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# Nanoindentation of CAM:OMA polymer thermoplastic layers

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## ABSTRACT

The polymer layers from carbazolylmethacrylates (CAM) with oktylmethacrylates (OMA) were prepared and investigated by us. The investigation of mechanical properties of such materials are extremely important, whatever the successful application might be. Load and depth sensing indentation with a Berkovich indenter were performed in order to evaluate the mechanical properties of polymer films. The effective elastic modulus and the hardness were determined on the basis of load – displacement data. The reliability of the chosen analytical method was checked using of number of repeats. The influence of chemical composition, action of UF-light and aging on the mechanical properties of CAM:OMA polymer materials was investigated.

**Keywords:** Polymer films, Carbazol, Cross-linking process, Nanoindentation, Elastic modulus

## 1. INTRODUCTION

A great attention has been focused now on polymer materials because of its unique chemical and physical properties as well as its industrial applications. New carbazole-containing polymer materials were prepared by us. These materials can be used as information storage media in the photonics, photolithography and holography [1-10].

Carbazole polymers can be cross-linked under the action of UV-light. As a result the layers change the coloration, become mechanically hard, strength, adhesive stable, without solubility in organic solvents and with stability to high temperature. The polymer materials have quite different mechanical behaviour in comparison with other types of materials. For studying of the mechanical properties of such materials it is necessary to use special method. It was stipulated by a set of reasons. Firstly, materials can be received only on rigid and flexible substrate. Secondly, the thermoplastic layers are soft before the cross-linking. Thirdly, the polymer films have a small thickness. The thickness of the recording thermoplastic layers depends on the concentration of polymer solution and is equal to 3-30 μm. Only the nanoindentation technique satisfies these entire requirements [11-17]. On the base of obtained experimental data will be find out of knowledge about physical processes taking place in the during cross-linking process, the possibilities of strengthening of polymer media and receiving materials with given properties.

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## 2. EXPERIMENTAL DETAILS

### 2.1. Materials

New polymer layers from 80% of carbazolylalkylmethacrylates (CAM) and with 20% of oktylmethacrylates (OMA) were obtained by the method of radical polymerization. The radical polymerization is a typical chain reaction. A free radicals are present in a reaction medium from a beginning up to the end of polymerization process. The chemical formulae of such polymer compound is given in Fig.1.

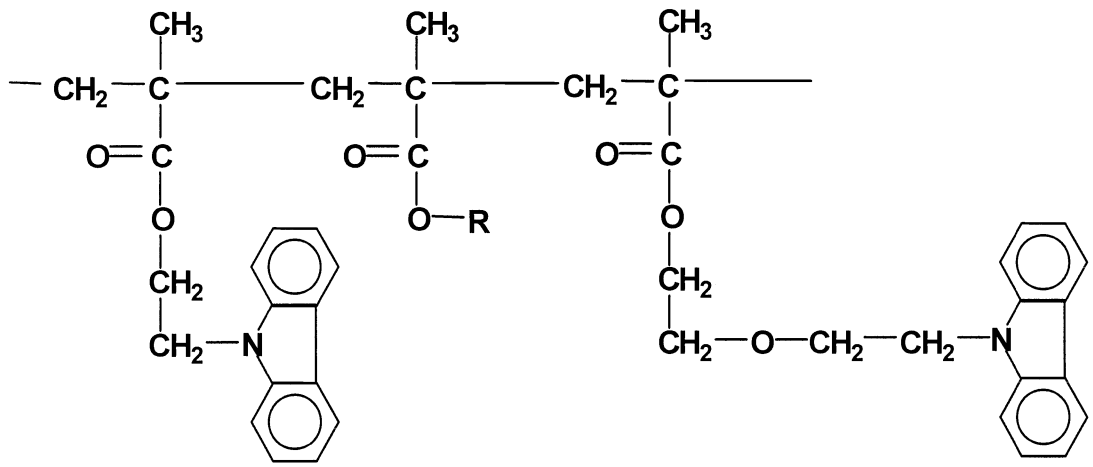



**Fig. 1** The chemical formulae of CAM:OMA polymer thermoplastic layers

All films had a good transparency and showed a good adhesion to hard (optical glasses) and flexible (transparent poly(ethyleneterephthalate)) substrates. The thickness of the samples ranges from 3 to 35 μm. The layers were exposed to ultra-violet light with incident energy E=10-20 mW/sm$^{-2}$ and also to white light (as sources was used mercury-quartz lamp PRK-4 with power of 500W). The photo-structural transformations for carbazole-containing materials were observed visually as a coloration changing of irradiation sites, losing of solubility in organic solvents. Quantitatively, the photo-structural modification is well seen from the spectra of absorption intensity in visible region. The effective elastic modulus and the hardness were determined on the basis of load–displacement data.

### 2.2. Nanoindentation tests

The elastic modulus and the hardness can be determined from indentation data obtained during one complete cycle of loading and unloading, shown in Fig.1.

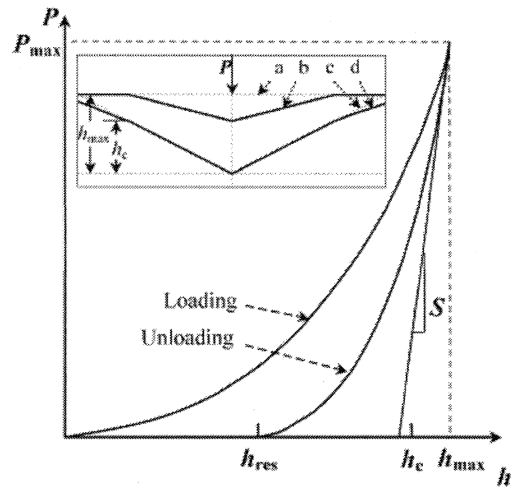



**Fig. 2** A schematic representation of load P versus indenter displacement h: (a) – initial surface; (b) – surface profile after load removal; (c) – indenter; (d)- surface profile under load [ 17].

The effective elastic modulus can be calculated using the following equation

$$E_{eff}=\frac{1}{\beta}\frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}} \tag{1}$$

Where A is the projected contact area, S is the experimentally measured unloading stiffness and β is a geometry constant, equal to 0.034 for a Berkovich indenter [6]. The projected contact area for a perfect Berkovich indenter is

$$A=24.5h_c^2 \tag{2}$$

where $h_c$ is the contact displacement (or the contact depth). For a non-ideal indenter typically a polynomial in $h_c$ is used. The contact depth, along which contact is made between the indenter and a specimen, can be estimated from the load-displacement data

$$h_c = h_{max} - \in \frac{P_{max}}{S} \tag{3}$$

where $h_{max}$ is the maximum displacement, which corresponds to $P_{max}$ , the maximum load, and $\epsilon$ is a constant, which depends on the geometry of the indenter, equal to 0.75 for a Berkovich indenter [6]. The unloading stiffness, which is the slope of the unloading curve during the initial stage of unloading, S=dP/dh, can be obtained by fitting the unloading curve by

$$P=B(h-h_{res})^m \tag{4}$$

and taking the derivative at the maximum displacement, $h=h_{max}$. Here P is the indentation load, h is the displacement, B and m are fitting parameters and $h_{res}$ is a residual displacement after complete unloading. The effective elastic modulus, used because elastic deformation occurs in both the specimen and the indenter, is related to the specimen elastic modulus by

$$\frac{1}{E_{eff}}=\frac{1-\nu}{E}+\frac{1-\nu_i}{E_i} \tag{5}$$

where E and ν are Young's modulus and Poisson's ratio for the specimen, respectively, and $E_i$ and$\nu_I$ are the same quantities for the indenter. For the diamond $E_i$=1141 GPa and $\nu_i$ 00.07 [8] were used.
Finally, the hardness H is defined from:

$$H=\frac{P_{max}}{A} \tag{6}$$

The indentation experiments were carried out at room temperature using a Nanoindenter II. A Berkovich-type diamond indenter was used. The apparatus only allowed experiments under displacement control to be performed. The calibration procedure suggested by Oliver and Pharr [17] was used to correct for the load frame compliance of the apparatus and the imperfect shape of the indenter tip. The maximum force was equal 500μN and twelve indentations were performed for each sample. The loading and unloading rate was 5 μN/s.

## 3. RESULTS AND DISCUSSION

The cross-linking process takes place in CAM:OMA polymer materials under action of UV radiation[1-4]. The absorption of light quantum by a polymer compound causes a disruption of chemical bonds of a macromolecule with formation of free radicals. As a result the polymer material become essentially hardened, the adhesive properties are improved, the coloration of irradiated sites are changed (in the dependence from the radiation dose from light up to dark green), the material is not dissolved in organic solutions.

The influence of irradiation time on the photo-structuring process was carried out. As following from Fig. 3 the time of photostructurization depends from the sample thickness. The time of the full structurization is equal to 22 minutes.

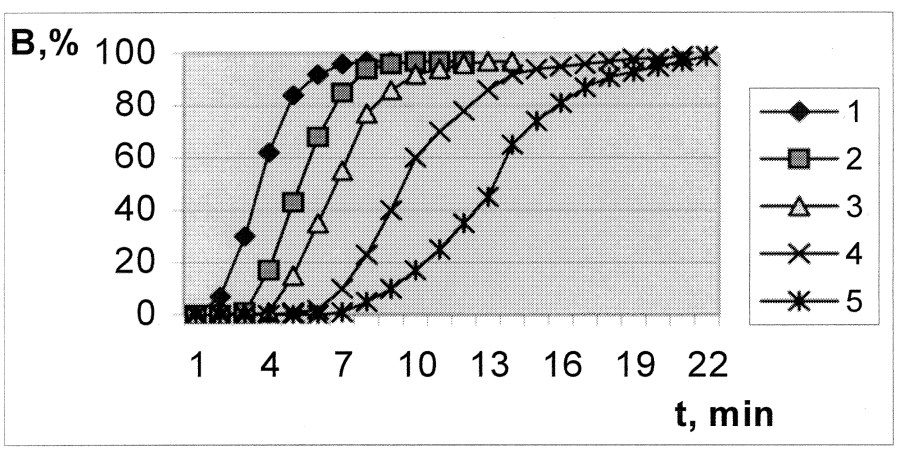
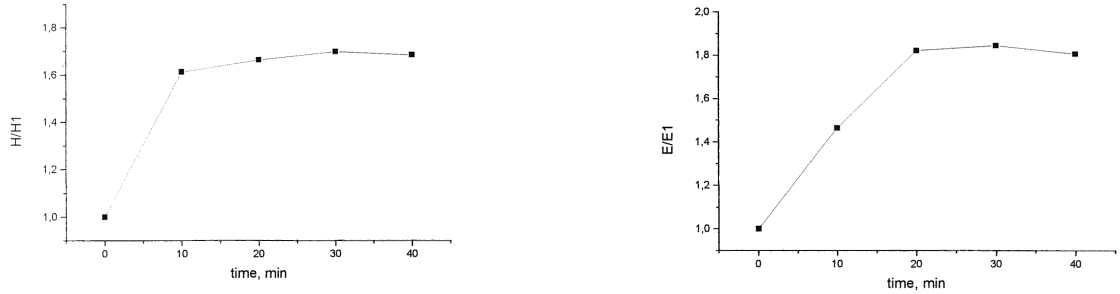



**Fig. 3** Modification of the photostructurization degree (B) with the irradiation time (t) for CAM:OMA thermoplastic layers. The thickness of layers : 1- 1μm; 2 - 2 μm ; 3 - 3 μm; 4 – 4 μm; 5 – 5 μm

We investigated the influence of irradiation time on the nanomechanical properties of CAM:OMA thermoplastic layers (Fig.2).

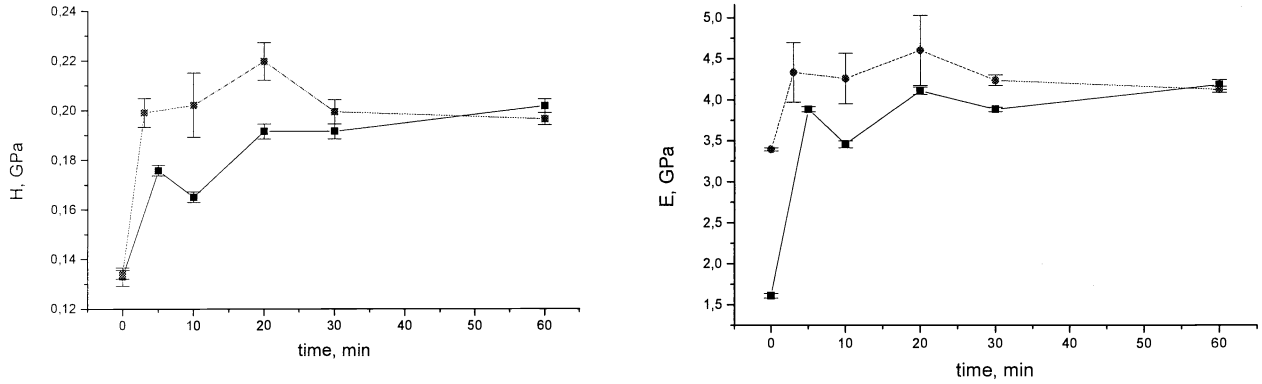



a) b)

**Fig. 4** Relative H (a) and E (b) versus irradiation time for CAM:OMA compositions

As it is visible from Figure 2, the nanohardness and the elastic modules increase almost in 2 times. However the behaviour of these nanoparameters during a cross-linking process is a different. The nanohardness practically achieves the maximal value for 10 minutes of an irradiation. The $E_{maz}$ observes after 20 minutes. The time necessary for full cross-linking of CAM:OMA polymer layers is equal 30 minutes. However at the further increasing of an irradiation time, especial at the presence of oxygen, the destruction begins to prevail above across-linking, the H and E decreasing takes place, the properties of a polymer material are worsened. For the successful using of polymer thermoplastic layers is extremely important to determine the cross-linking time. The nanoindentation technique is very suitable for this purpose.

The influence of aging on nanomechanical properties of carbazol containing materials (CAM:OMA) was investigated. The comparison of mechanical properties in dependence of irradiation time for fresh and old (are aged in during one month at room temperature) is presented on Figure 5.




a) b)

**Fig.1** The nanohardness (a) and elastic modulus (b) versus of irradiation timefor fresh (•) and ageing (■) during one month CAM:OMA

As we can see from Figure, the good correlation between H and E changes for fresh and ageing layers takes place. The CAM:OMA polymer layers are hardening and stability at full cross-linking (the irradiation time is equal from 30 to 40 minutes). The materials, received by us, are high-quality and can successfully be applied in practice. Nanoindentation technique can be used to accurately estimate the hardness and the elastic modulus of cross-linked layers on the basis of load-displacement data, originally proposed by Oliver and Pharr [17].

## 4. CONCLUSIONS

1. A set corbazole-containing polymer materials before and after cross-linked process by nanoindentation technique was investigated.
2. The conditions of mechanical properties improvement by different type of treatment were established.
3. Load and depth sensing indentation has shown itself as a powerful tool for an accurate estimation of mechanical properties of cross-linked CAM:OMA layers on hard and soft substrates.

## ACKNOWLEDGEMENT

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