

# Diffraction optical elements stored on photopolymers

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**Abstract**—In this work we study the capabilities of the PVA/AA based photopolymers to record diffractive optical elements (DOEs). A double beam interferometer is constructed, both in transmission and in reflection, in combination with the setup to expose the recording material. Some benefits are provided by this approach: direct calculation of the properties of the material is possible, index and surface modulation can be decoupled, and additional information can be obtained since the results are not influenced by diffusion processes. With this scheme we mainly characterize the properties at very low spatial frequencies, which can be useful to analyze the applicability of holographic recording materials in another range of applications, such as recording of DOEs. The material response is characterized for different recording intensities. The good results when diffractive gratings are stored are related.

**Key Words**—Diffractive optics, optical materials.

## I. INTRODUCTION

Photopolymers started to be used as optical material during 70's. Actually, photopolymer are used in many optical technological devices and applications. Holography is one of the most important applications where photopolymers play an important role; in particular, many important companies have focused their attention to develop a new generation of holographic memories [1]-[4]. The importance of the photopolymers as holographic recording media is due to their good properties. These materials are suitable for different wavelength, have good spatial resolution and are very inexpensive.

Photopolymers based on polyvinylalcohol (PVA) and acrylamide (AA) are used for many research groups in Europe. These materials have been deeply studied in holographic applications. On the other hand due to their good

optics characteristics PVA/AA based photopolymers can be used to record diffractive optical elements in the range of low spatial frequencies. In the present work we evaluate the possibilities of the PVA/AA based photopolymers to store diffractive optical element in the range of low spatial frequencies (less than 100 lines/mm). In order to achieve this goal we have characterized the behaviour of the material to the zero spatial frequency limit for different recording intensities. We have analyzed the changes in the material thickness and in the refractive index using interferometric methods[5]-[6].

Taking into account the results obtained we can calculate directly many important material parameters, such as the material shrinkage, the polymer refractive index, the optimum recording intensity, etc. As conclusion we demonstrate the viability of PVA/AA based materials to record diffractive optical elements and others applications as the alignment of liquid crystals

## II. EXPERIMENTAL

In Figure 1 we show the experimental setup in transmission geometry to measure the phase-shift as a function of the exposure energy. The setup has two arms with an angular separation of 30°, one to expose the recording material, whereas the second arm is the interferometer used to measure, in real-time, the phase-shift. The recording material is perpendicularly oriented with respect to the interferometer axis in order to ease the analysis of the interferometric results: at an oblique incidence we should take into account both the Fresnel coefficients at the interface and the increase of distance in the propagation across the layer.

In the first arm, the exposure beam provided by a solid-state

Nd-YVO4 Verdi laser with a wavelength of 532 nm (at this wavelength the dye presents the maximum absorption) is expanded and collimated using a spatial filter and a lens, obtaining a beam with 1.5 cm of radius. A wave plate and a neutral filter (attenuator) are added before the spatial filter to control the orientation and the intensity of the linearly polarized beam produced by the laser Nd-YVO4. A polarizer (P), with its transmission axis oriented along the vertical of the lab, is introduced to produce a beam with TE polarization incident onto the recording material. This incident beam forms an angle of  $30^\circ$  with respect to the photopolymer layer. We adjust the laser power so that the exposure intensity that impinges on the layer is  $0.4 \text{ mW/cm}^2$  (this is the value corrected from the Fresnel coefficient at the air-photopolymer interface at an incidence of  $30^\circ$  for TE polarization). A half-opened diaphragm is used to leave an unexposed area in the photopolymer layer.

In the interferometric arm, to generate the interferences pattern we use a He-Ne laser, since the photopolymer does not present any absorption at 633 nm. We have implemented a Young's fringes based two beams interferometer. This interferometer has been successfully applied in the phase-shift characterization of liquid crystal displays (LCDs)[7]. It shows a good precision, and due to its quasi-common path architecture is a robust setup, less sensible to changing environmental conditions and simpler to construct than Mach-Zehnder type interferometers. We use a grating with a spatial frequency of 4 lines/mm to generate a series of diffracted orders from the unexpanded He-Ne beam; we block all the orders except -1 and +1. One of the two orders impinges on the exposed zone (illuminated by the Nd-YVO4 laser) and the other one impinges on the non-exposed zone. The distance between the two orders is about 1 cm, so as to eliminate the influence of the monomer diffusion in the polymerization process. Once the two orders have propagated throughout the photopolymer, a lens is used to make them interfere. A microscope objective is used to amplify the interference pattern onto a CCD camera. This pattern is captured in real-time as a function of exposure at specific time intervals. The measurements and the results obtained using this setup is presented in Section 3.1.

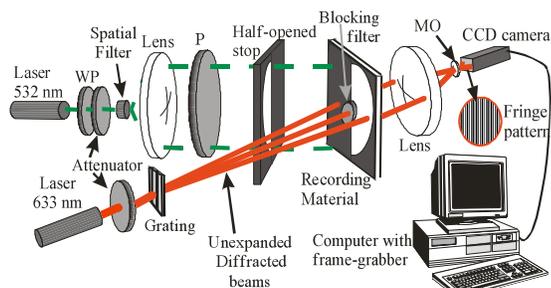


Figure 1. Experimental setup. The recording material is exposed with the green laser beam ( $\lambda=532 \text{ nm}$ ) and the phase-shift is measured with the red beam ( $\lambda=633 \text{ nm}$ ). P is polarizer, WP is wave plate, MO is microscope objective.

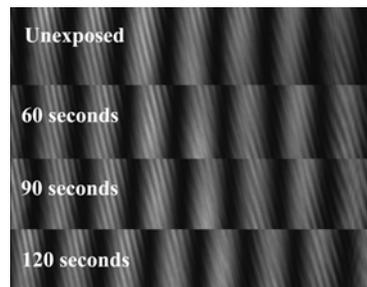


Figure 2. Fringe pattern for different exposure times (before exposing the material, after 60 s, 90 s and 120 s respectively). In particular, these images correspond to material 2 (see Table 1).

The PVA/AA formulations contain a dye, a cosensitizer which is triethanolamine (TEA), one or two monomers (AA and or not BMA) and a polymer (PVA). Let us introduce some basic details related to the design of the composition of PVA/AA photopolymer layers. Since the molecular weight of the PVA plays an important role in the monomer diffusion during the polymerization process, different types of PVA have been used in the literature. Moreover, different dyes and different triethanolamine (TEA) concentrations are normally used to obtain different material properties (TEA is a liquid at ambient temperature and plays an important role in the monomer and polymer diffusion during the polymerization process too<sup>1</sup>).

Table 1. Water solutions used to obtain photopolymerizable "dry" layers.

Component	Type 1	Type 2
PVA $M_w=130000$	8.5% w/v	8.5% w/v
TEA	0.4 M	0.4 M
YE	2.5 $\times 10^{-4}$ M	2.5 $\times 10^{-4}$ M
AA	0.45 M	0.40 M
BMA	Non	0.05 M

In this work, we consider PVA with a molecular weight of 130000, and the TEA concentration is varied between 0.4 M and 0.15 M (see Table 1). The photopolymerizable solution is prepared mixing yellowish eosin (YE, the dye), together with a mixture of acrylamide (the monomer) and triethanolamine (the co-initiator), and adding the PVA (the binder). In this study the solutions are prepared using a conventional magnetic stirrer, under red light and in standard laboratory conditions (temperature, pressure, relative humidity). The solutions are deposited, by gravity, over glasses (size  $20 \times 40 \text{ cm}^2$ ). Afterwards the solutions are left in the dark to allow the water evaporation. When a high percentage of the water content has already evaporated, the material is cut into squares ( $6.5 \times 6.5 \text{ cm}^2$ ) using a glass cutter. The water solutions used in this paper are presented in Table 1. Compositions type 1 and 2 are

used to obtain layers with thickness between 60 and 120  $\mu\text{m}$ ; in the case of composition type 2 the BMA is included in the solution<sup>[9]</sup>. In reflection we have studied the influence of BMA (crosslinker) in the shrinkage of the layers.

### III. RESULTS AND DISCUSSION

#### A. Results in transmission

We present the experimental data obtained for different material compositions and different thicknesses. The size of the error bars included in the figures indicates the repeatability or our experiments. This repeatability decreases when there are variations of the humidity and temperature in our laboratory during the drying process.

Let us begin the analysis with the basic material composition (type 1). In Figure 3 we show the phase-shift between the bright and dark zones as a function of the exposure time for material type 1; these layers have a thickness of 70  $\mu\text{m}$ . We see that after an exposure of 400 s (160  $\text{mJ}/\text{cm}^2$ ), the material is in the saturation region and no more changes can be observed: it is possible to assume that the polymerization process is finished. The saturation energy value is in the range obtained when characterizing the material at high spatial frequencies (about 120  $\text{mJ}/\text{cm}^2$ ). The maximum phase-shift value is around 192°; this value is sufficient in order to store binary-phase DOEs but it is too small to record non-binary DOEs, as diffractive lenses, blazed gratings or kinoforms, where a 360° phase-shift depth is generally required.

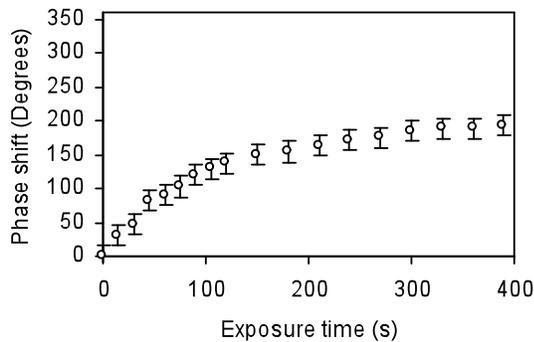


Figure 3. Phase-shift as a function of the exposure time for layers type 1 and 70  $\mu\text{m}$  thick.

In order to achieve higher values of phase-shift, there are two possibilities: to increase the thickness or to increase the refractive index modulation. In order to increase the refractive index, we can use crosslinker monomers as BMA. In Figure 4(a) we present the results provided for material type 2 (for the same thickness of material type 1, 70  $\mu\text{m}$ ). In Figure 4(b) we present the results provided for material type 2 with a thickness of 115  $\mu\text{m}$ . It is possible to observe that if we use

BMA in the chemical material composition, we obtain higher values of the phase-shift. Particularly, in Figure 4.b we achieve phase shifts significantly larger than 360°: that is, we can use this material to store non-binary DOEs as lenses. The only important disadvantage is the non-linearity between exposure time and phase-shift. Moreover, it is important to note the difference between the saturation exposure times for material type 1 (without BMA), shown in Figure 1, and type 2 (with BMA). Material type 1 presents saturation exposure times around 300 s whereas in the case of material type 2 these times are around 200 seconds. This effect clearly shows the increase in the polymerization rate when BMA is present<sup>[9]</sup>.

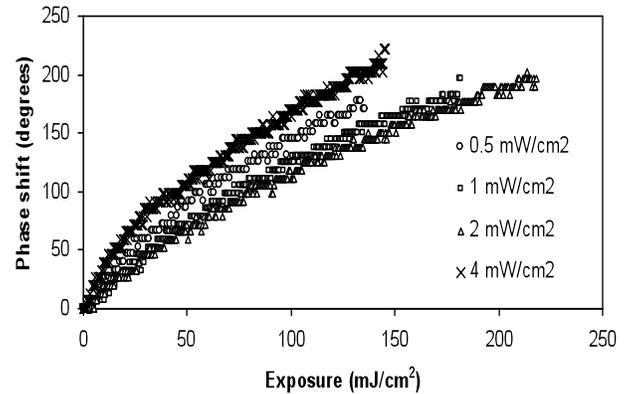


Figure 4. Phase shift as a function of the exposure time for layers type 2 for 70  $\mu\text{m}$  thick using different recording intensities.

Eventually, once we have characterized the different layers, it is important to remark that the huge phase-shift between the bright and dark zones cannot only be explained by a refractive index modulation, that is, a certain degree of thickness variation between the bright and dark regions should clearly contribute to the phase-shift. If we assume that there is no thickness variation, the saturation refractive index modulation should be around  $5 \times 10^{-3}$  for material type 1, and  $8 \times 10^{-3}$  for material type 2. Taking into account these results, the values are 30% higher than the typical values of refractive index modulation obtained in the holographic range where the spatial frequencies are around 1000 lines/mm. Furthermore, in the case of the holographic high spatial frequencies, there is an important contribution of free monomer coming from the non-exposed zones (monomer diffusion plays an important role for high spatial frequencies), which contributes to increase the refractive index modulation. These results suggest that PVA/AA based materials present a swelling or a shrinkage during the polymerization process in the experiments carried out. In this sense it is well known that volume shrinkage acts during the homogeneous polymerization of polymers. In the next Section we focus on the study of the thickness variations, using the phase-shift measurements obtained with the reflection type interferometer.

### B. Results in reflection

We analyze the thickness variation for two different compositions, with and without crosslinker, at zero frequency. Once obtained the phase shift between exposed and non exposed zones as a function of the exposure with the reflection interferometer, the shrinkage of the layer during exposure can be directly calculated using the following expression,

$$\Delta d = \frac{\Delta\Phi\lambda\cos\alpha}{4\pi} \quad (1)$$

where  $\Delta d$  is the thickness variation,  $\Delta\Phi$  is the phase-shift between exposed and non-exposed zones (expressed in radians),  $\lambda$  and  $\alpha$  are the wavelength and the incident angle of the reading beam respectively.

### C. Layers without crosslinker

The layers without crosslinker are characterized by shorter polymer chains, less energetic sensitivity, higher values of inhibition period and low values of diffraction efficiency when this type of layers are used in holography. In Figure 5(a) we show the phase shift between exposed and non exposed zones as a function of the exposure measured with the reflection type interferometer. Using Eq. (1) we calculate the shrinkage of the layer during exposure. We show the results in Figure 5(b). The shrinkage suffered by the sample during exposition is around  $2\ \mu\text{m}$  after 300 seconds. Due to this effect appears a variation of the Bragg angle in holographic application (i.e. when slanted grating are stored). Note that this shrinkage value exceeds the 0.5% defined as the upper limit for commercial availability of a recording medium[4].

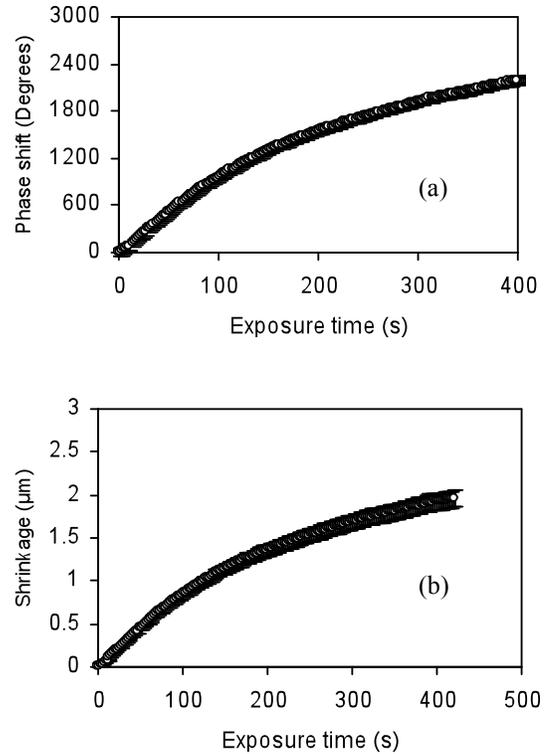


Figure 5. Layers without crosslinker. (a) Phase-shift as a function of the exposure time measured with the reflection interferometer. (b) Shrinkage as a function of the exposure time.

#### III.II.I Layers with crosslinker

Next we study the influence of the crosslinker in the material behaviour. In our experiments we use BMA as crosslinker. It is well known the capability of a crosslinker to increase the refractive index modulation of the polymer, the energetic sensitivity and the polymer length chains. On the other hand it is interesting to analyze the influence of the crosslinker in the layer shrinkage. We present the results for the phase shift as a function of exposure time in Figure 6(a). It is interesting to note the high values obtained in this case, due to the higher compaction produced by the BMA. Now the shrinkage is 33% higher than the case without crosslinker ( $3\ \mu\text{m}$ ) (Figure 6(b)).

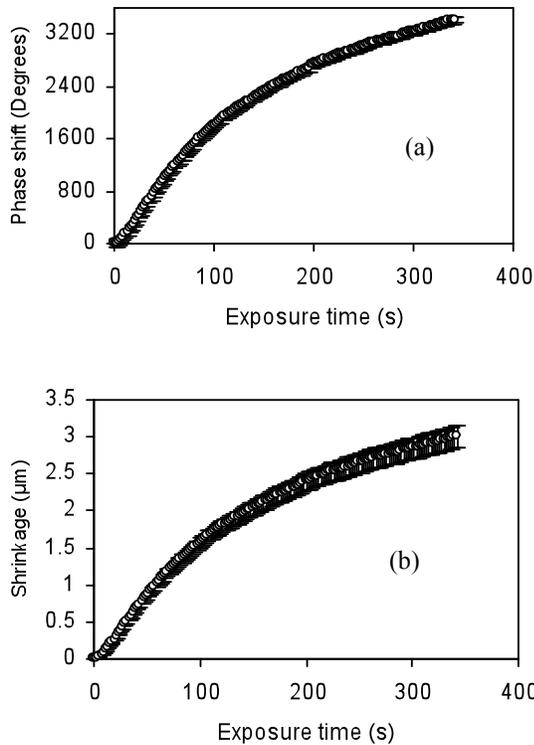


Figure 6. Layers with crosslinker. (a) Phase-shift as a function of the exposure time measured with the reflection interferometer. (b) Shrinkage as a function of the exposure time.

Now, in figure 7, the comparison for different recoding intensities is shown. Analyzing this figure it is clear than the higher profiles in the material surface are obtained for low exposure intensities.

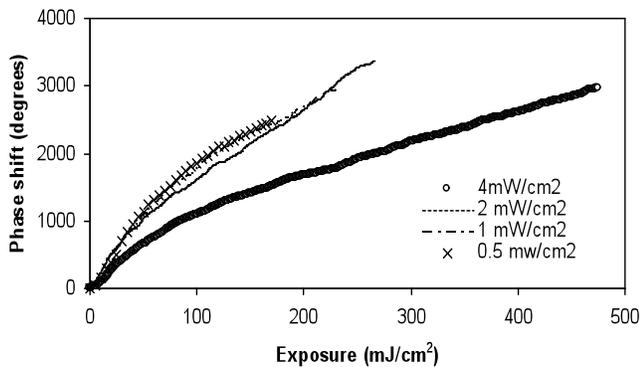


Figure 7. Phase-shift as a function of the exposure time measured with the reflection interferometer for different exposure intensities.

D. Diffractive gratings recorded

In order to record diffractive gratings on the photopolymer we use an experimental setup similar than figure 1. This new setup is shown in figure 7. Now the LCD is used as a master to record the diffractive gratings. The more important diffraction orders are analyzed to estimate the profile of the phase

modulation stored in the material.

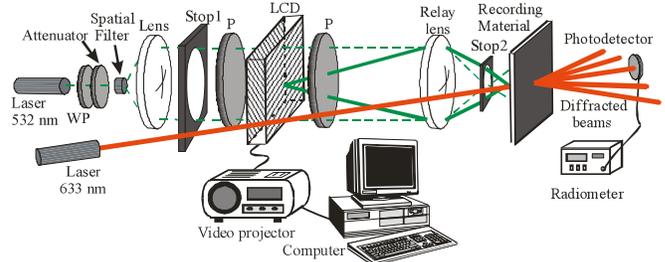


Fig. 8. Experimental set-up. The recording material is exposed to the green laser beam ( $\lambda=532$  nm) and diffraction efficiencies are measured with the red beam ( $\lambda=633$  nm). P are the polarizers and WP the wave plate.

In the first attempt a sinusoidal grating with a period of 0.16mm is recorded. In figure 9.a the diffraction efficiencies of the first 4th diffraction orders as a function of the exposure time is presented. Taking into account the efficiencies of the main important diffraction orders we can estimated the grating phase profile (Figure 9.b). As it can be seen the depth of the grating is close to  $2\pi$ , that's indicates that the materials is available to record diffractive elements as a lenses.

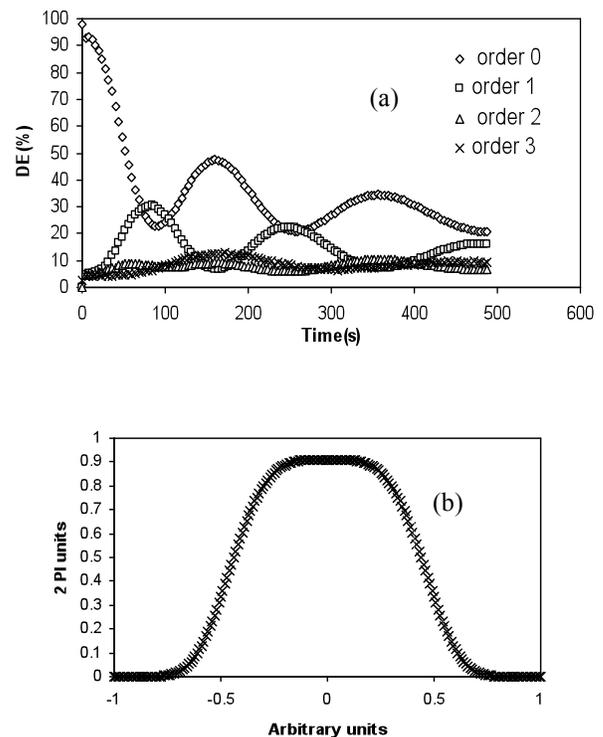


Figure 9.- Diffractive gratings : a)Diffraction efficiencies of 4<sup>th</sup> first orders for a period of 0.16 mm. b) Estimated phase profile.

IV. CONCLUSION

In this work we have characterized the optical modulation properties of PVA/AA based layers with different

compositions and thicknesses. A technique based on a Young's based double beam interferometer is proposed, which allows obtaining in real-time direct values for the phase-shift modulation of the recording material as a function of exposure. The characterization technique proposed does not depend on monomer diffusion processes, since a uniform exposure (zero frequency) is recorded onto the material. We have demonstrated the capability of some layer compositions to store phase elements under red illumination. Using the interferometer in reflection we have calculated the shrinkage for two compositions with and without BMA as crosslinker at zero spatial frequency limit. We have calculated values of shrinkage about 2 % (without crosslinker) and 3% (with crosslinker) in the layers analyzed, these values show a potential for the application to relief structures on the photopolymer, on the other hand the shrinkage is too high for holographic applications. We have characterized the material response for different recording intensities. We have stored diffractive gratings with phase depth around 2 PI.

#### ACKNOWLEDGMENT

This work was supported by the "Ministerio de Educación y Ciencia" (Spain) under projects FIS2008-05856-C02-01 and FIS2008-05856-C02-02 and by Generalitat Valenciana under project GVPRE/2008/137.

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