Relief diffracted elements recorded on absorbent photopolymers

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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 for characterizing and understanding the material behavior. In this paper we use a 3-dimensional model, based on direct parameter measurements, for predicting the relief structures generated on without-coverplate photopolymers. We have analyzed different spatial frequency and recording intensity distributions such as binary and blazed periodic patterns. This model was successfully applied to different photopolymers with different values of monomer diffusion.

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OCIS codes: (050.2770) Diffraction and gratings, Gratings, Holography, (090.2900) Holography: Optical storage materials.

References and links

1. Introduction

Photopolymer materials are interesting materials to be used as holographic recording media since they are inexpensive, self-processing, and have the ability to record low loss, highly diffraction efficient, volume holographic gratings. In general these materials absorb light of the appropriate wavelength, causing photo-polymerization of the local monomer, inducing a change in the material refractive index and thickness. Photopolymers have been largely studied in the range of holographic spatial frequencies (over 500 lines/mm) where they have found widespread application [1–9]. A photopolymer is basically made up of one or several monomers and crosslinkers, a sensitizer, binder and initiator. The composition of photopolymers may vary greatly and the recording layer can be manufactured in a wide range of possible thicknesses. These properties make them an interesting material for generating phase diffractive optical elements. Recently the capacity of photopolymers to record diffractive elements has been demonstrated [5,7,9].

Frequently in the literature, polyvinyl alcohol (PVA) materials, as opposed to commercial materials [1], 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 [10–12]. In the absence of cover plating, the layer may be more affected by the environment. For example, water may be absorbed or evaporate 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. Relief surface changes provide interesting possibilities for storing diffractive optical elements on photopolymers and are an important source of information for characterizing and understanding the material behavior. In this sense, classically, PVA materials are prepared with acrylamide as the main monomer, and this compound has an important drawback - it is carcinogenic [13]. Therefore, we substituted acrylamide by sodium acrylate with good results [14–16]. In this paper we study both materials.

We have made the first attempts to record diffractive optical lenses onto PVA/Acrylamide materials with relative success [9]. 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. Once we have determined the parameters involved on the
diffractive phase image formation, we proposed a model (Appendix I) to predict the surface variations in PVA materials using different monomers with different values of polymerization rates and diffusions velocities [16]. We demonstrated the utility of this model for exposures shorter than 30 seconds, and the in-dark evolution (post-evolution in absence of recording light) due to monomer diffusion [16].

In the present work we want to determine the utility of a 3-D diffusion model (Appendix I) for predicting the surface formation and evolution during exposure in order to make the theoretical predictions as accurate as possible in the recording of more complex diffractive structures.

Once a wider validation of 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. In this work we analyze all these questions taking into account experimental and theoretical data.

2. Experimental set-up

In this section we briefly describe the two different materials compared. The first is PVA/acrylamide (PVA/AA) material. Some variations of this material have been widely studied in the literature with good results [17]. However, since recent investigations confirm the toxic potential of AA [13], in the second material analyzed we substituted AA monomer by sodium acrylate (NaAO) [12] (PVA/NaAO), see Table 1. Both have a thickness of around 90 ± 5 μm. It is important to remark the presence of N-N‘dimetil-bis-acrylamide (BMA) as crosslinker in the PVA/AA material used in this work. The presence of crosslinker prevents the polymer diffusion from the bright to dark zones. Furthermore the presence of crosslinker has another effect in the material behavior: an increase of the polymerization rate about 28% as can be deduced from ref [15]. In addition other important difference between these two compositions is the initial monomer volume fraction, 0.22 for PVA/AA and 0.13 for PVA/NaOA [15]. Both materials contain the same co-initiator, triethanolamine (TEA), and dye, yellowish eosine (YE). Furthermore both materials are analyzed without cover plating to obtain direct information of the changes produced on the surface due shrinkage and swelling; nevertheless, the first attempts to use a PVA material with cover plating in order to avoid formation of relief gratings have been recently reported [12]. It is important to remark that the drying process to obtain a “solid” layer should be accurately fixed (time, humidity and temperature) in order to reproduce the same values of monomer diffusion, polymerization rate, etc. PVA materials are extremely sensitive (changes of factor 2 in monomer diffusion and polymerization rate when the temperature increases 1°C during the 32 hours of drying process) for any change in the drying condition.

Table 1. Chemical Composition of the Water Solutions

<table>
<thead>
<tr>
<th>Composition type</th>
<th>NaAO (g)</th>
<th>AA (g)</th>
<th>BMA (g)</th>
<th>H2O (ml)</th>
<th>TEA (ml)</th>
<th>PVA (ml) (15% w/v)</th>
<th>YE (0.8% w/v) (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA/AA</td>
<td>-</td>
<td>0.84</td>
<td>0.25</td>
<td>12.5</td>
<td>2.5</td>
<td>12.5</td>
<td>0.6</td>
</tr>
<tr>
<td>PVA/NaAO</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>12.5</td>
<td>2.5</td>
<td>12.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The experimental set-up is presented in Fig. 1 and is similar to the one used in ref [16], to measure the phase-shift as a function of exposure energy. In order to record phase diffractive gratings we introduced a spatial light modulator (SLM) working in the amplitude only mode [18] to modulate the green beam.
We have 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 a 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 use the electronics of the video projector to send the voltage to the pixels of the LCD. The LCD is used in the amplitude-mostly modulation regime by proper orientation of the external polarizers (P) [9,18,19]; then the pattern is imaged onto the material with an increased spatial frequency (a demagnifying factor of 2). The use of 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 use 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) is placed in the focal plane of the relay lens so as to eliminate the diffraction orders produced by the pixelation of the LCD. It can be expected that the final pattern imaged onto the recording material will be low-pass filtered due to the finite aperture of the imaging system and especially due to the filtering process produced by stop2. Therefore to record binary gratings we have substituted the LCD by a binary grating of 5 lines/mm (chrome on glass Ronchi ruling provided by Edmund Optics).

3. Results and discussion

In this section 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.

The results obtained at the zero spatial frequency limit and for very low spatial frequencies help researchers to directly determine the main parameters of photopolymer behavior, such as polymerization rate, shrinkage, monomer diffusion, etc [15]. Taking these values into account, we designed a surface model to predict the relief structures formed in photopolymers without cover plating. The model is based on the diffusion equations used in standard holographic models as can be seen in ref [16]. The predictions for the surface structures provided by this model were confirmed by the experimental results obtained in the recording of diffractive gratings for photopolymers without cover plating. In particular, gratings with a spatial period of 168 µm were recorded using a spatial light modulator [20]. The good agreement between the values for the four main diffracted orders predicted by the model and the experimental results shows the importance of the real zero frequency characterization in order to understand the material behavior. Using these simulations we accurately found the value of the monomer diffusion, \( D_m \), for PVA/AA materials (1.5x10^{-8} cm²/s) and for PVA/NaAO (1.2x10^{-9} cm²/s).
As we have already described, in a previous work [16] we have analyzed the recording of sinusoidal gratings for short exposure times. Now we want to analyze long exposure times to validate our model and study its range of applicability. Firstly we have studied the real time evolution of the recorded profiles for a sinusoidal intensity exposure pattern. Then, in the following subsections we have obtained the response for different intensity distributions, and we have also analyzed the deviations between theoretical simulations and experiments studying the profiles of monomer and polymer concentrations for sharp and for slanted surface profiles.

3.1. Sinusoidal illumination

For long exposures, it was experimentally shown that the combined energy of the first four orders represents less than 10% of DE due the high phase depth values [19]. The good agreement between simulation and experiments can be deduced from Fig. 2. The simulation and experiments were done using PVA/AA materials 90 µm thick, and the other parameters introduced were taken from the “zero spatial frequency” analysis \( D_m = 1.5 \times 10^{-8} \text{ cm}^2/\text{s} \); (polymerization constant) \( k_R = 0.007 \text{ cm}^2/(\text{s \cdot mW}) \) [16], (shrinkage) \( S_h = 4\% \) [16], \( \alpha = 0.02 \ \text{µm}^{-1} \) [16], \( M_0 = 0.22 \), volume fraction [16], \( I = 0.5 \text{ mW/cm}^2 \), (relationship between intensity and polymerization rate) \( \gamma = 0.50 \). Nevertheless some differences between simulated and experimental results for order 1 appear for exposure times higher than 70 s. There are two possible effects that may explain this phenomenon: the superficial tension when deep relieve profiles are formed, and the short polymer chains diffusion in opposite sense of monomer movement.

To validate the usefulness of the model in predicting the behaviour 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 were: \( D_m = 1.2 \times 10^{-8} \text{ cm}^2/\text{s} \); \( k_R = 0.0032 \text{ cm}^2/(\text{s \cdot mW}) \) [16], \( S_h = 1.7\% \) [16], \( \alpha = 0.02 \ \text{µm}^{-1} \) [16], \( M_0 = 0.15 \), \( I = 1.1 \text{ mW/cm}^2 \), \( \gamma = 0.50 \) and \( d = 90 \ \text{µm} \). The simulation for the first 4 orders is presented in Fig. 3 together with the experimental results. The good agreement between the model and the experiments confirms the importance of the direct determination of the parameters enabled by the zero spatial frequency limit technique and also confirms the value of monomer diffusion in Biophotopol. In addition we can also see the deviation between experiments and simulation for order 1 (cross dots) after 70 s of recording. It is important to note that in the case of the PVA/NaAO the values of shrinkage are clearly smaller due to the absence of crosslinker: therefore the surface tension is clearly weaker than in the previous case. The simulated response is a little bit faster than the one obtained in the experiments: this result can be due to small changes in the thicknesses or in the polymerization velocity (this depends on the drying process). In order to compare the results obtained by PVA/AA and PVA/NaAO materials, due to the different gratings buildup time constants, it can be seen that the decreasing of the order 0 and the increasing of order 1 is 4 times faster in PVA/AA materials than PVA/NaAO. In this sense it is important to remark that PVA/AA materials have BMA as crosslinker in the composition, which makes the grating formation faster.
The influence of recording intensity on the phase image formation is related with the value of parameter gamma. In this sub-section we have exposed PVA/NaOA material at three more recording intensities to check our results against the value predicted for parameter gamma in our measurements reported in [15], which is around 0.5. In addition the importance of species diffusion depends strongly on spatial frequency. In this sense it is interesting to analyze the material behaviour for different spatial frequencies. In particular in this sub-section we study the behaviour for grating period of 0.664 mm and 0.084 mm. Firstly, we analyze PVA/NaAO composition behaviour for different recording intensities with grating period of 0.664 mm. We have presented the results obtained for \( I = 1.1 \text{ mW/cm}^2 \) in Fig. 3. Now, in Fig. 4 a), b) and c), we present respectively the results for 0.5, 2 and 4 mW/cm². For this long period the profile depth is very similar to the one achieved at zero spatial frequency recording, as has
been shown in previous works [20], due to the low influence of species diffusion inside the material.

![Graph](attachment:image.png)

Fig. 4. Simulated and experimental diffraction efficiencies for order 0, 1, 2, 3 as a function of time for PVA/NaAO composition for different recording intensities a) 0.5 mW/cm$^2$, b) 2 mW/cm$^2$ and c) 4 mW/cm$^2$. Spatial period of 664 μm.

As we can see in Fig. 4 the predictions of our model agree with the experiment for exposure times shorter than 50 s in all cases. In particular for the weakest intensity we can...
reproduce the material behaviour for 100s; on the other hand for the highest intensity our simulations present deviations after 50 s of recording. Nevertheless we can affirm that the simulated fitted value of gamma is adjusted to predict the material behaviour between 0.5 and 4mW/cm².

It is interesting to emphasize that for smaller spatial periods than 168 µm. We cannot create this sinusoidal pattern onto the photopolymer using the LCD described in the experimental section due to its large pixel size.

3.3. Different spatial profiles

In order to record more complex diffractive optical elements, for example diffractive lenses, different profiles should be recorded; in particular more abrupt and sharper profiles are required. In this line it is interesting to analyze the photopolymer response for different recording intensity profiles. Throughout this work we have analyzed the results in the material surface for sinusoidal illumination. In this subsection we analyze the profiles formed when binary and blazed exposures are used. As we said in section 2 it is not possible to obtain accurate binary gratings using our LCD set-up. Therefore we substituted the LCD by a binary grating provided by Edmund Optics, with a spatial frequency of 5 lines/mm. In this case the magnification of the optic set-up used is 1.

In Fig. 5 we present simulation and experimental results for our PVA/AA (Fig. 5.a) and PVA/NaAO (Fig. 5.b) compositions. In the PVA/AA case the agreement between experiment and simulation decreases significantly after 40 s. It is possible that the non-local polymerization [21-22], not taken into account in our model prevents the recording of very sharp surface structures. In other words there is polymer in the dark zone due to the finite size of crosslinked monomer chains. In the case of composition with sodium acrylate and without crosslinker the agreement between simulations and experiments continues up to 60 s: the absence of crosslinker generates shorter polymer chains and produces a lower depth in the relief profiles, thus smaller surface tension effects. From the results in Fig. 5 we also note that a 40% of diffraction efficiency is achieved in the first order (for t = 10 s in PVA/AA, and t = 50 s in PVA/NaAO), which corresponds to the maximum value reachable by binary structures.

Blazed gratings are interesting for many applications in diffractive optics [23-24]. These gratings are characterized by a clear asymmetry in the diffraction efficiency between positive and negative diffraction orders. The efficiency of order 1, theoretically, may achieve the value of 100% when the phase depth takes the value of 2π. One possible way to record blazed gratings onto photopolymers is by using the LCD. The display modulates the amplitude profile of the recording beam by selecting the proper configuration of input and output external polarization systems. In Fig. 6 the DE of the most significant orders are presented using the simulation provided by our model. We observe the clear asymmetry and that the maximum DE for the order 1 is about 62%. This means that a blazed illumination does not produce a blazed relief on the surface, due to the monomer diffusion. In the following section we analyze some ideas to improve the material response both for sharp profiles and for slanted or tilted profiles.
Fig. 5. Simulated and experimental diffraction efficiencies for order 0, 1, 2, 3 as a function of time for a) PVA/AA and b) PVA/NaAO compositions and spatial frequency of 5 lines/mm for binary grating.

Fig. 6. Simulated diffraction efficiencies for orders −1, 0, 1, 2, 3 as a function of time for PVA/AA and for spatial period of 168 µm.
3.4. Sharp and slanted surface profiles

In order to analyze the viability 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 volume profile achieved during recording and the monomer and polymer spatial distributions. In previous works we have demonstrated that for sinusoidal and low-pass filtered recording intensities, both PVA/AA materials and PVA/NaOA present non-abrupt profiles [16]. Now we analyze the profiles obtained when the material is exposed to binary and blazed patterns. In particular we are interested on the polymer profiles achieved. Due both to the monomer diffusion following the Fick’s law and to the important reduction of polymer diffusion when using crosslinker monomers [25], at the end of the stabilization process the relief profile obtained should be produced by the polymer concentration distribution. In this sense we have represented in Fig. 7 the thickness of the surface profile along two periods obtained after 100 s of recording with incident intensity of 1 mW/cm² using a binary pattern. As can be deduced from this figure the phase shift between the middle of the bright and dark zones is around 2π (around 0.3 µm) after 100s of recording even in the case of PVA/NaOA, the case with less shrinkage. Thus the main problem with PVA materials is not to obtain the desired phase depth value but an accurate relief structure. It is interesting to remark that in the vicinity of the border the simulation predicts huge gradients in the material surface. That is due to the incorporation of monomer to the bright zones through the border and the higher polymerization of these zones. In order to avoid this phenomenon it is necessary to smooth the recording pattern around the border. In the experiment there are two phenomena that reduce these peaks at the borders: the finite length of the polymer chains and the superficial tension.

![Fig. 7. Surface profile after 100 s of recording, simulated for PVA/NaAO material.](image)

As we have commented before, we are interested on the polymer distribution. Opposite to the monomer concentration, the polymer concentration profile does not change with time when crosslinker are used [25]. In comparison, the monomer concentration, after an interval of several hours, for these very low spatial frequencies [20], due to diffusion, flattens, thus eventually evolving onto a constant profile. Using the 3-Dimensional model we have simulated the polymer profile after 100 s of recording for the two materials in order to analyse the influence of the monomer diffusion in the polymer distribution. The results are presented in Fig. 8, where we observe that the polymer presents slightly higher concentration near the borders due to monomer diffusion from dark zones to the bright ones. The width of these peaks depends on the value of monomer diffusion, i.e. for faster values (PVA/AA material, Fig. 8.a) the penetration of the monomer in the bright zones is deeper and the width higher than the values obtained in materials with slower diffusion (PVA/NaAO material, Fig. 8.b)
In the previous section we detected some difficulties in order to store highly efficient blazed gratings onto photopolymers. Now we analyze which profiles and polymer distributions are formed onto photopolymer materials when a blazed intensity distribution is used. The photopolymer distribution after 100s of recording exposure using 0.5 mW/cm$^2$ is depicted in Fig. 9. This simulation corresponds to PVA/AA material, and it can be seen that the polymer distribution, very important, to obtain stable relieve diffractive elements, does not correspond to a blazed grating due to monomer diffusion during the recording process.

Taking into account the results presented in Fig. 9, it is straightforward to propose alternative precompensated intensity recording profile in order to improve the linearity in the recorded polymer distribution. One possible alternative is the utilization of quadratic illumination, as described in the following equation, for values of $x$ between 0 and 168 µm and $I_0$ is 0.5 mW/cm$^2$

$$I(x) = \frac{I_0 x^2}{168^2} \quad (1)$$
Fig. 9. Polymer profile after 100 s of recording using blazed illumination profile and PVA/AA material.

For this intensity distribution we obtain the polymer distribution described in Fig. 10. As it can be observed in this Fig. 10 for this intensity the polymer distribution obtained after 100s is close to a blazed grating. This shows the possible application of the model to design and optimize the recording intensity to obtain a desired polymer profile.

Fig. 10. Polymer profile after 100 s of recording using “quadratic” illumination and PVA/AA material.

In order to study the influence of this new intensity distribution on polymer surface we have presented Fig. 11, where the DE of main diffracted orders is represented as a function of time. In this case the DE of the order 1 is increased to 70%, and the DE of the other orders is in each case lower than 5%. These results improve clearly the values presented in Fig. 6. Nevertheless the influence of the monomer distribution prevents achieving higher values of DE. Now it is important to note that the initial monomer volume fraction in PVA/AA material is around 0.22. The monomer distribution after 100 s. is presented in Fig. 12. We note, as previously commented, that after an interval of several hours the monomer concentration flattens becoming homogenously distributed.
Fig. 11. Simulated diffraction efficiencies for orders 0, 1, 2, 3 as a function of time for PVA/AA and compositions and spatial period of 168 µm.

Fig. 12. Monomer profile after 100 s of recording using “quadratic” illumination and PVA/AA material.

4. Conclusions

We have checked the validity of the 3-Dimensional relief model to predict the behavior of two different photopolymers. The range of validity of the model depends on the monomer diffusion and the recording intensity distribution. With these materials, we recorded gratings with different spatial periods, intensity amplitudes, and profiles. In all the cases our model provides very accurate predictions for each of the diffracted orders analyzed for exposure times under 50 s and for the various recording intensities. This confirms that the relation of intensity and polymerization ($\gamma$) in these materials is about 0.5 and the monomer diffusion is around $1.5 \times 10^{-3}$ cm$^2$/s in PVA/AA, and $1.2 \times 10^{-9}$ cm$^2$/s in PVA/NaAO. In order to obtain accurate binary or blazed gratings and the desired polymer distribution we can analyze the relief model simulations to precompensate accordingly the recording intensity distributions.

Appendix 1

Here we present the diffusion model used to predict the materials surface variations. 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:

$$\frac{\partial [M](x, z, t)}{\partial t} = \frac{\partial}{\partial x} D \frac{\partial [M](x, z, t)}{\partial x} + \frac{\partial}{\partial z} D \frac{\partial [M](x, z, t)}{\partial z} - F_x(x, z, t)[M](x, z, t) \tag{A1}$$
\[
\frac{\partial[P(x, z, t)]}{\partial t} = F_R(x, z, t)[M](x, z, t) 
\]  
(A2)

\[
F_R = k_R \cdot I^\gamma(x, z, t) = k_R \left( I_0 \left[1 + V \cos(K_g x) \right] e^{-\alpha t|z|} \right)^\gamma 
\]  
(A3)

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, \(\gamma\) indicates the relationship between intensity and polymerization rate \((F_R)\), \(K_g\) 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:

\[
M_{i,j,k} = \frac{\Delta t}{\Delta x^2} D_m M_{i+1,j,k-1} - 2 \frac{\Delta t}{\Delta x^2} D_m M_{i,j,k-1} 
+ \frac{\Delta t}{\Delta z^2} D_m M_{i-1,j,k-1} + \frac{\Delta t}{\Delta z^2} D_m M_{i,j+1,k-1} 
- 2 \frac{\Delta t}{\Delta z^2} D_m M_{i,j,k-1} + \frac{\Delta t}{\Delta z^2} D_m M_{i,j-1,k-1} - \Delta t F_{R,i,j,k-1} M_{i,j,k-1} + M_{i,j,k-1} 
\]  
(4)

\[
P_{i,j,k} = \Delta t F_{R,i,j,k-1} M_{i,j,k-1} + P_{i,j,k-1} 
\]  
(5)

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

\[
\Delta t \leq \frac{1}{2} \left( \frac{\Delta x}{D_m} \right)^2 
\]  
(6)

In this paper, we chose \(\Delta t = 0.4 (\Delta x^2/D)\), Once the monomer and polymer concentrations are calculated, we can obtain the relief surface formed:

\[
d = d_b + d_m + d_p 
\]  
(7)

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, 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:

\[
d = d_b \left(1 - M_0 - M\right) + d_p \left(1 - \frac{Sh}{100 M_0}\right) 
\]  
(8)

Where \(Sh\) is the shrinkage of the whole layer in \(\mu m\) where all the monomer is consumed and \(d_0\) is the initial physical thickness of the layer.

Acknowledgments

This work was supported by the Ministerio de Economía y Competitividad of Spain under projects FIS2011-29803-C02-01 and FIS2011-29803-C02-02 and by the Generalitat Valenciana of Spain under project PROMETEO/2011/021.