Direct analysis of monomer diffusion times in polyvinyl/acrylamide materials

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We propose an alternative, direct method to calculate monomer diffusion times in photopolymer materials. Very long period gratings are recorded in the photopolymer, and the real time variation in diffraction efficiency due to monomer diffusion is then analyzed. In photopolymers, monomer diffusion plays a fundamental role in hologram formation. However, since many interrelated parameters affect hologram formation, the usual techniques do not allow for an independent estimation of monomer diffusion times. The direct method proposed is applied to two polyvinyl based photopolymers with different molecular weights. © *2008 American Institute of Physics.*
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Polyvinyl/acrylamide (PVA/AA) photopolymers have very good properties as holographic recording materials. In order to characterize the hologram formation in this type of material, many parameters must be taken into account: the diffusion of components inside the material,[1,2] the relation between intensity and polymerization, the nonlocality of the polymerization process, the higher harmonics in monomer and polymer concentrations, the importance of dye variations, diffusivity variations, etc. Therefore, if we use a diffusion model, we can obtain only an indirect estimation of monomer diffusion times. This means that depending on the importance given to the different interrelated processes, enormous differences in the estimation of this important parameter, monomer diffusion times, could appear. There are studies that propose values of 10^{-14},[3,4] 10^{-10},[5,6] or 10^{-7} cm^2/s for the initial monomer diffusion coefficient (D_0).[7] It is obvious that each group uses different PVA molecular weights, different PVA refractive indexes and different component concentrations. Furthermore, the drying process depends on the temperature and humidity of each individual laboratory. Besides, the differences in the refractive indexes of the binder and monomer are critical in determining the refractive index modulations achieved.[8] However, these effects alone cannot explain the enormous differences observed. Some recent studies[5,7] propose very short exposures using a holographic setup to obtain an estimation of D_0. Nevertheless, important drawbacks have to be solved to apply this method. Firstly, the influence of the refractive indexes of the components involved in the process must be correctly estimated,[5] and secondly the grating evolution due to monomer diffusion after exposure lasts for only around 0.1 s (the time that it takes to stop the diffraction efficiency variation in the dark for spatial frequencies around 1000 lines/mm).[5] Furthermore, this effect can only be observed for very weak diffraction efficiencies.[5] Therefore, we can conclude that monomer diffusion should be estimated using only direct real time determination methods. We thus propose a direct method to determine the monomer diffusion times in photopolymers.

Our proposal consists in recording very long period gratings in the photopolymer to observe the monomer diffusion directly: this process is very fast at holographic spatial frequencies.[5,9] Afterward, we analyze the real time variation in the diffraction efficiency of the transmitted order due to monomer diffusion. Using this technique, we can obtain interesting additional information about the material's behavior. When a photopolymer is exposed using a periodic light pattern, free monomer, dye, and radical generator are consumed in the bright zones producing polyacrylamide chains. In this way, a gradient of components is produced inside the material: diffusion of components from the dark zones to the bright zones creates holes in the former.[5] These two effects increase the phase modulation of the grating stored in the material. The diffusion time[10] indicates the average time that one molecule takes to move across one grating period and is given by

$$\tau_D = \frac{\Lambda^2}{D_0 4\pi^2},\tag{1}$$

where D_0 is the molecular diffusion coefficient and Λ is the fringe period.

When gratings with spatial frequencies of around 10 lines/mm are stored in the photopolymer, the variations in the diffraction efficiency of each order can be observed several seconds after exposure (due to the high values of τ_D). We note that at these optical frequencies we are in the Raman-Nath regime. This high value of the grating period enables the diffusion times to be measured directly. The movement of components from the dark zones to the polymerized ones increases the phase modulation in the grating. To measure the velocity of the transformations in the material when recording has finished, we assume an exponential variation in the zero order diffraction efficiency (η_0) as follows:

$$\eta_0(t) = \eta_0(t \to \infty) + \Delta\eta_0 \exp\left(-\frac{t}{\tau_D}\right).\tag{2}$$

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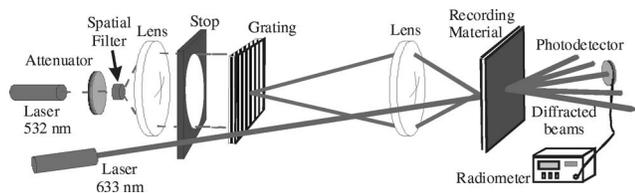
FIG. 1. Experimental setup. The recording material is exposed to the green laser beam ($\lambda = 532$ nm) and zero order diffraction efficiency is measured with the red beam ($\lambda = 633$ nm). *P* are the polarizers and WP the wave plate.

The experimental setup proposed is shown in Fig. 1. We use the expanded, collimated recording beam provided by a solid-state Verdi laser (Nd-YVO$_4$) with a wavelength of 532 nm (at this wavelength the dye exhibits maximum absorption). The recording intensity is 0.4 mW/cm^2 and the exposure time is 50 s. The periodic pattern is introduced by a liquid crystal display (LCD) working in the amplitude-mostly modulation regime by proper orientation of the external polarizers (*P*),[11] and is imaged with an increased spatial frequency onto the recording material (demagnifying factor of 2). A diaphragm (stop2) in the focal plane of the relay lens eliminates the diffraction orders due to pixelation of the LCD. Use of the LCD allows the period of the grating recorded in the photopolymer to be changed without moving any part of the recording system. To analyze in real time the variation in efficiency of the diffraction orders, we use the unexpanded beam of a He-Ne laser (633 nm) incident at a small angle with respect to the normal of the recording material.

The photopolymeric material used is composed of PVA as binder (with a molecular weight of 130 000 amu (Atomic Mass Unit)), acrylamide as monomer, N,N' methyl-bis-acrylamide as cross-linker, yellowish eosin as dye, and triethanolamine as radical generator (coinitiator), and has a thickness of around 80 μm.[6]

In order to determine the diffusion time in PVA materials, we recorded gratings with three different spatial periods: 84, 168, and 334 μm, respectively. Afterward, we analyzed the decrease in zero order diffraction efficiency (η_0) so as to obtain the characteristic time for this type of material. In Fig. 2, we present the evolution of η_0 once exposure is over. We also present an exponential fitting using Eq. (2) for a grating period of 84 μm. Using these data, it is possible to obtain a diffusion time of around 34 s, that is, a value for D_0 of $\sim 5 \times 10^{-8}$ cm^2/s. For this period, the value of η_0 becomes constant after 100 s. A good fitting is observed when exponential decay is assumed ($R^2 = 0.9899$).
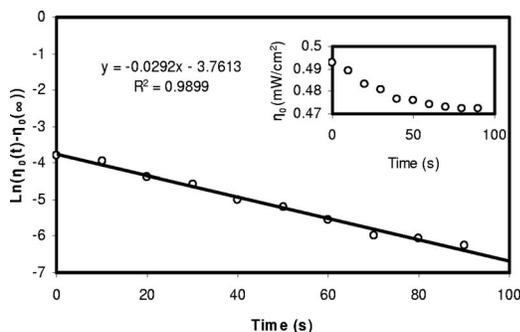

FIG. 2. η_0 after exposure as a function of time (dots, experimental data). The fitting of the logarithmic decay of η_0 is represented by a solid line. Grating period of 82 μm.
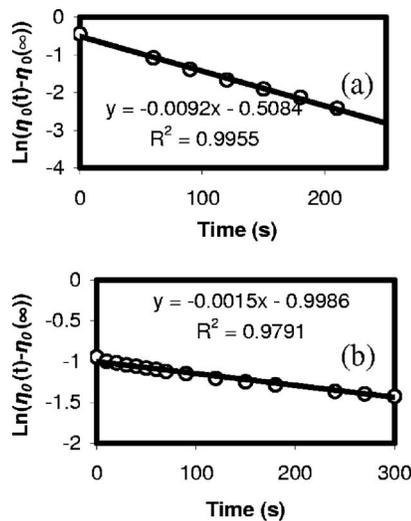

FIG. 3. Fittings of the variation in η_0 after exposure for two different grating periods: 168 μm (a) and 336 μm (b).

In order to verify that this phenomenon is due to component diffusion inside the material, it is necessary to analyze other spatial frequencies. Figures 3(a) and 3(b) show the fittings for grating periods of 168 and 336 μm respectively. The diffusion times obtained are 109 s ($D_0 \sim 6 \times 10^{-8}$ cm^2/s) and 667 s ($D_0 \sim 4 \times 10^{-8}$ cm^2/s). As can be seen, the higher the period, the longer the time needed to stabilize the grating. This is directly related to the influence of component diffusion on the variations in diffraction efficiencies.

It is important to note that the molecular weight of the PVA influences the diffusion of components. It is well known that a lower PVA molecular weight implies that there is less water retained in the "dry" film[12] and lower values of component diffusion times are obtained. In order to demonstrate this effect, we used a PVA with a lower molecular weight (27 000 amu). The results for a grating period of 82 μm are presented in Fig. 4. It is possible to obtain a characteristic diffusion time of 108 s ($D_0 \sim 1 \times 10^{-8}$ cm^2/s), i.e., monomer diffusion decreases.

To conclude, an alternative, completely direct method to measure the diffusion time in photopolymers has been proposed. This method is based on recording diffraction gratings with very low spatial frequencies. For long periods, the diffusion time increases and can therefore be directly measured. The use of a LCD provides additional flexibility to change the spatial frequency recorded without moving mechanical parts in the setup, thus increasing the robustness of this method. We applied the method to determine the diffusion of components inside PVA materials. We checked the results using different spatial frequencies and different PVA molecu-
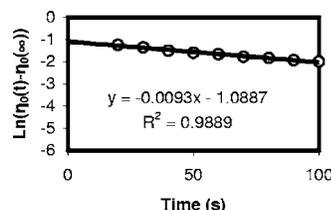

FIG. 4. Fitting of the variations in η_0 after exposure for a grating period of 82 μm for PVA with a molecular weight of 27 000 amu.

lar weights. Values of $D_0 \sim 5 \times 10^{-8}$ with an error of 20% (repeatability) for PVA (molecular weight of 130 000 amu) and $D_0 \sim 1 \times 10^{-8}$ with an error of 20% (repeatability) for PVA (molecular weight of 27 000 amu) were obtained.

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