Study of reflection gratings recorded in polyvinyl alcohol/acrylamide-based photopolymer

Rosa Fuentes,^{1,*} Elena Fernández,¹ Celia García,¹
Augusto Beléndez,² and Inmaculada Pascual¹

¹Departamento Óptica, Farmacología y Anatomía, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

²Departamento de Física, Ingeniería de Sistemas y Teoría de la Señal,
Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

*Corresponding author: fuentes@ua.es

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High-spatial-frequency fringes associated with reflection holographic optical elements are difficult to obtain with currently available recording materials. In this work, holographic reflection gratings were stored in a polyvinyl alcohol/acrylamide photopolymer. This material is formed of acrylamide photopolymer, which is considered interesting material for optical storage applications such as holographic memories. The experimental procedure for examining the high-spatial-frequency response of this material is explained, and the experimental results obtained are presented. With the aim of obtaining the best results, the performance of different material compositions is compared. © 2009 Optical Society of America

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1. Introduction

Because of the importance acquired by new technologies (computers and the Internet), the demand for storage techniques with more capacity, more density, and faster readout rates has increased considerably. Conventional optical memory technologies, such as CD-ROMs and DVDs, are two-dimensional (2-D) surface-storage techniques and, so, have almost arrived at the limit of their capacity. For this reason, in recent years much attention has been centered on three-dimensional (3-D) holographic disks [1–3]. Recently, many studies have focused on the characterization and optimization of thick holographic recording materials in order to obtain maximum data storage capacity [4–6], and transmission holographic memories have been designed [7]. However, in order to obtain more compact systems, it would be interesting to design reflection holographic mem-

ories to which the current technology for reading CDs and DVDs (reflective disks) may be applied.

Reflection holographic optical elements can be recorded, for instance, in silver halide sensitized gelatin emulsions [8] with good results, but this recording medium has a thickness of $7\text{ }\mu\text{m}$, which is very low if the aim is to store a great number of holograms in the same volume of material, as in the case of a holographic memory.

Since photopolymers have excellent holographic characteristics, such as high refractive index modulation [9,10], large dynamic range [2,11,12], good light sensitivity, real-time image development, high optical quality, and low cost, they have been used as the base of new 3-D holographic disks. In addition, their properties, such as energetic sensitivity or spectral sensitivity, can be easily changed by modifying their composition [9,11,13,14].

The photopolymer is composed of acrylamide (AA) as the polymerizable monomer, triethanolamine (TEA) as the radical generator, N,N'-methylenebis-acrylamide (BMA) as the cross-linker, yellowish

Eosin (YE) as the sensitizer, and a binder of polyvinyl alcohol (PVA) [9,13]. The resulting layers are about $80 \pm 10 \mu\text{m}$ thick.

Reflection holograms with an AA-based photopolymer have been investigated for bit-format holographic data storage, and holographic reflection gratings have been recorded with a diameter of a few micrometers and 0.28% diffraction efficiency [15]. This type of hologram has also been used for other applications, such as a visual indication of environmental humidity [16].

In this work, we focus on the study of different compositions of a polyvinyl alcohol/acrylamide (PVA/AA)-based photopolymer, as well as exposure time and intensity, with the aim of recording reflection holograms with a spatial frequency of up to 5000 lines/mm with the best results.

2. Experimental

A. Different Compositions for Recording Material

The holograms are registered in a photopolymer composed of AA as the polymerizable monomer, TEA as the radical generator, BMA as the cross-linker, YE as the sensitizer, and a binder of PVA. Adding BMA to the composition improves the energetic sensitivity and diffraction efficiency of the material and, in addition, gives a greater stability to the stored grating, thereby preventing it from disappearing with time.

A solution of PVA in water forms the matrix, and this is used to prepare the mixture of AA, BMA, and a photopolymerization initiator system composed of TEA and YE. The mixture is made under red light, deposited by gravity on a $22 \text{ cm} \times 40 \text{ cm}$ glass plate, and left in the dark for 18–20 h to allow the water to evaporate in normal environmental conditions (temperature $\approx 20^\circ\text{C}$ and relative humidity $\approx 35\%$). The drying time is optimized to obtain the maximum diffraction efficiency of the gratings with the environmental conditions of our laboratory. After the drying step, small plates of $5 \text{ cm} \times 5 \text{ cm}$ are cut.

Three different compositions were studied. Composition A has only AA as a monomer, composition B also contains bis-acrylamide as a cross-linker, and composition C includes sodium formate, a chain transfer agent (CTA) [17]. Table 1 shows the component concentrations of the photopolymer compositions used to obtain layers about $80 \mu\text{m}$ thick.

B. Mechanism of Hologram Recording

A photoreduction reaction is produced when the material is illuminated with a light beam of 514 nm. The dye is excited to the high-energy state and then reacts with the coinitiator TEA, which is the electron donor, to produce a dye radical anion and a TEA radical cation. The dye radical is not usually reactive enough to initiate polymerization, but the TEA radical will react with an AA molecule and polymerization may then occur. The reaction occurred in a PVA matrix, and we consider that the PVA matrix is inert. When the material is exposed to an interference

Table 1. Concentrations of the Photopolymer Compositions

	Composition A	Composition B	Composition C
Polyvinyl alcohol	8.26% w/v	8.26% w/v	8.26% w/v
Acrylamide	0.44 M	0.44 M	0.44 M
Triethanolamine	0.2 M	0.2 M	0.2 M
Yellowish Eosin	2.4×10^{-4} M	2.4×10^{-4} M	2.4×10^{-4} M
N,N'-methylene-bis-acrylamide	—	0.026 M	—
Sodium formate	—	—	0.026 M

fringe pattern, more monomer is polymerized and the amount of polymer formed increases with exposure.

In some papers [17], the spatial-frequency response of a PVA/AA-based photopolymer is improved by adding a CTA, sodium formate. CTAs are added with the aim of reducing the length of the polymer chains formed. These agents have the ability to stop the growth of a chain. Thus, the spatially periodic concentration distribution in the material formed by polymer chains can disperse more rapidly. This paper [17] presents the results for transmission holograms analyzing a range of spatial frequencies from 500 to 2750 lines/mm. It is proposed that the addition of a CTA will decrease the average length of the polymer chains formed and, hence, localize the chain growth to the bright regions of the interference pattern. Thus, more but shorter polymer chains are expected to be formed. If a reduction in the non-local effect can be achieved, the potential improvements in high-spatial-frequency material response will be significant.

In this work, the influence of this component (CTA) on reflection holograms with a spatial frequency of up to 5000 lines/mm is studied and compared with other compositions that do not contain this component. We replaced the cross-linker (bis-acrylamide) in composition B by the same concentration of CTA (sodium formate) to obtain composition C.

C. Holographic Setup

The basic setup used to record holographic reflection gratings is shown in Fig. 1. Two beams, each with an intensity of 20.3 mW/cm^2 , from an Ar-ion laser overlap at a photosensitive plate, producing an appropriate interference pattern at the plane of the material due to the formation of PVA in the regions of constructive interference.

Holographic reflection gratings were recorded using the output beam from the laser, which was split into two beams and then spatially filtered, using a microscope objective and a pinhole, and collimated to yield a plane-wave source of light at 514 nm. The diameter of these beams was 1.5 cm. The two laser beams were spatially overlapped at the recording medium but reached the opposite sides of the holographic plate with symmetrical geometry. Both beams impinged at an angle $\alpha = 45^\circ$ with respect to normal incidence. The incident angles inside the material were 28° in both cases, therefore, a symmetrical

Fig. 1. (Color online) Experimental setup: BS, beam splitter; M1, mirror; L1, lens; D1, diaphragm, SF1, microscope objective and pinhole.

grating was recorded. The spatial period of the grating, Λ , established by the experimental recording condition, was $0.193 \mu\text{m}$, applying Eq. (1) (therefore, the spatial frequency of the recorded reflection grating was 5174 lines/mm), where λ is the wavelength of the laser light used for the recording a hologram, Λ is the closest separation between the fringes of the interference pattern in the recording layer, n is the refractive index of the photopolymer 1.506 [18], and θ is the angle between writing beams inside the recording material (in this case $\theta = 124^\circ$):

$$\Lambda = \frac{\lambda}{2n \sin\left(\frac{\theta}{2}\right)}. \quad (1)$$

3. Results

The high spectral selectivity [19] of the reflection holograms means that light of a specific wavelength is reflected when the hologram is illuminated with white light. The color observed depends on the holographic fringe spacing, Λ , and the reconstruction angle.

Each reflection grating was optically characterized by measuring its transmission spectrum. The dependence of transmittance on the wavelength was measured using a double-beam spectrophotometer; therefore, the transmittance values take into account Fresnel reflections and the absorption of the glass substrate. The plate was placed perpendicular to the beam of the spectrophotometer.

The depth of the reflection peak on the transmittance curve allowed us to calculate the diffraction efficiency of the recorded reflection grating. Applying Eq. (1) where now $\theta = 180^\circ$, we obtain a theoretical value of $\lambda = 582 \text{ nm}$, at which point the reflection peak should occur.

Figure 2 shows the transmittance versus wavelength when a reflection grating was recorded on a

plate. As can be seen, it was possible to separate the dye absorption peak ($\lambda = 532 \text{ nm}$) from the reflection peak.

Figure 3 shows the diffraction efficiency as a function of exposure for the different compositions used. The energetic sensitivity is defined as the minimum energy required to achieve the maximum diffraction efficiency. It shows that the plates with compositions A and B were more sensitive than those with composition C since an exposure of only 0.4 J/cm^2 was necessary to reach the maximum diffraction efficiency, whereas with composition C, an exposure of 4.7 J/cm^2 was necessary. The maximum diffraction efficiency obtained was 4.2% for composition A, 9.1% for composition B, and 1.5% for composition C. The values represented in Fig. 3 do not represent the maximum diffraction efficiency values since the angle of incidence of the probe beam (normal incidence) of the spectrophotometer is different from that used during the recording (45°).

Figure 4 shows the transmittance of the plates with different compositions for a given exposure that gave the highest diffraction efficiency, versus wavelength. They show the formation of the reflection peak and its wavelength shift.

The concentration of the chain transfer agent used (0.026 M) is different from that used in other studies [17] (0.007 M), and in our case, addition of a CTA was not seen to increase the diffraction efficiency when a high spatial frequency of up to 5000 lines/mm is required. We believe that the next step will be to determine the concentration of this component that is necessary to improve the response of reflection holograms.

Dimensional changes in the recording medium can occur after recording. Unfortunately, during the photopolymerization process, the monomer used usually undergoes volumetric changes; conversion of the monomer molecules into a polymer network is accompanied by close packing of the growing polymer chains and a subsequent reduction in volume. This phenomenon, known as photopolymerization shrinkage, is particularly relevant in the case of reflection gratings whose pitch becomes lower than that defined by the geometric conditions of the recording.

Fig. 2. Transmittance versus wavelength when a reflection grating was recorded on a plate.

Fig. 3. (Color online) Diffraction efficiency as a function of exposure for reflection gratings recorded on plates, with composition A represented by squares, composition B represented by circles, and composition C represented by triangles.

Shrinkage of the material induces a change in the fringe spacing, Λ , in the thickness of the material. This results in a relevant shift of the wavelength at which the reflection peak appears. The ultimate effect is a change in the wavelength of the diffracted light with respect to the recording laser wavelength if the reconstruction takes place under the Bragg condition. However, in our case, the reconstruction was at normal incidence, which does not satisfy the Bragg condition. Therefore, our theoretical wavelength was considered as $\lambda_{th} = 582$ nm, which is inferred by Eq. (1), and we calculated the final wavelength displacement with respect to this theoretical value.

It is possible to introduce a parameter called optical shrinkage [20] as

$$s_{opt} = \frac{\lambda_{th} - \lambda_{exp}}{\lambda_{th}}. \quad (2)$$

This parameter represents the ratio between the final reflection wavelength displacement observed by spectral analysis ($\lambda_{th} - \lambda_{exp}$) and the theoretical reflection wavelength of the grating if there was no shrinkage, and it was reconstructed not satisfying the Bragg condition λ_{th} . The behavior of our samples

Fig. 4. (Color online) Transmittance as a function of wavelength for reflection gratings recorded on plates, with composition A represented by dashed curves ($E = 0.4$ J/cm²), composition B represented by solid curves ($E = 0.4$ J/cm²), and composition C represented by dotted curves ($E = 4.7$ J/cm²).

shows a peak shift of 9 nm corresponding to 1.5% of optical shrinkage, for compositions A and C, and 10 nm corresponding to 1.7% for composition B. Therefore, it may be seen that the holograms recorded using composition B had the maximum diffraction efficiency (9.1%), and the optical shrinkage was very similar to that of the other compositions.

These reflection gratings were also studied by subjecting them to a bleaching process. The bleaching provides temporal stability to the resulting holographic grating and enables it to be subsequently used in another optical device. However, the bleaching process makes the diffraction efficiency decrease. In this case, the diffraction efficiency attained was 1.3% with composition A, 2.2% with composition B, and 0.8% with composition C.

Experimentally, a range of concentrations of both the chain transfer agent and the cross-linker should be examined so as to better understand the process that takes place in our photopolymer material when holographic reflection gratings with high spatial frequency are recorded.

4. Conclusions

The capacity of AA-based photopolymer with different compositions to record holographic reflection gratings with high spatial frequency has been investigated for optical storage applications. In this work, our preliminary results on recording and readout of reflection holograms are presented. The high spatial resolution of the photopolymer material is demonstrated by recording reflection gratings with a spatial frequency of 5174 lines/mm. Three different compositions of recording material were studied, and the best results in terms of diffraction efficiency were obtained for the composition, which included bis-acrylamide. In this case, the gratings were characterized by a diffraction efficiency of 9.1% and an optical shrinkage of 1.7%, which represent the relative displacement of the reflected wavelength from the theoretically expected value.

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