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Holographic recording in charged photopolymerisable nanocomposites

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Abstract. The holographic recording properties of charged zeolite containing photopolymerisable nanocomposites were studied. Photopolymer samples doped with pure silica MFI-type zeolite nanoparticles were charged using corona discharge. The holographic properties of the nanocomposites were characterised in real time using the Stetson geometry of recording. The influence of the type of charge – positive or negative on the dynamics of holographic recording and the final diffraction efficiency was studied.

Keywords: photopolymerisable nanocomposites, holographic recording, zeolite nanoparticles, photopolymers.
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INTRODUCTION

Self – processing photopolymers have a large number of different applications due to their versatile properties as holographic recording materials. A significant effort has been directed towards the development of photopolymers for holographic data storage [1, 2], holographic sensors [3], holographic optical elements [4] and display holograms [5]. The Centre for Industrial and Engineering Optics has been developing acrylamide based photopolymers for the last decade [6-8]. The main parameters requiring improvement in these types of photopolymers are their dynamic range and their mechanical stability during the holographic recording. Recently we have successfully used zeolite nanoparticles as dopants in order to increase the dynamic range and lower the shrinkage in acrylamide-based photopolymers [9]. The advantages of using zeolite nanoparticles in colloidal form are their stability in water suspension: they have the same pH as the photopolymer and can be synthesized with different shape, size and chemical composition. Depending on the chemical composition and types of the structure, the zeolites will exhibit variable refractive index. Among the different types of zeolite nanoparticles used for doping of photopolymers, the pure silica MFI (Si-MFI) has shown the best results [9]. Having in mind that the zeolites are negatively surface charged it is expected to be an appropriate dopant for photopolymers [10].

We studied the effect of the charging of the photosensitive layers on their holographic recording properties. The charging was achieved by exposure to corona discharge. Different types of charges – positive and negative were deposited on the layer surfaces. It was observed that their presence influences the diffraction efficiency of recording.

THEORY

When a sample surface contacts some medium (gas or liquid), adsorption and desorption processes of medium particles occur [11]. In the case of a dynamic equilibrium between the two processes, there is an equilibrium concentration for the adsorbed particles. Some of these particles interact electrically with the adsorbent surface (physical adsorption), while others form chemical bonds with molecules from adsorbent surface. In the latter case, oxygen is very active. The equilibrium concentration of adsorbed particles may change under the influence of various external factors such as temperature, pressure, and electric field.

When polymers layers are subjected to corona discharge in air, various ions and ion groups are created. Some of the ions recombine on the surface of the material, giving rise to chemical changes in it, while the remaining ions penetrate into the bulk of the materials, where their charge becomes trapped [12]. It was demonstrated [13, 14] that a stable surface charge but not a volume charge is formed at relatively mild corona charging parameters like room temperature ($20^{o}C$) and 5kV corona voltage. In this case during the charging samples one can assume that only adsorption and a desorption processes of charged particles take place. These particles are accelerated by the electric field of the corona and interact with the surface of the samples. The authors in [15] have ascertained that ac air corona is characterized by high concentrations of O, HO_2, H_2O_2, OH and O_3 groups. At the same time, the corona discharge forms water-soluble, low-molecular-weight, oxidized materials (LMWOM). According to [16], if a positive corona occurs in air, the prevailing ions are of the type $(H_2O)_nH^+$, $(H_2O)_nNO^+$ and $(H_2O)_n(NO_2)^+$. If negative corona occurs in air, the most important ions are the $(H_2O)_n CO_3^-$ and CO_3^- ions.

Positively or negatively charged oxygen-containing ions deposited on the sample surface, during the charging process, generate a constant electric field in the sample volume. This additional electric field can induce additional charges or cause orientation of charged structures (such as zeolite nanoparticles) in the volume.

Previous studies of the holographic recording process in acrylamide based photopolymers [6-9] reveal that this process leads to a spatially modulated refractive index due to – monomer to polymer conversion, concentration driven monomer diffusion from the dark to the bright fringes, short polymer diffusion in opposite direction and, in the case of zeolite doped layers, facilitates the special redistribution of the zeolite nanoparticles. The rise of the refractive index modulation can be observed in real time by measuring the diffraction efficiency of the recorded volume phase holographic gratings.

EXPERIMENTAL

Materials

The holographic recording material consists of a soft polymer matrix containing porous zeolite nanoparticles of 60 nm size with concentrations in the range from 0wt.% to 10wt.%. 40μm thick layers are obtained by casting the photopolymer nanocomposite solution on glass substrates. The photopolymer matrix contains two monomers – acrylamide and N,N Methylene bisacrylamide, an initiator – triethanolamine, a binder – polyvinyl alcohol and a dye sensitiser Erythrosin B.

Charging of the samples

The charging of the samples was carried out using a point-to-plane three-electrode corona discharge system. The system consisting of a corona electrode (needle), a grounded plate electrode and a grid placed between them is represented in Fig. 1. The distance between the grounded plate electrode and the grid was 10 mm; the distance from the grid to the corona electrode was 7 mm. The samples were placed on the grounded plate electrode and were charged for 3min at RH 45%, $23^{o}C$ and atmospheric pressure of 101.3kPa. Positive or negative 5kV voltages were applied to the corona electrode. A 1kV voltage with the same polarity was supplied to the grid. Introducing a grid between the corona electrode and sample limits the sample surface potential to that of the grid and produces a more uniform distribution of charge on the sample surface.
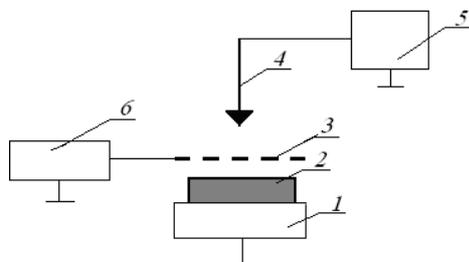

FIGURE 1. Experimental set up for corona charging: 1 - Grounded electrode; 2 - Sample holder; 3 – Grid - ± 1 kV; 4 - Corona electrode (needle) - ± 5 kV; 5 - Bias supply to the corona electrode; 6 - Bias supply to the grid.

Holographic recording set-up

The experimental set up is shown in Fig. 2. The light from a 532nm solid state laser was expanded and split into two recording beams which were then directed towards a total internal reflection prism (TIR) (as shown in Fig.2) in contact with a glass substrate. The substrate side facing the TIR prism was index matched by a high refractive index liquid – benzyl alcohol; the photopolymerisable nanocomposite was cast on the other side of the substrate. The recorded holographic grating was probed by a 633nm probe beam. The layer is not sensitive to this wavelength. The recording intensity was 25mW/cm^2 and the total exposure was 550mJ/cm^2.
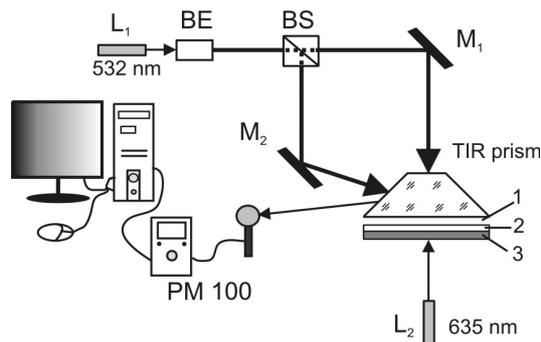

FIGURE 2. L1 - 60 mW/532 nm semiconductor laser; L2 – 1.5 mW/635 nm semiconductor laser; BE – beam expander; BS – beam splitter; M1,2 – mirrors; TIR prism - Total internal reflection prism of refractive index 1.522; 1 – Benzyl alcohol; 2 – glass substrate; 3 – Si-MFI nanozeolite doped samples; PM 100 – power meter.

RESULTS AND DISCUSSION

The results in Fig. 3 show a comparison of the diffraction efficiency dynamics in undoped and doped layers. It is seen that the addition of nanoparticles leads to an increase in the diffraction efficiency most probably due to nanoparticle redistribution. The optimum concentration of the nanoparticles was 2.5wt%. Because the nanoparticles are porous and their density is relatively low (1.78g/cm^3) the volume fraction of the nanoparticles in the photosensitive layer corresponding to this concentration is in the order of 13.5%.
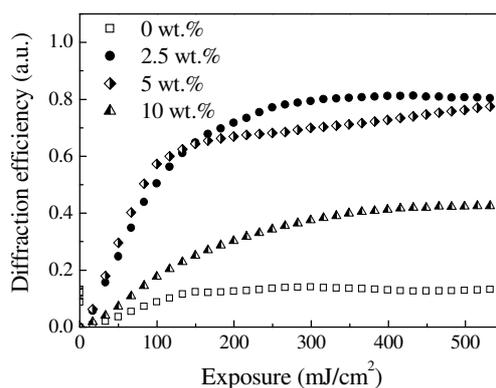

FIGURE 3. Diffraction efficiency of undoped, 2.5wt.% doped, 5wt.% doped and 10wt.% doped layers.

The influence of the electrical charging on undoped and 2.5wt.% doped layers can be seen in Fig. 4.
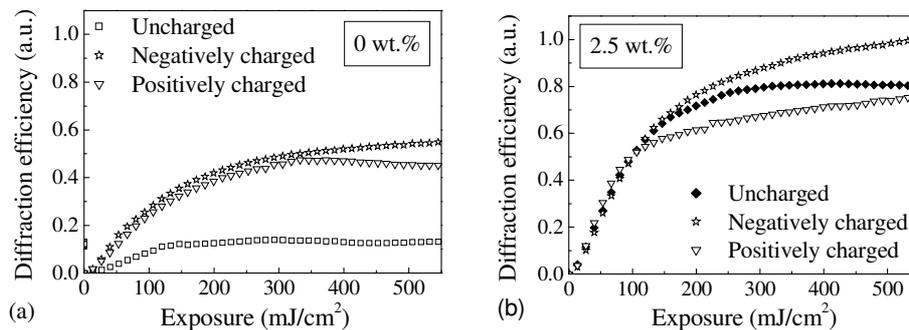
FIGURE 4. Influence of the corona charging on the real time diffraction efficiency in: (a) undoped layers and (b) 2.5wt.% doped layers.

It is seen that both undoped and doped layers are influenced by the corona charging. During the charging process positively or negatively charged ions, created in the corona discharge, are deposited on the sample surface. The observed differences in the diffraction efficiency dependencies could be explained by the difference in the electric field created by the corona discharge. In doped layers there is a superposition of two electrostatic fields. The first field (also present in undoped layers) is due to deposition of corona discharge ions on the layers surface and the second (not present in undoped layers) is created by the zeolite carried charge distributed in the sample volume.

CONCLUSIONS

In summary, there is an optimal concentration of (2.5 – 5) wt.% of zeolite Si-MFI nanoparticles for which maximum diffraction efficiency is achieved during holographic recording in the nanocomposites layers. Negative corona discharge is preferable for samples treatment before holographic recording. It was observed that the prerecording exposure to corona discharge of undoped layers improves their efficiency of recording.

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