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Authors(s)	Liu, Shui, Gleeson, M. R., Sheridan, John T.
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Analysis of the photoabsorptive behavior of two different photosensitizers in a photopolymer material

Shui Liu, Michael R. Gleeson, and John T. Sheridan*

UCD School of Electrical, Electronic and Mechanical Engineering, Optoelectronic Research Centre, SFI Strategic Research Centre in Solar Energy Conversion, College of Engineering, Mathematical and Physical Sciences, University College Dublin, Belfield, Dublin 4, Republic of Ireland

*Corresponding author: john.sheridan@ucd.ie

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Photopolymer materials are practical materials for use as holographic recording media. To further develop such materials, a deeper understanding of the photochemical mechanisms present during the formation of holographic gratings in these materials has become ever more crucial. This is especially true of the photoinitiation process, which has already received much attention in the literature. Typically the absorption mechanism varies with exposure time. This has been previously investigated in association with several effects taking place during recording. Since holographic data storage requires multiple sequential short exposures, it is necessary to verify the temporal change in photosensitizer concentration. Postexposure effects have also been discussed in the literature, however, such studies do not include effects such as photosensitizer recovery and bleaching. We report on experimental results and theoretical analysis of the recovery and bleaching mechanisms, which arise during exposure and postexposure for two different types of photosensitizers, methylene blue and erythrosine B in a polyvinylalcohol–acrylamide based photopolymer material.

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1. INTRODUCTION

The storage capabilities of self-processing photopolymer materials are under constant study due to their ability to record low loss, low shrinkage, and high diffraction efficient volume gratings. To obtain the full potential of these materials requires quantitative insight into the processes present during recording [1,2]. Therefore, the developments of accurate theoretical models, which are validated using reproducible experiments, are needed to allow important material parameters to be identified and controlled.

A study of the photochemical kinetics involved during holographic recording in a polyvinylalcohol–acrylamide (PVA–AA) based photopolymer material [1,3–7] is presented here. Such materials have received much attention in the literature [1–11] and are relatively simple to work with. In particular, in this paper our aim is to increase our understanding of what takes place inside the material during exposure when using different photosensitizers. If it is possible to precisely measure the number of photons being absorbed by the photosensitizer in the photopolymer material, and the amount of resulting initiation, then an accurate theoretical representation of the photopolymerization process can be made. Therefore, in order to fully predict the temporal evolution of holographic grating formation, it is necessary to thoroughly examine the kinetics of photoinitiation in photopolymer materials, which includes taking account of the effects of photosensitizer recovery and bleaching [2]. Thus we aim to further develop the theories of the photoinitiation processes

[2,4–6,10] by theoretically and experimentally examining such temporal effects during exposure and postexposure.

To systematically present the results of this study, the paper is structured as follows: in Section 2 we first discuss the photochemical rate equation, which determines the photoinitiation mechanisms present during grating formation. We then incorporate the temporal effects of absorption during exposure into this rate equation, and a flow chart of these processes is presented. In Section 3, we examine the photoabsorptive behavior experimentally for two different photosensitizers: methylene blue (MB) and erythrosine B (EB), respectively. Work done on extending the analysis of the recovery and bleaching processes is presented in this section. Then the developed model is fit to the experimentally obtained results using a numerical least squares fitting algorithm. Estimations of absorption parameter values are then extracted using the fitting procedure and are presented and discussed. Finally, in Section 4, a brief conclusion is given.

2. PHOTOINITIATION MECHANISM

A. Photochemical Reactions

During holographic exposure a PVA–AA material undergoes a set of three main photochemical processes [2,7,8]: initiation, propagation, and termination. In this work we focus on the mechanisms involved in the first of these processes, initiation. Photoinitiation involves the production of free radicals by photon absorption by the photosensitizer. The initiator consists of a photosensitive dye and a

reducing agent, i.e., a tertiary amine [triethanolamine (TEA) [1,2,8,12]]. The photosensitive dyes examined in this paper become excited in the presence of a photon and when excited can accept an electron from the reducing agent, and can then produce a free radical, $R^\cdot$. When the dye molecule is exposed to light of a suitable wavelength, it absorbs a photon of light and is promoted to a singlet excited state $^1Dye^*$ [2,13]. The singlet-excited dye can return to its ground state by radiationless energy transfer to another molecule such as TEA, the electron donor, ED , and by the emission of a photon by a process called fluorescence [1,12].

The singlet state dye can also undergo intersystem crossing into the more stable and longer-lived triplet state $^3Dye^*$ [2,13] (see flow chart in Fig. 1). This triplet state dye molecule can return to the ground state by radiationless energy transfer or by delayed emission of a photon, by collision with another dye molecule, and also by the presence of initially dissolved molecular oxygen [14–16] resulting in an unreactive oxygen species 1O_2 .

The dye molecules can also undergo a reaction whereby it abstracts two hydrogen molecules (atoms) from the ED to form the transparent (leuco [1,9,11]) form of the dye. The production of free radicals takes place when the triplet state dye reacts with ED . The ED donates an electron to the excited “triplet state,” $^3Dye^*$, of the dye leaving the dye with one unpaired electron and an overall negative charge, $Dye^{\cdot-}$ [1,2,7,8,11].

The ED radical cation then loses a proton and becomes a free radical. When an acrylamide monomer is present, the free radical can undergo *two different reactions* [1,2,7,8,11]. The *first* possible reaction is the initiation of the monomer radical $M_1^\cdot$ [1,8,17,18]. The *second* possible reaction the radical can undergo is dye bleaching [1,11]. This occurs when the dye radical formed abstracts a hydrogen molecule from the ED free radical. An unstable ED intermediate, $[(HOCH_2CH_2)_2NCH=CHOH]$ [1,2,11], and the transparent di-hydro dye, H_2Dye , are formed in

Fig. 1. Flow chart illustrating the photoinitiation mechanisms of the photosensitizer, MB, and EB.

this reaction, [2]. Dye bleaching is an important process because it allows a grating to be fixed after recording. By bleaching any remaining dye, no new free radicals can be formed. This results in the photopolymer layer becoming transparent.

B. Photosensitizer Rate Equation

Photopolymer materials can be made sensitive to different wavelengths using particular photosensitive dyes. Let us consider a photopolymer material layer with thickness d (centimeters) and initial photosensitizer concentration A_0 (mol/cm³), which is exposed to an incident intensity. The rate equation for the photosensitizer concentration changing with exposure time t can be expressed as [2,10,11]

$$\frac{dA(t)}{dt} = -\frac{\phi I_a(t)}{d} + k_r[A_0 - A_b(t) - A(t)]. \quad (1)$$

$A(t)$ (mol/cm³) is the photosensitizer concentration remaining at time t ; ϕ is the quantum yield or quantum efficiency of removal of the photosensitizer; $I_a(t)$ (Einstein/cm² s) is the absorbed intensity with time t ; k_r (s⁻¹) [2,10] is the rate constant of recovery of excited dye molecules back to their ground state, where it is then available for further photon absorption. $A_b(t)$ (mol/cm³) is the amount of photosensitizer concentration that has been bleached for an exposure of time t , following the work by Gleeson *et al.* [2]. To reduce the complexity of Eq. (26) from [2], we assume a simple linear relationship between the free radical, $ED^\cdot$ and incident intensity, I'_0 . This is governed by the rate equation,

$$\frac{dA_b(t)}{dt} \approx k_b I'_0 A(t), \quad (2)$$

where k_b (cm²/Einstein s) is the rate constant of bleaching, I'_0 (Einstein/cm² s) is the incident intensity corrected by the transmission fraction $T_{sf} = T_s \times T_f$, where T_s is the transmission fraction after the material scattering loss and T_f is the transmission fraction after the Fresnel boundary loss [2,10,11]. Examining Eqs. (1) and (2) we can identify two limiting cases, which describe these equations appropriately. Letting t_{exp} represent the exposure time, the two cases identified are as follows:

I. When $t \leq t_{exp}$, we assume that the recovery effect is negligible during the exposure [2]. This gives,

$$\frac{dA(t)}{dt} \approx -\frac{\phi I_a(t)}{d}. \quad (3)$$

The absorbed intensity $I_a(t)$ is described using the Lambert–Beer law [11,19],

$$I_a(t) = I'_0 \{1 - \exp[-\epsilon A(t)d]\}, \quad (4)$$

where ϵ (cm²/mol) is the molar absorption coefficient. Substituting Eq. (4) into Eq. (3) and integrating with respect to time, an expression for the time varying photosensitizer concentration, $A(t)$ (mol/cm³) can be obtained [10,11],

$$A(t) = (\varepsilon d)^{-1} \log\{1 + [\exp(\varepsilon A_0 d) - 1] \exp(-\varepsilon \phi I_0' t)\}. \quad (5)$$

Solving Eq. (2), $A_b(t)$ can be expressed as

$$A_b(t) = \frac{k_b}{2\varepsilon\phi^2 d} \left(\varepsilon \phi I_0' t \left\{ \varepsilon \phi I_0' t - 2 \log \left[\frac{1 + \exp(\varepsilon \phi I_0' t) / (\exp(\varepsilon A_0 d) - 1)}{1 + \exp(-\varepsilon \phi I_0' t) (\exp(\varepsilon A_0 d) - 1)} \right] \right\} + 2Li_2 \left[\frac{1 + \exp(\varepsilon \phi I_0' t)}{1 - \exp(\varepsilon A_0 d)} \right] - 2Li_2 \left[\frac{1 - \exp(\varepsilon \phi I_0' t)}{1 - \exp(\varepsilon A_0 d)} \right] \right). \quad (6)$$

where $Li_n(z) = \sum_{k=1}^{\infty} z^k / k^n$ is the dilogarithm function [20]. The light incident upon the photopolymer material layer can be broken down into three parts: (i) lost through scatter and due to Fresnel T_{sf} , i.e., $I_0' = I_0 \times T_{sf}$, where I_0 is the incident intensity before taking account of the loss fraction, (ii) light that is absorbed $I_a(t)$, and finally (iii) light that is transmitted $I_T(t)$. Then the normalized transmittance, $T(t)$, i.e., the ratio of the transmitted intensity to the incident intensity, $T(t) = I_T(t)/I_0$, can be expressed as a function of time [10,11],

$$T(t) = \frac{T_{sf}}{1 + [\exp(\varepsilon d A_0) - 1] \exp(-\varepsilon \phi I_0' t)}. \quad (7)$$

II. When $t > t_{\text{exp}}$, the incident light is turned off, and as a result no new photons are absorbed by the photopolymer material layer, i.e., $I_a(t) = I_0' = 0$, [2]. Equation (1) reduces to

$$\frac{dA(t)}{dt} = k_r [A_0 - A_b(t_{\text{exp}}) - A(t)]. \quad (8)$$

Solving Eq. (8) provides an analytical expression for the time varying recovery of photosensitizer, when $t > t_{\text{exp}}$,

$$A_r(t) = [A_0 - A_b(t_{\text{exp}})] - [A_0 - A_b(t_{\text{exp}}) - A(t_{\text{exp}})] \times \exp[-k_r(t - t_{\text{exp}})], \quad (9)$$

where $A(t_{\text{exp}})$ and $A_b(t_{\text{exp}})$ represent the concentrations of photosensitizer and bleached photosensitizer, respectively, at time $t = t_{\text{exp}}$.

In this section, we have described the photoinitiation mechanisms in detail using photochemical rate equations. Development of the flow chart presented in Fig. 1 succinctly illustrates these processes. A set of rate equations is presented that includes the mechanisms of photosensitizer recovery and bleaching. Next, we experimentally examine these mechanisms of recovery and bleaching for two photosensitive dyes, and quantify their postexposure effects.

3. EXPERIMENTAL WORK

To optimize the process of fabrication of holographic recordings, it is necessary to quantify three main parameters [2,10,11]: (a) the quantum yield, ϕ ; (b) the molar-absorption coefficient, ε ; and (c) the loss fraction, T_{sf} , which determine the absorptive effects present in a pho-

topolymer material, as they control the temporal evolution of absorption effects and thus the photopolymerization mechanisms during grating formation. We now estimate these parameters using fits to experimentally obtained transmittance curves.

A. Photosensitizer I—Methylene Blue

To obtain estimates for the values of these absorption parameters, we begin by examining the standard PVA-AA material [1–3,6–8,10,11] with MB, i.e., $C_{16}H_{18}ClN_3S$, used as the photosensitizer.

1. Photon Absorption

In accordance with the absorption spectrum of MB [21], an experiment was performed to measure the time varying transmittance of a normally incident plane wave of wavelength $\lambda = 633$ nm (red). To remove any effects arising due to diffusion of the photosensitizer from outside the exposed regions, the area of illumination was made the same size as the area of the material layer being exposed. The photopolymer material was prepared in the standard manner [1,2,7,8,10] with a dry material initial photosensitizer concentration $A_0 = 2.11 \times 10^{-6}$ mol/cm³ for recording.

As discussed in [2], the normally incident transmitted intensity I_0 is measured using a photodetector in units of mW/cm² s, and is necessarily converted to Einstein/cm² s [2,10]. Using three material layer thicknesses, 80, 120, and 160 μm , experimental transmittance curves were obtained for an exposure intensity of 5 mW/cm² s. Equation (7) was then fit using a nonlinear fitting algorithm, and the resulting estimations of the absorption parameters are presented in Table 1. The parameters obtained for the different thicknesses tend to converge well and a mean parameter value for each is displayed.

To further determine the convergence and accuracy of these parameter values, the experiments were repeated using three different exposure intensities, 2, 4, and 6 mW/cm² s, and a constant material layer thickness of

Table 1. Absorption Parameter Extraction from Fits to Experimentally Obtained Transmittance Curves of MB for Different Illumination Intensities and Layer Thicknesses

Intensity (mW/cm ²)	ε (cm ² /mol) ($\times 10^7$)	ϕ (mole/Einstein)	T_{sf}
2	7.707	0.067	0.796
4	7.803	0.070	0.766
6	8.080	0.070	0.788
Mean	7.86 ± 0.216	0.069 ± 0.001	0.783 ± 0.0123
Thickness (μm)			
80	7.902	0.066	0.782
120	8.029	0.063	0.761
160	7.858	0.064	0.831
Mean	7.93 ± 0.099	0.064 ± 0.001	0.7913 ± 0.0396

$d=120\text{ }\mu\text{m}$. The estimated parameter values are presented in Table 1. As can be seen, good agreement between the two sets of estimated values indicates the reproducibility of the results. Also, these results are consistent with the values obtained in the literature [2,10,11,22].

Figure 2(a) shows a typical average experimental transmittance curve, for a material layer thickness of $d=100\text{ }\mu\text{m}$ under an illumination intensity of $I_0=4\text{ mW/cm}^2\text{ s}$ for 75 s exposure time. The data were fit with the inclusion of error bars to indicate experimental reproducibility. The corresponding time evolution of the photosensitizer concentration, found using Eq. (5), is presented in Fig. 2(b). The transmittance in cases 1–4, i.e., for the exposure times t_1 – t_4 , results in particular fractions of the maximum intensity being transmitted through the photopolymer layer at saturation: $T_1 \approx T_{sf}/4$, $T_2 \approx T_{sf}/2$, $T_3 \approx 3T_{sf}/4$, and $T_4 \approx T_{sf}$. In these cases $A(t_1)$, $A(t_2)$, $A(t_3)$, and $A(t_4)$ are the instant photosensitizer concentrations for each corresponding exposure time. We can see that the longer the exposure the greater the intensity transmitted, and the less intensity absorbed. In this way we can quantify the amount and the rates of photosensitizer recovered and bleached during exposure [8]. This is now discussed in Subsections 3.A.2 and 3.A.3.

2. Recovery Process

Extending the work in Subsection 3.A.1 on the relationship between the time evolution of transmittance characteristics and the photosensitizer concentration, the recovery process can be numerically analyzed. When photopolymer material is exposed, the excited states of

photosensitive dye molecules are formed, i.e., singlet, $^1Dye^*$, and/or triplet, $^3Dye^*$. They either result in production of radical ED^* 's, or can be converted to the leuco or di-hydro state, H_2Dye , or can return to the ground state by relaxation and the fluorescence quenching process, i.e., combination, oxidation and reduction of the radicals, as indicated in Fig. 1. Therefore some of the photosensitizer recovers to the ground state, Dye .

In this section, the recovery process is examined and its rate constant, k_r (s^{-1}) is estimated. This is done by applying discrete timed, normally incident exposures of intensity $4\text{ mW/cm}^2\text{ s}$ to photopolymer layers of thickness $100\text{ }\mu\text{m}$. As illustrated in Fig. 2(a), the exposure times to reach (T_1 , T_2 , T_3 , and T_4) are identified as t_1 – t_4 . The experiment was carried out as follows:

- 1 The photopolymer material layer was exposed for time t_I (seconds) and the amount of light transmitted was monitored, i.e., t_I stands for the individual exposure times from t_1 to t_4 .

- 2 The exposing laser source was turned off by closing a mechanical shutter for a relatively longer time, t_{OFF} (minutes), than the exposure time t_I (seconds).

- 3 Reopening the mechanical shutter at t_{II} , the transmittance was again monitored until 100% saturation, T_{sf} , occurs.

- 4 The difference in transmittance, $\Delta T = T(t_I) - T(t_{II})$, was found for $t_{OFF} = t_{II} - t_I$; see Fig. 3. These differences were then converted into the corresponding photosensitizer concentrations $A(t_I)$ and $A(t_{II})$.

- 5 This process was then repeated for different values of t_{OFF} , in order to quantify the time evolution of the changes in transmittance and thus of the photosensitizer concentration.

Due to the large time scale, the experimentally observed transmittance curves, which determine the recovery behavior, are illustrated using the schematic presented in Fig. 3. The recovery process was numerically analyzed by combining Eqs. (5) and (7). During the post-exposure period, t_{OFF} , the photosensitizer concentration that the dye recovers to can be calculated at any particular time using $A_r(t_{OFF}) = A(t_{II}) = A(t_{III})$, since $T(t_{II}) = T(t_{III})$. From Fig. 3, we see that $T(t_I)$ is the transmittance when the exposure stops. The drop in the transmittance is due to the increase in the photosensitizer concentration at t_{II} , which indicates the existence of an absorption recovery

Fig. 2. (a) Experimental data and curve fits $T(t)$ with error bars, and (b) photosensitizer as functions of time $A(t)$.

Fig. 3. Representation of normalized transmittance curves obtained experimentally for estimation of recovery mechanism of active photosensitizer.

mechanism. In this way, we can find the amount of recovery during the postexposure period, t_{OFF} ,

$$\Delta A_r = A(t_{\text{III}}) - A(t_I). \quad (10)$$

To estimate the rate constant of recovery of MB, k_r (s^{-1}), four different exposure times, $t_1 = 5, 10, 20$, and 75 s, were examined (see Table 2). In each case, a range of values of t_{OFF} were chosen, resulting in experimental transmittance curves, from which photosensitizer recovery can be observed using Eq. (5). The resulting experimental values of $A_r(t_{\text{OFF}})$ are presented in Fig. 4. Fitting these four recovery curves using Eq. (9), the time evolution of the recovery process can be determined.

As can be seen, appreciable recovery occurs over long periods, with the MB photosensitizer recovering to almost its initial concentration. The extracted rate constant of recovery k_r (s^{-1}) for MB decreases in going from case 1 to case 4, i.e., as the exposure time increases, $k_{r1} > k_{r2} > k_{r3} > k_{r4}$; see Table 2. This appears reasonable, since the longer the photosensitive dye is initially exposed, the more dye molecules become excited. However, these excited MB dye molecules then react strongly with any oxygen dissolved in the material during manufacture, and which also diffuses from the air into the unsealed layer during recording (see Fig. 1). Therefore, the larger the number of excited dye molecules, the longer the time required for the dye to recover; see case 4 in Fig. 4. To study the effect of oxygen diffusion into the layer, the layers were then cover plated. In this way, the total amount of oxygen available to facilitate recovery can be reduced. The results of this process are discussed in Subsection 3.A.4.

3. Bleaching Process

To develop a physical description of the bleaching process, the recovery process must first be understood (this was discussed in Section Subsection 3.A.2). As illustrated in Fig. 1, the amount that is bleached depends on the exposure necessary until the dye is fully bleached. Because of the bleaching process, 100% recovery cannot be achieved, which means that a certain amount of photosensitive dye will never be able to return to its ground state. Thus, for the exposure times previously examined, we can predict that as t_{OFF} approaches infinity, and once the recovery process is complete, the photosensitizer concentration cannot recover to its initial value, A_0 . We illustrate this behavior schematically in Fig. 5.

Taking the decaying curve for $A(t)$ from Fig. 2(b), and inserting it into Fig. 5 graphically, for different initial exposure times (t_1 – t_4) the photosensitizer concentration is

Table 2. Extracted Parameter Values of Recovery Produced by Fitting Experimental Data for MB

	t_{exp} (s)	$T(t)$	$A(t_{\text{exp}})$ (mol/cm ³) ($\times 10^{-6}$)	k_r (s ⁻¹) ($\times 10^{-3}$)	$A_b(t_{\text{exp}})$ (mol/cm ³) ($\times 10^{-7}$)
Case 1	$t_1 = 5$	T_1	1.57	3	0.85
Case 3	$t_2 = 10$	T_2	1.152	1.6	0.95
Case 3	$t_3 = 20$	T_3	0.568	0.84	0.99
Case 4	$t_4 = 75$	T_4	0.042	0.72	1.66

Fig. 4. Fit to experimental data of recovery versus postexposure time off (t_{OFF}) of MB for different exposure times: $t_1 = 5$ s (solid curve), $t_2 = 10$ s (long dashed curve), $t_3 = 20$ s (dashed curve), and $t_4 = 75$ s (short dashed curve).

shown to recover to approximately the same value $A(t_{\text{OFF}} \rightarrow \infty)$ with different rates. It can be seen that there is a gap between the initial photosensitizer concentration A_0 and final value $A(t_{\text{OFF}} \rightarrow \infty)$. Hence, the amount of photosensitizer concentration bleached by exposure time, t , can be estimated by taking their differences,

$$A_b(t) = A_0 - A(t_{\text{OFF}} \rightarrow \infty). \quad (11)$$

To study the bleaching process, a larger range of exposure times were used, spanning the entire duration of the transmittance curve illustrated in Fig. 2(a). Experiments were carried out similar to those performed using the recovery process set up, except that in this case $t_{\text{OFF}} = 12$ (hours) is treated as being effectively $t \rightarrow \infty$ for each particular length of exposure. When the recovery process is complete, the laser is then turned back on, and the light transmission is monitored until saturation. By converting $T(t_{\text{II}})$ (see Fig. 3) into the corresponding photosensitizer concentration, the time evolution of bleaching was found by calculating the differences to the initial concentration, A_0 , for each exposure time. In each of these experiments,

Fig. 5. Schematic representation of the combining of the photosensitizer concentration (decaying curve) and recovery of MB for $t_{\text{OFF}} \rightarrow \infty$ with different initial exposure times: $t_1 = 5$ s (solid curve), $t_2 = 10$ s (long dashed curve), $t_3 = 20$ s (dashed curve), and $t_4 = 75$ s (short dashed curve).

a constant intensity, $I'_0 = 4 \text{ mW/cm}^2 \text{ s}$, is normally incident on the photopolymer material layers of thicknesses, $d = 100 \text{ }\mu\text{m}$.

The amount of photosensitizer bleached not only depends on the exposure time, t , but also on the exposure intensity I'_0 . Fitting the experimental data using Eq. (6), the rate constant of bleaching is determined to be $k_b = 4.26 \times 10^5 \text{ cm}^2/\text{Einstein}$; see Fig. 6. As can be observed, $A_b(t)$ increases in an exponential manner, as exposure time increases. However, the trend indicated by the approximate model (solid curve), shows a bleached concentration of approximately $A_0/6$, where $A_0 = 2.11 \times 10^{-6} \text{ mol/cm}^3$, over the examined exposure time, i.e., $t = 200 \text{ s}$. This appears to be because, as noted, MB has a strong reactivity with oxygen (initially dissolved and diffusing in from the air [11–13]). Thus more excited dye molecules are being continually returned to the ground state by the oxygen present, both during exposure and postexposure, than are transformed into the transparent states.

4. Cover Plating and Recovery

In Subsection 3.A.3 we noted that a significant amount of oxygen could diffuse into the material layer from the air during exposure and postexposure periods. In an effort to eliminate the effects of such diffusion, the material was cover plated using an index-matched fluid, silicon oil (500 times the viscosity of water), and a glass plate [7]. Figure 7 contains two recovery curves: curve (1) represents the results of repeated recovery experiments for case 2, i.e., when $t_2 = 10 \text{ s}$, but cover plated. Curve (2) shows the equivalent results for the uncover-plated case, i.e., case 2 extracted from Fig. 4. As can be seen from curve (1), significantly less photosensitizer recovers when the material is cover plated. As t_{OFF} increases, the amount of oxygen available to react with the excited MB dye molecules decreases, furthermore, and as a result that recovery takes place with a relatively slower rate constant, $k_r = 1.16 \times 10^{-3} \text{ s}^{-1}$, than for the uncover plated case in curve (2), $k_r = 1.6 \times 10^{-3} \text{ s}^{-1}$.

Fig. 6. Concentration of the bleached photosensitizer MB (dots), obtained experimentally as a function of exposure time, along with a best fit (solid curve).

Fig. 7. Fit to experimental data of recovery versus postexposure time off (t_{OFF}) of MB for curve (1) material cover plated (short dashed curve with big dots) and curve (2) uncover plated (long dashed curve with small dots).

B. Photosensitizer II—Erythrosine B

In this section, using the same experimental procedure and theoretical analysis, we examine the photoabsorptive behavior of our standard PVA-AA photopolymer material containing a different photosensitizer EB, $\text{C}_{20}\text{H}_6\text{I}_4\text{Na}_2\text{O}_5$ [1,2,7,8,10].

1. Photon Absorption

Once again, in order to estimate the absorption parameters, experiments were carried out with an input exposing intensity of $4 \text{ mW/cm}^2 \text{ s}$ normally incident on the material layers of thicknesses, $d = 100 \text{ }\mu\text{m}$. Almost the same experimental setup was used. However, in this case, the wavelength of the incident plane wave is $\lambda = 532 \text{ nm}$ (green), in accordance with the absorption spectrum of EB [23]. The initial photosensitizer concentration of the dry material is, $A_0 = 1.22 \times 10^{-6} \text{ mol/cm}^3$. Once again, the transmittance curves were monitored for a range of layer thicknesses with a fixed intensity, and for a range of intensities with a fixed thickness. The material parameters were extracted and are presented in Table 3.

The exposure times to reach (T_1 – T_4) and thus $A(t_1)$, $A(t_2)$, $A(t_3)$, and $A(t_4)$, as in Fig. 2 are identified for exposure times of, $t_1 = 5 \text{ s}$, $t_2 = 10 \text{ s}$, $t_3 = 20 \text{ s}$, and $t_4 = 75 \text{ s}$. The EB transmission curves are almost identical to those of MB. However, it is important to notice that the recovery and bleaching processes, which are taking place simultaneously, have significantly different rates. These are discussed in Subsections 3.B.2–3.B.4.

2. Recovery Process

Using the same experimental steps discussed in Subsection 3.A.2, the recovery experiments were performed for four exposure times t_1 , and the transmittance curves were obtained for the same range of exposure time off values, t_{OFF} . The photosensitizer concentration recovered was then estimated; see Fig. 8. The experimentally obtained results (dots) are then nonlinearly fit using Eq. (9).

Fitting the experimental data the rate constant of recovery for EB, $k_r (\text{s}^{-1})$, is then estimated; see Table 4. As can be seen, the rate constant of recovery tends to agree

Table 3. Absorption Parameter Extraction from Fits to Experimentally Obtained Transmittance Curves of EB for Different Layer Thicknesses and Illumination Intensities

Thickness (μm)	ε (cm^2/mol) ($\times 10^8$)	ϕ (mole/Einstein)	T_{sf}
80	1.333	0.0356	0.742
120	1.437	0.0370	0.780
160	1.549	0.0350	0.766
Mean	1.44 ± 0.109	0.036 ± 0.001	0.763 ± 0.017
Intensity ($\text{mW}/\text{cm}^2 \text{ s}$)			
2	1.416	0.0390	0.776
4	1.452	0.0326	0.780
6	1.450	0.0330	0.758
Mean	1.390 ± 0.127	0.0348 ± 0.001	0.771 ± 0.0086

well for each of the different exposure times. This is not surprising, because of the following:

- (i) The possible effects of photosensitizer diffusion from outside the exposed regions have been removed, i.e., the total layer area is exposed. However, even if this were not the case, it is unlikely that photosensitizer diffusion would have a significant effect, as the EB molecular weight is 879.92 g/mol, making it relatively large and immobile in the cross-linked PVA-AA photopolymer system.
- (ii) The excited EB dye molecules do not have as strong a reactivity with oxygen as MB [24]. This can be observed in Fig. 8.

The longer the photosensitive dye is initially exposed, the lower the maximum amount to which the photosensitizer concentration can recover. This indicates that the amount bleached gets larger, and thus less of the dye is available to recover. Therefore, we can see that the

Fig. 8. Fit to experimental data of recovery versus postexposure time off (t_{OFF}) of EB for different exposure times and rates: $t_1 = 5$ s (solid curve), $t_2 = 10$ s (long dashed curve), $t_3 = 20$ s (dashed curve), and $t_4 = 75$ s (short dashed curve).

Table 4. Extracted Parameter Values of Recovery Process from Fits to Experimental Data of EB

	t_{exp} (s)	$T(t)$	$A(t_{\text{exp}})$ (mol/cm^3) ($\times 10^{-6}$)	k_r (s^{-1}) ($\times 10^{-3}$)	$A_b(t_{\text{exp}})$ (mol/cm^3) ($\times 10^{-7}$)
Case 1	$t_1 = 5$	T_1	1.096	1.19	0.85
Case 3	$t_2 = 10$	T_2	0.894	1.22	1.38
Case 3	$t_3 = 20$	T_3	0.810	1.17	2.96
Case 4	$t_4 = 75$	T_4	0.152	1.18	6.89

bleaching process is quite active during exposure. This is now discussed in Subsection 3.B.3.

3. Bleaching Process

Based on the analysis of the recovery process, the bleaching process of EB can be analyzed by quantifying its rate constant k_b ($\text{cm}^2/\text{Einstein}$) estimated from its time evolution. Experiments were carried out in exactly the same manner as in Subsection 3.A.3, with $t_{\text{OFF}} = 12$ h, being again treated as $t_{\text{OFF}} \rightarrow \infty$. The time evolution of the bleaching process (curve) is determined by fitting Eq. (6) to the experimentally obtained data (dots), shown in Fig. 9.

The value of the bleaching rate constant for EB is estimated to be, $k_b = 6.85 \times 10^5 \text{ cm}^2/\text{Einstein}$. As can be seen, in Fig. 9, $A_b(t)$ continues to increase exponentially, even at longer exposure times. Therefore 100% bleaching of the photosensitizer, A_0 , appears possible if the recovery effect is eliminated by exposing it for a sufficiently long time, e.g., three or more times the exposure time necessary for the transmittance to saturate, as indicated in Fig. 2(a).

4. Cover Plating and Recovery

To determine the reactivity of EB with the oxygen, cover plated recovery experiments were identically performed. The results in Fig. 10 show that, for the cover plated case, curve (1), there is a significant drop in the amount of EB photosensitizer concentration that has recovered initially (i.e., $t_{\text{OFF}} = 1\text{--}3$ min). This is as a direct result of the cover plating leading to a reduction in the amount of oxygen

Fig. 9. Concentration of the bleached photosensitizer EB (dots), obtained experimentally as a function of exposure time, along with a best fit (solid curve).

Fig. 10. Fit to experimental data of recovery versus postexposure time off (t_{OFF}) of EB for (1) material cover plated (short dashed curve with big dots) and (2) uncover plated (long dashed curve with small dots).

available to enable recovery. We note that the rate of reaction of EB with oxygen, (i.e., k_z for EB), is not as fast as the reaction between MB and oxygen, (i.e., k_z for MB). Therefore oxygen is less reactive with the excited EB dye molecules, and this results in a much slower recovery, i.e., $k_r = 5.94 \times 10^{-4} \text{ s}^{-1}$ and a smaller concentration of recovered EB dye molecules during the initial stages than in the cover plated case of MB. However, over long periods of t_{OFF} the other possible recovery mechanisms that can still take place in the layer, i.e., molecule collisions, radiationless energy transfer, etc., enable the recovery of EB to reach the same amount maximally as curve (2) does. This behavior further indicates that the recovery of EB is less dependent on the presence of the oxygen, since its dye molecules do not react as readily with oxygen as MB.

4. DISCUSSION AND CONCLUSIONS

Starting with a detailed description of the photoinitiation mechanisms taking place in a PVA-AA based photopolymer material, we have further developed the governing rate equation to include the effects of the recovery and bleaching processes arising during photosensitive dye absorption. Quantifying these effects increases our ability to determine the time evolution of grating formation during holographic exposure.

It was previously shown that the main process responsible for the consumption of photosensitizer concentration was by photosensitive dye absorption [2,7,8]. In this paper, the analytic solutions of the time evolutions of recovery $A_r(t)$ governed by Eq. (9) and bleaching $A_b(t)$ governed by Eq. (6) are presented.

The photoabsorptive behaviors of two common types of photosensitizers, methylene blue (MB) and erythrosine B (EB) used in PVA-AA based photopolymer materials are examined, and shown to exhibit different behaviors under similar conditions. The key material parameters for both photosensitizers controlling the absorption characteristics in each process have been estimated using fits to the experimental transmission data.

In the recovery processes, both the MB and EB dyes need significant postexposure periods to fully occur. However, unlike EB, MB reacts strongly with any oxygen present, thus most of its excited dye molecules can be recovered rather than being bleached. Comparing Fig. 4 to Fig. 8, it can be seen that, k_r of MB varies but that of EB tends to be constant over the same range of exposure times. This clearly impacts the bleaching rate constant values k_b .

In the bleaching processes for both dyes, the amount of photosensitizer bleached $A_b(t)$ is proportional to the exposure time, as presented in Tables 2 and 4 for $A_b(t)$. Furthermore, in both cases, the bleaching process takes place much faster than the recovery process, i.e., $k_b \gg k_r$. $A_b(t)$ for EB continues to increase progressively up to A_0 as the exposure time increases. However, in Fig. 6 it appears that $A_0/6$ is the maximum bleached concentration of MB, which can be produced for that particular exposure time under the experimentally examined conditions. Thus, this suggests that MB has a much slower rate constant, k_b , than EB (see Fig. 9).

Examining the results for the cover plated cases, it was found that the rate constants of recovery, k_r , of both photosensitizers are reduced, but k_r of EB reduces more than the k_r MB dose. While there is a reduction in the maximum concentration that MB can recover to, EB still recovers to almost the same maximum concentration by other possible mechanisms but with much smaller recovered concentrations during the initial stage as in the previous uncover plated case. Therefore, it is shown that EB is less dependent and reactive with oxygen than MB.

The results obtained have been shown to converge well and have good reproducibility. In conclusion, MB behaves quite differently than EB, and this is most clearly observable postexposure. In particular, since excited MB molecules react strongly with oxygen, MB recovers more than EB, but bleaches less than EB.

Future work is required to more accurately describe the behavior of photosensitizers during exposure and postexposure. This work includes the examination of (i) longer exposure times, (ii) larger ranges of intensities, (iii) measurement of the concentration of dissolved oxygen in the photopolymer material, and (iv) the estimation of the diffusion rate of oxygen into the layer. However, this work clearly indicates that the postexposure photosensitizer effects taking place in such photopolymer materials can be significant enough to require their inclusion in any comprehensive material model.

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