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Authors(s)	Gleeson, M. R., Kelly, John V., Close, Ciara E., Sabol, Dušan, Sheridan, John T.
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Holographic Grating Evolution in Photopolymer Materials

Michael R. Gleeson, John V. Kelly, Ciara E. Close, Dusan Sabol, John T. Sheridan*

UCD School of Electrical, Electronic and Mechanical Engineering,

College of Engineering, Mathematical and Physical Sciences,

University College Dublin, Belfield, Dublin 4, Republic of Ireland.

*Corresponding Author: e-mail: john.sheridan@ucd.ie

Tel: +353-1-716-1927; Fax: +353-1-283-0921

Abstract: A generalized non-local polymerization driven diffusion (NPDD) model is presented, including the effects of absorption and inhibition. Experimentally obtained growth curves are fit using a four-harmonic numerical fitting algorithm and key material parameters are extracted.

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1. Introduction

To obtain the full potential of photopolymer materials for holographic data storage requires quantitative insight into the processes present during gratin fabrication. Developing accurate theoretical models, which are validated using reproducible experimental data sets, will allow crucial material parameters to be identified and controlled. A study of the photochemical kinetics involved during holographic recording in our Acrylamide (PVA/AA) based photopolymer has been presented previously [1,2]. Our specific aim is to increase our understanding of what takes place inside the photopolymer material during exposure, i.e. to explain the effects of the variation of the absorbance of the photosensitive dye with time [3-5], and the suppression of monomer radical production due to the presence of inhibitors [5-7]. We thus aim to extend the validity of our Non-Local Photopolymerization Driven Diffusion (NPDD) model [8-12], based on a deeper understanding of the photochemical and mass transport effects.

2. Theory

Using standard notation, the steady state assumption for radical concentration can be given by [2],

$$d[M^\bullet]/dt = R_i - 2k_t[M^\bullet]^2 - k_z[Z][M^\bullet] = 0. \quad (1)$$

where $[M^\bullet]$ is the monomer radical concentration, R_i is the rate of production of monomer radicals, k_t is the rate of polymer chain termination, k_z is the rate constant for the inhibition process and $[Z]$ is the concentration of inhibiting species. If it is assumed that much more monomer is consumed due to polymerization than is consumed in the initiation reaction, then the rate of polymerisation R_p can be given as,

$$R_p \cong -d[M]/dt = k_p[M^\bullet][M], \quad (2)$$

where k_p is the propagation rate constant. It is difficult to measure the concentration of monomer radicals, $[M^\bullet]$ therefore we eliminate $[M^\bullet]$ from Eq. (1) using Eq. (2) and rearrange giving [12]

$$\frac{2R_p^2k_t}{k_p^2[M]^2} + \frac{R_p[Z]k_z}{k_p[M]} - R_i = 0. \quad (3)$$

Solving the quadratic equation in Eq (3) for R_p , and choosing the root which was physically reasonable, gives

$$R_p = \left(k_p/4k_t\right)[M] \left(\sqrt{8k_tR_i + k_z^2[Z]^2} - k_z[Z] \right). \quad (4)$$

Formation of monomer radicals are dependent on the quantity of free radicals formed per photon absorbed and the intensity of the light used for recording. The inhibitor present indirectly consumes some of the absorbed photons resulting in a reduction in the number of free radicals available for the initiation of monomer radicals and thus for the formation of polymer chains. Thus the rate of initiation, R_i can be given by

$$R_i = f \left(\Phi' - R_p' \right) I_a(t), \quad (5)$$

where Φ' is the number of radicals produced per photon absorbed, f is a constant, R_p' is the number of radicals removed per photon absorbed due to the presence of inhibitor and $I_a(t)$ is the intensity of light absorbed in moles of

light quanta per litre per second [5,11]. We assume co-sinusoidal spatially modulated illumination, $I(x) = I_0^\gamma [1 + V \cos(Kx)]^\gamma$, where γ describes the non-linear response of the material to the exposing intensity, V is the fringe visibility, $K = 2\pi/\Lambda$, the grating vector magnitude, and Λ is the grating period. The concentration of photosensitizers, is related to the absorbed intensity by *de Beer's Law*:

$$I_a(x, t) = I(x) \left\{ 1 - \exp[-\varepsilon P_s(t)d] \right\} = I(x)A(t), \quad (6)$$

where ε is the molar absorptivity, $P_s(t)$ is the time dependent concentration of the photosensitizers (initiators) and d is the photopolymer layer thickness. Since the concentration of photosensitizers is a function of time, the absorption of the layer, $A(t)$ also depends on time. We relate the absorbance, $A(t)$ of the material to the measurable transmittance $T(t)$ of the material [2,5] by, $A(t) = 1 - BT(t)$, where B is a loss fraction which accounts for non-absorptive losses, i.e. Fresnel boundary coefficients. The polymerization rate, R_p , can now be written as

$$R_p = [M] [I(x)]^{1/2} \frac{k_p}{4k_t} \left\{ \sqrt{8k_t f(\Phi' - R_p')} A(t) + \frac{k_z^2 [Z]^2}{I(x)} - \frac{k_z [Z]}{[I(x)]^{1/2}} \right\} = \kappa [I(x)]^{1/2} H[t][M], \quad (7)$$

where κ , is the polymerization rate constant. In standard notation the general 1-D NPDD equation governing the evolution of the monomer concentration distribution becomes [8-10,12],

$$\frac{\partial u(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[D(x, t) \frac{\partial u(x, t)}{\partial x} \right] - \int_{-\infty}^{+\infty} \int_0^t R(x, x'; t, t') F(x', t') \times \left[u(x', t') \right]^\beta dt' dx'. \quad (8)$$

where $u(x, t)$ is the free-monomer concentration, $D(x, t)$ is the monomer diffusion constant, $F(x, t) = F_0[1 + V \cos(Kx)]^\gamma$ is the polymerization rate, with $F_0 = H(t)\kappa I_0^\gamma$, and $R(x, x'; t, t')$ is the non-local material response function. The non-local response function represents the effect of initiation at location x' and t' on the amount of monomer being polymerized at location x and time t . Assuming rapid chain growth, compared to other temporal effects, we can neglect the time non-locality and let the non-local response function be $R(x, x')$, in this way assuming an action-at-a-distance in our response. We assume a Gaussian spatially non-local material response function

$$R(x, x') = \left(1/\sqrt{2\pi\sigma} \right) \exp[-(x - x')^2 / 2\sigma], \quad (9)$$

where σ is the normalised non-local response parameter. The diffusion constant is defined by the expression $D(x, t) = D_0 \exp[-\alpha F(x)t]$ where D_0 is the initial diffusion constant and α is the diffusion coefficients decay parameter.

3. Results

Using a previously described holographic recording set-up [1], for recording 1000 lines/mm with a recording wavelength $\lambda = 532\text{nm}$ and probe wavelength $\lambda = 633\text{nm}$, we experimentally obtained a set of growth curves with 3 different exposure intensities. In each case the material was prepared in the manner described in [2], with Erythrosin B as the photosensitive dye. Fits to the experimental data were performed using our adjusted NPDD model applying a four harmonic numerical fitting algorithm [8-10] and are presented with the experimental data in Fig.1. The characteristic parameters extracted from the fits to the experimental data and fits to the experimental data $\pm 5\%$ are shown in Table 1, where t_i is the period of inhibition (negligible compared to the large exposure time), S is related to the non-local variance by $S = \exp(-K^2\sigma/2)$ and MSE denotes the Mean Squared Error of the fits.

Table 1.								
Parameter	I_0 mW	t_i s	D cm ² /s ($\times 10^{-11}$)	C cm ³ /mol ($\times 10^{-5}$)	κ cm ² mWs ⁻¹	S	R	MSE ($\times 10^{-10}$)
Case1	1.5	0.4	8.33	2.07	0.058	0.94	4.62	0.87
			± 0.41	± 0.88	± 0.004	± 0.01	± 0.48	± 3.73
Case 2	3.9	0.2	6.02	2.67	0.057	0.95	2.10	0.79
			± 1.92	± 0.24	± 0.004	± 0.01	± 0.6	± 4.12
Case 3	4.8	0.1	6.01	3.40	0.066	0.94	1.62	1.23
			± 0.85	± 0.1	± 0.006	± 0.01	± 0.3	± 5.01

Table 1. Characteristic parameters extracted from fits to experimental data. Note the short initial inhibition time values t_i .

Fig.1. Fit to the experimentally obtained growth curves of refractive index modulation (with Error Bars of $\pm 5\%$) versus exposure time for different recording intensities.

From the figure it can be seen that the fits to the experimental data and the low MSE values suggest good agreement between the experiment and the theory. Also, the extracted parameter values shown in Table 1. are comparable to those presented in the literature [1-12].

4. Conclusions

Future work includes the full analysis and comparison of previous models to that of our current model. It also includes the development of a more accurate function describing the change in inhibitor concentration with time and improving the model for the time varying absorption of the material. Models, which describe performance variations with material layer thickness and depth, must also be developed. A more exact expression for the refractive index modulation calculated using the Lorentz-Lorenz equation should be included [12]. Our understanding of other effects such as the chain termination mechanisms and material shrinkage must also be improved and then included in the model to enable a more accurate physical picture to emerge. However, given the variety of photopolymer material in which dye bleaching and inhibition effects have been observed, even the incomplete results presented here are significant for a range of applications, including holographic data storage, diffractive optical element fabrication, and photo embossing.

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