

# Linear response deviations during recording of diffraction gratings in photopolymers

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**Abstract:** In a holographic recording is advisable that the diffraction efficiency increases linearly with the exposure in a wide zone of the curve of diffraction efficiency versus energetic exposure and the slope of the curve must be approximately constant before saturation in order to improve the energetic sensitivity and to get reproducibility in different recordings with the same kind of photopolymer, although to find examples of deviations to this behavior it is usual. The more important deviation experimentally observed in photopolymers with high thickness happen when the first maximum in the curve is lower than the second one. This effect is opposed to an overmodulation. We present a main hypothesis related to the dye concentration into the layer and with the molecular weight of the polymer chains generated in the polymerization process in order to explain this effect.

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## 1. Introduction

Acrylamide (AA) photopolymers with a poly(vinyl alcohol) (PVA) binder are very versatile holographic recording materials [1]. Their most important characteristics include high diffraction efficiency, ease of preparation and the fact that they do not need post-processing after the hologram has been recorded [2]. These properties make them very suitable for studying factors relating to the process of hologram recording, or changes in the photopolymer composition. Recently, acrylamide based photopolymers have been developed in 1 mm thick layers by our research team, and these are ideal for use as recording medium in studies relating to hologram recording process [3,4].

The photopolymer used in this study is composed of acrylamide as polymerizable monomer, triethanolamine as radical generator, yellowish eosin as sensitizer and a binder of PVA [3]. We analyze the holographic behavior of the material during recording of diffraction gratings using a continuous argon laser (514 nm) at an intensity of 5 mW/cm<sup>2</sup> as recording laser. The response of the material is monitored with an He-Ne laser. We study the recording process of diffraction gratings of 1125 lines/mm, in 700-900 μm photopolymer thick layers with PVA M<sub>w</sub> = 130000 u binder.

The acrylamide photopolymers with poly(vinyl alcohol) binder are a very versatile materials in the preparation of solid layers with different thickness [5]. The diffraction gratings with relatively low thickness, registered in these materials show a behavior as volume gratings. We obtain the same behavior for high thickness around 1 mm. The refractive index modulation is proportional to the energetic exposure in these cases and Kogelnik's coupled wave Eqs. are valid during recording stage. The curve of diffraction efficiency versus energetic exposure must have a wide linear zone with an approximately constant slope before saturation in order to improve the energetic sensitivity in a hologram recording and to get reproducibility in different recordings with the same kind of photopolymer. Nevertheless it is possible to find examples of deviations to this behavior [3,6,7].

In this investigation, we study different cases in which there are deviations to this behavior, proposing different hypothesis in order to explain the situations that can be experimentally obtained. A main hypothesis related to Kogelnik's theory is presented and the experimental results obtained are according to the theory.

## 2. Preparation of the material

In recording materials based on PVA/AA, a solution of PVA in water forms the matrix and this is used to prepare the solution of monomer AA and the photopolymerization initiator system: yellowish eosin (YE), triethanolamine (TEA). The PVA was supplied by Fluka, AA and TEA by Sigma and YE by Panreac.

We prepare the solutions using a conventional magnetic stirrer, under red light and in laboratory conditions (T = 20 °C, relative humidity = 45%). In Table 1 it can be seen the concentrations of the components in the optimized photopolymer solution which is deposited in order to obtain solid layers of recording media [3]. The solutions are deposited by gravity, in polystyrene circular molds to avoid strain and distortion in the material during the water evaporation process, and left in the dark to allow the water to evaporate, while recording the laboratory conditions (T, relative humidity) during the process. When part of the water has evaporated, the “dry” material is removed from the mold, cut into squares and adhered, without adhesive, to the surface of glass plates measuring 6.5 × 6.5 cm<sup>2</sup>. The plates are then ready for exposure, which takes place immediately. The thickness of the material is measured using a conventional micrometer.

**Table 1. concentrations of the components of optimized photopolymer solution**

Component	Concentration
Poly(vinyl alcohol) $M_w = 130000$ u	13.30% w/v
Triethanolamine	0.15 M
Acrylamide	0.34 M
Yellowish eosin	$9.00 \times 10^{-5}$ M

### 3. Holographic set-up

To study the behavior of the photopolymer as a holographic recording material, we obtained unslanted diffraction gratings using a holographic set-up. The experimental device is shown in Fig. 1. An Argon laser at a wavelength of 514 nm was used to store diffraction gratings by means of continuous laser exposure. The laser beam was split into two secondary beams with an intensity ratio of 1:1. The diameters of these beams were 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  $\theta$  ( $16.8^\circ$  to the normal) with an appropriate set of mirrors, and the spatial frequency obtained was 1125 lines/mm. The working intensity at 514 nm was  $5 \text{ mW/cm}^2$ . The diffracted and transmitted intensity were monitored in real time with a He-Ne laser positioned at Bragg's angle ( $\theta' = 20.8^\circ$ ) tuned to 633 nm, where the material is not sensitive. The diffraction efficiency (DE) was calculated as the ratio of the diffracted beam to the incident power.

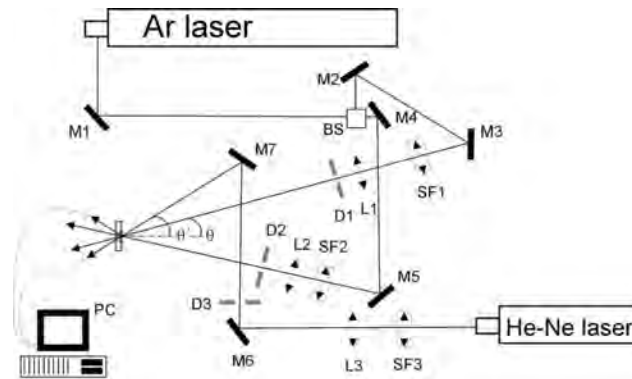


Fig. 1. Experimental set-up: BS, beamsplitter, Mi, mirror, SFi, spatial filter, Li, lens, Di, diaphragm, PC, data recorder.

### 4. Planning the problem

The experimental data obtained for a  $750 \mu\text{m}$  photopolymer layer with an estimated theoretical adjust by Kogelnik, Eq. (1), are shown in Fig. 2 [7].

$$DE(t) = \frac{I_D}{I_0} = \Gamma \sin^2 \frac{\pi n_1(t)d}{\lambda' \cos \theta'_i} \quad (1)$$

In this Eq.  $\Gamma$  is the absorption, diffusion and reflection losses factor.  $\theta'_i$  is the reconstruction beam angle (Fig. 1), measured into the material, which is calculated with refraction Snell law.  $\lambda'$  is the reconstruction beam wavelength.  $n_1(t)$  is the refraction index modulation and  $d$  is the diffraction grating thickness [8].

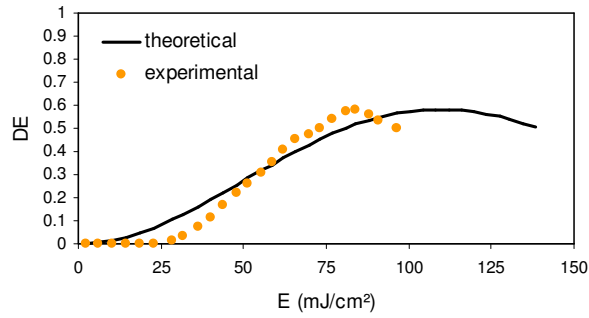


Fig. 2. Diffraction efficiency versus exposure for a 750  $\mu\text{m}$  photopolymer layer.

It is shown that the behavior of the photopolymer layer is very close to theory, specially in reference to the shape of the diffraction efficiency development during recording except by some details as induction period or inhibition at start of record, factors that are not included in the theoretical expression [6]. In the theoretical adjust the coefficient  $\Gamma$  is constant during the recording and the  $n_1(t)d$  product is proportional to energetic exposure.

In layers with high thickness, an index refraction overmodulation due to the quick raising of  $n_1(t)d$  product [9,10] it is easy to see in some recordings. The Fig. 3 shows an example of refraction index overmodulation in a 1000  $\mu\text{m}$  photopolymer layer and the theoretical adjustment by Eq. (1) considering the inhibition effects at the start of recording and a linear decreasing of the  $\Gamma$  coefficient that is equivalent to an increase of the losses by light diffusion proportional to the index refraction modulation [15].

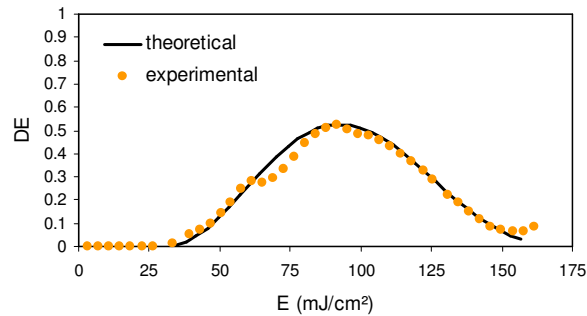


Fig. 3. Diffraction efficiency versus exposure for a 1000  $\mu\text{m}$  photopolymer layer with refraction index overmodulation.

In a recording as in Fig. 2, the curve of diffraction efficiency versus energetic exposure has a linear zone with constant slope at around 50% of the maximum diffraction efficiency as it can be seen in Fig. 4, which belong to record stage of a diffraction grating in a 700  $\mu\text{m}$  photopolymer layer.

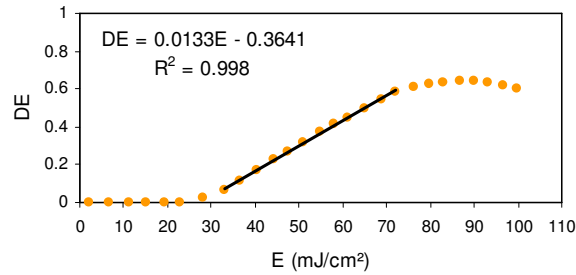


Fig. 4. Diffraction efficiency evolution during recording for an ideal situation in a 700  $\mu\text{m}$  photopolymer layer.

This behavior is desirable in most cases because implies a proportional evolution of diffraction efficiency with energy supplied to the photopolymer, and this is very useful to improve the energetic sensitivity and the reproducibility in the practical applications for these materials, for example in recording of holographic optical elements [11]. This type of behavior has occasionally some deviations, therefore in some cases it is not possible to obtain this linear relation, as in A, B and C curves in Fig. 5 for a 900  $\mu\text{m}$  photopolymer layer.

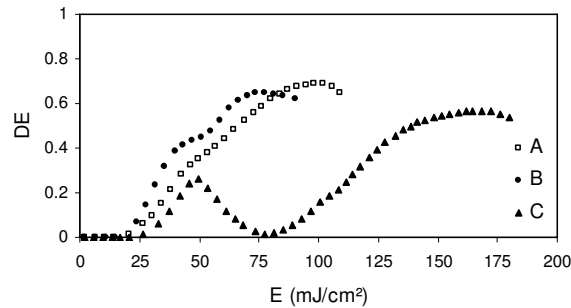


Fig. 5. A, Decrease of the slope with an inflection point in the curve. B, decrease of the slope with a transition zone. C, graph with a maximum lower than  $\eta_{\text{max}}$ . Hologram recordings in 900  $\mu\text{m}$  photopolymer layers.

“A” curve correspond to an example of slope change during recording, in this case, for 50  $\text{mJ}/\text{cm}^2$  exposure the slope decreases up to saturation. This behavior could imply a polymerization rate decreasing and could be explained by photopolymer properties change during recording, for example, with an increase of the media viscosity, which produces a slow down of the molecular movements [12,13].

A more extreme situation is for “B” curve, with a transition zone, that it could be a “plateau”, where DE is constant when the exposure increases. This case has no sense with previous explanation, since subsequently the slope is recovered, so in case of photopolymer properties change, due to polymerization, the slope couldn’t increase again because the increase of the media viscosity is proportional to the polymerization progress.

The “C” curve is another different situation that it must not confused with a refraction index overmodulation as in Fig. 3. In this case, the curve has a zone in which the diffraction efficiency decreases (in this example down to  $\text{DE} \approx 0$ ) before an later increasing up to saturation.

These three examples could be the same phenomenon. Thus, this behavior could be explained by several hypothesis:

Hypothesis 1. For A, B or C curve the refraction index modulation increases with the energetic exposure at the start of recording. At the same time, the diffusion of polymer chains

towards non exposed zones could decrease the refraction index modulation and therefore to produce the decreasing of the diffraction efficiency before the maximum diffraction efficiency is reached. But this is not possible in this photopolymer formulation because the diffusion coefficients of the polymer chains are not high enough to allow a quick migration to non exposed zones during recording. Moreover the diffraction efficiency after recording could decrease quickly around zero and it has not been observed [14].

Hypothesis 2. Another explanation is also based in diffusion phenomena and it considers the influence of monomer concentration modulation in the refraction index modulation. The monomer diffuses from non-exposed zones to exposed zones, where the polymerization takes place and it could imply an additional increase of the refraction index modulation [15].

## 5. Results

We have revised about 300 holograms registered in around 1000  $\mu\text{m}$  layers of PVA/AA photopolymer made at our laboratory in the last years, in order to check the experimental conditions of the recordings. The C curve type as in Fig. 5 is mainly obtained when the dye concentration is lower than the optimum and when the layers are not completely dry. This last situation is equivalent to a low dye concentration due to the water of the layer has not completely been evaporated and therefore the dye concentration is lower than expected [3].

When the monomer concentration is very high these deviations are also obtained and the curves have more relative maximums. This have been observed by C. García et al. in PVA/AA photopolymer layers with 150  $\mu\text{m}$  thickness [16].

We make three photopolymerization experiments without register diffraction gratings, simplifying the experimental set-up in order to check the diffusion hypothesis and the dye concentration relationship.

### Experiment 1

The experimental set-up is simplified in this experiment. We use only one argon laser beam (514 nm) to avoid a possible effect of diffusion between zones with different concentration. For this one beam exposure, a layer without glass support is placed perpendicular to the beam. Now, there is not a fringe structure in the photopolymer, the monomer and polymer concentrations are homogeneous in the exposed zone and therefore the diffusion effects are not possible. The Fig. 6 shows that the transmitted intensity is increased with the energetic exposure due to the decreasing of the dye concentration.

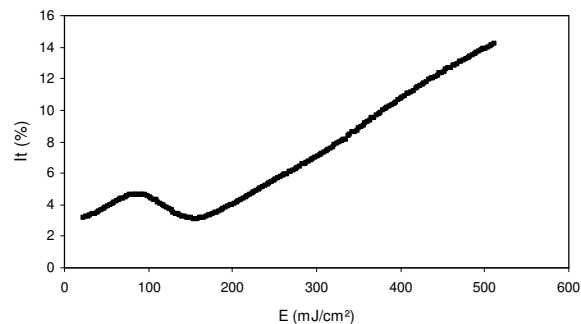


Fig. 6. one beam recording in a photopolymer layer without glass plate.

At the start of the recording there is a deviation of the linear response that produces a relative maximum in the graph. As in this experiment the diffusion effects are not possible the diffusion hypothesis can be ruled out.

The exposure to the green light produces a decreasing in the dye concentration which implies a progressive decreasing in the photopolymer absorption and a higher transmission. At

the same time the polymerization of the monomer increases the light diffusion that produces a decreasing in the transmission. The last effect is less important than the increase of transmission by the decrease in dye concentration except at the start of recording where the combination of both effects produces the relative maximum. It is important to see that the deviation of the linear response occurs at the start of recording as in the C curve in Fig. 5 which is we want to explain.

### Experiment 2

We use now a 633 nm reconstruction beam and one 514 nm beam in the standard experimental set-up. A 1 mm thick photopolymer layer is used without glass plate to simplify the system. In Fig. 7, the 514 nm curve shows the transmission intensity percentage at 514 nm multiplied by five to compare both curves. This curve produces the same effect showed in the experiment 1. The 633 nm curve shows the transmission intensity percentage at 633 nm.

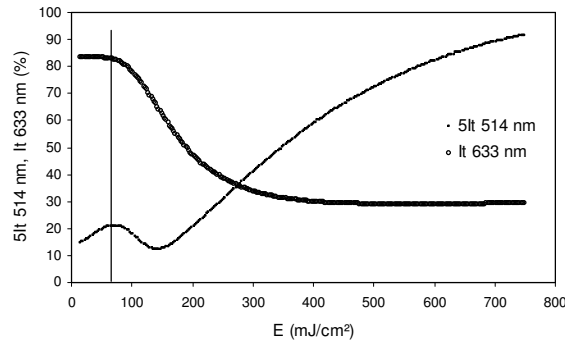


Fig. 7. one beam recording in a photopolymer layer without glass plate.

In the 633 nm curve, the transmission is constant at the start of recording because the dye does not absorb light at that wavelength. For the 514 nm curve, the transmission increases at the start because the dye concentration is reduced by the photopolymerization. When  $E = 65 \text{ mJ/cm}^2$ , the transmission intensity is maximum  $5It = 21\%$ , the dye concentration is decreasing more but now the transmission at 633 nm decreases by the light diffusion produced by the polymer chains. It can be seen that the start of decreasing of  $It_{633 \text{ nm}}$  match up with the maximum in  $It_{514 \text{ nm}}$  which implies a decreasing in  $It_{514 \text{ nm}}$  to a minimum value ( $5It = 12\%$ ,  $E = 145 \text{ mJ/cm}^2$ ). From this minimum value, the predominant effect is the increase in transmission due to the decreasing in the dye concentration.

The  $It_{514 \text{ nm}}$  variation between the relative maximum and the minimum is  $\Delta It_{514} = 1.8\%$ .  $It_{514 \text{ nm}}$  reaches  $16.4\%$  at  $600 \text{ mJ/cm}^2$ . The deviation of the linear response occurs at the start of recording.

### Experiment 3

We repeat the same experiment 2 but with a photopolymer layer with  $1/3$  in dye concentration, Fig. 8. Now the 514 nm curve shows a higher amplitude in the transmission intensity variation at the start of recording and a minor transmission at the end of recording. The  $\Delta It_{514} = 9.0\%$  at the relative maximum and  $It_{514 \text{ nm}}$  reaches  $6.4\%$  at  $600 \text{ mJ/cm}^2$ . This result is due to a minor dye concentration and therefore the dye concentration cannot decrease as in the experiment 2 when the energetic exposure increases. The dye concentration reaches a minimum value at the start of recording and produces a more pronounced effect in the light transmission.

In the other hand, the light diffusion ( $\Delta R_0$  Eq. (2)) is higher than in the experiment 2 because now the dye concentration is low and the polymer molecular weight ( $M_w$ ) is high

due to the decreasing in the chain starting moieties number caused by the low dye concentration [12].

The light diffused by a polymer solution with a molecular weight  $M_w$  can be expressed by Eq. (2), where: polymer concentration ( $c$ ), light diffusion angle ( $\theta$ ), solution refraction index ( $n$ ), incident light wavelength ( $\lambda_0$ ), polymer chains mean quadratic radius ( $R_G^2$ ), system optics characteristics constant ( $K$ ) and  $A_2, A_3, \dots$  are the virial coefficients [17,18].

The polymer rayleigh relation ( $\Delta R_\theta$ ) is proportional to the diffused light at  $\theta$  angle divided by incident light. Polymer chains with high  $M_w$  have a high  $\Delta R_\theta$  and thus the light diffusion is also high.

$$\frac{K c (1 + \cos^2 \theta)}{\Delta R_\theta} = \frac{1}{M_w} + \frac{16\pi^2 n^2}{3\lambda_0^2 M_w} R_G^2 \text{Sen}^2 \frac{\theta}{2} + 2A_2 c + 3A_3 c^2 + \dots \quad (2)$$

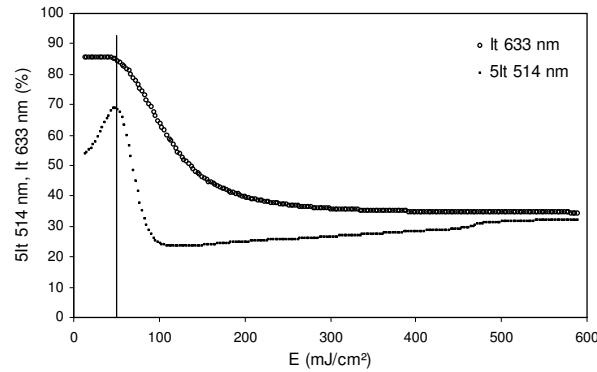


Fig. 8. one beam recording in a photopolymer layer without glass plate, 1/3 dye standard concentration.

With the limitation in the dye concentration, the predominant effect is the light diffusion by the polymer chains and therefore the  $I_t$  514 nm is lower than in a standard dye concentration ( $I_t = 6.4\%$  at  $600 \text{ mJ/cm}^2$  experiment 3 versus  $16.4\%$  experiment 2).

We can deduce from these experiments that the particular deviations to the photopolymer response are produced without polymer diffusion effects, and they are related with the dye concentration.

In hologram recording, a low dye concentration implies a high grating thickness because the light reaches deeper zones in the photopolymer layer due to the high light transmission [8]. By the other hand, a low dye concentration also implies a lower starting polymer chain moieties number  $\gamma$  therefore polymer chains with higher molecular weight [12]. Thus, the photopolymer reaches a higher index refraction modulation and grating thickness with a lower exposure, at the start of recording. In this situation, the factor  $n_1(t)d$  from Eq. (1) must be very high at the start of recording and after increases slowly. We introduces these considerations in Eq. (1) in order to check if the theoretical expression offers a result according to experimental results in the low dye concentration cases.

In order to simulate theoretically a hologram recording in a low dye concentration photopolymer we consider the  $n_1(t)d$  product very high at the start of recording and after an increasing evolution proportional to exposure as the indexmodul curve shows in Fig. 5. The indexmodul curve is  $5 \times 10^5(n_1(t)d)$  to compare the graphs. We also consider increasing light looses depending on exposure, thus the  $\Gamma$  factor decreases proportional to exposure [19]. DEsimulation is the diffraction efficiency calculated with Eq. (1).



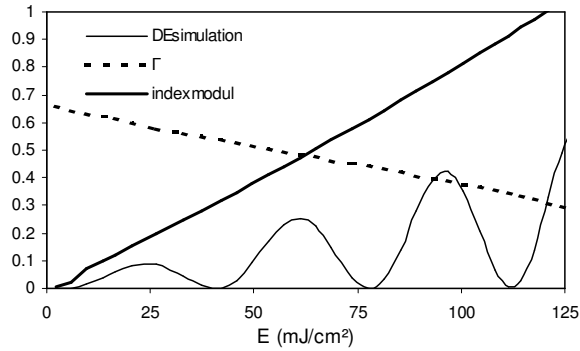


Fig. 9. Low dye simulation by Eq. (1). DEsimulation = diffraction efficiency obtained with Eq. (1),  $\Gamma$  decreases proportional to refraction index modulation,  $\text{indexmodul} = 5 \times 10^3(n_1(t)d)$ ,  $n_1(t)d$  has a light deviation at the start of recording from linear increasing proportional to E.

In DEsimulation it can be seen as the first maximum is lower than the second one and so on. The more important of this simulation is that the relative maximums are increasing progressively with the exposure, which is according to the experimental results with a low dye concentration in which the second maximum is higher than the first one (C curve in Fig. 5).

## 6. Conclusion

Different cases where there are deviations to ideal behavior during recording of diffraction gratings in photopolymers have been analyzed. The more important deviation experimentally observed and not explained to date is when the first maximum is lower than the second one in the diffraction efficiency versus exposure curve during recording. We check that this situation occurs experimentally when the dye concentration in the photopolymer is lower than the optimum value.

The experiments made with an one beam exposure show that there are not implied diffusion effects. In the other hand, these experiments prove that the linear deviations are related to the dye concentration. The dye concentration in the photopolymer layer is related to the polymer chains molecular weight and therefore to light diffusion, but also, in a hologram recording, with the grating thickness and with the index refraction modulation capacity of the material.

In a hologram recording with a photopolymer layer with low dye concentration, a high index refraction modulation and high grating thickness are produced at the start of recording and thus the  $n_1(t)d$  product is very high. After, the index modulation and grating thickness increases proportionally to exposure. This produces a first peak with lower diffraction efficiency than the second one in the response curve of the photopolymer. The theoretical simulation by Kogelnik's Eq. with these considerations offers a result according to the experimental.

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