New recording material with AgBr nanoparticles for optical holography

M Květoň\(^1\), M Škereň\(^1\), P Fiala\(^1\) and A Havránek\(^2\)

\(^1\) Department of Physical Electronics, Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University in Prague, 115 19 Prague 1, Czech Republic

\(^2\) Department of Macromolecular Physics, Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic

E-mail: milan.kveton@fjfi.cvut.cz

Abstract. A new recording material with silver bromide nanoparticles and photopolymerization system has been prepared and tested as a recording medium for optical holography. Through the method of the real-time measurement of a diffraction grating growth, we have shown that an efficient volume phase grating is formed during a holographic exposure. The material response on different exposure parameters has been measured and obtained results have been discussed. The transfer of nanoparticles within the recording layer, which is the main cause of the grating growth, has been experimentally verified through the direct observation of the grating micro-structure with the scanning electron microscope.

1. Introduction

Photopolymerizable recording materials with nanoparticles are the subject of an intensive study in last ten years (e.g. [1–5]). In comparison with common photopolymers, they contain inert inorganic particles with a high refractive index. Similarly as in the case of common photopolymers, the materials are self-developing and no additional wet chemical developing process is needed. The refractive index modulation, which is formed already during a holographic exposure, is relatively high and stable. Hence, the materials are attractive for applications such as image holography, for fabrication of diffractive optical elements, optical security elements, integrated optics, etc. The development of our photopolymer with silver bromide (AgBr) nanoparticles was inspired by the phenomenon of light induced mass transport in volume phase recording materials which can lead to redistribution of components (polymers and nanoparticles) within the medium and hence formation of a refractive index modulation. It is known that a transport of mass is the main cause of local changes of the refractive index in all efficient holographic recording materials. However, the mechanisms of molecules or particles redistribution differ.

In photopolymers, during a holographic exposure, polymer chains are formed in bright regions of the interference field. As the mobility of growing polymers is much lower than that of monomers, the polymers remain at their places of origin and so the modulation of polymer density is formed. The value of the refractive index modulation caused by the modulation of polymer density is relatively low. It has been recently shown that addition of inert particle into the photopolymerizable medium can increase the refractive index modulation. TiO\(_2\), SiO\(_2\), or ZrO\(_2\) nanoparticles with different refractive indexes from that of the host material are used...
most often. The particles are spatially redistributed due to the inhomogeneous polymerization initiated by a holographic exposure.

Mass transport is running also in silver-halide emulsions (SHE) when the process of the rehalogenization bleach is used for conversion of an amplitude hologram into a phase hologram [6]. SHE are composed of gelatin matrix in which grains (nanoparticles) of silver halide are dispersed in a high concentration. With the rehalogenization bleach technique, the developed metallic silver particles are oxidized into silver ions which became a part of the bleaching solution. The bleaching solution contains also halide ions. Due to the affinity of silver and halide ions to original grains in the unexposed areas, the grains grow at their expense and migration of silver ions occurs from exposed to unexposed areas. The formed refractive index modulation is high as the difference between the host gelatin matrix and the bulk silver halide material is high. However, the rehalogenization technique causes that the size of grains increases and so does the scattering of light which is an unwanted effect.

The basic idea of our concept is to add a suitable photopolymerizable system into the gelatin matrix with silver halide nanoparticles. When the material is holographically exposed, the photopolymerization process will cause the redistribution of nanoparticles. The advantage of the recording system is that silver halide nanoparticles are redistributed without additional developing processes and remain of the same size after the holographic exposure. AgBr nanoparticles have been chosen because of the fact that the refractive index of AgBr material is relatively high (about 2.3 for visible light) in comparison with gelatin or polymers and the preparation procedure of AgBr nanoparticles in a gelatin matrix is well developed for production of SHE.

2. Mechanism of polymer recording
In recent years we have formulated the immobilization-diffusion theory (ID-theory) of photopolymer holographic recording [7; 8] where we described why the growing photopolymer was located in the illuminated parts of the recording medium and why its position was practically fixed after the exposure. Details of the argumentation are thoroughly given in the cited references. The location of the photopolymer remains the same in the recording materials with nanoparticles as it has been in the previously studied acrylamide-based recording materials. However, as the nanoparticles are not compatible with the polymer, they are extruded out of the illuminated parts of the recording material and create an inverse distribution with respect to the interference field and polymer density. In a simple way, the mechanism of polymer recording is described in Fig. 1.

![Figure 1](image_url)

**Figure 1.** Distribution of monomers, nanoparticles, and polymers before (case a) and at the end (case b) of a holographic exposure within the recording layer.

The extrusion may be more seriously described by physical chemistry of polymers, namely by the Flory-Huggins theory of polymer solutions (e.g. [9–11]). Some attempts to solve this
problem have been done in the work [12]. According to our opinion, neglecting the Flory-Huggins interaction parameter \( \chi \) in their calculations is misleading. Namely, this parameter describes the polymer-monomer interaction in a solution and we think that the idea may be widen also to the polymer-nanoparticles mixture. More detailed discussion on the physical chemistry description of the grating growth in composite systems lies beyond the capacity of this short article. In practical evaluation of our experimental results, we continue in our previous techniques and for the specific features combined with nanoparticle systems, we were inspired by the works [1; 13].

3. Experimental

The recording material is composed of a gelatin binder with AgBr nanoparticles and acrylic monomers with a photoinitiation system. Typically, the diameter of nanoparticles is about 30 nm and they have relatively narrow size distribution. The preparation procedure of a recording layer consists of several steps which involve controlled precipitation of AgBr grains in gelatin solution, addition of a photopolymerization system, and coating thin layers on glass plates. The prepared layers are typically 20 \( \mu \)m thick and are deposited on a glass plates. The absorption maximum of the material is at a 550 nm wavelength (green light), its optimal exposition dose ranges from 5 to 10 mJ/cm\(^2\), and the diffraction efficiency of a formed grating (volume phase transmission grating) reaches 80\%.

Unique self-developing characteristics of photopolymers enable the real-time measurement of a forming diffraction grating. With the method, a response of the recording material on exposure of the harmonic interference field is studied for different recording parameters such as recording intensity, grating spatial period, or exposure time. The redistribution of AgBr nanonoparticles within the recording layer is also studied with a scanning electron microscope (SEM) JEOL JSM750.

3.1. Material composition and preparation

The initial ingredients for preparation of fine grains in a gelatin binder are water solutions of silver nitrate (AgNO\(_3\)) and potassium bromide (KBr) with a small amount of potassium iodide and a growth stabilizer. At first, a water solution is homogenized in a paddle-agitated reaction vessel which is temperature controlled. At second, solutions of AgNO\(_3\) and KBr are supplied through two vertical mixing jets to the agitated gelatin solution. In the vessel, the AgBr grains of a controlled size are precipitated and fall out of the solution. The gelatin acts as a stabilizer for the individual grains, preventing them from coagulation to form larger aggregates. After the precipitation, the gelatin solution contains a number of soluble by-products which are removed by washing as they may adversely affect the shelf-life or performance of the emulsion.

The radical photopolymerizable system is added to the melted gelatin-nanoparticles mixture. The system is composed of two liquid monomers, namely acrylic acid and N,N-Dimethylacrylamide, photoinitiator H-Nu 535 (2,4,5,7-tetraiodo-6-hydroxy-3-fluorone), and co-initiator borate V (butyryl choline butyltriphenylborate). The prepared mixture is poured over a leveled glass plate, spread with a stick or other coating tool and gravity settled. The amount of solution is a function of the desired thickness of the sensitive layer. For example, if we want to obtain a 20 \( \mu \)m dry layer, we are to take 0.02 cm\(^3\) of the solution on each 1 cm\(^2\) of a glass plate. After deposition, the layer is cooled down and dried in dark for about 4 hours. To prevent evaporation of liquid monomers, the sticky gel layer is covered with a thin PET foil. Concentrations of components of the prepared recording layer are summarized in Tab. 1.

3.2. Detection of a diffraction grating growth

With the detection method, a response of the recording material on exposure of the harmonic interference field is tested. A volume phase diffraction grating is formed already during the exposure and so its diffraction efficiency can be continuously measured. The diffraction grating is characterized with the diffraction efficiency, but the main quantity of the recording material
**Table 1.** Typical chemical composition of the photopolymer with nanoparticles.

| Chemical          | function               | weight fraction |
|-------------------|------------------------|-----------------|
| Gelatin matrix    | matrix                 | 20%             |
| AgBr nanoparticle | nanoparticle           | 15%             |
| Acrylic acid      | liquid monomer         | 57%             |
| N,N-Dimethylacrylamide | liquid monomer      | 7%              |
| H-Nu 535          | photoinitiator         | 0.2%            |
| Borate V          | co-initiator           | 0.8%            |

**Figure 2.** Schema of the experimental setup. Legend: L - recording laser (532 nm), SF - spatial filter, Le - collimating lens, M - plane mirror, RM - recording material, LD - laser diode (656 nm), D1, D2 - photo-detectors.

is the refractive index modulation. It can be evaluated from the measurement of the diffraction efficiency with Eq. (1) derived in the coupled wave theory [14]. The material parameter refractive index is connected with the chemical composition of the recording material. So measured changes of the refractive index may also be used for characterization of recording processes (polymerization, diffusion) and their further optimization.

In Fig. 2, a schema of the recording and detection setup is given. With the setup, an unslanted transmission grating is recorded with two ”s” polarized waves. For the exposure, the diode-pumped, frequency-doubled Nd:YAG laser, that emits at a 532 nm wavelength, is used (Coherent model 532-400). A narrow beam of the detection laser diode, which wavelength is out of the absorption band of the material, is used for the measurement of the diffraction efficiency. The beam is adjusted at the Bragg angle of the recorded grating. The length of the exposure is controlled with an electronic shutter which also triggers the real-time measurement of the diffraction efficiency \( \eta(t) \). The refractive index modulation \( n_1(t) \) is evaluated as an inverse function from the expression which was derived in the coupled wave theory [14]

\[
\eta(t) = \sin^2 \frac{\pi n_1(t) d}{\lambda_r \cos \theta_B},
\]

where \( d \) is the thickness of a recording layer, \( \lambda_r \) is the reconstruction wavelength and \( \theta_B \) is the Bragg angle. The obtained dependence of the refractive index modulation on time we call the grow-curve and is used for characterization of self-developing recording materials. More details about the detection method and experimental setup can be found in our recent paper [8] which deals with the acrylamide-based photopolymer.

4. Results and discussion
In this section, an experimental verification of transfer of nanoparticles during holographic exposure is given through the measurement of a grating growth and direct observation of the
microscopic structure of the grating.

4.1. Formation of a refractive index grating
The first experiments verified the ability of the recording material to form a volume phase diffraction grating. The process of a grating formation was measured with the method described in the previous section. A typical grow-curve obtained from the real-time measurement is presented in Fig. 3. Within several seconds, a grating with diffraction efficiency of 60% was formed in the layer of the photopolymer which was about 20 \( \mu \)m thick. The recording intensities, exposure time, and period of the recording interference field used in the experiment were 1.8 mW/cm\(^2\), 2 s, and 700 nm respectively.

The grow-curve describes the process of the diffraction grating formation through the parameter \( n_1 \). At the beginning of the exposure, a short induction period is observed. In spite of no detectable change of the refractive index, some initiation processes may be running in the recording material. After the induction period, the growth of the grating begins. This phase is interrupted when the recording laser is switched off. The rate of a grating formation depends on exposure parameters and chemical composition of the material. Typically, the formation rate increases in the beginning of this phase. The grow-curve goes through its inflexion point and the formation rate decreases at the end of the exposure phase. An additional increase of the refractive index modulation occurs even if the exposure is switched off. It runs out successively and saturates as the formation rate decreases to zero. This phase also strongly depends on exposure parameters. In the final period, the refractive index modulation remains stable or it may slowly decrease in time. The decrease is caused by degradation processes and its rate depends on the value of \( n_1 \) and chemical composition of the material. In fact, the degradation process may already be running from the beginning of the grating growth, but it is observed only at later exposure times when the grow rate decreases.

4.2. Influence of exposure parameters
The grow-curve depends on exposure parameters which are mainly recording intensities \( I_1 \) and \( I_2 \), spatial period of the interference field \( \Lambda \), and exposure time \( t_e \). An influence of the recording intensities was measured at first and the results are given in Fig. 4. In the case of a higher recording intensity, a higher recording rate is detected than that in the case of a lower intensity. The effect of intensity can be theoretically explained by the fact that the polymerization rate
increases with increasing intensity of light as more radicals are produced. The polymerization process is assumed as the driving mechanism and so the higher polymerization rate causes faster formation of a grating. Next to the rate of the grating growth, the final value of the refractive index modulation depends also on the recording intensity. This effect is still not very clear although it is also observed in other types of photopolymer recording materials.

![Figure 4](image1.png)

**Figure 4.** Influence of recording intensities on the process of a grating formation ($\Lambda = 700$ nm and $t_e = 5$ s for all curves).

![Figure 5](image2.png)

**Figure 5.** Influence of spatial period $\Lambda$ on the process of a grating formation ($I_1 = I_2 = 1.8$ mW/cm$^2$ and $t_e = 8$ s for all curves).

The grating growth depends strongly on the spatial period of the recording interference field (see Fig. 5). In the case of a long period, the grating grows up rapidly and a high value of $n_1$ is reached. On the other hand, a short spatial period is difficult to record and a low value of $n_1$ is reached. We assume that this effect of the limited resolution is caused by the size and mobility of the growing polymers. Hence their positions are not located only in bright areas of the interference field, which are very narrow in this case, and the separation process of nanoparticles and polymers does not proceed optimally.

### 4.3. SEM observations

The direct observations with SEM microscope give evidences of redistribution of nanoparticles within the layer. With SEM, only AgBr nanoparticles can be observed; the other components such as monomer, polymers, or gelatin matrix are not visible. Before a holographic exposure, the distribution of nanoparticles in an unexposed material is homogeneous. SEM images of cross section of an exposed material (grating) in the thickness direction are shown in Fig. 6. In the figure, a grating, which follows the intensity distribution of the recording interference field, can be seen. When the higher magnification of the microscope is applied, a periodic distribution of nanoparticles can be seen. The observation has verified that the refractive index grating is formed due to the transfer of nanoparticles caused by the inhomogeneous polymerization.

### 5. Conclusions

We have introduced a new photopolymer recording material with AgBr nanoparticles. We have demonstrated that a volume phase grating can be formed in the recording material when it is exposed with the harmonic interference field. The performance of the material has been tested at different exposure conditions. It has been found that high values of the refractive index modulation are reached for broader spatial periods and higher recording intensities. The evidence, that the grating is produced due to redistribution of nanoparticles during a holographic exposure, has been given from SEM observations of the grating microstructure.
Figure 6. SEM images of the cross section of a grating recorded in photopolymer with AgBr nanoparticles. The grating microstructure is magnified 3000x (image on the left) and 13000x (image on the right).

Acknowledgments

This work was supported by the Grant Agency of Academy of Sciences of the Czech Republic under the project KAN 401220801.

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