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Santiago de Compostela, 26 – 29 August 2014

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(Keynote invited talk)

Photopolymer characterization for diffractive and holographic applications

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1. Introduction

Photopolymers are classically used in the massive production of holograms for security systems and holographic based memories due to their appealing optical properties [1-6]. They enable modulation of the material permittivity and thickness, they are self processing, layers with a wide range of thicknesses can be obtained and properties can be fabricated on demand, they present low scattering and are reasonably cheap. These characteristics altogether make photopolymers a versatile and advantageous material to fabricate diffractive optical elements and holograms [1-12]. The material response depends on many parameters. When all of them are accurately determined the material behavior can be modeled, enabling to find easily the optimum schedule to multiplex many holograms, in holographic memories, or the intensity distribution to obtain the desired diffractive optical element (DOE) with the required relief structure or refractive index distribution [13-21]. In the case when the material presents a non-linear response, the recording intensity must be adequately modified, by means of the appropriate mapping function between phase modulation and exposure time, to obtain an optimum DOE or hologram. To manufacture DOEs we have used a hybrid optical-digital system with a liquid crystal spatial light modulator (LC-SLM) performing the function of the master [22-25]. There are certain properties of LC-SLM, such as the level of detail (resolution), non-linearity and contrast that we need to optimize. In the manufacture of DOEs we need to characterize the phase modulation properties as a function of exposure that the photopolymer provides. To do this, novel real time measuring techniques have been proposed, incorporating an interferometric system in the recording set-up [26-29]. For this application and for the characterization of various more generic properties of photopolymer layers, we have developed new measurement techniques. Partly, we adapt existing interferometric, polarimetric and spectrophotometric techniques to be specifically applied to the metrology of a series of parameters involved in the development of recording materials. Some of the parameters that can be determined by these techniques are: the refractive index of the chemical component, monomer diffusion inside the material, polymerization rate, the dependence of the polymerization on the recording intensity and the variation during the exposure. In this paper we show how it is possible to measure these parameters that have been tested with four different polymeric systems and we explain the influence of these parameters on the final DOE fabricated. The photopolymer systems where these techniques demonstrated their feasibility were polyvinyl alcohol acrylamide (PVA/AA)[25], biophotopol [30], holographic polymer dispersed liquid crystal (H-PDLC) [31] and the photopolymer commercialized by Bayer-Material Science [32]. We have introduced the obtained parameters in a diffusion based model that represents the material behavior where different intensity distributions are projected on the material.

In particular, the most studied materials are polyvinyl alcoholacrylamide (PVA/AA). They have been deeply analyzed in holography [33-38] and data storage [39-42]. Some theoretical models have been proposed [43, 36, 33, 18] to study these applications and to predict the material behavior during the recording process. To obtain the values for the changes in the material properties, mainly the index modulation, nonlinear fitting of multiparametric models, such as the rigorous coupled-wave theory (RCWT) [44], are applied to the experimentally measured diffracted and/or transmitted intensity. Even

though accurate values may be obtained with the holographic approach, it would also be very useful to obtain a direct measurement of the modulation properties of the material. It is also remarkable that the values obtained for the optical modulation properties at high spatial frequencies (more than 500 lines/mm) contain both the influence of photopolymerization reaction and diffusion of the components in the material between the exposed and unexposed zones [35]. Depending on the strength assumed in the models for the two processes (photopolymerization and diffusion), the values for the material parameters may largely vary. This is partly the reason for the huge differences in the values of the characteristic parameters provided by different research teams [35]. In principle the variation of monomer concentration and polymer concentrations, M and P , for a periodic illumination in X axis can be described as follows:

$$\frac{\partial M(x, z, t)}{\partial t} = \frac{\partial}{\partial x} \left[D(x, z, t) \frac{\partial M(x, z, t)}{\partial x} \right] - \int_{-\infty}^{+\infty} G(x, x') F(x', z, t) M(x', z, t) dx' \quad (1)$$

$$\frac{\partial P(x, z, t)}{\partial t} = \int_{-\infty}^{+\infty} G(x, z, x') F(x', z, t) M(x', z, t) dx' \quad (2)$$

In this equation $D(x, z, t)$ is the diffusion coefficient, $G(x, x')$ is the non-local response function and $F(x', z, t')$ represents the rate of polymerisation at point (x', z) and time t' . The non-local response function $G(x, x')$ is supposed to have a Gaussian form [16]:

$$G(x, x') = \frac{\exp[-(x - x')^2 / 2\sigma]}{\sqrt{2\pi\sigma}} \quad (3)$$

The square root of the variance $\sqrt{\sigma}$ characterizes the length scale over which the non-local effect is significant.

For holographic diffraction gratings the intensity distribution is assumed constant along the Y-axis, but attenuated in depth along the Z axis. The depth attenuation changes the angular response of the grating stored in the material [44] and determines the optical thickness and ultimate storage capacity of each material composition [45-48]. Beer's law explains the attenuation of light intensity with depth, the recording intensity can be written as:

$$I(x, z, t) = I_0 [1 + V \cos(K_g x)] e^{-\alpha(t)z} \quad (4)$$

where V is the fringe visibility, K_g is the grating number of the recorded grating, which depends on the grating period and may be written as:

$$K_g = \frac{2\pi}{\Lambda} \quad (5)$$

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. For example in some materials [48] for layers with a physical thickness around 800 μm , the transmittance is around 0.82%; in other words, the values of α_0 for this composition are around 0.006 μm^{-1} [48]. The absorption of the layer changes as a function of the time it takes the dye to be consumed. In a first approximation, it can be written as:

$$\alpha(t) = \alpha_0 \exp(-K_\alpha \cdot I_0^\beta \cdot t) \quad (6)$$

where β is a constant that determines the influence of the intensity on the rate of consumption of the dye and depends on many factors (chemical composition of the material, temperature, humidity, etc.). The absorption decay depends on the dye and the intensity used, and K_α defines the rate at which the dye is consumed. For example in some materials [48] for a power intensity of 5 mW/cm^2 and $\beta = 0.5$, the constant takes the following value: $K_\alpha = 0.005 \text{ cm mW}^{-0.5} \text{ s}^{-1}$ for an initial approximation [48].

Therefore for holographic diffraction gratings it can be assumed the following general dependence for the polymerization rate:

$$F(x, z, t) = F_0 [1 + V \cos(Kx)]^\gamma \quad (7)$$

where

$$F_0 = k_R I_0^\gamma \quad (8)$$

and γ indicates the relationship between intensity and polymerization velocity (k_R). One of the simplest ways to describe the behavior of polymerization during recording is to assume that the polymerization rate increases very fast due to the Trommsdorff effect and then, decreases because it is limited by the viscosity of the material [49]. Therefore it is given by:

$$k_R(t) = k_R \exp(-\varphi I_0 t) \quad (9)$$

where φ is the attenuation coefficient of the polymerization rate. In general there are many models for formation kinetics; these models take into account the roles of the photoinitiation, the co-initiator, the crosslinker, etc. during the grating formation. Other important novelties introduced in the study of photopolymers are the cut-off intensity for very low recording patterns or the inhibition period presented by some materials. For example in PVA/AA materials the lower cut-off intensity is around $50 \mu\text{W}/\text{cm}^2$ [48].

The question is how is it possible to develop measurement techniques and models to fit properly all these parameters for different types of photopolymers. In this paper we want to show this characterization from the beginning applying different methods to measure the parameters independently and afterwards describe how employing these parameters we can design models to simulate and reproduce the material behavior for many interesting applications such as holographic data storage.

2. Experimental set-up

We propose three different experimental set-ups, the first two set-ups permit us studying separately the processes of polymerization, shrinkage and diffusion. The third is a classic holographic geometry to record diffractive gratings or data pages depending on the object beam used for each particular case. In Fig. 1 we show the experimental setup in transmission geometry to measure the phase-shift as a function of the exposure energy without monomer diffusion. The setup has two arms with an angular separation of 14° , 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 14° with respect to the photopolymer layer. We adjust the laser power so that the exposure intensity that impinges on the layer is $1 \text{ mW}/\text{cm}^2$ (this is the value corrected from the Fresnel coefficient at the air-photopolymer interface at an incidence of 14° 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) [25]. It shows a good precision, and due to its quasi-common path architecture is a robust setup, less sensitive 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 scheme for the setup to measure the phase-shift in reflection is basically the same as in Figure 1. Instead of measuring the interference between the two transmitted beams, the measurements are done for

the reflected beams. The interferometric arm is, thus, located on the same side of the incident He-Ne probe beam at an angle, so as to separate the incident and reflected He-Ne beams. With these measurements the thickness variation, the shrinkage, can be measured as a function of the exposure energy. Therefore, with this setup it is possible to plot the fringes moving as a function of the exposure time during the polymerization process, and without the influence of monomer diffusion. In this sense, we have verified that once we stop the exposition, the shift in the interference fringes freezes. This indicates that the measurements taken in this setup are not affected by diffusion processes. In the case of the photopolymer studied in this paper we obtained that the exposed zone shrinks with respect to the non-exposed area.

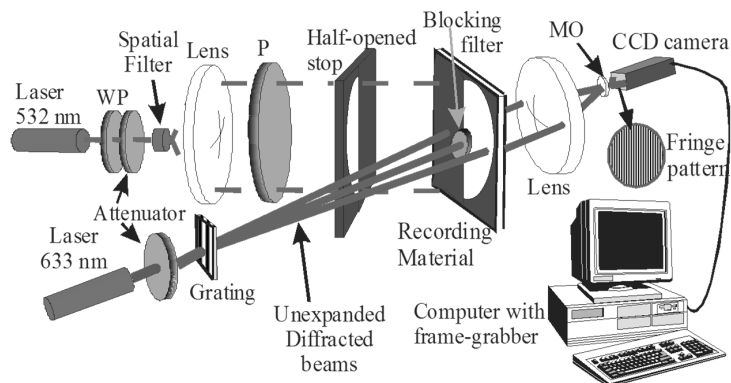


Figure 1 Experimental set-up 1 for zero spatial frequency recording.

Once the materials are characterized in the case of no diffusion, we proceed to measure the velocity of monomer diffusion in the material recording very low spatial frequency diffractive gratings. The experimental set-up is presented in Figure 2 [22] 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 [22] to modulate the green beam. 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) [22]; 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).

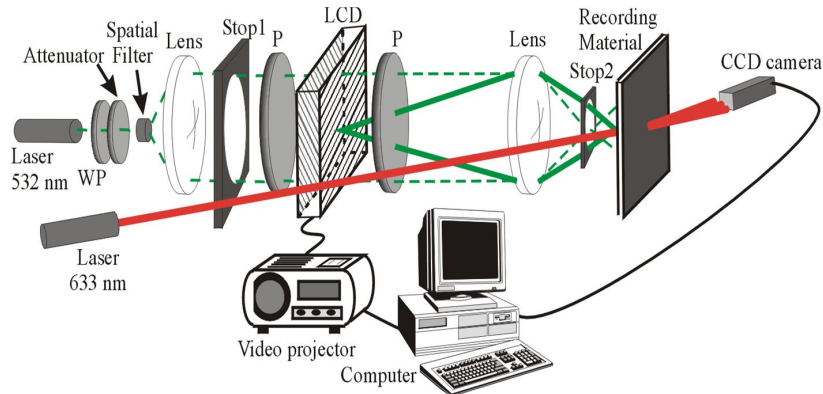


Figure 2 Experimental setup 2 to record diffractive optical elements using the LCD as a master.

The holographic device is shown in Figure 3 [50]. An Nd:YAG laser tuned at a wavelength of 532 nm was used to record diffraction gratings by means of continuous laser exposure. The laser beam was split into two secondary beams with an intensity ratio of 1:1. The diameter of these beams was increased to 1 cm by means of lens, while spatial filtering was ensured. The object and reference beams were recombined at the sample at an angle of 16 degrees to the normal with an appropriate set of mirrors, and the spatial frequency obtained was 1036 lines/mm. The working intensity at 532 nm was 7 mW/cm^2 . The diffracted and transmitted intensity were monitored in real time with a He-Ne laser positioned at Bragg's angle (19.1°) tuned to 633 nm, where the material does not polymerize. The diffraction efficiency was calculated as the ratio of the diffracted beam (I_D) to the incident power (I_0).

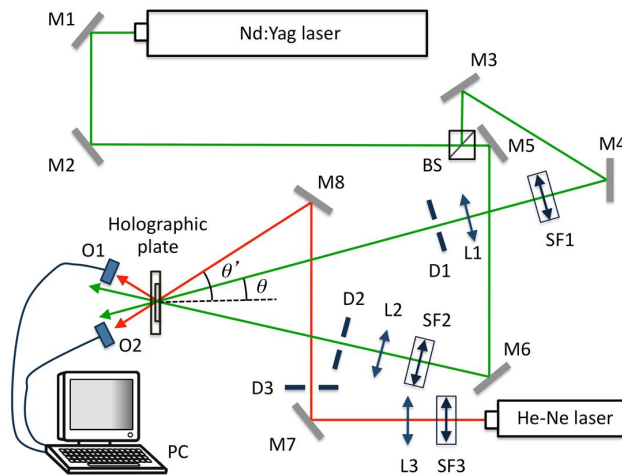


Figure 3 Experimental setup 3 to record and multiplex holographic diffraction gratings.

3. Results and discussion

3.1. Zero spatial frequency

In this section we present the main results obtained using the three set-ups previously described, in the same order. As we commented before, in our works we have analyzed four families of photopolymers, PVA/AA, biophotopol, H-PDLC and the photopolymer provided by Bayer-Material Science. Firstly we studied the response of the materials at zero spatial frequency for different recording intensities. In transmission analysis we can observe the effects of the refractive index changes and thickness variation

during polymerization [26, 28, 29, 51]. In Figure 4 we present the phase shift between the exposed and non exposed zones for PVA/AA materials for transmission geometry, experimental set-up 1. Comparing the material response for different intensities it is possible to fit the parameters K_R and γ as shown in references [26, 51].

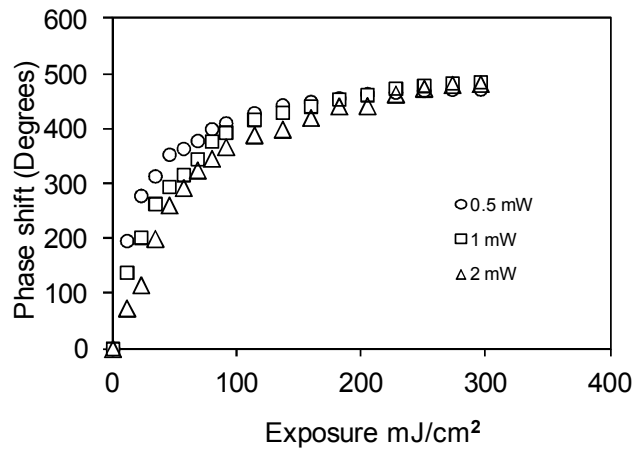


Figure 4 Phase shift as a function of exposure in transmission using the set-up 1 for PVA/AA materials.

Using reflection experiments we can obtain the thickness variation for different compositions (with and without crosslinker, with different monomer and TEA concentrations), at zero frequency [26, 29]. These results for the different composition based on biophotopol chemical formulation are presented in Figure 5 [26]. 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 [26]. With the comparison of the experiments in transmission and reflection for the same layer and with the previous calculus, using a simple refractometer, of the refractive index of the chemical compounds of photopolymer we can obtain the refractive index of the polymer formed during the polymerization process. Therefore we can calculate the refractive index modulation generated during the diffraction gratings recording in this kind of materials.

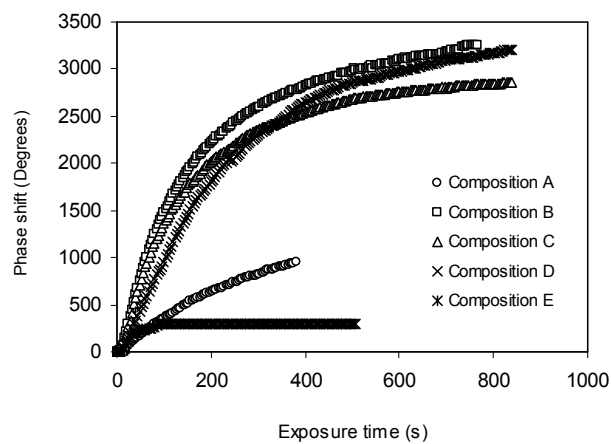


Figure 5 Phase shift as a function of exposure in reflection using the set-up 1 for different variations of biophotopol material.

3.2. Low spatial frequency objects

Once we have measured using the zero frequency response all the parameters involved in the polymerization process we can continue with the next step: obtaining the values for the monomer diffusion inside the material to finish the basic photopolymer characterization. To observe the effects of monomer diffusion in the material without polymerization we study the evolution of material after the recording of very low spatial frequency gratings. This recording can be done using the set-up 2 analyzing the reflected diffraction orders or the transmitted ones. In Figure 6 we show the evolution of the reflected diffraction orders after 16 s of recording. A sinusoidal pattern with spatial frequency of 6 lines/mm with amplitude of 1 mW/cm^2 was recorded. With the data provided by this experiments we can directly obtain the monomer diffusion following the steps presented in [23]. In addition, we can calculate the variation of the monomer diffusion exposing the material at different recording times. With these experiments we found that the velocity of monomer diffusion decreases with the creation of polymer chains. The results are depicted in Figure 7 for PVA/AA formulation [51].

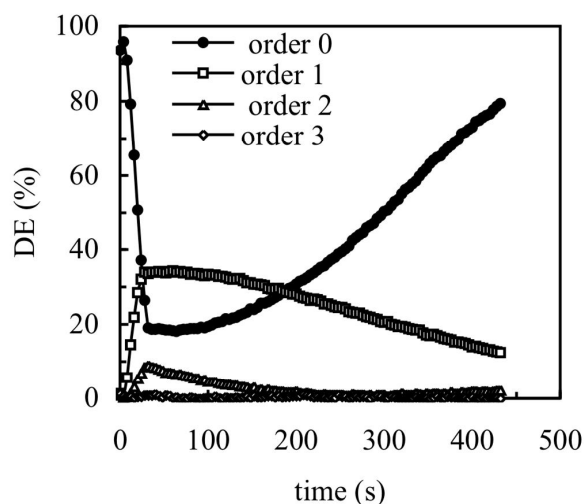


Figure 6 Experimental reflected diffraction efficiency for order 0, 1, 2 and 3 as a function of time for biophotopol composition.

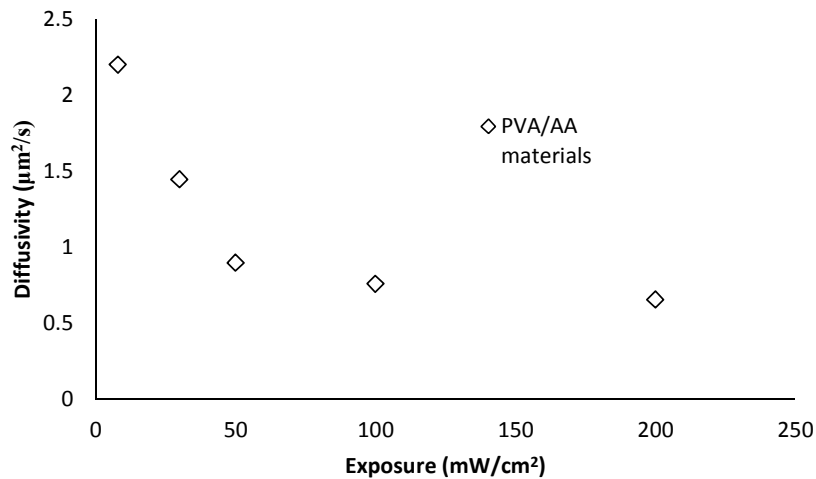


Figure 7 Calculated monomer diffusivity as a function of exposure time for diffraction gratings with spatial frequency of 6 lines/mm.

3.3 Models to predict the holographic and diffractive objects formation

After the calculations of the main parameters involved in the photopolymerization and diffusion processes we can introduce these values in the equations 1 and 2. To solve these differential equations we can use different methods, one of them is the decomposition of monomer and polymer concentrations in harmonics, and assume that only two or three of them are significant [16, 18]. Using this method we can obtain analytical expressions [15, 18] that provide us interesting physical information. In our last works [33, 51] we have solved the equations using finite difference method [36], this method is slower than the harmonics development but can be applied for very complex recording intensities, not only for sinusoidal cases. In Figure 7 we represent the comparison of the simulations using the model with the experimental data for a sinusoidal grating of spatial frequency of 6 lines/mm recorded in PVA/AA photopolymers [51]. In this Figure the main transmitted diffraction orders are measured using high dynamic CCD camera [22]. As can be seen there is good agreement between the experiments and our simulations.

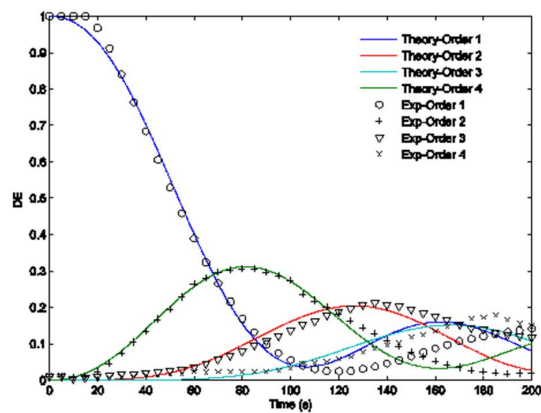


Figure 8 Recording of sinusoidal grating with spatial frequency of 6 lines/mm in PVA materials, experimental data and simulation.

In addition, these models can be applied for holography and also for very thick layers, more than 200 μm . This kind of layers is interesting to be the basis of holographic memories. As we have said in the introduction photopolymers are absorbent recording materials, therefore the recording intensity travels inside the materials and a big part of this intensity is absorbed and only a small part arrives to the back side. This effect is described in figure 9 and it has a huge importance in the hologram multiplexing schedules. In other words the optical thickness of each hologram depends strongly on this effect [44]. Initially, for a small hologram number, the hologram's effective optical thickness (the length of the zone where the hologram exists) is very low due to the short penetration depth of the light inside the material and only the monomer that is near the incident recording wave is consumed. When the hologram number increases, the monomer in this zone has been consumed and the following holograms are recorded deeper in the layer but the hologram's effective optical thickness decreases. This effect can be also predicted by the models when the parameters are correctly determined. In our works we have demonstrate how these models can predict the formation of holographic gratings in very thick PVA/AA layers. In Figure 10 we present the prediction of the model for the recording of a layer with different physical thickness and the experimental data for a 0.8 mm thick layer. This phenomenon cannot be predicted using 1-dimensional models. In these models if higher thickness is studied the grating strengths are higher too [44], and to correctly fit the data obtained with one layer it is necessary to determine the effective optical thickness beforehand; in other words you need to fit the angular response first [43]. For this value of absorption, the results using a 1-dimensional model and the model used in this work are similar only when the thickness of the layer is less than 500 μm .

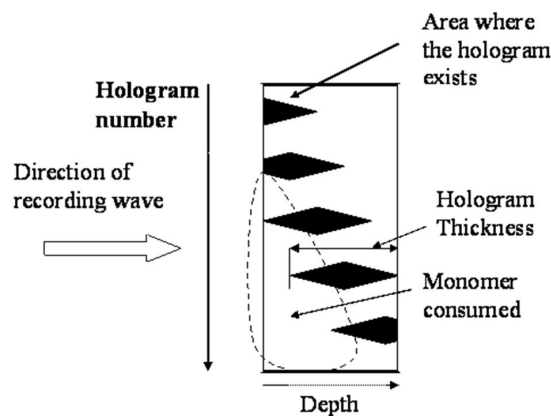


Figure 9 Diagram of the hologram formation as a function of hologram number.

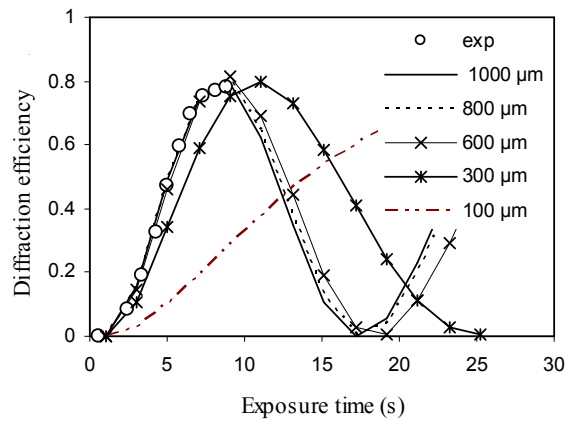


Figure 10 Diffraction efficiency versus exposure time for one grating with a physical thickness of 900 μm , the experimental data (white dots) and the simulations using the theoretical model for different thicknesses (1000 μm , 800 μm , 600 μm , 300 μm , 100 μm).

The electromagnetic theory to analyze the holograms recorded in photopolymers is an important tool to optimize and develop the material [52-56]. To analyze this depth attenuated gratings we have proposed a new algorithm based on the Rigorous Coupled Wave, RCW, method [57]. Using this algorithm and the results provided by the model it is possible to obtain the angular response of the diffraction gratings stored. We take into account the values of refractive index obtained in each sub-layer using the model to calculate the diffraction efficiency with an algorithm based on RCW, we can see the smoothing of the secondary lobes in the angular scan due to attenuation of the refractive index modulation in depth [44]. We can see in Fig. 11 how the diffusion model presented predicts the smoothing of the angular response and diffraction efficiency of the thick layers. In this case the effective optical thickness [44] of the layer is $690 \pm 20 \mu\text{m}$ and the initial value of the refractive index modulation is 3.10×10^{-4} .

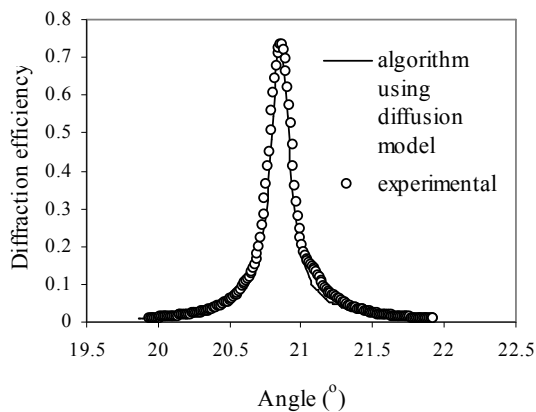


Figure 11 Diffraction efficiency as a function of replay angle for the grating presented in Fig. 1 (800 μm of physical thickness and spatial frequency: 1125 lines/mm).

The importance of the model is not reduced to the diffraction gratings. We have also demonstrated the utility of the model to obtain the optimum time schedule to multiplex many gratings or data pages in the material [46]. The important effect of this model is the prediction of the effective optical thickness for each hologram, thus we can calculate the minimum separation between two consecutive holograms. It can be seen in Fig. 12, the evolution of effective optical thickness as a function of the multiplexed holograms. It presents a maximum around 600 μm after 350 holograms are recorded and then the effective optical thickness decays. This effect has been observed before in PVAAA based polymer and is due to the consumption of 90% of the monomer in the first 190 μm of the layer.

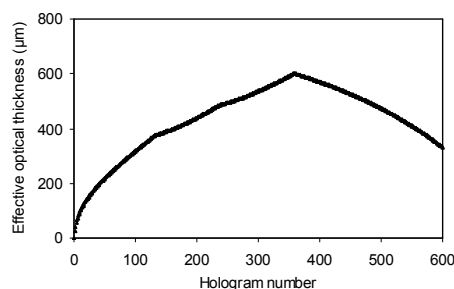


Figure 12 Experimental effective optical thickness as function of hologram number to record 60 holograms with diffraction efficiency around 2%.

4. Conclusions

We have presented a complete method to characterize photopolymers. Using the parameters measured by these techniques we have designed a model to predict many aspects of the photopolymers as optic recording material. We have demonstrated the usefulness of the model for predicting the material behavior for diffractive and holographic applications. 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. We have demonstrated that the model can be applied for different families of photopolymers compositions.

Acknowledgments

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