International Journal of Latest Research In Engineering and Computing (IJLREC)
Volume 1, Issue 1 : Page No.110-115, September-October 2013
www.ijlrec.com

A Focused UV laser for Optimal Photo-polymerization in Thick Medium

Jui-Teng Lin

New Vision Inc, Room 826, No. 144, Sect 3, Minchuan E. Rd, Taipei,Tawan

Abstract: Modeling of a focused UV laser photoinitiated polymerization in thick polymer absorbing medium is presented. Optimal focusing offers more uniform polymerization and larger volume than the collimated or non-optimal cases. A scaling law governed by f*=1.6/S is derived numerically, where S is the product of the extinction coefficient and concentration of the initiator. The focusing technique and analytic formulas developed provide useful guidance for further experimental study and system design for efficient photoinitiated polymerization, particularly for thick medium.

Keywords: modeling, photoinitiated polymerization , UV laser, focused beam

INTRODUCTION

UV light photoinitiated polymerization provides advantageous means over the thermal-initiated polymerization, including fast and controllable reaction rates and without a need for high temperatures or pH conditions [1-4]. Furthermore, it also offers controllable process which is light wavelength selective and maximum rate can be achieved by optimal polymer parameters such as its concentration.

The kinetics of photoinitiated polymerization systems have been studied by many researchers analytically, numerically and experimentally [2-12]. In general, the laser may still be absorbed by the photolysis product, the kinetics of photoinitiated polymerization, specially in thick polymer systems, becomes difficult to be solved analytically and only numerical results have been reported in previous literatures [9-12]. Commercial Type-I photoinitiators with two radicals following photon absorption using visible laser absorbance have limited water solubility and high cell toxicity [1]. Photoinitiator of poly(ethylene glycol) diacrylate (PEGDA) using UV laser at 365 nm has been recently explored for improved polymerization kinetics, at lower initiator concentrations [4].

It was known that the photoinitiated photopolymerization is always faster at the entrance and slower at the output end of the absorbing medium. Therefore, thick absorbing medium (>1.0 cm) can not be completely and uniformally photopolymerized, especially at its bottom portion within a limited time. This issue exists in all photoinitiated systems illuminated by a collimated laser beam which is an exponentially decreasing function of z inside the absorbing medium. To overcome the drawback of a collimated laser system and achieve a more uniform photopolymerization through out a thick medium, this study presents a focused laser system. We will first introduce a focusing function to compensate the laser power exponentially decay inside the absorbing medium. The polymerization equation is analyzed for optimal conditions. The polymerization process will be shown by its time evolution of polymerization boundary.

To our best knowledge, this study presents for the first time, an optimal focusing condition for uniform photopolymerization governed by the extinction coefficient and the initial concentration of the initiator. The focusing technique also provides a novel and unique means (within a limited time of irradiation) which can not be achieved by any others means. This paper will focus on the analytic formulas and comprehensive illustration for the focused system, whereas a complete numerical simulation will be presented elsewhere.

METHODS

A. The Focused Laser System

As shown in Fig. 1, a UV laser is focused and propagating along the z-direction, or the thickness of the absorbing medium having UV photoinitiator. The initial (at t=0) laser intensity (or fluence) of a focused beam may be expressed by an analytic form of

$$I(z,t=0)=I_0F(z) \tag{1}$$

where we have introduced a focusing function F(z) given by

$$F(z)=\left(1-\frac{1-w}{f}z\right)^{-2} \qquad \text{for } z<f, \tag{2.a}$$

$$F(z)=\left(w+\frac{1-w}{f}(z-f)\right)^{-2} \qquad \text{for } z>f \quad . \tag{2.b}$$

In Eq. (1), I_0=I(z=0, t=0) is the initial (at t=0) laser intensity on the entrance plan (z=0) of the medium and w is a ratio between the beam spot size at z=0 and at the focal point (z=f).

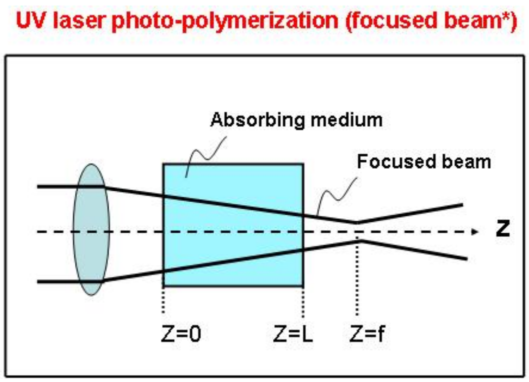


Fig. 1 The Schematics of a focused UV laser propagating in an absorbing medium having a thickness L..

B. *The Kinetic Equations*

For a thick polymerization system illuminated by a UV laser, the laser intensity and the photoinitiator and the photolysis product concentration, in general, should be governed by a 3-dimensional diffusion equation which can be solved only numerically. For comprehensive analysis emphasizing on the focusing features, we will ignore the diffusion effects such that the initiator profile may be described by a set of first-order differential equation. The molar concentration of the photoinitiator $C(z,t)$ and the focused UV laser intensity $I(z,t)$ described by a 1-dimensional kinetic model [9-12] is revised in this study to include the focusing effect as follows.

$$\frac{\partial C(z,t)}{\partial t}=-aI(z,t)F(z)C(z,t) \tag{3.a}$$

and

$$\frac{\partial I(z,t)}{\partial z}=-2.303\left[(\varepsilon_1-\varepsilon_2)C(z,t)+\varepsilon_2C_0\right]I(z,t), \tag{3.b}$$

where F(z) is the focusing function defined by Eq. (2); C_0 is the initial value, $C_0=C(z,t=0)$; and $a=83.6\lambda\phi\varepsilon_1$, with ϕ being the quantum yield and λ being the laser wavelength; and ε_j ($j=1$, 2) are the molar extinction coefficient of the initiator and the photolysis product, respectively. In our calculations, the following units are used: $C(z,t)$ in mM, $I(z,t)$ in (mW/cm^2), λ in cm, z in cm, in second, and ε_j in (mM·cm)$^{-1}$.

The differential coupled equations will be solved with the initial and boundary conditions $C(z,0)=C_0$ and $I(0,0)=I_0$. According to Eq. (3), we can also obtained the additional conditions $C(0,t)=C_0\exp(-aI_0t)$ and $I(z,0)=I_0F(z)\exp(-2.303\varepsilon_1C_0z)$. For the simplified case with $\varepsilon_2=0$ and for the collimated beam with F(z)=1.0, the analytic solutions for the photoinitiated polymerization process have been derived by previous researchers [5-8]. For the general case with $\varepsilon_2\neq 0$, which indicates that the photolysis product may still partially absorb the UV laser, the coupled differential Eqs. (3.a) and (3.b) become very difficult to be solved analytically and only numerical results (and limited to the collimated case) were reported so far [9-12].

RESULTS AND DISCUSSIONS

C. *Analytic Formulas*

Using the first-order solution of Eq. (3.a), we obtain the first-order solution of Eq. (3.b) which in term gives the second-order solution of Eq. (3.b) as follows

$$I_{(1)}(z,t) = I_0 F(z) \exp\left\{-[bC_{(1)}(t) + hC_0]z\right\}. \tag{4.a}$$

where

$$C_{(0)}(t) \cong C_0 \exp\left[-aF(z) I_0 t\right] \tag{4.b}$$

and $b = 2.303(\varepsilon_1 - \varepsilon_2)$ and $h = 2.303\varepsilon_2$.

By taking the Taylor expansion of Eq. (3.a) up to the third-order of $C_{(0)}(t)$ and solving for Eq. (1) to obtain the first-order solution for the initiator concentration

$$C_{(1)}(z,t) = C_0 \exp\left[-Q(z)F(z)G(t)\right] \tag{4.a}$$

$$Q(z) = \exp\left[-2.303\varepsilon_1 z\right] \tag{4.b}$$

$$G(t) = \left[\exp(bC_0 X) - 1\right]/(bC_0) \tag{4.c}$$

where X= $aI_0 t$.

The above equations provide an explicit formula for $I_{(1)}(z,t)$ as a function of z , t , C_0 , and I_0 . Eqs. (4) and (5) show that the initiator concentration is a deceasing function of time (t), but the laser intensity increases with time due to the photobleaching of the initiator. Furthermore, Eq. (5) shows that $C_{(1)}(z,t)$ has two competing components in z, the increasing component due to focusing aF(z), and the exponential decreasing function of z due to the Y term, and both aF and Y are proportional to ($\varepsilon_1 C_0$). Therefore, stronger compensation, or shorter focusing, smaller f in F(z) is needed for larger ($\varepsilon_1 C_0$). These two competing factors in z provide us the important feature that there is an optimal focusing such that uniform profile (up to certain medium thickness) of $C(z,t)$ is achievable.

D. *The Optimalization*

The focusing function F(z) in Eq. (2) defined by w and f, in which the value of w depends on the beam divergent angle and beam quality of the focused laser. In this study, we will assume w=0.2 for a typical diode laser as the UV light source. If one uses a LED as the light source, w will be larger (0.4 to 0.6). Figure 3 shows the numerically generated profiles (at t=60 seconds) of the normalized concentration $C(z,t)/C_0$ for a fixed ε_1 =0.4 (mM·cm)$^{-1}$ with ignored ε_2 , and various initial value C_0 .

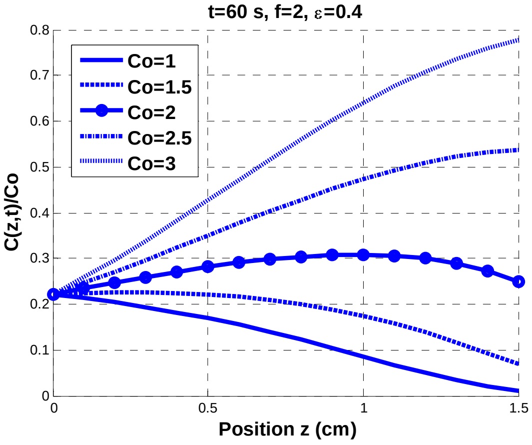


Fig. 2 the profiles of normalized initiator concentration C(z,t)/C_0 for a focused beam (with focal length f=2.0 cm), at t=60 seconds and a given extinction coefficient of the initiator ε_1 =0.4 (mM·cm)$^{-1}$, but for various initial concentration C_0= 1.0 to 3.0 mM.

In Figure 2, a focused UV laser with a focal length f=2.0 cm is used to suppress the increasing profiles of C(z,t) such that a more uniform distribution (along the medium thickness direction z) may be achieved. It may be seen that f=2.0 cm is an optimized focal length for almost uniform C (z,t) along the z-direction, up to the medium thickness L=1.5 cm. However, it is only apply to the profile of C_0 =2.0 mM. It is too much focused for smaller C_0 <2.0 mM and not enough for large C_0 >2.5 mM. In other words, shorter focal length is needed for larger C_0 . As shown by Figures 3 that the optimal focal length (f*) should be governed by the product of ε_1 and C_0 . This feature leads us to search for a scaling law of f* defined by (ε_1 C_0) in the next section.

E. *The Scaling Law*

From Eq. (5), for a given optimal focal length (f*), there will be a range of z, such that the profiles of C(z,t) achieve an almost flat top which defines the uniform photo-polymerization in thick medium and can not be achieved by a collimated beam. The flat-point of C(z,t) may be found by taking the derivative dC(z,t)/dz (at z=z*) =0. This condition provides us

$$f'z^* = 1 + \left(\frac{2aI_0 f'}{bC_0}\right)^{1/3} \quad (6.a)$$

$$f' = \frac{1-w}{f} \quad (6.b)$$

Due to the complex of the z-dependence of C(z,t) and I(z,t), the exact optimalization condition can only be numerically obtained. However, the qualitative trend is that long focal length will provide a large range (z) of flat-profile, and the optimal focal length (f*) shall be governed by a scaling law of $f^* \propto 1/(\varepsilon_1 C_0)$. This scaling law is predicted from our analytic Eq. (6). Our numerical simulation (to be published) confirms a scaling law given by a fit equation $f^* = 1.6/(\varepsilon_1 C_0)$ which is consistent with Eq. (6).

F. *The Kinetic of Polymerization*

For the case of collimated beam (with F=1), Eq. (4) and (5) show that the initiator concentration C(z,t) is a decreasing function of time but an increasing of z, that is to say the depletion of the initiator concentration (or the polymerization boundary) always moves from the top portion (z=0) to the bottom (z>0). This general trend in a collimated beam may be changed by a focused beam as follows.

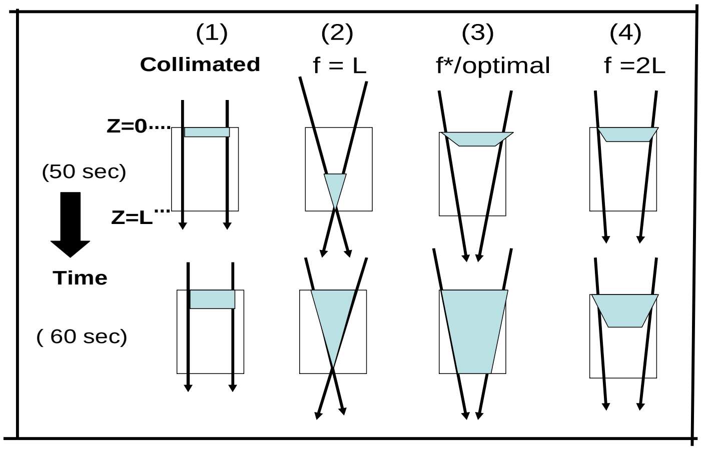


Fig 3. Schematics of time evolution of photo-polymerization via: (1) collimated beam, (2) tightly focused (with F=L); (3) optimal focusing (f=f*), and (4) slightly focusing (f=2L), where the polymerized portions are shown by shaded areas.

As demonstrated by Figure 3 for the schematics of time evolution (at t=50 and 60 seconds) of photo-polymerization via: (1) collimated beam, (2) tightly focused (with F=L), (3) optimal focusing (f=f*), and (4) slightly focusing (f=2L), where the polymerized portions are shown by shaded areas and the un-polymerized areas are shown by white areas. This schematic is further interpreted as follows.

For a collimated beam shown by case (1) of Figure 10, the top portion (about 0.3 cm) of the medium is always polymerized starting from the surface (z=0) which has the highest polymerization rate.

For a tightly focused case (with f=L=1.5 cm), the medium is polymerized starting from the bottom portion which has a higher laser intensity initially, and therefore initiator concentration C(z,t) is depleted faster than the top portion. For a slightly focused case (with f=2L>f*, not optimized), the polymerization process of collimated case is improved, but not enough. At the optimal focusing, with f=f* given by the scaling law, the photo-polymerization process starts from both ends (top and bottom)and gradually move to the central portion until the whole medium is polymerized.

The tightly focused, case (2) in Figure 10 with f=L, provide the fastest process than others. However, the optimized case (3) with f=f*, provides a larger volume of completed polymerization at a given time. We choose f* as the optimal condition based on not only the uniform polymerization distribution, but also by its large volume than the tighter focusing case.

CONCLUSION

This paper has presented a comprehensive modeling for the kinetic of UV laser photoinitiated polymerization in thick polymer systems in which the photolysis product still partially absorbs the laser after polymerization. It was demonstrated that the focused beam at an optimal condition (f=f*) achieves uniform polymerization and eliminates the intrinsic drawback of collimated beam in thick medium. The initiator concentration profiles at various focusing conditions are analyzed to define the polymerization boundary and to demonstrate the advantage of optimal focusing for more uniform polymerization and larger volume than the collimated or non-optimal cases. Too much focusing (with f<f*) provides fast process, however, it has a smaller polymerization volume at a given time than the optimal focusing case. Finally, a scaling law governed by $f^* = 1.6/(\varepsilon_1 C_0)$ is derived numerically and shows that larger extinction coefficient or larger initial concentration of the initiator, that is larger value of ($\varepsilon_1\ C_0$) requires a tighter focusing, or a smaller f*. The scaling law provides useful guidance for the prediction of the photoinitiated polymerization particularly in thick polymer systems under a focused UV laser illumination. The focusing technique also provides a novel and unique means for uniform photopolymerization (within a limited time of light irradiation) which can not be achieved by any others means. The dynamic profiles of the photoinitiated polymerization and the polymerization rate and the concentration profiles corresponding to Fig. 3 will be presented elsewhere by numerical simulations.

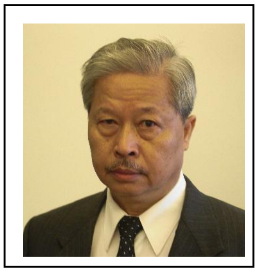
ACKNOWLEDGMENT

This work is partially supported by the grant from Xiamen-200 program (Xiamen Science & Technology Bureau, China). The author thanks assistance from Dr. D. C. Cheng (at Chinese Medical University) for the drawing of Fig. 2 based on numerical simulation..

REFERENCES

[1] S.J. Bryant , C. R. Nuttelman, K. S. Anseth , “Poly(vinyl alcohol)-heparin biosynthetic microspheres produced by microfluidics and ultraviolet photopolymerisation,” *J Biomater Sci, Polym Ed* 11, 439–457(2000).
[2] Fouassier J-P., *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*. Munich: Carl Hanser Verlag, 1995.
[3] Odian G., editor. *Principles of Polymerization*. New York: Wiley, 1991.
[4] Fairbanks B.D., Schwartz M.P., Bowman C.N., Anseth K.S. *Biomaterials* **2009**, 30, 6702–6707.
[5] Terrones G., Pearlstein A. *J. Macromolecules* 34, 3195–3204 (2001).
[6] Terrones G., Pearlstein A. *J. Macromolecules* 34, 8894–8906 (2001).
[7] Terrones G., Pearlstein A. *J. Macromolecules* 36, 6346–6358 (2003).
[8] Ivanov V.V., Decker C. *Polymer Int* 50, 113–118 (2001).
[9] Miller G.A., Gou L., Narayanan V., Scranton A.B. *J Polym Sci, Part A: Polym Chem* 40, 793–808 (2002).
[10] Stephenson N., Kriks D., El-Maazawi M., Scranton A.B. *Polym Int* 54, 1429–1439 (2005).
[11] Stephenson N., Kriks D., El-Maazawi M., Scranton A.B. *Polym Int* 55, 994–1006 (2006).
[12] Kenning N.S., Ficek B.A., Hoppe C.C., Scranton A.B. *Polym Int* 57, 1134–1140 (2008).

BIOGRAPHY



Jui-Teng Lin received his Ph.D in Chemical Physics from the University of Rochester in 1980. He is currently the Chairman and CEO of New Vision, Inc. (Taiwan) and a visiting Professor at He Medical University (China). He was a visiting Professor at the National Chiao-tung University and National Taiwan University (2007-2010), a faculty at CREOL,UCF(1986-1991) and founder and CEO of two US Nasdaq listed companies (1991-2004). He holds over 50 international patents and is the inventor of LASIK procedure (US Pat, 1991) using flying-spot scanning laser currently used in all major eye hospitals worldwide. Lin has published over 50 book chapters and 60 SCI journal papers. His achievements include WHO's WHO in Leading American Executives (1993), Model of oversea Chinese Young Entrepreneur (1997), Chair and/or co-chair in SPIE Conferences. Prof. Lin is a Fellow of American Society of Laser Medicine and Surgery ASLMS).