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The Process of Periodic Structures Fabrication in Photocurable Composite Materials

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Possibility of interference method realization using monomeric compositions and nanocomposites is shown. Periodic structures with submicronic and nanoscale elements and diffraction efficiency up to 50 % were obtained. It is shown that ZnO nanoparticle doping and nanoparticle concentration increasing leads to diffraction efficiency growth. Probable mechanisms and a role of diffusion processes at structures formation are determined.

Key words: interference lithography, polymer structures, nanocomposite, diffraction efficiency

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Introduction

In recent years, there has been increasing interest in methods and technologies for small-sized polymer elements of various configurations, including periodic structures that are of interest as photonic crystals and Bragg structures. A large number of publications consider processes of periodic structures production by laser interference lithography using SU-8 photoresist [1, 2]. However with this material, there is an application problem for a thicker layer. This is due to the need to remove the residual solvent, which requires labor-intensive high-temperature treatment. This paper focuses on the use of photocurable composite materials based on acrylic monomers with a photopolymerization initiator [3, 4]. The use of such materials is more advantageous when thick layers are formed as the former are applied without solvent, and they can affect material properties including the refractive index. Previously, composite materials were used to produce microlenses by tone lithography [5], optical fiber-end elements [6], and three-dimensional structures of high aspect ratio by deep lithography [7].

The purpose of this study was to investigate the possibility of using composite materials based on acrylic monomers enabling production of periodic structures by laser interference lithography and the factors determining their diffraction characteristics.

I. Experimental technique

Periodic structures were produced by the interference method using a two-beam interference scheme (Fig. 1). GKL-40I helium-cadmium laser was the radiation source emitting a 325 nm wavelength, which is associated with the photopolymerization initiator absorption band. The recording scheme provided the fine alignment of the interfering beams, the ability to change the angle between the beams, the equality of their intensities, the equality of optical paths in the scheme arms, and the horizontal position of the sample.

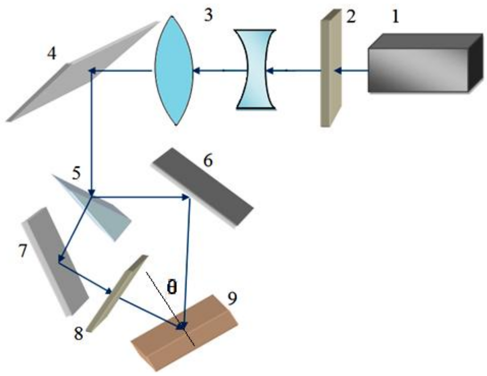
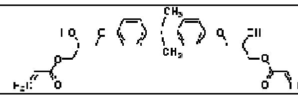
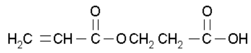
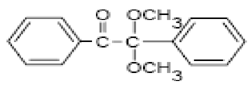


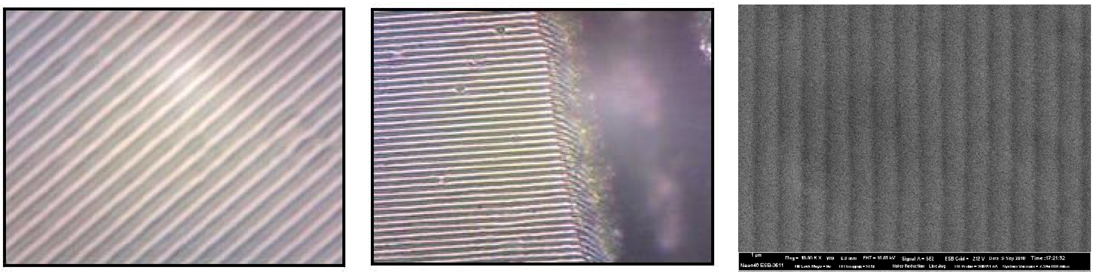
Figure 1. Optical scheme of the setup for periodic structures fabrication by interference method.
1 - a helium-cadmium laser, 2,8 - light filters, 3 - a quartz telescope, 4,6,7 - mirrors, 5 - quartz wedge, 9 - registration material.

The process of structures fabrication consisted of three stages: applying the layer, exposing, and removing the uncured material. A drop of the liquid monomer composition was deposited on a glass substrate; mechanical pressure generated a layer, the thickness of which was adjusted by the size of the spicers.

Table 1

Components included in the monomer compositions

№	Name	Refraction Index	Chemical Formula
1	Bisphenol A Glycerolate (**BisA**)	1.557	
2	2 Carboxyethyl Acrylate (2**Carb**)	1.457	
3	Nanoparticles	2.0	ZnO
4	Dimethoxyphenyl Acetophenone (Photoinitiator)		



a) b) c)

Figure 2. Photographs of the surface (a) of the section (b) of 2 micron periodic structures and a SEM-photograph of the surface of a 0.8 micron periodic structure (c). Composition: BisA/Carb 30/70, ZnO 10%

To avoid oxygen inhibition of the curing process, the layers were protected with a polyester film. When exposing with the interference structure, a polymer periodic structure was produced in the photocurable material. The uncured material was removed when treated with isopropyl alcohol.

The diffraction efficiency of the structures was determined by the ratio of the radiation intensity in the first-order diffraction to the intensity of incident light at a wavelength of 633 nm. This wavelength is usable due to the absence of absorption.

A binary monomer composition based on the components listed in table 1 was used as the material under study, with the percentage of 3/7 at the 0.2 % concentration of the photopolymerization initiator, and a nanocomposite based on the same components with 10 % ZnO nanoparticles introduced.

II. Results and discussion

As a result, 6, 2 and 0.8 micron periodic structures were produced. Figure 2 shows photographs of 2 micron periodic structures produced using the Labomed-3 optical microscope (1000^x magnification) and a SEM-photograph of a 0.8 micron periodic structure.

It was found that the structures have high diffraction properties. In this regard, a study was conducted to identify the diffraction efficiency dependence on the composition, structure frequency, exposure parameters, and post-exposure treatment. Figure 3 shows the diffraction efficiency dependence on the exposure duration (at the density of energy of $5 \cdot 10^{-2}$ J/cm^2) for the binary monomer composition and the nanocomposite for 2 micron and 0.8 micron periodic structures.

It is seen that the diffraction efficiency is higher for the ZnO nanoparticles composition in comparison with the monomer composition. For the nanocomposite, sufficiently high values of the diffraction efficiency are saved at up to the structure frequency of 1,200 mm^{-1}. For the monomer composition, a more significant decrease in the diffraction efficiency with a frequency increasing is observed. This may be due to the differences in the mechanisms of structure formation and the refractive index modulation, which determines the diffraction efficiency.

Figure 4 presents the results of the study of the periodic structures formation kinetics. The photographs were taken using the Labomed-3 optical microscope for the 6 microns structure period. It is evident that at the initial stage, individual elements are formed in the area of peak intensity in superimposed interference pattern. With the increasing exposure, connecting elements are formed and increase in number. With the further increase in exposure, the elements extend and there is a superimposed sinusoidal light-intensity distribution reflected. At larger exposure times, the elements almost completely fuse and a "solid" structure with surface relief emerges.

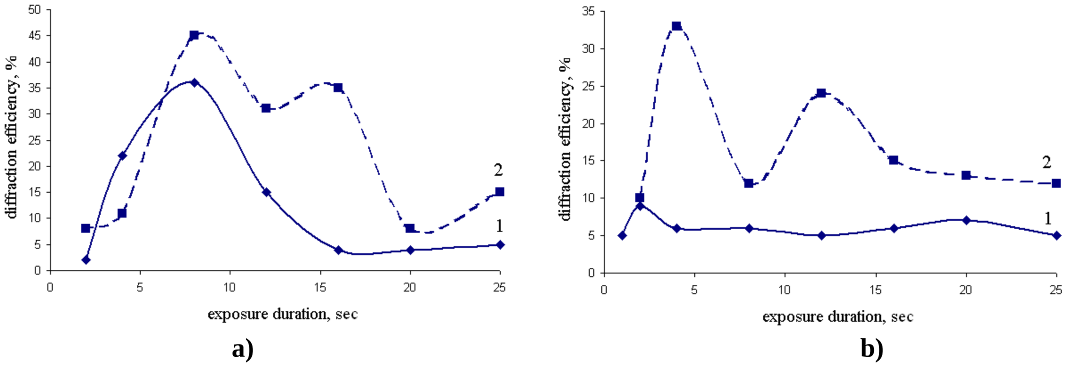
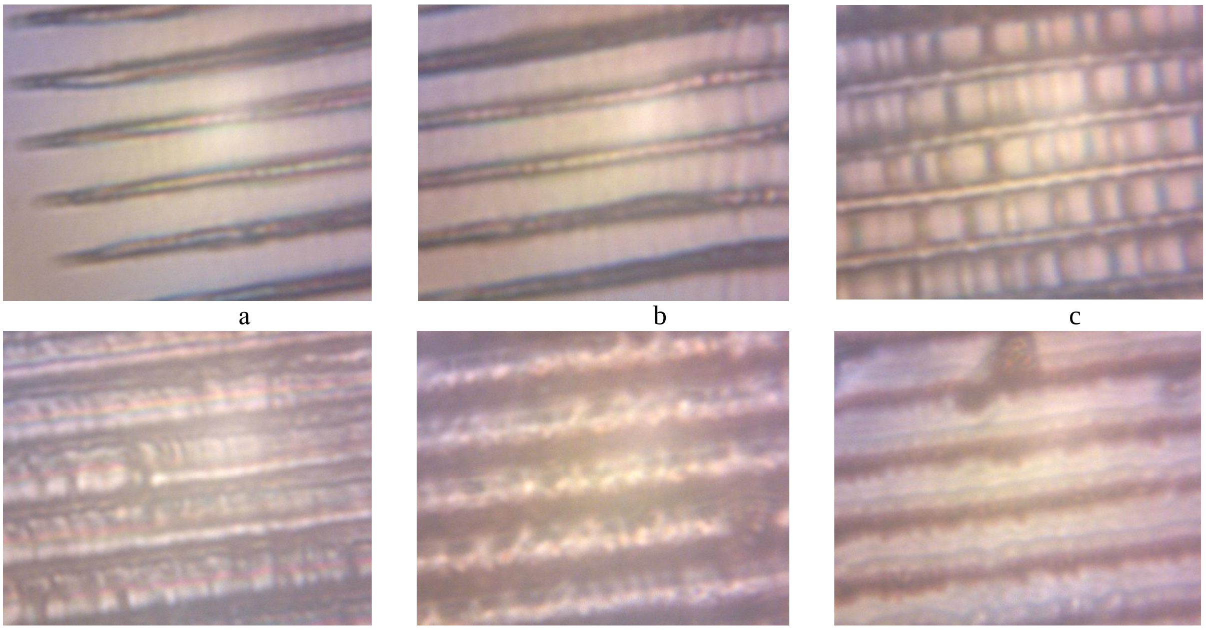


Figure 3. The diffraction efficiency dependence on the exposure duration for structure period: 2 μm (a) and 0.8 μm (b). Compositions: BisA/2Carb 3/7 (1) и BisA/2Carb 3/7, ZnO 10% (2). Layer thickness: 20 μm



a b c d e f

Figure 4. Periodic structure formation kinetics. Composition: BisA/2Carb 3/7, ZnO 10%. Exposure duration: 2 (a), 3 (b), 4 (c), 5 (d), 6 (e) and 8 (f) seconds

According to the mechanism discussed herein [8], in the process of photopolymerization, for the nanocomposite the photoinduced transfer of nanoparticles from the illuminated area (photopolymerization area) to the unlit area is allowed. According to this mechanism, nanoparticles may be contained in the gaps between the elements especially when the structure period decreases. Perhaps, the observed increase in the diffraction efficiency (Figure 3) and the decreasing differences in the diffraction efficiency at the increasing structure frequency of the nanocomposite compared with the monomer composition are linked with the photoinduced movement of nanoparticles.

The possibility of this mechanism is also confirmed by the studies of the diffraction efficiency of the structures immediately after exposure and after isopropyl alcohol treatment. Table 2 compares the results of the maximum values of the diffraction efficiency.

It is seen that the diffraction efficiency of the structures formed in the nanocomposite as a result of the exposure is much larger than in the monomer composition. Isopropyl alcohol treatment leads to a certain increase in the diffraction efficiency, which, however, is significantly lower compared with the monomer composition. This result confirms the possibility of photo-induced movements of nanoparticles in the process of photopolymerization. The refractive index modulation is formed mainly at the stage of exposure and the modulation is determined, according to the supposed mechanism, between the solid polymer which is formed in the region of maximum intensity, and the nanoparticles. It should be noted that as a result of the exposure (without further processing), quite high (up to 30%) values of the diffraction efficiency are achieved at the layer thickness of 20 microns, which is of independent practical interest.

For the monomer composition, a more significant change in the diffraction efficiency as a result of treatment is observed. This may be due to the fact that after exposure non-polymerized material is residue in the gaps between the elements, which is washed away during the isopropyl alcohol treatment. The modulation of the refractive index of the structure produced after

Table 2

The diffraction efficiency of the structures after exposure and after treatment

№	Name	Composite	DE_{max} , %	
			after exposure	after treatment
1	Monomer composite	BisA/2Carb 3/7	11	37
2	Nanocomposite	BisA/2Carb 3/7, ZnO 10%	28	45

developing is determined, apparently, between the solid polymer and the porous structure (air-polymer).

Thus, these results show that the mechanisms of the structure formation in the nanocomposite significantly differ from the monomer composition while the transport processes in the nanocomposites are currently poorly understood and require further investigation.

Conclusions

The possibility of periodic structures recording in photocurable materials based on acrylic monomers, with up to 400 nm elements, has been confirmed. It has been found that the introduction of ZnO nanoparticles increases the diffraction efficiency as compared with the monomer composition. High (up to 50%) values of the diffraction efficiency have been achieved, including no subsequent treatment values (up to 30%) with the layer thickness of 20 microns. Possible mechanisms of periodic structures formation have been identified.

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