Biophotopol's energetic sensitivity improved in 300 μm layers by tuning the recording wavelength

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Abstract

In order to obtain a highly environmentally compatible photopolymer to replace the well-known acrylamide photopolymer we optimized the previously developed Biophotopol composition to obtain volume transmission gratings in 300 μm layers, at a recording wavelength of 488 nm. The results obtained show an improved energetic sensitivity with similar diffraction efficiency to that obtained at the standard recording wavelength of 514 nm.

1. Introduction

Holographic techniques require a recording material with specific characteristics in terms of dynamic range, energetic and spectral sensitivity, layer thickness, post-processing, etc. Depending on the application —holographic memories, holographic and diffractive optical elements or other applications where light sensitive material is required— certain characteristics are more important than others [1-3].

One such application would be to replace a conventional optical element by its equivalent holographic optical element (HOE), which has significant advantages such as its smaller size and lower cost [4-6].

Usually, photopolymers have a photoinitiator system that absorbs light and generates free radicals that initiate the radical polymerization reaction of one or various monomers. In the case of holographic recording, the basic mechanism of hologram formation involves modulation of the refractive index between polymerized and non-

polymerized zones, corresponding to the “bright” and “dark” zones respectively, in the diffraction grating generated due to the interference of the recording beams [7].

Traditionally polyvinyl alcohol/acrylamide has been considered versatile holographic recording material; however, this type of photopolymer has low environmental compatibility. In opposition with other chemical formulations erroneously called “green photopolymer”, our formulation does not contain a toxic dye [8]. The PRF dye and all components in our formulation are really not toxic. The commonly used yellowish eosin and erythrosine B dyes are toxic [9]. Biodegradability, biocompatibility and low toxicity are new properties that have become essential in the design of a new recording material and so must be taken into account [10-12]. These properties are very interesting for a wide spectrum of applications such as those mentioned above or as a recording medium in photochemistry studies based on holographic techniques.

In a previous paper we developed the biocompatible photopolymer ‘Biophotopol’ in 900 μm thick layers for use as holographic memories [13]. However, such thick layers are not suitable for recording HOEs [14].

In this study, we optimized the Biophotopol photopolymer composition in order to obtain volume transmission gratings in 300 μm layers. This thickness is more suitable for recording HOEs. We used a recording wavelength of 488 nm and the results were compared with those obtained at the standard recording wavelength of 514 nm.

Therefore, the results provided here changing the recording wavelength open a new way to work with this truly “green photopolymer” and show the utility of this kind of photopolymer for holographic applications.

Finally, we demonstrate that the refractive index attenuation with layer depth may be disregarded in 300 μm thick layers at both recording wavelengths.

2. Material preparation

The composition studied is based on that described in our previous paper in which the Biophotopol composition was optimized to achieve 900 μm thick layers [8]. In particular, the photopolymer solution for 300 μm (Table 1) with water as solvent is composed of sodium acrylate (AONa) as polymerizable monomer, triethanolamine (TEA) as coinitiator and plasticizer, sodium salt 5'-riboflavin monophosphate (PRF) as dye and poly(vinyl alcohol) (PVA) as binder ($M_w = 130000$ u, hydrolysis degree = 87.7%). It also contains the crosslinker *N,N'*-(1,2-dihydroxyethylene) bisacrylamide (DHEBA). Figure 1 shows the molecular structures of the components.

Table 1. Composition of the photopolymer solution in molarity, PVA in percentage.

The composition of the photopolymer solution is deposited in circular glass molds by gravity. Initially the liquid solution has around 1450 μm thickness. The molds are then left inside an incubator (Climacell 111) with controlled humidity and temperature ($H_r = 60 \pm 5\%$ and $T = 22 \pm 1^\circ\text{C}$, respectively). When part of the water has evaporated (drying time 40 h), the “solid” film thickness decreases to 300 μm . At this time, the layer has enough mechanical resistance and it can be extracted from the mold without deformation. Then, the solid film is cut into $6.5 \times 6.5 \text{ cm}^2$ pieces and adhered to the surface of glass plates without the need of adhesives. The plates are then ready for exposure, which takes place immediately.

The thickness of the solid films is measured using an ultrasonic pulse-echo gauge (PosiTector 200) after exposure.

The Argon laser wavelength used in the hologram recording experiments was 514 nm and 488 nm where the dye absorbs.

In the previous Biophotopol composition the primary plasticizer (TEA) had a low concentration and the secondary plasticizer (water) a higher concentration. Therefore the water/TEA fraction was high. Now the situation is completely different since the thickness of the layers (300 μm) means there is less water content in the dry layer. A higher TEA content is necessary to plasticize the layer and therefore the water/TEA fraction in this polymer formulation is low. This implies that it is possible to use a relatively high DHEBA concentration since this molecule forms H-bonds with TEA (Figure 1) preventing crystals from growing inside the layer during the drying process. A high DHEBA concentration is necessary in order to obtain a photopolymer with the best energetic sensitivity.

Figure 1. Molecular structures of the components in the prepolymer syrup.

3. Holographic Set-Up

Figure 2 shows the experimental holographic set-up to obtain unslanted diffraction gratings. We used an Argon laser tuned at wavelengths of $\lambda_1 = 514 \text{ nm}$ and $\lambda_2 = 488 \text{ nm}$ with continuous laser exposure. The laser beam was split into two secondary beams with an intensity ratio of 1:1. The diameter of these beams was increased to 1.5 cm with an expander, while spatial filtering was ensured. The object and reference beams were

recombined at the sample at an angle $\theta = 17.1^\circ$ to the normal for both recording wavelengths with an appropriate set of mirrors, and the spatial frequency obtained was 1205 and 1144 lines/mm, for recording laser wavelengths of 488 and 514 nm, respectively. The working intensity for both recording wavelengths was 6 mW/cm². The diffracted and transmitted intensity were monitored in real time with a He-Ne laser positioned at Bragg's angle ($\theta' = 22.4$ and 21.2° for recording laser wavelengths of 488 and 514 nm respectively) emitted at 632.8 nm, where the material does not polymerize. In order to obtain diffraction efficiency (DE) and transmission efficiency (TE) as a function of the angle at reconstruction we placed the plates on a rotating stage. DE and TE were calculated as the ratio of the diffracted beam or transmitted beam to the incident He-Ne laser power. In order to take into account Fresnell losses the expression was multiplied by an appropriate factor.

Figure 2. Experimental set-up. BS: beamsplitter, Mi: mirror, SFi: spatial filter, Li: lens, Di: diaphragm, Oi: optical power meter, PC: data recorder.

During recording, a constructive interference is produced at the bright zones of the diffraction grating, where a photopolymerization reaction takes place according to the scheme in Table 2 [15].

Table 2. Radical polymerization mechanism.

Where k are the kinetic constants, $^1PRF^*$ is the PRF molecule in the singlet excited state, $^3PRF^*$ is the PRF molecule in the triplet excited state, $PRFb$ represents the decomposition byproducts from PRF, TEA is the amine radical derived from TEA, M is the monomer AONa, Mx , My , $Mx+y$, Mn ($n=1,2..n+1$) are polymer chains with a different number of monomer units.

4. Results and discussion

4.1 Spectral properties

The hydrogel photopolymer type we are using is very versatile because it allows the change of its composition to obtain the desired characteristics or as in this work the change of the absorption coefficient of the material by varying the wavelength to optimize their performance record.

The spectral properties of the solid films were measured with a Jasco UV-VIS V-650 spectrophotometer as a function of the wavelength. Figure 3 shows the absorption for a 300 μm photopolymer layer. The PRF dye is mainly absorbed in the 400-500 nm range so the highest transmittance occurs at wavelengths higher than 525 nm. We first used a wavelength of 514 nm to record the holographic diffraction gratings because this wavelength has the high output intensity of an Argon laser. The behavior of Biophotopol at this wavelength was good; however, the repeatability of the results was low. For this reason we decided to change the recording wavelength.

As can be seen in Figure 3 the absorption coefficient at $\lambda_1 = 514$ nm is $\alpha_1 = 7$ cm^{-1} , so we decided to tune the Argon laser to a shorter wavelength. The next short wavelength emitted by the Argon laser with high output intensity is $\lambda_2 = 488$ nm, at which the photopolymer absorption coefficient is one order of magnitude higher ($\alpha_2 = 91$ cm^{-1}). Therefore, greater absorption may be expected to improve the holographic photopolymer properties.

Figure 3. Absorption for 300 μm thick Biophotopol layer.

In photopolymers, during the recording stage, the light is exponentially attenuated in depth inside the material, as described by Beer-Lambert's law (or Beer's law)[16]. This attenuation produces a non-uniform refractive index profile limiting the grating thickness. This effective thickness may be clearly less than the physical thickness and depends on the chemical composition of the material.

To analyze the limitation on the effective thickness we assume that the attenuation of the refractive index profile is similar to the absorption of the recording light (α_i) inside the material. Figure 4 shows the index modulation normalized to the index modulation at the surface as a function of the depth for α_1 and α_2 . As can be seen for layer thicknesses of 300 μm , at a recording wavelength of 488 nm more than 34% of the initial refractive index modulation remains at this depth as compared to 91% that keeps at 514 nm.

Figure 4. Exponential decay of n_1 , modulation of the refractive index divided by the index modulation at the surface (n_{10}) as a function of depth plotted for Biophotopol layers ($\alpha_1 = 7$ cm^{-1} and $\alpha_2 = 91$ cm^{-1}).

The index modulation needed to obtain the same optical and physical thicknesses was 20% [17]. Therefore, for 34% and 91% of the initial value of the refractive index modulation the optical thickness will be practically the same as the physical thickness

(300 μm) at both wavelengths as can be seen in section 4.2. Hence, the holographic grating is recorded in the throughout physical thickness. The attenuation of the refractive index profile does not affect the holographic storage and there is no problem of using the 488 nm to record the holographic gratings due to low PRF concentration introduced in the chemical composition. The Figure 5 shows the angular response of the material for different film thicknesses for a record wavelength of 488 nm. We have fitted the experimental data using Kogelnik's coupled wave theory [18] to obtain the optical thickness. The narrowing of the main lobe can be observed when the thickness increases up to 500 μm since the attenuation in depth of the refractive index profile is negligible, however from 500 μm onwards the attenuation in depth of the refractive index profile begins to be considerable and therefore the narrow main lobe stops and the optical thickness remains constant, as we can see on Figure 6.

Figure 5. The experimental (physical thickness, symbols) and theoretical (optical thickness, lines) angular scan around the first Bragg angle is plotted for six layers recorded at 488 nm with different physical thicknesses.

Figure 6. Theoretical thickness versus physical thickness.

Figure 7 shows a 300 μm photopolymer layer. As can be seen the film is uniform and transparent over the whole surface. We can note the white light diffraction produced by the recorded diffraction gratings.

Figure 7. 300 μm Biophotopol photopolymer layer recorded at 488 nm.

4.2 Holographic recording

We have measured more than one hundred samples for each wavelength. Figure 8 shows DE versus exposure (E) for four representative samples recorded at two wavelengths, λ_1 and λ_2 . The photopolymer reached a similar DE (around 90%) at both recording wavelengths. However, the energetic sensitivity (S), defined as the minimum energy required to achieve the maximum diffraction efficiency (DE_{max}), is 0.3 J/cm^2 (at 488 nm) and 1.1 J/cm^2 (at 532nm), that means 30 and 150 s for an exposure intensity of 6 mW/cm^2 , respectively.

Figure 8. DE versus E for samples recorded at wavelengths of 488 nm (blue) and 514 nm (green).

In order to analyze this effect, Figure 9 shows S versus layer thickness (h). As can be seen, for both photopolymers, the energy needed to reach S decreases when h is increased. Moreover, S is lower for the photopolymer recorded at a wavelength of 488 nm than for the photopolymer recorded at 514 nm in the thickness range studied. It is interesting to note that the sensitivity of the photopolymer recorded at 488 nm remains practically constant for thicknesses greater than 300 μm .

Figure 9. S versus h for photopolymers recorded at 488 (blue squares) and 514 nm (green circles).

A possible explanation is related to the initiation step in the radical polymerization mechanism (Table 2). A PRF excited molecule generates a radical derived from TEA that initiates the propagation in Eq. (4). Nevertheless it is necessary for a PRF molecule to reach the triplet excited state, Eq. (2), before it can react with TEA to generate an initiating radical in Eq. (3). After light absorption, Eq. (1), the PRF molecule may be deactivated before it reaches the triplet excited state, Eq. (2). At 488 nm, the PRF molecule has higher absorbance than at 514 nm (Figure 3) and therefore the probability that the PRF molecules reach the triplet excited state is increased. In these conditions, k_1 Eq. (2) has a high value and the polymer chains are generated faster, leading to a high level of polymerization in a short time [19]. Therefore, a greater energetic sensitivity (lower S value) is obtained.

Figure 10 shows the angular reconstruction, taking into account Fresnell losses for both interfaces (air/layer and glass/air), after recording the photopolymer at two wavelengths (488 and 514 nm). It can be seen that both angular reconstructions have the same shape and, therefore, similar holographic parameters.

Figure 10. Angular scan obtained for the holograms recorded in photopolymers at two wavelengths.

We also fitted the experimental data using Kogelnik's coupled wave theory [18] and obtained the main holographic parameters: refractive index (n_0), index modulation (n_1), thickness (h), full width at half maximum (FWHM) and absorption coefficient α_{HeNe} (Table 3), at the reconstruction wavelength (633 nm).

Table 3. Main holographic parameters h , n_0 , n_1 , α , FWHM and R^2 obtained for the samples shown in Figure 10.

As can be seen the parameters are very similar for both photopolymers. The values of R^2 represented show that there is good agreement between the experimental angular response data and the theoretical model proposed by Kogelnik.

It is interesting to note that the secondary lobes (Figure 10) are in agreement with Kogelnik's coupled wave theory. As noted in previous studies [17, 20] the effect of an attenuated grating is to smooth the secondary lobe responses. Therefore, this supports our affirmation that for thicknesses less than 300 μm the optical thickness is similar to the physical thickness at both recording wavelengths.

We have on going experiments to fit the time that the information remains in our material and we can say at this time it is longer than one year. Furthermore, we are developing preliminary studies to record binary data pages in this environmental compatible material. Nevertheless further studies will be done in order to optimize the experimental setup and the chemical composition.

Conclusions

In the field of green photonics the employment of photopolymers with high environmental compatibility that avoids waste problems it is fundamental.

In this paper, we obtained transmission diffraction gratings in 300 μm layers of Biophotopol, a non-standard thickness for this photopolymer. The material reached high diffraction efficiencies of about 90%. Furthermore, we improved the energetic sensitivity by 50% tuning the recording wavelength to higher absorption values (488 nm) without a significant increase in the refractive index attenuation. This result could be related to the photopolymerization mechanism, in particular to a greater number of excited molecules leading to a high level of polymerization in a short time.

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Molecular structures

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Experimental set-up

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Absorption
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Exponential decay
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Figure5
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Figure6
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Figure9
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Figure10
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Table1

PVA (% w/v)	AONa (M)	TEA (M)	PRF (M)	DHEBA (M)
15	0.34	0.15	$1.00 \cdot 10^{-3}$	$6.40 \cdot 10^{-3}$

Table2

Initiation	
$PRF \xrightarrow{h\nu} {}^1PRF^*$	(1)
${}^1PRF^* \xrightarrow{k_1} {}^3PRF^*$	(2)
${}^3PRF^* + TEA \xrightarrow{k_2} PRFb + TEA\cdot$	(3)
Propagation	
$M_1\cdot + M \xrightarrow{kp} M_2\cdot$ $M_2\cdot + M \xrightarrow{kp} M_3\cdot$ $M_n\cdot + M \xrightarrow{kp} M_{n+1}\cdot$	(4)
Termination	
$M_x\cdot + M_y\cdot \xrightarrow{k_{tc}} M_{x+y}$	(5)
$M_x\cdot + M_y\cdot \xrightarrow{k_{td}} M_x + M_y$	(6)

Table3

λ_{rec} (nm)	h (μm)	n_0	n_1	α_{HeNe} (μm^{-1})	FWHM($^{\circ}$)	R^2
488	286	1.501	0.00088	0.00040	0.138	0.999
514	307	1.497	0.00086	0.00044	0.134	0.997