NON-LINEAR RESPONSE OF PHOTOPOLYMERS FOR REAL-TIME HOLOGRAPHY: COPOLYMERIZATION PROCESS

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ABSTRACT

A model is proposed which would allow us to justify and obtain the diffraction efficiency of photopolymeric materials with a non-linear response to the refraction index, using as a base the equations on the evolution of co-polymerization reactions. The photochemical material being analyzed can be optimized by correctly selecting the model's parameters.

Processes based on the light-induced polymerization of monomers are currently used in the curing of inks, coatings, printing plates, electronic integrated circuitry, optical data storage, microlithography, stereolithography, and Holography. Photopolymers are considered to be one of the most promising recording materials for Holography because with them it is possible to achieve high diffraction efficiencies and low signal-to-noise ratios while working in real time [1]. Moreover, they are self-developing mediums. Photopolymer materials have potential for use in optical interconnect applications and high-density optical storage [2]. Holographic photopolymer systems basically consist of a monomer, or a mixture of monomers, and a photoinitiator. Upon radiation, active species, radicals or ions are produced which initiate the polymerization chain reaction, with selective conversion of monomers into polymers in the irradiated areas. In this way it is possible to obtain refractive index modulations, and then photopolymers are capable of forming volume phase holograms.

In this letter we describe and analyze the non-linear response of holographic photopolymers formed with a mixture of two monomers, i.e., when copolymerization processes are considered. Up to now, a linear relation between exposure and the refraction index modulation was believed to exist [3]. However we believe that this relation is non linear. Previous studies have shown that this non-linear relationship is possible, but the relation between the photochemical reaction and its form has not been justified [4].

In a photopolymer system exposure to the holographic interference pattern modulates the refractive index n of the material, in accord once the

Lorentz-Lorenz relation, and for a photosensitive material whose N components form an ideal compound it is possible to write the following equation [5]:

$$\frac{n^2(t) - 1}{n^2(t) + 2} = \sum_{i=1}^N R_i A_i(t) \quad (1)$$

where $n(t)$ is the refraction index as a function of time, R_i is the molar refraction of the i -th component and $A_i(t)$ is the concentration of the A component at the time of " t ".

The majority of photopolymerizable systems that are currently used as holographic recording materials are made up of more than one monomer and these systems are based on copolymerization phenomena. In these cases it is possible to obtain greater index modulations as well as improved energetic sensitivity.

If the system has two monomers, A and B , which are transformed into polymer C , by a copolymerization reaction initiated by the absorption by the sensitizer of at least one photon, the following will be true:

If $A(t)$, $B(t)$ y $C(t)$ are the concentrations of components A , B y C , respectively, at the time of t , the overall change in the concentrations of A and B with time can be given simply by the rate equations:

$$-dA(t)/dt = k_{AA} A(t) + k_{AB} B(t) \quad (2)$$

$$-dB(t)/dt = k_{BA} A(t) + k_{BB} B(t) \quad (3)$$

Furthermore, $A(t) + B(t) + C(t) = A_0 + B_0$ where $A_0 = A(0)$ and $B_0 = B(0)$ will be true when $t = 0$. In equations (2) and (3), k_{ij} are the overall reaction rates. Constants k_{AA} y k_{BB} are related to the polymerization processes of components A and B, respectively, while constants k_{AB} y k_{BA} refer to the copolymerization processes of A with B. With the integration of equations (2) and (3), using equation (1), it is possible to obtain the refractive index as:

$$n(t) = [(2H - 1)/(1 - H)]^{1/2} \quad (4)$$

where:

$$H(t) = R_A A(t) + R_B B(t) + R_C C(t) \quad (5)$$

and:

$$A(t) = -[(m_1 + k_{BB}) q_1 \exp(m_1 t) + (m_2 + k_{AA}) q_2 \exp(m_2 t)] \quad (6)$$

$$B(t) = q_1 \exp(m_1 t) + q_2 \exp(m_2 t) \quad (7)$$

$$C(t) = A_0 + B_0 - A(t) - B(t) \quad (8)$$

being: $q_1 = B_0 - q_2$ and $q_2 = -[k_{BA} A_0 + (m_1 + k_{BB}) B_0]/(m_2 - m_1)$.

$$m_1$$

$$= -(k_{AA} + k_{BB}) \pm [(k_{AA} - k_{BB})^2 + 4 k_{AB} k_{BA}]^{1/2} \quad (9)$$

$$m_2$$

where the upper sign corresponds to m_1 and the lower sign corresponds to m_2 . If we define the refractive index modulation as $\Delta n(t) = n(t) - n_0$, where n_0 is the initial refractive index, refractive index modulation will be a function of:

$$\Delta n(t) = f(A_0, B_0, k_{AA}, k_{BA}, k_{AB}, k_{BB}, R_A, R_B, R_C; t) \quad (10)$$

This refractive index modulation has been plotted in Figure 1 for the following values of the parameters: $A_0 = B_0 = 1 \text{ mol}$, $k_{AA} = k_{BB} = 0.001 \text{ s}^{-1}$, $k_{BA} = k_{AB} = 0.00014 \text{ s}^{-1}$, $R_A = 0.24 \text{ dm}^3$, $R_B = 0.05 \text{ dm}^3$, $R_C = 0.15 \text{ dm}^3$.

where exposure is given by $E = I \times t$, I being the incident irradiance and t the exposure time. As can be seen, a clear non-linear relation is established between exposure and the modulation index.

We consider that volume-phase transmission holographic gratings are stored in real time in photopolymers, for which the diffraction efficiency DE is [6]:

$$DE = \sin^2[\pi d \Delta n(t) / \lambda \cos \theta] \quad (11)$$

where λ is the readout wavelength, d is the thickness of the hologram, and θ is the Bragg angle. Figure 2 shows the DE for the parameters considered in Figure 1 and for a transmission holographic grating with $d = 45 \text{ }\mu\text{m}$, $\lambda = 633 \text{ nm}$, and $\theta = 15^\circ$. This Figure shows that, DE does not have a periodic response as predicted by Kogelnik's theory [6] when Δn is a linear function of exposure

because the behavior of the modulation index is non-linear. At high exposures, DE remains constant. Eq. (10) and (11) indicate the existence of a clear relation between composition and the properties of the materials on one hand, and the DE obtained on the other. Likewise, it allows for the optimization of the material according to its composition, quantum yield and irradiance intensity. The form and behaviour of the diffraction efficiency shown in Figure 2 which was calculated using the theoretical model we have described here is similar to the diffraction efficiencies obtained experimentally with polymers made up of two monomers [7].

In summary, using Kogelnik's DE equation for volume-phase transmission holographic gratings, and introducing the non linear response of refractive index modulation caused by changes in concentration photopolymerization reactions, we have shown that photopolymerizable materials have non-linear behaviour when working in real time Holography.

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FIGURE CAPTIONS

Figure 1.- Modulation index as a function of time exposure.

Figure 2.- Diffraction efficiency as a function of time exposure.

FIG. 1

Fig. 2