Material response of photopolymer containing four different photosensitizers

CrossMark

Yue Qi [a], Haoyu Li [a], Jinxin Guo [a,b], Michael R. Gleeson [a,c], John T. Sheridan [a,*]

[a] School of Electrical, Electronic and Communications Engineering, Communications and Optoelectronic Research Centre, The SFI-Strategic Research Cluster in Solar Energy Conversion, College of Engineering and Architecture, University College Dublin, Belfield, Dublin 4, Ireland
[b] Department of Engineering Science, University of Electro-Communications, 1-5-1 Chofu-gaoka, Chofu, Tokyo 182-8585, Japan
[c] III–V Materials and Devices, Photonics Centre, Tyndall National Institute, Lee Maltings, Dyke Parade, Cork, Ireland

ARTICLE INFO

ABSTRACT

Building on a previous studies, the behaviour of four different photosensitizers in an acrylamide/polyvinyl alcohol (AA/PVA) photopolymer material are examined using a 1-D Nonlocal Photo-polymerisation Driven Diffusion (NPDD) model. In order to characterise the effects of using different photosensitizers, holographic illuminations with different spatial frequencies and intensities are applied. Material parameters, i.e., the nonlocal response parameter, σ, the diffusion rate of monomer, D_m, the chain initiation kinetic constant, k_i, and the termination rate, k_t, are extracted by numerically fitting the predictions of the NPDD to experimentally measured refractive index modulation growth curves. Four photosensitizers, [Erythrosin B (EB); Eosin Y (EY); Phloxine B (PB); and Rose Bengal (RB)], are examined.

1. Introduction

The first step in any photo-polymerisation process involves the absorption of light by the photosensitiser in the material. Depending on the material and dye type, this leads to an initiation process. Clearly this first step is critically important in determining the material response characteristics. In earlier models it was generally assumed that the exposing intensity [1–5] directly determined the rate of initiation or the rate of polymerisation (and thus the process of grating formation) in the layer.

To concisely characterise the material response Zhao and Mouroulis [1], whose model well describes the behaviour of photopolymers for larger period and lower exposure intensities, introduced the parameter

$$R = K^2 D_m / F_0. \tag{1}$$

In this equation, $K = 2\pi/\Lambda$ is the magnitude of the grating vector, D_m is the diffusion constant of the monomer, and $F_0 = \kappa I_0^\tau$, is the polymerisation rate [1,4]. The κ parameter is a material constant, while τ describes the nonlinear response of the material to the exposing radiation and I_0 is the average exposing irradiance [1,4]. When the material layer is illuminated by a cosinusoidal

interference pattern a holographic grating of fundamental period Λ is formed. The R parameter is useful because it can be shown that the larger the value of R the higher the fidelity and strength of the recorded grating [1]. For low spatial frequency (SF) cases, the recorded cosinusoidal grating period Λ is large, i.e., SF$=1/\Lambda$. Larger grating periods mean that the monomer must diffuse a longer distance from the dark interference fringe regions into the bright regions, in order to equalise the monomer concentration in the layer. Returning to the R parameter we note that as Λ increases K decreases and thus R decreases, and therefore one might expect a weaker grating to be recorded. For low exposing intensity (or low absorptivity dyes) the values of I_0 (or κ) are smaller and therefore R is bigger. In these cases the monomer is used up (polymerised) more slowly. Therefore the monomer has time to diffuse into the brightly illuminated regions and be polymerised there, and thus a stronger grating will be formed. High exposing intensity will cause fast growth of the grating but will also lead to poor fidelity recording, because of the formation of higher harmonic of the refractive index modulation. Such higher harmonic can be formed even if $\tau = 1$ (i.e., linear material response), e.g. if monomer, diffusing from the dark regions does not penetrate into the centre of the bright regions, but is rapidly polymerised at the edges of these regions. For this case the spatial distribution of the photo-polymer becomes less sinusoidal, thus higher harmonics of the photopolymer concentration becomes more significant leading to the generation of the higher harmonics of the refractive index

modulation, i.e., n_2, n_3 etc. We note that in the model used in this study n_2, n_3 are not included. Nonlinearity of the material response gives rise to values of τ not equal to one appearing in R, resulting in the first harmonic amplitude of the grating being weaker because of the use of monomer to form higher harmonics.

For higher spatial frequency cases, the grating period is smaller, and the monomer has a shorter distance to diffuse from the darker regions into the more brightly illuminated fringe regions. R is larger and the grating is expected to be stronger, compared to the lower spatial frequency cases. However, the nonlocal effect [5] plays a more significant role in the small period cases, leading to a smearing effect in the material response and thus to the formation of a weaker grating modulation [5,6]. The Nonlocal Photo-polymerisation Driven Diffusion (NPDD) model was developed to include and explain such effects.

An extended NPDD model [6–10] was presented in [7] describing the effects of holographic exposure. The model in [7] includes a more general description of the initiation process. This is necessary here in order to quantitatively compare the effects of the different dyes examined. The photopolymer model includes (i) initiation, (ii) propagation, (iii) termination, and (iv) inhibition. These processes, in acrylamide/polyvinyl alcohol (AA/PVA) based photopolymer materials are examined in [11]. A detailed discussion of the photo-chemical processes involved, for dyes such as those examined here, is given in [7]. The dye related processes include: (i) time-varying photon absorption, (ii) recovery, and (iii) bleaching [12–15]. We note that, the study [7] focused on determining the values of dye absorption, recovery and bleaching related parameters.

Applying the notation and methods developed in [7], in this paper, the validity of this kinetic model is further examined by applying it to fit the experimental diffraction efficiency data measured during grating formation for a range of AA/PVA materials. Specifically dry AA/PVA photopolymer layers, containing four different photosensitizers are studied, i.e., Erythrosin B (EB); Eosin Y (EY); Phloxine B (PB); and Rose Bengal (RB). The effects of using these four different photosensitizers are examined, when holographically exposing with both different spatial frequencies and different intensities. In each case key material parameters related to the photopolymerization process [16,17], e.g., the nonlocal response parameter, σ, the diffusion rate of monomer, D_m, the chain initiation kinetic constant, k_i, and the termination rate by combination and disproportionation, k_t, are extracted by performing fits using the NPDD model to the experimentally obtained growth curves. The effect of changing the dye used on the various parameter values is examined and the consistency (validity) of the parameter values extracted are discussed.

We note that in order to simplify the fitting process the NPDD model is reduced in complexity. For example starting with the model developed in [7], it is assumed that the monomers diffuse at a constant rate, D_m, and that the value of the propagation rate constant, k_p is equal to that of the initiation rate, i.e., $k_p = k_i$ [6]. Furthermore it is assumed that the rate constant of primary radical termination is 10 times larger than the rate of bimolecular termination, $k_{tp} = 10k_t$ [6].

The paper is structured as follows: in Section 2, the refractive indices and the initial volume fractions of the main components of the material are presented. The temporal evolution of the grating refractive index modulation is then calculated by applying a volume fraction analysis and using the Lorentz–Lorenz relation [18,19]. It is shown how the first harmonic of grating refractive index modulation, $n_1(t)$, can be extracted from the measured diffraction efficiencies using Kogelnik's two wave coupled wave theory [20]. In Section 3, simulations of the first harmonic refractive index modulation are presented for five different spatial frequencies and three different exposing intensities. In Section 4,

the corresponding experimental results are shown, with the measured diffraction efficiencies (gratings growth curves) being examined for materials containing the four different photosensitizers. The first harmonic amplitudes of the refractive index modulations n_1, are then extracted from the experimental diffraction efficiency data. Key parameters, which determine the material response during holographic recording, are then extracted by numerically fitting the predictions of the NPDD model to the refractive index modulation growth curves obtained. Finally, in Section 5 a brief conclusion is presented.

2. Index modulation

During holographic exposure at wavelength $\lambda = 532$ nm, and throughout the resulting grating formation process [21,22], a probe beam replays the recorded unslanted transmission geometry gratings on-Bragg at $\lambda_p = 633$ nm, to which the material is insensitive [7]. The temporal evolution of the resulting Fresnel coefficient corrected first-order diffracted, I_d, and transmitted intensities, I_t, of the probe beam are measured, e.g., see the experimental setup shown in Fig. 2 in [23] or Fig. 8 in [24]. In this case the diffraction efficiency is well approximated by the diffraction selectivity

$$\eta(t) \approx \frac{I_d(t)}{I_d(t) + I_t(t)}. \tag{2}$$

The first harmonic of grating refractive index modulation, $n_1(t)$ [8], can then be found using Kogelnik's two wave coupled wave theory [20],

$$\eta(t) = \sin^2\left[\frac{\pi d n_1(t)}{\lambda_p \cos \theta_{in}}\right], \tag{3}$$

where θ_{in} is the on-Bragg replay angle inside the layer.

The time varying value of the refractive index modulation n_1 must be predicted. Applying the Lorentz–Lorenz relation [25], and using the volume fractions and index values of the various material components, the index n of the material can be expressed as

$$\frac{n^2-1}{n^2+2} = \varphi^{(m)}(t)\frac{n_m^2-1}{n_m^2+2} + \varphi^{(p)}(t)\frac{n_p^2-1}{n_p^2+2} + \varphi^{(b)}(t)\frac{n_b^2-1}{n_b^2+2}, \tag{4}$$

where n_m [$\varphi^{(m)}$], n_p [$\varphi^{(p)}$], and n_b [$\varphi^{(b)}$] are the refractive indices [volume fractions] of monomer, polymer, and background material, respectively [9]. Neglecting shrinkage and swelling effects during holographic grating formation, [25], the sum of the volume fractions of the individual component is assumed to be conserved during and post exposure, i.e.,

$$\varphi^{(m)}(t) + \varphi^{(p)}(t) + \varphi^{(b)}(t) = 1. \tag{5}$$

The temporal evolution of the refractive index modulation can then be expressed as [25]

$$n_1(t) = \frac{(n_{dark}^2+2)^2}{6n_{dark}}\left[\varphi_1^{(m)}(t)\left(\frac{n_m^2-1}{n_m^2+2} - \frac{n_b^2-1}{n_b^2+2}\right) + \varphi_1^{(p)}(t)\left(\frac{n_p^2-1}{n_p^2+2} - \frac{n_b^2-1}{n_b^2+2}\right)\right], \tag{6}$$

where n_{dark} is the refractive index of the photopolymer layer before exposure, and $\varphi_1^{(m)}(t)$ and $\varphi_1^{(p)}(t)$ are the time varying first harmonic volume fraction components of monomer and polymer respectively.

Initial material parameter values, when $t=0$, are also required: Φ^m, Φ^p and Φ^b are the initial monomer, polymer and background volume fractions before exposure. These can be directly estimated from the initial material composition, see Table 1. In our studies the initial photosensitizer concentration in all the cases is $[A_0] = 1.22 \times 10^{-6}$ mol/cm^3, while the initial concentrations of monomer