Analysis of Holographic Polymer-dispersed liquid crystals (HPDLCs) for tunable low frequency diffractive optical elements recording

R. FERNÁNDEZ^{1,*}, S. GALLEGÓ^{1,2}, A. MÁRQUEZ^{1,2}, J. FRANCÉS^{1,2}, F. J. MARTÍNEZ^{1,2},
I. PASCUAL^{1,3}, A. BELÉNDEZ^{1,2}

¹*Instituto Universitario de Física Aplicada a las Ciencias y las Tecnologías, Universidad de Alicante. Apartado 99, 03080 Alicante, Spain*

²*Departamento de Física, Ingeniería de Sistemas y Teoría de la Señal. Universidad de Alicante. Apartado 99. E03080 Alicante, Spain*

³*Departamento de Óptica, Farmacología y Anatomía, Universidad de Alicante, P.O. Box 99, E- 03080, Alicante, Spain*

*roberto.fernandez@ua.es

Abstract: Holographic polymer dispersed liquid crystals (HPDLCs) are the result of the optimization of the photopolymer fabrication techniques. They are made by recording in a photopolymerization induced phase separation process (PIPS) in which the liquid crystal molecules diffuse to dark zones in the diffraction grating originated. Thanks to the addition of liquid crystal molecules to the composition, this material has a dynamic behavior by reorientation of the liquid crystal molecules applying an electrical field. In this sense, it is possible to use this material to make dynamic devices. In this work, we study the behavior of this material working in low frequencies with different spatial periods of blazed gratings, a sharp profile whose recording is possible thanks to the addition of a Holoeye LCoS-Pluto spatial light modulator with a resolution of 1920x1080 pixels (HD) and a pixel size of $8 \times 8 \mu\text{m}^2$. This device allows us to have an accurate and dynamic control of the phase and amplitude of the recording beam.

Keywords: Polymer dispersed liquid crystals; holographic recording materials; photopolymer formulation; electro-optical polymer devices

1. Introduction

Photopolymers are one of the most promising recording media for many holographic applications [1-3] such as optical waveguides [4], holographic-based memories [5] or optical data storage [6].

These kind of materials exhibits an outstanding versatility and new possibilities can be exploited by including new components into the classic formulations, such as nanoparticles or dispersed liquid crystal (LC) molecules. The incorporation of liquid crystals in photopolymers makes it possible to obtain composite materials [7-9]. These materials are made by recording in a photopolymerization induced phase separation process (PIPS) [10, 11], 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. When the HPDLC layer is exposed, PIPS results in spatially periodic structures alternating polymer and LC. The orientation of the liquid crystal produces a refractive index modulation between polymer and LC [12]. Therefore, the grating recorded onto the photopolymer gains a dynamic behavior and the possibility of being modified by electrical means [13-15]. In this sense, it is feasible the development of optical switching devices [16, 17], tunable-focus lenses [18], sensors [19], phase modulators [20], or prism gratings [21].

We have widely analyzed in previous studies the viability of different photopolymeric materials to record diffractive optical elements (DOEs) like lenses or blazed gratings [22-24]. In this case, as an extension of the results shown in [25], we continue exploring the behavior of a HPDLC material to record low frequency DOEs with different spatial periods using a Liquid Cristal on Silicon (LCoS) display working in mostly amplitude mode as a master.

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 (NMP) acts as unreactive solvent, decreasing the dye concentration. It was used in combination with NVP to control the overmodulation during hologram recording. Table 1 shows the composition of the material and Fig. 1 shows the molecular structure of the components of the material

The composite solution was made by mixing the components under red light at which the material is not sensitive. The solution was sonicated at 35°C in an ultrasonic bath, deposited between two ITO conductive glass plates 1mm thick, and separated using 30 µm glass microspheres from Whitehouse Scientific Ltd (Fig. 2).

Once exposed, 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.

Dipentaerythritol penta/hexa-acrylate	4'-Pentyl-4-biphenylcarbonitrile (CL036)
Ethyl eosin	N-Phenylglycine
N-methyl-2-pyrrolidone	N-vinyl-2-pyrrolidone
Octanoic acid

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

Fig. 1. Molecular structure of the components of the material

Fig. 2. Scheme of the HPDLC device: 1 glass plate, 2 ITO coating on glass plate, 3 electric connection zone, 4 glass microspheres, 5 polymer rich zone, 6 liquid crystal rich zone.

To record and evaluate the recording of sharp DOEs, the setup shown in Fig. 3 was used. A solid-state Verdi laser (Nd:YVO4) with a wavelength of 532 nm (green light), at which the material exhibits maximum absorption, was used during the recording process.

In the setup, we can distinguish two beams, the recording beam and the analyzing beam. The periodic pattern, in this case the blazed grating, is introduced by a LCoS modulator placed along the recording arm of our setup and sandwiched between two polarizers (LP) oriented to produce amplitude-mostly modulation. Then, with a 4f system the intensity distribution generated by the LCoS is imaged onto the recording material and we can analyze the diffraction efficiencies (DEs) in real time, defined as:

$$DE = \frac{I_i}{I_I} \quad (1)$$

Where I_i is the intensity of the diffraction orders and I_I is the incident intensity.

The analyzing arm is made up of a He-Ne laser at a wavelength of 633 nm, at which the material exhibits no absorption, and TE (vertical) polarization used to analyze in real time the elements formed on the material. This arm is designed to collimate the light incident on the recording material and a diaphragm (D1) was used to limit the aperture of this collimated beam of light. A non-polarizing beam splitter (BS) was used to make the two beams follow the same path up to the red interference filter (RIF) placed behind the recording material to ensure that only the analyzing beam is incident on the CCD placed at the end of the setup. To separate the different diffraction orders, we placed a lens behind the material, obtaining the Fraunhofer diffraction pattern on the camera. We used a high dynamic range CCD camera model pco.1600 from pco.imaging. This camera has a resolution of 1600 x 1200 and a pixel size of 7.4 μm x 7.4 μm . The camera was also used in the plane of the recording material to evaluate the intensity pattern imaged from the LCD plane. The recording intensity used is 0.2 mW/cm².

Fig. 3. Experimental setup. BS: beam splitter, Mi: mirror, SFi: spatial filter, LP: lineal polarizer, Li: lens, Di: diaphragm, RIF: red interference filter and PC: data recorder.

The intensity distributions provided by the LCoS across a vertical line for two different spatial periods are shown in Figs. 4 and 5. Different images were obtained placing the CCD camera in the plane of the material and recording the image of the blazed grating provided by the LCoS. The intensity distributions were extracted from a vertical line of the images corresponding to each period. These figures shown the effects of the lowpass filtering introduced by the setup to the final DOE, especially due to the diaphragm

(D3) placed to eliminate the diffraction orders produced by the pixilation of the LCD screen of the SLM. Both figures present a smoothness of the abrupt edges of the blazed profile and this effect is more accused as the size of the grating is smaller. In the most extreme cases that can cause the total loss of the grating shape, having a sinusoidal type form.

These patterns are the ones to be recorded on the photopolymer, converted into phase elements, with the great improvement added thanks to the inclusion of the LCoS SLM with a small pixel size of $8\ \mu\text{m}$ and HD resolution which improve the one of the DOE recorded. The Fraunhofer diffraction pattern obtained on the camera is shown in Fig. 6a).

After the recording, an electrical field is applied to evaluate the electro-optical response. The setup used to carry out this analysis includes a Tektronik TDS1012B oscilloscope, a Tektronic AFG3022B dual channel arbitrary function generator, a N4L voltage amplifier, and an impedance control circuit designed in our laboratory. The signal generated is a AC 1KHz bipolar square waveform. The impedance control circuit attenuates the high intensity spikes associated with capacitance effects produced by the steep voltage changes in the applied voltage. These intensity spikes reach values higher than the ones allowed by the amplifier protection circuit, thus switching it off and limiting the range of the applicable high voltage amplitude values. The capacitance is due to the capacitor structure of the HPDLC cell, composed of the two ITO electrodes and the HPDLC dielectric layer in between. An example of the diffraction pattern shown in Fig. 6a) after applying an electrical field is shown in Fig. 6b), it can be observed the changes on the grating by the effect of the LC reorientation.

Fig. 4. Intensity profile provided by the LCoS across a vertical line of the grating for an $80\ \mu\text{m}$ period blazed grating.

Fig. 5. Intensity profile provided by the LCoS across a vertical line of the image for a $336\ \mu\text{m}$ period blazed grating.

Fig. 6 a). Fraunhofer diffraction pattern captured by the CCD camera before applying an electrical field, b) applying an electrical field of 23.3 V/μm.

3. Results

Along this section different results are presented. Firstly, an analysis of the influence of the period of the grating in the final DE achieved by the recorded DOE, then, the electro-optical response of these DOE is studied. In addition to this, the conservation of the grating is also analyzed by the recording of the DOE during certain exposure time and shutting off the recording laser to observe the post-evolution of the grating. This section is finished with the results of a zero-spatial frequency recording to quantify the phase shift between exposed and nonexposed areas and a simulation to quantify the effects of the diffusion in this kind of materials.

Fig. 7 shows the comparison between the diffraction orders of a 1448 μm, 168 μm and 80 μm blazed grating recorded onto the HPDLC material with a recording intensity of 0.2 mW/cm². The figure shows how the DE of the first orders increase and reach a value above the 20% for the 168 μm and 80 μm gratings and near the 15 % for the 1448 μm grating. These values are obtained after about 40 s of exposure time for the 1448 and 168 μm gratings. The 80 μm grating reaches a higher value of DE, near the 40 %. This is due to the importance of diffusion for smaller spatial periods. For these exposure times, diffusion helps to increase the phase modulation of the grating, as in holography, but transforms it on a sinusoidal one, smoothing the sharp edges of the blazed grating.

Fig. 7. Diffraction efficiency of the zero and first orders as a function of time for a 1448 μm, 168 μm and 80 μm period blazed gratings recorded onto the HPDLC material

To analyze the conservation of the grating and the effects of the monomer diffusion, we studied the post-exposure evolution of the material. In Fig. 8 it can be seen the post-exposure evolution for two

168 μm , turning off the recording beam after 30 s of exposure time.

In previous works, based on PVA/AA and Biophotopol materials [23, 24, 26], we studied the application of an index-matching system. This index-matching system allowed us to separately measure the fast changes produced by the relief structure formed on the surface of the material from the internal diffusion. The fast changes due to thickness variations, are the so-called “apparent diffusion” and the diffusion due to the internal monomer motion is the so-called “real diffusion”.

In this case, we have measured the effects of the “apparent” monomer diffusion, as we cannot distinguish between surface and internal diffusion due to the confinement of the material between two ITO glasses. These effects are more accused for the 168 μm . In this case, the DE drop is near the 9 %. For the 336 μm one, the drop of DE is around the 4.5%.

The fittings of the measurements, following the same equations than in reference [27], are represented in Fig. 9. It can be seen how the value of the slope is higher for the 168 μm period blazed grating. Thus, the value obtained for the diffusivities are $3 \pm 1 \cdot 10^{-8} \text{ cm}^2/\text{s}$ and $2 \pm 1 \cdot 10^{-8} \text{ cm}^2/\text{s}$ for the 336 μm and 168 μm gratings respectively.

Fig. 8. a) Post-evolution of the zero and first orders after 30 s of exposure time as a function of time for a 336 μm period blazed grating, b) Post-evolution of the zero and first orders after 30 s of exposure time as a function of time for a 168 μm period blazed

Fig. 9. a) Fitting of the experimental values obtained for a 336 μm period blazed grating and for b) a 168 μm period blazed grating

Once the gratings were recorded, the material is placed into the electro-optical setup to analyze the electro-optical response of it. Fig. 10 and Fig. 11 show the response in terms of the changes in the intensity of zero orders for the different gratings showed in Fig. 7 as a function of the voltage applied. In Fig. 10a), it is shown how as the electric field is increased, the intensity of the zero order decreases a 60% of its initial value for 15 V/ μm and increases slightly, a 15 %, from this point to the limit allowed by the ITO glasses before rupture, near 23.3 V/ μm . In the case of the 168 μm blazed grating represented on Fig. 10b), the intensity value drops until near the 10% of its initial value for an applied voltage of 18.3 V/ μm . From this point to the rupture limit, the intensity value continues at its minimum value. In both cases,

from this point going back to 0 V/ μm , the intensity increases progressively recovering almost all the starting intensity value.

In Fig. 11, which shows both the response of the zero and first orders of an 80 μm blazed grating, the zero order presents similar behavior than the 168 μm grating. The first order shows an increase of the intensity with the electric field applied near the 20 % of its initial value. It can be seen as not all the intensity of the zero order is concentrated onto the first order due to a loss of the blazed profile of the grating towards a more sinusoidal shape. The hysteresis is related to the period of the grating, showing larger hysteresis for the larger grating periods, due to the influence of the period on the LC vacuoles size. Shorter periods create smaller size LC vacuoles; therefore, they are easier to reorient by electric field.

Fig.10. (a) Intensity of the zero order as a function of the applied electric field for a 336 μm period blazed grating, (b) Intensity of the zero order as a function of the applied electric field for a 168 μm period blazed grating.

Fig. 11. Intensity of the zero and first order as a function of the applied electric field for an 80 μm period blazed grating.

To have a first approach to the effects of the layer refractive index and thickness changes during the polymerization process, a zero spatial frequency limit analysis was carried out. We illuminated with a uniform beam with wavelength of 532 nm, where the material is photosensitive, and section of 1 cm^2 . Simultaneously using two He-Ne beams, one that goes through the middle of the green spot, the phase of this beam varies with the changes in the material, and the other unaltered as a reference. We made them interfere and we store the interference pattern on a CCD camera [28]. We measured the phase changes produced by the light between the illuminated and non-illuminated areas in real time. The result of this analysis for a HPDLC material with a thickness of about 30 μm is presented in Fig. 12, which represents the changes in the phase between exposed and non-exposed zones.

As it can be seen, the material starts to react quickly and after 30 seconds of exposition the phase shift is over 250°. The phase shift of 360° is reached after 160 s of exposition, confirming the possibilities of this material to fabricate low frequency DOE and explode its tunable capabilities to fabricate tunable DOE by means of an electrical field, as it was already shown in the previous figures. The main drawback is the high value of scattering that this kind of materials present, together with the shrinkage effects and the impossibility of using an index matching system [26] to minimize the surface changes which affect to the final shape of the DOE recorded. To quantify the effects of this fast surface diffusion, we have used our model [24, 27] to simulate the recording of a blazed grating onto a HPDLC material, considering the diffusivities measured for the material in this work, and compared it with the lower diffusivities measured for index matched materials [26]. The results of the simulation are shown in Fig. 13. It can be seen how the maximum DE that could be achieved by the material with the measured diffusivities is around the 30 %, because of the fast matter transfer. As opposition to this, with lower values of diffusivity, the maximum DE limit is increased in more than the 20 %, reaching the 50% of DE.

Fig. 12. Phase shift as a function of the exposure time

Fig. 13. Simulation of the recording of a blazed grating onto a HPDLC material

4. Conclusions

Along this work, we have analyzed the capabilities of HPDLC materials to work with low spatial frequencies and explore the tunable capabilities of these materials. In this case, we have studied the recording of blazed gratings of different periods using a spatial light modulator based on an LCoS screen to work with periods between 80 μm and 1448 μm . The setup used allowed us to record and analyze on real time the grating formation onto the photopolymers, measuring the DE in each case. The maximum values of DE obtained are near the 40 % for an 80 μm period grating. We have also observed how the influence of the “apparent” monomer diffusion is greater for smaller periods. After the recording of the gratings, we placed the material into an electrical field to evaluate the electro-optical response of the material for the zero and first diffraction orders of gratings of three different periods. The zero order decreases its intensity with the increment of the electric field until the 20% of its initial value. In opposition to that, the first order increases its intensity with the increment of the electric field a 20% of its initial value. There is not a total concentration of the intensity of the zero order into the first order due to a loss of the blazed profile towards a more sinusoidal profile.

In the last place, we have studied the phase shift of the material using a zero spatial frequency limit analysis and observed that the phase shift of this material is above 360° , required to work with certain types of DOE. We have also studied the effects of the diffusivity in this material using our simulation model, observing that for the diffusivities measured in this work the maximum DE is around the 30%, a 20% less compared to the diffusivities measured for index matched materials. In this point, it is mandatory to reduce the diffusion and possible shrinkage effects to achieve larger DEs, considering the impossibility of using an index matching system. To improve the results are some possibilities: to include additional nanoparticles in the formulation and to improve the recording intensity distribution.

Acknowledgments

This work was supported by the “Ministerio de Economía, Industria y Competitividad” (Spain) (FIS2014-56100-C2-1-P and FIS2015-66570-P) and by “Generalitat Valenciana” (Spain) (PROMETEO II/2015/015).

References

1. M. S. Weiser, F. K. Bruder, T. Fäcke, D. Hönel, D. Jurbergs, and T. Rölle, “Self-processing, diffusion-based photopolymers for holographic applications,” *Macromol. Symp.* 296(1), 133–137 (2010).
2. J. Neumann, K. S. Wiekling, D. Kip, “Direct laser writing of surface reliefs in dry, self-developing photopolymer films” *Appl. Opt.* 38, 5418–5421 (1999).
3. X. T. Li, A. Natansohn, P. Rochon, “Photoinduced liquid crystal alignment based on a surface relief grating in an assembled cell,” *Appl. Phys. Lett.* 74, 3791–3793 (1999).
4. C. P. Jisha, V. C. Kishore, Beena Mary John, V. C. Kuriakose, K. Porsezian, and C. Sudha Kartha, “Self-written waveguide in methylene blue sensitized poly (vinyl alcohol)/acrylamide photopolymer material,” *Appl. Opt.* 47, 6502–6507 (2008).
5. M. D. Lechner, “Photopolymers for optical memories and waveguides,” *Electron. Prop. Polym. Relat. Compd.* 63, 301–308 (1985).

6. H. J. Coufal, D. Psaltis, G.T. Sincerbox, "Holographic Data Storage" Springer-Verlag: Berlin, Germany, (2000).
7. E. Hata, K. Mitsube, K. Momose, and Y. Tomita, "Holographic nanoparticle-polymer composites based on step-growth thiol-ene photopolymerization," *Optical Materials Express*, vol. 1, no. 2, pp. 207–222, 2011.
8. Y. J. Liu and X.W. Sun, "Holographic polymer-dispersed liquid crystals: materials, formation, and applications," *Advances in OptoElectronics*, vol. 2008, Article ID 684349, 52 pages (2008).
9. S. Massenot, J.-L. Kaiser, R. Chevallier, and Y. Renotte, "Study of the dynamic formation of transmission gratings recorded in photopolymers and holographic polymer-dispersed liquid crystals," *Applied Optics*, vol. 43, no. 29, pp. 5489–5497, (2004).
10. S. Meng, H. Duran, J. Hu et al., "Influence of photopolymerization reaction kinetics on diffraction efficiency of H-PDLC undergoing photopatterning reaction in mixtures of acrylic monomer/nematic liquid crystals," *Macromolecules*, vol. 40, no. 9, pp. 3190–3197 (2007).
11. M. Mucha, "Polymer as an important component of blends and composites with liquid crystals," *Progress in Polymer Science*, vol. 28, no. 5, pp. 837–873 (2003).
12. L. V. Natarajan, D. P. Brown, J. M. Wofford et al., "Holographic polymer dispersed liquid crystal reflection gratings formed by visible light initiated thiol-ene photopolymerization," *Polymer*, vol. 47, no. 12, pp. 4411–4420 (2006).
13. J. Yan, L. Rao, M. Jiao, Y. Li, H.-C. Cheng, and S.-T. Wu, "Polymer-stabilized optically isotropic liquid crystals for next generation display and photonics applications," *Journal of Materials Chemistry*, vol. 21, no. 22, pp. 7870–7877 (2011).
14. T. J. Bunning, L. V. Natarajan, V. P. Tondiglia, and R. L. Sutherland, "Holographic polymer-dispersed liquid crystals (HPDLCs)," *Annual Review of Materials Science*, vol. 30, pp. 83–115 (2000).
15. H. Ren, S. Xu, and S. T. Wu, "Gradient polymer network liquid crystal with a large refractive index change," *Optics Express*, vol. 20, no. 24, pp. 26464–26472 (2012).
16. M. S. Li, A.Y.-G. Fuh, J.-H. Liu, and S.-T. Wu, "Bichromatic optical switch of diffractive light from a BCT photonic crystal based on an azo component-doped HPDLC," *Optics Express*, vol. 20, no. 23, pp. 25545–25553 (2012).
17. V. K. S. Hsiao, C. Lu, G. S. He et al., "High contrast switching of distributed-feedback lasing in dye-doped H-PDLC transmission grating structures," *Optics Express*, vol. 13, no. 10, pp. 3787–3794 (2005).
18. H. Ren, Y.-H. Fan, Y.-H. Lin, and S.-T. Wu, "Tunable-focus microlens arrays using nanosized polymer-dispersed liquid crystal droplets," *Optics Communications*, vol. 247, no. 1–3, pp. 101–106, 2005.
19. M. S. Li, S. T. Wu, and A. Y. G. Fuh, "Sensor for monitoring the vibration of a laser beam based on holographic polymer dispersed liquid crystal films," *Optics Express*, vol. 18, no. 25, pp. 26300–26306 (2010).
20. Y. H. Fan, Y. H. Lin, H. Ren, S. Gauza, and S.-T. Wu, "Fast-response and scattering-free polymer network liquid crystals for infrared light modulators," *Appl. Phys. Lett.* 84(8), 1233–1235 (2004).
21. H. Ren, Y. H. Fan, and S. T. Wu, "Prism grating using polymer-stabilized nematic liquid crystal," *Appl. Phys. Lett.* 82(19), 3168–3170 (2003).
22. A. Márquez, S. Gallego, M. Ortuño, E. Fernandez, M. Alvarez, A. Beléndez, I. Pascual, "Generation of diffractive optical elements onto a photopolymer using a liquid crystal display," *Proc. SPIE* 7717 (art. 77170) (2010).
23. R. Fernández, S. Gallego, A. Márquez, J. Francés, V. Navarro, I. Pascual, "Diffractive lenses recorded in absorbent photopolymers," *Opt. Express*, 24, 1559–1572 (2016).
24. R. Fernández, S. Gallego, A. Márquez, J. Francés, V. Navarro-Fuster, and A. Beléndez, "Blazed Gratings Recorded in Absorbent Photopolymers," *Materials (Basel)*, vol. 9, no. 3, p. 195, (2016).
25. R. Fernández, S. Fenoll, S. Gallego, A. Márquez, J. Francés, V. Navarro Fuster, A. Beléndez, I. Pascual, "Influence of the spatial frequency on the diffractive optical elements fabrication in PDLCs," *Proc. SPIE* 9970 (art. 997019) (2016).
26. R. Fernández, S. Gallego, A. Márquez, J. Francés, F. J. Martínez and A. Beléndez, "Influence of index matching on AA/PVA photopolymers for low spatial frequency recording," *Applied Optics*, 54(11), 3132–3140 (2015).
27. S. Gallego, A. Márquez, F. J. Guardiola, M. Riquelme, R. Fernández, I. Pascual, A. Beléndez, "Linearity in the response of photopolymers as optical recording media," *Optics Express*, 21(9), 10995–11008 (2013).
28. S. Gallego, A. Márquez, D. Méndez, C. Neipp, M. Ortuño, M. L. Alvarez, E. Fernandez, A. Beléndez, and I. Pascual, "Real-time interferometric characterization of a polyvinyl alcohol based photopolymer at the zero spatial frequency limit," *Appl. Opt.* 46(30), 7506–7512 (2007).