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Research Article

Experimental Conditions to Obtain Photopolymerization Induced Phase Separation Process in Liquid Crystal-Photopolymer Composite Materials under Laser Exposure

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We analyze the experimental conditions necessary to obtain a photopolymerization induced phase separation process inside liquid crystal-photopolymer composite materials. Composites stored for 24 hours perform poorly in hologram recording but a good result is obtained if they are used recently prepared. We use a procedure combining heat and sonication to disarrange the liquid crystal structures formed during storage of the composite. We also propose incoherent light treatment after recording the hologram in order to evaluate if the phase separation evolved correctly during hologram recording.

1. Introduction

Nowadays, the materials with a nonhomogeneous internal structure undergo quick development. Concepts as nanoarchitectonics have been proposed to arrange structural units in a required configuration. Thin film preparation is an important subject related to the structural development of photonic and electronic devices [1–3].

The combination of polymer chemistry with liquid crystals allowed obtaining light sensitive composites for advanced applications in which the thin film preparation and the structural modification have a fundamental importance [4–6].

The incorporation of liquid crystals in photopolymers makes it possible to obtain composite materials which can vary their optical properties by means of an electric field. The liquid crystal molecules add optical anisotropy to the photopolymer and therefore it is possible to change the response modifying the electric field applied [7–14].

Holographic polymer dispersed liquid crystals are known as H-PDLC. They are made by holographic recording in a photopolymerization induced phase separation process (PIPS) in which the liquid crystal molecules diffuse to dark zones in the diffraction grating where they can be oriented by means of an electric field. The orientation of the liquid crystal produces a refractive index variation which changes the diffraction efficiency. Therefore, the grating develops a dynamic behavior that may be modified by means of an electronic device. In this manner, it is possible to make dynamic devices such as tunable-focus lenses, sensors, phase modulators, or prism gratings [15–18].

The PIPS effect takes place inside the material during hologram recording. Phase separation must evolve correctly in order to obtain a device with high diffraction efficiency and the capacity to change the optical response by modifying the electric field applied. The device will not have a dynamic behavior if the phase separation does not evolve correctly.

In this study, we show how the response of a H-PDLC material differs depending on whether phase separation is complete or not. To do so, we study the experimental conditions that are necessary in order to obtain a correct phase separation. These conditions are related to the prepolymer solution homogenization. We also propose incoherent light treatment after the hologram is recorded in order to evaluate if the phase separation evolved correctly during hologram recording.

2. Experimental Section

The monomer used was dipentaerythritol penta/hexa-acrylate (DPHPA) with a refractive index $n = 1.490$. We used the nematic liquid crystal CL036 (LC) from Qingdao Intermodal Co., Ltd., which is a mixture of 4-cyanobiphenyls with alkyl chains of different lengths. It has an ordinary refractive index $n_0 = 1.520$ and a difference between extraordinary and ordinary index $\Delta n = 0.250$.

N-Vinyl-2-pyrrolidone (NVP) was used as crosslinker and octanoic acid (OA) as cosolvent and surfactant. We used ethyl eosin (YEt) as dye and N-phenyl glycine (NPG) as radical generator. N-Methyl-2-pyrrolidone was used in combination with NVP (a solution obtained in a previous study [19]) in order to control the overmodulation during hologram recording. Table 1 shows the composition of the material.

The composite solution was made by mixing the components under red light where the material is not sensitive. The solution was sonicated at 35°C in an ultrasonic bath, deposited between two ITO conductive glass plates 1 mm thick, and separated using 30 μm glass microspheres from Whitehouse Scientific Ltd. The device was exposed to a laser beam ($\lambda = 532$ nm) in a holographic setup in order to record a diffraction grating in the photopolymer layer. A photopolymerization reaction takes place in the bright zones of the diffraction grating and a highly reticulated polymer network is generated. During the PIPS, the liquid crystal molecules diffuse to the unexposed region where they remain as droplets.

After recording, the diffraction grating in the H-PDLC was reconstructed ($\lambda = 632.8$ nm) and the diffraction efficiency was obtained.

2.1. Holographic Setup. We obtained diffraction gratings using a holographic setup to study the behaviour of LC-photopolymer composites as a holographic recording material. The experimental device is shown in Figure 1. An Nd : YAG laser tuned at a wavelength of 532 nm was used to record diffraction gratings by means of continuous laser exposure. The laser beam was split into two secondary beams with an intensity ratio of 1 : 1. The diameter of these beams was increased to 1 cm by means of lens, while spatial filtering was ensured. The object and reference beams were recombined at the sample at an angle of 15.8 degrees to the normal with an appropriate set of mirrors, and the spatial frequency obtained was 1024 lines/mm. The working intensity at 532 nm was 4 mW/cm^2. The diffracted and transmitted intensity were monitored in real time with a He-Ne laser positioned at Bragg's angle (18.9°) tuned to 633 nm, where the material does not polymerize. The diffraction efficiency was calculated as the ratio of the diffracted beam (I_D) to the incident power (I_0). The recordings were made at room temperature (20°C).

Table 1: Composition for LC-photopolymer composite in wt%.

DPHPA	CL036	YEt	NPG	NVP	OA	NMP
46.52	29.31	0.08	0.94	15.80	4.22	3.13

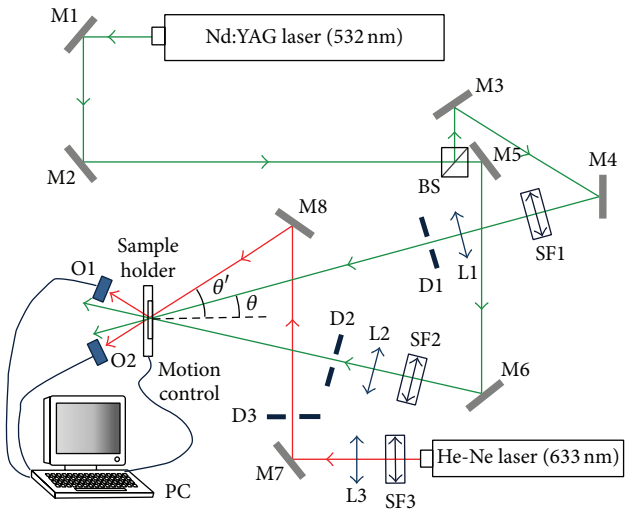

Figure 1: Experimental setup. BS: beam splitter, Mi: mirror, SFi: spatial filter, Li: lens, Di: diaphragm, Oi: optical power meter, and PC: data recorder.

3. Results and Discussion

3.1. Phase Separation. Figure 2 shows diffraction efficiency as a function of energy exposure during recording of the holograms. Plate A was made using the composite solution prepared according to the experimental procedure explained above. The solution was stored overnight at 20°C in an oven with temperature control and plate B was made using this solution the following day.

Plate A had a Demax of 12% and plate B a poor Demax of 5% although the same composite solution was used for both plates. In order to explain this behavior, it is necessary to study the mechanism for diffraction efficiency generation in these materials.

Two complementary gratings are obtained when light polymerizes the monomer. One is the grating formed by the polymerized monomer located mainly at the bright zones, and the other is the grating formed by the LC droplet bands located mainly at the dark zones. If the PIPS is adequate, the phase separation is optimal and the refractive index in the liquid crystal grating is higher than that in the polymerized monomer grating. Therefore, a relatively high diffraction efficiency was obtained with plate A. If the phase separation is not complete a weak liquid crystal grating is obtained with

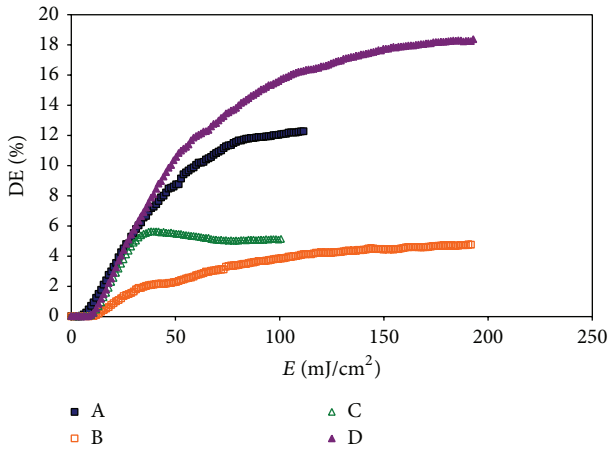

Figure 2: A fresh composite solution, B one day aged solution, C heated solution, and D solution activation process.

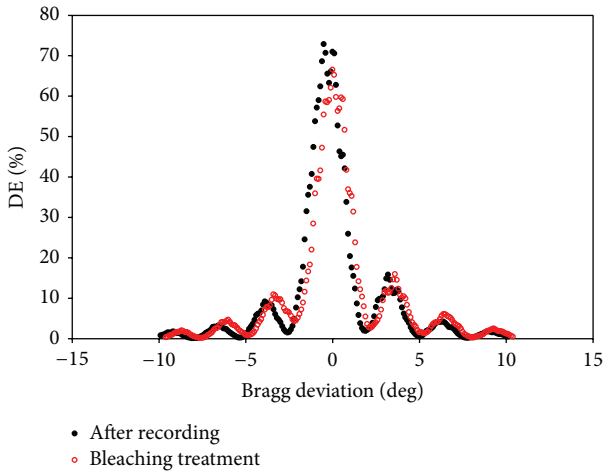

Figure 3: Angular scan after recording and after bleaching.

a small difference between the refractive index of the polymerized monomer grating and that of the liquid crystal grating. This is the case of plate B.

3.2. Solution "Activation" Process (SAP). We used an activation process in order to improve phase separation in the composite solution during hologram recording. This process combines heat and prolonged sonication in order to disarrange any ordered LC structures formed in the solution during storage. The same solution used to make plates A and B was heated to 30°C to make plate C. The heated solution was then sonicated for 7 minutes and used to make plate D.

Plate C had a poor Demax of 6% but plate D had a relatively high Demax of 18%. A possible explanation to this behavior is next. In a recently prepared solution the LC molecules are dispersed homogenously in the liquid. When the solution is stored for 24 hours the LC molecules form ordered structures. This solution is transparent and looks the same as it did when recently prepared but the LC molecules could be now arranged and a temperature of 30°C is not enough to disarrange these structures. In this case, when the monomer polymerizes phase separation does not occur homogeneously.

The monomer is the main component of the photopolymer and it has a high viscosity of 16000 mPas at 20°C, so this hinders the dispersion of LC molecules. Therefore, a SAP implies a relatively high temperature (30°C) in order to decrease the viscosity of the solution. With a low viscosity, sonication treatment can homogenize the solution and the LC structures are broken down. The activated solution may now be used in holographic recording and the LC will act as individual molecules during monomer polymerization and phase separation. Therefore, the liquid crystal grating is now more homogeneous and its refractive index is higher than that of the polymerized monomer grating.

3.3. PIPS Evaluation. In this experiment, one plate was prepared using a SAP and a hologram was recorded. The angular response after recording was obtained and then the plate was exposed to incoherent light (5400 lx halogen lamp, 15 minutes) in order to bleach the dye in the dark zones. Figure 3 shows the angular scan after recording and after bleaching.

As can be seen in this figure, after recording the plate has a Demax of 71% and after bleaching a Demax of 67%. The decrease in diffraction efficiency was only 4%. This indicates that the PIPS was done correctly and the liquid crystal is mainly located in the dark zones. A possible explanation is that bleaching polymerizes the monomer in the dark zones. LC molecules stay in the dark zones if the polymer network in the bright zones was correctly formed during hologram recording. As the index of the liquid crystal is higher than that of the polymerized monomer, polymerization in the dark zones does not increase the index modulation. Therefore the DE curve after bleaching is very similar to the one before bleaching. The decrease in DE is due to diffusion of a small fraction of LC droplets to the bright zones.

The result was completely different in the case of a photopolymer without LC. The experiment was repeated with an acrylamide based photopolymer without LC and Figure 4 shows the angular responses after recording and after bleaching [20].

Demax was 71% after recording and 48% after the bleaching treatment—a decrease of 23%. The plate has only one grating, the polymer grating, since this photopolymer has no liquid crystal. In this situation polymerization by incoherent light in the dark zones notably decreases the index modulation.

Bearing this in mind, bleaching treatment could be used as a quick and simple procedure to check if the PIPS evolved correctly in photopolymers with LC. A decrease in DE of less than 5% may be related to a correctly performed PIPS, whereas a decrease in DE of about 20% or higher indicates a poor phase separation during hologram recording.

4. Conclusions

In holographic recording, low diffraction efficiency is usually related to the composition: incorrect component proportions, low LC concentration, nonoptimized photopolymer,

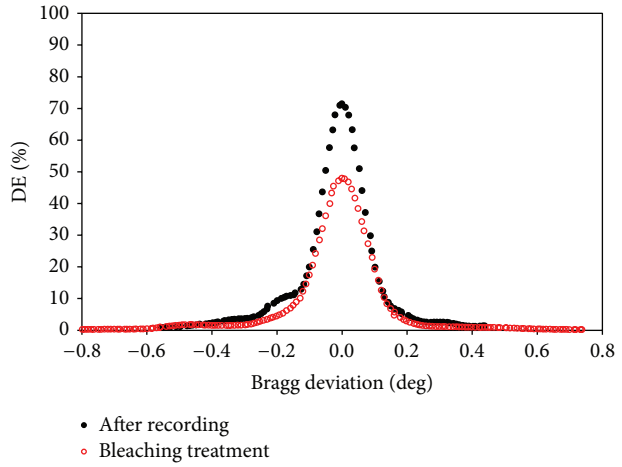

Figure 4: Angular scans after recording and after bleaching treatment for a photopolymer acrylamide based without LC.

and so forth. However, an optimized LC-photopolymer composite material may have low diffraction efficiency if the solution is stored and used without a previous treatment. This behaviour could be related to LC molecules form ordered structures in the solution during the storage. In this study, we found that this effect could be detected in the DE versus E curve during holographic recording. The arrangement of the LC molecules could be broken down by means of a solution activation process that combines heating to 30°C followed by prolonged sonication. This process should be carried out before each hologram recording in order to ensure the PIPS evolves correctly; that is, a high DE value is obtained.

We observed that a bleaching treatment with incoherent light yields a decrease in Demax in the angular response. This decrease in DE is related to the PIPS effect. If the PIPS evolves correctly, the decrease in DE after incoherent light treatment is small—less than 5%. This could be explained by the difference between the refractive index of the LC and that of the polymerized monomer located in the dark zones. Therefore if the decrease is small the PIPS effect was adequate. But if the decrease is high, typically around 20%, the situation is similar to that of photopolymers without LC. The phase separation is not complete and the device may not work under an electric field. The bleaching treatment could be easily carried out under experimental conditions, so this is a quick and effective procedure to check the quality of the LC-photopolymer composite.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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