of porosity	97%	99%
Punch density (punch/cm^2)	228	228

Table 1: Properties of nonwoven layers.

2.2 Electrospinning Apparatus

As it is shown in Figure 1, horizontal electrospinning apparatus with a cylindrical collector (with take-up speed of 100 RPM) was used. A 22 G needle (inner diameter: 0.4 mm and length: 34 mm) was chosen. For creating an electric field between the needle and the collector, a high-voltage power supply which can generate DC voltage up to 40 kV was utilized that leads to polymer ejection of drop from tip of the needle toward the collector. The solution flow rates were controlled by a pump at a rate of 0.25 ml/h. The electrospinning process parameters were adjusted to: solution concentration of 10 and 9 w/v %, applied voltage of 12 and 16 kV for providing PAN and PU nanofiber, respectively. Tip to collector distance was fixed on 12 cm.

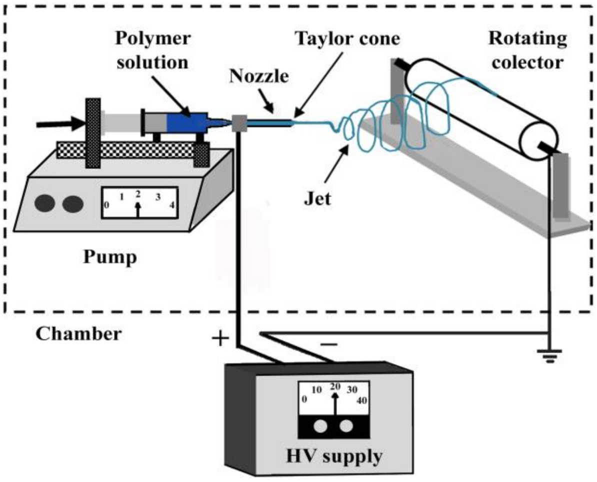

Figure 1: Schematic of electrospinning apparatus.

2.3 Sample Preparation

Nanofiber webs with determined surface density (i.e. 1, 3, 5 g/m^2) were placed within nonwoven layers. The properties of all nonwoven samples were the same as listed in Table 1. After layering 1, 2 or 3 nanowebs within four nonwoven layers, a sandwich structure was produced. The schematic of prepared sample is shown in Figure 2. 1, 3 and 5 g/m^2 nanofiber webs was obtained by 3, 8, 12 hr and 3, 9, 15 hr for PAN and PU, respectively, by electrospinning apparatus. The structures of all samples together with their code are defined in Table 2.

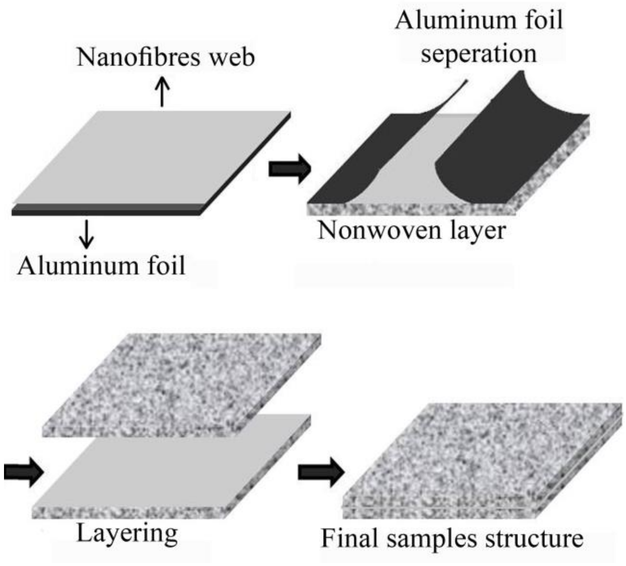

Figure 2: Schematic of prepared samples.

Sample code	nanofiber layers No.	Nanofiber surface density	Nanofiber layer	Nonwoven
P-PAN1	3	1	PAN	Polyester
P-PAN3	3	3	PAN	Polyester
P-PAN5	3	5	PAN	Polyester
P-PU1	3	1	PU	Polyester
P-PU3	3	3	PU	Polyester
P-PU5	3	5	PU	Polyester
W-PAN1	3	1	PAN	Wool
W-PAN3	3	3	PAN	Wool
W-PAN5	3	5	PAN	Wool
W-PU1	3	1	PU	Wool
W-PU3	3	3	PU	Wool
W-PU5	3	5	PU	Wool
P-PANI	1	5	PAN	Polyester
P-PANII	2	5	PAN	Polyester
P-PANIII	3	5	PAN	Polyester

Table 2: structures of all samples together with their code.

2.4 Characterization and Measurement

Scanning electron microscopy (SEM; model AIS 2100, Seron Technology, Korea) at an accelerating voltage of 25 kV was used to investigate the surface morphology of nanofiber webs. Samples were gold-coated before SEM. The nanofiber diameter was determined by 100 measurements using Image J software.

The transfer function method (ASTM E 1050) covers the use of an impedance tube (model: 4206, B&K, Denmark), with two microphone locations and a digital frequency analysis system (model: 550 & BZ5051, B&K, Denmark) for measuring the normal incidence sound absorption coefficients. Transmission Loss factor (TL) is the loss as sound passes through a barrier. In particular, TL can be defined as the difference between the sound pressure level (SPL) on the source side of the barrier and the SPL on the receiver side. ASTM E 2611-09 (Standard test method for measurement of normal incidence sound transmission of acoustical materials based on the transfer matrix method) was used for measuring of TL factor. An additional tube extension impedance tube with four microphone and different setup was utilized. By measuring the sound pressure at the four microphones (two microphones located in front of samples and the other placed behind it) location, the TL value of the material can be determined. To measure over the complete frequency range from 50 Hz to 6.4 kHz, the components can be assembled into two different setups: a 100 mm diameter tube (for frequencies from 50 Hz to 1.6 kHz) and a 29 mm diameter tube (for frequencies from 500 Hz to 6.4 kHz). A loudspeaker (sound source) is mounted at the one end of the impedance tube, and the test sample is installed at the middle of the tube. In the impedance tube method, sound waves are confined within the tube and thus the size of the sample required for test needs to be only large enough to fill the cross-section of the tube properly.

Air permeability of samples was measured according to BS 5636 (standard test method for determination of permeability of fabrics to air) in pressure of 100 Pa after and before placing of nanofiber layers within nonwoven layers.

3 RESULTS AND DISCUTIONS

3.1 Nanofiber Diameter

Figure 3 (a, b) shows the surface morphology of nanofibers. The average diameter of PAN and PU nanofibers are 121 and 203 nm, respectively. As it is clear in Figure 3, narrower fiber diameter distribution was observed in case of PAN sample.

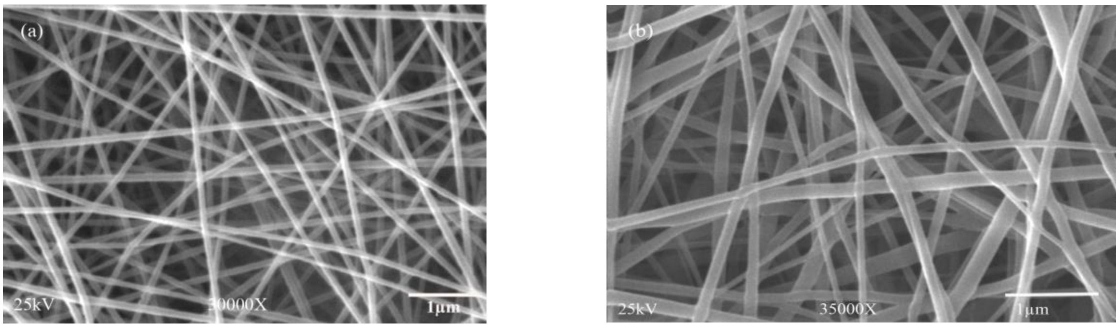

Figure 3: SEM micrograph of surface morphology of (a): PAN and (b): PU nanofibers

3.2 Effect of Surface Density

The ability of a material to resist the flow of sound energy through its structure is termed as sound insulation and this is largely determined by its mass. According to mass law in acoustic (equation (1)), heavy materials stop more noise passing through them than light materials. For any impermeable material there will be an increase in its noise stopping ability of approximately 6 dB for every doubling of mass per unit area (m) or frequency (f)[21].

$$TL = 20\log(fm) - 33 \tag{1}$$

However, increasing in mass of an insulator for improving nonwoven sound transmission loss is not acceptable in most industries. Figure 4 (a-d) show transmission losses of PAN and PU nanofiber layers placed within polyester and wool nonwovens layers. As it is shown, TL was increased by the presence of PAN or PU nanofiber layers. Moreover, increasing in surface density of both nanofiber layers resulted in higher sound transmission loss in both wool and polyester nonwoven substrates. Higher sound transmission loss was observed in case of samples produced from PAN nanofiber layers.

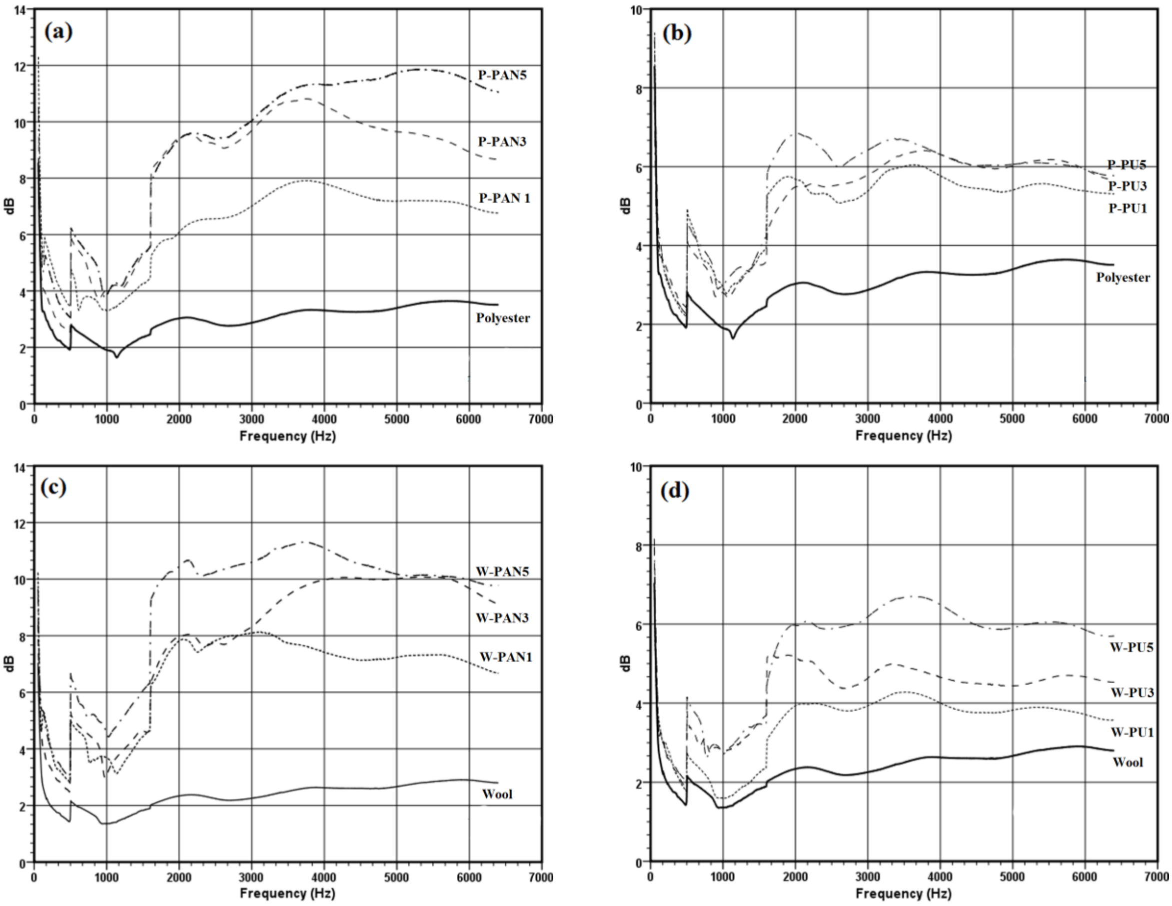

Figure 4: Changes of sound transmission loss against mass per unit area; samples containing (a): PAN nanofiber layers within polyester layers, (b): PU nanofiber layers within polyester layers, (c): PAN nanofiber layers within Wool layers, (d): PU nanofiber layers within wool layers

3.3 Effect of Nanofiber Layers

Figure 5 shows the enhancement of sound transmission loss by increasing the number of PAN nanofibers layers within polyester nonwoven layers from one to three. While sound waves pass through the first to the last (third) layer, their intensity is suppressed step by step. By comparing of the results presented in Figure 5 and Figure 4(a), it can be concluded that increasing in the number of nanofiber layers is more effective than increasing in the mass per unit are of the layers. For example, the sample of P-PAN3 demonstrates better sound transmission loss than the sample of P-PANII.

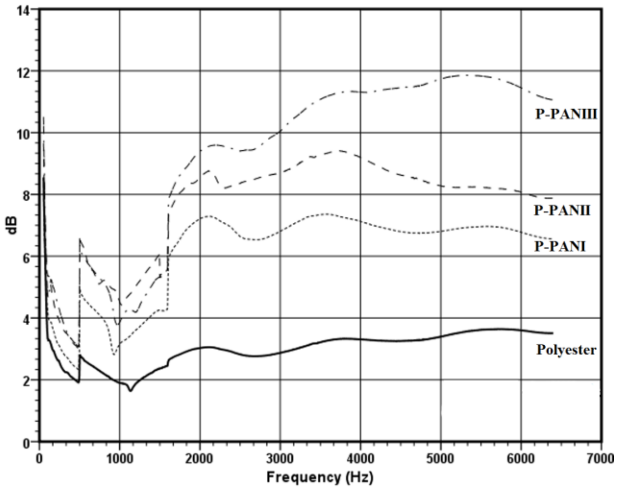

Figure 5 Changes of sound transmission loss against number of PAN nanofiber layers within polyester layers

3.4 Air Permeability

Air permeability is a very important parameter for thermal and acoustical insulation of nonwoven fabrics. Lower air permeability causes lower sound transmission, consequently more sound insulation [18]. The air permeability of samples is shown in Table 3. According to the table, samples containing PAN nanofiber layers presented less air permeability. This behavior can be attributed to the finer diameter of PAN nanofiber comparing to PU nanofiber diameter.

Sample	Before layering ($cm^3/s/cm^2$)	After layering ($cm^3/s/cm^2$)
W	334	—
P	297	—
P-PAN1	289	29
P-PAN3	292	20
P-PAN5	295	13
P-PU1	300	44
P-PU3	286	38
P-PU5	297	31
W-PAN1	338	27
W-PAN3	331	21
W-PAN5	340	15
W-PU1	339	50
W-PU3	333	41
W-PU5	337	34
P-PANI	302	31
P-PANII	291	19
P-PANIII	295	13

Table 3: Air permeability of samples

As can be seen, by increasing the number of nanofiber layers, lower air permeability was achieved confirming the relation of this important parameter with sound insulation ability [19]. Generally, some sound energy is radiated by the vibration of nanofiber layer [21] m. Because of high elasticity of PU nanofibers [22], more sound energy can be created by PU nanofiber vibration; therefore, less sound transmission loss was achieved by PU layers comparing to PAN layers. Moreover, samples with polyester nonwoven substrates presented higher sound transmission loss because of their lower porosity (97%) in comparison with wool substrate (99%).

The TL test shows improvement in sound insulation ability of samples containing lightweight nanofiber layers. Although sound reflection can restrict sound wave to pass, sound intensity in front of a hard surface is enhanced because the reflected wave adds to the incident wave[21]. Impedance tube measurements show that adding of nanofiber layers within nonwoven layers lead to considerable increase in the sound absorption coefficient, in which polyester nonwoven layers sound absorption coefficient of 0.40 increased to 0.67 and 0.71 by presence of PAN and PU nanofiber layer, respectively, at the frequency of 2000 Hz. At present time, intensive studies about sound absorption by nanofiber layers under progress by the authors[23], and the detailed results will be published at separated paper.

According to the very interesting results it seems that these innovative composite materials can introduce a new branch of acoustic materials that can improve both sound absorption and sound transmission loss, simultaneously, especially in low and mid frequencies which are difficult to take by conventional materials. Meanwhile, the weight and the thickness can be reduced by the presence of nanofiber layers that show economic benefits of using this kind of materials. Moreover, because of the easier electrospinning, affordably and easier solubility of PAN comparing with PU polymer, PAN nanofiber is preference.

4 CONCLUSION

The effects of applying polyurethane and polyacrylonitrile nanofibers within polyester and wool nonwoven layers on sound proofing behavior have been studied. The results show enhancement in sound transmission loss by increasing the number and the weight per unit area of both nanofiber layers. Higher sound transmission loss was observed in case of samples containing PAN nanofiber layers, which has been attributed to higher air permeability and elasticity of PU comparing to PAN nanofiber layer. Samples with polyester nonwoven layers presented higher sound transmission loss due to their lower porosity (97%) comparing to wool nonwoven layers (99%). Moreover, Sound absorption coefficient measurements show that adding of nanofiber layers within nonwoven layers lead to increase in the sound absorption. We have shown in this study, the acoustic material can enhance both sound transmission loss and sound absorption, simultaneously, especially in low and mid frequencies, which are difficult to take by conventional materials. Furthermore, weight and thickness were reduced by means of nanofiber layers.

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THE ROLE OF NANOFIBERS DIAMETER IN THE ENHANCED THERMAL CONDUCTIVITY OF ELECTROSPUN NANOFIBERS

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Keywords: Electrospinning, Nanofiber, Thermal Conductivity, Surface Density, Porosity

Abstract. *In this paper, the effects of variation in average nanofibers diameter and nanofibers web surface density on thermal conductivity of polyacrylonitrile (PAN) nanofibers web was examined. The results reveal using thinner nanofibers resulting in lower limit of thermal conductivity, better thermal insulation performance and higher amount of Roseland mean extinction coefficient that means lower conductivity. It can be related to higher specific surface of thinner nanofibers that means more surface area for radiative scatter and absorption lead to lower conductivity. With increasing in surface density of nanofibers web, the thermal conductivity reduced and water vapor transmission rate and thermal insulation ability improved. Higher porosity percentage and smaller pores size in the web with higher surface density could be resulting in lower thermal conductivity.*

1 INTRODUCTION

Energy keeping is one of the vital and important problems in nowadays human life. One of the key solutions to eliminate this problem is thermal insulation. Thermal insulation is used in various applications for abate heat transfer between a medium and its environment. Heat transfer involves the transport of energy from one place to another by energy carriers. In a gas or liquid phase energy can be transported by motion of molecules but in solids by phonons, electrons, or photons[1]. Fibrous insulators because of their high tortusity and porosity have most efficiency among the various materials for thermal insulation[2]. Heat flow passing through a fibrous material may be exhibited by three mechanisms: convection, conduction in air or solid part and radiation[3]. Some parameters such as fibers diameter, density, thickness and pores size of fibrous insulators can be affected total heat transferred by every mechanism. Thermal conductivity through fibrous structures has been studied widely in order to optimize product design and development[4]. Increasing in thermal insulation efficiency was achieved by these extensive studies but there are some weaknesses such as high thickness and weight that should be eliminated or reduced. In recent years, there has been a growing interest in the nanomaterials due to their uniquely promising properties and applications. Electrospun nanofibers by showing unique characteristics such as extremely low diameter and high specific surface area have applications in filtration, tissue engineering, waterproof breathable fabrics, microwave absorption and thermal insulation[5,6].

Electrospinning offers a simple, flexible, and low-cost technique for the creation of superfine fibers and enabling to produce membrane-like structure with high porosity but very small pores size[7,8]. There are few published reports on the thermal properties of the nanofibers. Carbon nanofiber mats with diameter of 200-1000 nm were fabricated via electrospinning method and the results of thermal properties measurements showed carbon nanofiber mats posses great potentials in applications for thermal management materials[9]. Reports on an experimental investigation of the thermal radiative properties of electrospun superfine fibrous polyvinylealchol (PVA) films containing or without TiO_2 nanoparticles showed that electrospun fibrous PVA and PVA/TiO_2 films had significantly greater Rosseland extinction coefficients and lower thermal radiative conductivities than the conventional polymer foams[3]. The anisotropic thermal conductivity of vapor grown carbon nanofiber based paper-like mats was measured. The in-plane thermal conductivity of the mats varied from 12 W/m.K to 157 W/m.K for volume fractions of 0.067 and 0.462, respectively, while the corresponding through-plane thermal conductivities were measured to be 0.428 W/m.K and 0.711 W/m.K [10]. In another research is shown thermal conductivity of PAN-based carbon nanofiber decreased by decreasing fiber diameter [11].

As far as we know there have been a few experimental studies on the effects of nanofibers web morphology on thermal properties. In the present study is focused on effects of variation in average nanofibers diameter and surface density of web on thermal conductivity and thermal insulation performance. For this aim, PAN nanofibers webs in three various surface densities (1, 3 and 5 gr/m^2) and nanofibers diameter (416, 261 and 108nm) are prepared and placed between PE nonwoven layers to measurement thermal conductivity and insulation efficiency.

2 EXPERIMENTAL

PAN powder ($M_w = 10^5$ g/mol , $M_n = 0.7\times10^5$ g/mol), consisting of 93.7 wt% acrylonitrile (AN) and 6.3 wt% methylacrylate (MA) was supplied with Polyacryl Co.(Isfahan, Iran) and N,N dimethylformamide (DMF) were obtained from Merck, respectively, as polymer and solvent. The PE nonwoven layers with various weight per unit area, thickness of 2.53 mm and fibers diameter of 19 µm were produced by carding machine, followed by needle punching.

Horizontal Electrospinning apparatus with a cylindrical collector was used. A 22G needle (inner diameter: 0.4 mm and length: 34 mm) was chosen. For creating an electrical field between the needle and the collector, a high-voltage power supply which can generate DC voltage up to 40 kV was utilized that leads to the ejection of polymer drop from tip of the needle toward the collector. The nanofibers web was provided by electrospinning process on an aluminum foil and then was separated from the foil and placed between nonwoven layers that shown schematically in Figure 1. After placing the nanofibers web within the nonwoven layers, a sandwich structure was produced. Specimen’s construction parameters were mentioned in Table 1.

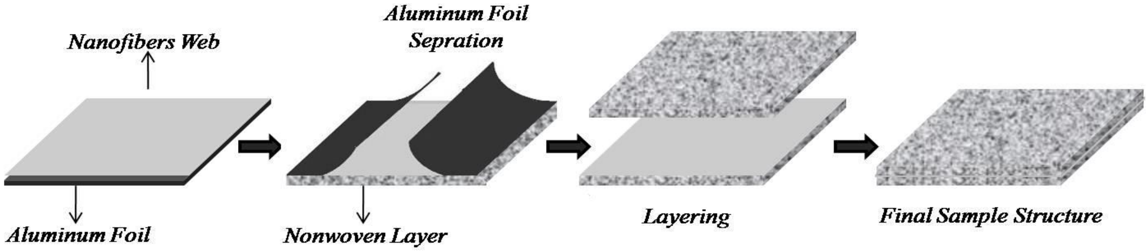


Figure 1: Schematic Diagram of Sample Preparing.

No.	Surface Density (g/m^2)	Nanofibers Diameter (nm)	Number of Nonwoven Layer
N00	-	-	2
N01	3	416	2
N02	3	261	2
N03	3	108	2
N04	1	261	2
N05	5	261	2

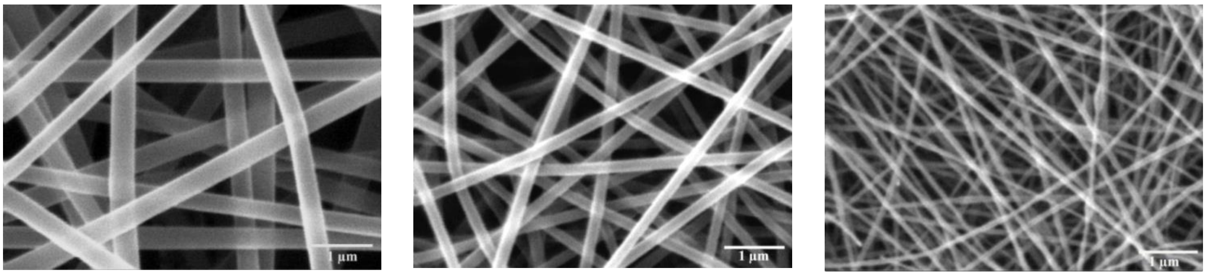
Table 1: Specimens construction parameters.

The morphology of the electrospun nanofibers was examined by scanning electron microscope (SEM, AIS-2100, Seron. Co., Korea) at an accelerating voltage of 25 kV under magnification of 30000X and the average nanofibers diameter was measured with the SEM images using Image J software (National Institute of Health, USA) from 200 nanofibers/sample. Nicolet Nexus 670 FTIR spectrometer was applied to determine the Rosseland mean extinction coefficient. The WVTR was measured under an environment with a temperature of 22 ^oC and a relative humidity of 65% with the water vapor transmission dish method according to British Standard BS7209. To investigate the thermal conductivity of samples, heat flow meter apparatus is used according to ASTM C-518. Typical test conditions are 50°C on the upper plate, and 10°C on the lower plate. Thermal insulation test was performed using two boxes with dimension of 20 cm × 20 cm × 20 cm. The inside of one box was covered with neat nonwoven and another with nonwoven having nanofibers web. The temperature decrease in each box was measured using thermometer every 5 min and finally when room temperature became equal to that of box covered inside with neat nonwoven[8].

3 RESULTS AND DISCUTIONS

3.1 Nanofibers Morphology

Figure 2 shows the SEM images of the electrospun PAN nanofibers in three average diameters (416, 261 and 108 nm). Different average diameters of nanofibers can be obtained with changing in three important electrospinning parameters: polymer concentration (w/v%), applied voltage (kV) and the nozzle-collector distance (cm)[5]. The nanofibers with diameter of 108 nm were prepared in polymer concentration of 8 w/v%, applied voltage of 14 kV and 15 cm in nozzle-collector distance. With increasing in the polymer concentration, nanofibers with higher diameter were achieved[12].



(a) (b) (c)

Figure 1: SEM Micrographs of PAN Nanofibers with Mean Diameter of a) 416 nm b) 261 nm c) 108 nm.

3.2 Effect of Nanofibers Diameter

Thermal conductivity as a function of density for neat nonwoven and nonwovens containing nanofibers web is shown in Figure 3. As shown in Figure 3, thermal conductivity of the PE nonwoven decreased with increase in density and then enhanced again. This can be explained by the fact that as the density increases, making the fibrous structure more packed. This causes the mean free path (distance traveled by a photon before it collides to another fiber surface[13]) for a photon movement decreased thus causing a decrease in the heat transfer due to radiative conduction. When the density comes to a critical point, the increase in conduction through solid phase (fibers) and decrease in radiation conductivity resulting in a raise in the total thermal conductivity[14,15].

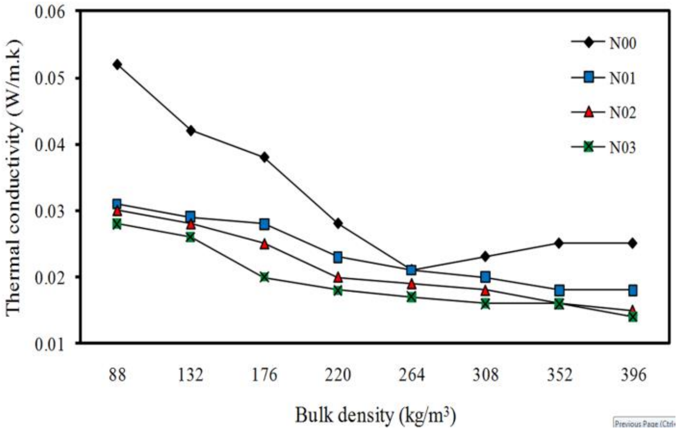
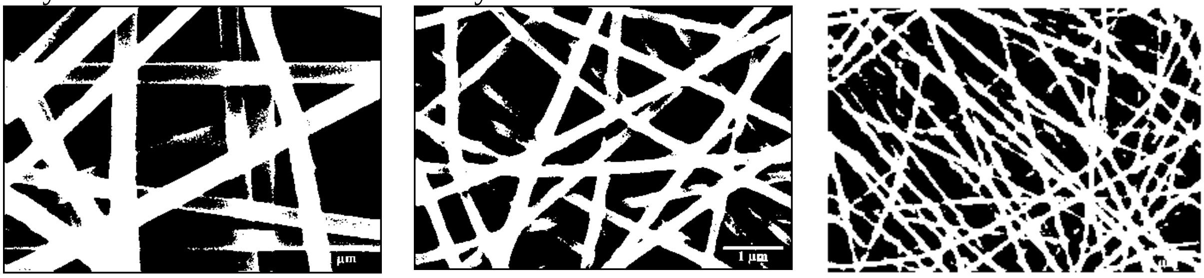


Figure 3: The Thermal Conductivity Results as a Function of Bulk Density for N00, N01, N02 and N03.

In fact, in fibrous structures the small size of the pores and the tortuous nature of air channels present prevent any heat transfer by convection[3]. Moreover, in fibrous insulation materials because of low fiber volume fraction, heat conduction through the solid phase (the fibers) is not significant and conduction through air is usually considered to be the conductivity of still air that is poor (0.17 BTU.in/ hr. ft^2.°F) at room temperature. Thus radiative conductivity is prevalent mechanism of conductivity since high porosity percentage of fibrous structures. By adding of nanofibers web, thermal conductivity was enhanced noticeable that is believed to be because of their extremely fine fibers and very high porosity of web. The superfine fibers in nanofibers web have better radiation absorption and extinction since their higher surface-area-to-volume ratio leading to decrease in the thermal conductivity. Moreover, smaller pores size between nanofibers causing a decrease in the mean free path for photon movements resulting in lower radiative energy transfer. This improvement becomes more significant when bulk density increased. In high densities, increase in the thermal conductivity of the sample contain nanofibers web was diminished that may be attributed to nanofibers presence effects and their natural compact structure that could compensate increased nonwoven thermal conductivity. According to thermal conductivity curves which is apparent in Figure 3, decreasing in the average nanofibers diameter lead to lower limit of conductivity. Higher specific surface of thinner nanofibers[16] means more surface area for radiative scatter and absoption that resulting in lower thermal conductivity. Further, higher porosity of the web with nanofibers diameter of 108 nm could be other reason of their lowest thermal conductivity. Another plausible explanation for reduction in conductivity can be smaller pores size in the web containing thinner nanofibers leading to lower radiative conductivity. For better understanding how reduction in nanofibers diameter affected porosity of the web, Image J analysis on SEM images are shown in Fig. 4. By considering to percentage of black areas which is apparent in Figure 4 (a, b and c) it is reasonable to assume that reducing in average nanofibers diameter have indispensable effect on create more tiny pores (black areas) in the nanofibers web. With regard to this context, it could be understood that using thinner nanofibers have noticeable performance to achieve very low limit of thermal conductivity.



(a) (b) (c)

Figure 4: Image J Analysis on SEM Micrographs of Nanofibers with Mean Diameter of a) 416 nm b) 261 nm c) 108 nm

3.3 Effect of Nanofibers Surface Density

For evaluating the effect of changing in nanofibers web surface density, three nanofibers webs in 1, 3 and 5 gr/m^2 surface density are prepared using changes in electrospinning process time. As illustrated in Figure 5, the thermal conductivity declined with rising surface density of the nanofibers web.

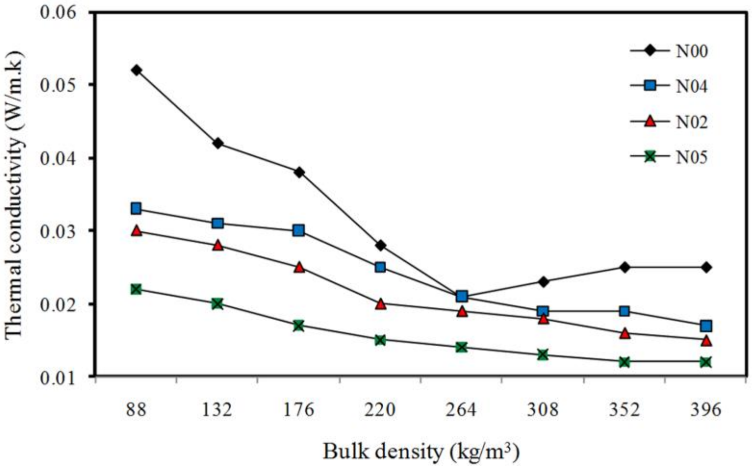


Figure 5: The Thermal Conductivity Results as a Function of Bulk Density for N00, N04, N02 and N05

Increase in electrospining time lead to more volume fraction of nanofibers in the web and so higher surface density. Accordingly, more volume fraction of nanofibers with their very high specific surface means there is excessive surface area for radiative absorption that create fewer limit of radiative heat transfer. Another reason for demonstrate this result can be related to the nanofibers web porosity. As confirmed by theoretical and experimental studies in the literature, mean pores size is one of the most important parameters influencing radiation heat transfer in fibrous structures[3,11]. According to Table 2, it can be found that increasing in the nanofibers surface density creating lower mean pores size.

Surface Density (g/m^2)	Nanofibers Diameter (nm)	Pores Size of Nanofibers Web (Average ± S.D.)
1	261	476 ± 48
3	261	321± 52
5	261	179 ± 33

Table 2: The mean pores size of nanofibers web in various surface density.

It is evident as mean size of the web pores become smaller, the radiation mechanism of thermal conductivity reduced because less photon can pass through the open spaces between the nanofibers. In other word there is a higher eventuality of a photon getting intercepted by the nanofibers through these smaller pores. This event is exhibited schematically in Figure 6. Hence, with considering to test results, it could be said that surface density of nanofibers web have a noticeable direct effect on the achieved thermal conductivity.

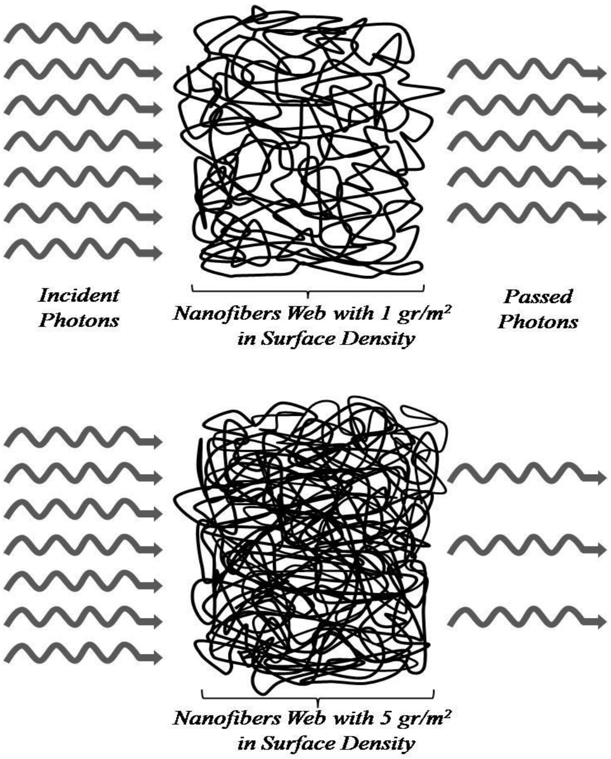
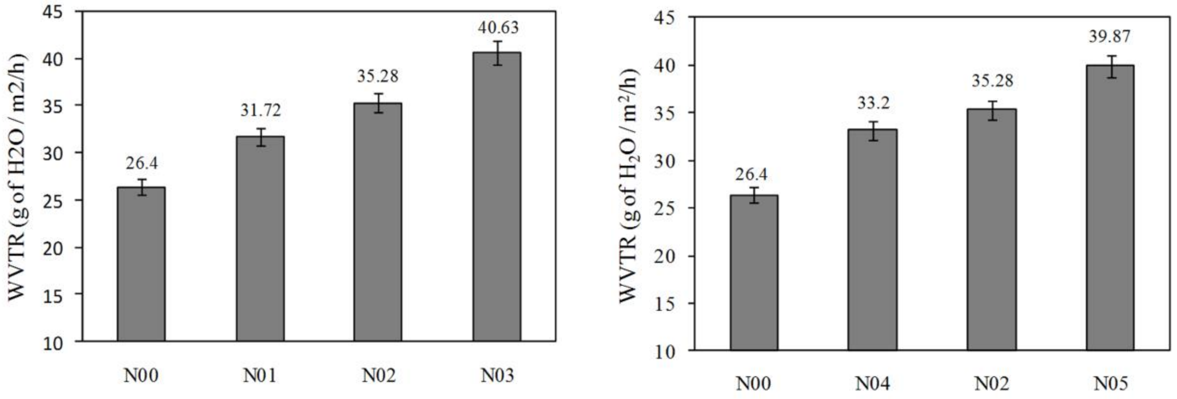


Figure 6: Schematic of Intercepting of Photons by the Nanofibers Web.

3.4 Examination of Thermal Insulation Ability

Figure 7 shows the WVTR results of the neat nonwoven and the nonwoven with nanofibers web in various surface densities and average nanofibers diameter. In presence of nanofibers web, higher WVTR observed that could be referred to huge specific surface area of nanofibers. This excessive surface area may cause water molecules slip at the nanofibers surfaces and water vapor transfer improvement. Further, very high percentage of porosity in the nanofibers web structure could be another reason of more water transfer ability. As shown in Figure 7 (a), the water transfer rate improved approximately 28.08% with declining in the average nanofibers diameter of 416 nm to 108 nm. This behavior was expected since as commonly known from the previous studies, there are a reverse relation between specific surface area and diameter of nanofibers[16]. As can be seen in Figure 7 (b) increasing in surface density of nanofibers web resulting in higher percentage of water vapor transfer. It can be related to increase in volume fraction of nanofibers with their huge surface area. The WVTR enhancement could denote better thermal insulating performance since with considering to high thermal conductivity of water it can be anticipated that the accumulation of water vapor leading to weaker thermal insulation efficiency.

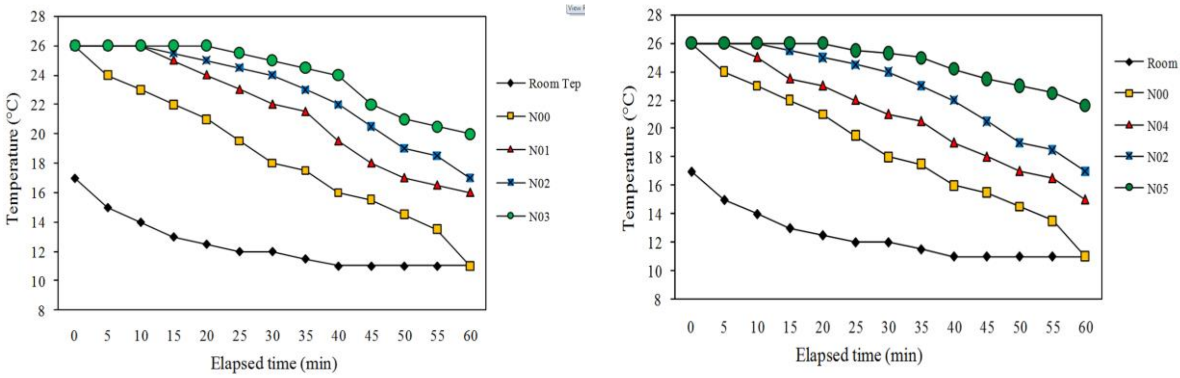
In order to explored integrity of the WVTR test results, thermal insulation as a function of time has been evaluated using two boxes in a cold environment that results are shown in Figure 8.



(a) (b)

Figure 7: The WVTR Results for (a) N00, N01, N02 N03 and (b) N00, N04, N02 and N05.

Sluggish temperature reduce rate was observed in the box covered inside with nonwoven containing nanofibers web. In presence of nanofibers web inside the box is kept warmer comparing to using neat nonwoven. As confirmed by Figure 8 (a) inside temperature of the box covered with nonwoven involving thinnest nanofibers (108 nm) got equal to 20°C after 60 min, that was higher than 17°C and 16°C for nanofibers diameter of 261 nm and 416 nm respectively. Figure 8 (b) demonstrates with applying nanofibers web with 5 g/m^2 of surface density, inside temperature of the box kept warmer longer period of time comparison with using nanofibers web with 1 and 3 g/m^2 of surface density. These results confirm the WVTR results and evidence employing nanofibers could enumerate as novel potential technique to improved thermal insulation efficiency in many applications such as cold-weather clothing, sleeping bags, building construction and aircraft.



(a) (b)

Figure 8: The Thermal Insulation Results for (a) N00, N01, N02 N03 and (b) N00, N04, N02 and N05.

4 CONCLUSION

Electrospun PAN nanofibers in three various diameters (416, 261 and 108nm) and surface density of webs (1, 3 and 5 gr/m^2) were produced and placed between PE nonwoven layers to thermal conductivity measurement. Results show the thermal conductivity reduced using of thinner nanofibers and also webs with higher surface density. It was observed, the Rosseland mean extinction coefficient with applying nanofibers in average diameter of 108nm to be higher than using nanofibers with 261nm and 416nm in average diameter. Moreover, the nanofibers webs with more surface density have shown higher amount of the Rosseland mean extinction coefficient. Thus, it can be concluded, applying thinner nanofibers and nanofibers webs with more surface density can decrease radiative heat transfer. The WVTRs improved approximately 28.08% with declining in average nanofibers diameter of 416nm to 108nm.

Further, increase in surface density of nanofibers web resulting in higher percentage of water vapor transfer. As a conclusive result it could be said nanofibers are very susceptible materials to improve thermal properties without any penalties in thickness and weight. In addition, using nanofibers in lower average diameters and surface density of webs could be a promising way to achieve noticeable develop in thermal insulation performance. Nonetheless, this research is not adequate and more studies need to investigate effects of other nanofibers parameters on thermal properties.

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MORPHOLOGICAL AND MECHANICAL CHARACTERIZATION OF POLYURETHANE FOAMS CONTAINING MULTIWALLED CARBON NANOTUBES AND NANOCLAY

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Keywords: Polyurethane foam, Carbon nanotubes, Nanoclay, Morphology, Mechanical properties

Abstract. *Polyurethane (PU) nanocomposite foams were prepared by In-Situ polymerization. The effects of nanoparticles assimilation on the morphological and structural progresses and the relation between this increases and mechanical properties of the PU foam were established. The effects of three different contents of nanoclay and Multi Wall Carbon Nanotubes (MWNTs) loading on foam morphology, structure, kinetic of foaming reactions and mechanical properties were separately examined. By adding of MWNTs and nanoclay in foams, the foam morphology improved, in which cell density increased and smaller cells were obtained. The mechanical properties of foam especially tensile strength have been increased in presence of nanoparticles. With enhancing nanoclay content, nanocomposite foam tensile strength has been improved but in case of MWNTs contrary effects was observed. Increase in nanoparticle amounts leading to lower cell density. In general, the incorporation of both nanoparticles in foam structure leads to lower foaming reactions rate that affected mechanical properties of foam.*

1 INTRODUCTION

Polyurethanes are a wide-ranging class of materials utilize in a broad variety of applications. Changing the effective parameters such as reactivity, chemical component, molecular weight of monomers can produce a great potential to fabricate various types of polyurethanes with different properties.[1] This variety caused PU to be used in different forms such as foams, elastomers, resins, covers.[2-4] The most consumption of polyurethanes is in the form of polyurethane foams, in which about 80 percent of polyurethanes are used in this nature.[4] Polyurethane foams are prepared by the polymerization of a polyol with an isocyanate, in which the reacting mixture is foamed using a blowing agent.[5] Depending on the composition, cell morphology, and physical properties, the PU foams can be classified as rigid or flexible foams. The PU foams can also be categorized as closed or open cell foams. Open cell foams are made up of broken cell walls and the structure consists of mainly ribs and struts. In closed cell foams, the foams cells are separated from each other and pores are surrounded by cell walls.[6] There are two main reactions in the production of flexible polyurethane foams: the “blow” reaction and the “gelation” reaction. The blow reaction involves the reaction of water with an isocyanate to yield an amine, carbon dioxide and heat. The evolved gas (carbon dioxide) and the reaction exotherm help the fluid to expand into a cellular structure. The gelation reaction occurs between the isocyanate groups and the hydroxyl functionalities of a polyol. Balancing of these two reactions rates provides the open-celled morphology in the foam that is highly affecting the physical properties.[7] Formation of a gas/polymer solution in the blow reaction is followed by a rapid drop in pressure and/or an increase in temperature during the gelation reaction. This gives rise to large number of cell nucleations because the gas tends to escape out of the polymer matrix. As the morphology development depends on the cell formation in a polymer therefore, cell nucleation is of great importance in the foaming process.[8]

The unique properties of PU foams such as low density, porous structure, lightweight and diversity of manufacturing, has provided a wide application like insulators, sound absorbers, building, transport, furniture, textile.[9-10] For increasing PU foams performance in the mentioned fields and eliminating or reducing its weaknesses like low mechanical strength and thermal stability, in recent years researchers have attempted to produce PU nanocomposite foams.[12] Morphological develops in the PU nanocomposite foams lead to various structures that create desired properties. It is reported that incorporation of a low percent of nanoparticles due to their extraordinary characteristics like extremely low size, high aspect ratio and high specific surface, can significantly improve foam properties.[13-15] Nanoclay hybrid syntactic foams are developed for applications requiring high energy absorption and damage tolerance. Presence of nanoclay particles plays a significant role in delaying crack initiation and growth, resulting in enhanced tensile strength and toughness.[16] In polyurethane foam made of high molecular weight polyols increasing in compressive strength and modulus have been observed when 5 wt.% modified nanoclay was employed.[17] Nanoclay infused foam sandwich structures exhibited higher peak loads compared with neat foam sandwich structures. Also damage analyses showed that nanoclay infused foams had smaller damage area than their neat counterparts.[18] Nanoparticles (SiC and TiO_2) loading cause significant changes in the cellular structures of the PU foam. Cell dimension almost doubles with the inclusion of 3% by weight of TiO_2 nanoparticles.[19] Moreover, in case of adding CNTs in PU foam, it is claimed that both ends of carbon nanotubes and its side walls act as heterogeneous nucleation sites so more nucleation efficiency can be achieved.[20] In the other work the effect of three different types of nanoparticles, namely spherical TiO_2, platelet nanoclay, and rod-shaped carbon nanofibers (CNFs) are considered. In all cases only 1 wt.% nanoparticles are used, and have found significant thermal and mechanical properties enhancement of the nanophased PU foam.[21] The compressive modulus and the storage modulus of the rigid PU foams increased and the mean cell size decreased with addition of nanoclay.[22]

Though, some researches in the literature about the effect of using nanoparticles in foam structure can be found, more studies for establishing deep understanding are still needed. In this work, effects of different contents of nanoclay and MWNTs on morphological, structural and also mechanical properties of flexible PU foam were investigated. For this aim, nanocomposite foams loaded with three different contents (low, moderate and high) of each nanoparticle were synthesis and then the foaming reactions rate, the morphological developments like cell density and cells size and their effects of these alterations on tensile and tear strength and other mechanical properties were determined.

2 EXPERIMENTAL

2.1 Materials

A polyether based polyol (ULTRACEL U-3000) having OH value: 30.0 ±2.0 mgKOH/g and viscosity of 1700 cP at 25°C, was obtained from Bayer group. Diphenylmethane 4, 4´-diisocyanate (MDI) was supplied from Merck Co.. Silicone surfactant (DABCO DC 2585) and the catalyst; that is a solution of 33% triethylenediamine and 67% dipropylene glycol (DABCO 33-LV), were obtained from Air products and chemicals Co.. Distilled water used as blowing agent. Modified nanoclay (Cloisite 30B), was purchased from Southern clay products Co.. Multi wall carbon nanotube (MWNT) having a diameter of 10-30 nm and 10 µm length was obtained from Research Institute of Iran Petroleum Industry (RIPI).

2.2 Electrospinning Apparatus

For synthesis of PU nanocomposite foams the provided polyol and isocyanate were dehydrated for 4 h at room temperature. The MWNTs and nanoclay also were dehydrated under vacuum oven at 60 °C and 100 °C for 4 h, respectively. In the first step, nanoclay was mixed with the polyol at 1600 rpm for 10 min by using a mechanical stirrer and followed by a dispersion process for 30 min with sonication. Then the catalyst, the surfactant and the distilled water at required amounts, were added to the mixture and mixed for 1 min, afterward, the isocyanate was added to this mixture. At last step, the whole components were mixed again with the mechanical stirrer until foaming occurred and then the mixture immediately was poured into an open mold. When the foam rose completely, it was put in the oven at 50 °C for 4 h to be cured. The same process for adding MWNTs was also performed. Different contents of nanoparticles and foam materials are listed in Table 1.

NO.	Polyol (g)	MDI (g)	Surfactant (g)	Catalyst (g)	Water (g)	MWNT (g)	Nanoclay (g)
NP0	70	27.2	0.5	0.9	1.4	_	_
NP1	70	27.2	0.5	0.9	1.4	0.05	_
NP2	70	27.2	0.5	0.9	1.4	0.1	_
NP3	70	27.2	0.5	0.9	1.4	0.15	_
NP4	70	27.2	0.5	0.9	1.4	_	0.5
NP5	70	27.2	0.5	0.9	1.4	_	1
NP6	70	27.2	0.5	0.9	1.4	_	1.5

Table 1: Different contents of nanoparticles and other materials in nanocomposite foams.

2.3 Characterization

The morphology of nanocomposite foams was evaluated by scanning electron microscopy (AIS-2100, Seron Technology, Korea) after coating the samples with gold. The foam mean cells size was measured by Image J software, and the cell density was calculated from SEM micrographs.[23] Ultrasonic (UP to 200 from Hielscher) was used for dispersion process of nanoparticles in polyol solution. The wide-angle X-ray diffraction analysis was performed by E Quniox 3000 (from Inel Co.). The tensile strength and the elongation of the samples were determined according to ASTM D3574 (Test E) by using a universal testing machine (Instron 5566). The sample size was 1 × 2.5 × 2.5 cm^3 and a cross-head speed was set on 8 mm/s. The tear strength was measured by the same Instrone machine according to ASTM D3574 (Test F). The resilience was examined by following ASTM D3574 (Test H). The density of foams was calculated from the mass and volume of samples.

3 RESULTS AND DISCUTIONS

3.1 Foam Morphology

Two types of nanocomposite foams (using nanoclay and MWNTs) under similar reaction process were prepared then their morphological and mechanical properties were compared. Table II shows the morphological properties of prepared nanocomposite foams comparing to neat foam. The morphology of nanocomposite foams was examined by SEM that is shown in Figure 1. The mean cells size was measured by Image J software from Figure 1. The cell density was calculated according to the following[24] and then normalized to the ratio between the nanocomposite foam density and the neat PU foam.

$$N_f = \left(\frac{nM^2}{A}\right)^{\frac{3}{2}} \tag{1}$$

Where N_f is the cell density, n is the number of cells, A is the area of SEM micrograph and M is the magnification factor. According to Table 2 and Figure 1, by incorporation of each type of nanoparticles, the cell density of foams was increased and the cells size was reduced comparing to neat foam sample. The morphology of the final foam is influenced considerably by cell nucleation and hence it plays important role in foaming process. The nucleation theory classifies the cell nucleation into two different types: homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation occurs in a pure gas/polymer when no impurities are added to the solution. In the presence of nucleating agents, heterogeneous nucleation takes place in the polymer matrix. It occurs at the interface between the polymer/gas solution and the nucleants.[8] In fact, nanoparticles in polymer solution act as nucleation agents and causing effective decrease in the required energy for creating bubbles and hence promoting the cell nucleation. Nanoparticles in comparison with conventional nucleating agents have a very extensive surface contact with polymer matrix and with gas molecules due to their extremely fine dimensions and very high surface density. This means that the optimum nanoparticle content can be achieved at a low nominal particle concentration. Due to high nucleation ability in foams involving nanoparticles that lead to more number of cells, the produced CO_2 from reaction between water and isocyanate must be spent to growth more number cells that culminated in smaller cells. On the other hand in cell growth process, the cells come to close to each other as they grow. The increased pressure inside the cells stretches the cell walls to their rupture and two adjacent cells becomes a single large cell. This transformation is referred to as cell coalescence. The cell coalescence has an adverse effect on the cells size that decreasing the flexibility of the polymer by cooling down the polymer is common way to prevent it.[8] The presence of nanoparticles in polymer matrix because of higher amount of hydrogen bonding among urethane chains can lead to lower polymer flexibility and also low cell coalescence. This lower flexibility of polymer means difficult and few evolving of the gas (carbon dioxide) leading to smaller cells size. Increasing in polymer mixture viscosity (when a good dispersion happened) could be presented as the other reason for limitation in cells expansion and low cells size was achieved.

To compare the effect of nanoparticles levels on foam morphology, three different contents for each nanoparticle were selected: 0.05, 0.1 and 0.15 wt% as low, moderate and high contents for MWNTs and 0.5, 1 and 1.5 wt% as low, moderate and high contents for nanoclay. The effect of nanoprticles contents on foam morphology is shown in Table II. As can be seen, in general, by nanoparticles (nanoclay and MWNTs) incorporation lower cell size and higher cell density comparing to neat foam were obtained. However by transferring from low to high contents of MWNTs, reduction in cell density (from 4.35 to 2.82) can be observed. In case of nanoclay same trend was observed, in which cell density decreased from 4.16 to 2.83 by increasing in nanoclay content from 0.5 to 1.5 wt%. In case of MWNTs these observations can be related to weak dispersion ability of nanoparticles in high consumption contents. The aggregations with more size taken place in case of MWNTs comparing to nanoclay. In case of MWNTs, in high contents (≥ 0.1 wt%), aggregations leading to decrease in the number of nucleation sites. This lower nucleation sites can decrease cell density and create cells with bigger size.

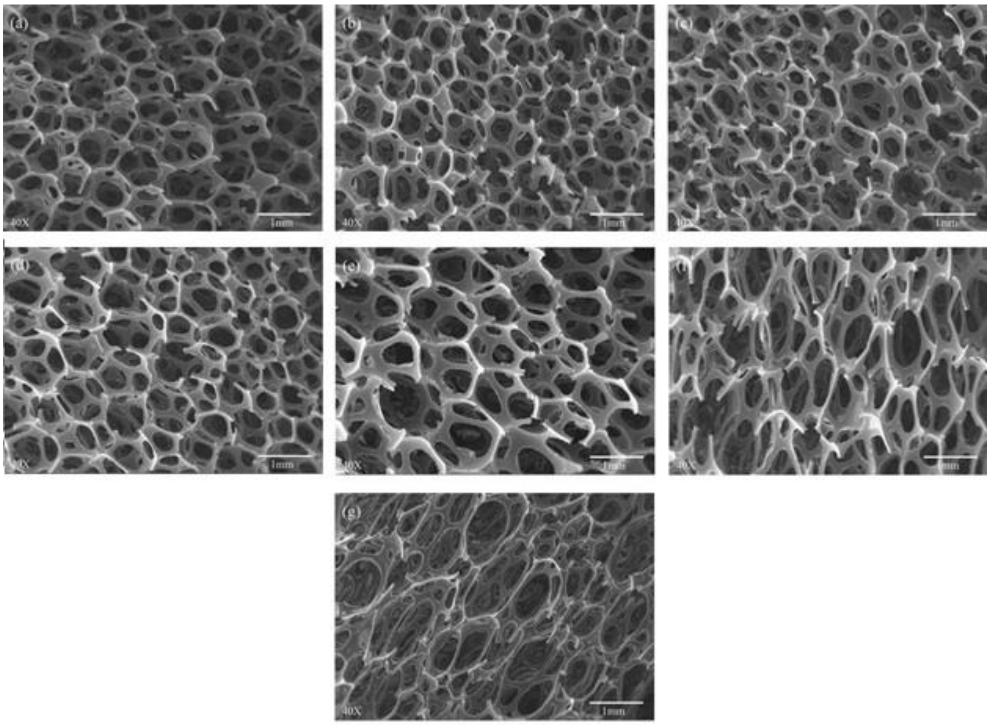

Figure 1: SEM micrographs of: (a) NP4, (b) NP5, (c) NP6, (d) NP1, (e) NP2, (f) NP3, (g) NP0.

NO.	Bulk density (kg/m^3)	Mean cell size (μm) (Average ± S.D.)	Cell density (cell/cm^3)×10^5 (Average ± S.D.)
NP0	45.20	397 ± 11	2.42 ± 0.23
NP1	51.84	232 ± 9	4.97 ± 0.10
NP2	60.43	245 ± 8	4.82 ± 0.11
NP3	74.22	264 ± 9	4.63 ± 0.12
NP4	55.85	221 ± 10	5.12 ± 0.13
NP5	76.23	197 ± 10	5.37 ± 0.15
NP6	92.27	162 ± 13	5.78 ± 0.14

Table 2: Morphological properties of neat and nanocomposite foams.

Figure 2 shows X-ray diffraction profiles of neat nanoclay (Cloisite 30B) and foams containing different contents of nanoclay. It indicates that the characteristic peak of the crystallinity in the nanoclay disappears in nanocomposites foams. It can be shown that good dispersion was taken placed in case of nanoclay comparing to MWNTs. Hence, other reason for reducing of cell density in high amounts of nanoclay should exist that may be limit nucleation ability of nanoclays. According to results in Table II, it can be conclude that MWNTs have more potential for improved foam morphology because lower amounts of MWNTs (0.05 wt%) can give better results (more cell density) in comparison with nanoclay of 0.5 wt%. This can be related to cylindrical shape of MWNTs in comparison with nanoclay.

In MWNTs structure, both ends of carbon nanotubes and its side walls can act as heterogeneous nucleation sites so more nucleation efficiency can be achieved.[20]

Table 3 shows the foaming reactions time. The cream time corresponds to the time distance between blending of materials and beginning of cells production that can be distinguished with color change in polymer mixture caused by saturation with gas bubbles. In foams containing MWNTs and nanoclay, the cream time became longer in comparison with neat foam. Also increase in nanoparticles quantity give rise to longer cream time. The gel time and rise time were increased at the same procedure. The comparison between nanoclay and MWNTs indicate that nanoclay has a stronger effect in foaming rate. According to SEM micrographs, decrease in foaming rate can lead to low elongation and stretching of foam cells in the rise direction. It results in fewer fractions of struts oriented in the rise direction and consequently lower anisotropy in nanoparticles/PU composite foams. This alteration is clearer in low and moderate contents of nanoparticles where good dispersion take place.

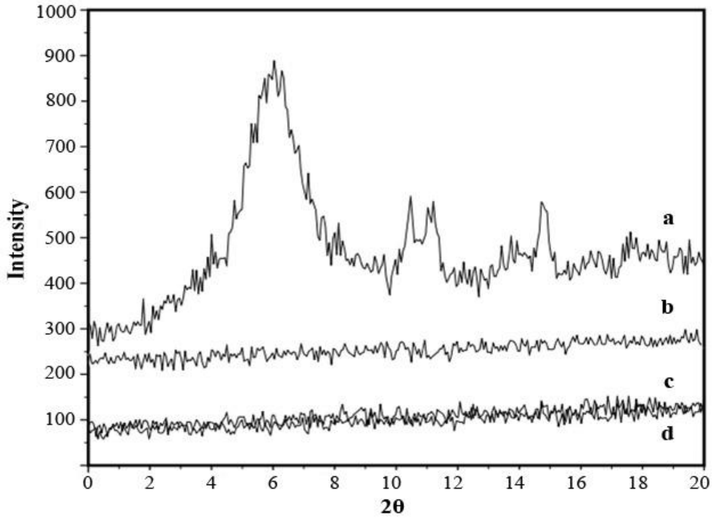

Figure 2: X-ray diffraction profile of: (a) pristine nanoclay, (b) NP4, (c) NP5, (d) NP6.

No.	Cream time (s) ± 2s	Gel time (s) ± 2s	Rise time (s) ± 2s
NP0	10	47	68
NP1	22	71	107
NP2	24	84	121
NP3	25	92	132
NP4	25	73	109
NP5	30	90	128
NP6	34	97	136

Table 3: Cream, gel and rise times of neat and nanocomposite foams.

3.2 mechanical Properties

Mechanical properties of nanocomposite foams are shown in Table 4. These results show by incorporation of nanoparticles, mechanical properties of foam were improved. According to introduction part, the second major reaction in the foaming process occurs between the isocyanate groups and the hydroxyl functionalities of the polyol. Because the polyol usually has a functionality between two and three, this process leads to a three dimensional covalent network. Higher amounts of hydrogen bonding among urethane chains in this network and fine morphology of foam have been described as two important parameters for obtain high strength in PU foam.[25] It was shown in previous sections that nanoparticles incorporation can improve foam morphology with increasing in cell density and producing smaller cells. These morphological modifications are the most important reason for improving in mechanical properties especially tensile strength. The increase of foam density is another important effect of nanoparticles. Foam density has a linear relationship with mechanical properties so that, higher density as shown in Table 2 means greater content of struts and polymeric cell walls in volume resulting in greater tensile strength. On the other hand, prevention of the H-bond formation in PU network due to reactions between MWNTs and nanoclay surface hydroxyl groups with –NCO groups of isocyanate, can decrease the foam strength. The tensile strength of PU nanocomposite foams depends on the competition between the positive effects of nanoparticles on polymer reinforcement (improvement in foam morphology), and the negative effects on H-bond formation and network structure. The positive effects are stronger when urethane content is low (less rigid foams) while the negative effects dominate when the urethane content is high (more rigid foams).[17] According to Table 4, the tear strength in the presence of nanoclay and MWNTs slightly increased. This could be attributed to nanoparticles ability in load transferring and also barrier effect to hinder of crack expansion. Elongation of foam was reduced by adding of nanoparticles because of chain mobility prevention. Figure 3 shows tensile stress-strain curves of neat and nanocomposite foams. It can be observed, the tensile strength increased by increasing of nanoclay content but in case of MWNTs, contrary effect was observed. This can be related to the aggregation of nanotubes and consequently lower nucleation sites leading to unsuitable morphology. This unsuitable morphology is the main reason for decrease in tensile strength in higher amounts of MWNTs (≥ 0.1 wt%). But in the case of using nanoclay contrary to unsuitable morphology (lower cell density) that achieved in high contents, higher tensile strength was obtained. This may be due to using lower contents of nanoclay in all samples comparing to critical contents (≥ 2 wt%) as reported in literatures. The benefit of using these low amounts of nanoclay is less prevention in the H-bond formation among urethane molecular chains that contributes to strength of polyurethane foams.[17] This result was in good agreement with others reports.[16, 25] Also they showed using high percents of nanoclay (>2 wt%) cause aggregations leading to low tensile strength.

No.	Tensile strength (MPa)	Tear strength (MPa)	Elongation (%)	Resiliense (%)	Volume change (%)
NP0	0.446 ± 0.081	0.446 ± 0.019	97.91 ± 15.19	26 ± 2	1.47
NP1	0.719 ± 0.032	0.461 ± 0.021	66.65 ± 12.14	30 ± 3	0.92
NP2	0.675 ±0.038	0.495 ± 0.011	35.00 ± 14.20	33 ± 1	0.89
NP3	0.592 ± 0.043	0.502 ± 0.015	54.16 ± 12.10	35 ± 2	0.85
NP4	0.533 ± 0.041	0.556 ± 0.017	71.86 ± 13.13	37 ± 2	0.71
NP5	0.899 ± 0.066	0.563 ± 0.021	48.33 ± 10.11	40 ± 2	0.68
NP6	1.024 ± 0.072	0.573 ± 0.018	39.16 ± 13.17	42 ± 1	0.64

Table 4: Mechanical properties of neat foam and prepared nanocomposite foams.

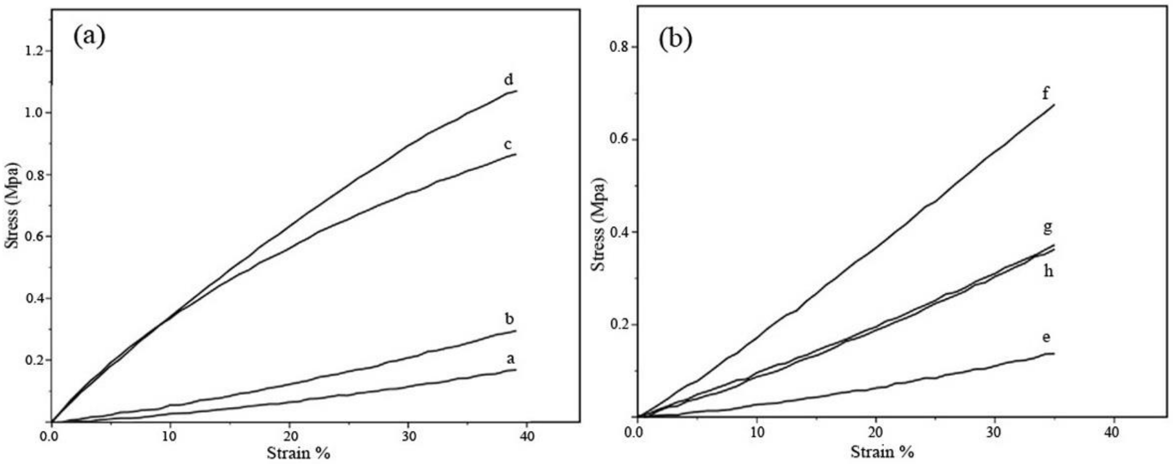

Figure 3: Tensile stress-strain curves of: (a) NP0, NP4, NP5, NP6, and (b) NP0, NP1, NP2, NP3.

4 CONCLUSION

The effects of nanoclay and MWNTs on morphology, structure, kinetic of foaming reactions and mechanical properties of flexible polyurethane foam were studied. The results indicate that in the general PU foams involving nanoparticles present greater cell density and smaller cells size in comparison with neat foam. Incorporation of nanoparticles in foam leads to improvements in mechanical properties especially in tensile strength. Reduction in elongation is another result of nanoparticles incorporation that was more obvious in case of nanoclay. With rising of nanoclay content, the tensile strength increased and in the optimized condition that relevant to foam having 1.5 wt% nanoclay, the improvement of about 129% was observed. The inverted effect by increasing of MWNTs contents to amounts beyond the critical limitations (≥ 0.05 wt%) was shown and the highest improvement (about 59%) in the presence of 0.05 wt% MWNTs was reached. The reaction between MWNTs and nanoclay surface groups with –NCO group of isocyanate caused longer foaming process that recognized with higher cream, gel and rise times. Increase in cream, gel and rise time reduced anisotropy in the nanoparticles/PU foam nanocomposites which can results in isotropic mechanical properties; similar properties in parallel and perpendicular to rise direction.

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ELECTROMAGNETIC RADIATION ABSORPTION BEHAVIOR OF ELECTROSPUN NANOFIBER LAYERS CONTAINING MULTI WALLED CARBON NANOTUBES

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Keywords: Carbon Nanotubes; Poly (vinyl alcohol); Nanofibers; Electrospinning; Microwave absorption

Abstract. *In this paper, poly (vinyl alcohol) (PVA) nanofibers with various multi walled carbon nanotubes (MWCNT) contents (up to 10 wt%) were produced by electrospinning process and their microwave absorption properties were evaluated by a vector network analyzer in the frequency range of X-band at room temperature. The uniform, steady dispersion and well oriented MWCNT within the PVA matrix were achieved through using sodium dodecyl sulfate (SDS) as dispersing agent. The morphological analysis of the nanofiber layers revealed that the deformation of the nanofibers raises with increasing MWCNT concentration. Very soft surface of the composite electrospun nanofibers even for the nanofibers with concentration of 10 wt% MWCNT have been successfully prepared because of the high stability dispersion of MWCNT. It was observed that microwave absorption properties improved with increasing in the loading levels of MWCNT. Finally, the electrospun composite nanofiber sample with the 10 wt% content of MWCNT has revealed the reflection loss of 15 dB at the frequency of 8 GHz.*

1 INTRODUCTION

Electromagnetic interference (EMI) is a main kind of environmental pollution that recently with rapid growth of using electrical and electronic devices have been increased. EMI consists of any unwanted emitted electromagnetic wave which can cause harmful disturbance of system performance[1]. In recent years, this interference has been increased because of significant developments in electronic systems causing serious problems, such as disturbance of performance and malfunctions of these systems and even can affect the human body[2]. Therefore, EMI shielding materials are necessary because of health concerns and protecting electrical and electronic equipment when these equipments interfere with each other[3,4]. The amount of attenuation in the electromagnetic field by a shield is defined as shielding efficiency (SE). There are three mechanisms for control this electromagnetic pollution which is consisting of surface reflection, absorption and multiple reflections of the electromagnetic wave. Among them, absorption is best mechanism for shielding of the electromagnetic wave and using microwave absorption materials is great technique to prevent EMI[5].

In the past, typical metals such as copper or aluminum were the most common materials for EMI shielding, which had excellent shielding effectiveness[6]. High conductivity and dielectric constant of materials result in high shielding effectiveness. Some metals such as silver and copper have high conductivity and high dielectric constant leading to excellent shielding effectiveness[5,7]. The main mechanism for the EMI shielding by metallic materials described by radiation reflects, therefore these materials cannot be used in applications where absorption is important like stealth technology. Furthermore, they have some disadvantages like high density especially in high loading of metal filler, easy corrosion and complex processing[8,9].

Recently, carbonic materials have been also used in EMI shielding and microwave absorbing applications, as conductive fillers. Various carbonic microwave absorber media have been investigated, which includes carbon nanotubes (CNT), carbon fibers (CF), carbon nanofibers (CNF), and carbon black (CB). Among mentioned media, microwave absorption by CNT has been of great concern. CNT are classified in two general types, namely single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT). MWCNT with their exceptional mechanical, electrical and thermal properties are reported to be excellent shielding materials for electromagnetic interference, because of their high conductivity and low density characteristics. The main mechanism described for shielding by the MWCNT is the radiation absorption, therefore MWCNT can be useful for applications where absorption is important[2,6,10].

Several experimental and theoretical studies, using different techniques, have been focused on microwave absorption on CF, CNF, and CB in composite structures with controversial results[11-14]. Currently, there are few studies in the literature regarding the use of MWCNTs in composite for improving their microwave absorption[15]. In the present study, the synthesis of novel poly (vinyl alcohol) (PVA) / MWCNT composite nanofibers by electrospinning process has been reported. The microwave absorption behaviors in these composite nanofibers have been investigated using vector network analyzer. Also the effect of MWCNT amounts on the absorption capacity of the composite nanofibers is also investigated.

2 EXPERIMENTAL

2.1 Materials

PVA powder (M_w=72000 g/mol, 98 % hydrolyzed) as a polymer was obtained from Merck and MWCNT (purity > 95%, diameter< 8 nm, Length: 30µm) were supplied from Neutrino Company. Sodium dodecyl sulfate (SDS) was obtained from Sigma-Aldrich. The solvent used for dissolving PVA and PVA/SDS/MWCNT dispersion was distilled water. All reagents used were of analytical grade and were used as received without further purification.

2.2 Electrospinning Solutions

Electrospping solutions were prepared in three steps (Figure 1). First, the solution samples were prepared by dissolving 1 wt% SDS in distilled water using magnetic stirrer (corning hot plate stirrer PC-351) at 25 °C for 1 hr. In the second step; different weights of MWCNT were dispersed in the SDS/H_2O solutions by using a high power ultrasonic homogenizer (UP200, Germany) at 0 °C for 20 min. Finally, the electrospinning solutions were prepared by dissolving 8 wt% of PVA in sonicated solutions by using a magnetic stirrer at 80 °C for 2 hr. The calculated MWCNTs concentrations in each composition of any sample are listed in Table 1.

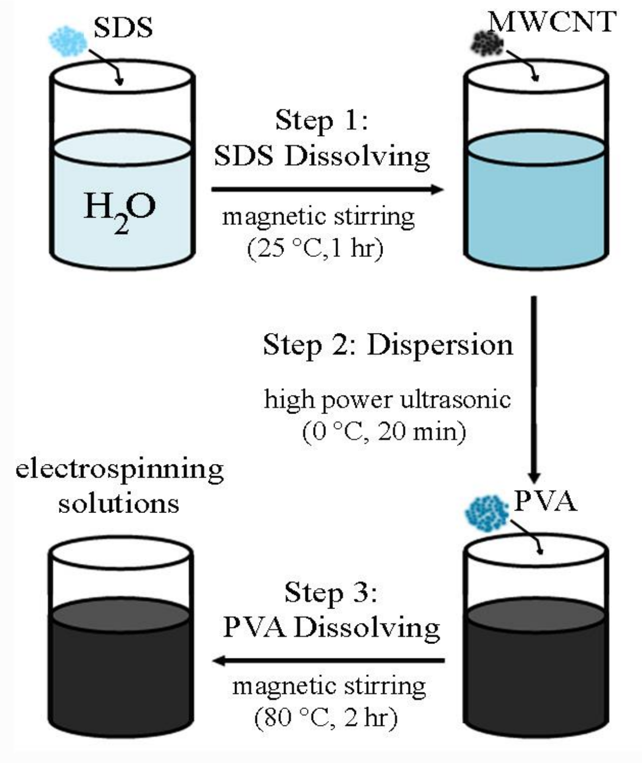


Figure 1: Illustration of the dispersion process steps.

Code.	Mass in 100ml H_2O			MWCNT mass ratio (wt %)
	PVA (mg)	SDS (mg)	MWCNT (mg)	
CNT-0	8000	920	0	0
CNT-2	8000	920	180	2
CNT-5	8000	920	450	5
CNT-10	8000	920	900	10

Table 1: Concentrations of MWCNT, SDS, and PVA in the mixed solutions

2.3 Composite Nanofibers Synthesis

The prepared PVA/SDS/MWCNTs solutions were added to a glass syringe with a needle tip (22G, L=34 mm, O.D=0.7 mm, and I.D=0.4 mm). The feeding rate of the polymer solutions was 0.25 ml/hr, electrospinning voltage at 15 kV was applied to the needle, the distance between the needle tip and collector was set for 17 cm and then the electrospun nanofibers was collected on take-up drum under speed of 100 RPM. The electrospinning of PVA/SDS/ MWCNTs solutions were performed at 22±2 ºC and constant relative humidity of 35-40 %.

2.4 Measurement and Characterization

The surface morphology of the nanofibers was examined by SEM (Philips, XL-30) at an accelerating voltage of 25 kV under magnification of 10000X, and the average fibers diameter was measured with the SEM images using Image J software (National Institute of Health, USA) from 100 fibers/sample. The microwave-absorbing properties of the composite nanofibers were investigated using HP Vector Network Analyzer (Model 8510ES) in the frequency range of 8-12 GHz at room temperature. All samples were cut into a rectangular shape (22.86 mm × 10.16 mm, thickness 1mm) to fit in rectangular wave-guide of X-band.

The wave-guide fitted with the sample was backed by a metal layer for measurement of reflection loss.

3 RESULTS AND DISCUTIONS

3.1 Optimized Dispersion of MWCNT

The difficulty in preparing well dispersed MWCNT composite solutions have been related to their high specific surface area and consequently, possessing very stronger van der Waals interactions. Generally, to improve the morphological properties of the fabricated films containing MWCNT, the dispersion condition is very significant. It is important that MWCNTs to be dispersed uniformly without breakage and aggregation. The SDS/MWCNT solution presented highly stable dispersion behavior without any precipitation at room temperature even after two months. The schematic mechanism of dispersion process has been presented in Figure 2. SDS surfactant is a class of molecules exhibiting a strong tendency to adsorb at interfaces. This is characterized by the presence of both polar (hydrophilic) and nonpolar (hydrophobic) segments. The hydrophilic polar group in SDS dissolves well in water. On the other hand, the hydrophobic backbone in SDS interacts with the MWCNT. Finally, by following this route complete and efficient surface coating of MWCNT by SDS molecules preventing re-aggregation can be achieved.

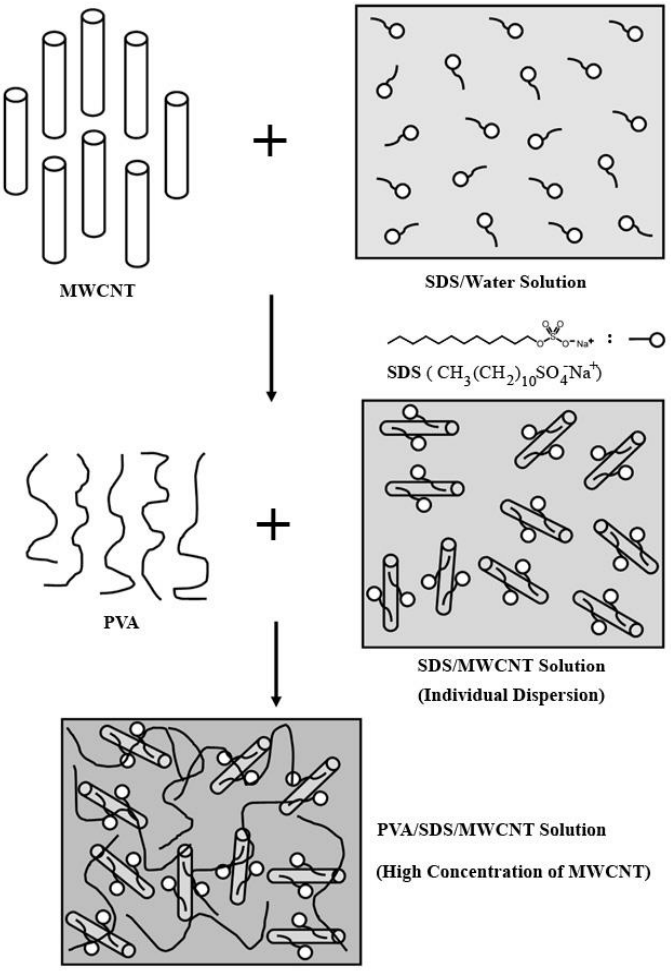
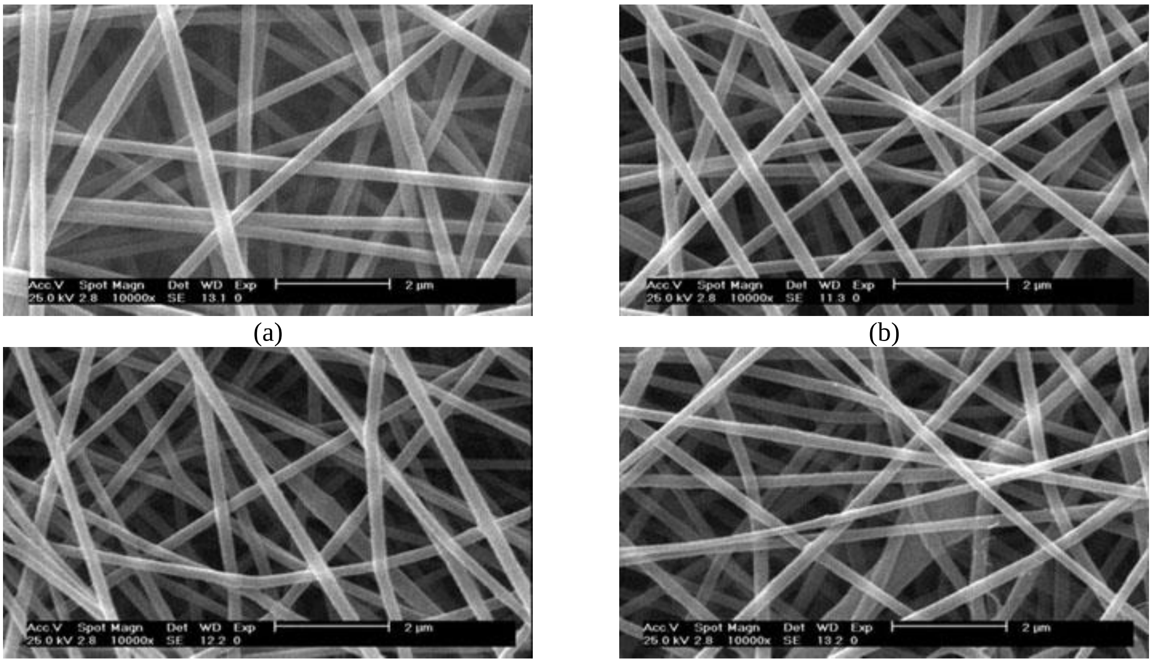


Figure 2: Schematic mechanism of dispersion process.

3.2 Morphplogy of Composite Nanofibers

Figure 3 display SEM photographs of the PVA/SDS/ MWCNT composite nanofibers. The surface of the CNT-0 and CNT-2 electrospun nanofibers is very smooth, as shown in Figure 3a and 3b, respectively. Low surface roughness and unevenness in the CNT-5 sample was observed, while still good alignment in the sample structures can be seen (Figure 3c). However, considerable aggregation and local irregularities were observed as the MWCNT content increased to 10 wt % (see the sample CNT-10 in Figure 3d). However, considerable aggregation and local irregularities in nanofibers structure by incorporating low concentrations of MWCNT (1-2 wt %) have been also reported by other researchers[16].



(a) (b)

(c) (d)

Figure 3: SEM photographs of electrospun composite nanofibers samples: (a) CNT-0, (b) CNT-2, (c) CNT-5, and (d) CNT-10

The dispersion condition is a very important step in electrospinning process and plays a significant role in achieving the good morphological properties of the fabricated composite nanofibers containing MWCNT. The high stability dispersion of MWCNT leads to very smooth and soft surface of the composite electrospun nanofibers even for nanofibers with high concentrations of MWCNT (~10 wt %). The SDS/MWCNT solution presented high stable dispersion behavior without any precipitation at room temperature for one month. So, it is believed that good dispersion of MWCNT in the prepared solutions and their high stability performances even at high concentrations of MWCNT have loaded to smooth and soft surfaces in all samples.

Changes in the average diameter of the various nanofibers samples produced versus increasing the MWCNTs concentration is shown in Figure 4. With increasing the concentration of MWCNTs in the solution from 0 to 5 wt%, the mean diameter of nanofibers decreased from 291±22 nm for CNT-0 to 216±20nm for CNT-5. When MWCNTs concentration was increased to 10 wt% the average diameter increased to 224±30 nm. The average nanofibers diameter for 10 wt% MWCNT sample was not significantly different from previous group ($P<0.05$) but significantly different from all other groups. As described in the literature, decreasing polymer concentration cause reduction in the viscoelastic force versus the electrostatic force and when the viscoelastic force is lower than the electrostatic force, the average diameter of nanofibers decreased[17,18].

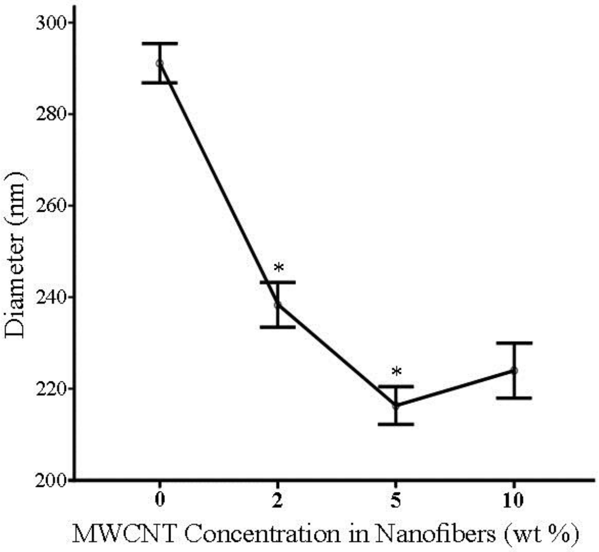


Figure 4: Error plot of composite nanofibers average diameter versus concentration of MWCNT. (*: $P < 0.05$, values are significantly different from the previous group compared)

3.2 Electromagnetic Properties

Reflection loss (RL) is the ability of electromagnetic wave absorption. The absorption of the electromagnetic wave by any absorber can be predicted from the value of RL, so that the larger the negative value of RL, the better microwave absorption behavior of absorbers[11-14]. In case of a metal backed single layered absorber, RL is expressed as:

$$RL\,(dB) = 20\log\left|\frac{Z_{in} - Z_0}{Z_{in} + Z_0}\right| \tag{1}$$

Here, Z_0 is the impedance of air, and Z_{in} is the input impedance of the absorber, which were given by:

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}} \tag{2}$$

$$Z_{in} = \sqrt{\frac{\mu_0.\mu_r}{\varepsilon_0.\varepsilon_r}}\tanh\left[j(\frac{2\pi fd}{c})\sqrt{\mu_0.\mu_r.\varepsilon_0.\varepsilon_r}\right] \tag{3}$$

Where μ_0 and ε_0 are the permeability and permittivity of vacuum, μ_r and ε_r are the relative complex permeability and permittivity of the composite structure, c is the velocity of electromagnetic wave in free space, f is the frequency, and d is the thickness of the absorber[11].

The frequency dependencies of the microwave absorbing properties of the PVA/SDS/MWCNT nanofibers samples are shown in Figure 5. For the CNT-0 sample, the maximum reflection loss has reached -6 dB at frequency of 11.5 GHz. For the CNT-2 sample, the maximum absorption peak has increased to -8 dB at the frequency of 11.5 GHz. With increasing of MWCNT concentration to 5 wt% for the CNT-5 sample, the maximum absorption peak did not changed, however the electromagnetic absorption properties have improved to 2 dB in the lower frequency range. However, for the CNT-10 sample with content of 10 wt% MWCNT, the absorption peak at the frequency of 11.5 GHz did not changed, but the reflection loss increased to -15 dB at the frequency of 8 GHz.

Compared to the result of electromagnetic absorption properties of this sample with other samples, generally, electromagnetic absorption properties have improved with increasing the content of MWCNT. As described in the literature[19,20], by increasing the MWCNT content, the electrical conductivity is increased and this improvement in electrical properties can lead to increase in the conductive current and dielectric properties. On the other hand, the loss tangent (tan δ) is an important parameter in describing electromagnetic absorbing properties in such a way that electromagnetic absorbing properties can be improved with increasing the loss tangent value. With the increase in MWCNT content, the dielectric loss tangent becomes larger leading to increase in the absorption loss. However in this work the lowest reflectivity (-15 dB at 8 GHz) obtained by PVA/SDS/MWCNT composite nanofibers sample with corresponding thickness of 1 mm. Thus it can be concluded absorbing composite nanofibers with thin thickness, can lead to stronger absorption with lower cost.

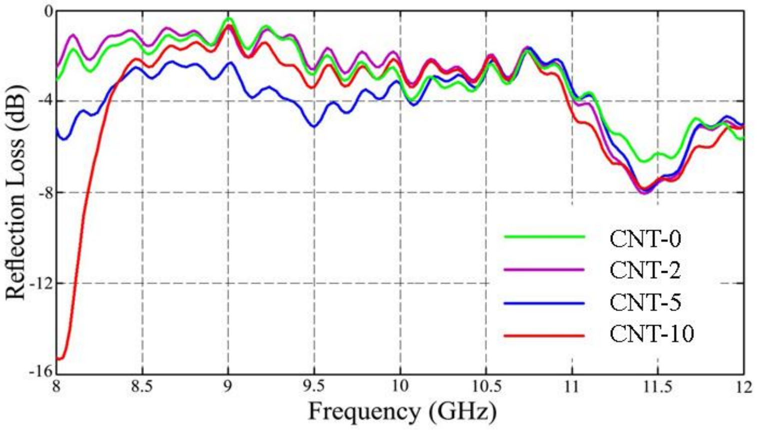


Figure 5: Reflection loss dependency on the frequency for the PVA/SDS/MWCNT nanofibers

4 CONCLUSION

In the present work, the composite solutions of PVA/SDS/MWCNT prepared under various MWCNT contents up to 10 wt% have been successfully fabricated to composite nanofibers made by electrospinning process. The MWCNT concentration varied from 0 to 10 wt%. With increasing the concentration of MWCNT in the solution from 0 to 5 wt%, the average nanofibers diameter decreased from 291±22nm to 216±20nm. When MWCNTs concentration was increased to 10 wt% the average diameter increased to 224±30nm. The high stability dispersion of MWCNT leads to very smooth surface of the nanofibers even for the PVA/SDS/MWCNT composite nanofibers with the content of 10 wt% MWCNT. The maximum reflection loss have improved with increasing the content of MWCNT from -6 dB at the frequency of 11.5 GHz for the pure PVA/SDS nanofibers to -15 dB at the frequency of 8 GHz for PVA/SDS/MWCNT sample with the content of 10 wt% MWCNT.

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INTEGRATION OF LEDS ON SCREEN PRINTED SILVER CIRCUITS

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Keywords: silver conductive paste, screen printing, LED, textiles

Abstract. *The objectives of the research paper consisted in printing circuits onto textile fabrics with conductive silver paste and to integrate LEDs on the thus completed circuits.*
The silver conductive paste was printed using a semi-automatic machine, and a roller-type mold steel with a definition lines of 400-500L/inch allowing the deposition of ink emulsion thickness around 10-15 microns. After printing, the circuits were thermally treated for 30 minutes at 100°C and 150°C.
The circuit lines are composed of microstructured agglomerated silver particles with different size and shapes. Most of the particles are in fine contact each other ensuring a good electrical conductivity. The printed lines contain 87% silver demonstrating that almost all the organic compounds used to formulate the conductive paste have been evaporated during the curing step. The silver lines show a high adherence to the substrate and a good conductivity. LEDs and connectors were integrated on the silver printed lines. The LEDs were welded with gold and powered with thin battery.

1 INTRODUCTION

The integration of electronic devices into flexible textiles could open new markets and offer great possibilities to different sectors: from patient monitoring via smart clothes (healthcare & telemedicine) to the trace of a specific item or innovative wearable computing applications such as flexible sensing, chemicals detection, and mobile power generation.
Until now the electronic textiles have been produced by weaving, wiring, sewing or embroidering. These solutions, incorporating on different levels conductive yarns under different forms, have drawbacks in costs, weight and stiffness.
To overcome such disadvantages, many researches are directed to print the electrical circuits by different printing techniques such as ink-jet, screen, rotary or gravure one [1-3].
The use of printing processes assures high integration and production flexibility due to high speed production, high reliability, throughput and low costs [4].
The printing processes, combined with bonding, lamination will reduce the manufacturing cost compared to standard batch processing and patterning. This reduction is expected in the order of 30% of the final components encompassing materials, cabling and assembly costs.

2 GENERAL SPECIFICATIONS

2.1 Electrical circuits design

To achieve the integration requirements of electronic components (LEDs, thin battery, etc.), the following specifications for electrically conductive network have been established:

- width of electrical conductors: 100 µm (+ / -10%);
- thickness of electrical conductors: approx. 5 µm to 1mm;
- electric conductors must allow a current of 500 mA / 6-24V;
- distance between two lines (conductors): 1000 µm (±10 µm);
- electrical conductors should be up to 15 cm;
- must allow the deposition of connectors (Pads) with approx. 200 micron diameter from the same conductive ink;
- should allow up to 100 conductive lines with terminal connector type (pad).

2.2 Materials

a. Textiles: 100% polyester covered with polyurethane film was used as support, the characteristics being shown in table 1. The material withstands operating temperatures of 150-170 ° C.

Analysis		Values	Standard
Total material weight, g/m^2		200	SR EN 12127/2003; SR EN ISO 5084/2001
Textile (polyester) support weight, g/m^2		140	
Polyurethane film weight, g/m^2		60	
Total material thickness, mm		0,28	SR EN ISO 5084/2001
Polyurethane film thickness, mm		0.03	
Tensile strength, N	warp	1403	SR EN ISO 13934-1/2002
	weft	675	
Ellongation, %	warp	33.8	
	weft	20.9	
The abrasion resistance, cycles, pressure- 9Kpa, (Nu-Martindale)		100000	SR EN ISO 12947-2/2002
Resistance to surface wetting (Spray test), grade		ISO scale : 2 AATCC scale: 70	SREN 24920-1996
Air permeability, l/m^2/sec		impermeable	SR EN ISO 9237/1997
Permeability to water vapours, %, 3h		5.18	SR 9005/1979
Colour fastness to dry/wet rubbing		5/5	SR EN ISO 105-X12-2: 2004
Resistance to artificial weathering, 108hours; grade		5	SR EN ISO 105-B04: 99

Table 1 Technical specifications of textile support

b. Conductive pastes: two conductive pastes based on silver acquired from TOYO INK Japan were tested**: REXALFA RA FS 045** and **RA FS 045**.

These conductive pastes are recommended to print fine lines used for electrically conductive touch-screen displays and photovoltaics. The printed lines (10 microns thickness) have a volume resistivity of $5x10^{-5}$ Ω•cm and a surface resistivity of 0.05 Ω/sq.

RA FS 045 is a one-component system (viscosity: 85+/-10Pa•s/25°C) for direct use. If desired thinning RA FS 200 solvent can be used. For 1% thinning, the viscosity reaches up to 20-30 Pa•s/25°C.

2.3 Screen printing technique

The silver conductive paste was printed using a semi-automatic machine, a flat squeegee and a roller-type mold steel (SUS screen mesh) with a definition lines of 400-500L/inch allowing the deposition of ink emulsion thickness around 10-15 microns. After printing, the printed circuits were thermally treated for 30 minutes at 100°C and 150°C.

The achieved printed electrical circuits are shown in the figure 1:

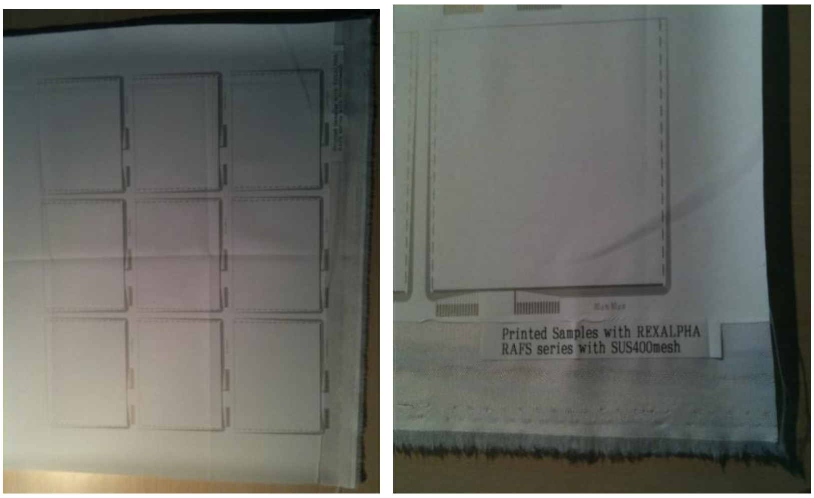

Figure 1 Printed electrical circuits based on silver

3. Analyses

Circuits were evaluated in terms of morphological aspect, silver content, adhesion to the substrate and electrical resistance obtained.

3.1 Scanning Electron Microscopy

The shape and surface area characteristics of the silver conductive particles have been analyzed by Scanning Electron Microscope Quanta 200 (FEI, Holland). The samples were prepared by using a double conductive adhesive tape to bind small portions of the printed material to a metallic support (stab).

The morphological aspect of the printed circuits are shown in the figure 2.

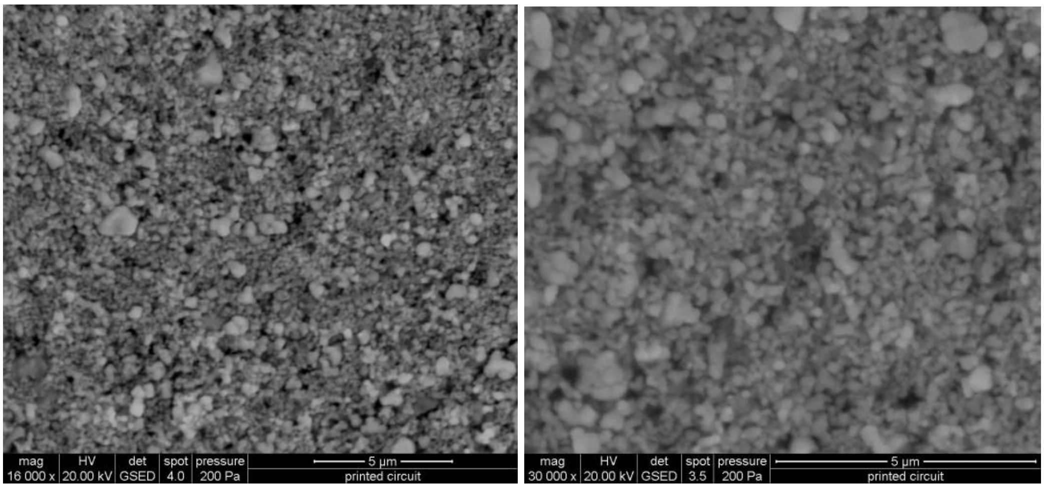

Figure 2. SEM micrograph of silver printed circuits

As seen from Figure 2 , the circuit tracks are composed of microstructured agglomerated silver particles with different size and shapes. Most of the particles are in fine contact each other ensuring a good electrical conductivity.

The quantification of the silver amount contained in printed lines was performed on SEM / EDAX and is presented in table 2 .

Element	Mass, %	At, %	K- repport	Z	A	F
C K	6.69	33.09	0.0393	1.2483	0.4704	1.000
O K	3.91	14.52	0.0056	1.2264	0.1172	1.0001
Al K	1.54	3.39	0.0083	1.1383	0.4716	1.0066
Ag L	**87.02**	**47.94**	**0.8436**	**0.9549**	**1.0150**	**1.0002**
Ti K	0.85	1.05	0.0068	1.0566	0.7603	1.000
Total	100.00	100				

Table 2. The quantification of the silver amount contained in printed lines

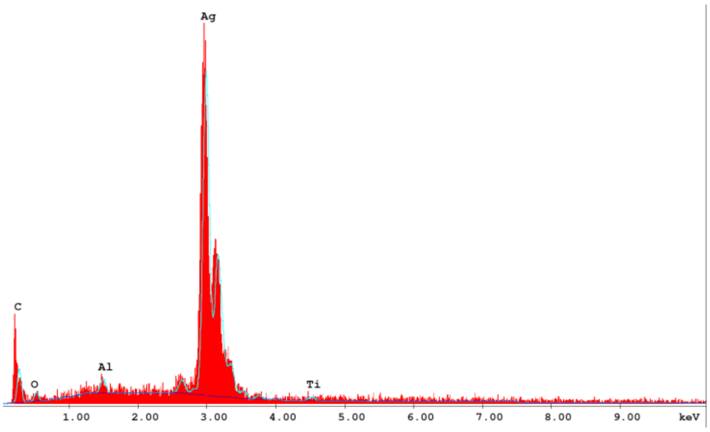

Figure 3. SEM/EDAX spectrum of the silver printed circuit

As it is shown in table 2, the most part (87%) of the printed circuits are composed of silver demonstrating that almost all the organic compounds used to formulate the conductive paste have been evaporated during the curing step.

3.2 Adhesion test:

The adhesion of the printed lines have been tested according to ASTM D-3359 tape test standard by applying, pressing and pulling out a transparent scotch tape (2.5 cm).

	Thermal treatment				**Standard**
	100°C, 30 min.		**150°C, 30 min.**		
Conductive paste	**RA FS 007**	**RA FS 045**	**RA FS 007**	**RA FS 045**	
Adhesion	Surface delamination	No delamination	No delamination	No delamination	ASTM D-3359 - adhesion tape test
Surface resistance, Ω/sq	0.090	0.098	0.134	0.100	

Table 3. Surface resistivity and delamination of printed circuits

During pulling of the tape, the removal of the silver from the coating is observed on the material printed with **RA FS 007** while no silver particles could be observed on material printed with **RA FS 045,** regardless of the temperature applied during the curing treatment.

Finally, RA FS 045 conductive paste was selected due to lower surface resistance and high degree of attachment to the substrate.

3.3 Electrical resistance of the printed circuits

Electrical resistance values determined by a digital ohmmeter are presented in Table 4.

L [cm]	1	2	3	4	5	6	7	8	9	10	11	12
R [Ω]	5.4	10.7	13.1	16.0	22.6	23.5	26.5	30.2	32.4	36.9	40.0	45.8

Table 4. Electrical resistance, R , according to the length L of the conductor track (width of 1 mm)

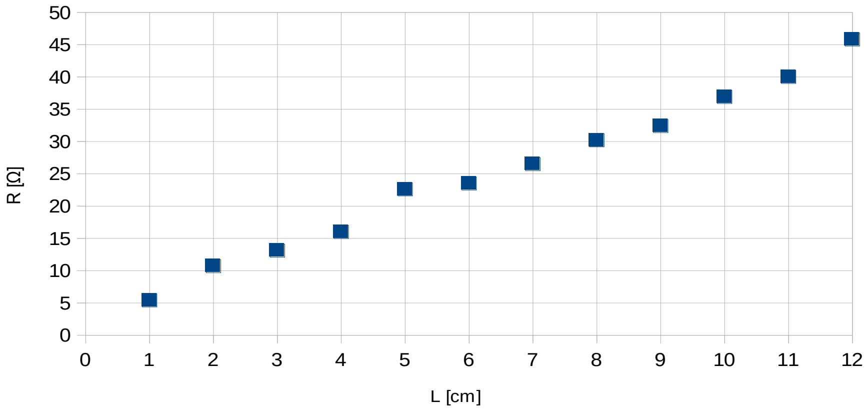

Figure 4. Electrical resistance depending on the length L of the conductor track

A linear dependence is observed between R and L, within the measurement errors. The electrical resistance values of the printed electrical lines indicate that the conductive lines (1mm thick) can be used for making electronic circuits. In contrast, the electrical resistance of thin lines measured between contacts of their heads is 32 ÷ 33MΩ. This value indicates that these lines present some interruptions due to possible cracks or narrowing of conductive film deposited on substrate.

3.3 LEDs integration on conductive lines

Different electronic devices could be integrated on the printed electrical lines, such as LED chips, photodiode as sensor lights or micro-controllers to produce luminous advertising articles, improving in this way, the final aspect and ability to capture customers' attention. Such advertising articles require a relatively low brightness level, around 2cd/m^2, which means that a single point could be illuminated by a maximum two single LEDs or OLEDs.

LEDs and connectors with specifications listed in tables 5-8 were integrated on the silver printed lines. The LEDs were welded with gold (25µm thin gold wires acquired from Dr. Mueller) and powered with thin battery.

Parameter	Symbol	Value			Unit
		Minime	Typical	Maxime	
Length of the chip edge (x- direction)	L_x	0.17	0.22	0.24	mm
Length of the chip edge (y- direction)	L_y	0.17	0.22	0.24	mm
Diameter of the wafer	D		100		mm
Die height	H	130	150	170	µm
Diameter of the bondpad	d		90		µm
Additional information					
Metallization frontside	Gold				
Metallization backside	Gold alloy				
Die bonding	Epoxy bonding				

Table 5. Mechanical values of the integrated microstructures

	620-623nm	623-625nm	625-627nm	627- 630nm
250-320 mcd	A31	B31	C31	D31
320- 400mcd	A32	B32	C32	D32
400-500mcd	A33	B33	C33	D33
500-640mcd	A34	B34	C34	D34

Table 6. Binning

Parameter	Symbol	Value	Unit
Maximum operating temperature range	T_{op}	-40…+100	^{0}C
Maximum forward current (T_A = 25^{0}C)	I_F	50	mA
Maximum surge Current, (T_A = 25^{0}C) Tp = 10µs, D= 0.05	I_{peak}	0.1	A
Maximum junction temperature	T_j	125	^{0}C

Table 7 Maximum Ratings

Parameter	Symbol	Value			Unit
		Minime	Typical	Maxime	
Dominant weavelength I_F = 20 mA, tp = 30ms	λ_{dom}	620		630	nm
Reverse voltage, I_R = 10µA	V_R	5			V
Forward current, I_F =f(V_A) I_F = 20mA; t_p = 30ms	V_F	1.90		2.40	V
Luminous intensity*, I_F = 20mA; t_p = 30ms	I_V	250	350		mcd

Table 8 Electrical values (T_A = 25^{0}C)

* Relative luminous intensity: $I_V/I_{V(20mA)}$ =f(I_F); $I_V/I_{V(25^0C)}$ =f(T_j)

4. Conclusions

► the conductors printed with REXALFA RA FS 045 and cured for 30 minutes at 100°C show good values of surface resistance, high conductivity and adhesion to the substrate.

► Selected printing parameters have ensured the development of conductive lines with a maximum thickness of 1mm. In principle, it is considered that the thickness of the lines should be in the range 0.5 - 1mm to have a high conductivity, to eliminate any overheating due to a single LED chip management and to prevent disruption of printed lines and connectors.

► Screen printing technology of the electric circuits is advantageous in terms of flexibility and bending ability of the printed materials, the cost and the existent machinery in textile enterprises.

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CLUSTERIZATION IN TEXTILE AND CLOTHING INDUSTRY

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Key words: cluster, clusterization process, textiles and clothing, textile clusters

Abstract: *In Romania, textile industry is one of the fundamental branches of the national economy in terms of employees number (approx. 170,000 employees) and of exports (approx. 11% of the national exports).*

Relying on strengths and transforming weaknesses into opportunities, the Romanian textile industry faces an important challenge: to become an intelligently specialized industry based on strong regional clusters. These clusters can provide the energy and the means to focus the economic development efforts. Their set-up and development is a driving force for healthy and profitable regional growth.

The paper presents aspects of the clusterization process, characteristics of the textile – clothing industry and specific clusters in Romania.

1 INTRODUCTION

The textile and clothing industry has a long-lasting tradition and it is one of the basic industrial sectors of the European economy. The UE 27 textile and clothing industry had in 2012 a turnover of 165.3 billion EUR and the investments amounted to approx. 5 billion EUR[1]. Despite the strong negative impact of the world economic crisis, the sector had in 2012 over 181,400 enterprises and approx. 1.78 millions employees.

Textile industry is in Romania one of the fundamental branches of the national economy in terms of number of employees (approx. 170,000 employees) and of exports (approx. 11% of the national exports). The textile industry contributes to social stability and is represented all over Romania (approx. 6000 active textile companies) and detains approximately 3% of Romania GDP.

At the end of 2012 Romania had:

- 1.59 % of the turnover of textile-clothing industry of UE 27;
- 12.27% of the labour force employed in this sector at European level;
- 2.99 % of the enterprises in the textile-clothing industry of UE 27;
- 0.8% of the total textile export amount outside UE;
- 0.57 % of the total clothing export amount outside UE.

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[1] EURATEX 2012 Annual Report

These figures indicate the special importance of the sector. Relying on strengths and transforming weaknesses into opportunities, the Romanian textile industry faces an important challenge: to become an intelligently specialized industry based on strong regional clusters.

These clusters can provide the energy and the means to focus the economic development efforts. Their set-up and development is a driving force for the regional healthy and profitable growth.

2 CLUSTER CONSIDERATIONS

Michael Porter is considered today to be "Spiritus Rector" of the economic policy based on cluster development and the one who formulated the following definition: "Clusters are geographic concentrations of interconnected institutions and companies from a certain domain. Clusters consist of a group of related industries and other important entities from a competitiveness point of view. These include, for example, specialized input (such as components, machines and services) suppliers or specialized infrastructure suppliers. Clusters often expand downstream towards various distribution channels and clients sideways towards complementary product manufacturers and towards industries that are related to them by mutual qualifications, technologies or inputs. Finally, some clusters include governmental institutions and other types of institutions, such as universities, standardization agencies, think tanks, professional training suppliers and employers' associations, which ensure specialized training, education, information, research and technical support". (Porter M., 1998)

The definition of a cluster can also be found in the Romanian legislation (HG 918:2006 – the "Impact" Program), according to which a cluster is a group of producers, users and/or beneficiaries, aiming to implement best practices in the EU in order to increase the competitiveness of economic operators.

The European Commission's Communication COM (2008) 652/2008 ***"Towards world-class clusters in the European Union – Implementing the broad-based innovation strategy"*** defines a cluster as a group of firms, related economic actors and institutions that are located near each other and have reached a sufficient scale to develop specialized expertise, services, resources, suppliers and skills.

The "Competitiveness pole" is an association of companies, research-development and training organizations, which act in partnership in order to implement a joint development strategy. This strategy is built around innovative projects, its final goal consisting in approaching one or more markets[2].

The first economist to describe clusters from a "supply chain" point of view was Alfred Marshall (1842 – 1924) (Marshall, 1920), who, by analyzing the industrial agglomerations in England, has found that these geographic concentrations of companies from a certain sector create involuntary positive economic effects – the so-called externalities:
- effects on the labour force: the fact that a large number of companies supply themselves from the same labour pools results in the increase of wages, on one hand, and in the increase of its training level, on the other hand;

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[2] http://competitivite.gouv.fr/politique-des-poles/quest-ce-quun-pole-de-competitivite-472.html.

- effects regarding suppliers specialization: in order to avoid competition, companies in an industrial agglomeration tend to specialize themselves on a certain segment of the value added chain, leading to the increase of product quality and to cost reduction;
- technological transfer: Marshall found that information and knowledge are "floating in the air" between the existing companies in the geographical concentration. This is, in fact, the „avant la lettre" definition of technological transfer.

Subsequently, looking from the economic geography point of view, Jane Jacobs (Jacobs, 1969) emphasized the role of big cities in economic development, these cities playing the role of what is known today as "urban growth poles".

In his paper, "Competitive Advantage of Nations", Michael Porter (Porter M., 1990) has demonstrated that, in order to explain a country or a region's economic success, it is not enough to rely on the classical factor endowment theory, as it depends on the complex interaction between the factors reunited in what is known today as "Porter's Diamond": demand, firm strategy, structure and rivalry, production factors, supply chains and horizontal integration.

Also, innovation is today a sine qua non condition for economic success and for maintaining companies on the market. For a long time, and unfortunately, still, innovation has been regarded as a linear process: invention – prototype – testing – mass production – market. This model that draws through its simplicity nowadays proves itself to be obsolete. Innovation is a complex process, based on the interaction of the actors involved in innovative systems. Essential contributions to the systemic approach of innovation were made by Lundvall (Lundvall, 1992), Nelson (Nelson, 1993) and more recently Guth (Guth, 2004).

All these considerations have lead to the unanimously accepted "triple helix" model, which joins together, within a cluster, representatives of:

- companies – representing the economic part of the cluster;
- universities and research institutes – representing the suppliers of innovative solutions, applicable to the real needs of the companies that are part of the cluster;
- local and regional public authorities, etc.

However, in Romania, experience has proved that the three natural partners of the "Triple helix" model not only do not cooperate, but they also do not know each other and do not get to discuss with one another. There is a need for adapting the model and for turning it into a "Four clover" model, the fourth actor being the catalyst organizations – consulting firms, specialized in the technology transfer and innovation field, technology transfer centres, etc. (Cosnita, D., Guth, M., 2010).

Obviously, different categories of actors within this model have different contributions and stakes, which must be harmonized. They can be synthesized in the following form (Table 1):

Table 1 Stakes of various actors in the „Four clover“ Model

Partner	Contribution	Effects/Benefits
R&D sector	- Up to date and applied research - Information, know-how transfer	- adaptation of the curriculum - new laboratories sponsored by the industry - continuous learning - research nuclei
Industry	- cooperation - making available production facilities	- increase of added value - other competitive advantages
Public Authorities	- mediator - dissemination at central, regional and local level - direct support	- central, regional and local economic development
Specialist Consultants	- know-how transfer	- added value
Generalist Consultants	- Coordination Dissemination at national and international level Know-how transfer	- participation in an innovation network

Referring to the effort to analyse the clusters/competitiveness poles, we should proceed from the following premises:

- relationship between the National vs. Regional Level involving a multitude of interested players;
- approach from the standpoint of existing financing sources;
- existence of several denominations that are fully assigned to or are connected with the same concept: cluster, competitiveness pole, excellence pole, urban growth pole.

The main player at a national level is the Ministry of Economy with its General Direction for Industrial Policies and Business Environment which sets the industrial policy frame for the clusters’ activity and through POS CCE Management 5 Authority it provides financial support The Ministry for Regional Development and Tourism (MA European Territorial Cooperation, AM POR) National Authority for Scientific Research (OI POS CCE Axis 2) are involved in the management of financing programmes for clusters at a central level.

At a regional level ADR plays a double role, as Intermediate Body for the Regional Operational Programme and also as initiators/catalysts for some clusters (eg. ICT Vest, Automotive Vest, ASTRICO NE etc). Also at a regional and sub-regional level there are existing clusters that are registered with the General Direction for Industrial Policies in MECMA.

It is worth noting, for conceptual clarity, that there was initially no difference between the term cluster (Anglo-Saxon origin) and competitiveness pole (French origin), however in Romanian they tend to be used in different contexts, therefore conceptual demarcation is welcome.[3]

Thus, the term „cluster" chiefly indicates industrial agglomerations and stresses concentration of enterprises active in the same field or in connected fields, with the economic effects, as identified by Marshall, on the labour force, on the suppliers' specialization and related to technology transfer and innovation. There structure may or may not be „triple helix" complete structure.

The „Competitiveness Pole" is an association of enterprises, research and development and training organizations that form a partnership to apply a joint development strategy. This strategy is based upon innovative projects whose final objective is to approach one or several markets.[4] Therefore, from our perspective, the pole has a complete triple helix (authorities - R&D- industry) or four clover (a catalyst organization being added) structure.

Table 2 presents specific differences between competitiveness poles, clusters, excellence poles and urban growth poles.

Table 2 Conceptual demarcations

Nr.	Denomination	Characteristics	Theoretical basis
1	Competitiveness Pole	- complete triple helix or four clover structure - strategy subordinated to the objective of being active on one or more markets - orientation to exports - focus on innovative projects - national and international impact - focus on production activity	Porter's Diamond
2	Cluster	- industrial agglomeration - stress on enterprises relationship - structure in various maturity phases	Marshall Theory
3	Excellence	- represents a competitiveness pole highly orientated towards research - innovation - stress on R&D and innovation	Lundvall, Nelson, Guth Theories
4	Urban growth pole	- has in view the geographic dimension of the term, the role of the towns in the crystallization of competitiveness poles	Jane Jacobs' Theory

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[3] *However, there is no way to avoid the alternative use of the two terms in the future, especially given the trend to unify the terms in the European Union towardsinnovative cluster*

[4] *http://competitivite.gouv.fr/politique-des-poles/quest-ce-quun-pole-de-competitivite-472.html.*

3 INNOVATION IN CLUSTERS

3.1 Systemic Theory of Innovation

Innovation can be described as a result of the interactions of various actors in the so called innovative systems. The systemic view on innovation was discussed by LUNDVALL[5] (1992), NELSON[6] (1993) and more recently by GUTH[7] (2004). Considering these new approaches, the traditional linear model of innovation, becomes less and less relevant.
Learning, trust and the so called social capital become the main pillars of this new model.

Individual and institutional learning

In systemic models learning or the capacity to learn is an essential prerequisite for innovation and ultimately for the increase of economic competitiveness.[8] A distinction should be made between individual and institutional learning. Their interactivity (learning by interaction) is the key instrument to transform individual learning into institutional learning. In the end, success does not exclusively reside in a high degree of interactivity in an organization, but more and more in the interactivity between organizations.

Trust and social capital

Individual learning normally occurs in classical situations centred on teacher – student relationship. Students rely upon the teacher's competence. In this case learning is a social interaction developed in a certain framework. Information is "coded" (in books) and also "tacit". Trust plays a very important role in the learning process, both in relation with the "teacher" and with the "student". Translating this to the level of successful innovative processes based on inter-institutional relations it is easy to understand that success relies on a certain amount of trust. These thoughts bring us closer to the "social capital" concept. This was coined by Coleman in 1990. The social capital means a group of objectives, norms and social relations. This capital makes it easier for the players involved to reach their objectives by coordinating their activities.[9]

The new innovation diamond

The model to be discussed below was recently developed by the **Centre for Innovation and Technique of Rhine North Westphalia (ZENIT**, based on Porter's theory of competitive advantage and individual and institutional learning concepts). [10]

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[5] *See LUNDVALL, B.A., Ed. (1992), National Systems of Innovation: Towards a Theory of Innovation and Interactive Learning, London.*

[6] *See NELSON, R.R., Ed. (1993), National Systems of Innovation: A Comparative Analysis, Oxford.*

[7] *See Guth, Innovation, Social Inclusion and Coherent Regional Development: A new diamond for a socially inclusive innovation policy in regions, Discussion paper on the Conference on Territorial Cohesion, Galway, 2004*

[8] *Florida, R., Towards the Learning region, in Futures, 27, p. 527-536, 1995*

[9] *See Meyer Stammer, J., Was ist Meso? Systemische Wettbewerbsfaehigkeit: Analyseraster, Benchmarking-Tool und Handlungsrahmen, INEF Report 55/2001, p. 34, Duisburg, 2001*

[10] *Research financed by Hans Böckler Foundation, Germany (www.boeckler.de)*

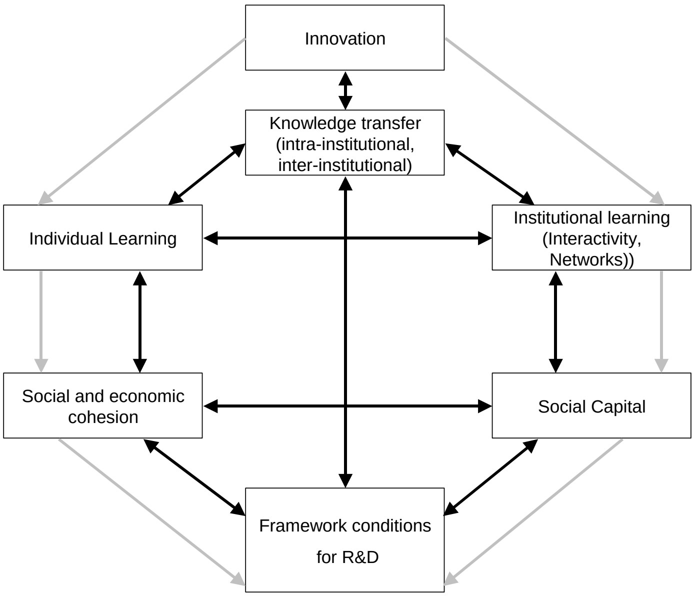

Figure 1 The new innovation diamond

Thus, the model is built on the following considerations:

- Innovation is founded on in-depth scientific knowledge supported by modern infrastructure;
- Technology transfer and innovation processes are impossible in a polarized economic – social environment. A certain economic and social cohesion is needed as a prerequisite for the implementation of innovative processes;
- Innovation is built on individual and institutional learning;
- Individual and institutional learning can take place if a common set of norms, rules and visions was set;
- One can talk about innovation only when knowledge materializes either in a new management product, service, process or instrument.

3.2 APPLICATIONS OF THE NETWORK MODEL OF INNOVATION. TRIPLE HELIX AND FOUR CLOVER

An application of the systemic theory of innovation correlated with the individual and institutional learning concepts can be found in the “triple helix” innovation concept (in clusters, these being by definition a non-linear concept). To have technology transfer and innovation (in a cluster) the following categories of players need to participate[11]:

- universities and research institutes representing the offer of products, processes and innovative services;
- industry, especially SMEs that represent the demand for innovation; ideally, these should determine and absorb the above mentioned offer;

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[11] Vezi Etykowitz, H., The Triple Helix of University-Industry-Government Implications for Policy and Evaluation, Institutet för studier av ut b i ldning och forskning, Stockholm, 2002

- the state authorities that are competent in facilitating innovative processes (ministries, regional authorities etc).

Figure 2 Triple Helix Model

This model is successfully applied in Sweden. The implementation of innovation programmes in Sweden is managed by the Government Agency for Innovative Systems (VINNOVA – www.vinnova.se), subordinated to the Ministry for Enterprises, Energy and Communications. VINNOVA's annual budget is 200 mil. EURO, that is 6% of research and development public investment in Sweden. This budget is allocated between academic environment - 40%, research institutes - 20% and private companies - 30%.

The priority intervention fields were defined: ICT (30%), biotechnologies (20%), production systems and materials (20%), automotive sector (20%) and labour sciences (10%). These fields have corresponding finance programmes that can be accessed. The membership of the management committees strictly respects the partners' representation in the „triple helix", including representatives of the academic environment, of the state and of the business environment.

In Romania the 3 natural partners of the triple helix do not cooperate, they don't even know each other and do not communicate. There is a need to adapt the model and transform it into a "four clover model". The fourth player is represented by catalyst organizations – consulting firms in the field of technology transfer and innovation, technology transfer centres etc.[12]

"Pro Wood", an innovative cluster in the wood sector, was set up in Braşov-Covasna region with the support of FP7 project conducted in 2008-2010. After a detailed analysis of the SMEs situation in that region, a plan of measures was elaborated and pilot activities were conducted. The main action directions focused on the improvement of the cooperation between industrial high-schools in the wood sector and SMEs, improvement of the companies' marketing strategy and of the association in general, collaboration between research centres and the industry. The project resulted in signing a protocol for cluster set-up in April 2010.

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[12] Coşniţă, D., Triple helix of four clover, speech at the sixth Forum for Innovation and Technology Transfer, Bucharest, 2007

Figure 3 Four Clover Model applied to Pro Wood.

The model used for “Pro Wood” cluster is “four clover” (Cosnita, D., Guth, M., 2010) which besides the regular participants in the triple helix model: Faculty for Wood Industry - The “Transilvania” University in Braşov, County Council Covasna and the Association for SMEs in the Wood Industry in Covasna county (KO FA), included and/or was supported by organizations with a catalyst role in the cluster establishment and consolidation ().

There are two types of such organizations: experts (Fraunhofer Institute in Braunschweig, Institute for the Optimization of Production Processes – TTS Helsinki, the competitiveness pole CRITT Bois in Metz) and with general expertise (Centre for Innovation and Technique of Rhine North Westphalia ZENIT, Inno Consult and the German Society for Technical Cooperation – GTZ).

“Pro Wood” cluster is managed by the Regional Branch Association KO-FA.

4. TEXTILE CLUSTERS IN ROMANIA

In Romania, in recent decades, due to the new political, economic and social conditions and to the restructuring process, the textile industry has gone through significant changes at each stage of the value chain. The considerable development of the private sector is due to this branch adapting easily to the consumers’ needs and requirements and to the massive development of lohn production.

The market economy mechanisms had a major impact on the development of the textile industry and created an actual balance of supply and demand as a result of market forces. The big number of companies on the market in this sector, and especially in the clothing subsector led to a real competition environment and to the creation of clusters.

At this moment, there are 4 developing textile clusters in Romania.

In the North – East Region the *cluster ASTRICO NE* was created. Astrico producers association is already operating for some time and it is a strong industrial group in the field of knits production and sales, based on Rifil company, the most important producer of knitting yarns in Eastern Europe.

The quality of this group's products ranges at medium – high level and the products are predominantly – over 80% - exported on the European market (France, Italy, Germany, Spain, Belgium, Great Britain etc.) and USA.

The group comprises 12 companies, 11 of them being SMEs, and each of the members has a range of representative products such as: knitting yarns (Rifil SA is one of the most important producers of acrylic yarns), circular knitting products (Ema SA), knitted garments (pyjamas, body wear - Sofiaman Impex SRL), knits combined with leather and leather garments (Staro SA), knits with embroidery elements (Anca Rom SA and Ema SA), knitted products made on linear electronic machines (Anca Rom SRL, S&B Comp SRL, Smirodava SA, Sporul CM, Jatex SA, Bucovina Tex SA). These companies have market recognition of their brands (Ema, Sense, Smirodava, Sofiaman, Sofiaman Kids, Sporul, Anca Rom, Jatex, Staro, S&B, Bucovina, Rifil, Kinga Varga).

The cluster includes 2 research entities (National Research and Development Institute for Textiles and Leather and the Faculty for Textiles and Leather Iasi), a public authority (ADR North East) and a catalyst company (Inno Consult SRL).

The c*luster Romanian Textile Concept* was formed in 2011 in the Bucharest – Ilfov and Muntenia South Regions. The cluster has 22 partners representing the economic environment and is centred on an association of 27 producers with established tradition in the garments, knitwear, footwear and leather products.

The companies in this cluster produce a large variety of products: light and heavy garments (Conflux, Frangipani Fashion, Mod Conf Trend, Tanex, Focus, Samric, Katty Fashion, Glamour Fur, Rexton, Caremil, BD International, Ring Textile Production, Madirom Conf, Practic Prodcom), knitwear (Impex Trading, Tanex, Datsa Textil, Eurotricot), socks (Overall Co), footwear/leather products (Import Export Gygy, Angela Internaţional, Sfera Factor Association), cotton and denim type fabrics (UCO Tesatura, UCO Filatura, Sigma Filatura, Iasitex, Siderma).

All the members of the association have their own brands, such as: Tata şi fiul (Father and Son), Andreea Vrajitoru, Papucei, Corvari's, Miracat's, Glamour, Miragal, 27th Avenue, Andreea Tincu, Sense, with which they participate in international specialized fairs in Paris, London, Dusseldorf, Tokyo, New York etc.

The catalyst companies and organizations offer a wide range of services such as consulting, marketing, advertising, transportation, logistics, storage, human resources, event organizing.

The cluster includes 1 research entity (The National Research and Development Institute for Textiles and Leather), 4 universities (the Faculty for Textiles and Leather Iasi, the University of Art and Design Cluj Napoca, the Academy of Economics Studies Bucharest and the National Arts University Bucharest), 1 public authority (local town hall of Sector 6, Bucharest) and 14 catalyst companies.

In the South – East Region the *cluster Traditii Manufactura Viitor - TMV Sud –Est* was formed. The organizations in this cluster have previous collaboration relations. In this cluster, the companies that represent the industrial sector are big, medium and small enterprises, and their experience is based on at least 15 years of tradition in the textile field.

The range of products and services in this cluster is broad: high quality men, women and children garments from the whole range of raw materials (Artifex SRL, Sorste SA), chemical finishing (Textile Blue Wash SRL), high complexity garments (Pandora Prod SRL), women's garments (Contempo Tex SRL, Ro-Design SRL), various clothing items (Tricotton Junior SRL, Ardesa SRL), various textile products and fashion (Verona Mode SRL), trade with industrial equipment, consumables and accessories specific to the field (Migami SRL), cardboard package production (Comunivers 912 SRL), transportation and commerce (Eltra Logis SRL).

The cluster includes 3 research entities (National Research and Development Institute for Textiles and Leather and the Faculty for Textiles and Leather Iasi and the University of Art and Design Cluj Napoca), 2 public authorities and 3 catalyst organizations.

In the Centre Region the cluster *„Transilvania" Textile & Fashion* was formed, and its objective is to strengthen the already existing relations in the field of student internships and specialist training and also to identify all the opportunities to make innovative products with a higher added value by technology transfer and applied research. The stated objective is to support the activity of professional groups in the textile industry for more efficient and effective services, to set up communication channels, to develop experts and enterprises networks of cooperation, to identify the possibilities to assimilate innovative products and to ensure a high performance management.

Representative for this cluster are the clothing products and accessories (excluding body wear), travel articles and harness articles. This group is formed of 11 companies: Favorit Bradul SA, Secuiana SA, Super Home Textil SRL, Exopalma PROD-COM-CONFECTII SRL, Variart SRL, Dreiconf S.A, Rustica Comerţ SRL, George SRL, New- Fashion SA, Producţie Prestări Comerţ Dia-Dal SRL and Ban Import Export SRL.

The cluster includes 1 research entity (National Research and Development Institute for Textiles and Leather), 2 public authorities (Local Council Sf. Gheorghe municipality, Local Council of Covasna), 1 catalyst company (Grupul şcolar Kós Károly, Sf. Gheorghe), 3 banking units (OTP Bank SA, Suc. Sf. Gheorghe, CEC Bank SA, Suc. Sf. Gheorghe, Transilvania Bank SA, Suc. Sf. Gheorghe), 2 agencies (Agency for Environmental Protection Covasna, Local Agency for Labour Force Occupation in Covasna).

A number of the organizations in this cluster form *NOATEX* - the *pole of competitiveness in the textile – clothing industry* whose objective is to support competitiveness, innovation and productivity.

5. Competitiveness of Textile Clusters.

The textiles and leather sector contributes 12% to Romanian exports and is the largest employer in manufacturing industry (25%). Its contribution to the GVA has increased by 30% between 2005 and 2008. R&D expenditure in the sectors recovered in 2010 after a significant decline in 2009 due mainly to the contribution of the leather sector which accounted for 70% of R&D expenditures in the sector in 2010. While the overall trade balance is positive it should be noted that this is as a result of the positive trade balance of wearing apparel (clothing). Overall the sector ranks 4th in number of SMEs (3904 enterprises in 2009) and contributes approximately 10% to the overall GVA produced by SME businesses.

In 2010, Romania accounted for 1.59% of European Union turnover, represented 9.6% of the labour force, 4.7% of the number of enterprises, 0.71% of clothing exports and 0.61% textile exports. (Bucur., 2012). Technical textiles, intelligent textiles and costumized apparel are seen to be the most important development trends of the Romanian textile industry. Textile exports are mainly represented by the classical wearing apparel (clothing) component.

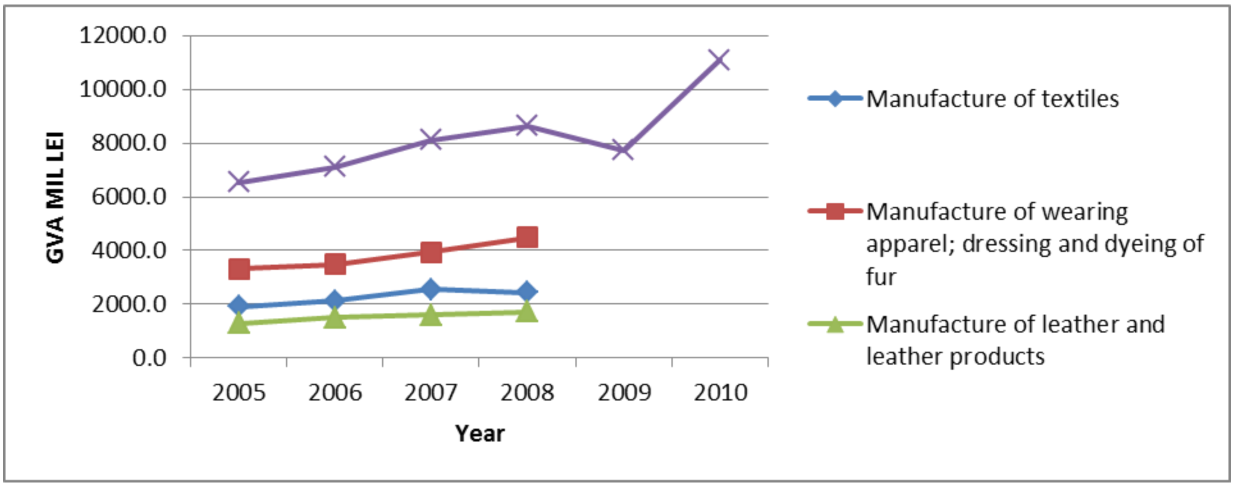

Figure 4 Romania: Gross Value Added in the Textile and Leather Sectors Source: Statistical Yearbook of Romania 2012, NACE Rev. 2

It is however considered a modest innovator assessed by means of turnover produced by innovative SMEs (Paslaru, 2012). Research and development in leather and textiles in 2010 is dominated by leather and leather products (69%) with textiles and clothing representing 25% and 6% respectively of R&D expenditure.

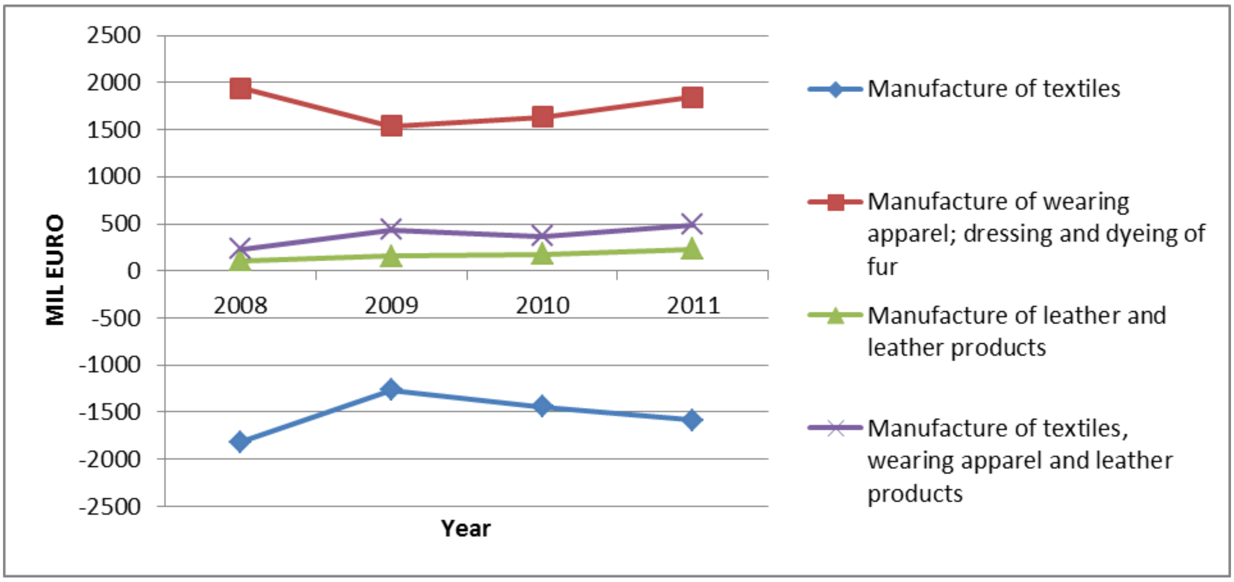

Figure 5 Romania: Trade balance in Textiles and Manufacturing 2008 to 2011 Source: Statistical Yearbook of Romania 2012, NACE Rev. 2

Euro Monitor International in their market research report "Apparel in Romania" published in August 2012 (EuroMonitor International, 2012) identified that "the apparel market experienced one of the best-case scenarios in 2011, almost managing to maintain the sales recorded in 2010, and it managed to maintain consumers' attention through frequent discounts and special marketing strategies."

Euro Monitor (EuroMonitor International, 2012) also identified that, "the apparel market is expected to see gradual, mild recovery throughout the five year forecast period. One of the key factors influencing this trend will be Romanians' shift in purchasing behavior, from extensive to cautious. Discounts and promotions generate most of the sales in the market, by providing consumers with the perception of saving money. Thanks to the strong interest of international fashion retailers in the market and the increasing economic upsurge, consumers will be offered an even wider array of apparel options; thus both value and volume sales are expected to increase. The presence of online retailers and the possibility to order items from home will be other drivers of sales in terms of both demands, as consumers have to invest less effort in shopping, and supply, as e-stores are cheaper to launch, manage and promote."

2 recent studies have dealt with the competitiveness of Romanian industrial sectors, namely the Cluster Analysis performed by the Romanian Cluster Association (Cosnita, 2012) and a study undertaken on behalf of the National Commission of Prognosis (Cojanu, 2012). It should be noted that both methods work with a composite index, i.e. P with importance, size, innovation, exports and ICCS with production, technology, structure and exports (Cojanu, 2012), however both studies have adopted different indicators. In addition the analysis by the Romanian Cluster Association takes into consideration the consistency between the national (sectors) and regional (clusters) level. Therefore, it comprises more economical sectors (e.g. non-industrial); including services e.g. IT and logistics; and additionally some of the sectors have been combined e.g. textile and leather or wood, furniture and paper, reflecting the actual composition of clusters and sectors in Romania.

The textile sectors marks a normalized competitiveness index P* = 0,47 (maximum=1 in the automotive industry) in the Cluster Study and a ICCS* = 0,24 (maximum =1 in the food industry). The difference highlights the importance of the sectors in terms of employment.

Coming to the cluster level, ASTRICO NE and Romanian Textile Concept mark a competitiveness index C= 18,62 and respectively 17, 61 (maximum=24,71 automotive Dacia-Renault).

6. **TRENDS IN TEXTILE CLUSTER DEVELOPMENT**

At the moment there is a gap of at least one stage of cluster development between Romanian and European clusters (if seen in a 4 stage cycle: generation – development - excellence - internationalisation), i.e. Romanian clusters are in the generation (very few have passed into the development phase) while European ones find themselves in development-excellence phase, e.g., only 5 Romanian clusters have been benchmarked according to ESCA (The European Secretariat for *Cluster* Analysis) methodology to be awarded bronze label (ESCA), out of which Romanian Textile Concept

Another problem lies in the "vertical" way of considering industrial sectors according to NACE codes etc. This model, unfortunately still persisting in Romania, becomes more and more obsolete. Clusters are innovative structures per se which imply cross-sectorial cooperation: creative industries, mechatronics, energy, green technologies, smart cities are topics that become more and more relevant.

Therefore, the Romanian Cluster Association has started the shaping up of 2 cross-sectorial cluster networks, i.e. creative industries and green technologies, the textile clusters playing the central role in the first one.

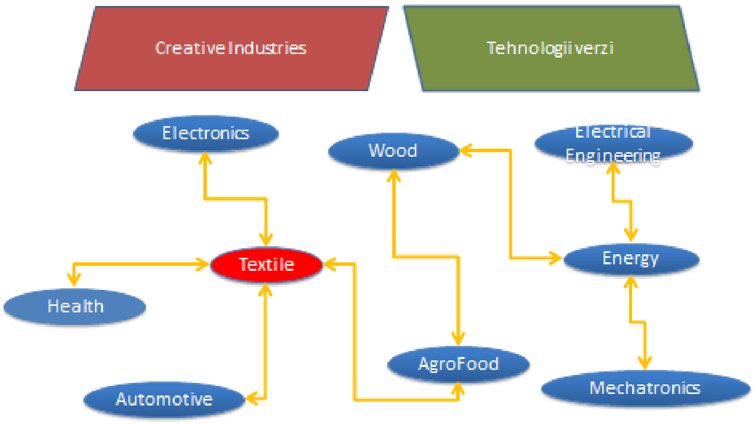

Figure 6. The role of textiles in cross-sectorial cluster cooperation.

7. CONCLUSIONS

At present, the textile industry in Romania is a fundamental economic branch at national level and it covers the whole country, with concentration in 4 regions: NV, NE, Centre and Bucharest. It also represents an important social stability factor, as the clothing subsector employs the highest number of people in Romania's processing industry.

As SMEs have a high weight in the structure, the sector employs highly qualified professionals, but there are low investments in high technology.

The industry has a low volume of production in the primary sector (yarns, woven fabrics, knitted fabrics, nonwoven etc) relying on the import of raw materials.

Romania has the natural resources to develop the production of yarns and silk and wool fibres, as well as the production of bast fibres of flax and hemp but the investments are expensive.

In the clothing subsector, in recent years, there is a constant renewal of the own creations, with detrimental effects for lohn.

The development of technical textiles, of products with destination specific functionalities (antibacterial, antifungal, fire proof, conductivity, high comfort) can be, according to EURATEX [13], a chance for the future development of the textile industry.

The world trends give hope that the textile industry can be energized in countries with an average development, including Romania.

Taking into consideration the weight of SMEs in the textile industry, the development of organizational structures in support of SMEs, such as clusters, is a necessity.

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THE “ROMANIAN TEXTILE CONCEPT” CLUSTER AND THE “NOATEX” POLE OF COMPETITIVENESS

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Keywords: Textile, garments, cluster, Pole of competitiveness

Abstract. *After the integration in the European Union, and in the context of the international crises, the Romanian textile companies must align themselves to the international trends in order to face the competition and manage to not only survive, but to gain a good position on the market and establish themselves as important players on the market.*

This is possible by abandoning the traditional methods of a traditional factor-driven economy, methods already obsolete, by conquering a new position in the market by means of high quality and a strong brand image.

But, as only the strong and united industries have the power to find the resources to invest in innovation, marketing, promotion, creative design, the clusters and Poles of competitiveness prove to be the best form of organization for commercial information, communication and business cooperation, the adoption of these organizational forms representing an important milestone in the evolution of the Romanian economy.

An example in this sense is the Romanian Textile Concept Cluster, member of the Noatex Pole of Competitiveness. Both entities have assumed the role of these types of organizations, not just at micro level, but also at macro level, striving through their activities to achieve the development not only of their members, but also the development of the regions and of the industry in which they operate and, through inter-disciplinary activities, the development of the entire economy.

1. INTRODUCTION

After the integration in the European Union, and in the context of the international crises, the Romanian textile companies must align themselves to the international trends in order to face the competition and manage to not only survive, but to gain a good position on the market and establish themselves as important players on the market.

Thus, they must abandon the traditional methods of a traditional factor-driven economy that are still functioning in Romania although they have been proven by M. Porter to be obsolete, they must abandon the advantage of the cheap workmanship and conquer a new position in the foreign market, i.e. the medium and high segment, which corresponds to a high quality and a strong brand image.

The individual companies, especially the small and medium ones that usually form this industry do not have though the power to forge themselves, by themselves, on a mature market, only the strong and united industries being able to find the resources to invest in innovation, marketing, promotion and creative design.

Therefore, the idea of cluster has become more and more present in the Romanian industries, being considered the best form of organization for commercial information, communication and business cooperation.

2. THE ROMANIAN TEXTILE CONCEPT CLUSTER

2.1 The organisation and structure of the cluster

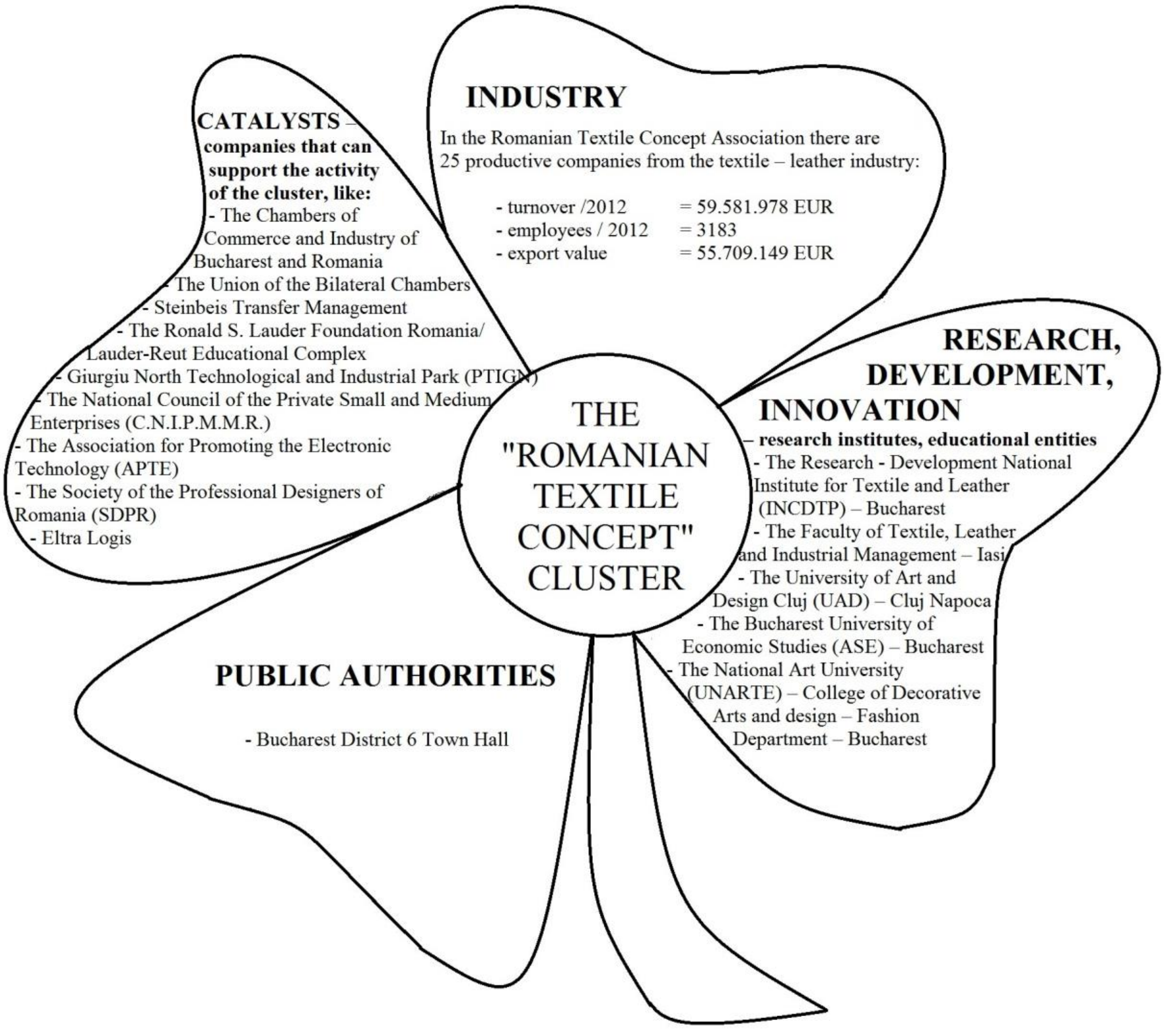

Figure 1: Organisational system of the Romanian Textile Concept Cluster

The Romanian Textile Concept (RTxC) cluster is organized as a natural platform for public-private partnership, on the "Four Clover" model, model that best adapts to the Romanian reality[1].

In the “Four Clover” model, it appears a 4th player besides the ones from the classic “Triple Helix” model[2], the following categories being represented in the cluster:

- The industry, as a driving force of cluster
- The research - development sector (universities, research institutes)
- Public authorities, with role of active support of the business environment
- Catalyst organisations and companies, with role in the functioning of the cluster (consulting companies, advertising, media, etc.).

2.2 The objectives of the cluster

The driving force of the Romanian Textile Concept (RTxC) cluster is the professional association with the same name, an association that represents also the cluster management entity. Romanian Textile Concept (RTxC) is a professional association founded in 2011 by the unconditional agreement of 10 founding companies, manufacturing companies with old traditions in the garments, knitwear, footwear and leather goods industry from the Bucharest - Ilfov area, which have found this form to formalize the collaborative relationships they already had. In the last 2 years other companies from the textile and leather industry, productive companies or performers of services, have joined the Association of Romanian Textile Concept (RTxC), reaching a number of 28 members of the association.

The main objectives of the cluster were grouped into four main directions:

1) INNOVATION, RESEARCH, DEVELOPMENT
- Creating and organising a "Textile Technological Centre "
- Creating and promoting the brand of the cluster
- Promoting new innovative technologies and developing new sub-sectors: technical textiles, intelligent textile, nanotechnologies, eco-design, a.o., for cooperating with other interdisciplinary sectors
- Promoting new and more efficient methods of using both the materials and energetic resources
- Promoting methods of increasing the added value of the products made

2) EDUCATIE, INSTRUIRE
- Implementing systems of training, qualification
- Implementing systems of perfecting the professional training
- Facilitating the connection between the producers and the young designers
- Improving the existing working conditions for the members of the association by offering guidance for obtaining funds and implementing the OHSAS 18001 and SA 8000 systems of certification

3) MARKETING, INTERNATIONALISATION, COMMERCIAL
- Facilitating the participation at domestic and international fairs and exhibitions
- Elaborating market researches for approaching other markets then the UE one
- Creating a portal for the members of the cluster, which to include: raw materials

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[1] ; Michael Guth, ZENIT GmbH; Daniel Cosnita, Inno Consult - *R E P O R T - Clusters and Potential Clusters in Romania - A Mapping Exercise* (February, 2010).

[2] ETYKOWITZ, H, *The Triple Helix of University-Industry-Government Implications for Policy and Evaluation*, Institutet för studier av ut b i ldning och forskning, Stockholm. (2002)

and accessories data base, requests, a.o.

- Promoting the activity of the association and cluster by website, flyers, a.o.
- Organising promotional and informational events

4) PROJECT MANAGEMENT

- Elaborating the strategy of the association and cluster
- putting into practice the existing cooperation through joint projects
- Initiating and managing fundraising projects

2.3. Projects of the cluster

According to Good Practice Guide for Clusters[3], "The clusters are a long-term solution, they are not suitable for a thinking limited to a short-term approach, since they represent a strategic dimension that lays the basis of the integration of all the key actors. Each cluster must be dynamic and have the ability to respond to new conditions. Foreseeing this and establishing strategies for future success are the results of implementing an organizational culture, a specific brand and its strategic management specific to the cluster."

These points were taken into account also by the Romanian Textile Concept (RTxC) Cluster in the strategy developed for 2012 - 2017, according to which it has already acted in various ways, our of which we mention the development and submission of projects of common interest to all the members of the cluster.

The Training, Education Department of the Romanian Textile Concept (RTxC) Association has elaborated 2 projects and submitted them for obtaining European funding from the Sectoral Operational Programme Human Resources Development (SOP HDR), which would meet the requests of the members of the cluster to have trained workers:

- **"TEXFEM – INCREASING WOMEN'S SKILLS AND QUALIFICATIONS – PROMOTING THE EQUALITY OF CHANCES IN THE TEXTILE SECTOR"**

This project aims to provide the members of the cluster the opportunity to qualify theirs workers. It also wants to solve a problem the industry is facing now, namely to provide training courses in trades for which no other school system exists: pattern makers, sample maker, etc.

The project also intends to support and innovation and management course, too, a specialization very current and that will be very useful in the future.

Partners in this project are ICPE - Research Design Institute of Energy – project leader, INCDTP - National Research and Development Textile and Leather Institute, the RTxC Association and the Gheorghe Asachi University - Faculty of Textile and Leather Industrial Management

Among the activities proposed in this project are:

- attracting and establishing a target group of 325 women for training or changing their qualification
- an attracting and improving a target group of 216 women for training courses: pattern makers, sample makers, ICT, innovation management
- counselling/guidance for 50 women, who will have a chance to a career after 1 year
- campaign to promote success stories of women in management positions in the textile sector

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[3] coordonator Adrian Dumitru Tantau, *Ghid de buna practica pentru clustere* , Free Group, Bucuresti (2011)

The project has a two year implementation period and will cover the Bucharest – Ilfov, South Muntenia, Southeast and Northeast regions

- **“PROMISE – PRACTICUM IN FASHION – THE TRANSITION FROM SCHOOL TO ACTIVE LIFE”**

This project aims to meet the future fashion designers’ need to perfect their training by practicum (practical studies) in the companies from our cluster, with the hope that in the future these young people will collaborate on the development of collections for both cluster, and for the brands owned by the companies in the cluster.

The project's partners are the Romanian Textile Concept (RTxC) Association – leader, Gea Strategy & Consulting and the University of Art and Design Cluj-Napoca - the Fashion Design Department and the activities proposed are the following:

- collaboration with the National University of Art Bucharest (Fashion Design Department) and Gheorghe Asachi University - Faculty of Textile and Leather Industrial Management
- career counseling and guidance
- study visits for 300 students in various Romanian textile companies
- preparing training internships in companies
- organising and offering internships in companies for about 100 students
- selecting 10 students that will collaborate with 10 companies for making 10 mini collections (minimum 10 pieces)
- "Fashion in context" gala – fashion show for presenting the collections created by the aforementioned 10 students

The project implementation period is 18 months and the area of development will include the Bucharest – Ilfov, South Muntenia, Southeast, Northeast, Northwest and Centre region

The Project Management Department of the Romanian Textile Concept (RTxC) Association has initiated a project for the cluster’s management with structural funding through the Sectoral Operational Programme Increase of Economic Competitiveness (SOP-IEC), priority axis 1.3.3., by which to be able to achieve part of the objectives proposed, especially on the Internationalisation, Marketing and Commercial line.

- **“CLUSTER MANAGEMENT” PROJECT**

Collaborators on this project, initiated and led by the Romanian Textile Concept (RTxC) Association, as management entity of the cluster with the same, name will be all the cluster members (research institutes, educational institutions, manufacturing companies, companies with a catalyst role, etc.).

From the proposed activities we mention:

- Establishing the cluster development plan
- Developing strategies and campaigns to promote the cluster
- Developing market researches in order to tackle new markets
- Organising workshops, seminars, "Cluster Day"
- Identification of new customer services
- Participation in international trade fairs and trade missions
- services of training and qualification of the personnel, exchanges of experience

The project will have an implementation period of two years.

The Marketing, Internationalisation, Commercial Department of the Romanian Textile Concept (RTxC) Association is involved in various projects designed to promote the image, the activities and the products of the cluster members, from which we mention:

- **“PROMOTING THE CREATIVE POTENTIAL OF THE ROMANIAN TEXTILE INDUSTRY”**

This is a cultural project included in the contest for Cultural Projects for 2013, launched by the Administration of the National Cultural Fund from Romania.

Partners in this project are the Romanian Cluster Association (CLUSTERO), INCDTP - National Research and Development Textile and Leather Institute, the Romanian Textile Concept (RTxC) Association, the National University of Art Bucharest – the Faculty of decorative Arts and Design.

The Innovation, Research, Development Department of the Romanian Textile Concept (RTxC) Association has initiated various projects in collaboration with INCDTP – the National Research and Development Textile and Leather Institute, with financing from various European sources (Eureka, FP7, and other programmes), for applying in production the latest researches in the field (textiles with medical purposes, customised garments for people with disabilities, smart-specialisation - intelligent, thermoregulatory textiles, with nano-particles, etc.)

One of the most important projects of this department is the one for creating and organising a Textile Technological Centre - CTT RO TEX Bucharest, with which the management of the cluster intends to assure that the productive companies are up to date with the latest pieces of information regarding the technology in the field, have an easiest access to the technological transfer of the newest research – development projects. Not lastly, this Centre is intended to be a first step in the establishment of new innovative companies that can lead to the development of the textile – leather sector (the reindustrialisation being also a point in the strategy of the country).

- **“TEXTILE TECHNOLOGICAL CENTRE – CTT RO TEX BUCHAREST” PROJECT**

The main activities of the centre will be of innovation – research support, commercial and informational support and will be divided in departments specialised on specific directions:

- Health and hygiene department (prostheses, orthoses, implants; sterile fields; antimicrobial textiles, bandages, dressings, gowns etc.; hygiene and beauty)
- Fashion Department (fashion trends, fashion design, technical documentation, etc.)
- Yarns, fabrics, non-woven and textile chemistry Department (pilot plant for parameter measurements in industrial regime, specific treatments for each area of application, etc.)
- Military equipment and protective work Department (camouflage equipment; fire retardant products; tents, parachutes, bags; workwear; uniforms; shoes and leather products; sport outfits, etc)
- Transport, construction Department (thermo, phonic, UV, shock insulation materials; geo-textiles; composites; automotive specific fabrics; filter systems)

The technology transfer center will serve not only the members of the cluster and of the Pole of competitiveness, but is intended to be a center open to all the companies in the industry in the country and even from abroad.

3. THE “NOATEX” POLE OF COMPETITIVENESS

3.1 The organisation and structure of the Pole

The management of the Romanian Textile Concept (RTxC) Cluster has initiated in 2012 the establishment of a Pole of competitiveness with national representativeness, called “NOATEX”, which is formed by the 3 clusters existing then in the textile field, namely:

- The “Romanian Textile Concept (RTxC)” cluster – South Muntenia and Bucharest - Ilfov regions
- The “Astrico NE” cluster –Northeast region, with headquarters in Piatra Neamt
- The “Traditii Manufactura Viitor” Cluster (TMV) – Southeast region, with headquarters in Focsani

Besides the members of the 3 clusters other Higher education institutions, R&D institutes and catalyst companies have joined the Pole.

The exclusive management of the Pole was entrusted to a consulting firm specialised in management.

3.2 The objectives of the Noatex Pole of competitiveness

Amongst the objectives proposed by the members of the Pole we mention:

- The Pole aims to position itself as a best practice example, valuing the expertise of the management entity, the successful examples from other European countries, etc.
- The development and integration of high-potential niches: technical textiles, smart textiles, fashion design, etc.
- Increasing the innovation capacity of the members
- Increasing the attractiveness of new markets outside the EU (Middle East, Asia, Russia)
- Increase technological level by investments

3.3 The projects of the Noatex Pole of competitiveness

In order to achieve the objectives proposed, the management of the Pole has decided to issue a package of projects of common interest (23 projects) by forming some consortiums between the members of the Pole, as it comes out from the strategy of the Pole.

As an opportunity for accessing structural financing appeared from the Sectoral Operational Programme Increase of Economic Competitiveness (SOP-IEC), priority axis 1.3.1, out of the 23 projects, 13 have been selected and submitted for approval, being now in the last evaluation stage.

The package is grouped on the following types of projects:

INVESTMENT PROJECTS

- Technology upgrade / production capacities increase
- Upgrading / building production facilities
- Technological and ICT acquisitions for a more efficient use of the raw materials

RESEARCH PROJECTS

- Making Eco products through organic processes of finishing the 100% natural textiles
- Customised clothing - Made to measure

SOFT PROJECTS

- The management of the Pole of competitiveness

- Supporting the access to new markets by organizing trade missions and market researches
- Expanding the access to new markets / customers through participation in fairs
- Innovative solutions to capitalize the Romanian traditional elements in fashion lines in order to achieve a country brand
- Developing strategies for implementing innovative solutions and creating new products in order to access new markets through the integration of young designers in the production process
- Increasing the economic competitiveness through the development of strategic marketing activities

4. CONCLUSIONS

The Romanian Textile Concept (RTxC) cluster was formed as a response to the needs of the textile companies to be united, both in what regards their own individual interests, and of the common ones, in order to be a promoter of this field, to be the engine of the technology transfer and of the innovation from the research stage to the industrial production.

The positive reactions, both from the companies, and the authorities, to the existence, activity and importance of the clusters and poles of competitiveness make us believe that the Romanian economy is in a good, although rather slow and lengthy, process of upgrading from the traditional models and becoming a competitive sustainable one.

These are the aspiration based on which the strategies of the Romanian Textile Concept Cluster and of the Noatex Pole of Competitiveness are build, both entities having assumed the role of these types of organizations, not just at micro level, but also at macro level, striving through their activities to achieve the development not only of their members, but also the development of the regions and of the industry in which they operate and, through inter-disciplinary activities, the development of the entire economy.

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THE ADVANTAGES OF USING WOOL FIBERS EMBEDDED IN THE INSULATION SYSTEMS FOR CONSTRUCTION

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Keywords: wool, fiber, insulation, construction, system

Abstract. *This paper presents aspects of the advantages of using wool fiber construction. By using wool fibers in construction is included in the European eco trend. Insulation of buildings and reduce carbon dioxide emissions is concerned both at national and European level. By efficient thermal insulation of buildings is reduces energy consumption or gas used for heating. Also use natural materials for insulation, allow good breathing walls and reduce the formation of condensation on the walls and the destruction walls. The usage ways of the wool in construction may be like a panel or like waves fibers rolls. Regarding the costs for this natural wool insulation, this type of insulation is more expensive than traditional insulation materials like fibreglass. It is also 100% natural, renewable, sustainable, and recyclable. This insulation is safer and easier to install.*

1 INTRODUCTION

Intense concerns for using wool as insulating material in construction have been in Ireland, UK, U.S. and New Zealand. In New Zeeland the Ecowool product made by Eco Insulation Ltd. (1) is available as natural Ecowool and recycled Ecowool. Natural Ecowool and EarthWool insulation products are 100% pure New Zealand fine, white wool. Recycled Ecowool is coloured wool sourced from New Zealand woollen product manufacturers [1].

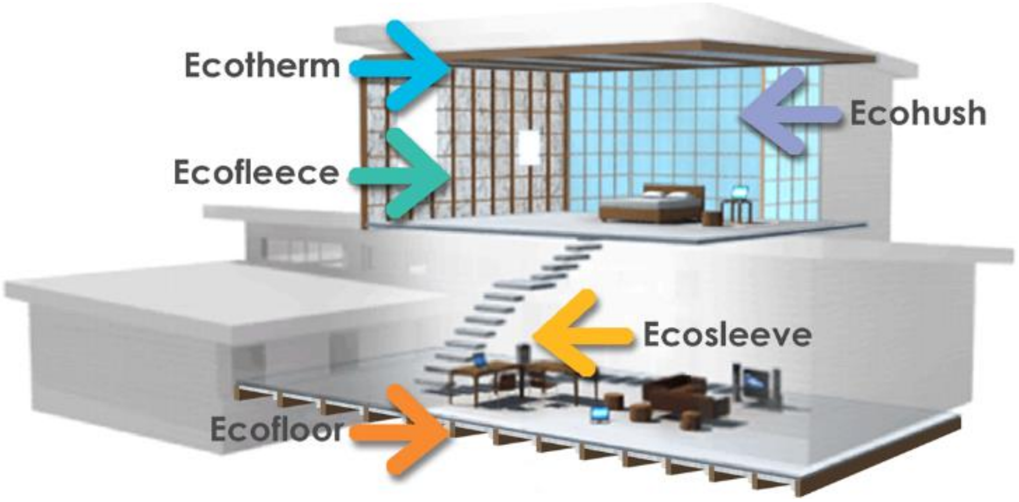

Figure 1: System insulation for house – produced by Eco Insulation Ltd. New Zeeland [1]

In Ireland the company Sheep Wool Insulation Ltd. produce Sheep Wool Insulation Premium product that is a range of grey coloured sheep's wool thermal / acoustic insulation rolls [2]. Premium rolls are suitable for a wide use of applications, including internal & external walls, ceiling & rafter level applications and floors. This thermo insulation product is a safe material to handle and install. Wool fibres are completely safe to touch and work with, requiring no special handling or protective equipment. The insulation rolls can be installed on top of existing glass or mineral wool, reducing the opportunity for their potentially hazardous particles to become airborne [2].

Figure 2: Wool thermo insulation produced by Sheep Wool Insulation Ltd. Ireland [2]

In UK the company Black Mountain Insulation Ltd. Has developed the product thermo insulation based on wool fibres. Black Mountain sheep’s wool insulation has approximately 95% natural fibre content – one of the highest available on the market. This combined with the resilient nature of sheep wool insulation ensures that this natural insulation will maintain its structure and performance throughout the life of the building. This product has recently submitted to independent endurance testing to be used in the project to build a roof over the collapsed Chernobyl power station - they were proven to perform for the equivalent of over 100 years absorbing and releasing moisture, treatment longevity, nor did they compact even when subjected to continued condensation cycles [3] .

Figure 3: Wool insulation waves - Black Mountain Insulation Ltd. UK [3]

In the US the Oregon Shepherd company is producing the wool insulation products: PermaLoft and PermaBatt [4]. These products can be used in exactly the same way as traditional insulation products, providing excellent warming and cooling properties for walls, floors, ceiling and roofs of homes, commercial and industrial buildings. The PermaBatt product is designed to fit between vertical timber framing, or lay in a blanket form. The batting comes in a variety of widths and thicknesses [4].

Figure 4: PermaBatt and Permaloft wool insulation products–Oregon Shepard US [4]

In Germany the company Alchimea Naturwaren GmbH is producing the Alchimea wool insulation product that has good thermal insulation properties, preserved even wet [5]. The moisture absorption and rapid failure attenuates excellent extreme temperature variations [5].

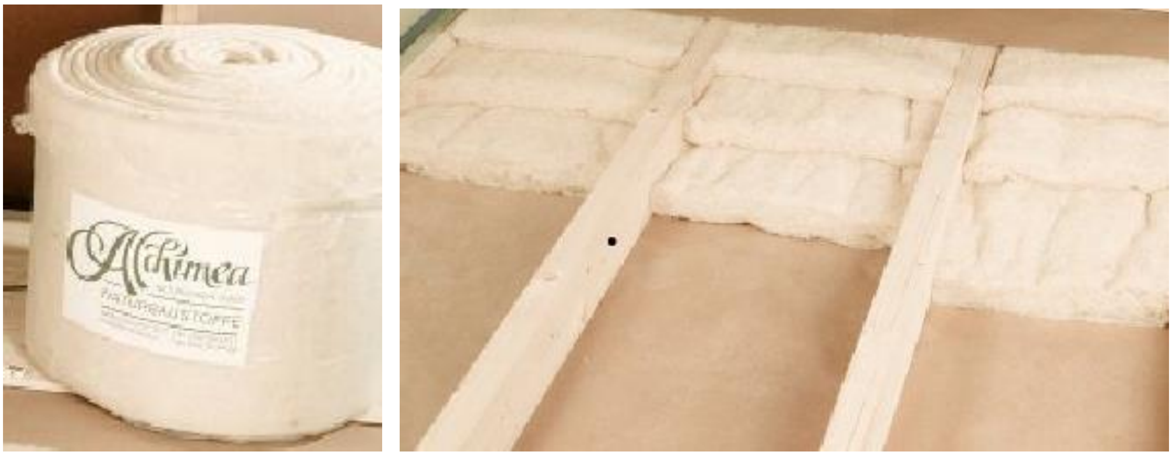

Figure 5: Alchimea wool insulation product – Germany [5, 6]

Unfortunately in Romania currently is not produced thermo insulation materials made by wool fiber for construction. Currently in Romania is present the Alchimea wool insulation product made in Germany.

Despite this we want a revival of this sector in Romania which will be materialized in the next future by getting an experimental model of wool insulating material.

2 GENERAL SPECIFICATIONS

Wool insulation commonly can be used like panels or from wave fibers roll. Generally, wool panels have thicknesses of 50 mm to 100mm, with widths of 400 mm and 600 mm, and lengths of 1000 mm. Most manufacturers provide custom sizes as well and bats and ropes are easy to cut once on site. Wool insulation costs is higher than conventional fiberglass insulation, but does not require the use of protective gloves, and may have significantly lower health risks to both the building occupants and the installation workers. Installing wool insulation is very similar to installing conventional insulation.

Wool fibers are hygroscopic, absorbing and releasing moisture without reducing thermal performance. The fibers are breathable. While absorbing this moisture, the wool releases energy in the form of heat, raising the temperature of surrounding areas. In warmer weather the process is reversed – as the wool releases this moisture it creates a cooling effect. The wool insulation has a highest performing fibrous insulation, maximizing energy efficiency. The thermal conductivity values (0.036-0.039 W/ m·K) from table 1 it is show that sheep wool insulation have appropriate values by classical insulation materials used in building, and this is an important point to sustain the usage of the sheep wool panels for interior building insulation.

Sample name	Thermal conductivity **λ**[W/ m·K]	Thickness [mm]
1.Sheep wool insulation- Germany	0,036	50
2.Sheep wool insulation -Ireland	0.039	50
3.Sheep wool insulation -UK	0.039	50
4.Fiberglass insulation ISOVER	0,039	50
5.Mineral wool insulation ISOVER N	0,036	50
6.Extruded polystyrene insulation	0,045	40

Table 1: Thermal conductivity

3 WOOL INSULATION ADVANTAGES IN SUPPORTING THE PRODUCT DEVELOPMENT

The wool insulation has several advantages, even the production costs make to product to more a little bit expensive:

- Health and Safety

The wool insulation it is easy to handle, requiring no special protective clothing or equipment during installation or throughout the serviceable life of the building. The product made by using the mineral or glass fibers it is have a toxicity for worker when this waves or panels are mounted on the walls.

- Resistance to mold and fungus - walls breathings

Wool naturally resists mold and fungus due to its natural moisture transfer properties. Wool Insulation allows your home to breathe by absorbing moisture, chemical, and/or odor laden air and transferring it outside as temperatures change [4]. A permeable house wrap applied over exterior subsiding provides for this passive exchange. If it is used the extruded polystyrene insulation inside this is cause the formation of mold on the walls.

- Formaldehyde absorption

The natural fibers have the capability to absorb chemical substances. Tests carried out by the Central Testing Facility in Tokyo, Japan found that when formaldehyde was released into a chamber, wool was able to absorb 96% of the formaldehyde within several hours [4].

- Acoustic

Wool insulation products naturally enhance the acoustic properties of a building. This advantage is due to the bulky shape and presence of the interstationary air.

- Friendly environment

The production of wool insulation is energy efficient, using approximately 10% of the embodied energy it takes to manufacture fiberglass insulation. Is knows the fact that mineral – glass wool production process is energy intensive process.

The natural insulation products made by using the wool fibers are 100% sustainable, biodegradable, and renewable. This type of insulation is a part of eco trend system (figure 6).

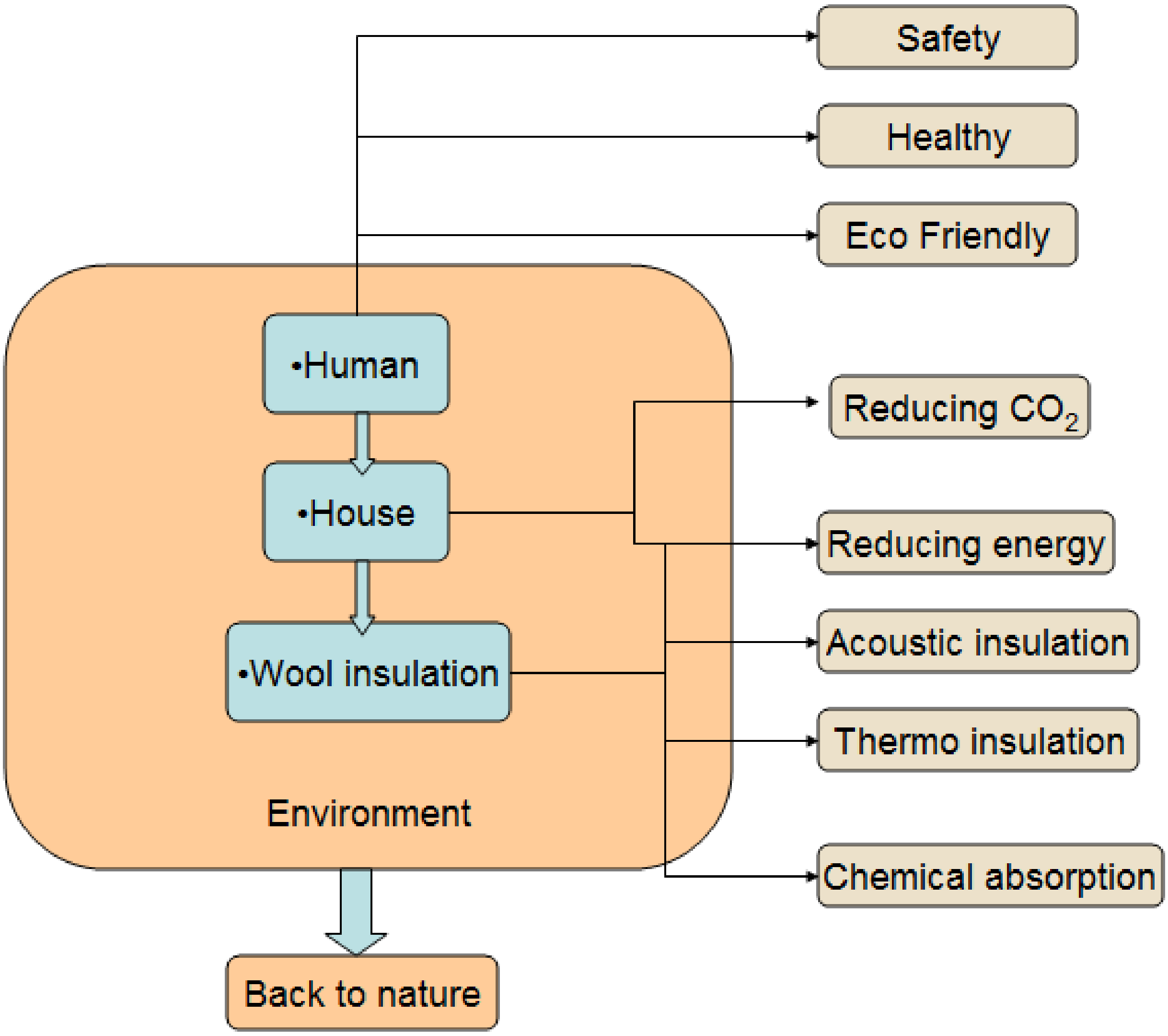

Figure 6: Human-House-Natural Insulation integrated in eco environment system trend

4 CONCLUSIONS

Wool Insulation is made from 100% natural wool and is eco friendly. It is a sustainable and renewable resource. By using the wool insulation it is contributing to a healthy and natural clean environment.

The natural insulation folds perfectly on green building trend by reducing carbon dioxide emissions and energy consumption.

By acoustic and thermal insulation of buildings using natural wool is made for people a healthy and pleasant habitat.

The wool thermo insulation system acts as a buffer between the cold damp weather outside and the warm dry environment inside your home. Wool fibres absorb moisture to keep the building warm during winter, and releases moisture in summer to keep the building cool. This moisture transfer is not possible if there are used the extruded polystyrene on internal insulation. The same moisture transfer can be realized by using the mineral/glass wool, but the disadvantage is that more energy is necessary to obtain mineral wool and this product is toxic and is needed for an increased protection for the worker that mount this insulation. The sheep wool insulation can be used only for interior building insulation. A little disadvantage in using the wool insulation is that it is necessary a moth treatment. The other insulation mineral wool and extruded polystyrene are not destroyed by mites. The interior sheep wool insulation is mounted on wood structure.

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MULTIFUNCTIONAL WOVEN FABRICS FOR EMERGENCY SHELTERS AND OTHER APPLICATIONS

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Keywords: Woven fabric, emergency shelters, tents, multifunctional textiles

Abstract. *Modern textile technology comprises accomplishing of innovative high-value added textile products with multi-functional character. For materials manufacturing, the textile products have some substantial advantages, like light-weightiness, flexibility and resistance and this is a reason for producing technical textiles. A research is conducted upon a need of the market. The aim of our research was the manufacturing of several types of woven fabrics from cotton and polyester with special treatments and multi-functional character for various types of destinations: emergency shelters, tents for tourism and leisure etc. This type of fabric has special hydrophobic, fire-proof, anti-microbial and resistance properties and was accomplished by a team of INCDTP and Technical University "Gh. Asachi"-Iasi.*

1 INTRODUCTION

Technical textiles are a field envisaged by the European strategy, and consist of textile materials with technical applications, in fields like: medicine, industry, safety, agriculture etc. This categories of new high-added value textile products ensemble the good properties of textile materials (light-weightiness, flexibility, resistance) and offer adequate solutions for the specific technical purpose. Their implementation on the market has to fulfill both customer needs as well as technological possibilities. Textile producers share an intelligent market and have to compete very hard in order to satisfy the consumer. Various marketing trends are used by textile companies in this competition. We would like to focus upon two of them, highlighting the implementation of a research result into production.

The major complementary marketing trends distinguished are:

- ➔ Technology Push
- ➔ Market Pull

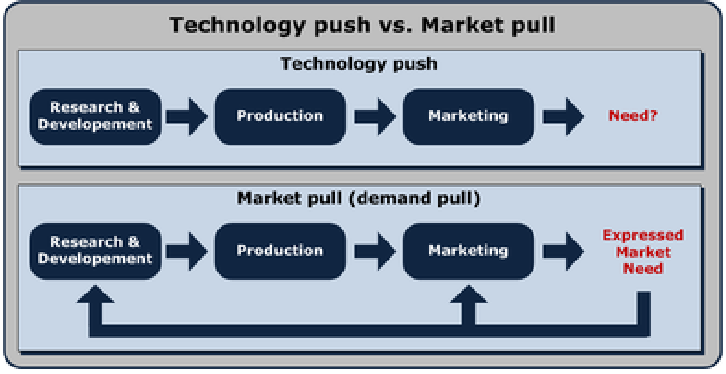

Fig. 1. Marketing strategies

Technology Push is a strategy of a company to propose for the market the latest technology trends, developed inside the company. Market Pull is a strategy of a company to search upon the latest requirements of the market.

Research and development is performed as result of an identified need on the market. Both strategies are relevant for an innovating producer, and we have to take into consideration their concurrence in order to implement research results on the market.

The main research result presented in this paper is a technical textile product, performed after identification of a major need: emergency shelters for distressed people.

The sheltering of people in emergency situation like floods, fire or other natural disasters is a very important aspect in national security. The accomplishing of a new, modern solution for this type of problem, offers safety and confidence to distressed people.

The obtained products consist in a multifunctional woven fabric, having as destination emergency shelters and other applications. The market imposes the following requirements for technical fabrics:

- fire proof character – for emergency shelters;
- water proof character – for textile architecture and consumer goods;
- anti-microbial treatments or combinations of such treatments – for hygienic-sanitary destinations;
- light coatings – for applications in tourism and leisure.

For this purpose, several woven fabrics, from cotton and polyester have been performed. The design of the new woven fabrics with destination tents, tarpaulins and textile architectures, aimed reaching the following parameters:

- Fabric mass between:
    400-450g/mp, for cotton fabric;
    100-250g/mp, for fabrics from Polyester filamentary yarns;
- Breaking force: minimum 300N;
- Breaking elongation, 20-28 %,
- Thickness, 0,3-2,9 mm;

Recommended finishing: dyeing followed by fire-proofing treatment, hydrophobic treatment or coating.

The development of equipments and products destined for emergency situations consists in the accomplishing of the following activities:

- Identification of new types of yarns and categories of finishing products, enabling processing by non-conventional weaving;
- Designing and performing of new fabrics destined especially for performing tents for protection in emergency situations, but also for tents with touristic destination;

- Finishing by covering with multi-functional coating, using new generation of finishing products;
- Testing by laboratory investigation of the raw materials, semi-finished materials and finished products;

The production of an innovative technical fabric with multifunctional properties aims to cover a stringent necessity identified in emergency sheltering of distressed people.

2. EXPERIMENTAL PART

Technological design elements for fabrics structures have been used, multi-functional finishing and treatment (fireproof and hydrophobic), in order to ensure safety elements and comfort for the people in shelters. The technological flow for the accomplishing of new fabrics, destined for tents for sheltering humans, involves the processes in figure 2:

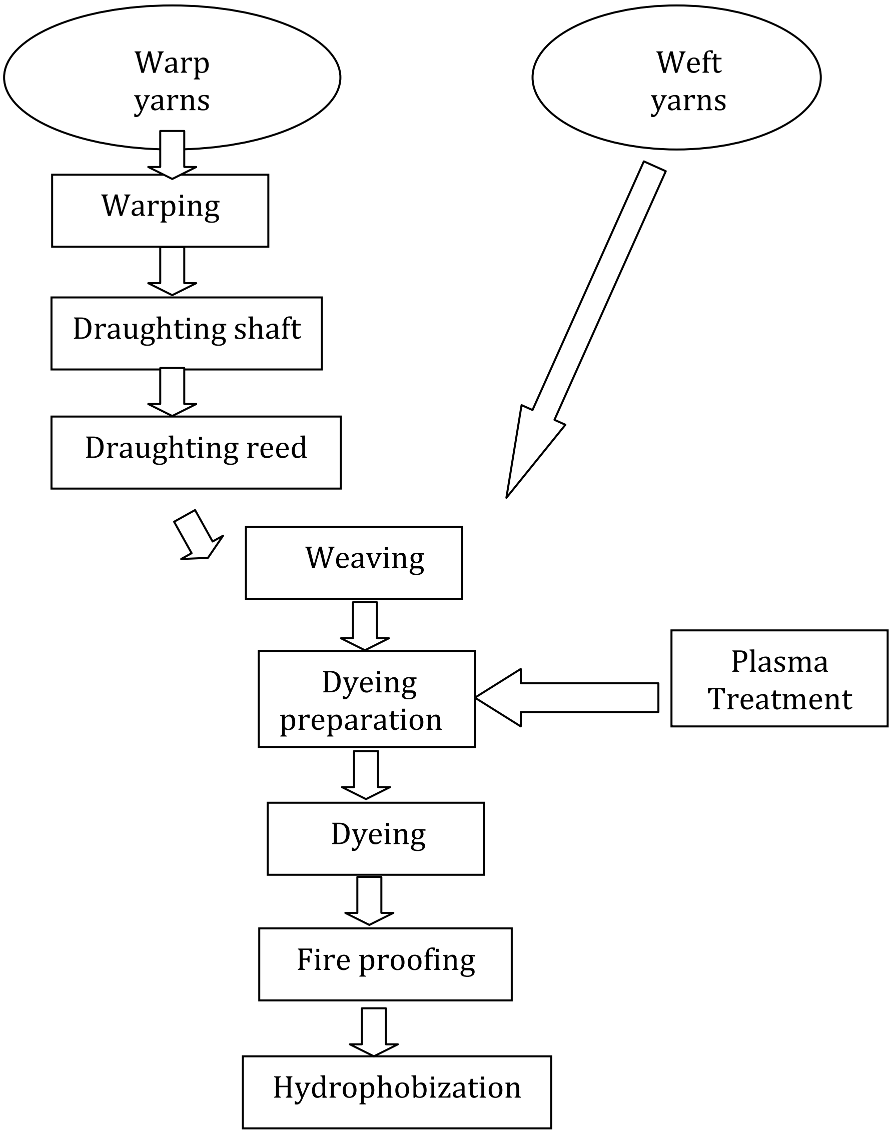

Fig. 2. The technological flow for performing fabrics, destined for shelters

The technology flow presented in figure 2 is accordingly to the technical possibilities of INCDTP with physical mechanical parameters specific for tents and shelters.

Fig. 3. Finishing of the fabric

The technical fabrics performed have specific properties destined for satisfying the basic requirements, ensured by raw materials, structure and finishing. Several doubled and twisted yarns from cotton and filamentary yarns from Polyester or Polypropylene have been experimented, on classical and non-conventional weaving machines. The weaving machines used in manufacturing the new types of woven fabrics are the non-conventional weaving machine type SOMET THEMA11 for Polyester yarns and the weaving machine type STB2-216 for cotton yarns.

The selected raw materials: cotton twisted yarns Nm20/4 and Nm 10/2, processed on the machine STB2-216 and polyester filamentary yarns 80dtex/32f/350z, processed on the machine Somet Thema11.

Three new types of fabrics have been performed within the research activities: woven fabric from 100% twisted cotton yarns (performed on non-conventional weaving machine with micro-shuttle STB 216), woven fabric 100% multi-filamentary Polyester (on the gripper weaving machine SOMET THEMA11) and a woven fabric from Polypropylene (on a classical weaving machine with shuttle).

The justification for the selection of these raw materials consists in the following specific characteristics:

Cotton yarns:

- large variety of types and linear density;
- low cost;
- good process-ability;
- may be subjected for finishing of the surface by immersion, coating, calender finish;
- absorption and releasing of humidity, generating the effect of auto-water-proofing in case of the long-drawn contact with water;
- capable of processing on gripper or shuttle weaving machines, specific for many industrial companies;

Polyester yarns:

- large variety of types and structures;
- good tenacity and tear resistance;
- UV resistant;
- reduced ratio mass/ surface unit

The yarn properties are presented in table 1.

Table 1 – Physical-mechanical parameters for Cotton and Polyester yarns

Yarn type / Parameter /measurement unit	Nm20/4 Cotton 100%	Nm10/2 Cotton 100%	80dtex/ 32f/350z PES 100%	167 dtex/ 144f rotoset PES100%	Standard method
	V1 Warp	V1 Weft	V2 Warp	V2 Weft	
Linear density: dtex (den) Tex Nm	 - 100,57x2 9,94/2	 - 51,4x4 19,5/4	 83,1 (74,8) - -	 168 (151,5) - -	SR EN 2060/97
Breaking force (N)	24,47	30,06	2,64	5,77	SR EN 2062/2010
Breaking elongation (%)	8,31	10,69	31,96	20,35	SR EN 2062/2010
Torsion (tors/m)	339	562	350	Without torsion	SR EN ISO 2061/2011
Yarn Twisting (tors/m)	311	306	-	-	SR EN ISO 2061/2011
Diameter (mm)	0,875	0,762	0,25	0,79	SR EN ISO 13152/93

As consequence of the processing of the raw materials accordingly to the technology flow in fig. 2, several types of woven fabrics resulted. In Table 2, two of them are described.

Table 2 - Physical mechanical properties for raw and finished fabrics

No	Fabric type / Parameter / measurement unit		**Raw fabrics**		**Finished fabrics**	
			Cotton 100% V1	Poliéster 100% V2	Cotton 100% V1	Poliéster 100% V2
1	Width (cm)		130	168,5	121	153
2	Mass on surface unit (g/sqm)		430	130	442	148
3	Density no.yarn/10 cm	Warp	105	742	110	808
		Weft	84	370	96	418
4	Maximal breaking force (N)	Warp	134	973	142	1168
		Weft	129	1145	141	1262
5	Breaking elongation (%)	Warp	28,9	36	31,2	34
		Weft	13,59	28,6	17,6	37,8
6	Thickness (mm)		1,16	0,36	1,21	0,32
7	Air permeability (l/sqm/sec)		400	95,7	247	112

From the analysis of this data it results that the fabric types obtained within the project, present the suitable parameters for performing temporary shelters for emergency situations.

A slight increase of the density and compactness with direct effect and the increase of the breaking load can be observed after the finishing process. The decrease of the permeability to minimal values which ensures water-proofing can be also observed.

The maintaining of approximately the same values of the finished fabric compared to the raw fabric can be explained by the high level of compactness in the weaving stage. This fact does not permit contraction in wet environment, although the fabric has been finished without tensioning.

The final width of the fabric has been ensured by its free contraction. At the variant performed from polyester fibers, the use of fibers with micro-filamentary yarns has ensured a high level of compactness, stressed by the thermo-fixation operation.

The following warping installations have been used for manufacturing the warp.

Table 3 - Warping installation characteristics

Type of article Characteristic	I -130/430	II -150/140
Raw material		
- Warp	(V1) Cotton Nm10/2	(V2)PES 80dtex/34f/350z
- Weft	(V1) Cotton Nm 20/4	(V2) PES167/144/rotoset
Number of warp yarns	1260	6375
Draughting	8 shaft, dispersed	right
Draughting order	1, 5, 2, 6, 3, 7, 4, 8	1; 2; 3; 4; 5; 6; 7; 8
Draughting reed	2 yarns	5 yarns
Reed linear density:	45 places/10cm	75 places /10cm;
Binding	Plain weave	Satin

Compactness: maximal for each linear density of weft yarns used.

The binding chosen is the plain weave for variant (V1), cotton woven fabric, considered to have the most balanced repartition of the modality for taking over the stresses, the best tear resistance and the best coefficient of filling the blank spaces between the component yarns. The obtaining of balanced properties on the two directions was envisaged for this variant.

For variant (V2) from Polyester yarns, the Satin 8/5 binding has been chosen. This fabric has a smooth, glossy aspect and a high capacity for covering the pores. The shiny aspect of the yarns as well as the effect caused by the Satin binding, determines a reduced capacity of water and impurities retention for the front of the fabric, easiness in mounting and plying, reduced volume in the deposition spaces.

This variant is designed especially for the tents of small sizes with especially applications for touristic purposes.

The width of the fabric – the fabric has been performed with the width of 140 cm in the reed (V1) and 170 cm in the reed (V2).

A raw fabric with the width of 130 cm (V1), which has reached after finishing the width of 120 cm, resulted after weaving.

The fabric from Polyester yarns resulted after weaving in of 168 cm (V2) and reached after finishing the width of 150 cm.

These values of the width have been imposed by the width parameter of the machines in the factory (treatments for boiling, dyeing, fireproof finishing, oil repellent finishing) and of matching the confectioning dimensions with minimal losses.

The technological parameters used have been chosen accordingly to physical-mechanical properties of the yarns, as follows:

For the warping operation

Both warping variants have been accomplished on the Textima warping machine, by using the following parameters:

Number of yarns in band: 100;
Warping speed : 300 m/min;
Warp length : 100 m;
Cone height: 35 mm;
Speed for advance: 0,25 mm/rot;
Speed for plying: 30 m/min;

Several specific adjustments regarding the yarn tension and control in the warping process have been performed.

For the shaft draughting operation

The preparation of the shaft has been performed manually by verifying and placing on each frame of a number of 1000 lamellar heads with oval orifice.

The order for distributing the yarns was: 1, 5, 2, 6, 3, 7, 4, 8 for V1 and 1, 2, 3, 4, 5, 6, 7, 8 for V2, for ensuring a uniform distribution of the stresses.

For the reed draughting operation, there was used a manual method and an alternative repartition of 2 yarns in a reed joint (V1) and 5 yarns in a reed joint (V2).

This procedure has ensured the desired density. By weaving and contracting as consequence of the finishing treatments, resulted the parameters presented in table 2.

For the weaving operation, there were used the current devices for mounting the basis warp as well as the devices for controlled tension for the weft yarns.

The working parameters of the SOMET weaving machine, such as the order of lifting the healds, the tension in warp and weft, have been introduced on the machine console.

At the STB machine there have been performed mechanical adjustments for establishing gauges and replacing changing wheels.

3. DISCUSSION

After the laboratory tests we have selected the variant named CORTINA, presented in table 4.

Table 4 – Woven fabrics type CORTINA

Physical –mechanical parameter	Unit of measurement	Value	Standard method
Width	cm	150 ± 3	SR EN 1773:2002
Mass	g/mp	430 ± 10	SR EN 12127:2003
Mass	g/ml	645 ± 10	SR EN 12127:2003
Warp density	fire/10cm	350 ± 5	SR EN 1049-2:2000
Weft density	fire/10cm	195 ± 3	SR EN 1049-2:2000
Warp breaking force, min.	N	1000	SR EN ISO 13934-1:2002
Weft breaking force, min.	N	1000	SR EN ISO 13934-1:2002
Breaking elongation warp, min.	%	10	SR EN ISO 13934-1:2002
Breaking elongation weft, , min.	%	10	SR EN ISO 13934-1:2002
Air permeability, min.	l/m2s	25 ± 10	SR EN ISO 9237:1999

In order to improve the dyeing fastness and to decrease the temperature of the dyeing bath, the CORTINA fabric was treated with Plasma in the INCDTP laboratory. The laboratory is endowed with a CD 400 Roll-to-roll plasma installation from Europlasma NV. The fabric was treated with Oxygen in order to scour the surface of the cotton material before dyeing and finishing. Other plasma treatment parameters: Type of gas: Oxygen; Frequency domain: MHz; Power: 50W; Work pressure: 20 mTorr; Process time: 80 s.

For the finishing treatments the fabrics were dyed with specific resistant dyes, specific to both types of raw materials, followed by coating with Polyurethane. This type of woven fabrics is cleaned after performing of the clothing shelter structure, with water jets and detergents and mechanical or manual brushing.

The drying is performed by exposure to hot atmospheric air or in hot rooms. In order to obtain a good cleaning effect, the surface of the fabric has to be smooth and flat and the treatments should be compatible with used detergents. Light resistant colorants will be used in the finishing process. Toxic or dangerous products will not be used in the finishing or cleaning process. The fabric was also treated for hydrophobic, fireproofing and anti-microbial properties. The following finishing agents were used for this purpose:

Table 5 – Special finishing agents

Special property	**Applied finishing agent**
Hydrophobic character	Evo Protect FSV
Fireproofing	Flamentin APF
Anti-microbial	Eosy / Unitika

The hydrophobic effect of the multifunctional fabric CORTINA was evidenced by contact angle determination.

We can see in the following pictures the high hydrophobic property of this fabric and the table with contact angles.

Fig. 4 – Contact angle images

Table 6 - Contact Angle values

	Measurement 1	Measurement 2	Measurement 3	Average
Left Angle	148.60°	139.30°	142.10°	143.33°
Right Angle	147.90°	136.70°	141.40°	142.00°

The average contact angle of 143,33° / 142.00° proves a very good hydrophobic character.

4. CONCLUSIONS

Multifunctional fabrics have been performed within this research activity with destination temporary shelters for emergency situations and tents for tourism and leisure.

Technological elements for designing woven structures, finishing and multifunctional treatment (fire proof, hydrophobic and anti-microbial) have been used with the purpose of ensuring safety and comfort.

Several aspects have been complied in order to manufacture these fabrics:

- The dimensional calculation of the fabric has been performed accordingly to the “mass” parameter.
- The densities have been correlated with the reed linear density of the weaving machine STB 2-216 (45/10) and Somet Thema11 (75/10) as well as with the apparently diameter of the selected yarns, such as d= 0,875 mm for Nm 10/2; d = 0,25 mm for yarn 80 dtex).
- Before the finishing process the fabric surface have been activated and cleaned in the Plasma installation 400 Roll-to-roll from INCDTP laboratory.

Fig. 5 - Shelter for emergency situations

Technical fabrics with specific properties destined for satisfying technical and social requirements, have been characterized by the parameters of raw materials, structure and finishing. The finishing ensures water proofing, fire proofing and/or anti-microbial properties.

New technologies have been also experimented: processing of doubled and twisted yarns or of filamentary yarns, by using machines and equipment with high productivity.

In consequence, for the diversification of multifunctional technical textiles, the purpose was to produce superior properties regarding tear, proofing and resistance to changing weather conditions. These properties are mandatory for performing of constructions destined for the protection of people.

New possibilities of plasma treatment have been identified: coating, hydrophobic, anti-microbial treatments or combinations, for the durable effect on technical fabrics.

After the finishing treatment, the fabrics have been investigated on modern equipment in the INCDTP laboratory and a shelter for emergency situations was manufactured. The material has been tested in continuously utilization conditions and no visible degradations of the material have been observed. The parameters obtained in the laboratory investigation do not show significant depreciation of the main physical-mechanical characteristics. A tent as functional model has been exposed to air at atmospheric conditions in Bucharest. Periodically, at an interval of 30 days, the cleaning of the tent has been performed, with water jets and specialized textile detergents.

This textile product is a research result in the field of technical textiles and it covers an important application: sheltering people in emergency situations. For the new characteristics of the fabric a patent request was issued.

The new textile product is a consequence of both technology push and market pull. Its benefits have been largely disseminated in the textile industry field.

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ITPROTECH PROJECT: IT PRODUCTION TECHNOLOGY FOR CUSTOMIZED GARMENTS

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Keywords: customization, platform, technology

Abstract. *Most industries these days use computers to test their products before they produce them in real-life. Rather than producing a physical sample before a garment's look and fit is tested, virtual fitting means seeing the garment on the computer first, to detect and correct problems early in the development process, rather than weeks down the line.*

The novelty of the project consists in gathering the software and equipments in one IT based production technology platform that will increase the access of the SME's from clothing industries to technologies that create personalized garments for their clients according to the fashion trends. Also, the utilization of the IT production technology platform will increase the flexibility and adaptability of the SME's, sustaining the development of competitiveness in knowledge based economy and society.

1 BACKGROUND

Coordinated by the Region of Nord-Pas de Calais, CROSSTEXNET programme draws together 17 research funding agencies on regional and national level in a co-operation project aiming at "making more and smarter funding available to European textile research, on a permanent basis, by exploiting the potentials of international co-ordination and programming of research programmes."

Within the context above, CROSSTEXNET is distinguished to be an operative initiative supplying resources for cooperation. Its ambition is to transfer policy and strategy oriented documents to the level of beneficiaries, hereby providing a tool for implementation of research policies and strategies.

The project proposal was submitted to the 4th Call of the CROSSTEXNET programme and was declared eligible for funding. The ITProTech project started on July 31th, 2013 in Bucharest.

Figure 1: ITProTech Project's logo

2 OBJECTIVES

- Elaborate the technical specification of the IT production technology platform for design and fitting the custom garments;
- Design, develop and continually upgrade the database with garments models and pattern according to the classic style and the fashion trends;
- Design and develop the IT production technology platform for design and fitting the garments providing users with information and tools as well as an integration framework including all the software and equipment from 3D scanning to production;
- Development of new technical solutions to manufacture personalised garments enabling a fast reaction to the new trends. For achieving these objectives, ITProTech will address the whole design process.

3 IMPLEMENTATION

In order to achieve the project objectives, project activities are structured in four workpackages, which are generally, correlated leading to added value of the results. The project consortium involves institutions of different kinds that complement each other in terms of capacities and expertise but also of visions and attitudes.

Over its 24 months duration the ITProTech project plans actions in two European counties according to 4 major WPs:

- WP1: System requirement specifications;
- WP2: Production technology platform design and development;
- WP3: Production technology platform integration and tests;
- WP4: Management, dissemination and exploitation.

4 EXPECTED EXPLOITABLE RESULTS:

- Design, develop and continually upgrade the database with garments models and pattern according to the classic style and the fashion trends;

- Design and develop the IT production technology platform for design and fitting the garments providing users with information and tools as well as an integration framework;
- Development of new technical solutions to manufacture personalized garments enabling a fast reaction to the new trends.

5 CONCLUSIONS

The European textile & clothing industry is one of the most important industrial sectors for EU countries. To maintain its current important competitive position in the European economy, it has to aim for innovative and high technology products, where the know-how and the educational skills are an important factor in the production process. If new characteristics as design and fitting can be added to the garments, new markets with a high turnover are possible.

Mass customization is a new technology that has a vital and direct affect upon market participants: consumer, manufacturers, retailers and wholesalers. Customized Clothing is becoming an important part of business, by filling a global niche market.

This project addresses the market niche of custom designed apparel that includes garments for people with emphasis on functionality and perfect fit. The customized clothing developed in the project will be most practical, functional, highest quality and most fashionable available for consumers.

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SUSTAINABLE TOOLS FOR IMPROVING TEXTILE SME'S COMPETITIVENESS

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Keywords: sustainable innovation, sustainable tools, green marketing tools, green public procurement

Abstract: *The "Sustainable innovation for textile in South East Europe" project funded by the European Union under Transnational Cooperation Programme South East Europe has the mission to create a new synergy between the public and private sector in order to disseminate knowledge, to promote the application of eco-design tools and to spread product sustainability principles in manufacturing productions and consumptions, encouraging the Public Administrations to purchase them. The competitiveness of enterprises gets through to the response to the needs of customers (buyers, consumers, users) and to the improvement of the quality of products and services offered. This paper analyzes the way in which textile SMEs can competitiveness can be improved through sustainable tools.*

1. INTRODUCTION

As new markets are becoming increasingly strong in manufacturing textile products, the markets in the EU region have to take up the challenge in order to keep up with worldwide competitors, especially in a moment in which low-wages are no longer the solution to improve competitiveness. In this context, the strategy around the overall quality and value of the textile product emerged make the manufacturers and stakeholders understand that the winning strategy to become world leader revolves around improving the quality and the value of what they produce.

Every textile item releases effluents that are harmful to the environment. Eco-friendly fabrics can substitute normal products. Reducing the environmental impact throughout the life-cycle of a fabric item or using lower impact products can contribute actively to the improvement of the situation. In general, there are four major environmental key factors associated with the production of textiles: water, energy, pollution, and use of non-renewable resources.

Green certification for textile products is a useful tool available to the entire textile sector that can be used to lower the impact on the environment of such industries as well as to boost their credential in terms of respect of the environment and promotion of sustainable practices. In parallel, environmentally-friendly initiatives including efforts towards energy efficiency, renewable energy and waste recycling, are all technology useful to “green” the industry segment. However, in addition to such strategies, getting certified is an essential step for the textile industry in order to demonstrate and show they comply with the existing environmental laws and certifications. Labels are also an effective way to show consumers you care for the environment and that you comply with the strictest standards available. The latest trends show that consumers, especially in the EU, are becoming increasingly conscious of their purchases: as a matter of fact, consumers are starting to question about their choices in products and also in relation to the companies that produce what they buy. The green wave and the organic movements are not new, and in some cases, they date back to past decades, but the outbreak of the financial crisis has brought about careful considerations among consumers and had the effect of further reinforcing and diffusing such attitudes. In addition, studies on green consumers’ attitudes show that those who choose to buy green, tend to choose easily recognizable symbols that testify that such products comply with rules and regulations protecting the environment. In this sense, manufactures are called to provide clear, persuasive and comprehensive information on what sets their product apart environmentally. Certifications are clear and easily recognizable symbols of such values: certified products show that what you produce is eco-friendly and safe for human beings as certified systems and products are traceable and verifiable in their impacts. In other words, getting certified is the first step to implement concrete and effective measures to improve the impact of your SME on the environment. The growing importance of green certification is also supported by the number of private and public organization that decide to undergo the process to obtain a green certification [1].

Green public procurement (GPP) is a tool with great potential, able to play a very strategic role within the framework of the strategies for sustainable development of a Local Authority. The purchase of goods and services with reduced environmental impact may be made functional for reaching specific environmental protection objectives (for example, reduction of energy consumption, reduction of waste production, etc.), in addition to providing an important contribution to the achievement of sustainability objectives defined in the framework of national and European policies and have a significant influence also on suppliers of goods and services, thus on the dissemination of environmental technologies.

Public authorities are major consumers in Europe: they spend approximately 2 trillion Euros annually, equivalent to some 19% of the EU’s gross domestic product. By using their purchasing power to choose goods and services with lower impacts on the environment, they can make an important contribution to sustainable consumption and production. By promoting and using GPP, public authorities can provide industry with real incentives for developing green technologies and products.

In its GPP Training Toolkit, European Commission has defined ecological criteria for the textile products. The GPP criteria are designed to reflect the key environmental risks. Two sets of criteria are presented. On one hand, the Core GPP criteria that address the most significant environmental impacts, and are designed to be used with minimum additional verification effort or cost increases. On the other hand, the Comprehensive GPP criteria that are intended for use by authorities who seek to purchase the best environmental products available on the market, and may require additional administrative effort or imply a certain cost increase as compared to other products fulfilling the same function [2].

The main aim of the project is twofold as it addresses both the private sector (SME) and the public systems (Public Administrations). The project aims to improve the knowledge and the development of methods and tools targeted to the eco-friendly manufacturing of the textile sector within the SME and at the same time it aims at fostering the adoption of public procurement procedures complying with environmental sustainable practices.

2. METHODOLOGY

To achieve the project objectives a threefold strategy was adopted:

A) Harmonization of the operators competences and knowledge with regard to green marketing tools, so to individuate homogenous methods of application;
B) Testing of the tools in SMEs, so to increase the enterprises awareness on green approach and to promote new targeted project initiatives ;
C) Enhancement of eco-sustainability principles in Public Administration internal management, so to encourage Public Administration in assuming the role of potential buyer and supporter of more favourable market conditions for the diffusion of environmentally friendly products.

The project actions are organized into three different categories:

1) **Research Activities:** definition of the work strategy starting from the standardization and strengthening of the partners’ knowledge on textile manufacturing industry and market trends, as well as Green Public Procurement in force legislation.

2) **Applied Actions**: definition and testing of an **“Eco-Design” Handbook** for SMEs taking into account eco-sustainable tools, methodologies and techniques for the textile industry such as: product certification, product traceability, Environmental Management System, Corporate Social Responsibility. The Handbook contents will be diffused among SMEs and Public Administrations.

3) **Network of Excellence**: creation and maintenance of on line Forum and Focus Group for information exchange and diffusion on the sector technological development and normative regulation. The outputs and results capitalization will reinforce networking between the project partners and stakeholders.

Recent trends in development of industries in the European Union are moving towards on development of production processes, improvement of product quality and environmental protection in the different processes and final products.

Taking into account open market and new products which are not controlled and do not meet certain standards, particularly in terms of safety to human health, new set of standards is introduced as well as certification needed to make the product (including textile products) safe, environmentally acceptable with high quality standards.

Specifically, for textile products, several certifications have been introduced to guarantee the accuracy, safety and "green" components in the process of production and processing.

Among the ecological system certifications the ISO 14001 standard is certainly the most widely used, followed by EMAS Regulation (Regulation (EC) n. 761/2001) the EU eco-management and audit system.

Both are voluntary certifications to businesses and organizations, public or private, who want to be responsible for assessing and improving their environmental performance.

It is not a certification specific to the textile sector, nor a product mark, that is they do not give guarantees for a green product but ensure that the certificate holder complies with mandatory environmental requirements and set goals for improving its environmental performance (e.g. reduction of waste production, reduction of water consumption, etc.).

As for the ecological product labels, the most popular one in the textile industry is definitely the Oeko-Tex Standard® 100, certified companies in the world are about 7.000, and many more products. This is a private standard that certifies the compatibility of textiles with the intended use from the standpoint of human health. To achieve this certification certain chemicals must be selected and laboratory tests on the finished product must be performed.

This mark is not a guarantee of an ecological product, either during production or end of life, but states that the product is free from harmful substances while using; the standard also includes some product performance requirements (e.g. colour fastness).

Another product label, specifically for textiles, which has success, is the Global Organic Textile Standard (GOTS) that is the certification of textile products made from organically grown natural fibers.

This certification begins with recognizing the growing environmental, social and health problems associated with the production and use of conventional cotton. To obtain such certification supplies must be certified from organic natural fibers, and we must select and limit the chemicals used during the finishing of the fabric.

Another ecological label product is the Community Ecolabel Mark (Regulation EC n.1980/2000), not primarily in textiles but also applicable to textiles, for which there are specific requirements. It is a European mark for a product that guarantees environmentally friendly characteristics throughout its life cycle (raw materials, production, end of life). In addition to the ecological requirements some performance requirements are also needed.

The so-called environmental product declarations are little known but deserve attention. It is a tool designed to improve environmental communication between producers on one side (business to business) and other distributors and consumers (business to consumers). These statements report the environmental impacts of a product throughout its life cycle (cradle to grave, that is from the production of raw materials to end of life). For environmental impacts, for example, it refers to the emission of carbon dioxide or the production of waste of a functional unit, which may be a square meter of fabric or clothing. This information, validated by an independent third party, may be useful to purchasers to compare two similar products and choose the one with the lowest environmental impact. The problem today is that such statements are not widely used, although it is a very interesting tool to make purchasing decisions on the environmental awareness based on objective data and validated.

In conclusion we can say that, before applying for, or purchasing on the basis of, any ecological label you should have clear understanding of the needs of the public or private entity on whose behalf you buy a product. Besides possibly you should deepen the specification of any certification; only in this way you will be engaged in a focused and conscious choice.

3. RESULTS AND DISCUSSION

After evening out and sharing information about the textile sector in each country, the challenge was how to shift from theory to operational work, how to move to that innovation we wanted to promote.

For SMEs we tried to provide simple, clear useful information and tools. We submitted over 50 questionnaires and performed over 20 audits. The aim was to make entrepreneurs easier to understand their needs and opportunities.

As regards PAs we realized we knew very little about Public Administration purchasing behavior, before talking about GPP. Laws can be in force, but GPP experience is so poor, that we felt we need to better understand how PAs approach the public purchasing, then to investigate the “green” part of it, to finally come to textiles, possibly green textiles.

Due to the lack of knowledge in the area of GPP, our public tender authorities make no attempt to announce “green” requirements, as competitive (low) price is still a priority. Therefore the improvement of knowledge and education are very important.

As a result of the above mentioned problem and the lack of the customers’ knowledge about the advantages of “green” products, such products do not have an appropriate market; therefore, this should be created in the first place, as companies will not manufacture such products without sufficient demand.

It is not necessary to define a “transnational tool”, as all countries involved in this project are familiar with the requirement systems that apply to products (i.e. EU ecolabel, Oeko-Tex® Standard 100) or the manufacturing process as a whole (i.e. EMAS, ISO 14001, Oeko-Tex® Standard 1000).

It is a serious problem that obtaining the distinctive marks for the products and the manufacturing process requires considerable funds, because of the test and license fees on the one part and because of any necessary investments on the other part. However, SMEs are struggling to survive because of the decreased purchasing power, and there are very few projects supporting such investments.

Education, as clearly shown by the “tool” created in this project, should be started with children so that a natural demand is created for green products for the future.

LCA could largely contribute to the extension of the knowledge of PAs

The best way to increase GPP acceptance in general, and for the textile sector in particular, is to increase stakeholder participation in procurement processes. The stakeholders identified and the role that each stakeholder may have in fostering the GPP are summarized in table 1.

Stakeholder	**Role**
Public Sector	
Policy makers	Introduce GPP by making an easy to apply legislation Start -up/initial incentives for green businesses
Public Administration	Organize green public procurement procedures and stop buying cheap products Promote education and information schemes Apply criteria in order to decrease costs and give value for money (minimum price for the best quality)
Private Sector	
Private companies (Small and Medium Enterprises)	Choose to produce green products in order to be more competitive (quality and characteristics) Improve communication and promote properly their added value
Chamber of Commerce	Educate the market Promote GPP products
Advertising companies	Indirect role Create messages that can easily reach the targeted groups
Consumer	
NGOs and civil society representatives	Put pressure on the Public Administration to buy and promote green products Act together with the Public Administration and policy makers to promote the GPP Make suggestions for new policies
The final consumers	Pay more attention to what they consume Demand for better quality and drive the market trends Be more informed about the green products
Certification Institutions	Act professionally in issuing the certifications Check the compliance with the GPP requirements

Table 1: Role of the stakeholders in fostering the GPP

Eco labels may help GPP in two directions:

- Helping in correct design and complete technical specifications of desired products

(definition of product/services characteristics)

- Helping in evaluation and compliance of concrete specifications (accepting the fact that certification also means compliance to certain specifications)

4. CONCLUSION

Working from theory to practice, we found out that:

- SMEs are confident in green tools, less confident in public market;
- PAs are interested in GPP, hindered by preconceptions and habits;
- Financial constraint is similar in SMEs and PAs, but those who trusted green tools and GPP won their challenge.

The best way to promote GPP within the textile sector is to inform and educate the market. Training programs need to be designed and implemented for public sector procurers and to be targeted at building expertise in integrating products and performance related criteria into the procurement process:

- evaluating procurement needs,
- determining specifications and award criteria,
- drafting and monitoring contracts , as well as
- assessing outcomes

These are the critical points in the textile procurements process, and the most practical elements about which procurers can dialogue with policy-makers and bidding companies not only on the most sustainable alternative, but also on the “most economically advantageous” one.

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INTEGRATED MANUFACTURING PROCESS FOR TEXTILES APPLICATIONS AND WOOD PROTECTION - MANUCOAT

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Keywords: photocatalytic materials, textiles, wood, plasma, sputtering

ABSTRACT: The main goal of MANUCOAT project is to manufacture new, long life and environmentally stable photocatalytic materials with sensitivity in the solar visible spectrum.

The result for textile and wood products will be water repellent and self - cleaning surfaces, with higher resistance to weathering and fungi, including antimicrobial properties.

This is ideal for home and medical textiles, because it can enhance the hygienic characteristics, and also for outdoor textiles or wood applications as it increases the resistance to damaging factors.

The MANUCOAT research is focused on obtaining the visible light photocatalytic effect of textile and wood surfaces by developing a system for plasma treatment of textiles and wood substrates and by deposition through physical methods of non – doped / doped nano-TiO2, where dopants envisaged are Ag and Si.

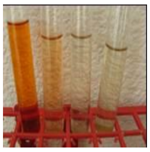
The doped Nanostructured Anatase (particle sizes < 20nm) will be developed and obtained in the project through hydrothermal procedure in aqueous media, at low temperatures (≤ 200ºC) and high pressures (> 200 atm), in one step without any further thermal treatment. In the project an equipment will be optimized in order to be used for both wood and textiles treatment and coating.

The project develops the physical methods for deposition of nanostructured films: the plasma technology for treatment of the textile surface for a better deposition of nano TiO_2 and the

sputtering technology for deposition of non-doped and doped TiO_2 on textile and wood substrates. The methods and equipment will be validated in industry.

Innovation elements:

1. Obtaining “in situ” TiO_2 nanoparticles doped with Ag, with reproducible phase composition and surface properties, by a low cost and scalable hydrothermal procedure starting from soluble inorganic salts of Ti. Hydrothermal procedure takes place at low temperatures (max. 2000 C) and high pressure (>200 atm) enabling the formation of stable nanostructures in which the dopant enters in B sites of TiO2 lattice.



2. New method to extend the absorption domain of photocatalytic compounds in the visible range, increasing the photocatalytic yield and photodegradation rate.

3. Development of plasma treatment to create active sites for the deposition of large quantities of nanoparticles with uniform, homogeneous, and well controlled composition.

4. Development of DC/RF sputtering technology to coat the textile and wood substrates with thin, transparent, nanostructured layers with high photocatalytic efficiency.

Until now, the only commercial applications for DC/RF reactive magnetron sputtering are mainly for electronics.

The project will develop the DC/RF sputtering method and equipment for work at low temperature and will create the possibilities to select deposition parameters to obtain thin film.

5. Correlation of complex data analysis (physical, mechanical, thermal, morphological and biological properties) to evaluate the functional effects (the photocatalytic activity, self-cleaning and auto-sterilizing, antibacterial/anti-fungal efficiency) and to elaborate a new "reference standard" to allow comparison of photo catalytic results of different methods of nanoparticles deposition on different textile substrates.

The international partner, IRIS will contribute in Manucoat: for one side, with their expertise in plasma technology applied to surface treatment of materials to develop and validate plasma for the treatment of textile surface before nanoparticles deposition to improve the performance of textiles; and, from the other side, his engineering and manufacturing processes knowledge to scale up the system from laboratory test rigs to a pre - competitive scale prototype that will be validated in the industry.

Expected exploitable results

1. The hydrothermal technology to obtain on larger scales on pilot installation of the doped/non-doped TiO_2 nanoparticles;
2. Sputtering technology for manufacturing the antimicrobial, self-cleaning textiles and wood;
3. Versatile equipment for sputtering treatment of textiles and wood;
4. Versatile equipment for plasma treatment of textiles;
5. Textile products with antimicrobial, antifungal and self-cleaning properties;
6. Wood product with high resistance to weathering.

The marketing potential for photocatalytic coatings is massive, including medical applications, architectural (particularly cultural heritage purposes, facade paints, indoor, wall paper, tiles, consumer goods etc.), automotive and food industries (cleaner technologies, non-fogging glass and mirrors, product safety), textile, wood and glass industry, and environmental protection (water and air purification and disinfection).

ROMANIAN FOLKLORE – A WAY TO BRING FORWARD THE TRADITIONAL VALUES THROUGH FASHION DESIGN

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Keywords: Fashion, tradition, Romanian costume, folk

Abstract. *Fashion and design involve changing. It was noted recently, frequent return to ethnic motifs, seen as a necessity regarding the inspirational mood, but also as a cultural reference present within the fashion system. The traditional Romanian costume has a great artistic value because of its spectacular cut and decorations. In Romania there are 112 traditional costumes, from Banat are twelve costumes and in Caras five costumes. The traditional Romanian costume is an emblem of recognition, a mark of ethnic identity, a document with certain historical and artistic value. The variety of clothing pieces and the complexity of the decorative elements became really fast the main inspiration for both local designers (Dorin Negrau, Adrian Oianu, Ingrid Vlaslov) and for international designers (Phillipe Guillet, Joseph Altuzarra, Tom Ford). The international designers' interest for the traditional Romanian costume constitutes a way of promoting the traditional Romanian values.*

1 INTRODUCTION

Fashion and design involve changing. This change means that the designers continue to be under constant pressure, to maintain their creativity always awake. The new developments in mass production and information technology have contributed to the increase of the changing speed by decreasing the time elapsed between the design process and the finished stocks entering the commercial environment.

On the threshold of the third millennium, bringing to light of the “antiques” across the globe and recombine them, took an unprecedented amplitude. The easiest way to get a new image from several old pictures is decomposing into their component elements and recombining them in a form that is more or less logical.

It was noted recently, frequent return to ethnic motifs, seen as a necessity regarding the inspirational mood, but also as a cultural reference present within the fashion system. This return to ethnic motifs are analyzed in terms of globalization and its effect on contemporary garment. With this return to ethnic elements and motifs persists the importance of social and cultural archetypes, developed during a major historical period, archetypes who kept meaning and essence until today. The ethnic motifs have a particular importance as a symbol and archetype in contemporary fashion. The analysis of these forms of cultural expression supports the conclusion, according to which the reuse of these decorative motifs can create products with a great effect in contemporary fashion. It is obvious, in this context, the importance of the source of inspiration, but also the presence of a relevant manner of reapplication and reinvention of these elements.

2 THE TRADITIONAL ROMANIAN COSTUME- DESCRIPTION

The traditional Romanian costume has a great artistic value because of its spectacular cut and decorations. The popular Romanian costume finds its roots in our ancestors costumes (Thracians and Dacians) being subject to continuous developments, but also keeping unchanged the essentials: its unity and continuity. Starting from the artistic achievements made with raw fabrics produced in peasant households, the traditional Romanian costume proved the Romanian peasant craftsmanship in both fabrics and embroidery decorating and also in obtaining vegetable colors. The traditional costumes are different, depending on the season, festive occasions, age and sex, adapting to the specific occupations of the area.

The traditional Romanian costume represents the eternity and individuality of an ethnic group. In Romania there are 112 traditional costumes, from Banat are twelve costumes and in Caras five costumes.

In ancient times, the folklore was integrated into a socio-cultural context that included all facts of life in the rural world. The secrets of crafts of manufacturing clothing couldn't be learned from books, only from the village women. They were transmitted from generation to generation-from mother to daughter. The traditional Romanian costume as general features, has the same resemblance across the country, with certain differences of details, changes of shape, cut, decoration and color. This unity gives the costume the popular and national character.

The national Romanian costume born from the Romanian peasant soul has the first meaning:

1. The significance of nakedness – that clothing is to cover the human body – as a divine requirement – and then, to protect it from the weather conditions, therefore it is different, depending on the season, being thicker in winter (wool fabric and fur) and thin in the summer (hemp, flax, cotton). Hemp fabric keeps warm in winter and it's also a good fabric for summer.

Figure 1: Traditional Romanian costumes

2. The social significance – the clothes shows the social status of the wearer to others. The difference is given by ornamentation, color and stitches. Some clothes indicated professions – for example shepherds, forest workers, farm work – when the costume is simple- compared to the one worn on holidays or at weddings.

3. Religious significance – The national Romanian costume, by its ornaments and decorations, had the purpose to defend the people who wear it from the evil spirits and bring them luck and health.

So, we can say that the traditional Romanian costume combines utility with beauty, achieving the necessary balance between soul and body, without the importance of one being exacerbated over the other.

The traditional costumes are still worn in many Romanian villages, especially on holidays. They differ by region: Banat, Transylvania, Bukovina, Moldavia, Crisana, Maramures, Dobrogea, Oltenia and Muntenia. Embroidery patterns have a meaning that differs from one area to another. In each region of the country the traditional combination of colors are strictly respected. In Transylvania, the villages from Sibiu Surroundings are famous for their glamorous and colorful traditional costumes. In Maramures, the folk creation is preserved in its original form; in the traditional costume the green color is predominant. The traditional costume from Moldavia is simpler, without many ornaments and with only three colors: black, red and white, later associating other colors (blue and orange combination, in northern Moldavia) but in a small degree.

The diversity of the traditional costume marked by particularities of ornamental and tailoring is also manifested structurally from one region of the country to the other.

The traditional Romanian costume is a combination of local traditions, the geographical location, climate and economic opportunities. It is an emblem of recognition, a mark of ethnic identity, a document with certain historical and artistic value. From birth to death, the traditional costume accompanied the human in all the events of his life, being a carrier of symbols.

3 THE TRADITIONAL ROMANIAN COSTUME- INSPIRATIONAL SOURCE

3.1. National level

Today the traditional Romanian costume became an inspiration source to the wholesale fashion production industry designers, both Romanian and international. They created clothing pieces with an unique design and distinctive details, based on the traditional models, with embrodeiry, specific colors and other elements, like tassels, to create unique clothing pieces. The national Romanian costume will remain an inspirational source because of the multitude of forms particular to each region of the country and decorative elements that can always be reinterpreted.

The interest for Romanian tradition and craftsmanship found itself in the Romanian designers collections. They created fashion collections having as an inspiration source the traditional Romanian costume.

Adrian Oianu is a very appreciated Romanian designer who launched three collections inspired by his native's country traditional costumes: "Suflecata pan' la brau" ("Turned up 'til the belt"), "Bucurie" ("Joy") and „Romanian punk". The collections conquered fashion enthusiasts around the world. Dorin Negrau had as inspiration for his "Lost" collection the traditional costume from the Bihor region.

Other designers influenced by the Romanian folk costume were Olah Gyarfas, Corina Vladescu and Ingrid Vlasov.

Figure 2: Adrian Oianu – Collection “Romanian punk”

3.2 International level

The traditional Romanian motifs were used by many Romanian designers, but a great interest for our folk costumes was shown by the foreign fashion designers.

French designer, Phillippe Guilet, launced the collection “Prejudices 100% RO” which focused on the traditional uniforms of the “Callus” (Calusarii), folk dancers from the south western part of Romania. Yves Saint Laurent had a collection inspired by the Romanian traditional flax blouses called “La blouse roumaine”. Joseph Altuzarra, the French designer who owns the American brand Altuzarra, found his inspiration for his Resort collection in Romanian folklore. The collection includes colorful clothing pieces, blouses that resemble the Romanian traditional flax blouse and pencil skirts with ethnic prints.

The American designer Tom Ford found his inspiration for his Spring 2012 collection in Spain, South America and also in Romania, in the Fagaras area.

Figure 3: Phiilipe Guillet- Collection Prejudices 100% ro

The American brand Atrophologie designed a whole collection for autumn-winter inspired by the traditional costumes from Maramures. This collection had a major impact in the world, being distributed in America, England, Canada and online in over 30 countries. The interest of the international designers for our traditional costume is a good way of promoting the traditional Romanian values.

4 CONCLUSIONS

Fashion and design involve changing. It was noted recently, frequent return to ethnic motifs, seen as a necessity regarding the inspirational mood, but also as a cultural reference present within the fashion system. The analysis of these forms of cultural expression supports the conclusion, according to which the reuse of these decorative motifs can create products with a great effect in contemporary fashion.

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Today the traditional Romanian costume became an inspiration source to the wholesale fashion production industry designers, both Romanian (Dorin Negrau, Adrian Oianu, Ingrid Vlaslov), and international (Philippe Guilet, Joseph Altuzarra, Yves Saint Laurent, Tom Ford). The interest of the international designers for our traditional costume is a good way of promoting the traditional Romanian values.

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MULTI-FUNCTIONALITY OF TEXTILE META-STRUCTURES

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Keywords: multi-functionality, textiles, meta-structures

Abstract. *During the last 20 years, spectacular results were obtained, not only from a theoretical standpoint, in the meta-materials field (materials with negative magnetic permeability and electric permittivity). To this purpose, the "invisible cloaks" and "acoustic cloaks" were conceived, first theoretically and later experimentally. It is natural to extend these concepts to textile structures and this should lead to the notion of multi-functional meta-textile structures (textile structures that ensure both "invisibility" and "phonic isolation"or other non-conventional material) that can be readily applied to various fields. The paper approaches these aspects in particular and highlights the specificity of such a research referring to the multi-functionality of textile meta-structures. The paper presents the elements that are necessary and sufficient to the understanding of the notion of multifunctional meta-textile structure.*

1 INTRODUCTION

Advanced industrial technologies, directly or indirectly, exert their beneficial influence, generated by progress, in the fields of the social-economic life, in such a way that these fields seek to harmonize the development in view of a common benefit. Since, from the social and economic points of view, textile industry represents a major technology user; it is natural that it should try to address all challenges in a positive way. The benefit is mutual: technology identifies a user (*consumer*) that is directly interested, willing to make investments in order to adapt both the methodology and the manufacturing process to the new technical requirements, while the *consumer* (user) assesses the effectiveness of the envisaged investment, following that it should be recovered during application of the accepted flow (raw-materials-manufacturing process-trading).

Technological advances achieved over the past 25 years have led not only to great technologic results, but also to theoretical reconsiderations which were unimaginable 30 years ago. It is enough to mention here only two very conclusive examples, namely ***metamaterial.***

"The concept of metamaterials was first introduced in the field of electromagnetic (EM) materials. Here it came to mean a material whose effective properties arose not from the bulk behavior of the materials which composed it, but more from their deliberate structuring. Therefore, metamaterials sit at the intersection of two classical categories, materials and devices. Our definition of metamaterials in this review is somewhat broader than what conventionally defined as it includes all MNSMs regardless of a relative scale ratio between the characteristic structural length and the wavelengths of EM or mechanical waves. In the conventional (narrower) definition of metamaterials, the characteristic length scale of their structures is one or more orders smaller than the wavelengths"[2]

2 THE MATHEMATICAL MODEL OF THE EXTERNAL LAYER FORMED OF AN INVISIBLE METATEXTILE STRUCTURE [1-2]

2.1 The material point hypothesis.

Each intersection between a warp yarn and a weft one is a distinct material point (figure 1), perfectly pointed out. This means that the two determined yarns have the same and only material point, as if they were connected. The mass of the material point results from the even distribution of the textile area mass on all over the material points above mentioned;

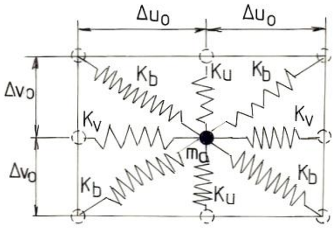

Fig. 1: The cloth ‘atom’

2.2 The hypothesis of the elastic bonds.

Each material point (“atom”) is connected with at the most eight neighboring material points, two by two on each warp and weft yarn and with other four on biè (figure1).This connection is a perfect elastic bond when it is subjected to tensile stresses, following Hook’s Law.

2.3 The hypothesis of the electrical properties of yarns.

The yarns are electro-conductible

2.4 Equations of motion

$$\begin{cases} m\ddot{\mathbf{X}}_i = \boldsymbol{\phi}_{ij} + \mathbf{F}_i + \mathbf{F}_{\mathbf{i,em}} - \beta\dot{\mathbf{X}}_i \\ i = 1,2,\ldots N_m,\ j \in V_i \end{cases} \qquad (1)$$

$\boldsymbol{\phi}_{ij} - elastic\ \ force$

$\mathbf{F}_i - exterior\ \ force$

$\mathbf{F}_{\mathbf{i,em}} - electromagnetic\ \ force\,(Lorentz)$

$-\beta\dot{\mathbf{X}}_i - damping\ \ force$

$V_m - N_m$ *the number of free nodes that belong to the texti le field*

2.5 Equations of Maxwell

$$\nabla\mathbf{E} = \frac{1}{\varepsilon_0}\rho \qquad (2)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (3)$$

$$\nabla \mathbf{B} = 0 \quad (3)$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} \quad (4)$$

2.6 Constitutive laws

$$\mathbf{D} = \varepsilon_0 \mathbf{E} \quad (5)$$

$$\mathbf{B} = \mu_0 \mathbf{H} \quad (6)$$

$$T_{ik} = \varepsilon_0 \left(E_i E_k - \frac{1}{2} \delta_{ik} e^2 \right) + \frac{1}{\mu_0} \left(B_i B_k - \frac{1}{2} \delta_{ik} B^2 \right) \quad (7)$$

where:

E - electric field
B - magnetic field
J - current density
ρ - change density
ε_0 - permittivity of free space
μ_0 - permeability of free space
T_{ik} - tensor of tension
e - electric charge
δ_{ik} - Kronecker symbol

The mathematical model obtained links variable to the electromagnetic variable permitting the interaction between the textile structure and the surrounding electromagnetic field.

Equations are written for each node (linking point) of the textile (structure) network therefore depending on the density there can be thousands of equations with partial derivatives to which the boundary conditions are added. It is clear that the solution to such a huge system of equations can only be found by GRID networks specific methodology, the only methodology that can lead to an acceptable numerical solution.

3. MATHEMATICAL MODEL OF THE DEFORMATION OF AUXETIC WOVEN TEXTILE STRUCTURES

The mathematical model used for the study of the deformation of auxetic textile structures can be, as a matter of fact, considered an adaptation of Butoescu V. model [3] to auxetic textile structures in a GRID network. In comparison with the initial model, the fundamental difference is the fact that GRID network equations accept millions of numerical solutions, and at the same time, it presents particular challenges for error control and for other specific characteristics of this work method. The fact that grid networks are compatible with the calculation of matrices of such dimensions leads us to formulate the essential work hypothesis which is that in this case each connection point is biunivocally represented in the model, so that each “atom” point is presented with the material specific characteristics. Because the study used the values obtained for parachute fabrics, this model eliminates the hypothesis of the existence of “oblique” reactions. Because the model is detailed in [3], we shall underline the essential elements specific to auxetic woven structures that can be solved as grid networks and the methodology for grid network calculation.

3.1 Description of the mathematical model specific to these auxetic woven structures

Butoescu model [3] shall be adapted to the grid network work method. Therefore, the work shall be done not with fictitious yarns, but with the yarns in the woven fabric, in this case the warp and weft yarns and the connection points shall be considered mass points – points in which the mass of each fabric “atom” is concentrated. Furthermore, rigidities K_u and K_b depend on Poisson ratio. The elastic forces in the yarns are given by the [2] expressions:

$$\boldsymbol{\Phi}_{ij} = \begin{cases} \boldsymbol{K}_{ij}(\nu)\left(1 - \dfrac{\left|\mathbf{X}^{o}_{ij}\right|}{\left|\mathbf{X}_{ij}\right|}\boldsymbol{X}_{ij}\right) \cdot \dfrac{\mathbf{X}_{ij}}{\left|\mathbf{X}_{ij}\right|}, & \boldsymbol{if} \quad \left|\mathbf{X}^{o}_{ij}\right| \le \left|\mathbf{X}_{ij}\right| \\ 0, & \boldsymbol{if} \quad \left|\mathbf{X}^{o}_{ij}\right| > \left|\mathbf{X}_{ij}\right| \end{cases} \qquad (8)$$

in which *i,j* are indices for the connection point situated at the intersection of the “i” weft yarn with “j” warp yarn. The index *j* takes values for the neighbouring nodes of *i* node rigidity values must be linked to Poisson ratio, corresponding to *ij* region in the system. $\mathbf{X}_{ij}$, is the position vector of *(i,j)* point and “0” index, indicates the initial position of a point. The equations of motion for point *I* are:

$$m\ddot{\mathbf{X}}_i = \boldsymbol{\phi}_{ij} + \mathbf{F}_i \qquad (9)$$

In which *i* takes values for all the network nodes and $\mathbf{F}_i$ is the external force acting in *i*.

3.2 Elastic equivalence of elastic membranes and certain textile structures [5]

There are many situations in which, in order to study certain characteristics (especially those related to elasticity and resistance) of the textile structures, we need to use numerical methods that evidence by means of calculations firstly, the “compatibilities” of the elastic behaviour of the studied samples.

This way we are led to the concept of elastic equivalence of two samples: when subjected to identical stresses, two geometrically identical bodies have identical behaviours. Thus, under identical loads we get the same results (tensions, deformations) for both. A concrete example is given by the walls of arteries in the human body – they are elastic and resistant walls that can be assimilated to an elastic membrane with similar properties. If there is a need to replace such arteries, one of the searched for characteristics is the elastic behaviour – a textile structure that, from an elastic perspective, behaves the same as the original artery. Once this concept is clear, we can work towards the proposed objective: a numerical model of the elastic behaviour of a membrane, a problem solved within the limits of the theory of elasticity by using dedicated products such as ABACUS, COMSOL MULTIPHYSICS. In the figure below the tension state is presented for two elastic membranes with opposite Poisson ratios – for the first case ν is 0.3 and for the second case it is -0.3. We can now approach the problem of finding a textile structure that is elastically equivalent to the elastic membrane. It is a challenging problem, as the textile structure is a discontinuous medium; therefore using the above products is forced upon this problem (meaning that in many instances the discontinuity of the textile structure leads to errors). There is a need for a closer method to have a correct modelling of the textile structures. One of the methods is the model presented in this paper. The work methodology shall be presented in the following part of the study.

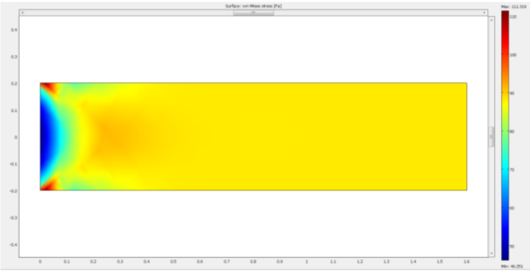

Fig. 2 a) Conventional case

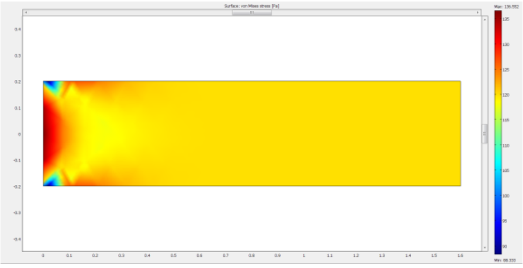

Fig. 2 b) Auxetic case

3.3 Results and discussion

For calibrating the model, parachute samples type T40-200 with the following characteristics were used: mass 60 g/m^2; thickness 0.13 mm, D_u = 628/10 cm; D_b = 615/10 cm; the yarn used was PA 6, warp yarn fineness was of 4.5 Tex and the warp yarn diameter was of 88 µm . As regards the weft yarn the diameter is 86 µm, fineness 4.5 Tex. Textile sample is treated as a membrane that is numerically simulated and then we compare the values obtained by the first method (the one using COMSOL MULTIPHYSICS) with those obtained using GRID networks. Some calculations are presented in Table 1. As can be seen in COMSOL MULTIPHYSICS product simulation (column 3 and 5), the values obtained in the auxetic case (Fig. 3 b) are superior to those obtained in the conventional case (Fig. 3 a.). As regards the second method, a number of 628x615 points were used for the connection points. It can be seen that generally the values obtained by GRID processing are ranging around the values obtained by the conventional method.

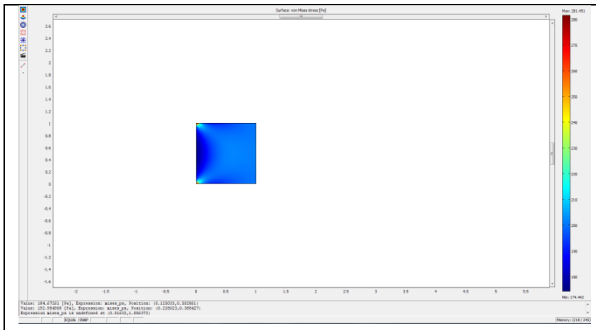

Fig. 3 a) Conventional case

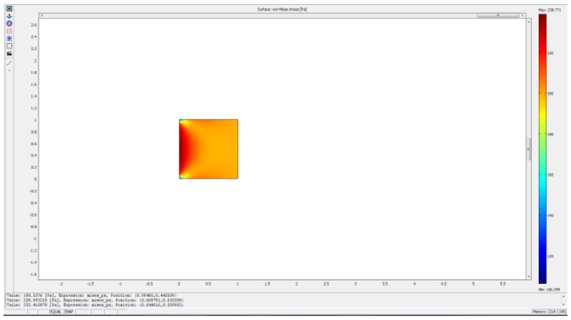

Fig. 3 b) Auxetic case

We used the following values: density 1150 kg/m3 wire, 2e9 Young's coefficient [Pa] and the Poisson ratio is 0.2. Auxetic case was considered for the Poisson value -0.2.

Table 1 Values calculated by simulation on COMSOL MULTIPHYSICS and grid network

Coordinate x	Coordinate y	Conventional Von Mises [Pa]	Conventional Grid	Auxetic Von Mises [Pa]	Auxetic Grid
0.25	0.55	193.5	191.8	208.4	205.6
0.48	0.45	201.1	199.7	212	210.9
0.59	0.45	201.7	200.1	199	200.6
0.49	1	193.7	194	207	205.7
0.48	0	193.6	191.8	206	204.7
0.4	0	191.7	193.	207.2	205.3
1	0.46	201.4	200.5	198.53	200.7
0.01	0.01	282.2	283.1	278.1	276.5
0.08	0.62	212.5	213.1	229	227
0.04	0.6	226.7	227.1	232	231.4

4. CONCLUSIONS

A hypothetical model of “multifunctional invisible” textile structure was presented. This structure is formed of two layers: an external one that ensures the “invisibility” of the textile structure as a whole and an internal one consisting of an auxetic structure.

For the internal layer, a concrete case of design of such a structure will be presented (mathematical modeling and numerical results).

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EVALUATION OF THE COLOR FASTNESS PROPERTIES OF DENIM GARMENTS DYED WITH NATURAL VEGETABLE DYES

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Abstract. *The desire to color textiles is as old as spinning and weaving. Natural dyes have been used since thousands of years for their long endurance, soft and elegant colors. But the invention of synthetic dyes has limited the application of natural dyes. The health hazards associated with the use of synthetic dyes and also the increased environmental awareness have revived the use of natural dyes during the recent years. The major performance characteristic of a dye is its ability to maintain the color in normal use and is known as color fastness. The study provides information regarding color fastness properties of naturally dyed denim fabrics.*

1 INTRODUCTION

Since textile materials were invented, humans have been searching ways to color them. The ability of natural dyes to color textiles has been known since ancient times. The earliest written record of the use of natural dyes was found in China dated 2600 BC. Chemical tests of red fabrics found in the tomb of King Tutankhamen in Egypt show the presence of alizarin, a pigment extracted from madder (*Rubia tinctorum*). In more modern times, Alexander the Great mentions having found purple robes dated 541 BC in the Persian royal treasury [1].

Natural dyes are derived from naturally occurring sources such as plants (example: indigo and saffron); insects (example: cochineal beetles and lac scale insects); animals (example: some species of mollusks or shellfish); and minerals (example: ferrous sulfate, ochre, and clay) without any chemical treatment [2]. A spectrum of beautiful natural colors ranging from yellow to black exists in the above sources. These colors are exhibited by various organic and inorganic molecules (pigments) and their mixtures are due to the absorption of light in the visible region of 400-800 nm. This absorption of light depends on the structure or constituents of the coloring molecules [3].

By the sixteenth century, dyes played a major role in political and economic history, as European nations looked out for the secrets of applying natural colors. *Indigofera tinctoria,* that yielded a brighter indigo blue, arrived in Europe from India and the East. Indigo and the madder were the most important natural dyes [4].

The affinity of a dye for a fabric depends on the chemical structure of the dye and fabric molecules and on the interactions between them. Unlike most organic compounds, dyes possess color because they:

- absorb light in the visible spectrum (400–700 nm), have at least one chromophore (color – bearing group),
- have a conjugated system, i.e. a structure with alternating double and single bonds,
- exhibit resonance of electrons, which is a stabilizing force in organic compounds [5].

As far as the chemistry of dyes is concerned, a dye molecule has two principal chemical groups, chromophores and auxochromes. The chromophore, usually an aromatic ring, is associated with the coloring property [6]. It has unsaturated bonds such as –C=C, =C=O, –C–S, =C–NH, –CH=N–, –N=N– and –N=O, whose number decides the intensity of the color. The auxochrome helps the dye molecule to combine with the substrate, thus imparting color to the latter [7].

Recently, a number of commercial dyers have started looking at the possibilities to overcome environmental pollution caused by the synthetic dyes, by replacing them with natural dyes. Natural dyes produce soft shades as compared to synthetic dyes. In spite of the better performance at multiple washing, recently the potential use of natural dyes on textile materials has been attracting more and more scientist to study the natural alternative for dyeing due to the following reasons:

- wide spread of natural dyes sources and huge potential
- available experimental evidence for allergic and toxic effects of synthetic dyes
- available information on different natural colorants, including methods for their extraction and purification.

Technology for production of natural dyes could vary from simple aqueous extraction to complicated solvent systems or to sophisticated supercritical fluid extraction techniques, depending on the product and purity required. Purification may consist in filtration or reverse osmosis or preparatory HPLC, and drying of the product may be obtained by spray or under vacuum or using a freeze-drying technique.

For successful commercial use of natural dyes, appropriate scientific techniques need to be established by scientific studies on dyeing methods, dyeing kinetics and compatibility of selective natural dyes, in order to obtain shades with acceptable color fastness behavior and reproducible color yield [8].

Although the Earth possesses large plant resources, only little has been exploited so far. More detailed studies and scientific investigations are needed to assess the real potential and availability of natural dye-yielding resources.

Almost all parts of the plants produce dyes. It is interesting to note that over 2000 pigments are synthesized by various parts of plants, of which only about 150 have been commercially exploited [7].

Denim has been a crucial textile to society ever since twill weaving was developed nearly one thousand years ago. In the last decade weaving of denim fabrics has undergone dramatic changes with a view to improving the comfort level and aesthetic aspects.

Denim is a strong, durable fabric. The warp yarn is traditionally dyed with the blue pigment obtained from indigo dye. In the twill weave used in denim, the fabric is constructed by interlacing warp and filling yarns in a progressive alternation, which creates a diagonal effect on the face. Denim is traditionally woven from 100% cotton yarn. However, today it is blended with polyester, in order to control shrinkage and wrinkles, and elastomeric fibers to add stretch. Today, denim has many faces. It can be printed, striped, brushed, napped and stonewashed, as well as the indigo.

In the last few decades, denim has gained unimaginable popularity for those who initially wore it for protection, rather than for fashion. Denim has become a wardrobe staple. Fit, comfort and price are the most important factors affecting the purchase of denim jeans. Due to longer life span of jeans, the denim industry continues to hold an advantageous position over other types of apparel [9].

A renewed international interest has arisen in natural dyes due to increased awareness of the environmental and health hazards associated with the synthesis, processing and use of synthetic dyes [10].

Synthetic dyes have been in use globally in textile industries due to their availability. For the last one decade or more research has been carried out to explore the hidden component found in plants which could be used as dye alternative to synthetic one. Extensive literatures have been reviewed on this subject.

Most of the natural dyes have no substantivity for the fiber and are required to be used in conjunction with mordants. A mordant, usually a metallic salt, is regarded as a chemical, which itself can be fixed on the fiber and which also combines with dyestuff. A link is formed between the fiber and the dye, which allows certain dyes with no or little affinity for fiber to be fixed [11].

2 MATERIALS, EQUIPMENT AND METHODS

The present research activity was carried out to evaluate the performance of naturally dyed denim fabrics with natural dyes extracted from walnut, pomegranate and indigo leaves.

Known natural destructive agents for vegetable dyes are light, weather, oxygen and other atmospheric gases which can lead to fading. In addition to natural agents, there are many chemicals and finishing treatments used in wet processing of textiles which may influence color fastness to some degree. Most dyes are organic compounds, therefore are to the action of destructive agents [8].

Several tests for the assessments of fastness of dyes are available. Tests may be divided into those of customer significance such as light, washing, rubbing, perspiration and those concerning only the producer such as fastness to treatments against shrinkage, carbonization etc.

For characterization and evaluation, the following tests were performed onto selected samples:

- color fastness to washing, according to SR EN ISO 105 C06: 2010
- color fastness to acid perspiration, according to SR EN ISO 105 E04: 2009
- color fastness to alkaline perspiration, according to SR EN ISO 105 E04: 2009
- color fastness to water, according to SR EN ISO 105 E01: 2013
- color fastness to artificial light, according to SR EN ISO 105 B02: 2003
- color fastness to organic solvents, according to SR EN ISO 105 X05: 2000

2.1 Materials

Denim naturally dyed samples, dyed with extracts of pomegranate, walnut and indigo – supplied by MODAZEN INC.

Adjacent multi-fiber from James Heal, England

ECE Detergent with phosphate without optical brighteners

ARIEL Detergent

2.2 Testing equipment

Scourotester – washing equipment

Stainingtester – rubbing equipment

Memmert – oven

Xenotest Appolo – light testing equipment

DataColor and Hunterlab – color difference equipment

2.3 Methods used for evaluation of color fastness

2.3.1 Color Fastness to Washing

Washing fastness of denim fabric samples dyed with natural vegetable dyes was analyzed by SR EN ISO 105 C06: 2010, method A1S. For this a dyed sample was sewed with a piece of adjacent multi-fiber of similar size. For washing solution preparation 4 g of ECE phosphate detergent with no optical brighteners was used and then diluted to a volume of 1L with distilled water. The solution was introduced with a stainless steel glass together with the sandwiched specimen and rotated at 40^0C for 30 minutes in Scourotester equipment. Then the specimen was removed, rinsed in cold and hot water, and treated with diluted acetic acid solution. To have a comparison, another sample was tested by using commercial detergent ARIEL for colored fabrics. After the samples were dried, the assessment of the change in color and staining of adjacent multi-fiber was made, using the grey scale. The change in color mas measured also with both Data Color and Hunterlab equipment.

2.3.2 Color Fastness to acid and alkaline perspiration

Denim samples, put in contact with adjacent multi-fibers were introduced in acid and alkaline solutions containing histidine, then squeezed and placed between two glass plates under a pressure of 12.5kPa inside an oven at a temperature of 37^0C, for a period of 4 hours. The change in color and staining were assessed by using grey scale. The color parameters were also determined by Data Color and Hunterlab equipment.

2.3.3 Color Fastness to water

A sample of dyed denim is sewed with the same size of adjacent multi-fiber, then placed in a Berzelius beaker and covered with grade 3 water and maintained for 30 minutes at room temperature for an efficient wetting. Afterwards, the sample is squeezed and placed between two glass plates under a pressure of 12.5 kPa inside an oven at a temperature of 37^0C, for a period of 4 hours. The change in color and staining were assessed by using grey scale. The color parameters were determined by Data Color and Hunterlab equipment.

2.3.4 Color Fastness to artificial light

Fastness to light of different dyed samples was analyzed using light fastness tester according to SR EN ISO 105 B02: 2003. For this, a dyed sample was cut according to size of clip. Half portion of the fabric was exposed and other half masked. A reference scale consisted in blue wool reference strips was simultaneous tested. The temperature inside the equipment was adjusted by circulating cold water. The sample holders were rotating in clockwise direction for 92 hours. The color fastness to light of specimen was evaluated by comparison of color change of the exposed portion to the masked control portion of test specimen or unexposed original material, using grey scale for color change and gradation was noted on the extent of fading. Another grade was given by comparing the fading of the tested sample to a similar contrast noticed on the blue wool reference scale. The color parameters were determined by Data Color and Hunterlab equipment.

2.3.5 Color fastness to organic solvents

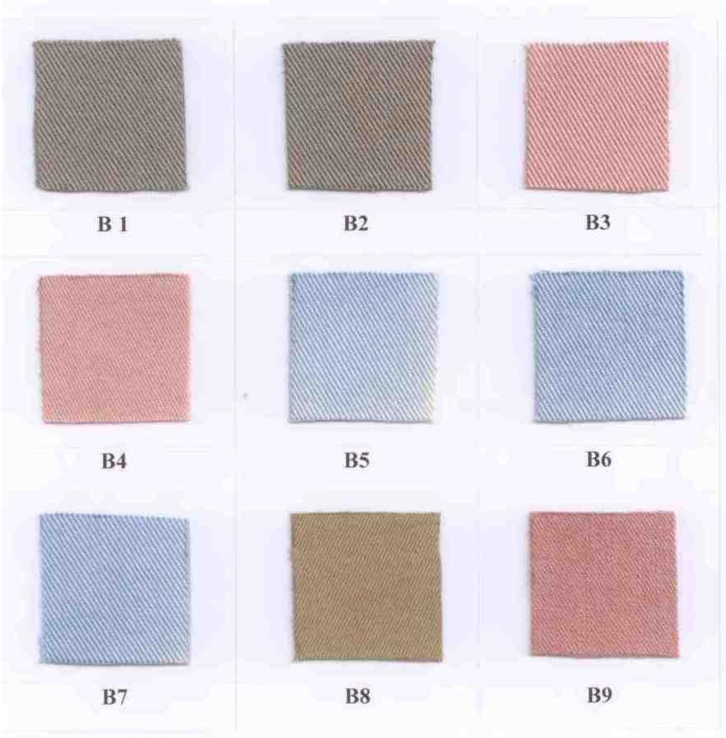
The organic solvent used was perchloroethylene. A sample of dyed denim was sewed with the same size of adjacent multi-fiber, then placed in a Berzelius beaker and covered with perchloroethylene at a ratio of 40:1. Continuous stirring of the sandwiched specimen was assured for 30 minutes. Then the specimen was removed from the solvent and dried in the air. The assessment of the change in color and staining of adjacent multi-fiber was made, using the grey scale. The change in color was measured also with both Data Color and Hunterlab equipment.

2.3.6 Color fastness to rubbing

Rubbing fastness was analyzed according to SR EN ISO 105 X12: 2003. The device used for rubbing fastness was Stainingtester. The force applied during rubbing: 9N. Both dry and wetting rubbing tests were performed.

3 RESULTS AND DISCUSSIONS

A number of 9 denim samples dyed with vegetable natural dyes prepared by MODAZEN INC. were tested by INCDTP in order to evaluate their color fastness properties. Preliminary chemical and physical–mechanical tests were performed in order to characterize the denim garment.



3.1 Characterization of the dyed denim samples

		Sample code								
Crt. No.	Test	B1	B2	B3	B4	B5	B6	B7	B8	B9
1.	Weight per unit area (g/m^2)	400	395	397	341	381	386	384	349	343
2.	Thickness (mm)	0.84	0.84	0.84	0.75	0.84	0.84	0.85	0.73	0.85
3.	Density (no. yarns/10 cm) warp	368	363	366	552	363	364	361	502	447

	Density (no. yarns/10 cm) weft	224	221	219	273	219	218	220	276	283
4.	Breaking force (N) warp	1647	1554	1607	1678	1685	1756	1792	1433	1184
	Breaking force (N) weft	1146	1133	1018	626	1200	1333	1240	765	778
5.	Elongation at break (%), warp	32.7	31.8	38.5	27.9	29.1	29.0	28.8	26.2	31.3
	Elongation at break (%), weft	18.58	17.7	20.1	12.2	17.73	18.56	18.22	13.25	12.2
6.	Tear resistance (N), warp	60.4	58.3	56.3	30.3	40.1	40.5	39.7	28.9	55.8
	Tear resistance (N), weft	57.8	55.5	44.5	18.49	29.5	32.1	28.5	20.9	31.7
7.	Air permeability (mm/sec.)	24.84	25.76	29.32	19.52	30.54	30.26	29.10	17.56	17.06

Table 1: Physical – mechanical characterization of denim samples

3.2 Evaluation of the property of color fastness

Assessing the change in color between tested samples and original samples has been highlighting the following behaviour: all the samples have lost their color intensity. The greatest modification has been observed for color fastness to light and color fastness to washing. Grades according to ISO 105 A02 have been attributed to each tested sample.

An interpretation of the attributed grades:
1 = Poor durability of the color
2 = Moderate durability of the color
3 = Good durability of the color
4 = Very good durability of the color
5 = Excellent durability of the color

Crt. No.	Test	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**B9**
1	Color fastness to washing, Detergent ECE	1-2	1-2	1-2	1	2	3-4	3	1-2	1
2	Color fastness to washing, Detergent Ariel	1	1	2	2	2	3-4	3	2-3	1-2
3	Color fastness to acid perspiration	4-5	4	3	2-3	3	4-5	4-5	4-5	3
4	Color fastness to alkaline perspiration	4-5	4	4	4	2-3	4-5	4-5	4-5	4

5	Color fastness to water	4-5	4	3-4	4-5	2-3	4-5	4-5	5	4-5
6	Color fastness to organic solvent	4-5	4	4-5	4	2	2-3	4	4-5	3-4
7	Color fastness to light	1	1	1	1	1	1	1	1	1

Table 1: Change in color of tested samples measured with DataColor and Hunterlab equipment

Since the introduction of color measurement instrumentation, there has been an international goal to describe color differences with numerical value. The first internationally accepted method, developed by the Commission International de l'Eclairage (CIE), was L*a*b* color tolerancing.

Color instruments generate tristimulus values in an X, Y and Z coordinate system. Depending on the specific instrument, these tristimulus values are converted to Hunter L, a, b or CIELAB L*, a* and b* units. The difference between the two systems is the mathematical manipulation of the basic tristimulus values.

Each color has its own distinct appearance, based on three elements: hue, chroma (saturation) and lightness (intensity of the color). By describing a color using these three attributes, you can accurately identify a particular color and distinguish it from any other.

Considering the above mentioned modalities to express the difference in color, all the received samples, were tested within INCDTP's laboratory, using two pieces of equipment for color evaluation: Hunterlab and Data Color.

A summary of the test results is presented below:

DL* : Lightness

		Sample								
Test	**Equipment**	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**B9**
Washing with ECE	HUNTERLAB	7,46	6,94	9,18	11,80	7,21	4,28	2,71	8,57	11,50
Washing with ECE	DATACOLOR	8,19	8,29	8,92	10,84	6,43	2,88	3,58	8,51	10,91
Washing with ARIEL	HUNTERLAB	10,52	9,54	6,11	6,33	6,65	3,63	2,08	6,81	9,17
Washing with ARIEL	DATACOLOR	10,46	10,17	5,75	5,39	6,50	2,18	3,25	5,72	8,50
Acid perspiration	HUNTERLAB	0,70	1,72	2,84	5,12	3,4	1,46	1,86	0,43	3,01
Acid perspiration	DATACOLOR	1,.04	1,86	2,77	4,58	2,60	0,44	0,62	0,40	2,58
Alkaline perspiration	HUNTERLAB	1,14	1,16	1,21	2,33	4,00	2,06	0,55	0,10	2,22
Alkaline perspiration	DATACOLOR	0,91	1,43	1,31	1,55	3,37	0,72	0,46	-0,15	1,65
Water	HUNTERLAB	0,22	0,43	1,94	-0,56	4,73	1,76	0,09	0,40	1,39

Water	DATACOLOR	0,03	1,08	2,11	-0,75	3,96	0,53	0,52	-0,01	1,02
Organic Solvent	HUNTERLAB	-0,43	0,48	0,27	1,53	6,53	5,08	1,56	-0,16	3,32
Organic Solvent	DATACOLOR	0,31	1,29	0,01	1,12	5,27	3,85	1,64	-0,34	2,21
Light	HUNTERLAB	23,90	24,06	19,70		19,55	19,58	17,76	12,62	24,93
Light	DATACOLOR	23,80	24,14	18,85	18,74	16,96	16,27	15,80	12,25	24,63

Table 2: DL* values obtained for naturally dyed denim samples

The experimental values obtained for this parameter, (DL*) highlight the fact that all the applied treatments have an obvious impact towards luminosity of the tested samples when compared to the reference (original) one. Washing the samples with neutral detergent with phosphate and without optical brighteners has conducted in all cases to positive results of the DL* parameter, which means that an increase in luminosity has been observed.

For samples B1 and B2 when treated with ARIEL detergent (which contains optical brighteners) the luminosity of the treated sample is greater than the reference one. For all the other samples the values of DL* parameter are lower in the case of using Ariel Detergent (with optical brighteners) as compared with ECE detergent (without optical brighteners).

When subjecting the samples to acid and alkaline perspiration, all the obtained values for luminosity were positive, which means that all the samples are modified compared to the reference material, in the sense that all those samples are lighter.

The same situation has occurred for color fastness to water, when for all the samples except for B4 a positive value of DL* has been obtained.

When testing the color fastness to perchloroetylene, all the values were positive, except for sample B8 for which the values of DL* are negative. For samples B1…B7 and B9, the luminosity is greater than the reference. In case of sample B8 the luminosity is lower than the reference.

When exposed to artificial light, all the samples have showed positive great values for DL* parameter compared to the reference. This states that the color modification is semnificative.

DC* : Saturation

		Sample								
Test	**Equipment**	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**	**B9**
Washing with ECE	HUNTERLAB	-3,91	-4,37	-5,21	-6,37	-3,81	-0,47	-0,11	-2,72	-7,75
Washing with ECE	DATACOLOR	-3,75	-4,07	-5,32	-6,97	-4,13	-0,01	-0,80	-2,65	-7,59
Washing with ARIEL	HUNTERLAB	-5,79	-5,55	-2,52	-3,82	-4,17	-0,63	-0,16	-0,90	-7,49
Washing with ARIEL	DATACOLOR	-5,39	-5,58	-2,88	-3,83	-4,77	-0,04	-0,95	-0,44	-6,39
Acid perspiration	HUNTERLAB	0,19	0,43	-0,16	-0,3	-2,05	0,18	-0,08	0,23	-1,71
Acid perspiration	DATACOLOR	0,44	-0,04	-0,13	-0,67	-1,79	0,92	0,12	0,64	-0,64

Alkaline perspiration	HUNTERLAB	-0,31	-0,49	-0,33	-0,37	-2,45	-0,08	0,08	0,72	-1,85
Alkaline perspiration	DATACOLOR	0,05	-0,46	-0,40	-0,47	-2,67	0,65	0,20	1,17	-0,75
Water	HUNTERLAB	-0,62	-0,11	-0,67	-0,15	-3,33	-0,16	0,31	-0,34	-1,79
Water	DATACOLOR	-0,03	-0,70	-0,73	-0,29	-3,21	0,48	0,12	0,03	-0,73
Organic Solvent	HUNTERLAB	-0,36	-0,28	-0,26	-1,12	-5,79	-4,01	-1,40	0,33	-3,27
Organic Solvent	DATACOLOR	0,18	-0,42	-0,23	-1,13	-5,12	-3,37	-1,25	0,61	-1,81
Light	HUNTERLAB	-2,87	-3,04	-10,10		-4,67	-5,98	-4,57	-4,24	-11,98
Light	DATACOLOR	-2,46	-3,45	-10,84	-9,85	-4,98	-4,82	-4,54	-4,75	-12,37

Table 3: DC* values obtained for naturally dyed denim samples

The values obtained for this parameter, DC*, after submitting the sample to different treatments described above, have showed that the samples become more saturated or less saturated, depending on the positive or negative registered result.

Both washing with neutral detergents such as ECE or ARIEL, which contains optical brighteners have showed that the samples become less saturated than the reference material.

For samples B1 and B2, the decrease in saturation becomes more obvious for ARIEL detergent. This is due to the presence of the optical agent which leads to a loss of coloristic intensity. For samples B3, B4, B8, B9, the recorded negative values have showed a lower decrease of saturation when using a detergent containing optical agents as compared to ECE detergent. For this specific case of natural dyes using a detergent with optical agents has lower influence on the degree of saturation of the samples.

In case of B5, B6, B7 samples the modification of saturation is comparable for ARIEL and ECE.

Testing the samples toward acid and alkaline perspiration has showed a greater variation. Negative results have been obtained, which suggests a decrease of saturation, but also some positive results have been obtained, which suggests an increase of saturation. This is also an indicator for the ne-uniformity of the dyeing process or the dye itself.

When tested for color fastness to water, all the samples give negative results. This leads us to the conclusion that nearly all samples became less saturated than the reference when tested against resistance to water. Positive and negative values obtained for the same sample is due to the ne-uniformity of the dyeing or the dye itself.

Regarding color fastness to light, all the samples have showed a loss of saturation.

10 CONCLUSIONS

Textile industry continuously searches for new technologies in order to accomplish the consumer’s demands. In recent years, there has been a revival of the use of dyes and colors of natural origin for coloring textile products. This increasing demand for the material with natural origin is because of the health hazards attributed to some of the synthetic dyes.

Natural dyes are subjected to more destructive agents who can fade significantly the color of a naturally dyed product. Considering the low affinity for natural dyes specific for cotton fibers used within traditional denim garments, the purpose of this study was to assess the fastness properties of the samples prepared by MODAZEN INC.

A number of 6 laboratory tests were performed, according to specific standardized methods. The visual assessment of the treated samples was confirmed by Data Color and Hunterlab results. All treated samples highlight a change in color in the sense of fading which has occurred to the highest extent at exposure to artificial light and washing. Slightly fading has been observed also for the other performed test, but to a much smaller extent. As a conclusion that can be extracted from the information gathered so far: color fastness of denim naturally dyed samples is generally poor. Optimization of the dyeing procedure is necessary.

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FABRICS ACQUIRING ANTIMICROBIAL PROPERTIES BY SONOCHEMICAL NANOPARTICLES EMBEDING

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Keywords: Antimicrobial activity, ultrasounds, MRSA, Acinetobacter baumannii, Candida albicans, copper oxide, wash durability

Abstract

The main focus of textile research in the last decade has been to develop processes and technologies which improve or add extra functionality to classical textiles. This paper presents the antimicrobial activity against a range of bacterial and fungal species of a PES/CO woven textile impregnated by means of ultrasound with nanoparticles of copper oxide. Supplementary data regarding textile and nanoparticle characterization, such as SEM coupled with EDS and IRT (Infrared Thermography) are also presented.

1. INTRODUCTION

Antimicrobial textiles

The use and applications of antimicrobial textiles has increased in recent years following a global trend in health care systems and a general societal concept, where personal and home hygiene have become an ever more important requirement for a healthier and better life.

The antimicrobial function is imparted to textiles by a range of chemical agents including: silver ions, natural biopolymers like the chitosan or vegetal extracts, N-halamine molecules, alkyl ammonium ions, metals and metallic salts and quaternary ammonium salts [1, 7].

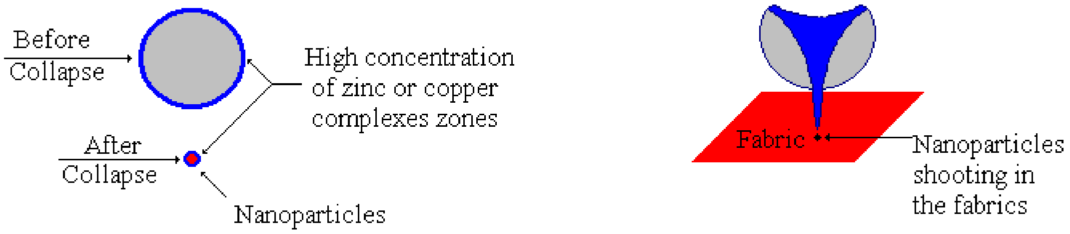
Antimicrobial agents act in various ways: disrupting the structure and integrity of the microbial cellular membrane; interacting with the genetic material (RNA and DNA); and altering the structure of essential proteins.

Maybe the most important application of antimicrobial textiles is the medical sector. Such textiles can be included in preventive measures taken by the hospitals to avoid the transmission of diseases [6]. Woven textiles may be used in hospitals as bed sheets and pillow covers as well as patient and medical personnel protective garments. The durability of

the antimicrobial property on the surface of textiles is one concern and serious challenge in developing such products [10, 11].
Depending of the type of textile fibre and upon the end use of the final product the antimicrobial functionality may be incorporated in three ways: (a) *direct incorporation* in to the fibres during their formation, especially in the case of artificial fibers (i.e Rhovil'As from Rhovil, Amicor and Amicor Plus from Courtaulds,; (b) *as finishing* on the fibers (i.e Eosy from Unitka); (c) and as a *finishing on the textile products* (i.e Sanitized from Sanitized AG).

Ultrasonic treatment

Ultrasound when a power threshold is reached induces voids, bubbles in liquid media. These bubbles are not stable and after several acoustic cycles collapse releasing locally tremendous amount of energy in terms of temperature (5,000ºK) and pressure (~2,000 atm). If there are some chemical compounds dissolved in the liquid, then they will suffer decomposition due to the bubble's collapse. If the compounds dissolved in the liquid generate metal oxides when the bubbles collapse, then they will end up as nanoparticles. Copper and zinc ammonia complexes in ethanol solution where chosen for this process. The addition of a fabric material in this setting will change some of the bubble collapse from a symmetrical mode to an asymmetrical mode (Figure 1).



Symmetric collapse generating nanoparticles

Asymmetric collapse shooting nanoparticles into the fabric

Figure 1. Acoustic bubble collapse

In this project a single step process in which ultrasound causes both the formation of metal oxide nanoparticles (CuO, ZnO) and simultaneously impregnates these nanoparticles in to textile fibres was employed [2, 4]. The pilot ultrasonic machines are based on the original laboratory scale unit, schematically presented in Figure 2.

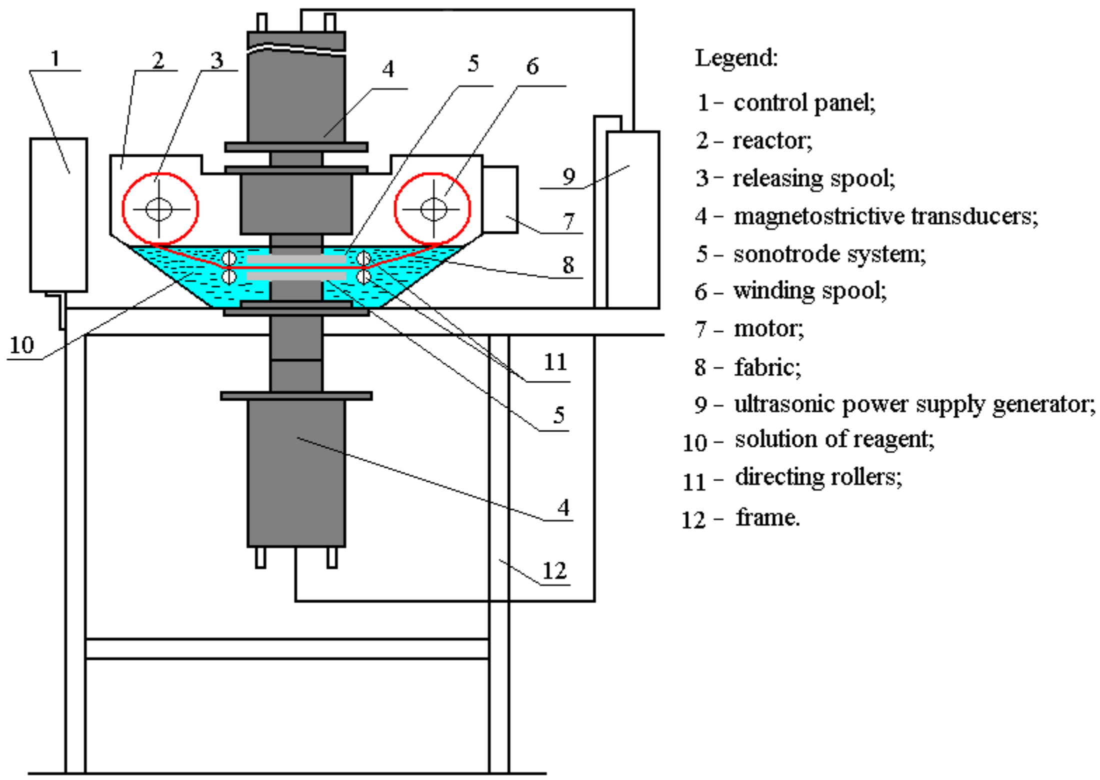


Figure 2. Schematic of laboratory scale machine for ultrasonic impregnation of textiles with antimicrobial nanoparticles

During this project two pilot ultrasonic machines designed to impregnate fabrics with nanoparticles were built. Each one was based on different ultrasonic transducers:

- The one existing in Romania was based on magnetostrictive flat ultrasonic transducers.
- The other one existing in Italy was based on piezoceramic tubular ultrasonic transducers.

Magnetostrictive transducers have the advantage of a high level of tolerance to process conditions, but they have a low level of efficiency in transformation of electricity in mechanical vibration, while the piezoceramic transducers are more sensitive to process condition, but have a higher transformation efficiency. Both prototypes were run in a continuous mode to produce 500 mm wide rolls of fabric impregnated with CuO NPs. Several samples are reported here for their antimicrobial properties.

New developments

This paper presents the antimicrobial activity of a PES/CO woven fabric that was coated with copper oxide nanoparticles (CuO NPs) with the aid of ultrasound energy. The microorganisms tested were represented by bacteria species *Acinetobacter baumannii* and MRSA and as fungal species, *Candida albicans*. The antibacterial and antifungal activities were maintained after 30 and 60 washing cycles. The ultrasound methods proved to be efficient in imparting antimicrobial function to the textile materials. The ultrasound treatment process was developed and optimized during the FP7 project SONO, that proposed to develop a technology able to deposit metallic oxide nanoparticles on the surface of textile materials for biomedical applications and related economic domains.

2. MATERIALS AND METHODS

2.1 Material

67 % polyester : 33 % cotton plain weave fabric (469 yarns/10 cm, yarn count 22.2 tex, in warp; 225 yarn/10 cm, yarn count 36.1 tex in weft; fabrics weight 198 g/m^2), of 50 cm width was used. Two types of samples were obtained: one on the Davo pilot scale (*sample D*) and the second on the Klopman pilot scale (*sample K*). Fabric pattern is diagonal 2/1.

2. 2 CuO Nanoparticles deposition

The sonochemical coating of the fabrics was carried out according to a previously published procedure [2]. In the pilot scale machines 500 mm wide rolls of fabric were fed on a motorized roller system through the acoustic cavitation zone close to the ultrasonic transducers. Both the fabric and the sonotrodes were submerged in a solution containing the precursors for the sonochemical production of CuO NPs. This solution contained between 0.01 and 0.05 M copper acetate dissolved in a 9:1 mixture of ethanol and water. For the coating procedure the solution was heated to approximately 50^{o}C the pH was adjusted to between 8 and 9. The fabric was then fed at a constant rate through machine. After this the fabrics were washed thoroughly with clean water and ethanol and then dried.

2.3 Washing of textiles

Specimens of both samples coated with CuO NPs on the ultrasound equipments were washed at 75 ^{0}C on a Rotawash (SDL Atlas) machine with a liquid, pH neutral detergent (4 g/L). The washing was done for 30 and 60 washing cycles according to SR EN ISO 6330:2001 standard (*Textiles - Domestic washing and drying procedures for textiles testing*).

2.4 Antimicrobial activity

Antimicrobial activity was carried out according to ISO 20743 standard (*Textiles. Determination of antibacterial activity of antibacterial finished products*), absorption method. The method gives a quantitative assessment of the antimicrobial activity at the surface of textile materials. The antimicrobial testing consists in establishing the cell reduction between a control sample and a treated sample after an incubation period of 24 -72 hours. The value of reduction is expressed as logarithm function after the following formula:

$$A = F - G \tag{1}$$

Where, **A** – antimicrobial (antibacterial/antifungal) efficiency value;
F – growth value on the control fabric sample;
G - growth value on the treated fabric sample

The antibacterial testing was carried out against methicillin-resistant *Staphylococcus aureus* (MRSA), strain NCTC 10442, and *Acinetobacter baumannii*, strain NCTC 10303. The

antifungal testing was carried out against *Candida albicans* AATCC 10231.
The tested microbial strains are considered important in causing nosocomial infections and they are also resistant to usual antibiotic therapy.

2.5 Scanning Electron Microscopy (SEM)

The surface morphology of coated samples was investigated by a FEI Quanta 200 Scanning Electron Microscope with a GSED detector, at a 8000X – 16 000X magnification and a accelerating voltage of 12,5 kV – 20 kV. The samples were examined before washing and after 60 cycles of washing and the copper oxide nanoparticles diameters were measured with the SEM xTm software.

2.6 Energy Dispersive X-ray analysis (EDX)

EDX was used to identify the elemental composition of the PES/CO coated fabrics. The analysis is done with a FEI Quanta 200 Scanning Electron Microscope coupled with a EDX detector. The detector has the ability to convert the X-ray energy emitted by the samples into voltage signals that are specific to different chemical elements. The EDX analysis was applied before washing and after 60 cycles of washing.

2.7 Infrared Thermography (IRT)

The uniformity of conductive thermal transfer was analysed with a FLIR P 620 thermocamera, towards a study of the thermophysiological comfort. The samples were fixed on the top of heating plate heated to 37°C, the normal temperature of human body. The thermal infrared radiation emitted by the textile fabrics were detected with the thermocam in the spectral band between 7.5 and 13 μm. Thermograms were generated from these results, which indicate the distribution of temperature on the surface of the analysed samples. The thermograms were analysed with the soft Flir Quick Report, adding the rectangle and isotherm function and samples emissivity with the value 0.95.

3. RESULTS AND DISCUSSIONS

3.1 SEM and EDX before and after washing

Scanning electron microscopy was used to investigate the surface morphology of the uncoated and coated textile materials and to identify the presence of CuO nanoparticles. Investigations were carried out before and after 60 cycles of washing (Figure 3 and 4). The nanoparticles of CuO were identified on the surface of the samples before washing, and after 60 cyles. The washing did not affect the Nps coating for any of the samples. The range of Nps diameters observed was between 70 – 600 nm.

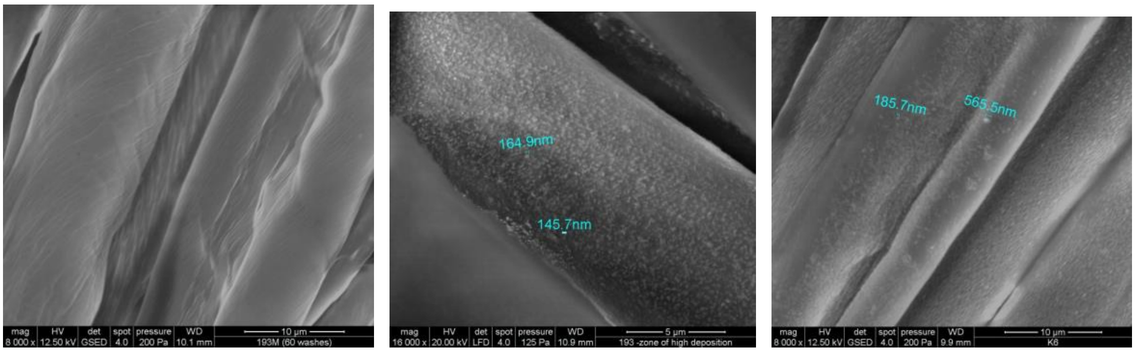


Figure 3. SEM micrograph of the uncoated samples (left), coated sample D (middle) and coated sample K (right) before washing

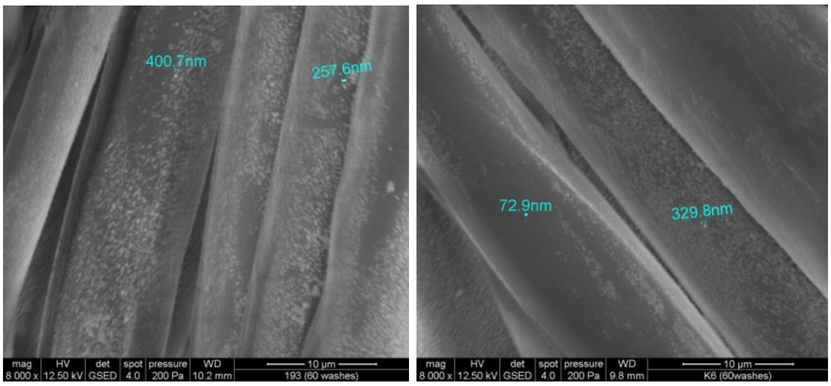


Figure 4. SEM micrograph of the coated sample d (left) and coated sample k (right) after 60 washes

The presence of CuO nanoparticles on the surface of d and k samples was further confirmed by the edx identification of cu emission line. the cu line was observed for the coated samples before and after 60 washing cycles. the coating was maintained after the laundering operation (figures 5 and 6).

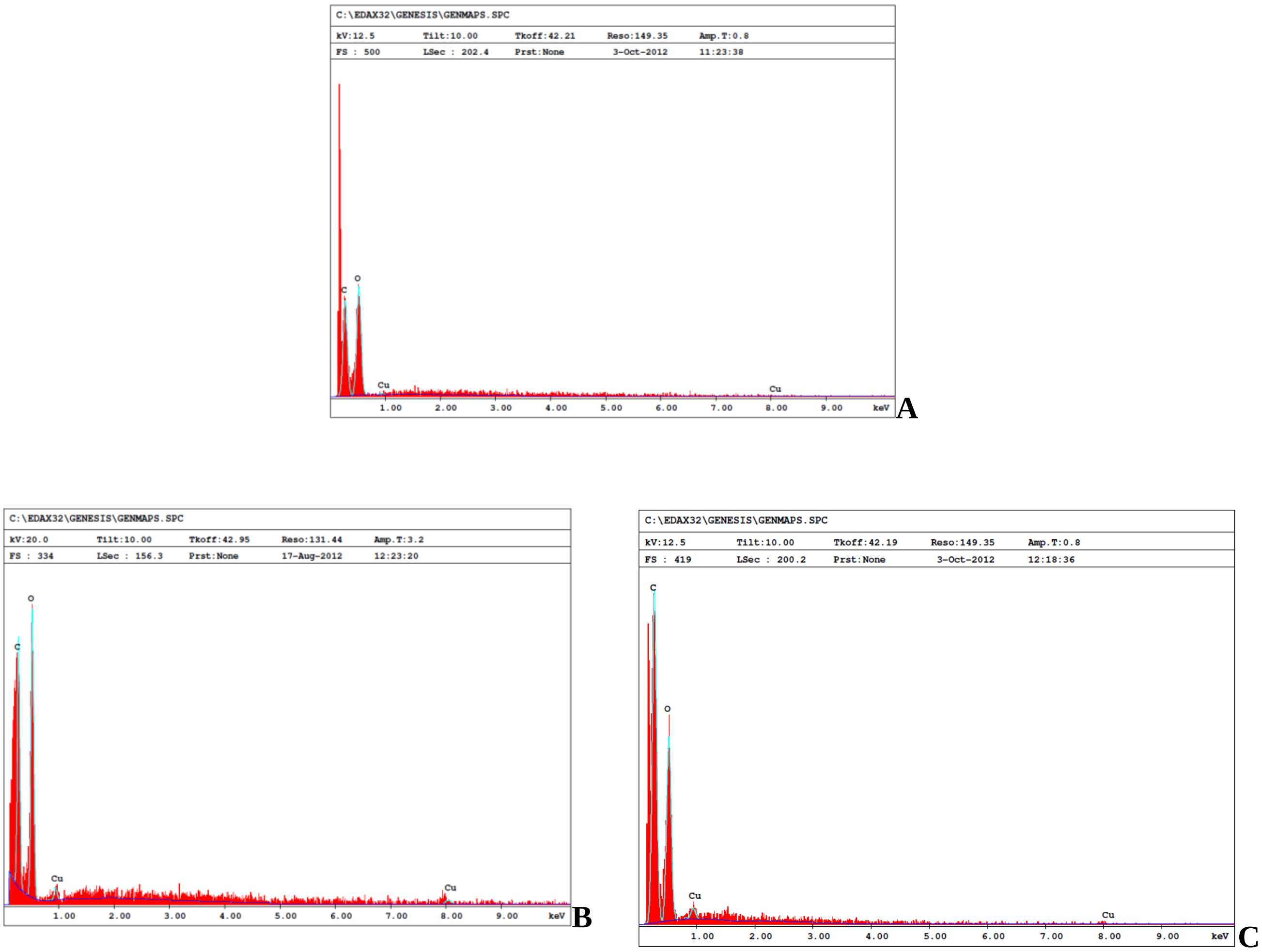


Figure 5. EDX spectra of sample D before (B) and after 60 washing cycles (C) and of uncoated fabric (A)

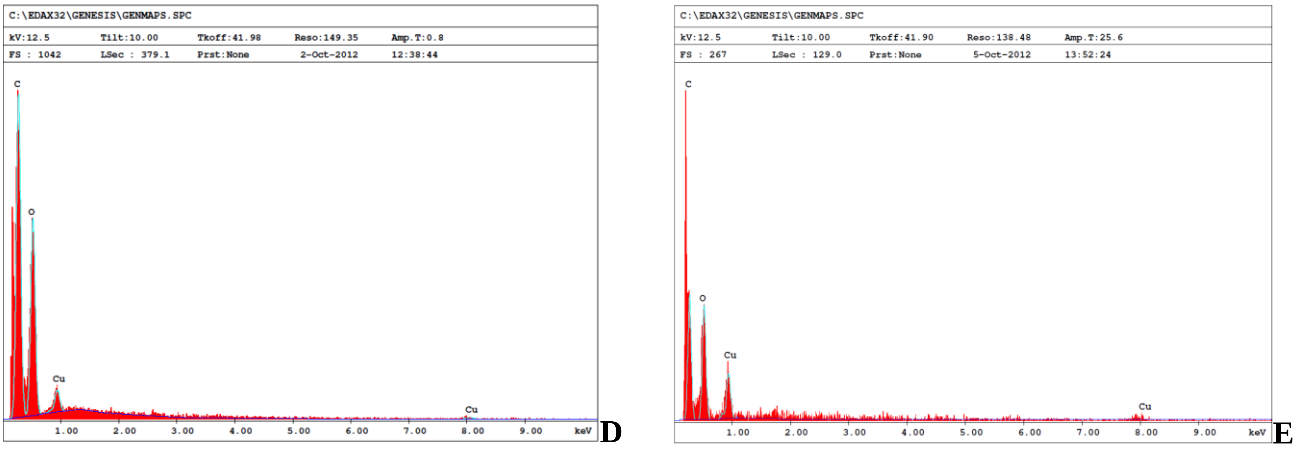


Figure 6. EDX spectra of sample K before (C) and after 60 washing cycles (D)

3.2 Infrared thermography (IRT) before and after washing

The following pictures are the thermograms for the uncoated and coated samples. the isotherm of 37±0.5 °c appear in thermograms with gray color. in the thermograms appear, also, the scale of temperatures which are represented by different colors. The thermograms of all samples (before and after washing) have a very large area of isotherm.This showed that they were thermally conductive, because a large area of the analysed surface had values of temperature near the temperature of the plate (37°c). For this reason, we can consider that the treatment and the washing doesn’t modify the thermal conductivity of material.

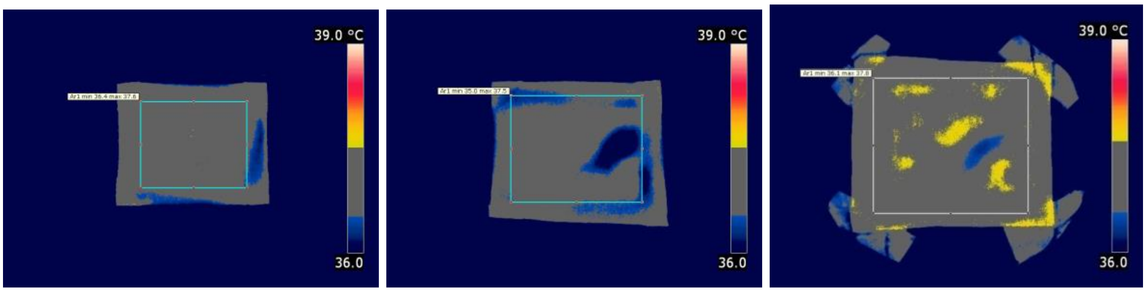


Figure 7. IRT thermograms for the uncoated (left), sample D (middle) and sample K (right) before washing

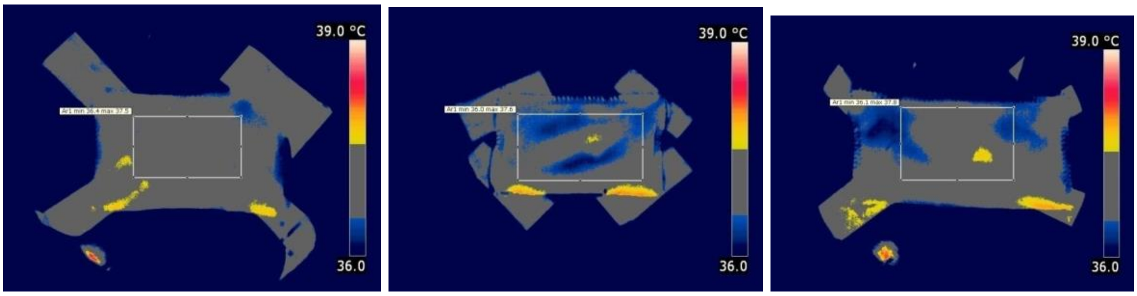


Figure 8. IRT thermograms for the uncoated (left), sample D (middle) and sample K (right) after 60 washes

The non-uniformity of the thermal transfer through uncoated and coated samples is measured with the help of parameter Δt (^{0}C) which represents the difference between the maximal (t_{max}) and minimal (t_{min}) temperature inside the rectangles from thermograms. In the following chart it is observed that, after washing, the uncoated and K samples maintain the non-uniformity values. For sample D the non-uniformity decreases.

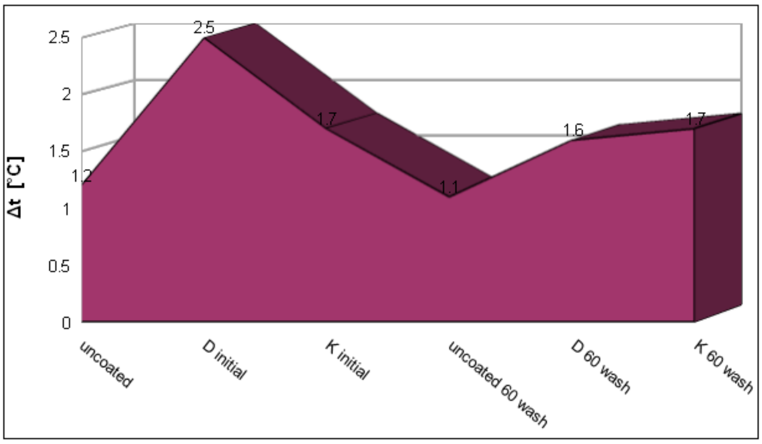


Figure 9. Infrared thermography analysis for uncoated and CuO Nps coated samples before and after 60 washing cycles

3.3 Antimicrobial testing before and after washing

3.3.1 Antibacterial assessment

The antibacterial assessment was performed on initial CuO Nps coated D and K samples and after the laundering operation for 30 and 60 washing cycles. The antibacterial efficacy was compared with the uncoated fabric and the viable cell reduction was logarithmically expressed by parameter A.

The results from antibacterial efficacy tests on the CuO NP PEC fabrics are presented in Figure 10. The antibacterial activity of both of the fabrics was very high, with A values >5. Following overnight incubation of the fabric samples with the test bacteria no viable bacteria cells were recovered. The antibacterial activity levels after 60 washing cycles were still high (A>2) and in Figure 4 CuO NPs can still be seen on the fibres after the washing treatment. There was some decrease in the antibacterial activity levels after washing presumably due to the loss of some CuO from the fabrics. Both fabrics lost between 0.16 and 0.17 % w/w of the CuO. The slightly greater drop in activity observed with the Davo fabric may have been due to the lower amount of CuO deposited in the first place (0.37 % w/w CuO on D and 0.9% w/w CuO on K) (Figure 11).

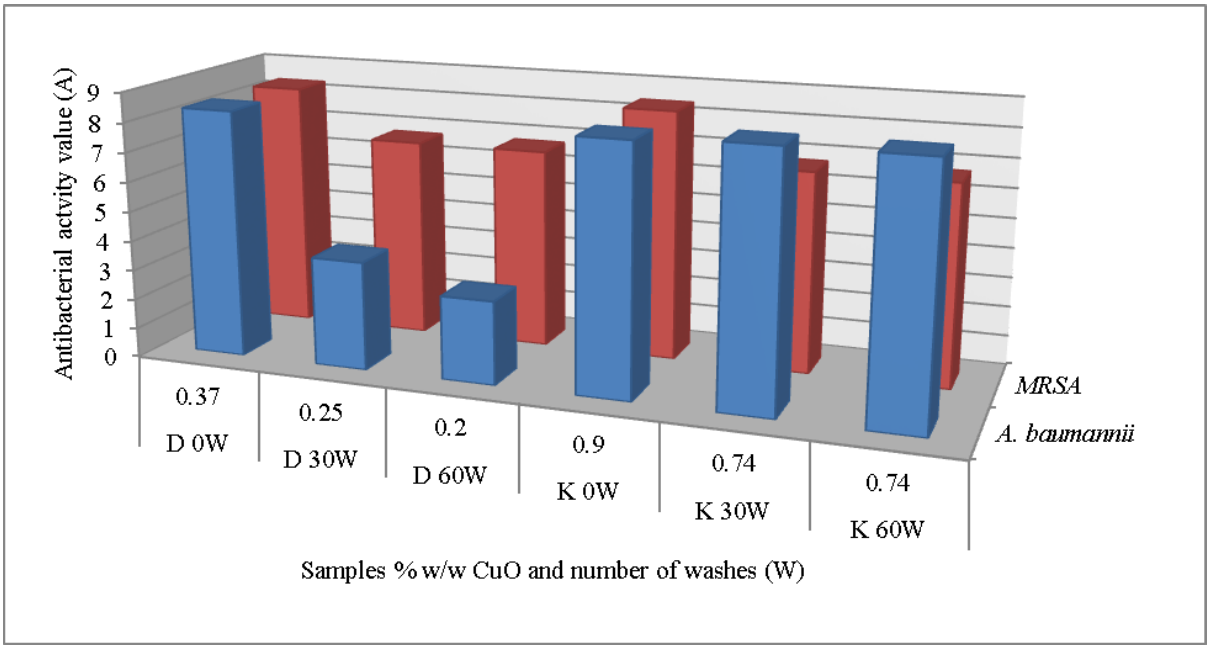


Figure 10. Antibacterial activity towards MRSA and *Acinetobacter baumannii* for samples D and K after 0, 30 and 60 washing cycles.

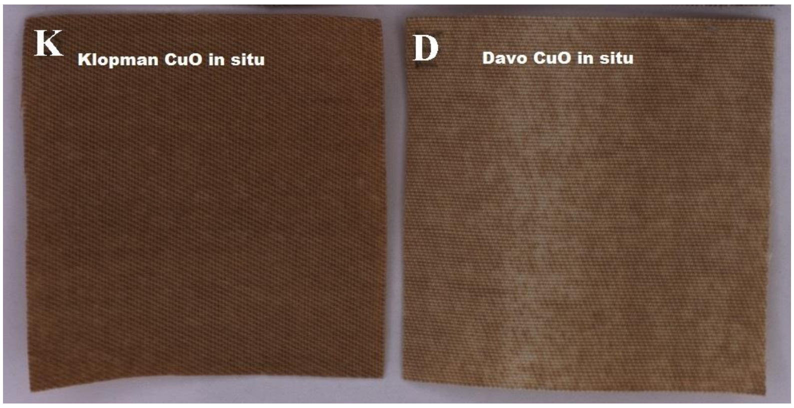


Figure 11. White PEC sonochemically impregnated with CuO NPs. (left) sample from Klopman machine (right) sample from Davo machine.

3.3.2 Antifungal assessment

The antifungal assessment was performed on initial CuO Nps coated D and K samples and after the laundering operation for 30 and 60 washing cycles. The antifungal activity efficiency was measured compared with the uncoated fabric and the cell reduction was logarithmically expressed by parameter A.

The initial coated fabrics, both samples D and K expressed a high antifungal value, close to 3, representing a cell reduction > 99.9%. The fungal cell reduction remained at the same value after 30 washing cycles as well as after 60 washing cycles, for each samples, which means that the laundering cycles will no longer affect the antifungal efficiency and that the CuO Nps are stable/permanent embedded on the surface of the fabrics. The fungal cell reduction is showing grater value for the K sample after 30 and 60 washing cycles, similar to the antibacterial cell reduction results, sustaining the correlation hypothesis between the antimicrobial activity and the amount of CuO deposited on the textile materials. The antifungal results are presented in Figures 12 and 13.

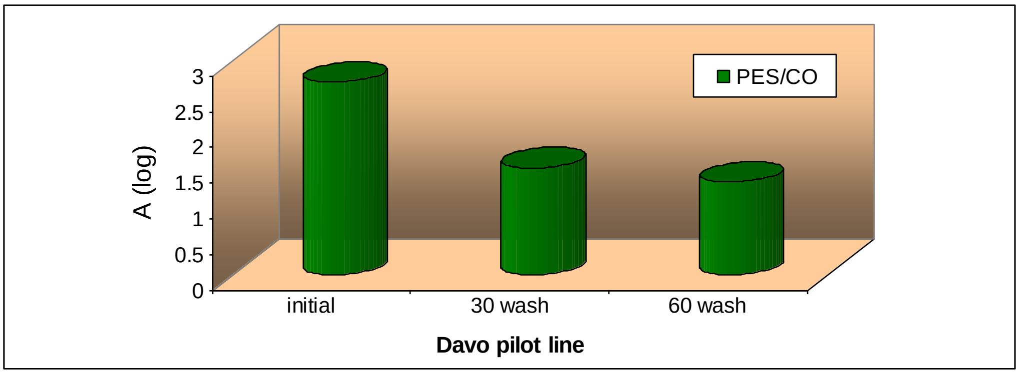


Figure 12. Antifungal activity towards *Candida albicans* for sample D obtained on the Davo pilot line before and after 30 and 60 washing cycles

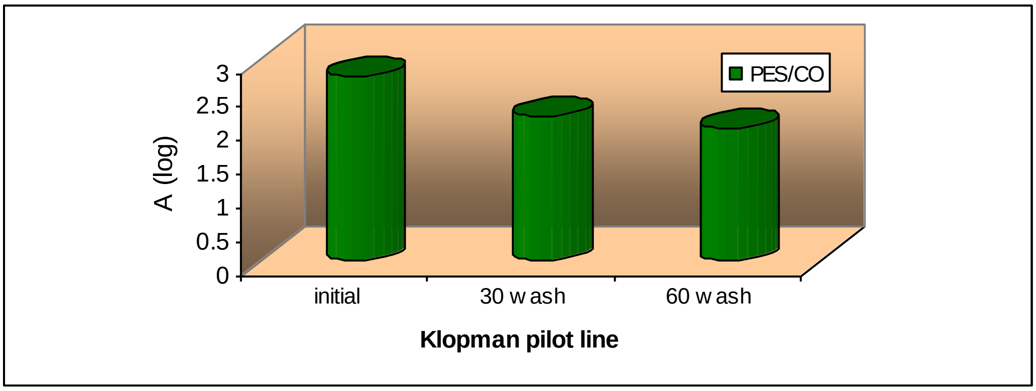


Figure 13. Antifungal activity towards *Candida albicans* for sample K obtained on the Klopman pilot line before and after 30 and 60 washing cycles

4. CONCLUSIONS

Nanoparticles of copper oxide have been embedded into a textile surface by means of ultrasounds. The CuO coating is analysed through Scanning Electron Microscopy (SEM), Energy dispersive x-ray analysis (EDX) and Infrared termography (IRT) and the antimicrobial efficiency of the CuO Nps is determined for the treated samples and for the treated samples after 30 and 60 cycles laundering. The antibacterial efficiency as well as antifungal efficiency are very high for the initial coated samples. Sample obtained on the Klopman pilot line is showing excellent antimicrobial activity also after 30 and 60 washing cyles. The antimicrobial activity is lower for the D sample after the washing cylces, being correlated with a smaller amount of CuO Nps deposited on the fabrics surface (0.37 % w/w CuO on D and 0.9% w/w CuO on K). The sonochemical process has can be used for a range of textiles and for various different nanoparticles. The technology has the potential to be both economically competitive and environmentally green. The formation of the nanoparticles and their impregnation are accomplished in a single step process, and no toxic chemicals are used.

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WOMEN SCIENTISTS IN THE TEXTILE – CLOTHING SECTOR

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Keywords: women scientists, woman, gender dimension, gender equality, textile-clothing

Abstract*:* Studies highlight that gender discrimination is still present in modern societies. In order to get promoted, a woman has to prove that she is more capable than a man in a similar position. In the research field, the increase of women participation is an objective shared by many scientific institutions in Europe, as evidenced by the public consultation initiated by the European Commission, with the purpose of defining Horizon 2020 framework programme for research and innovation.

The ERA (European Research Area) strategic vision, adopted in 2010, sets as an objective that until 2030, half of the total number of scientific personnel in all subjects and at all levels of scientific system should be women.

In comparison with other sectors, the textile-clothing sector employs women in majority. The paper presents aspects referring to gender dimension, especially in the research environment of the textile-clothing sector.

1 INTRODUCTION

The “gender” theme is very complex. Various studies conducted in some countries of the European Union show that, although formal legislation is an absolutely necessary condition, it does not guarantee gender equality. These studies underline the necessity of modifications at the mentality level and in work conditions. Various institutions need to get involved in supporting and encouraging these changes by the establishment of new standards and monitoring progress to allow women to benefit of the advantages stipulated in the legislation.

The textile-clothing sector, in comparison with other sectors, employs predominantly women employees.

2. THE TEXTILE – CLOTHING SECTOR IN ROMANIA

At present, we can describe the textile-clothing sector in Romania as a dynamic sector of the national economy, with a high degree of performance, employing female labour force and ensuring employment for approximately 167 thousand employees (out of which 140 thousand in clothing and approximately 27 thousand in textiles)[1].

Fig. 1 presents the evolution of the percentage of women involved in industry, processing industry and textile-clothing industry. A prominent fact is that the percentage of women employed in the textile – clothing sector is almost double compared to the one of women in industry, respectively 83.72% compared to 43% of the total number of employees in 2011.

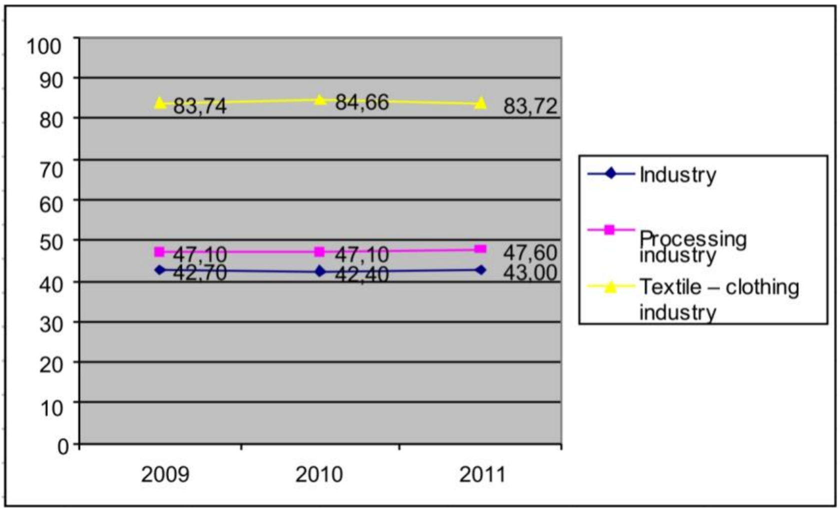

Fig. 1 Romania – Evolution of percentage of women employed in industry, processing industry and textile – clothing industry

It is also worth mentioning the fact that in the processing industry in Romania, comprising 24 branches, the clothing sub-sector is number 1 in terms of average number of employees. In this hierarchy this subsector is at the opposite pole, occupying the penultimate position (position 23) in terms of gross average salary. At the same time, the textile – clothing sector contributes to social stability being represented in all the counties (a total of 5 979 textile companies, out of which 4 480 with a clothing profile and 1 499 with a textile profile), has a significant weight in the national exports (10.89%) and it contributes with 3.39% of Romania’s GDP.

3. WOMEN SCIENTISTS

In the past, men were traditionally preoccupied exclusively with their professional career, ignoring their responsibilities for the family, but the situation at present has changed.

While in the second half of the XIX-th century women gained the freedom to access knowledge and social ascension, in the actual context the chances for women to develop a scientific career have considerably increased.

Researchers have discovered physiological differences between a man’s and a woman’s brain. On the other hand, the natural differences between men and women are certainly complemented by the social rules and cultural stereotypes that generate different expectations for boys and girls during growth stage, including differences related to professional activity.

This is one of the reasons why the studies indicate that gender discrimination is still present in modern societies. In order to get promoted, a woman has to prove that she is more capable than a man in a similar position. [2].

In the research field, the increase of women participation is an objective shared by many scientific institutions in Europe, as evidenced by the public consultation initiated by the European Commission, with the purpose of defining Horizon 2020 framework programme for research and innovation.

The ERA (European Research Area) strategic vision, adopted in 2010, sets as an objective that until 2030, half of the total number of scientific personnel in all subjects and at all levels of scientific system shall be women.

The Directorate - General for Research has mandated the elaboration of a report in order to analyse the conditions and status of women scientists in Central and East European countries and in the Baltic States. These countries are: Bulgaria, Czech Republic, Estonia, Latvia, Lithuania, Poland, Romania, Slovak Republic, Slovenia and Hungary. As a result of the action for promoting gender equality in science in Enlarged Europe, initiated by *"Science and Society Action Plan"*, this report follows the ETAN (European Technology Assessment Network) with the title "*Scientific Policies in United Europe. Promotion of professional excellence in the context of an integrative approach of gender equality"*, that treats mainly the situation of women scientist in EU member countries [3].

The group of Experts Enwise (**En**large **Wo**men **I**n **S**cience to **E**ast) was created with women scientists in various fields, representing science academies, universities, research institutes and business environment.

This report stipulates the fact that in the period before communism the professional evolution of women followed the same patterns as in West European countries. The report highlights the influence that the country specific "gender" policy had on Central and East European countries and in the Baltic states during the communist regime which included both equal rights and the obligation to have a full time job and access to education irrespective of gender. Moreover, this policy was supplemented by the existence of assistance for children care, legal protection and support offered by the state to employed mothers. But this formal gender equality was acquired and doubled by a censorship policy and through the suppression of women's freedom to travel and to free expression. Furthermore, this system perpetuated horizontal and vertical segregation in all fields of activity (including Higher Education and Research).

The report takes into account the communist legacy referring to "gender" policy. The quality of education and free access to education has determined the development of a significant number of highly qualified women who are active in all the public spheres, particularly in science.

The transition period that led to a restructuring of the research systems in these countries was characterized by an abrupt decrease of the funds allocated to science, the decrease of the number of researchers and the disappearance of the armament industry.

Although the changes equally affected men and women in research, women are those who are more vulnerable to transition consequences.

The perspectives of young female scientists are quite gloomy due to lack of funds, rigid promotion and recognition criteria and lack of adequate assistance policy. All these factors are potential causes of the “brain drain”.

Although the percentage of women among researchers is higher in these countries than in the rest of 15 EU member states, upon a more in-depth analysis of the economic situation the following are observed: women are better represented in the countries with smallest research population; for a longer period of time they constituted the majority of the highly qualified labour force and therefore there is a high probability that they are employed in strong research connected fields.

The demographic data are not the only explanation. The report shows that in countries where male and female representativeness in research is balanced, there are “gender” differences in the presence in various R&D sectors and various fields of science. This way, women are squeezed out of competitive sectors that benefit of more generous financing and absorbed as auxiliary human resources in the sectors with low funding.

The report sketches an image of day-to-day work conditions of women scientists in these countries. The women are still under-represented at top management level in academies and universities. They are the majority in teaching personnel (54%), but tend to be concentrated in the lower academic positions. Despite the fact that women representation in university staff is similar to the one in the researchers’ community, the probability for men to obtain a higher academic position is three times higher.

The scientists in these countries were associated with the Research Framework Programme since the beginning of 1990. Despite the interest shown by women scientists for such activities, their skills are used rather in support activities than in the monitoring of the Framework Programme or advisory work.

Inadequate funding, poor infrastructure and outdated equipment are factors that impede the development of research communities, especially in those RD sectors where expenditure is low, as it is the case in the textile – clothing sector.

These sectors tend to absorb a big part of the women scientists who under these circumstances face the risk of losing research opportunities.

At present, similar to other EU members, Romania faces the same problems. Although in order to comply with EU requirements, gender equality was formally declared in our country, there is still a long way to go with putting it into practice.

Amendments brought to legislation that favour gender equality are often faced with resistance. In the parliament, strongly dominated by men, there is strong resistance to the gender equality idea and sometimes gender equality is perceived as discrimination against men.

In the transition period in research in Romania, when there was an abrupt decline of funds allocated to science, a restructuring of the system took place and this led to the decrease of number of researchers and the disappearance of more industry branches. Although the changes produced have equally affected men and women active in research, women are those whom transition consequences place in a more vulnerable situation.

In Europe, the percentage of female researchers is increasing, but women continue to be under-represented in scientific subjects and careers. This is the message of the latest edition of the „She Figures" report, published by the European Commission [4]. Women represent only 33% of the total number of European researchers, 20% of the number of tenured university professors and 15.5% of the number of top managers of the higher education institutions. The European Commissioner for research, innovation and science, Máire Geoghegan-Quinn, stated: "Despite some progress registered during the last years, women are still a minority among researchers and there is an invisible but real barrier that blocks the access to the top positions. This is a serious injustice and an outrageous waste of talent. The objective of the Commission is to promote gender equality in our programmes and to do our best to change a deeply rooted institutional culture."

According to the report, women represent approximately:

- 40% of the total number of researchers in higher education;
- 40% in public sector;
- 19% in economic environment.

Although in all sectors their number grows faster than the number of men (+ 5.1% for women compared to +3.3% for men during 2002-2009), women researchers continue to face great difficulties in filling decision making positions, the ratio being one woman to two men in the scientific and management councils in all EU.

In 2010, the women ration among students (55%) and higher education graduates (59%) is higher than that of men, but the majority of PhD students and PhD graduates were men (women represent only 49%, respectively 46%). Moreover, higher in the academic career women represent 44% of the researchers with PhD degree on the first career level and only 20% of those in top positions. Women under-representation is even more striking in fields as science and engineering.

A great majority of the European officials consider that a higher involvement of women in science will contribute to social economic growth [5].

The slow progress in achieving gender equality is mainly attributed to:

- General persistence of gender stereotypes on the labour market;
- Lack of support at higher level in research institutes;
- slow progress in the modernization of research institutes

Among the European scientific institutions the idea of an insufficient presence of women in science and technology is a waste of resources that neither science nor economy can afford has become more and more accepted.

60% of the European university graduates are women. They graduate with excellent marks, many times better than those of their male counterparts. But these highly qualified personnel cannot find a place in the system. Many technology fields are dominated by men, the total number of women being below 30% out of the total number of students.

The National Research and Development Institute for Textiles and Leather has initiated a project having as objective to promote a better integration of the gender dimension in the textile –clothing field, both in research and education field and in the economic and cluster field.

Attention will be focused on the promotion of a better gender integration in science, research and technology through the dissemination of practices and research studies existing at international level.

The project includes actions in the following 4 directions, both for the research and education field and for the economic and cluster field:

i) Development of a better understanding of the gender dimension in the field of technology development and of innovation processes paying special attention to the challenges identified in Horizon 2020;

ii) Dissemination of policy measures orientated to the integration of the gender dimension in the context of science, research and technology;

iii) Analysis of case studies for successful women careers in the textile – clothing field;

iv) Dissemination of success stories for a better integration of the gender dimension in career opportunities for women.

The implementation of this project will be a starting point for the establishment of new partnerships at European and international level, all the more so as starting with 2013, INCDTP has become a member of COST Action TA 1201, a project that comprises representatives of the research, academic environment, of the business environment and of the women organizations in the entire world.

Participation of the institute to this consortium that promotes mobilities and good practice exchanges in a field of interest and good prospects for the scientific community shall contribute to the alignment of Romanian research to the strategic directions of HORIZON 2020, to the consolidation of the image and visibility of INCDTP on national and international level and last but not least will lead to a better involvement of women in the scientific activity and in the economic environment at a moment when industry is acutely lacking qualified personnel.

Thus, by convergent actions, aimed at increasing competitiveness in the research and innovation sector through research and innovation, professional training, professional evaluation, women participation stimulation, attracting young people to a successful career, INCDTP shall contribute to achieving its strategic objectives as a pillar of the textile – clothing field.

4. CONCLUSIONS

Promotion of gender equality is one of the key priorities set by the European Commission to establish the European Research Area (ERA). The Commission has asked the EU member states to eliminate the obstacles that impede on the recruitment, retention and promotion of women researchers. The Commission has also in view to solve the gender inequality problem at a decision-making level.

The HORIZON 2020 programme stipulates that this direction is a strategic measure and there is a need for actions meant to eliminate the obstacles that hinder women from having successful scientific careers. The European Commission committed to reaching the objective of 40% referring to the participation of women in the consultative structures and will guarantee that differences between women and men will be reflected by the content of the call for project proposals and in the evaluation process, as applicable. The Commission estimates that a higher participation of women will improve the quality of research and innovation and will at the same time contribute to solving the existing deficit of highly qualified and experimented scientists needed to increase competitiveness and for the growth of European economy.

HORIZON 2020 programme stipulates that at a national level, member states will need to promote new forms that reconcile the professional and private life and will increase gender equality. The research institutes need also to implement adequate strategies referring to gender equality in human resources management and in research programmes.

As the textile-clothing sector hires predominantly female personnel, in view of an integrative approach of gender equality, further research is needed on the "women scientists" theme and also a systematization of data referring to the men and women distribution.

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ROMANIAN WOOL FIBRES CHARACTERISTICS: CURRENT STATE AND PERSPECTIVES

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Abstract. *This paper presents a study referring to characteristics of Romanian wools produced in 2013. The evolution of wool production and consumption in Romania over the last 10 years has been analysed. Samples of wool produced in 2013 were gathered from all Romanian regions and were analysed from physical – mechanical, chemical and morphological perspective.*

1 INTRODUCTION

During recent years the textile sector in Romania has gone through deeper structural adjustments that were possible due to rapid privatization; reaching a reasonable level of profitability became possible only for clothing companies that import their raw material. Because a majority of weaving and spinning mills were closed down, the imports of clothing products and carpets especially from China and Turkey increased.

Wool local market barely survived, as the shepherds only commercialize the meat – especially around Easter – they are not interested anymore in the sheep wool that should be clean and have a high quality, motivating that they have no possibility to sell it anymore or that they are offered too low a price for selling it. As a consequence, wool is not considered an auxiliary product anymore, alongside milk, meat and lambs. Very few shepherds still active in the country, in Dobrogea, Buzău or Maramureş, raise authentic races such as Tsgai or Merino, with high quality wool, that they export especially to Asian countries. As for the rest, the luckiest shepherds are those who manage to sell the wool to construction companies that use it for thermal and phonic insulation of buildings[1].

2. CURRENT SITUATION IN ROMANIA

In 1980 Romania was ranked 10-th in a global ranking in terms of numbers of sheep and the same position in terms of wool production. It had also an important position among top meat producers. Compared to 1989, a reduction of numbers was registered – by 29.1% at the end of 1994, by 40.38% in 1997 and by 50.09% at the end of 2000.

Starting with 2006 the numbers of ovine and caprinae increased significantly and it reached in 2009 a level of 10.1 million, followed by a slight decrease, and in 2012 it reached again the same level as in 2009. **The total numbers of ovine and caprinae** increased by 3.4%, and the numbers of families (sheep, gimmers and goats) increased by 3.2% in 2012 compared to 2011(fig. 1) [2].

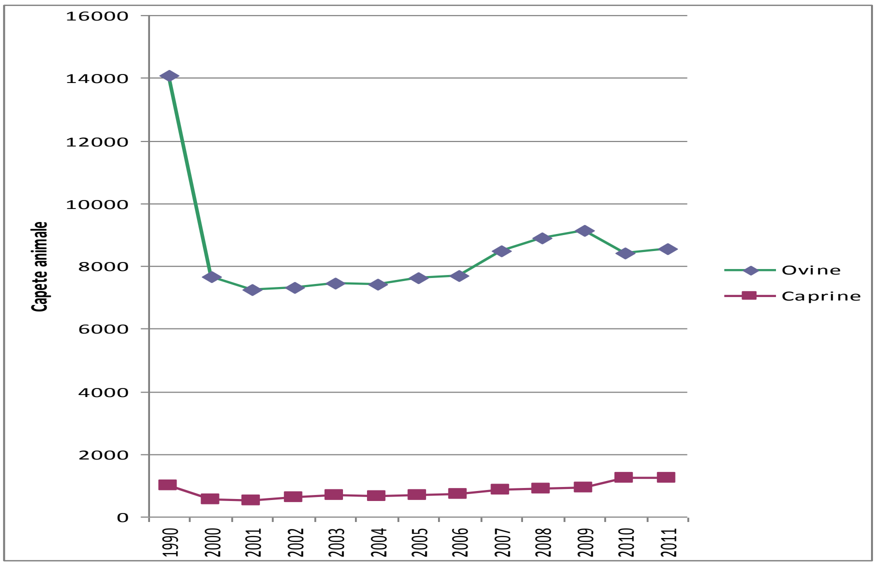

Figure 1 – Evolution of the numbers of animals in 2000 – 2012[2]

At the end of 2012, Romania is on fourth position within EU after United Kingdom, Spain and Greece in terms of numbers of ovine and caprinae.

As a consequence of the fluctuations of the animal numbers, wool production decreased significantly after 1990, by more than 50% until 2000 and then started to grow as can be noticed in the figure bellow.

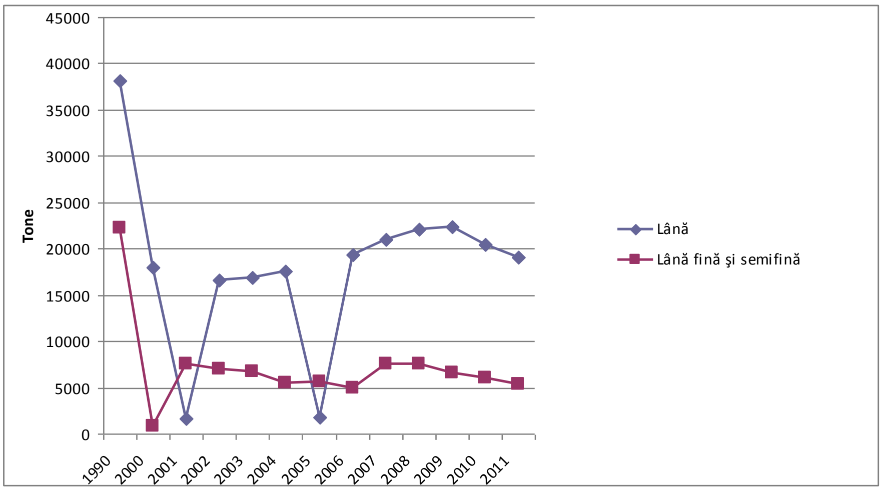

Figure 2 - Wool production in Romania[2]

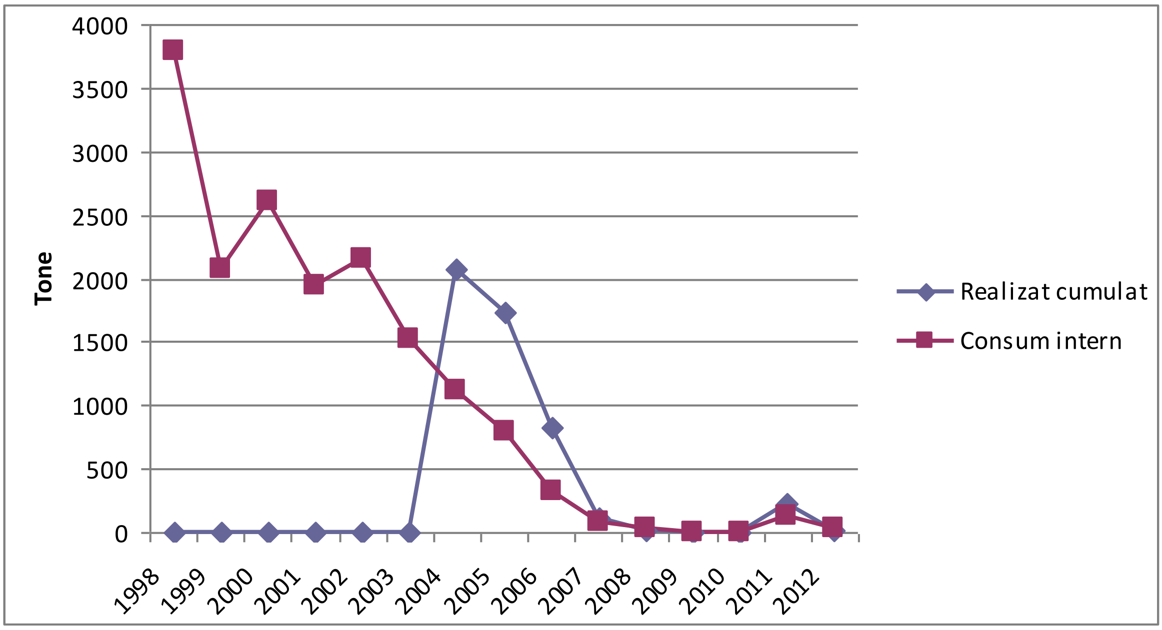

Figure 3 - Industrial Wool Production (2012) [2]
(product 30450, washed basis)

In 2012 Romania imported from outside European Union approx. 700 tons of wool, especially combed wool, the same as in 2011and approximately 50% more than in 2010.

3 RESULTS AND DISCUSSIONS

3.1 Complex quality testing of samples of collected fibres

The objective of this paper is to highlight the present quality characteristics of Romanian wools throughout Romania. Samples of wool produced in 2013 were taken from practically all the regions of the country - Ardeal, Muntenia, Banat and Moldova. A basis of raw materials was developed with samples of the most relevant ovine breeds presently grown in Romania. Wool samples were taken from the following breeds: Merino, Turcana, cross-breeds (Tsigai+Merino). In the study 21 wool samples were analysed. Because the breed was not known for all the wool samples, an attempt was made to categorize the wool according to the breeds specific to each region, based on the physical – mechanical, chemical and morphological characteristics resulted after tests.

Samples characterization was done by physical – mechanical, chemical and structural tests in the RENAR accredited laboratory of INCDTP.

From a **physical-mechanical** point of view the following parameters were determined:

a) **average diameter** of fibres using LASERSCAN equipment.

b) **average length** of individual fibres according to standard SR EN ISO 6989:1998.

The results obtained following the tests are presented in tables 1 and 2.

Table 1 Results of physical – mechanical analysis

	Average Diameter Laboratory method on LASERSCAN equipment			
Sample Code/breed	Average Diameter (μm)	Coefficient of Variation (%)	Comfort Factor	Standard Deviation (μm)
P 1.1	29,4	25,41	67,4	7,2
P 1.2	27,7	19,2	72,9	5,3
P 2.1	26,3	22,0	80,5	5,8
P 2.2	35,3	24,0	31,4	8,5
P 3	42,6	39,1	28,8	16,7
P 6.1	50,5	33,3	13,3	16,8
P 7	32.1	21.9	43	70
P 9.1	38.5	38.3	37	14.7
P 9.2	32.4	39.8	58.2	12.9
P 9.3	45.9	33.4	16.6	15.3
P 11	35,9	39,0	40,3	14,0
P 12	29,0	21,8	63,9	6,3
P 4	23,2	26,9	87,8	6,2
P 6.2	33,9	23,9	35,1	8,1
P 8	34.9	21.7	28.7	7.6
P 5.1	38,8	41,2	36,5	16,0
P 5.2	32,7	27,5	44,8	9,0
P 10	43,8	31,9	17,2	14,0
P 13	33,4	38,4	51,9	12,9
P 14	40,3	38,4	29,5	15,5
P15	40,7	40,7	33,1	16,6

Table 2 presents the quality technical conditions to be met by unwashed wool and its classification depending on the breed according to STAS 844-80

Table 2 Quality Technical Conditions according to STAS 844-80

Characteristics	Merino Wool	Spanca Wool	Tsigai wool	Stogosa wool	Turcana Wool
Fineness	Fine	Fine and semi-fine	Semi-fine and semi-thick	Semi-thick and thick	Thick
Average medium (μm)	Maximum 25	Maximum 30	Maximum 37	Maximum 45	Over 45
Average length (cm) min	5.1-6.1	6.1-7.1	6.5-7.5	Is not normed	Is not normed

Comparing the results obtained following the laboratory analysis with data from the technical quality conditions stipulated by STAS 844-1980 the following conclusions were reached:

- samples P 1.1 and P 1.2 declared by the ovine breeder as belonging to Merino breed have an average diameter specific to Spanca breed, which is considered a fine and semi-fine wool breed.

The values of comfort factor are quite high: 67 and 73 respectively. It is known that, the finer the wool, the higher the comfort factor (maximum 100).

- sample P 2.1 declared by the breeder as belonging to the cross-breed (Tsigai+Merino) with an average fibre diameter of 26 µm, corresponds to Spanca breed, and P 2.2 declared by the breeder as belonging to the same breed has a diameter of 35 µm, characteristic to Tsigai breed, and it belongs to the category of semi-fine and semi-thick wools, according to STAS 844-80.
- samples declared by the ovine breeders as belonging to Turcana breed belong according to the standard to four different breeds, as follows: P 12 – Spanca breed; P 7, P 9.1, P 9.2 and P 11 – Tsigai breed; P 3 - Stogosa; P 9.3 and P 6.1 – Turcana breed.
- sample P 4 declared as belonging to Carabașa breed, with a fibre diameter of 26 µm, belongs according to table 2 to Spanca breed, fine and semi-fine wool, *fact confirmed also by a comfort value of over 80%.*
- samples P 6.2 and P 8 declared as belonging to Tsigai breed, which is a breed of semi-fine and semi-thick wool corresponding to the characteristics of this breed.

Nevertheless, a very low wear comfort of 30% is noticed.

- the samples coming from unidentified breeds can be classified according to Table 2 in two breeds: P 5.1, P10, P 14 and P15 with a fiber diameter of max. 45 µm, belonging to Stogosa breed, and P5.2 and P 5.3 belong to Tsigai breed.

The data comparison leads to the conclusion that the breeds declared by the ovine breeders do not coincide with the standard classification of breeds.

Table 3 presents the results of the tests for the measurement of fibres' length according to standard SR ISO 6989:1998.

Table 3 Fibre length

	Fibre length	
Sample/ Breed code	Average length of single fibres	
	mm ± p %	cv %
P 1.1	72,58 ± 1,32	21,48
P 1.2	94,42 ± 1,93	32,29
P 2.1	83,05 ± 1,23	19,50
P 2.2	92,62 ± 3,82	44,53
P 3	94,49 ± 5,41	64,75
P 6.1	66,15 ± 3,72	44,40
P 7	120.59 ± 3.92	47.93
P 9.1	136.68 ± 7.26	84.85
P 9.2	84.55 ± 3.68	42.57
P 9.3	127.73 ± 5.31	61.83
P 11	126,09 ± 3,91	44,03
P 12	98,85 ± 3,87	41,47
P 4	93,67± 2,75	32,41
P 6.2	88,78 ± 1,73	19,43
P 8	87.77 ± 1.48	17.37
P 5.1	118,13 ± 7,14	85,41

P 5.2	107,84 ± 4,43	52,53
P 10	155,69 ± 5,35	61,39
P 13	86,12 ± 3,35	38,60
P 14	135,97 ± 6,92	81,08
P15	125,35 ± 6,05	68,42

Characterization of fibers in terms of their length shows that all samples fall into one of two categories: long wool or medium wool. Samples with the fibre length higher than 100 mm are considered long wool fibers, and those with the length ranging between 60 and 100 mm are considered medium wool fibres.

Samples P 7, P 9.1, P 9.3, P 11 and samples from unidentified breeds (except P 13) are considered long wool and the remaining samples represent medium wool.

The coefficient of variation has a large range of values which shows extremely high length non-uniformity. Distribution on such a wide range of length values is caused by a complex of factors comprising mainly food and shelter conditions of the sheep, as well as genetic features of Romanian breeds.

Although samples derive from different areas of the country, there is a fairly large homogeneity of sample characteristics from a physical -mechanical point of view and depend mostly on the breed and not on the geographic area.

Physical-chemical characterization of wool samples was performed in order to determine the following parameters:

- fat content, according to STAS 7690:1993 standard;
- alkali content according to ISO 3072:1996 standard;
- urea-bisulfite solubility according to STAS 11138:1978 standard.

The results of chemical analyzes are presented in Table 4.

Table 4 Chemical characterization of samples

Sample/breed code	Fat content %	Alkali content %	Urea-bisulfite solubility %
P 1.1	14,24	31,84	27,06
P 1.2	7,71	20,27	12,22
P 2.1	11,19	18,88	14,23
P 2.2	3,95	12,98	7,21
P 3	17,49	19,26	16,26
P 6.1	4,23	20,84	9,28
P 7	11,33	27,51	19,94
P 9.1	8,77	21,3	15,88
P 9.2	5,76	21,58	9,22
P 9.3	12,31	27,65	16,71
P 11	11,42	20,29	13,75
P 12	15,19	17,81	8,49
P 4	8,65	25,76	11,01
P 6.2	11,93	28,6	13,49
P 8	1,39	10,72	3,16

P 5.1	8,18	25,8	23,39
P 5.2	4,87	21,34	4,43
P 10	9,37	5,21	6,85
P 13	13,95	28,96	16,09
P 14	11,01	24,62	18,74
P15	8,97	34,04	15,68

Fat content shows the sebum percentage from wool fibers. The greater amount of fat, the higher protection is provided for the fibres.

Determination of wool solubility in urea - bisulfite solution is a method for determining alkaline degradation (washing control). It is believed that solubility in urea-bisulfite solution is important to control the washing process and wool thermal processes. Standard wool has a high solubility of 30-50%.

By its decreased value, urea-bisulfite solubility indicates bisulfite bond breaking and the degradation of the main chain; hydrolysis control is also indicated by this value.
Low solubility in urea - bisulfite solution obtained from the tested samples is explained by the formation of stable cross- links of lantionine which can not be subjected to urea - bisulfite mixture hydrolysis.
In order to show the degree of degradation of the wool fiber quality analyses were performed. Pauly test involves dyeing of wool fibers with a colored compound formed by coupling the sulfodiaz-benzoic acid with the aromatic group of tyrosinine. As this amino acid is missing from keratin molecules of the surface layer, the dye is formed only when the reagent can reach the cortex cells.

The results are shown in Figures 4a and 4b and the analysis is conducted only for white wool. Wool fibers are dyed in different shades of yellow to orange, depending on the degree of degradation, as follows:

a) *Light yellow*. In this case the dye did not penetrate deep into the fiber (cuticular layer), which shows a good fiber condition and quality level. Samples P 1.1, P 2.1, P 3, P 13 fall into this category.
b) *Bright yellow*. Cuticular layer is more degraded than in the first case. Samples P 1.2, P 5.1, P 7, P 12, P 15, P14 fall into this category.
c) *Yellow to orange*. Cuticular layer is degraded and dye reached the cortex. Samples: P 2.2, P 4, P 5.2, P 6.1, P 8, P 10, P 9.1 fall into this category.

Factors influencing erosion of cuticular structure may be influenced by:

- the type of animal - health status, quantity and type of food consumed (good or bad quality) food regime;

- Environment: animals reared indoors (winter stables), which are protected from the effects of the sun, wind and rain, providing greater protection for wool fibers compared to those reared in open places which can not provide protection against bad weather.

- the way in which pastures are maintained, which influences the increase of vegetable and mineral impurities of wool fibers.

In order to perform a complete characterization of wool fibers SEM images were made with FEI Quanta 200 Scanning Electron Microscope to mark out the structure of wool fibers.

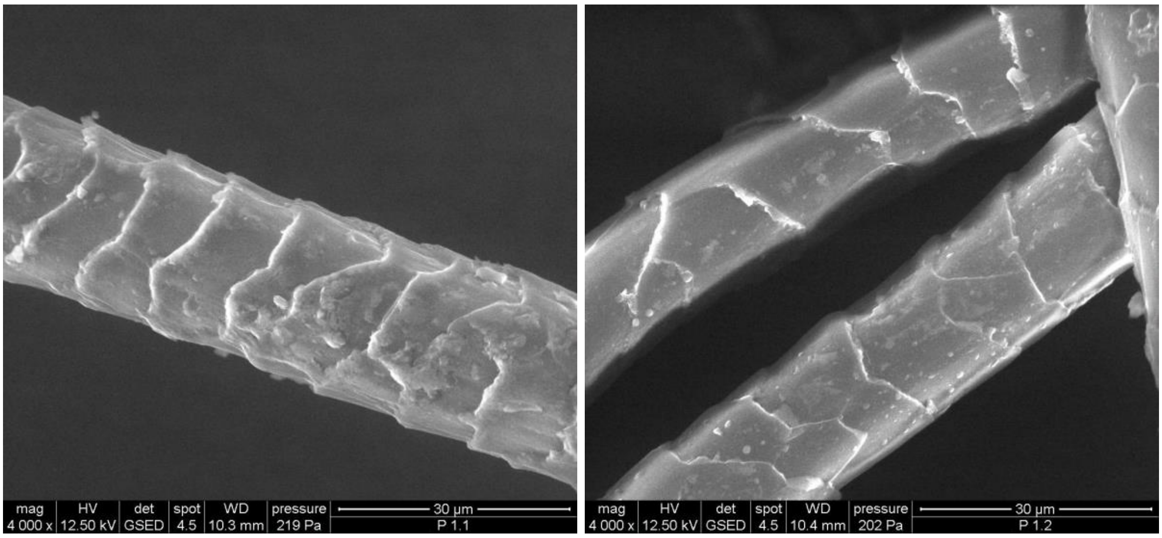

Figure 4 SEM images of samples P 1.1 si P 1.2

Samples P 1.1 and P 1.2 are samples of fine and semi-fine wool, Spanca breed, which have protuberant and wide scales, specific to the breed. Cuticular cells are fine and well marked out.

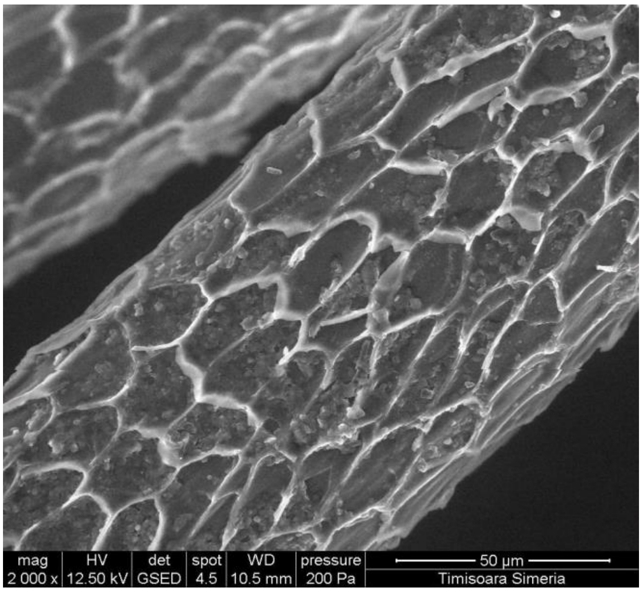

Figure 5 SEM image, sample 10

Sample P 10 belongs to Stogosa breed, the fiber surface is covered with polygonal scales and the fiber is thick.

3 CONCLUSION

Physical-mechanical, plysical-chemical and structural laboratory analyses have indicated the characteristics specific to the breeds from which wool samples were collected.

We have identified samples of fine wool (P 1.1, P1.2, P 4), semi-fine wool (P2.1 , 2.2 , 6.2, 8, 13) and thick wool (P 5.1 , P 5.2, P 10 , P 14 , P 15), depending on the breed. Results showed changes in the qualitative characteristics of Romanian types of wool, resulting in the increase of average diameter for fine wool until up to 26-27 microns and degradation of cuticular layer, as evidenced by Pauly test which shows orange tendency colors.

SEM images showed surface fiber structure specific to each sheep breed.

Depending on the geographic area, fiber characteristics do not differ greatly, but they are influenced by breed and the body area from the place they were selected.

Reviving Romanian wool production can only be achieved through close collaboration between animal husbandry, farmers, sheep breeders and processing industry, taking into account the control of cross-breedings, pasture condition, food and shelter conditions in order to produce high quality fine and semi-fine wool fibres.

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