Diffraction efficiency improvement in high spatial frequency holographic gratings stored in PVA/AA photopolymers: Several ACPA concentrations

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Abstract:

High spatial frequencies in holographic gratings are difficult to obtain due to limitations of the recording material. In this paper, the results obtained after storing holographic transmission gratings with a spatial frequency of 2656 lines/mm in a material based on polyvinyl alcohol and acrylamide (PVA/AA) are presented. A chain transfer agent, 4,4'-azobis (4-cyanopentanoic acid) (ACPA) was incorporated in the composition of the material to improve the spatial resolution. Different concentrations of ACPA were used in order to find the optimal concentration giving maximum diffraction efficiency for high spatial frequencies.

Keywords: Holography; Polymers; Holographic transmission gratings; chain transfer agent.

1. Introduction

Holography is the physical mechanism by which holograms can be stored by exposing a photosensitive material to the interference of two light beams [1–3]. In this way the amplitude and phase of a wavefront can be stored when the wavefront interferes with a coherent light background. When the material in which the interference pattern is stored is illuminated by the reference beams, a diffracted beam is observed that is an exact reproduction of the original wavefront. In the last decade holography has acquired great importance due to its numerous applications, for example, holographic interferometry to obtain information on the deformation of materials [4], in the manufacture of lenses [5,6] and holographic optical elements [7–9], or data encoding [10,11]. Moreover, holography can even be applied to manufacture solar concentrators [12] and in the field of medicine [13]. However, one of the major advances is that holographic devices can store information throughout the volume of the material, thereby increasing the storage capacity in comparison with two-dimensional devices that only store information on the surface [14–16].

A fundamental element of holographic data storage devices is the recording material where information is stored. Research groups around the world concentrate their efforts on obtaining a suitable material for this purpose [17–19]. It

is important to find a material with a high refractive index modulation and high energy sensitivity with good optical quality. And more recently materials with a high resolution are being sought [20–22].

One way to increase the storage capacity of these devices is to store data pages with a higher spatial frequency. Conventional recording materials reach diffraction efficiencies close to 100%, but only for spatial frequencies not much higher than 1000 lines/mm. However, when attempts are made to store objects with higher spatial frequencies, the diffraction efficiency drops dramatically and this is why materials with a higher spatial resolution are needed.

This study attempts to optimize the standard composition of a PVA/Acrylamide photopolymer in order to improve its spatial resolution. To do this, a chain transfer agent, 4,4'-azobis (4-cyanopentanoic acid) (ACPA) is introduced in the photopolymer and its concentration is modified [21,22]. Thus, the optimal concentration that gives maximum diffraction efficiency for high spatial frequencies may be determined.

To quantify the improvement achieved by including ACPA in a PVA/Acrylamide photopolymer, transmission gratings of 2656 lines/mm were stored (this spatial frequency was chosen because in this type of photopolymers, the diffraction efficiency is reduced by half compared with gratings of 1000 lines/mm). The diffraction efficiency obtained with the different concentrations of ACPA was measured and the results compared. Furthermore, the diffraction efficiency was fitted using the Coupled Wave Theory [23] to obtain parameters such as refractive index modulation, spatial period and thickness of the grating that give us an indication of the improvement in the stored gratings when ACPA is incorporated in the composition of the material. For the same purpose, shrinkage of the gratings was also calculated.

2. Chemical process

In this study, ACPA was used as a chain transfer agent (CTA), due to its capacity to generate two identical radicals. triethanolamine and yellowish eosin (TEA/YE) was the redox system with TEA as initiator. CTA's were introduced in photopolymers and developed by Gleeson *et al.* [20,24] in order to reduce the molecular weight of the polymer chains grown during the recording of holograms. When a diffraction grating is recorded in a photopolymer, a radical polymerization initiated by light takes place in the exposed zones. In photopolymerization, the mechanism of initiation is detailed in Refs. [25–27]. For this work we only consider the propagation reactions Eq. (1). The radicals R derived from the initiator molecule (TEA) react with the monomer M (AA) generating a growing macroradical $M_n \cdot$ in the propagation reaction system Eq. (1). Two growing macroradicals are deactivated by combination or disproportionation in the termination reactions. Kinetic constants of the propagation is denoted by k_p . The basic mechanism in a radical polymerization involves the following reactions in the propagation mechanism:

2.1. Chain transfer mechanism

Adding a chain transfer agent XA to the photopolymer composition introduces a new reaction in the propagation reaction system Eq. (1) of the kinetic scheme:

where $M_n \cdot$ is a growing macroradical that reacts with the chain transfer agent XA producing deactivation of the growing macroradical. The new radical A can start a new polymer chain according to the following reaction:

The main effect of a chain transfer is the decrease in polymer chain molecular weight due to the presence of XA molecules, which deactivate the growing macroradicals M_n . In this paper, the performance PVA/AA photopolymer layer with a thickness of a 70 μm , developed in our laboratory, is improved thanks to a chain transfer effect. ACPA is used as chain transfer agent XA in a photopolymer with TEA/YE as initiator system. The influence of the chain transfer effect on the holographic characteristics of the photopolymer is analyzed.

3. Preparation of the material

The holographic transmission gratings are recorded in a PVA/AA based photopolymer. The standard composition of this material contains acrylamide (AA) as the polymerizable monomer, triethanolamine (TEA) as radical generator, polyvinyl alcohol (PVA) as binder and yellowish eosin (YE) as sensitizer. Table 1 shows the concentrations of the components of this material (Composition 1) [28]. This composition provides diffraction efficiencies of 100% for holographic gratings with a spatial frequency of 1000 lines/mm.

Table 1: Concentrations of the photopolymer compositions

	Composition 1	Composition 2	Composition 3	Composition 4	Composition 5	Composition 6
Polyvinylalcohol (PVA)	8.26% m/v	8.26% m/v	8.26% m/v	8.26% m/v	8.26% m/v	8.26% m/v
Acrylamide (AA)	0.44M	0.44M	0.44M	0.44M	0.44M	0.44M
Triethanolamine (TEA)	0.20M	0.20M	0.20M	0.20M	0.20M	0.20M
Yellowish eosin (YE)	2.4x10-4M	2.4x10-4M	2.4x10-4M	2.4x10-4M	2.4x10-4M	2.4x10-4M
4,4'-Azobis(4-cyanopentanoic acid) (ACPA)	-----	0.006M	0.009M	0.012M	0.015M	0.018M

However, previous studies have shown that when you want to store holographic gratings with higher spatial frequencies, the diffraction efficiency decreases as the spatial frequency increases, and falls to a very small diffraction efficiency for spatial frequencies of 5000 lines/mm [22,29].

Fortunately, photopolymers are very versatile and it is possible to add new components to their composition. Therefore, it was decided to add a chain transfer agent (ACPA) to the standard composition in order to improve its spatial frequency. The main effect of this polymerization reaction is a reduction in the length of the polymer chain, which in turn leads to an improvement in the response of the material to the recorded spatial frequency. In order to optimize the composition and obtain gratings with maximum diffraction efficiency, five different concentrations of ACPA between 0.006 M and 0.018 M (compositions 2 to 6) were added to the photopolymer with composition 1. The concentrations of the components are shown in Table 1.

To obtain the materials included in Table 1, first a solution of PVA in water was prepared by heating and once all the PVA had dissolved it was allowed to cool. Simultaneously a solution of AA and TEA was prepared in water. These two components were mixed in the proportions necessary to obtain the concentrations of composition 1 (Table 1). Finally YE was added to the solution under red light because the material is not sensitive at this wavelength. In the case of compositions 2 to 6 (Table 1), ACPA was also added to the solution and stirred until completely dissolved. The mixture was then deposited by gravity on a 22 cm x 40 cm glass plate and kept in the dark for one day approximately to allow the water to evaporate in conditions of temperature, $T=20^{\circ}\text{C}$ and relative humidity, $\text{RH}=40\%$ and obtain layers of $70\pm 5\text{ }\mu\text{m}$ thick. Once dry, the glass was cut into squares of $6\times 6\text{ cm}^2$.

4. Holographic Setup

Fig. 1 shows the experimental setup used to store holographic transmission gratings [28]. During the recording stage two beams - the object beam and the reference beam - interfere at an angle θ with the normal to form the hologram. As the two beams can be considered plane waves, a diffraction grating is obtained. The laser used in the recording stage was a Nd: YVO₄ laser (Coherent Verdi V2) emitting a beam with a wavelength of 532 nm, at which the material is sensitive. To store the diffraction grating, the vertically polarized laser beam was split into two beams with a beam-splitter, passed through a microscope objective and a pinhole to expand and filter the beams and through a series of lenses and diaphragms to collimate them with the desired diameter (1 cm). Finally, some mirrors directed the beams to produce interference at the desired angle on the recording material. The total intensity of the recording beams was 5 mW/cm^2 .

The recording angle of the experimental setup was calculated according to Eq. (4) to achieve a spatial frequency of 2656 lines/mm:

$$\sin \theta = \frac{\lambda}{2\Lambda} \quad (4)$$

where Λ is the spatial period, $1/\Lambda$ is the spatial frequency and λ is the wavelength measured in air [1].

During the reconstruction stage, a HeNe laser with a wavelength of 633 nm was used to reconstruct the holographic grating, since the material is not sensitive at this wavelength. The laser beam fell on the material at an angle of θ' calculated from Eq. (4). A recording angle of 45° was used to achieve a spatial frequency of 2656 lines/mm and an angle of 57.2° , calculated from Eq. (4), was used to reconstruct the grating. The spatial period of the grating stored in the material was $\Lambda_{\text{th}}=0.3765\text{ }\mu\text{m}$.

The power of the diffracted beam was measured with a radiometer and the diffraction efficiency of the grating, DE, is defined as the ratio of the power of the diffracted beam to the power of the incident beam.

Fig. 1. Experimental setup for transmission gratings. Mi: mirrors, BS: beam splitter, Li: lenses, SFi: microscope objective lens and pinhole, Di: diaphragms, R: radiometer.

During the polymerization process, conversion of monomer to polymer molecules may be accompanied by shrinkage of the polymer chains producing a reduction in volume. In the case of transmission gratings, shrinkage of the material may be due to a change in the spatial period, which requires a shift in the reconstruction angle to obtain the maximum diffraction efficiency. Specifically, shrinkage occurs when the effective spatial period of the grating, Λ_{exp} , is smaller than the spatial period defined by the geometrical conditions of the setup, Λ_{th} . Shrinkage induces a change in the spacing of the Bragg planes defined by $\Delta\Lambda = \Lambda_{th} - \Lambda_{exp}$. Thus, shrinkage is defined as [30]:

$$S_{opt} = \frac{\Lambda_{th} - \Lambda_{exp}}{\Lambda_{th}} \quad (5)$$

5. Results and discussion.

After tuning the experimental setup, gratings with a spatial frequency of 2656 lines/mm were recorded in the photopolymer plates with six different compositions (see Table 1). Composition 1 corresponds to the standard composition of a PVA/AA photopolymer. Compositions 2 to 6 are modifications of the standard composition, to which different concentrations of a chain transfer agent, ACPA, were added to improve the response of the material to the spatial resolution. The ACPA concentrations used were 0.006 M, 0.009 M, 0.012 M, 0.015 M and 0.018 M in compositions 2, 3, 4, 5 and 6 respectively. The aim of this study is to find the composition with which the highest diffraction efficiency is obtained and then, in future works, take it as a reference to find the best composition for gratings with higher spatial frequency with a reflection geometry.

Fig. 2 shows the diffraction efficiency (DE) versus reconstruction angle obtained by recording the diffraction gratings in the six compositions in Table 1. The zero of the horizontal axis corresponds to the Bragg angle for a wavelength of 633 nm, which is 57.2° for this spatial frequency. The gratings in Fig. 2 were recorded with an exposure of 225 mJ/cm^2 , at which the maximum diffraction efficiency was obtained. The DE obtained with the standard composition is represented by black circles. As can be seen, the maximum DE obtained with this composition was 41 %. With composition 2 (ACPA concentration of 0.006 M) a DE of 38% was obtained (red squares); with composition 3 ($C_{ACPA}=0.009 \text{ M}$) the DE was 45% (blue triangles); with composition 4 ($C_{ACPA}=0.012 \text{ M}$) it was 51% (green circles); with composition 5 ($C_{ACPA}=0.015 \text{ M}$) it was 62% (violet squares); and with composition 6 ($C_{ACPA}=0.018 \text{ M}$) it was 60% (orange triangles). From the results in Fig. 2, it can be concluded that adding a concentration of 0.006 M ACPA is not enough to increase the DE of the stored gratings. However, with higher concentrations of ACPA, the material began to respond positively since the DE increased as the concentration of ACPA increased. The maximum DE was obtained with an ACPA

concentration of 0.015 M. Higher concentrations of ACPA were tested ($C_{ACPA} = 0.018$ M), but the DE did not improve. Therefore, for the spatial frequency studied, the optimal concentration of ACPA was 0.015 M.

Fig. 2. DE versus Bragg's angle for gratings stored with a spatial frequency of 2656 lines/mm in the materials with the compositions in table 1.

To see the evolution of the maximum of the diffraction efficiency when the concentration of ACPA is changed, Fig. 3 depicts the $DE_{MAX}(\%)$ of the gratings shown in Fig. 2 versus ACPA concentration (black circles). As can be seen, the increase in DE_{MAX} with ACPA concentration is not linear. DE_{MAX} increases up to a point beyond which it remains constant. In this case the limit is reached at an ACPA concentration of 0.015 M, since increasing the C_{ACPA} to 0.018 M, results in a slight decrease in DE_{MAX} .

Fig. 3. DE_{MAX} versus ACPA concentration for the gratings depicted in Fig. 2.

To obtain more information about the stored gratings, it was decided to fit the DE in Fig. 2 with the Coupled Wave Theory [23]. Refractive index modulation, Δn , effective spatial period, Λ_{exp} , and thickness, d [31] can be extracted from the fitting. The fittings are represented in Fig. 2 by a solid line.

Table 2 shows the parameters resulting from fitting the gratings in Fig. 2 (Δn , Λ_{exp} and d). In addition, the DE (%) of the gratings for each composition was also considered in order to analyze the results better.

With the values of the spatial period, Λ_{exp} , the shrinkage, S_{opt} , can be calculated from Eq. (5). Considering that the theoretical spatial period for a grating with a frequency of 2656 lines/mm is $\Lambda_{th} = 0.3765 \mu m$ (see section 2b), the

shrinkage values obtained are shown in Table 2. As can be seen, in the compositions in which ACPA is more effective (compositions 3, 4 and 5), the shrinkage is slightly greater than in the standard composition (composition 1) and the compositions in which ACPA is ineffective either due to too low or too high a concentration (compositions 2 and 6 respectively). However, in all cases the shrinkage is very small (less than 0.3 %), so APCA has very little effect on shrinkage.

Moreover, it should be noted that from the fitting made with the Coupled Wave Theory, the thickness of the grating can also be obtained. The thicknesses of the gratings stored with the six compositions are shown in Table 2. Their values range between 61 μm and 76 μm .

Table 2: Parameters obtained from the fitting of the gratings in Fig.2 for the compositions in Table 1.

	DE(%)	Δn	Λ_{exp} (μm)	d (μm)	S _{opt} (%)
Composition 1	41	0.0011 $\pm$ 0.0005	0.3761 $\pm$ 0.0004	70 $\pm$ 1	0.1
Composition 2	38	0.0012 $\pm$ 0.0004	0.3760 $\pm$ 0.0003	61 $\pm$ 1	0.1
Composition 3	45	0.0013 $\pm$ 0.0003	0.3759 $\pm$ 0.0004	64 $\pm$ 1	0.2
Composition 4	51	0.0013 $\pm$ 0.0003	0.3754 $\pm$ 0.0004	72 $\pm$ 1	0.3
Composition 5	62	0.0014 $\pm$ 0.0003	0.3759 $\pm$ 0.0004	76 $\pm$ 1	0.2
Composition 6	60	0.0014 $\pm$ 0.0003	0.3760 $\pm$ 0.0004	69 $\pm$ 1	0.1

Furthermore, Fig. 4 shows Δn versus ACPA concentration, obtained from fitting the data in Fig. 2 with the Coupled Wave Theory (red squares) [23]. As can be seen, Δn increases as the concentration of ACPA is increased from a value of 0.0011 (composition 1) to a value of 0.0014 (composition 6). Therefore, these results show that ACPA, besides improving DE, also improves Δn .

Fig. 4. Δn versus ACPA concentration for the gratings depicted in Fig. 2.

6. Conclusions

This study demonstrated the validity of using chain transfer agents, specifically ACPA, to improve the spatial resolution of photopolymers.

ACPA led to an increase in the response of the material to the spatial frequency recorded (2656 lines/mm), since the DE increased from 41% (composition 1 without ACPA) to 62 % (composition 5 with ACPA). The photopolymer without ACPA had a low DE, therefore it had a lower response to high spatial frequencies. With the incorporation of ACPA, the response of the material improved since a significantly higher DE was obtained. Moreover, Δn increased as the ACPA concentration increased. Therefore, ACPA improves the response for high spatial frequencies of materials which incorporate it in their composition.

Finally, it should be noted that for 2656 lines/mm, the addition of ACPA had very little effect on the shrinkage of the materials since this only increased from 0.1 % in the standard photopolymer to 0.3% in materials with an ACPA concentration of 0.015 M.

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