Analysis of the fabrication of diffractive optical elements in photopolymers

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ABSTRACT

Recently the possibility to record phase diffractive optical elements (DOEs) onto photopolymers has been explored. Two of their properties when they are illuminated are useful to this goal: the relief surface changes and the refractive index modifications. The recording intensity distribution with a sinusoidal profile is the easiest profile to record in a holographic recording material, i.e. it can be obtained by the simple interference of two plane wave beams or alternatively using a spatial light modulator. This second method is more flexible and opens the possibility to record a wide range of diffractive elements such as binary, blazed gratings, diffractive lenses, etc. Sharp profiles may as well be recorded. In general they present a clear smoothing of the edges due to various reasons: the cut-off frequency (a low pass filtering) of the optical system, quality of the spatial light modulation, inhibition period, finite size of polymer chains, monomer diffusion, and non-linearities in the recording process. In this work we have analyzed the importance of some of these aspects of the photopolymer and the experimental set-up in order to record high quality DOEs. The photopolymer analyzed is based on polyvinylalcohol/acrylamide. To achieve this goal we have used a diffusion model to simulate the DOE's recording with different recording intensities distributions.

Keywords: Diffractive optical elements, holographic recording materials, photopolymers, spatial light modulators.

1. INTRODUCTION

Photopolymer materials have a number of advantages over other photosensitive materials. Most of the materials are self-developing (self-processing) or require only some simple post-processing, such as an exposure to light or heat treatment post-exposure. This eliminates the need for wet chemical development.

In general, the composition of photopolymers includes one or more monomers, a photosensitive dye and an initiator resulting in either a liquid or a dry layer system. Dry photopolymers also usually contain a polymeric binder in addition to the other components. A dry Acrylamide, AA, (monomer) based polymer system is used for the studies reported here. Frequently in the literature, polyvinyl alcohol (PVA) materials, as opposed to commercial materials [1-2], are not cover plated. Cover plating can provide mechanical support and alter surface tension (energy) effects so as to change the profile of the surface relief grating formed during exposure [3-7]. In the absence of cover plating, the layer may be more affected by the environment. Furthermore, photopolymers without cover plating allow surface profiles and reflection diffractive elements to be generated, and provide new interesting information about the processes that take place in the materials during and after light exposure.

Low spatial frequencies are required in the fabrication of diffractive elements and to fabricate waveguides elements [8-12]. These elements can be generated due to two important properties of the photopolymers: the variations in refractive index and thickness during exposure [13-14]. To obtain a deeper insight into the profile of the generated gratings and especially into the sharpness of the edges and the phase modulation depth, we have obtained numerically the diffraction-

efficiency values for the different orders using a Fermi-Dirac function based profile [14]. Fitting the numerical results with the experimental ones we can sketch the grating profile.

We have made the first attempts to record diffractive optical lenses onto PVA/Acrylamide materials with relative success [15]. In these experiments we detected deviations between the focal length expected and the experimental results. Therefore we decided to analyze separately the two phenomena measurable in PVA materials without coverplate, the relief structures formed on the free material surface and the variation in the refractive optical index due to monomer polymerization [7]. Our goal for this work is to analyze the influence of some of these parameters on the final DOE fabricated. To achieve this goal we have used some theoretical models and we have obtained the experimental results using a photopolymer based on polyvinylalcohol/acrylamide. We want to analyze the response of two materials for some light intensity distributions (different shapes, intensities and spatial frequencies) and check the validity of our 3-Dimensional relief model.

2. THEORETICAL MODEL AND EXPERIMENTAL SET-UP

Therefore, three dimensional behaviors can be described by the following general equations:

$$\frac{\partial[M](x, z, t)}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial[M](x, z, t)}{\partial x} + \frac{\partial}{\partial z} D \frac{\partial[M](x, z, t)}{\partial z} - F_R(x, z, t)[M](x, z, t) \quad (1)$$

$$\frac{\partial[P](x, z, t)}{\partial t} = F_R(x, z, t)[M](x, z, t) \quad (2)$$

$$F_R = k_R \cdot I^\gamma(x, z, t) \quad (3)$$

where $[M]$ is the monomer concentration, $[P]$ is the polymer concentration, D_m is the monomer diffusion coefficient, I is the recording intensity, k_R is the polymerization constant, γ indicates the relationship between intensity and polymerization rate (F_R), Kg is the grating number and α is the coefficient of light attenuation. The initial value of α [$\alpha(t=0)=\alpha_0$] can be obtained if the transmittance and the physical thickness of the layer are known. In this paper we use the finite-difference method (FDM) to solve a 3-dimensional problem using a rigorous method. Therefore eqs. 1 and 2 can be written as:

$$\begin{aligned} M_{i,j,k} = & \frac{\Delta t}{\Delta x^2} D_m M_{i+1,j,k-1} - 2 \frac{\Delta t}{\Delta x^2} D_m M_{i,j,k-1} \\ & + \frac{\Delta t}{\Delta x^2} D_m M_{i-1,j,k-1} + \frac{\Delta t}{\Delta z^2} D_m M_{i,j+1,k-1} \end{aligned} \quad (4)$$

$$\begin{aligned} & - 2 \frac{\Delta t}{\Delta z^2} D_m M_{i,j,k-1} + \frac{\Delta t}{\Delta z^2} D_m M_{i,j-1,k-1} - \Delta t F_{R,i,j,k-1} M_{i,j,k-1} + M_{i,j,k-1} \\ P_{i,j,k} = & \Delta t F_{R,i,j,k-1} M_{i,j,k-1} + P_{i,j,k-1} \end{aligned} \quad (5)$$

In order to guarantee the numerical stability of the equations, the increment in the time domain, Δt , must satisfy the stability criterion

$$\Delta t \leq \frac{1}{2} \frac{(\Delta x)^2}{D_m} \quad (6)$$

In this paper, we chose $\Delta t = 0.4 (\Delta x^2/D_m)$.

In Eq. 1 and 2 we have to determine the dependence of D_m and F_R with the variables x , z and t . The simplest approximation is to assume that these variables are constant [16], but many works have focused their efforts calculating accurately these parameters [17-19]. In particular F_R has been very much studied since it includes all the chemical reactions that take place in the material during the exposure. In previous paper we have demonstrated the decreasing of D_m with the exposure for a spatial period of 168 μm and suggested that this variation should be faster for smaller spatial periods or higher spatial frequencies [20]. In addition we have approximated the dependence of the polymerization with the intensity only taking into account the last exponential decay of the polymerization constant with time [20], that allows us write:

$$k_R(t) = k_{R0} \exp(-\alpha_T t) \quad (7)$$

, where α_T is the attenuation of the polymerization due to the Trommsdorff's effect [16].

The volume fraction is given normally by $\phi_i = x_i v_i / \sum x_i v_i$, where x_i is the molar fraction and v_i is the molar volume of the i^{th} component [38-39]. In order to calculate the refractive index of the layer as a function of the variations in the volume fraction of each component, we can use the Lorentz-Lorenz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{n_m^2 - 1}{n_m^2 + 2} M + \frac{n_p^2 - 1}{n_p^2 + 2} P + \frac{n_b^2 - 1}{n_b^2 + 2} (1 - M_0) \quad (8)$$

where M_0 is the average initial value for the volume fraction of monomer, n_p is the polymer refractive index, n_m is the monomer refractive index, n_b is the binder refractive index. The effect of holes generation and collapse described in reference [16] does not affect, thus we assume that volume fraction of holes is constant.

For very low spatial frequency analysis, the diffractive-based experimental setup is shown in Fig. 1, where the periodic pattern is introduced using a LCD as the master which is copied onto the photopolymer. We used an expanded, collimated recording beam provided by a solid-state Verdi laser (Nd-YVO4) with a wavelength of 532 nm (at this wavelength the dye, yellowish eosine, exhibits maximum absorption). The periodic pattern, sinusoidal-like, is introduced by a liquid crystal display (LCD), a Sony LCD model LCX012BL, extracted from a video projector Sony VPL-V500. We used the electronics of the video projector to send the voltage to the pixels of the LCD. The LCD was used in the amplitude-mostly modulation regime by proper orientation of the external polarizers (P) [21, 22]; then the pattern was imaged onto the material with an increased spatial frequency (a demagnifying factor of 2). Using the LCD allows us to change the period of the grating recorded in the photopolymer without moving any mechanical part of the set-up. Nevertheless, the size of the pixel, 42 μm , of this LCD model limits the minimum value of the spatial period in the recording material to 168 μm (i.e. 8 LCD pixels to reproduce a period). To analyze in real time the variation in efficiency of the different diffraction orders, we used an unexpanded beam of a He-Ne laser (633 nm) incident at a small angle with respect to the normal axis of the recording material. A diaphragm (stop2) was placed in the focal plane of the relay lens so as to eliminate the diffraction orders produced by pixelation of the LCD. The final pattern imaged onto the recording material can be expected to be low-pass filtered due to the finite aperture of the imaging system and especially due to the filtering process produced by stop2.

Fig.1 Experimental set-up used to analyze the recording of gratings in real time.

3. RESULTS AND DISCUSSION

We have divided this section in different subsections in order to analyze the response of the material for different recording intensity patterns. Firstly we have analyzed the material response for a sinusoidal recording pattern. Secondly we have carried out some simulation to analyze the material response for binary intensity patterns. Analyzing the results we proposed which aspects should be improved to record high quality diffractive optical elements. Once a wider validation of the surface model has been presented, it is important, in order to record more complex diffractive optical elements (DOEs), the study of the material response for different intensity distributions, amplitudes and spatial frequencies. Moreover, in some additional cases (non-sinusoidal profiles), it is interesting to understand how the diffusion of the short polymer chains and non-local polymerization affects the profiles generated. We have analysed how the low pass filtering due to the optical system affect the final properties of the DOEs recorded.

3.1 Sinusoidal gratings

Sinusoidal illumination can be easily obtained using Fig. 1 or from interferential methods [6]. It is therefore the most studied case. We have analyzed on the first place the material under this recording pattern, to check the diffusion model for different spatial periods. A change in the spatial period of the recording illumination causes a variation of the influence of species diffusion in the formation of the DOE. We have compared our simulation with the experimental results for the recording of two sinusoidal gratings with periods of 168 μm and 336 μm . The results are depicted in Figure 2 and Figure 3 respectively. As can be seen in these figures the theoretical simulations fit perfectly with the experimental results until 160 s approximately. This fact indicates the utility of our model to predict the variations in the spatial frequency in the sinusoidal recording pattern. Moreover as can be seen in these figures the growth of the sinusoidal grating 336 μm (of illumination period) is slower than for the 168 μm due to the weaker presence of diffusion in the grating formation. It is important to remark that whereas in the simulation of the grating with 168 μm we have used the variation of D_m with time proposed in ref. [20], in the case of 336 μm we have assumed a constant value of D_m . This assumption is based on the limitation of D_m due to the growth of polymer concentration and the consequent increase of the material viscosity, and this effect is attenuated for longer periods.

Fig. 2.- Sinusoidal illumination with 168 μm of period. Simulations of the four main orders, with the experimental results for chemical PVA/AA based photopolymer.

Fig. 3.- Sinusoidal illumination with 336 μm of period. Simulation of the four main orders, with the experimental results for chemical PVA/AA based photopolymer.

3.2 Binary gratings

In order to analyze the feasibility of PVA materials to store diffractive elements the parameter of interest is the phase amplitude or the thickness modulation of the grating. In this sense the results presented in this section focus on the refractive index profile achieved during recording and the monomer and polymer spatial distributions. Now we analyze

the profiles obtained when the material is exposed to binary patterns. To record sharp profiles the experimental setup presents a clear drawback, the optical low pass filter due to the optical system and especially Stop 2 used to eliminate the pixilation of the LCD. We have presented the simulation for binary grating without low pass filtering, Figure 4, and with the binary recording intensity low pass filtered, Figure 5. As can be seen due to the low pass filtering the Figure 5 is similar to the sinusoidal response.

Fig. 4.- Binary illumination with 336 μm of period without any filter. Simulation of the four main orders.

Fig. 5.- Binary illumination with 336 μm of period low pass filtered. Simulation of the four main orders.

To have a deep insight about the refractive index profile recorded in the PVA/AA materials we have represented the refractive index distribution as a function of time in Figure 6: around the edges have been very sharp peaks due to monomer diffusion. We believe that in the real case these peaks should not be as sharp as predicted by the theoretical model. More realistic simulations can be done maybe introducing the dependence of the diffusivity with the whole volume (the sum of M and P) for each particular spatial point. Other mechanism to improve the model response is taking into account the diffusion of the short polymer chains from the bright zones to the dark ones [21].

Fig. 6.- Binary illumination with 336 μm of period without any filter: stored refractive index profile as a function of time.

4. CONCLUSIONS

We have checked the validity of the 3-Dimensional model to predict the behavior for some different recording intensities. We have increased the prediction capability of the model for sinusoidal gratings. An accurate determination of the temporal and spatial dependence of monomer diffusion is fundamental to improve the model response in sharp intensity distribution.

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