

NANOMECHANICAL PARAMETERS OF NEW CARBAZOLYLE-CONTAINING PHOTORESIST POLYMERS

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Abstract

The new photopolymer layers from carbazolemethacrylates (CAM) with oktylmethacrylates (OMA) and polyepoxypropylcarbazole (PEPC) were prepared and investigated by us. Load and depth sensing indentation with a Berkovich indenter were performed in order to evaluate the nanomechanical parameters of polymer films. The reliability of the chosen analytical method was checked using number of repeats. The influence of chemical composition, action of UF-light and aging on the nanomechanical properties of CAM: OMA and PEPC were investigated.

1. Introduction

A special attention has been given now to the problem of holographic registration of images and information with the purpose of a solution of various scientific and technical problems, as well as for protection of important documents from falsification. New carbazole-containing photopolymer layers from carbazolylalkylmethacrylates (CAM) with oktylmethacrylates (OMA) and copolymer layers from polyepoxypropylcarbazole (PEPC) were obtained and investigated by us [1- 3]. These materials can be successfully used as information storage media in photonics and photolithography.

CAM: OMA, CAM: M and PEPC materials under the action of a ultra-violet irradiation are exposed to the photochemical transformations that leads at the end to the deep photopolymer structurization [1-3]. Structurization of layers is accompanied by change of coloration of the irradiated sites, their solubility in the organic solvents, increasing of mechanical durability and adhesive properties of the materials. Generally, the investigation of the mechanical properties of such materials is extremely important, wherever the application might be. Load and depth sensing indentation, commonly referred to as nano-indentation, has shown itself as a powerful tool to characterize several mechanical properties of coating and has been broadly used for inorganic coatings for about ten years already [4, 5]. On the contrary, for the polymer layers this technique is limitedly applied. It will be shown in the paper that this technique can be used to accurately estimate the hardness and the elastic modulus of structurization polymer layers on the basis of load-displacement data, originally proposed by Loubert et al. [6] and Doerner and Nix [7] and later significantly developed by Oliver and Pharr [8].

In this paper we present the results concerning the possibilities of polymer media strengthening with the scope to improve mechanical properties of the relief image (hardness and elastic modulus). The influence of coating thickness, filler content and chemical composition on the mechanical properties polymer and copolymer layers was also investigated.

2. Experimental details

2.1. Materials

New aminostyrole and carbazole containing polymer materials were obtained by the method of radical polymerization. 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 $E=10\text{-}20 \text{ mW}/\text{sm}^{-2}$ and also to white light (as sources was used mercury-quartz lamp PRK-4 with power of 500W). The photo-structural transformations were observed by 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. The reliability of the chosen analytical method was checked using number of repeats. The information about polymer layers under investigation is presented in Table 1.

Table 1. The characteristics of investigated polymer layers

Sample code	Filler content	Chemical composition (%)	Thickness, μm
CAM:OM A	Carbazolylalkylmethacrylate:oktylmethacrylate (copolymer)	80:20	8
CAM:M	Polycarbazolylalkylmethacrylate (polymer analog)	30:70	7
PEPC	Polyepoxypropylcarbazole (homopolymer)		4,5

1. Results

1.1. Nanoparameters for as-grown polymer materials

Nanoindentation testing can be used as qualitative tool for the determination of mechanical parameters of thin polymer films. The nanohardness and elastic modulus for as-grown carbazole containing materials, determined by the method of Oliver and Pharr [8], are presented in Table 2.

Table 2. Elastic modulus (E) and nanohardness (H) for as-grown photoresist polymer layers

Sample	E, GPa	H, GPa
CAM:OMA	$3,39331 \pm 0,02647$	$0,1339 \pm 0,0018$
CAM:M	$3,39331 \pm 0,0178$	$0,13339 \pm 0,0018$
PEPC	$1,45668 \pm 0,02709$	$0,11449 \pm 0,0036$

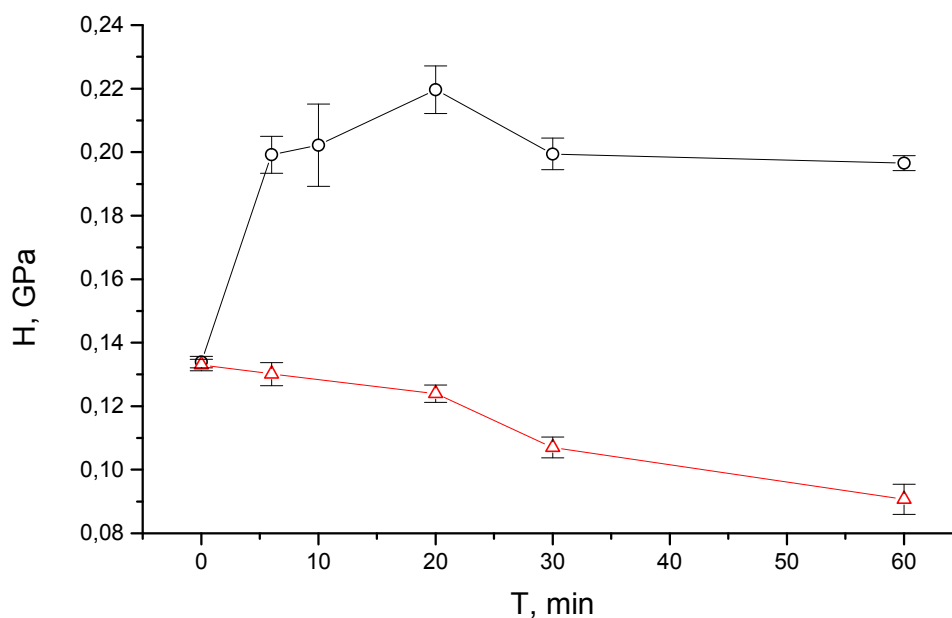
It is necessary to note (Table 2) that the influence of a chemical compound on nanomechanical parameters of CFM:OMA and CAM is not revealed (the values of H and E are equal). The values for PEPC homopolymer are lower in comparison with the previous materials (especially it takes place for the elastic module).

1.2. Influence of UV-irradiation on the nanomechanical properties

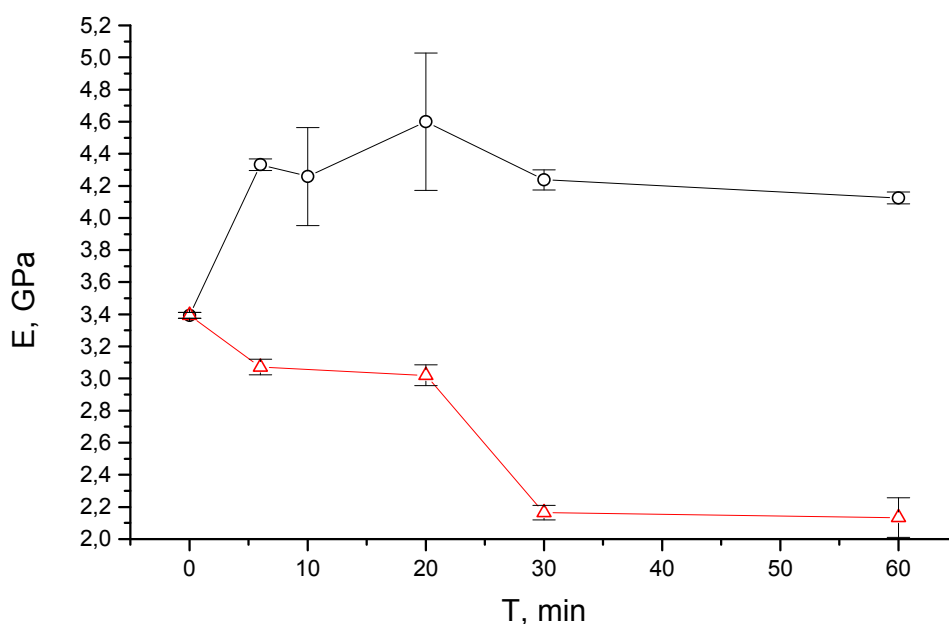
The process of photochemical structurization takes place under action of ultra-violet irradiation in carbazole containing photoresist polymers. Structurization of layers is

accompanied by changing coloration of irradiation sites, increasing of mechanical parameters (hardening of material), improving of adhesive properties.

Fig 1. shows the dependences of nanohardness (H) and elastic modulus (E) on time of UV-irradiation for CAM:OMA and CAM: M.



a)



b)

Fig. 1. The nanohardness H (a) and effective elastic modulus (b) versus time of irradiation (T) for CAM: OMA ($\circ$); and CAM: M (Δ)

The influence of the chemical composition on the mechanical properties of irradiated CAM:OMA and CAM:M photoresist polymers is of the main interest in the work. As was indicated above (Tabl. 2), H and E nanomechanical parameters were equal before action of irradiation. The behaviour of these materials after irradiation differs markedly: for CAM:OMA copolymer the hardening takes place (max values of H and P are observed at 20 min of irradiation), and softening revealed for CAM:M polymer analog. Such behaviour of investigated materials is connected by the fact that an irradiation causes the structure changes of polymeric materials which influences mechanical properties.

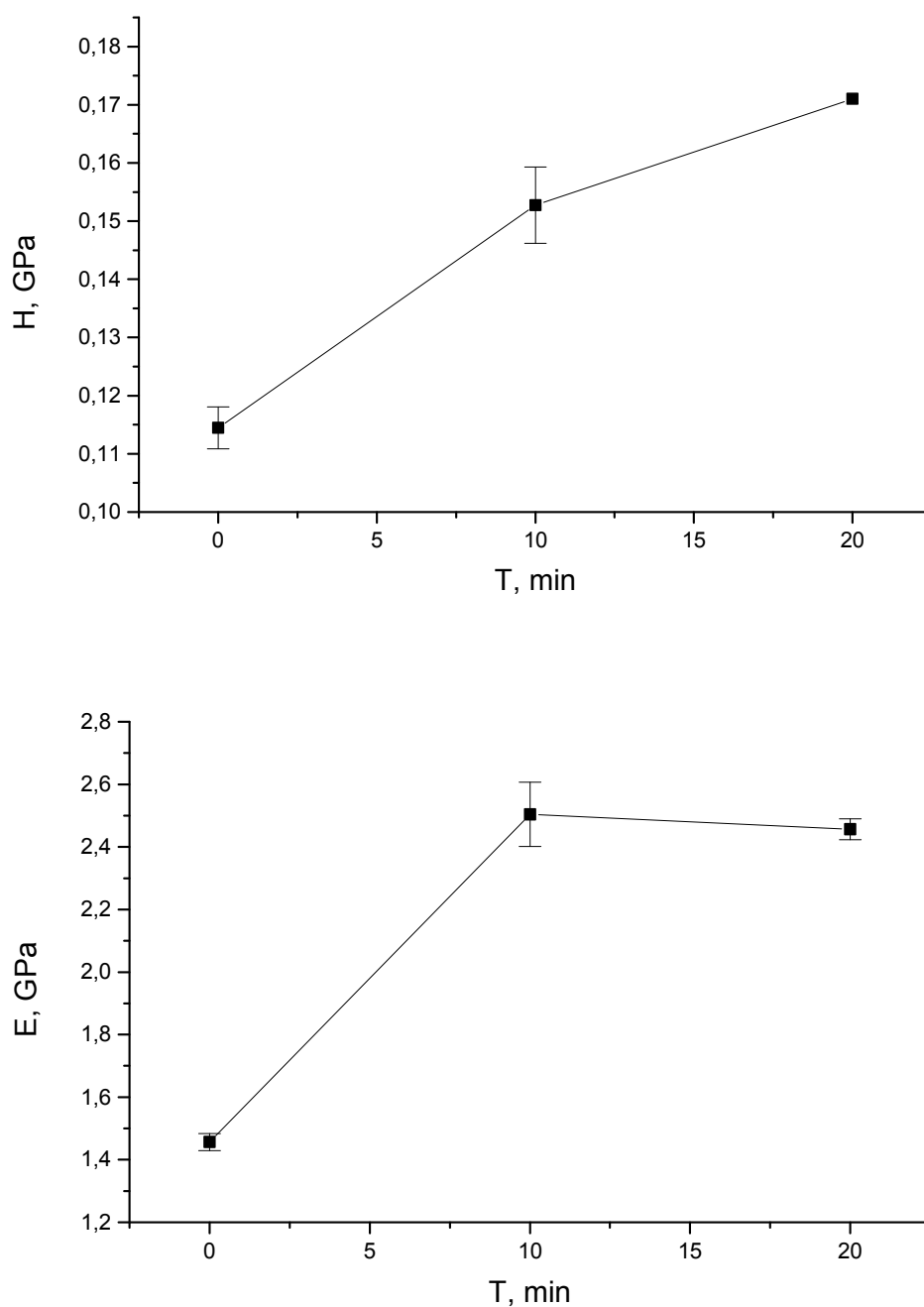


Fig. 2. The nanohardness H (a) and effective elastic modulus (b) versus time of irradiation (T) for PEPC homopolymer

The increases of H and E parameters are observed for PEPC homopolymers at irradiated time before 10 min, then nanohardness continues to grow with increase of irradiated time (20 min), but for elastic modulus the value diminution is observed (fig. 2, b).

It is known [9-11] that mechanical strength depends not only on chemical structure determined by composition, relative positions and sequence of nuclear groupings, but also on a degree of macromolecule branching. The vital influence on durability is especially rendered by a degree of the cross-section sewing changing during irradiation. Durability of polymers is determined by amount of cross-section connections between circuits. The growth of cross-section connections at small degrees of irradiation is accompanied by increasing durability. At achievement of the big degrees of cross-section sewing of chain molecules their orientation and crystallization are at a loss, and the further increase of quantity of cross-section connections is accompanied by reduction of durability. Such effect we can observe at big irradiated time for CAM:OMA and PEPC materials (Fig. 1 and 2). The influence of irradiation on CAM:M materials causes straightening of macromolecules and as a results the softening of the material. So, changing the chemical composition the technologist can obtain very strong or unsuitable materials for application. Therefore studying of mechanical properties of new polymer materials is extremely important.

Conclusions

1. A set of corbazole-containing polymer materials before and after cross-linked process by nanoindentation technique was investigated.
2. The conditions for improvement of mechanical properties after ultra-violet irradiation 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, CAM: M and PEPC layers.

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