Surface relief model for photopolymers without cover plating

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Abstract: Relief surface changes provide interesting possibilities for storing diffractive optical elements on photopolymers and are an important source of information to characterize and understand the material behaviour. In this paper we present a 3-dimensional model based on direct measurements of parameters to predict the relief structures generated on the material. This model is successfully applied to different photopolymers with different values of monomer diffusion. The importance of monomer diffusion in depth is also discussed.

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References and links
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1. Introduction

Photopolymers have been widely studied in the range of holographic spatial frequencies (over 500 lines/mm). The potential of these materials for use in holographic applications has been demonstrated with great success [1–5]. Their wide application [3–9] has made the use of photopolymers as optical materials an interesting field of research. They are useful for different applications, such as diffractive and refractive optical elements, due to the refractive index variations and relief profiles generated [4,5,7,9]. Photopolymers present a great flexibility in their composition, the recording layer can be manufactured in a wide range of possible thicknesses, and they are inexpensive. These properties make them an interesting material for generating phase diffractive optical elements. In particular, the possibility of recording diffractive lenses in polyvinylalcohol (PVA) based photopolymers has recently been demonstrated using a spatial light modulator [9].
Historically, there were huge discrepancies in the monomer diffusion determination for PVA material (from 10^{-14} \text{ cm}^2/\text{s} \ [10] to 10^{-7} \text{ cm}^2/\text{s} \ [11]). Nowadays, the values for this parameter range from 10^{-9} \text{ cm}^2/\text{s} \ [12] to 10^{-7} \text{ cm}^2/\text{s} \ [11], depending on the PVA used \ [13], environmental temperature and humidity \ [12], etc. Frequently in the literature, PVA materials do not have a cover plating design as opposed to commercial material \ [1]. 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 \ [14,15]. In the absence of cover plating, the layer may be more affected by the environment. For example, water may be absorbed or evaporated and the surface profile formed during exposure may be greatly changed. 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. The goal of this study is to determine the utility of a 3-D diffusion model for predicting the surface formation and evolution after exposure. To make the theoretical predictions as accurate as possible, the parameters are obtained from direct experimental measurements. Once the model has been experimentally validated, some different values for monomer diffusion are provided and analyzed in order to evaluate the importance of this parameter in the manufacture of diffractive optical elements. The theoretical simulations are compared with the experimental results reported in ref \ [16]. for the material with acrylamide as monomer and BMA as crosslinker (PVA/AA photopolymer) and for the Biophotopol (PVA/NaOA photopolymer) compositions analyzed in ref \ [17]. (compositions A and D described in the paper).

Shrinkage caused by polymerization is greatly reduced after exposure, due to monomer diffusion from the non-exposed to exposed zones \ [18–20]. In some cases this process produces swelling of the polymerized regions and the diffraction efficiency of the zero order rises to a maximum again \ [16]. In this post-exposure process, polymerization does not take place and only the species diffusion can modify the surface profile. We simulated different material behaviors and compared different materials in order to clarify the phenomenon of grating evolution in the dark.

2. Theoretical model

The main properties of photopolymer behavior are well known. Polymerization and diffusion govern the material behavior. For very low spatial frequencies, the non-local photopolymer behavior can be disregarded. Therefore, three dimensional behaviors can be described by the following general equations:

\[
\frac{\partial [M](x,z,t)}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial [M](x,z,t)}{\partial x} \right) + \frac{\partial}{\partial z} \left( D \frac{\partial [M](x,z,t)}{\partial z} \right) - F_\gamma(x,z,t)[M](x,z,t) \tag{1}
\]

\[
\frac{\partial [P](x,z,t)}{\partial t} = F_\gamma(x,z,t)[M](x,z,t) \tag{2}
\]

\[
F_\gamma = k_\gamma \cdot I^\gamma(x,z,t) = k_\gamma \left( I_0 \left[ 1 + V \cos(K_g x) \right] e^{-\alpha(tz)} \right)^\gamma \tag{3}
\]

where \([M]\) is the monomer concentration, \([P]\) is the polymer concentration, \(D\) is the monomer diffusion coefficient, \(I\) is the recording intensity, \(k_\gamma\) is the polymerization constant, \(\gamma\) indicates the relationship between intensity and polymerization rate \((F_\gamma)\), \(K_g\) is the grating number and \(\alpha\) is the coefficient of light attenuation. The initial value of \(\alpha\) \((\alpha(t=0) = \alpha_0)\) 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{equation}
M_{i,j,k} = \frac{\Delta t}{\Delta x^2} DM_{i-1,j,k-1} - 2 \frac{\Delta t}{\Delta x^2} DM_{i,j,k-1} + \frac{\Delta t}{\Delta x^2} DM_{i+1,j,k-1} + \frac{\Delta t}{\Delta z^2} DM_{i,j,k+1} - \frac{2 \Delta t}{\Delta z^2} DM_{i,j,k+1} + \frac{\Delta t}{\Delta z^2} DM_{i,j,k-1}
\end{equation}

\begin{equation}
P_{i,j,k} = \Delta t F_{R_i,j,k-1} M_{i,j,k-1} + P_{i,j,k-1}
\end{equation}

In order to guarantee the numerical stability of the equations, the increment in the time domain, \( \Delta t \), must satisfy the stability criterion [21,22]:

\begin{equation}
\Delta t \leq \frac{1}{2} \left( \frac{Ax}{D} \right)^2
\end{equation}

In this paper, we chose \( \Delta t = 0.4 (Ax^2/D) \), which is consistent with the Wu and Glytsis [22] and J. V. Kelly dimensionless analysis [21]. However, the diffusion model now includes diffusion in the z direction.

One of the most common problems in applying these equations correctly is the independent determination of all the parameters. Recently, some research groups have proposed different ways to obtain an accurate value for monomer diffusion inside the layer. In addition, analysis of these materials at the zero spatial frequency limit gave direct measurements of shrinkage and polymerization rates for different photopolymers [23]. For example, in a 100 \( \mu \)m thick layer, the total shrinkage when all the monomer is transformed into polymer is around 4 \( \mu \)m. We assume that for very low spatial frequencies the superficial tensions can be disregarded; therefore, we calculated the volume fractions of monomer and polymer. That is, the initial volume fraction of monomer was 0.22; therefore, the polymer volume fraction is 0.18 when all the monomer is polymerized. The difference between monomer and polymer volume is reported in reference [23] for some compositions and the initial volume fraction of monomer can be obtained taking into account the water evaporated in the drying process.

One of the problems associated with finite-difference codes is that the grid used for the simulations has a finite size. This implies that in order to simulate open regions some artificial tricks must be introduced when simulations are calculated using this method. In this study, we simulated the exact area of the exposed zone (8.5 mm). Now for polymer diffusion we want to find a suitable boundary condition to simulate the extension to large (1 cm in diameter) real gratings recorded on the outer perimeter of the grid. There are 2 types of boundaries in our problem:

The first are the boundaries of the polymer with other different media (the glass substrate and air). In this case, we assume monomer diffusion is only permitted in one direction, (parallel to the boundary interface) [24]. Therefore, for the boundary condition between medium 1 (air) and medium 2 (polymer) off the grid, the monomer concentration (Eq. (12)) can be written as:

\begin{equation}
M_{i,1,k} = \frac{\Delta t}{\Delta x^2} DM_{i+1,1,k-1} - 2 \frac{\Delta t}{\Delta x^2} DM_{i,1,k-1} + \frac{\Delta t}{\Delta x^2} DM_{i-1,1,k-1} + \frac{\Delta t}{\Delta z^2} DM_{i,2,k-1} - \frac{\Delta t}{\Delta z^2} DM_{i,2,k-1} + \Delta t k_2 \bar{I}_{i,1,k-1} M_{i,1,k-1} + M_{i,1,k-1}
\end{equation}

And for the boundary between medium 2 (polymer) and medium 3 (glass substrate):
where \( j_{\text{max}} \) is the maximum value of \( j \)

The second is the boundary of the recorded zone. In this area we have non-exposed photopolymer, where we assume that the monomer concentration is constant and takes the value \( M_0 \), the initial monomer concentration.

Once the monomer and polymer concentrations are calculated, we can obtain the relief surface formed:

\[
d = d_b + d_m + d_p
\]

Where \( d_b \) is the part of the thickness due to the binder, \( d_m \) the part due to the monomer and \( d_p \) the part due to the polymer. Using “zero frequency” interferometry [23], the differences between monomer and polymer volumes can be calculated. If we assume that \( d_b \) is constant we can obtain the thickness of the layer as follow:

\[
d = d_b (1 - M_0 - M) + d_p P \left( 1 - \frac{Sh}{100M_0} \right)
\]

Where \( Sh \) is the shrinkage of the whole layer in \( \mu \text{m} \) where all the monomer is consumed and \( d_b \) is the initial physical thickness of the layer.

### 3. Results and discussion

In this section both experiments and simulations are presented in order to explain the formation of different profiles observed in PVA materials. Firstly, we design our simulations introducing parameters for PVA/materials reported by different authors. During exposure, polymerization and diffusion have a direct influence on the profile formed. As in the experiments reported in [25], to fit the profile, using our technique based on measuring the diffraction efficiencies of the different diffraction orders [25], we have to apply a short exposure time. Longer exposure times generate large phase-modulation depths exhibited by the surface profile, the first nine orders present weak values and produce a large uncertainty in the fitting of the profile. On the other hand, during post-exposure only diffusion takes place. Although it may be assumed that monomer and short chain polymer diffusion takes place during post-exposure, monomer diffusion is clearly faster and more relevant for short times. Therefore for long time simulations polymer chain diffusion should be taken into account.

Attenuation of the light inside the material has been studied in previous papers and is due to the dye concentration [26,27]. High light absorption in PVA photopolymers creates an extra monomer gradient in depth. Propagation of monomer from deep zones to the surface has only a small influence on the hologram formation for monomer diffusion rates of around \( 10^{-10} \text{ cm}^2/\text{s} \) [24]. Currently new methods have obtained new values for acrylamide photopolymers of around \( 10^{-8} \text{ cm}^2/\text{s} \). Therefore, the importance of monomer diffusion in depth should be revaluated. In this paper we study the influence of this phenomenon for different materials and diffusivity values.

#### 3.1 Theoretical surface behavior

In this section we report some simulations using the parameters estimated in previous studies using direct, independent methods. Furthermore we discuss the differences in the relief profile when the material has other possible parameters.

For very high spatial frequencies a clear shrinkage in the exposed zones was measured by different authors [11]. When we introduce the parameters measured for PVA/AA based
photopolymers, we obtain the behavior represented in Fig. 1. The parameters introduced in the model are: $D = 1.5 \times 10^{-8} \text{ cm}^2/\text{s}$; $k_R = 0.007 \text{ cm}^2/(\text{s}\cdot\text{mW})$ [23], $Sh = 4 \mu\text{m}$ [23], $\alpha = 0.02 \mu\text{m}^{-1}$ [25], $M_0 = 0.22$ [23], $I = 0.5 \text{ mW/cm}^2$, $\gamma = 1$ and $d = 90 \mu\text{m}$. This figure shows the sinusoidal profile formed on the material due to polymerization and shrinkage for a layer of 90 μm.

After exposure, shrinkage due to polymerization stops immediately. On the other hand monomer diffusion continues to equilibrate the monomer concentration inside the material. The evolution of the simulated profile for the same layer is represented in Fig. 2. It can be seen that the shrunk zones swell due to monomer diffusion. After 100 s, the filling time, the thickness of the exposed zones is equal to that of the non-exposed ones. To have a whole view of recording and post-exposure processes we have included Media 1, where is simulated in real time the surface relief using our model. Some significant frames are depicted in Fig. 3.
Having discussed the general surface behavior, it is important to calculate the diffraction efficiency (DE) of the orders generated with the profiles simulated in order to compare it with that obtained in the previous experiments reported. Reversing the method used in [25] it is relatively simple to obtain the DE of the orders 0, 1, 2 and 3, etc. With “reversing” we mean that now we know the profile and we can calculate the diffracted intensity, whereas in [25] it was the other way round. In other words, once the profile is known we obtained the DE of the
different orders by the Fourier Transform of the profile. To have a complete view of the surface profile formed, we have observed that we need to consider some additional orders apart from order 0 and 1 [25]. Figure 4 shows the evolution of the first 4 orders as a function of time. It can be seen that there is good agreement between the model and the experiments reported in previous studies for the 4 different orders. This indicates that the model is useful for predicting relief diffractive objects recorded on photopolymers without cover plating such as PVA/AA materials.

Fig. 4. Simulated diffraction efficiency for order 0 (blue), 1 (green), 2 (red), 3 (black) and experimental dots as a function of time with diffusion in depth.

One of the most interesting parts of our simulation is the post exposure process, where only diffusion takes place. The “filling time”, $t_f$, is the time the material needs to fill the shrunken zones with monomer coming from the dark zones. This time can be easily determined experimentally. Once exposure stops, the zero order grows to almost 100% DE; thus the surface profile may be considered to have disappeared. We introduced different values for monomer diffusion in the model keeping the rest of the parameters constant, the values obtained for the filling time are presented in Table 1. In 2005, Blaya et al. [10], estimated $D \sim 10^{-14}$ cm$^2$/s. They and other authors noted that the matrix composition (PVA) [13,28,29] plays a very critical role in determining $D$. It is important to note that our PVA has a higher molecular weight than those reported by other authors; therefore, our $D$ values may possibly be assumed to be a fast limit for acrylamide diffusion. However Blaya et al. state that $D$ values of the order of $10^{-7}$ cm$^2$/s are not justifiable [10,12]. Since 2002, Sheridan and associates, in a series of papers applying the NPDD model, have consistently estimated $D$ to be of the order of $10^{-10}$ cm$^2$/s [30–32]. Recently this group has reported values of around $10^{-9}$ cm$^2$/s [12]. Another group, Dr. Toal and associates, fitted the $D$ value as $10^{-7}$-10$^{-8}$ cm$^2$/s [11,33]. From Table 1 we can extract one important result: monomer diffusion in our material is around $1.4-1.5 \times 10^{-9}$ cm$^2$/s. In addition the values of $10^{-9}$ and $10^{-7}$ cm$^2$/s cannot explain the response of our material.
Table 1. $t_f$ Obtained from the Model for Different Values of Monomer Diffusion ($D$)

<table>
<thead>
<tr>
<th>$D \times 10^{-8}$ (cm$^2$/s)</th>
<th>0.1</th>
<th>1</th>
<th>1.4</th>
<th>1.5</th>
<th>2</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_f$ (s)</td>
<td>500</td>
<td>147</td>
<td>99</td>
<td>85</td>
<td>60</td>
<td>8</td>
</tr>
</tbody>
</table>

3.2 Extension to other photopolymers

Recently, some studies have described substituting the acrylamide in PVA materials due to its elevated carcinogenic potential [34,35]. Changing the monomer obviously changes the material properties [23]. One of the most important changes observed is in the monomer diffusion inside the polymer matrix [23]. To validate the usefulness of the model in predicting the behavior of different photopolymers without cover plating, we introduced the parameters obtained from these photopolymers using zero frequency analysis in the diffusion model. The parameters introduced in the model are: $D = 10^{-9}$ cm$^2$/s; $k_R = 0.0032$ cm$^2$/(s·mW) [23], $Sh = 1.7$ μm [23], $\alpha = 0.02$ μm$^{-1}$ [25], $M_0 = 0.15$, $I = 1.1$ mW/cm$^2$, $\gamma = 1$ and $d = 100$ μm. The simulation for the first 4 orders is presented in Fig. 5 with the experimental results. The good agreement between the model and the experiments confirms the low values for monomer diffusion in Biophotopol. For a very long relaxing time, we observed a weak deviation from the theoretical prediction and experiment due to the diffusion of short chains of polyacrylamide. In this type of polymers no crosslinker has been used. This phenomenon should be taken into account in order to improve the model presented. To quantify the influence of short chain polymer diffusion, the average length and molar volume should also be estimated. Therefore, it is clear that further study is necessary to predict more accurately the stable relief profile.

Fig. 5. Simulated diffraction efficiency for order 0 (blue), 1 (green), 2 (red) and 3 (black) and experimental dots as a function of time.

3.3 Influence of depth diffusion

One of the main goals of the model is to introduce monomer diffusion in depth. For standard “solid” photopolymers with values of monomer diffusion of around $10^{-10}$ cm$^2$/s, the weak
influence of this phenomenon on hologram formation has been demonstrated [24]. Therefore, monomer diffusion along the z axis is usually disregarded. Nevertheless, for the recent estimations of monomer diffusion in PVA/AA materials, the importance of monomer diffusion in depth should be revaluated. In Fig. 6 we present the simulation with equal parameters disregarding the second term of Eq. (1). Then a difference of around 15% in the DE of zero order was detected after 16s of exposure. This makes sense if we compare the period of the recording grating, 168 μm, with the thickness of the sample, 90 μm where around 80% of the green light is absorbed. Therefore, for long exposures monomer diffusion in depth should be taken into account for PVA/AA materials.

![Fig. 6. Simulated diffraction efficiency for order 0 (blue), 1 (green), 2 (red), 3 (black) and experimental dots as a function of time without diffusion in depth for PVA/AA material.](image)

It is interesting to extend the analysis of depth diffusion in biophotopol photopolymers. We have demonstrated previously that monomer diffusion in these materials is around 10 times slower. In Fig. 7 the simulation disregarding Z diffusion is presented. In this case some differences are observed too, but they are weak, around 1%. It is important to note that the exposure time is longer; therefore, for slow monomer diffusion systems monomer diffusion in depth can be disregarded.
Fig. 7. Simulated diffraction efficiency for order 0 (blue), 1 (green), 2 (red), 3 black) and experimental dots as a function of time without diffusion in depth for biophotopol material.

4. Conclusions

We have presented a new way to model and predict the relief profiles formed in photopolymers without cover plating. We have demonstrated the usefulness of the model for predicting the relief changes in different materials. The model is an important tool for designing reflection and transmission diffractive elements recorded on photopolymers. One of the main goals of the method presented is the independent determination of the main parameters involved in recording diffractive elements to avoid multiparametric fittings with some possible convergent solutions. The importance of acrylamide diffusion in depth was measured and should be incorporated in the models to be applied to PVA/AA materials. We obtained clear evidence that monomer diffusion of acrylamide is $1.4-1.5 \times 10^{-8} \text{cm}^2/\text{s}$ and that of NaOA is $1.2-1.3 \times 10^{-9} \text{cm}^2/\text{s}$. The model can be improved estimating the effect of short polymer chains diffusion for long relaxing times especially for compositions without a crosslinker.

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