

# Study of the index matching for different photopolymers

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## ABSTRACT

One of the most promising phase optical recording mediums are photopolymers. In these materials, the use of an index matching component permits a better conservation of the stored information and, additionally, the study of the molecules migration and shrinkage/swelling phenomena separately. In general, the transmitted beam has the information of the thickness and refractive index modulation mixed. Therefore, we propose the introduction of a coverplate besides with an index matching liquid in order to improve the characterization and the conservation. The index matching techniques have been classically used for holographic recording materials. In principle, to obtain an accurate index matching we have to choose a liquid with refractive index very close to the mean of the polymer one. Then, when shrinkage takes place during recording, mainly due to the polymerization, the liquid will fill up the generated grooves minimizing the diffractive effects produced by the relief structure. In fact, in this work we study different index matching components for different photopolymers. The photopolymers analyzed in this work have a polyvinyl alcohol (PVA) as a binder and two different main monomers: one has acrylamide and the other one sodium acrylate. We have recorded very low diffractive gratings and studied their conservation for different index matching components.

**Keywords:** holography, holographic recording materials, diffractive optical elements.

## 1. INTRODUCTION

Photopolymers present appealing optical properties for holographic [1-3] and diffractive applications [4-7]. They enable modulation of the electrical permittivity and thickness, are self processing, layers with a wide range of thicknesses and properties can be fabricated on demand. Due to their importance, several models have been developed to simulate the recording step in these materials. The phase image formation is governed by two different phenomena, the photochemical reactions due to the illumination that conclude by the polymer chains formation, and the molecules migration due to the gradients in the concentrations produced by the photopolymerization. Once the importance and the magnitude of both processes are fitted, basics models can be implemented. One way to obtain a whole characterization of the material is the low spatial frequency because the migration can be observed in real time. In addition, it can be used to record low spatial frequency diffractive optical elements like sinusoidal, binary, blazed gratings ore lenses [6-7].

One of the most studied photopolymers has as a binder polyvinyl alcohol (PVA) [8-9]. These photopolymers have been used for many interesting applications such as the fabrication of waveguides [10], sensors [11], alignment of liquid crystals [12] or solar concentrators [13]. Nevertheless, from the beginning to nowadays, an interesting discussion has been carried out about the importance of the diffusion in this type of material [8,14-17]. Furthermore, the presence of PVA permits that the environmental humidity affects thickness of the layer by the continuous water exchange between PVA and the environmental [18-20]. To avoid this effect there were designed some encapsulation techniques, one of them include the index matching using liquids and coverplates [8, 21-22]. Additionally, a fitted index matching permits to avoid the effects of the thickness variation isolating the refractive index changes.

Along this paper, we want to study the influence of the liquid used for the index matching in different photopolymers using PVA as a binder. The first one has acrylamide, AA, as a main monomer and the second one is a high

environmental compatible photopolymer with sodium acrylate, NaAO. In addition to this, we have explored the possibilities given by the using of coverplate in the field of diffractive optical elements fabrication.

## 2. EXPERIMENTAL

As we have said in a previous section, the standard photopolymer is composed of AA as polymerizable monomer, triethanolamine (TEA) as coinitiator and plasticizer, yellowish eosin (YE) as dye, PVA as binder and a small proportion of water as additional plasticizer. It may also contains N,N'-methylene-bis-acrylamide (BMA) as crosslinking monomer. AA and BMA are toxic monomers, the former more than the latter. YE also introduces problems due to the four Br atoms in its molecule, but it is clearly the less toxic component. In this sense, in the chemical formulation analyzed in this work, we keep YE as a dye, to obtain a better comparison of the monomer importance.

For monomer substitution it is necessary to use another vinyl monomer that is less toxic than AA. We used sodium acrylate, NaAO, prepared in situ by means of a one-pot reaction with acrylic acid and sodium hydroxide in the prepolymer solution used to prepare the layers. The toxicity of sodium acrylate is lower than that of AA. We replaced AA by NaAO in the photopolymers BIO. BMA, a known also toxic, but clearly less than AA, is the crosslinker usually used in a standard AA-based photopolymer [21] and, in this case, we used it in the NaAO-based photopolymer too.

Biophotopol has also a hydrophilic binder as the AA-based standard photopolymer and this implies that during its production the main solvent used is water. Biophotopol does not use any additional co-solvent. Any products and devices made with this photopolymer can also be eliminated, once their useful life is over, by dissolving in water. Therefore, this material has an advantage over hydrophobic photopolymers because it avoids the use of petroleum-based solvents, which are toxic and flammable.

Analyzed solutions for AA and Bio, whose compositions can be seen in Table 1, are deposited using the force of gravity on a glass substrate (25 cm x 20 cm) and left in the dark (RH = 40–45%, T = 20–23 °C). When part of the water has evaporated (after about 36 hours), the layer has enough mechanical resistance and can be cut without deforming. The final “solid” film has a physical thickness around  $90 \pm 5$   $\mu\text{m}$ . In order to study the influence of the index matching liquid we have used different liquid listed with their respective refractive index in Table 2.

Table 1. Composition of photopolymer AA and BIO, liquid solutions.

Composition name	AA	BIO
NaAO(ml)	-----	3
TEA(ml)	0.5	2.0
PVA (ml) (8% w/v)	25	25
YE (0.8% w/v) (ml)	0.7	0.7
BMA(g)	0.25	0.15
AA (ml)	0.35	-----
Thickness $\pm 4$ ( $\mu\text{m}$ )	85	85

Table 2. Liquid for index matching and their refractive index.

Liquid	A	B	C	D	E
Refractive index	1.520	1.478	1.470	1.451	1.442

To evaluate the influence of the index matching in PVA photopolymers we store diffractive optical elements and study the effects of diffusion after recording with the set up presented in Fig. 2. In order to record phase diffractive gratings we introduced a spatial light modulator (SLM) working in the amplitude only mode to modulate the green beam (532 nm). The materials described in this work are sensitized to the green light and transparent for red light (633 nm). The periodic pattern, sinusoidal-like, is introduced by a liquid crystal display (LCD), a Sony LCD model LCX012BL, extracted from a video projector Sony VPL-V500. We use the electronics of the video projector to send the voltage to the pixels of the LCD. The LCD is used in the amplitude-mostly modulation regime by proper orientation of the external polarizers (P); then the pattern is imaged onto the material with an increased spatial frequency (a demagnifying factor of 2). The use of the LCD allows us to change the period of the grating recorded in the photopolymer without moving any mechanical part of the set-up. Nevertheless the size of the pixel, 42  $\mu\text{m}$ , of this LCD model together with the filtering of the pixelation of the LCD (by stop 2) limits the minimum value of the spatial period in the recording material to 168  $\mu\text{m}$  (i.e. 8 LCD pixels to reproduce a period).

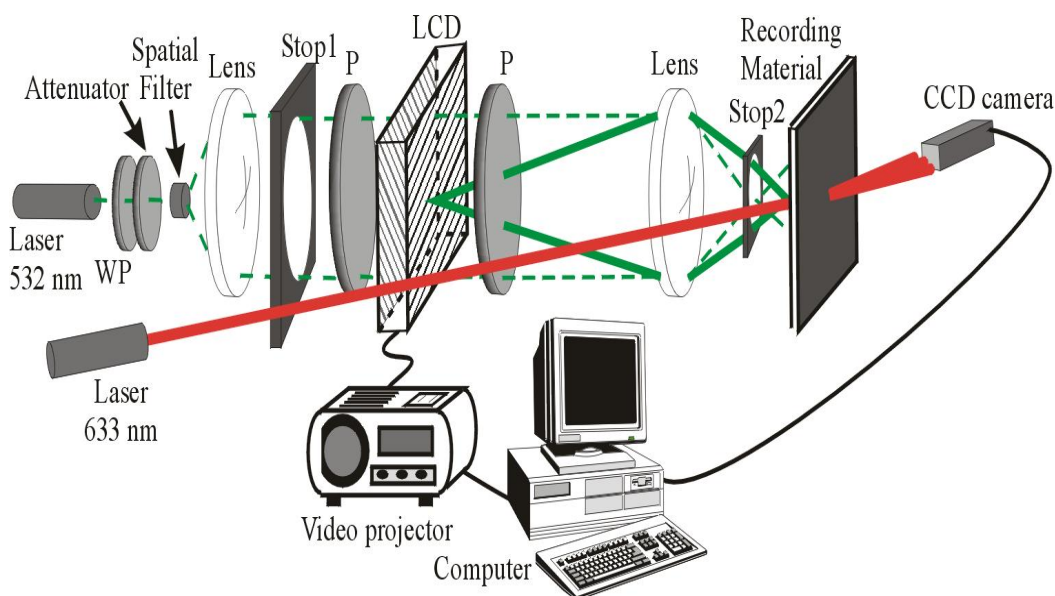


Fig. 1 Experimental setup to record sinusoidal gratings onto the photopolymer using the LCD as a master.

The recording process is presented in Figure 1. In this figure, we show firstly the shrinkage in the illuminated zones mainly due to the polymerization, the material becomes more compact. Secondly, after illumination, the illuminated zones swell due to the “apparent” monomer diffusion. The huge difference between the diffusion times estimated with and without index matching indicates that the changes observed on the surface (surface or “apparent” diffusion) are different than the “real” or internal diffusion. Furthermore, the incorporation of a coverplate and index matching systems improves the conservation and the lifetime of the recorded DOEs [8]. In addition, the reduction of the matter transfer produced by the presence of the sealant can be used to record sharp diffractive optical elements with insignificant smoothing of the refractive index profiles, as we will show in this work.

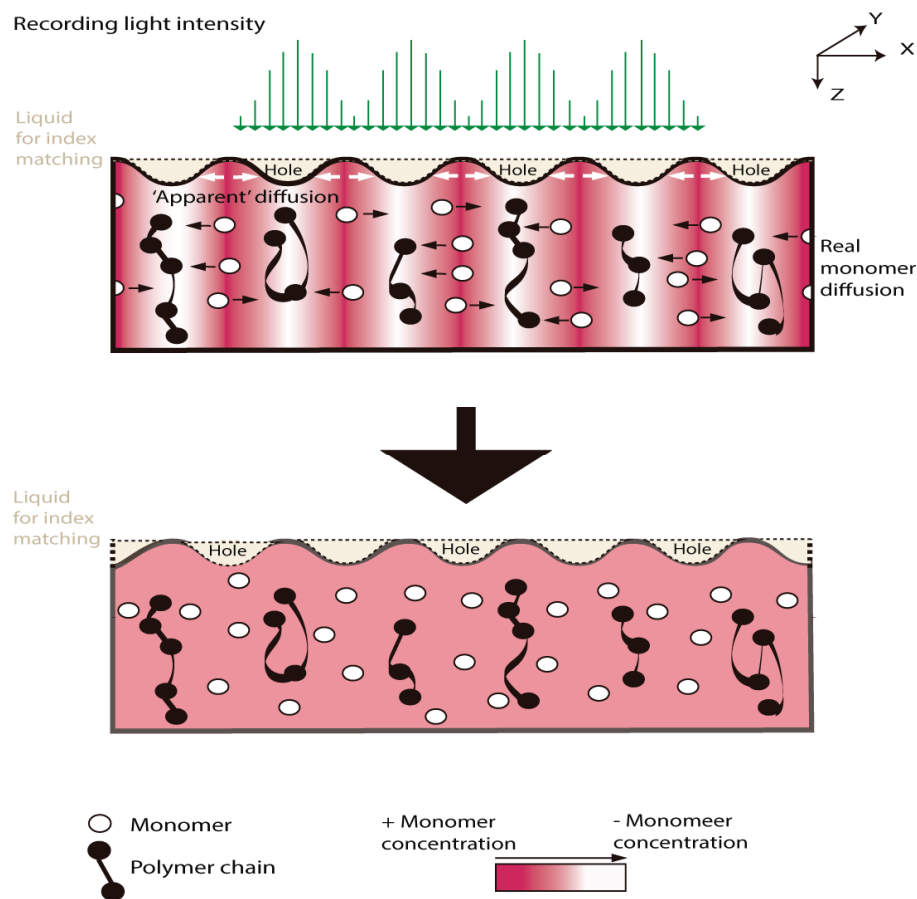


Fig. 2 Diagram of the grating recording in the photopolymers with index matching. The “apparent” diffusion is due to the recovering surface changes and the “real” diffusion is due to the internal monomer motion.

### 3. RESULTS AND DISCUSSIONS

In this section, we present the results of the use of different liquids for index matching the samples. In this sense, we have applied the liquids described in Table 2 to coverplate the photopolymers and to record sinusoidal gratings and blazed gratings. We expect that the liquid fill the grooves generated by the polymerization and help to increase the phase modulation and to improve the recording of sharp phase profiles as blazed gratings [23].

#### 3.1 Acrylamide photopolymer

In a previous studies we have demonstrated as the inclusion of coverplate together with a perfect index matching using glycerin,  $n=1.447$ , or “a body oil for babies” (99% is glycerin [22]) are perfect to be used with PVA/AA photopolymers [21]. In this sense, we present these cases in Fig.3. The Fig.3.a represents the diffraction efficiencies of the main orders during 100s under a sinusoidal pattern illumination and the following 500s of post evolution. The same experiment is depicted in Fig.3.b using liquid B and coverplated. As it can be seen, the higher value of DE of the order 1 is achieved earlier, at 90 s, than the in the non-covered case 450s. This coverplating method increase dramatically the viability to store sharp phase profiles such as blazed gratings as is shown in Fig.4.a and Fig.4.b where are non-covered and covered respectively are shown. It is important to note that in the no covered case, the DE of the order 1 only achieve a DE around 15%, very poor result, nevertheless only including the liquid B and the coverplate this efficiency can arise 60%.

This result is very important taking into account the low pass filtering made by the Stop 2 (see Fig.1) in order to eliminate the pixelation. Therefore, we expect better results just improving the recording pattern. As was discussed by some authors, a good index matching is fundamental technique to fit correctly the internal monomer diffusion in PVA/AA materials [21]. Let us now, have a deep insight in this aspect. We want to analyze the influence of the refractive index of the liquid used in the coverplate method in the post evolution of the diffractive optical element stored in photopolymers and as a consequence in the measurement of the monomer diffusion in the layer. In this sense, with the same PVA/AA material we have studied the response using the liquid of Table 2. Firstly, we have studied the effect of introducing the liquid A, a liquid crystal, Fig.5.a, which average refractive index is 1.52. In this case, it can be seen as the DEs do not keep constant after recording and they vary slowly in comparison with the no-covered case, Fig.3.a, but clearly faster than the case of liquid B, Fig.3.b. This variation can produce an over-estimation of monomer diffusion in this material. Besides, we present also the results using liquid C,  $n=1.470$ , in Fig. 5.b. It can be seen as despite having almost the same refractive index of liquid B, glycerin, there is a variation of DEs after exposure, 100s. That highlights the critical importance of obtaining a perfect index matching in order to characterize the photopolymers with PVA as a binder.

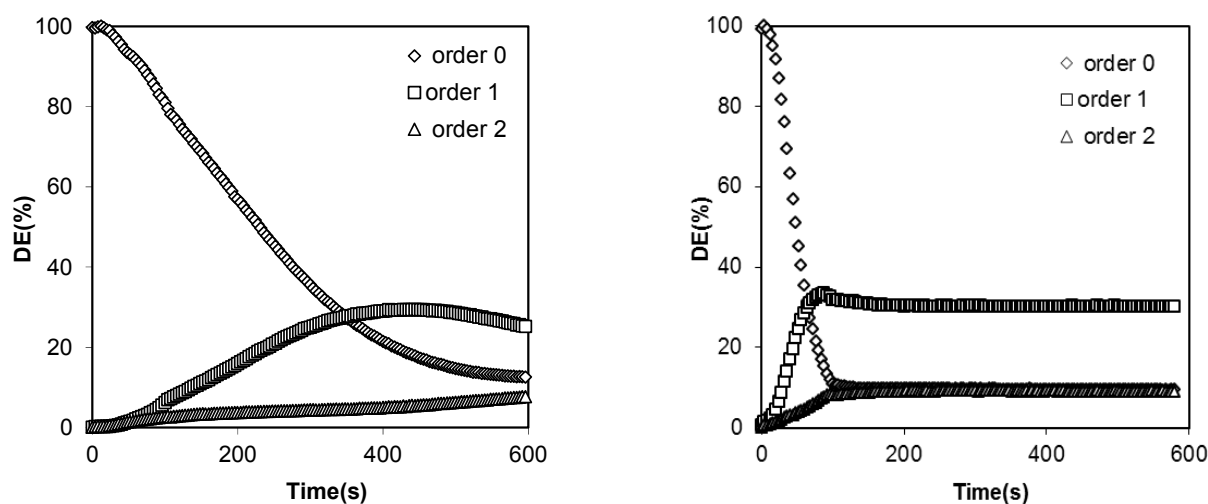


Fig 3. Sinusoidal grating registration during 100s and the post-evolution a) without index matching and b) with liquid B, glycerin.

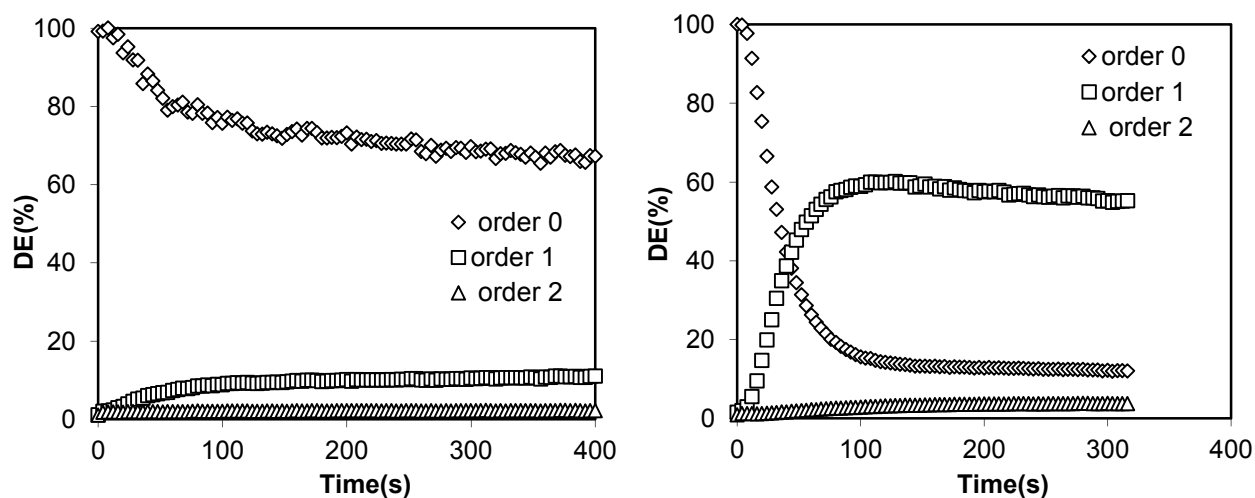


Fig 4. Blazed grating recorded with continuous recording, a) without index matching, b) using glycerin, liquid B, as an index matching agent.

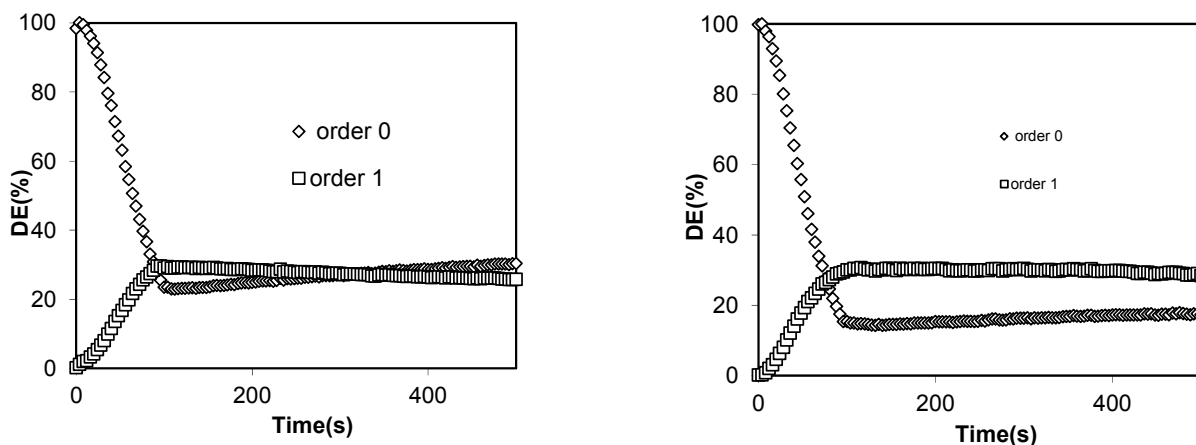


Fig 5. Sinusoidal grating recorded during 100s and the post-evolution using liquid A and liquid C as an index matching agent respectively.

### 3.1 High environmental compatible photopolymer, BIO

As we have related in the introduction, there are many efforts in order to obtain high environmental compatible photopolymers inside the new field of “green chemistry” [20]. In particular, some efforts have been done to substitute acrylamide as main monomer due to its high level of toxicity [20]. One of the first attempts was the introduction of sodium acrylate as a main monomer, using basically the same formulation of PVA/AA (dye, binder, and radical generator). We have used this to analyze how varies the index matching method just changing one component of the chemical composition. In this sense, in Fig. 6.a and in Fig. 7.b we present similar experiments to those shown in Fig. 3, without and with index matching. In Fig 6.a, we can observe similar behavior in BIO and AA polymers, fast DE variations after recording. Nevertheless, in the case of Fig. 6.b, it is important to note that DEs do not keep constant after recording using liquid B as index matching. In order to check the origin of these variations, maybe a higher diffusion or a wrong index matched agent, we have performed the same experiments using liquids D, A, C and E (Figures 7.a, 7.b, 8a, 8b respectively). From these data, we can extract that the best index matching is achieved with liquid C,  $n=1.470$ , therefore, the average refractive index of the layer is slightly lower in the case of BIO in comparison with AA. In addition, it is important to note the rapid reaction observed when liquid A, liquid crystal, is introduced as an index matching agent. Further investigations are being developed in this sense to analyze this surprising effect. We know that the presence of high refractive index liquid to coverplate and the filling of the grooves formed by polymerization can increase the phase modulation, but it looks so huge. Besides, this is also interesting because if we confine the liquid crystal in the polymerization zones a tunable diffractive optical element can be fabricated [12]. On the last place we present the influence of the index matching on the recording of blazed gratings, where we proof the improving in the results using this method. In Fig. 9 a diffraction around 60% is observed during recording of a blazed grating using index matching with liquid C.

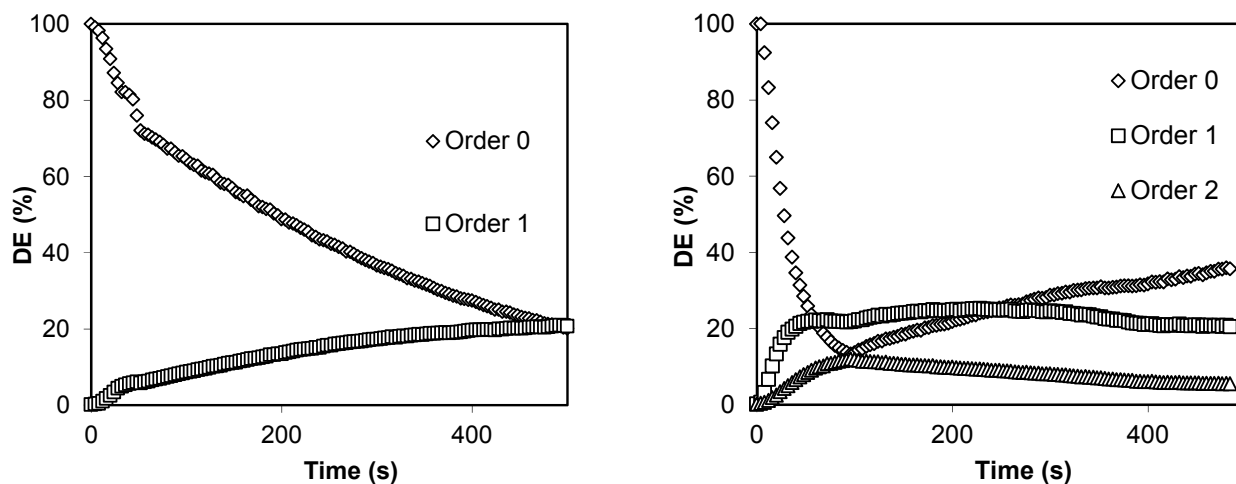


Fig 6. Sinusoidal grating, recorded during 100s and the post-evolution in BIO material A) no-covered material, b) material using liquid B as an index matching agent.

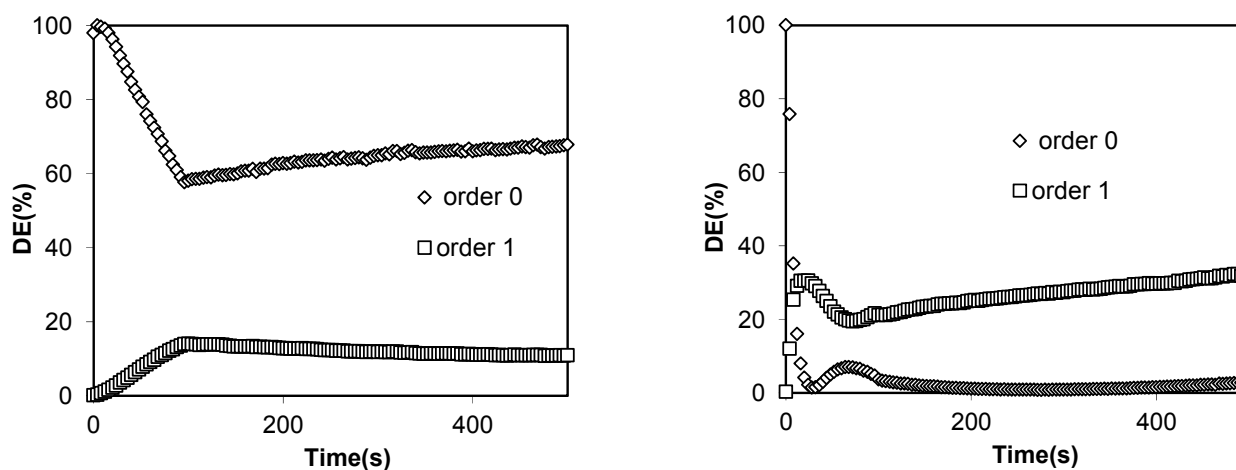


Fig 7. Sinusoidal grating recorded during 100s and the post-evolution in BIO material using liquid D and liquid A as an index matching agent respectively.

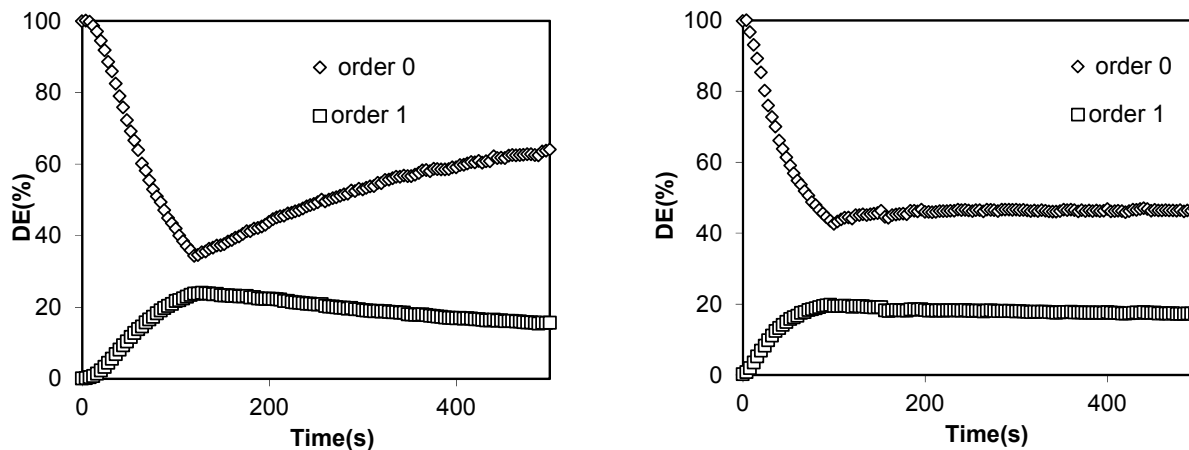


Fig 8. Sinusoidal grating recorded during 100s and the post-evolution in BIO material using liquid C and liquid E as an index matching agent respectively.

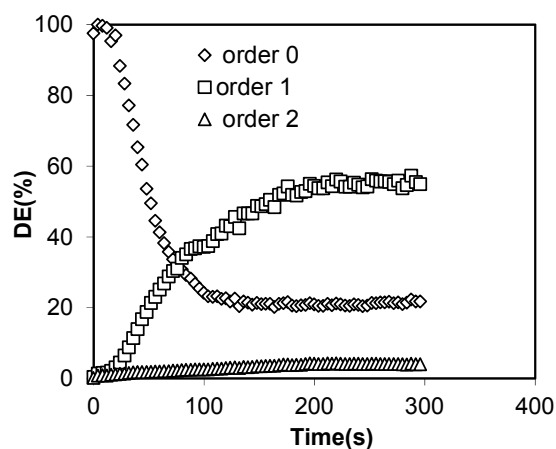


Fig 9. Blazed grating during continuous recording for BIO material using liquid C as index matching agent.

#### 4. CONCLUSIONS

Along this paper we have studied the influence of the index matching refractive index on the recording of DOE, in particular sinusoidal and blazed gratings. Two different photopolymers have been analyzed, AA and BIO. For the first one glycerin with  $n=1.477$  is a perfect index matching agent, and for the second one, the best results were obtained with a liquid with  $n=1.470$ . We have demonstrated as an incorrect index matching process can origin a miscalculation in the monomer diffusion in PVA materials due to the variations on the DE after recording. We have shown how with index matching DE higher than 60% can be achieved. Further experiments can be performed in order to study the viability of the index matching with liquid crystal to obtain higher values of phase modulation and tunable DOEs.

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