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Photostructure transformation effects of layer consisting from CAMC:OMA copolymers under the action of laser irradiation

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ABSTRACT

The photochemical method of image recording of carbazole - containing polymeric layers (f.e. PVC and its copolymers or poly -N - epoxypropylcarbazole, containing under 10% of photochemical cross-linking agents at the range of calcogen - derivatives of methane and etc.) attributes to well-known methods of image recording.

The carbazolalkylmethacrylate (CAMC) copolymer with octylmethacrylate (OMA) photoplastic carries has been investigated in details on the purpose to enlarge the image photographic characteristics of carbasolalkylmethacrylate. The photopolymer layers were made by pouring from solutions.

The structure of CAMC is 1:1 and contains OMA varying from 0 to 50mol%. There were additionally added about 5-16% iodinophorm CHI_3 for photo-cross-linking of given copolymer layers. The best results of macromolecular photo-cross-linking in UV-rays were obtained with 60-70mol% CAMC containing copolymers. It can be connected with good flexibility of polymeric macromolecules. Optimal concentration of iodinophorm was about 8-10%.

It has been used a coherent laser beam with λ=420 nm for holographic images recording (Ne-Cd-lazer). There were obtained holographic gratings with resolution 1500 mm^{-1} and diffraction efficiency 23%. This material has photographic sensitivity 10^3 m^2/J that allows using the explored copolymers for elaboration of a new optic media for holographic images recording.

Keywords: copolymer, layer, image, registration, cross-linking, recording, laser, holography, resolution, diffraction efficiency.

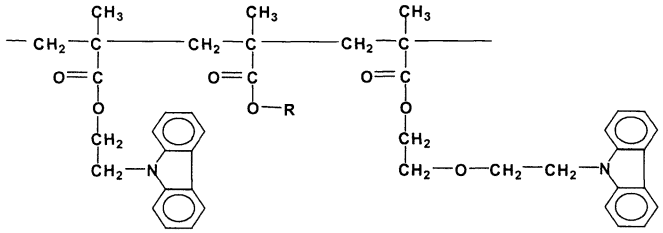
1. INTRODUCTION

Recently special attention was given 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. For solution of the given problem occupied reliefo-graphic methods of registration of holograms with application of inorganic semiconductors or organic photoconductors (PC) from carbazol-containing polymers sensitized by electron-donor additives the special place in the scientific and technical literature [1 – 4]. On photopolymer PC-layers from carbazol-containing polymers of the polyepoxypropilcarbazol type or vynilcarbazol with oktylmethacrylate copolymers the holographic images with good diffraction efficiency 10-12 %, resolution up to 500 mm^{-1} and photographic sensitivity 10^{-5} - 10^{-6} J/sm^2 were obtained by the photothermoplastic method of the recording [4] .

With the purpose of improving of the photographic characteristics, in particular the diffraction efficiency and the resolution, as well as for simplification of the process of production we studied and proposed photopolymer layers from carbazol-containing compositions with 4-10 % of the cross-linking agents capable to photostructurization. The possibility of using of the obtained mediums for registration of holographic images with better photographic characteristics is investigated.

2. EXPERIMENTS AND RESULTS

Carbazolylalkylmathacrylates (CAMC) copolymers with octylmethacrylates (OMA) of the common formula



containing about 60 mol % of carbazolyl links were obtained by a method of radical polymerization in a tholuen solution. Polyepoxypropylcarbazol (PEPC) is commercially available. The given photopolymer was synthesised from N-epoxypropylcarbazol by cation or anion polymerization methods.

For preparation of the samples mediums the solutions of above indicated CAMC and PEPC copolymers added with 0-10 % of iodophorm CHI_3 or other cross-linking agents were prepared. The photopolymer layers were applied both on transparent poly(ethylenethereftalat) films and on rigid substrates from an optical glass. The thickness of the samples ranged from 1,0 μm to 20,0 μm. The samples were dried up on air and then in a drying camber at $T^o \sim 40^oC$ within 24 hours.

The samples of carriers for photothermoplastic registration were prepared from tholuen solutions sensitized by electron-acceptor additions by deposition on metalized poly(ethylenethereftalat) films with transparency ~ 90%.

2.1. Sensitometric investigations

It is known [5, 6] that photo-chemical transformations in carbazol-containing polymers at the presence of cross-linking agents like iodinophorm CHI_3 occur according to the ion-radical mechanism with formation at the issue of spatially – cross-linked structures, that allows to use them for registration of information. In the given part of work the sensitometric characteristics (photo-sensitivity, coefficient of visibility and other parameters) in dependence from the concentration of CHI_3 in a photoconducting layers and from their thickness, from the kind of radiation etc were investigated. The trial study was carried out on PC-layers from PEPC taken as an analogy and from CAMC:OMA copolymers. The layers were exposed to ultra-violet light with incident energy E = 10 - 20 mW/sm^2 and also to white light (mercury-quartz lamp PRK-4 and 500 W incandescent lamp as sources). The photo-structural transformations were observed visually as modification of colour of the PC-layers and through losing of solubility of the irradiated areas. Quantitatively, the photo-structural modifications are well seen in the spectra of visible region.

The maximum of visible absorption spectra (Fig.1) is observed in the interval 630-650 nm. As follows from Figure 1 in a defined time t = 30 s the intensity of absorption becomes constant and corresponds to a full cross-linking of the PC-layers.

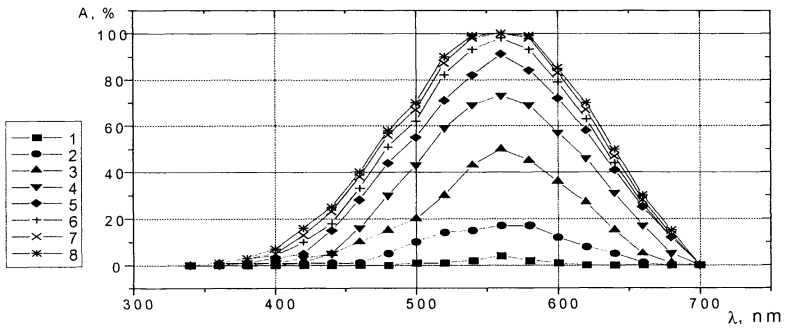


Fig. 1. Modification of the absorption intensity with the time of exposure of the layers:
1 - 0 s; 2 - 5 s; 3 - 10 s; 4 - 15 s; 5 - 20 s; 6 - 25 s; 7 - 30 s; 8 - 40 s;

The investigation of the polymeric composition influence on structural photo-cross-linking in dependence on carbazolic nucleus concentration (as CAMC-1 and CAMC-2) in polymers represents a great interest. There are investigated the process activation of layers photo-cross-linking with different additives (f.e. chloranyl etc.).
It was shown the layers photo-cross-linking acceleration in dependence on increasing of chloranyl (ClAn) concentration (1-2%) in polymeric compositions (CAMC-1:CAMC-2 (50:50mol%) was called as poly-CAMC, CAMC:OMA). The time of layers full photo-cross-linking regresses from 30-35 minutes to 18-20 minutes in the case of poly-CAMC (Fig.2) and CAMC:OMA(Fig.3) with UV-irradiation.

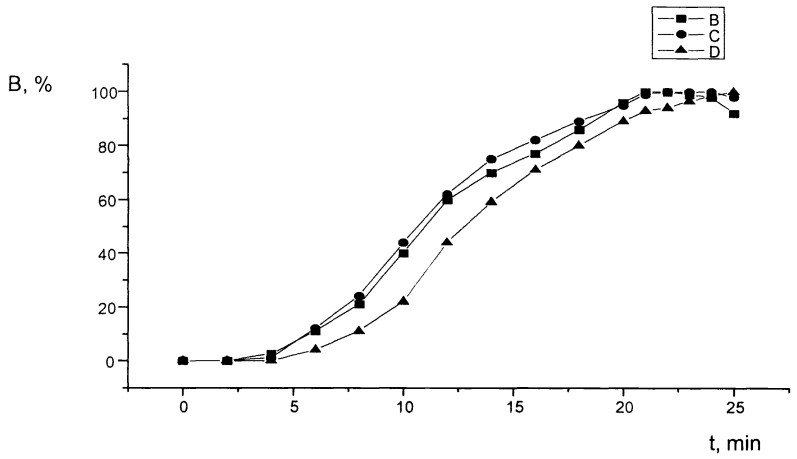


Fig. 2. Dependence of photo-structurization of layers with the time of UV-irradiation:
B – CAMC1:2(50:50)+10%CHI_3+1%ClAn;
C - CAMC1:2(50:50)+10%CHI_3+2%ClAn;
D- CAMC1:2(50:50)+10%CHI_3.

In the case of laser irradiation the photo-cross-linking time is about 3-5 min. The optimal concentration in photopolymer layers is about 2% as we can see from Fig.2, Fig.3 and especially from Fig.4.

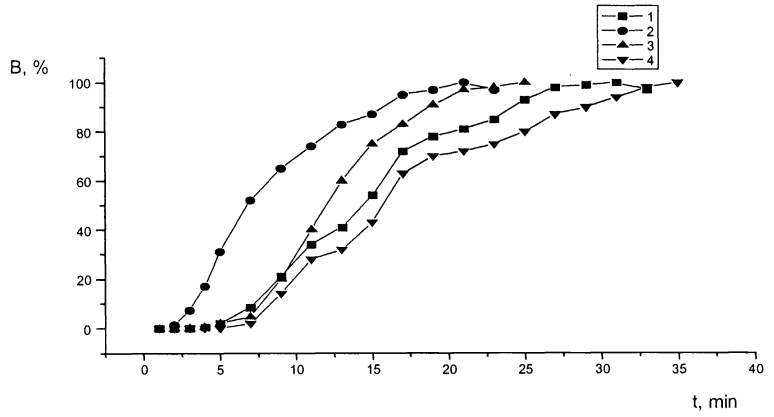


Fig.3. Dependence of photo-structurization of layers with the time of UV-irradiation:
1 – CAMC:OMA (60:40)+10%CHI_3+1%ClAn;
2 - CAMC:OMA (60:40)+10%CHI_3+2%ClAn;
3 - CAMC:OMA (60:40)+10%CHI_3+3%ClAn;
4- CAMC:OMA(60:40)+10%CHI_3.

With the following increasing of chloranyl concentration the photo-cross-linking process became less as we can see from Fig.4. It can be connected with carbasol nucleus isolation. Such effect we have observed in the case of OMA concentration increasing in the CAMC:OMA copolymers.
The increasing of OMA plastifier component concentration always results to the layers photo-cross-linking time increasing. The increasing of OMA molar concentration in copolymer layers from 0 to 40mol% results to the layers photo-cross-linking time increasing more than for 15 minutes.

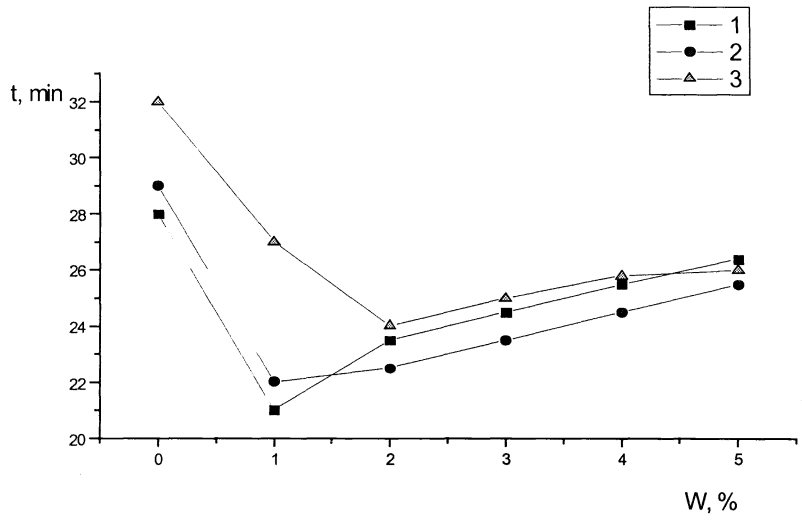


Fig.4. Dependence of the complete photo-structurization of the CAMC-layers with different OMA concentration on the concentration of ClAn:
1 – CAMC (1:2) (50:50);
2 – CAMC:OMA (80:20);
3 - CAMC:OMA (60:40).

2.2. Holography investigations

To obtain good holograms on the PC-polymer layers an installation on the base of 1W CW Argon - Ion laser and 20 mW He-Cd laser was mounted. An iris diaphragm was placed intra-cavity to select single mode output from Argon-Ion laser (type LG-106). This regime allows us to increase the length of coherence and, as a consequence, to obtain good holographic scene with the depth of definition up to 15 sm. The laser power in single mode output was 200 mW on wavelength λ=0,49 μm for Argon-Ion laser and 15 mW on wavelength λ=0,42 μm for He-Cd laser.
Optical set-up of the experimental holographic installation is presented in Fig. 5 and consists of: 1 - He-Cd laser; 2 - mirrors; 3 - PC-polymer layer; 4 - collimator system; 5 - He-Ne laser; 6 – photo-detector; 7 - optical power meter and transformation system; 8 - computer system; 9 - beam splitter.

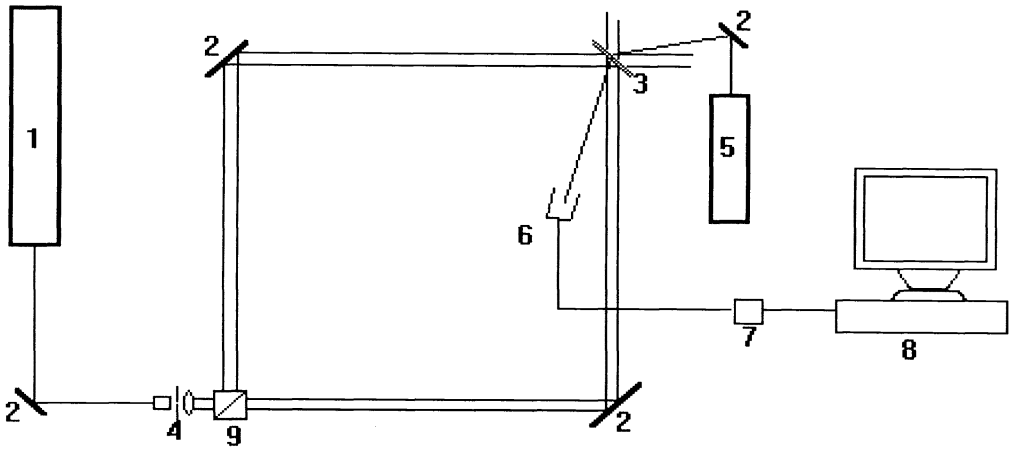


Fig. 7. Optical setup:
1 - He-Cd laser; 2 - mirrors; 3 - PC polymer layer; 4 - collimator system;
5 - He-Ne laser; 6 – photo-detector; 7 - optical power meter and transformation system; 8 - computer system; 9 - beam splitter.

The experimental results on reflection hologram recording have shown that the resolution of the holographic monolayer based on PEPC and CAMC:OMA photoconductor polymer layers is no less than 2000 mm^{-1}. The maximum of the diffraction efficiency of the reflection holograms is 1,5 % at the layer thickness of 5-6 μm. The following chemical treatment permits to increase the diffraction efficiency up to 20 %.
For the layers capable to photostructurization made from copolymers of carbazol-containig compositions with 4-10 % of cross-linking agents and with1-2% of ClAn, the dependence of diffraction efficiency of registered diffraction gratings on the time of exposition was investigated. The registration of diffraction gratings was carried out at spatial frequencies 1500 mm^{-1}. The results of measurements are shown in a Table 1.

Table 1

1 – PEPC+8%CHI_3+1%HlAn samples; 2, 3 – PEPC+8%CHI_3+2%HlAn samples;
4, 5 – poly-CAMC+8%CHI_3+2%HlAn samples; 6 – CAMC:OMA (80:20)+8%CHI_3+2%HlAn samples;
7 – CAMC:OMA (60:40)+8%CHI_3+2%HlAn samples;

$N_{sampl.}$	n, μm	$\eta_{1R} + \eta_{1'R}$, %	$\eta_{1T} + \eta_{1'T}$, %	t_{expos}, min	t_{treat}, s
1	5-6	1,5	2,7	4	10
2	5-6	1,8	3,5	4	10
3	5-6	2,2	15,3	8	10
4	5-6	5,4	3,1	4	10
5	5-6	23,0	12,0	8	10
6	5-6	19,6	10,3	8	10
7	5-6	16,3	8,2	8	30

λ=0,42 μm; W=7 mW; ν=1500 mm^{-1},

It is seen from the table that the diffraction efficiency of the poly-CAMC-layers with 2% of HlAn increases up to 23 % with the exposition time up to 8 min.

3. CONCLUSION

1. The photopolymer layers capable to photostructurization from carbazol-containing compositions with 4-10 % of the cross-linking agents are offered.
2. The contents of carbazol-containing copolymers has an influence at all photo-cross-linking process.
3. The increasing of carbazolic component in carbazolylalkylmethacrylate copolymers reduces the full photo-cross-linking time more than for 25%.
4. The optimum concentration of sewing component CHI_3 in PEPC and CEM:OMA PC-layers is 8-10%.
5. The activator presence (f.e. chloranyl – 1-2%) accelerates the photo-cross-linking process.
6. The obtained layers are examined with the aim of registration holographic images with improved photographic characteristics.
7. The diffraction efficiency of the registered diffraction gratings reaches 23 % with increasing of exposure time up to 8 min.

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