Recording of Diffraction Gratings in Polyvinyl Alcohol/Acrylamide Photopolymers by Pulsed Laser Irradiation.

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ABSTRACT

In this communication we present the experimental results obtained when diffraction gratings are stored using pulsed exposure in polyvinyl alcohol/acrylamide photopolymer deposited in a dry film. The influence of the energy of the irradiation pulse was studied and the number of pulses needed to reach maximum diffraction efficiency was obtained.

The recording was performed using an holographic copying process. The original pattern employed was a grating of 1000 lines/mm processed according to silver halide sensitized gelatin, with a beam ratio of 1:2 and transmittance of 75%. We exposed the samples by recording holograms with a collimated beam from a frequency-doubled Nd-Yag (532 nm) Q-switched laser.

The pulse duration was ~ 8 ns and the frequency of repetition varied between 2 and 10 Hz. The pulse fluence was increased from 0.07 mJ/cm^2 to 6.7 mJ/cm^2 .

Our initial results show that it is possible to obtain diffraction gratings with a diffraction efficiency of 60%. The energetic sensitivities achieved are close to those obtained when working with the same material and continuous irradiation, without processing of the gratings.

Keywords: Holography, holographic recording materials, photopolymers.

1. INTRODUCTION

Holography has been widely employed in the investigation of photochemical and photophysical processes using cw and pulsed laser irradiation. The rate constants, quantum yields and number of photons involved in reversible and irreversible photoprocesses have been determined by studying the change in diffraction efficiency of gratings stored using continuous wave laser¹

The phase modulated holographic technique has enabled the quantum yield and the effects of a photoinduced matrix to be determined by monitoring amplitude and phase gratings².

Carre et al.³ developed an alternative treatment, which makes it possible to obtain information from photochemical processes by using the bleaching of the sensitizer in a grating formed by the holographic method.

Recently, Blaya et al.⁴ by combining the formation of volume holograms with the temporal evolution of transmittance obtained a model which enables the polymerization constants of the radical polymerization mechanism involved during irradiation, the grade of conversion at any time, the quantum yield of initiation of radicals and the molar absorption of the dye to be determined.

The formation of dynamic holograms using ultrashort light pulses has also been analyzed in different holographic recording materials⁵⁻⁷. In photorefractive materials⁵ the technique used combines a pulsed signal beam with a continuous reference beam. In this way, the diffraction efficiency can be maximized and greatly increased in comparison with the traditional continuous recording technique. It has been demonstrated that reflection holograms may be recorded in Dupont

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photopolymer films by means of pulsed laser exposure⁶, and it was observed that continuous incoherent pre-illumination increased both diffraction efficiency and sensitivity.

Furthermore, pulsed laser exposure has been used for evaluation of photochemical rate constants and quantum yields. Olaj et al.⁸ developed the pulsed laser polymerization method as a tool for evaluating individual kinetic constants of free radical polymerization. The free-radical propagation rate coefficients of methyl methacrylate have been measured using a visible light wavelength⁹.

Decker et al.¹⁰ studied the kinetics of the polymerization of acrylic monomer exposed to a pulsed nitrogen laser tuned at 337.1 nm and determined the polymerization rate and the induction period. Deeg et al.¹¹ demonstrated that it is possible to perform single shot transient grating experiments, and thus in principle, investigate every photoinduced irreversible process. Unstable photochemical intermediates can be detected and their kinetics evaluated. Together with the quantum yield measured by a CW grating technique, this allows the photochemical rate constants to be calculated.

In this paper we study the response of a polyvinyl alcohol/acrylamide photopolymer deposited in the form of a layer when exposed to pulsed laser irradiation. Firstly, we analyze the variation in transmittance of this material as a function of both pulse energy and repetition rate. This enables information to be obtained about the rate of polymerization as a function of these parameters. Secondly, we present the experimental results obtained when holograms are stored using pulsed beams. We also study the effect of the pulse fluence as well as the total number of pulses employed during irradiation in order to obtain maximum diffraction efficiency. The holograms were generated by means of a copying process^{12,13}. This method enables transmission gratings to be obtained without having to make the optical paths of the object and reference beams coincide when a pulsed laser is used.

2. MATERIAL

The photopolymer used is based on acrylamides¹⁴. It consists of acrylamide (AA) as monomer, triethanolamine (TEA) as radical generator and yellowish eosin (YE) as sensitizer, all on a film of polyvinyl alcohol (PVA).

The photosensitive solution is prepared by adding 2 ml of a 8g/l solution of yellowish eosin (supplied by Panreac) and 6.4 ml of a solution of acrylamide (supplied by Sigma) and triethanolamine (supplied by Sigma) to 40 ml of 10% polyvinyl alcohol (supplied by Riedel-de-Haen and $M_w \approx 25000$). The concentration of the composition is summarized in Table 1.

The resulting solution is coated, using an automatic depositor, on a 20x40 cm² glass plate to give an initial thickness of 500 μ m. The plate is dried for 24 hours in the dark under normal laboratory conditions ($T \approx 21-23$ °C, $RH \approx 50-60$ %) and subsequently cut into plates measuring 6.5 x 6.5 cm². The thickness of the layer was measured with a PIG 455 apparatus supplied by Neurtek. The final thickness of the dry film is $70 \pm 5 \mu$ m.

Table 1. Concentration of the composition

TEA	0.199 M
AA	0.446 M
PVA	10 %
YE	2.5×10^{-4} M

3. EXPERIMENTAL SETUP

Firstly, the variation in transmittance of the material at the emission wavelength of the laser, $\lambda = 532$ nm, as a function of the number of pulses and fluence per pulse was analyzed. To do so, the laser beam was made to strike the photopolymer perpendicularly. The transmittance was measured with a Cary 3E spectrophotometer to obtain information about the photochemical behavior of the dye.

Figure 1 shows the geometry of the irradiation used to store the holograms by means of a pulsed beam. The process is a copying one, in which the master is placed in direct contact with the photopolymer in such a way that the transmitted and diffracted beams interfere in the photopolymer film, provided that the paths of the beams differ sufficiently to produce interference.

A beam splitter placed in the way of the pump beam directs about 10% of the laser beam energy towards a detector. The generated signal was a measure of the pump pulse energy and was recorded with an oscilloscope. The remaining 90% of the

pulse energy is incident on the original pattern at an angle so that the diffracted and transmitted beams impinge onto the photopolymer film. A computer controls both the number and repetition rate of the pump pulses. The diffracted intensity was monitored with a He-Ne laser tuned at 633 nm, at which wavelength the material does not absorb.

In a previous study we analyzed the coherence conditions of this geometry¹². If we consider that the master is a photographic emulsion 5 μm thick and that the photopolymer has a thickness of 70 μm , applying the results of this previous study we obtain a difference in path of 1.69 μm , which gives a coherence factor of 0.99.

Since the spectral width of the pulse is 1 nm, its temporal coherence factor is almost one, so the total coherence factor is greater than 0.98.

The original grating is formed in a photographic emulsion processed in silver halide sensitized gelatin. The ratio of the transmitted beam to the diffracted beam is 1:2 and it has a total transmittance of 75%, which gives a fringe visibility of 0.94. These data indicate that it is not possible to obtain a diffraction efficiency of 100% with this geometry, since the phase contrast is not one. Nevertheless, from the point of view of analysis and optimization of the photopolymer, the simplicity of the device compensates for this limitation in the diffraction efficiency

We exposed the samples by recording holograms with a collimated beam from a frequency-doubled Nd-Yag (532 nm) Q-switched laser. The pulse duration was ~ 8 ns and the frequency of repetition varied between 2 and 10 Hz.

Figure 1. Experimental Setup

4. ANALYSIS OF THE TRANSMITTANCE FUNCTION

The variation in transmittance of the material at the emission wavelength of the laser, $\lambda = 532$ nm, as a function of the number of pulses and fluence per pulse was analyzed. Figure 2 shows the variation in transmittance of the material, compared with the transmittance line of the unexposed plate, as a function of the number of pulses for different pulse fluences. This variation in transmittance indicates that the material is bleached when is illuminated with light at a wavelength of 532 nm, which corresponds to the absorption band of yellowish eosin (YE). Therefore, incident light produces consumption of the sensitizer due to a photoreduction reaction of the dye, giving rise to the formation of the alkyl-amino free radicals which initiate the polymerization reaction. When the fluence per pulse is increased, the variation in transmittance for a given number of pulses increases. This implies a greater consumption of the dye (bleaching) as well as an increase in the rate of generation of free radicals.

The curves can be fitted by using an approximation than can be easily obtained from the experimental characteristics of the holographic film¹⁵. We considered the formula:

$$\Delta T = \frac{T_{\infty}}{1 + \exp(a - b \log E) + \exp(c - d \log E)} \quad (1)$$

where T_{∞} is the maximum variation in transmittance, E is the exposure, a y b are parameters that can be determined from the experimentally obtained ΔT - $\log E$ curve, and c and d can be estimated by evaluating equation (1) at points $\log E = \log E_i$ y $\log E = (\log E_i)/2$. If E_i is the exposure of the inertial point and m is the slope of the characteristic curve in the linear region, from simple calculation it can be obtained¹⁵:

$$a = 2(1 + 2m \log E_i / T_{\infty}) \quad (2)$$

$$b = 4m / T_{\infty} \quad (3)$$

$$c = \ln \left(\frac{\left\{ \frac{\Delta T_{\infty}}{\Delta T(\frac{1}{2} \log E_i)} - \left[1 + \exp \left(2 + \frac{2m \log E_i}{\Delta T_{\infty}} \right) \right] \right\}^2}{\frac{\Delta T_{\infty}}{\Delta T(\log E_i)} - (1 + \exp 2)} \right) \quad (4)$$

$$d = \frac{c - \ln \left[\frac{\Delta T_{\infty}}{\Delta T(\log E_i)} - (1 + \exp 2) \right]}{\log E_i} \quad (5)$$

By means of numerical fitting, we can determine the slope of the linear zone together with the minimum activation energy of the dye necessary to initiate radical generation. Figure 3 shows the slope obtained and the activation energy as a function of the pulse fluence. When low pulse fluences are used a steeper slope is obtained, which implies a faster consumption of dye, but the activation energy is greater. When the pulse fluence is increased there is a decrease in the slope and in the activation energy. Above 0.67 mJ/cm² the slope remains constant and the activation energy increases, which means that although the rate of consumption of the dye is independent of the pulse fluence, when the fluence of the pulse is increased a higher energy is needed to activate the system and consequently to initiate the polymerization reaction. These results are important since they indicate the rate of variation of the dye in the sample and therefore the rate of generation of radicals and the minimum energy necessary in each case.

The measurements obtained and the fitted curves are shown in the figure 4. As can be seen from this figure, there is good agreement between theoretical and experimental results.

Figure 2. Variation in transmittance as a function of the number of pulses for a pulse frequency of 3 Hz.

Figure 3. Slope of linear region (solid circles) and activation energy (open circles) as a function of the pulse fluence.

Figure 4. Transmittance curves as a function of log of exposure for two pulse fluences: a) 0.67 mJ/cm² and b) 1.74 mJ/cm²

Another factor which affects the response of the material is the pulse repetition rate. In the theoretical models that explain the polymerization with continuous irradiation, a stationary state is assumed for the production and consumption of radicals that initiate the polymerization reaction. Therefore, since at $t = 0$ the concentration of radicals is 0 a minimum time is necessary to reach the stationary state. Under pulsed irradiation, the generation of free radicals is discontinuous. Consequently, the time during which the sample is not irradiated is important, since the number of radicals decreases during this time and so the rate of polymerization decreases. An increase in the irradiation frequency results in a reduction in the time during which there is no irradiation and therefore the process comes closer to the stationary state as in the case of continuous irradiation. This can be seen in figure 5 which shows the transmittance function evaluation versus pulse repetition rate for a pulse fluence of 2.2 mJ/cm^2 and 1000 pulses. As can be seen, the variation in transmittance increases when the pulse repetition rate is increased.

Figure 5. Variation in transmittance as a function of the pulses repetition rate for a pulse fluence of 2.2 mJ/cm^2 and 1000 pulses.

5. STORAGE OF HOLOGRAMS

As mentioned above, a copying process was used to generate the holograms. Figure 6 shows diffraction efficiency results of the +1 order in the case of different fluences per pulse, measured with an He-Ne laser tuned at 633 nm, at which wavelength the material does not absorb. It can be seen that diffraction efficiencies of 55% have been reached for a pulse fluence of 0.67 mJ/cm^2 . The sensitivity of the material in this case (235 mJ/cm^2) is similar to that obtained with continuous irradiation¹⁴, if we take the sum of the energy of each pulse. However, the diffraction efficiency decreases from 80% for continuous irradiation to 60% for irradiation with a pulsed laser. There is an optimum fluence per pulse (0.67 mJ/cm^2) at which the maximum diffraction efficiency and maximum sensitivity (defined as the minimum energy necessary to reach maximum diffraction efficiency) are obtained. For energies below 0.67 mJ/cm^2 , lower diffraction efficiencies and sensitivities are obtained. For energies greater than 0.67 mJ/cm^2 the sensitivity decreases.

If we compare figures 2 and 6 for the same fluence (figure 7), it can be seen that in order to obtain maximum diffraction efficiency, it is not necessary for the dye to be completely consumed. The consumption of dye necessary to reach the maximum diffraction efficiency depends on the pulse fluence. As occurs with the diffraction efficiency curves (figure 6), there is an optimum pulse fluence (0.67 mJ/cm^2) at which the maximum diffraction efficiency is reached with the lowest variation in transmittance (5%), at higher and lower fluences (figures 6a and 6c) the necessary variation in transmittance increases.

Figure 6. Diffraction efficiency as a function of exposure for different pulse fluences and a frequency of 10 Hz.

Figure 7. Transmittance (open circles) and diffraction efficiency (solid circles) versus exposure for a pulse fluence of a) 0.2 mJ/cm² b) 0.67 mJ/cm² and c) 1.7 mJ/cm² and a pulse frequency of 10 Hz

6. CONCLUSIONS

To conclude, we have analyzed the behavior of the dye when irradiated with a pulsed laser, and determined the influence of pulse fluence and repetition rate on the consumption of the dye. We have demonstrated the possibility of storing, using pulsed beams, diffraction gratings of 1000 lines/mm in a PVA/AA photopolymer with a diffraction efficiency of 55% and sensitivity similar to that obtained using the same material and continuous irradiation without the need for processing of the gratings obtained.

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