Photopolymerization Model for Curing BTA-Doped Photosensitive Polymers

We begin by calculating the exposure dose, i.e. the energy, required for photopolymerization. To do so, we first consider the penetration depth $D_p$. This parameter is defined as the location at which the ultraviolet energy incident on a photosensitive film decays to a value of $1/e$ of its maximum value. The thickness of the film that is cured is related to the penetration depth as follows:

\[ C_p = D_p \ln \left( \frac{E_{\text{max}}}{E_c} \right), \]

where $E_{\text{max}}$ is the energy at the surface of the film and $E_c$ is the minimum energy required to induce photopolymerization. \(^1\)

Furthermore, the curing energy as a function of film thickness follows the Beer-Lambert law:

\[ E_u(z) = E_{\text{max}} \cdot e^{-\frac{z}{D_p}}. \]

The subscript $u$ indicates the case of an undoped film. Substituting Equation (1) into Equation (2) yields

\[ E_u(z) = E_{\text{max}} \cdot e^{-\frac{z}{C_p} \ln \left( \frac{E_{\text{max}}}{E_c} \right)}. \]

The term $\frac{1}{C_p} \ln \left( \frac{E_{\text{max}}}{E_c} \right)$ has inverse length units. Thus, this term can be considered as an effective absorption coefficient and Equation (3) can be re-written

\[ E_u(z) = E_{\text{max}} \cdot e^{-\alpha_{\text{eff}} z}, \]

where

\[ \alpha_{\text{eff}} = \frac{1}{C_p} \ln \left( \frac{E_{\text{max}}}{E_c} \right). \]
Equation (4) evaluated at $z = n \times \delta$, where $\delta$ is the physical thickness of the film and $n$ its refractive index, is the minimum energy required to fully cure the film. The total exposure dose ($E_u$) as a function of film thickness is typically supplied by the manufacturer.

Let us now consider the case of a doped photosensitive pre-polymer film. The energy absorbed by the UV-absorbing compound reduces the energy available for curing. This effect is additive in terms of the absorption coefficient. The amount of energy available for curing a doped film becomes

$$E_d(z) = E_{\text{max}} e^{-\alpha_d z} e^{-\alpha_d z} = E_u(z) e^{-\alpha_d z},$$

where the parameter $\alpha_d$ is the additional attenuation resulting from introducing the dopant.

As Equation (6) shows, for large $\alpha_d$ as in the case for BTA, $E_d \ll E_u$. This implies that the energy received by the SU-8, $E_d$, will not be sufficient to induce polymerization. The loss of energy resulting from BTA absorption must be compensated by increasing the exposure time.

Thus, the energy required to cure the doped film, $E^*_d$, where the subscript “$*$” denotes the adjustment in exposure time, is:

$$E^*_d(z) = I_{\text{max}} (t_E + \Delta t) \cdot e^{-(\alpha_d + \alpha_d)z}.$$

$I_{\text{max}}$ is the irradiance of the UV lamp, $t_E$ is the time it would take to cure an undoped film of optical thickness $z$, and $\Delta t$ is the requisite additional time.

Simplifying Equation (7) we obtain

$$E^*_d(z) = I_{\text{max}} t_E e^{-\alpha_d z} e^{-\alpha_d z} + I_{\text{max}} \Delta t e^{-\alpha_d z} e^{-\alpha_d z}.$$

Since $E_{\text{max}} = I_{\text{max}} t_E$, we can write

$$E^*_d(z) = E_{\text{max}} e^{-\alpha_d z} e^{-\alpha_d z} + E_{\text{max}} \frac{\Delta t}{t_E} e^{-\alpha_d z} e^{-\alpha_d z}.$$

Recall that for polymerization to occur, the undoped film must be exposed with a minimum dosage of $E_u$. In order to have $E^*_d \geq E_u$, the condition required for curing the BTA-doped film, the following condition must hold:

$$e^{-\alpha_d z} \left( 1 + \frac{\Delta t}{t_E} \right) \geq 1.$$

Thus, the additional time required for successful curing must satisfy
\( \Delta t \geq t_E \left( e^{\alpha_d z} - 1 \right) \).

The total exposure time is thus:

\( t_E^* = t_E + \Delta t \geq t_E e^{\alpha_d z} \).

The parameter \( \alpha_d \) is a concentration and wavelength dependent absorption coefficient and it is given by the following formula:

\[ \alpha_d = \frac{\epsilon \cdot c}{M} , \]

where \( \epsilon \) is the extinction coefficient \(^1\), \( M \) is the molecular weight of the doping chromophore, and \( c \) is its concentration in the pre-polymer. For a model particular to the photolithography of SU-8-BTA composites at the i-line wavelength, we re-write Equation (13) as

\[ t_E^* \geq t_E e^{\left( \frac{\epsilon_i}{M} \right) \frac{c_{BT A}}{l}} \cdot \delta . \]

The i-line extinction coefficient \( \epsilon_i \) is obtained experimentally using the molecular formulation of the Beer-Lambert law, namely, \( A = \epsilon_i c l \), where \( A \) is the absorbance of the chromophore in solution at concentration \( c \) across an optical thickness \( l \). The chromophore concentration \( c_{BT A} \) is obtained by dividing the number of moles of BTA in the doping aliquot by the pre-polymer volume. (The solvent volume can be neglected because it evaporates during curing).

Scaling Equation (15) by \( I_{max} \) yields the minimum exposure dose needed for polymerizing the composite:

\[ E_d^* (\delta) \geq E_u (\delta) e^{\left( \frac{\epsilon_i}{M} \right) \frac{c_{BT A}}{l} \delta} . \]

**References**