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Thick Photopolymer Layers for Holographic Recording Materials

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ABSTRACT

In this article the behaviour of thick photopolymer layers as material for holographic recording is studied. The material used is a photopolymer based on acrylamides, consisting of acrylamide as monomer, yellowish eosin as sensitizer and triethanolamine as radical generator, all on a matrix of polyvinyl alcohol.

We studied the influence of the thickness of the layer on the behaviour of the photopolymer as a holographic recording material. According to Kogelnik's theory, the thickness determines the temporal or energetic evolution of the diffraction efficiency.

Layers of different thicknesses were used and it was observed that on increasing the thickness and maintaining the chemical composition of the material constant, the shapes of the curves of diffraction efficiency against time varied. As well as there being differences in the shapes of the curves, it was observed that the sensitivity of the layer increased with its thickness, while the diffraction efficiency remained constant.

The main problem when working with thick layers is that many noise gratings appear which make the diffraction efficiency decrease rapidly. In order to eliminate the noise gratings the composition of the material was modified when working with thick layers.

Keywords: photopolymers, holography, diffraction efficiency, scattering.

1. INTRODUCTION

Holography is a method of storing information by means of photochemical and photophysical processes.

Photographic emulsions, dichromated gelatin and photopolymers are some of the materials most frequently used in holography¹.

Due to the continuous development of applications such as optical storage, holographic memories, holographic interference and holographic displays, it is necessary to develop new holographic recording materials.

In recent years many types of photopolymer systems have been developed for holographic recording². Some of the most important characteristics that have motivated their development are their high energetic and spectral sensitivity, high resolution, high diffraction efficiency, good signal – noise ratio, temporal stability and processing in real time. Furthermore these materials are very inexpensive and have a wide variety of compositions.

Photopolymerizable dry films are basically made up of one or several monomers, a photosensitizer and a co-initiator on a suitable polymeric film acting as a binder.

When two beams originating from a laser are superposed on a photosensitive plate an interference pattern is formed in the plane of the material. In the constructive interference zones the optical properties of the material (refraction index and/or absorption) vary due to the formation of photoproducts. The polymerization mechanism in the constructive interference zones is initiated by the absorption of light by the sensitizer. The sensitizer reacts with the co-initiator producing radicals that bind with the monomer, thus initiating the polymerization reaction.

The photopolymer we used is made up of yellowish eosin as sensitizer, triethanolamine as radical generator and acrylamide as monomer, all on a film of polyvinyl alcohol.

Jenney³ was the first to develop a system based on acrylamides as a holographic recording material. This system was composed of acrylamide and N,N'-methylenebisacrylamide as monomers and methylene blue and p-toluenesulfonic as initiator. A diffraction efficiency of 20% was obtained with a sensitivity of 0.6 mJ/cm².

Later an improvement in the holographic characteristics was observed when the solution of acrylamide was used on a polymeric dry film. Jeudy et al.⁴ were the first to use these systems with polyvinyl alcohol as the binder. They obtained a diffraction efficiency of 80% with a sensitivity of 100 mJ/cm². Calixto⁵ developed a photopolymer made up of acrylamide as monomer, triethanolamine as initiator and methylene blue as sensitizer on a polyvinyl alcohol film. He obtained efficiencies of 10% with sensitivities of 94 mJ/cm², working with very low intensities.

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The continuous development of photopolymer systems is due, in large, to the development of optical storage as an information storage technique. Holographic memories are an example of this type of storage system. The principal obstacle to the use of these photopolymers in holographic information storage is their thickness.

Up to now the experiments carried out using Dupont photopolymers with a thickness of 100 μm have only enabled storage densities of 10 bits/ μm^2 to be obtained. To increase the storage density, it is necessary to obtain films of greater thickness.

In our study the influence of the thickness on the behavior of the material as a holographic recording material has been analyzed. According to Kogelnik's theory the thickness determines the temporal or energetic evolution of the diffraction efficiency.

We worked with layers from 50 μm to 200 μm thick, and observed that on increasing the thickness and maintaining the chemical composition of the material constant, the shapes of the diffraction efficiency curves as a function of energy varied. Firstly, we studied the influence of the thickness on the behavior of the material when its chemical composition remained constant. A diffraction efficiency of 80% with a sensitivity of 100 mJ/cm² was obtained for a thickness of 200 μm . Secondly, we analyzed the behavior of the material when the concentration of monomer was varied for a constant thickness. The principal problem posed is that the increase in thickness produces a great amount of scattering and consequently a decrease in the diffraction efficiency. It has been demonstrated experimentally that increasing the concentration of monomer reduces scattering.

2. EXPERIMENTAL

The photopolymer used is based on acrylamides⁶ and consists of acrylamide (AA) as monomer, triethanolamine (TEA) as radical generator and yellowish eosin (YE) as sensitizer, all on a polyvinyl alcohol (PVA) film.

As we have already mentioned, our objective was to study the behavior of the material for different thicknesses, and so we worked with thicknesses of from 50 μm to 200 μm approximately. To obtain plates with a thickness of less than 100 μm , 48 ml of the final solution were deposited and the PVA concentration was 10%. For thicknesses greater than 100 μm , 120 ml of solution were deposited and the PVA concentration was 15 %. This difference in the concentration of PVA is due to the fact that the PVA gives volume to the film so it is necessary to increase the concentration to obtain a greater thickness.

Table 1 shows the TEA and YE concentrations used for all the experiments. The concentration of AA is varied from 0.393 M to 0.593 M.

TEA	0.199 M
YE	2.5×10^{-4} M

Table 1: Composition of the solution.

The resulting solution is deposited using an automatic depositor on a 20x40 cm² glass plate. This automatic depositor enables the initial thickness of the plate to be varied. The initial thickness of the plate was 500 μm for a final thickness of less than 100 μm , and 1000 μm for a final thickness greater than 100 μm .

The plate was dried for a period of 24 h. in the dark and under normal laboratory conditions ($T \cong 21\text{-}23^\circ\text{C}$, $\text{RH} \cong 40\text{-}60\%$). Once dried, it was cut into plates measuring 6.5 x 6.5 cm².

The main problem arising on increasing the thickness is the appearance of many noise gratings, produced by this increase in thickness and by the increase in the PVA concentration, which causes the granular aspect of the material to increase.

Figure 1 shows the transmission spectrum of the photopolymer film, the absorption of the dye used is between 450 nm and 550 nm.

The experimental device used to store the holographic gratings is shown in figure 2. The holographic gratings were registered with an Argon laser tuned at 514 nm and with an incident intensity $I = 10 \text{ mW/cm}^2$. The laser beam was split into two secondary beams, referred to as the object beam and the reference beam, with an intensity ratio of 1/1. These two beams were recombined at the sample at an angle of 16.8° with respect to the normal, and the spatial frequency obtained was 1124 lines/mm. The diffracted intensity was monitored in real time with a He-Ne laser positioned at the Bragg's angle tuned at 633 nm, where the material does not absorb, with an incident intensity of 8 mW/cm². The diffracted and transmitted intensities were detected with two detectors connected to a computer.

Figure 1: Transmittance spectra of the material. The chemical composition of the material is AA: 0.446M, TEA:0.199 M, YE: 2.5×10^{-4} M and PVA:10%.

Figure 2: Experimental device

3. RESULTS AND DISCUSSION

As has been indicated before, we first studied the influence of the thickness on the behavior of the material. For this, we used a concentration of acrylamide of 0.518 M and the thickness was varied from 50 μm to 210 μm .

Figure 3 represents the energetic evolution of the diffraction efficiency (DE), transmission efficiency (TE) and the sum of both (DE+TE) for a thickness of 55 μm . Figures 4 and 5 show the same curves for the same concentrations and thicknesses of 110 μm and 210 μm , respectively.

Figure 3: Diffraction efficiency, transmission efficiency and the sum of both for a thickness of 55 μm .

Figure 4: Diffraction efficiency, transmission efficiency and the sum of both for a thickness of 110 μm .

Figure 5: Diffraction efficiency, transmission efficiency and the sum of both for a thickness of 210 μm .

According to Kolgenik's theory, the thickness determines the temporal or energetic evolution of the diffraction efficiency. The variation in thickness in this holographic material, with a constant chemical composition, produces changes in the behavior of this type of curves. This is observed on comparing figures 3,4 and 5. For a thickness of 55 μm the curve of

diffraction efficiency rises to a maximum value and then remains constant. On increasing the thickness to 110 μm , it can be seen that the curve rises until the maximum diffraction efficiency is reached and then falls, but in this case the drop is not very pronounced. If we carry on increasing the thickness to 210 μm , it can be seen that once the maximum value of diffraction efficiency is reached, the curve falls quickly.

It can therefore be deduced that when working with large thicknesses, the optimum zone is limited to the zone in which the diffraction efficiency increases. Once this reaches its maximum value noise gratings appear that cause a lot of light to be scattered, thus decreasing both the diffraction and the transmission efficiency.

The thickness also influences the sensitivity. It can be seen that on increasing the thickness of the material the sensitivity increases from 300 mJ/cm^2 for a thickness of 55 μm to 100 mJ/cm^2 for a thickness of 210 μm . With respect to the diffraction efficiency, there are no large variations on increasing the thickness – it varies between 80% and 90%.

The principal difference in the behavior of the material when the thickness is increased is that many noise gratings appear. Therefore, when the diffraction efficiency reaches its maximum value, it quickly decreases. However if we compare the points at which maximum diffraction efficiency is obtained, we can see that the scattering hardly varies with thickness.

Figure 6: Scattering at the maximum diffraction efficiency point and scattering at the final diffraction efficiency point against thickness.

This is shown in figure 6 where scattering at the maximum diffraction efficiency point and scattering at the final diffraction efficiency point against thickness is represented. The difference between the sum of the transmitted and the diffracted beam at a particular point and the initial value was taken as a measure of the scattering at that point. The thickness was varied from 50 μm to 210 μm .

When the thickness is increased, the final scattering increases from 2% for a thickness of 50 μm to 80 % for a thickness of 210 μm . However scattering at the maximum efficiency point does not exceed 10% for any of the thicknesses.

Consequently, this material may be considered suitable for the manufacture of holographic memories⁷. A. Pu and D. Psaltis⁸ established a linear relationship between the storage density and the thickness of the material, according to which 60 $\text{bits}/\mu\text{m}^2$ could be stored in a thickness of 200 μm .

The optimum work zone for this thickness would be below 100 mJ/cm^2 , beyond this exposure the diffraction efficiency decreases and many noise gratings appear.

For great thicknesses it is possible to reduce scattering by increasing the concentration of monomer. This is due to the polymerization mechanism⁹. Polymerization is initiated by the absorption of light by the dye. The dye reacts with the triethanolamine producing radicals that bind with the monomer, thus initiating the polymerization reaction. This reaction is propagated until the polymer chains bind with the remaining radicals and the reaction is terminated. When the concentration of monomer is increased, this reaction is very rapid, in other words, the rate of polymerization increases. As in the previous case, the reaction is terminated by the polymer chains binding with the radicals, but in this case the reaction

is so rapid that when the reaction terminates, the polymer molecules are very small. These molecules scatter less light and so scattering is reduced.

Figure 7 shows the diffraction efficiency, transmission efficiency and the sum of both for a thickness of 150 μm , a concentration of acrylamide of 0.393 M (the rest of the concentrations were not changed) and $I = 10 \text{ mW/cm}^2$.

Figures 8, 9 and 10 show the same curves for different concentrations of acrylamide: AA:0.446 M (figure 8), AA: 0.518 M (figure 9) and AA: 0.593 M (figure 10).

Figure 7: Diffraction efficiency, transmission efficiency and the sum of both for $d = 150 \mu\text{m}$. The chemical composition of the material is AA: 0.393 M, TEA: 0.199 M, YE: 2.5×10^{-4} M and PVA: 15%.

Figure 8: Diffraction efficiency, transmission efficiency and the sum of both for $d = 150 \mu\text{m}$. The chemical composition of the material is AA: 0.446 M, TEA: 0.199 M, YE: 2.5×10^{-4} M and PVA: 15%.

Figure 9: Diffraction efficiency, transmission efficiency and the sum of both for $d = 150 \mu\text{m}$. The chemical composition of the material is AA: 0.518M, TEA: 0.199 M, YE: 2.5×10^{-4} M and PVA: 15%.

Figure 10: Diffraction efficiency, transmission efficiency and the sum of both for $d = 150 \mu\text{m}$. The chemical composition of the material is AA: 0.593M, TEA: 0.199 M, YE: 2.5×10^{-4} M and PVA: 15%.

Upon increasing the concentration of monomer the rate of polymerization is greater, therefore the slope of the initial section is greater and the sensitivity is also greater. With respect to the diffraction efficiency, we can say that it oscillates between 65% and 80% for the different concentrations and there is no clear dependency on concentration.

Figure 11 shows scattering at the maximum diffraction efficiency point and scattering at the final diffraction efficiency point as a function of the concentration of acrylamide. When the concentration of monomer is increased, the final scattering increases, however scattering at the maximum diffraction efficiency is reduced.

If we compare the scattering at the maximum diffraction efficiency for the different concentrations we can see that this goes from 30% for AA:0.393 M to 10% for AA: 0.593 M.

It has been demonstrated experimentally that for large thicknesses it is possible to reduce scattering by increasing the concentration of acrylamide, due to the fact that the polymer chains formed are shorter and therefore less light is scattered.

Figure 11: Scattering at the maximum diffraction efficiency and scattering at the final diffraction efficiency as a function of the concentration of acrylamide.

In conclusion, variation in the thickness of this holographic material, with a constant chemical composition, produces changes in the behavior of this type of curves. On the other hand, in spite of the fact that once the maximum efficiency is reached, increasing the thickness causes the curve to fall, it can be seen that at the maximum diffraction efficiency point scattering does not vary, and the diffraction efficiency remains practically constant.

All these characteristics make it possible to consider using this material in the manufacture of holographic memories. The optimum behavior zone of the material is below 100 mJ/cm² for a thickness of 210 μm. In this zone it is possible to store holograms with high a diffraction efficiency and low scattering.

Finally it has been demonstrated experimentally that it is possible to reduce scattering when working with large thicknesses, d = 150 μm, by increasing the concentration of monomer.

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