Development of Polymer Microneedle upon Exposure of Hollow Gaussian Beam on Unconstraint Depth Resin

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Abstract. This paper presents characterization of unconstraint depth photopolymerization yielding different forms of cured voxel under exposure of hollow Gaussian beam. The governing model consists of nonlinear Schrodinger equation along with transient diffusion phenomenon and intensity dependent refractive gradient is considered in predicting the curing behaviour. The effect of various process parameters viz; intensity of and degree of hollowness of Gaussian beam, time of exposure on the formation of cured voxel is presented in this paper. Typical of cured voxel resembles hollow microneedle under certain conditions of exposure. The study proposes potential possibility to be used as one of the methods to develop hollow microneedle being used in many biomedical applications for effective drug delivery.

1. Introduction
Microneedles are the promising geometrical microstructures in the biomedical applications specifically for transdermal drug delivery [1]. These microneedles are used in various ways for the drug delivery. In one of the forms of drug deliver using microneedles, solid microneedles coated with desired drug on the surface is penetrated into the skin [1, 2]. The coated solid microneedle along with the drug dissolve into the skin in this way of drug delivery. In other forms of delivery technique the microneedle is formed of drug composition itself [2]. The full microneedle is then inserted into the skin for dose delivery. In one more variants the hollow microneedles are inserted into the skin for the drug delivery through the hollow portion [1-3]. This variant is found most effective for the delivery of drugs.

The microneedles required for drug delivery are formed by various microfabrication techniques [2-3]. Microstereolithography, from class of additive manufacturing process has demonstrated the capability to develop the microneedles of both solid and hollow forms. The developed microstructures are also used for the transdermal drug delivery [3]. However, the microstructure forms consist of stair-

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stepping effects on the surface due to layer-by-layer way of fabrication [13]. The stair-stepping effect is undesirable from needle insertion point of view in the drug delivery applications. To minimize stair stepping effect, the structure need to be developed from thin layers. This leads to increase in fabrication time for the microstructure. In above technique the photopolymerization is processed in constraint way (solid platform restricting the beam to travel further). Unconstrained depth photopolymerization is also one of the ways to develop different kinds of microstructures. 3D interference lithography [4–7], photopolymer waveguide prototyping [8–10], flow interference lithography, [11] and recently developed energy exposure controlled lithography or bulk lithography [12–16] are few of the lithography techniques illustrating formation of different variants of microstructures from unconstraint depth photopolymerization. Mostly these structures are used in developing micro-electromechanical systems. In all these techniques the unconstraint depth photopolymerization is explored under exposure of Gaussian beam with different orientations, interferences range of beam intensity and time scale. The physics of unconstraint depth photopolymerization under exposure of hollow Gaussian beam is not yet explored.

This paper discusses the physics of photo-polymerization when unconstraint depth resin is exposed to hollow Gaussian laser beam. The physics reveals the role of diffusion in evolution of different forms of cured voxel under simultaneous actions of change in refractive index [28–32] and absorption of photons. Developed cured voxel is observed under different degree of hollowness of Gaussian beam, exposure dose and duration.

![Intensity distribution in hollow Gaussian beam](image1)

**Figure 1.** Intensity distribution in hollow Gaussian beam.

![Schematic representation of unconstraint depth photopolymerization under hollow Gaussian beam](image2)

**Figure 2.** Schematic representation of unconstraint depth photopolymerization under hollow Gaussian beam.

2. Central theme of the process

Figure 1. shows intensity profile of incident beam (hollow Gaussian beam) used in the study of unconstraint depth photopolymerization yielding different cured voxels. The hollowness is achieved by applying boundary condition \( I=0 \) for \( r \leq r_h \) on intensity distribution,

\[
I(r; 0) = I_0 \exp \left( -\frac{2r^2}{w_0^2} \right)
\]

The radius, \( r_h \) (refer figure1) can be varied to set desired degree of hollowness. Process of forming cured voxel by allowing hollow Gaussian beam to propagate in resin of unconstraint depth (sufficient large depth) is illustrated in schematic way in figure 2. Physical set up consists of laser source, optical system for beam navigation and resin system. Ar+ laser of wavelength 351.1 nm is considered in this study. Physically the hollowness of the Gaussian beam is achieved by obstruction places centrally in
the path of the beam. The mirror is used to reflect the laser beam and to make it incident on resin system. Benzoil Ethyl Ether was used as a photoinitiator (4 % wt. concentration) in Hexane diol-diacrylate monomer to prepare UV curable resin [13]. The hollow Gaussian beam propagates in the resin under the action of diffusion of species and absorption of photons. Diffusion of photoinitiator takes place at inner zone (refer hollow part zone I in inset of figure. 2) and in zone exterior of Gaussian beam (refer II in figure. 2). Time available for diffusion of photoinitiator species in zone I decides the form of microneedle. Lesser time available for diffusion in zone I makes formed voxel to be hollow microneedle while large time for diffusion make solid cured voxel. This is typically the central theme of the process. This theme is presented in terms of quantified characterization presented in dimensionless manner in next sections.

3. Process Modelling

This section presents model of propagation of hollow Gaussian shaped laser beam in sufficient large depth resin. Propagation of hollow Gaussian shaped laser beam in absorbing (due to photoinitiator species in resin) and intensity dependent refractive index gradient resin medium along with diffusion of photoinitiator species taking place on zone I and II depicted in figure 2 is presented. Further section also presents one of the numerical schemes, split beam method used to solve the model of photo-polymerization under different physical phenomena.

Utilization of photoinitiator species due to exposure of hollow Gaussian shaped laser beam develops a concentration gradient both in hollow part of beam (refer hollow part zone I in inset of figure. 2) and exterior portion (refer II in figure. 2) of exposure. This concentration gradient is typically of photoinitiator species induced due to its consumption in reaction zone. Photoinitiator diffuses from high to low concentration due to developed concentration gradient [13]. The following equation represents the dynamic concentration of photoinitiator,

$$\frac{ds}{dt} = \frac{1}{2} \phi E IS + D_s \left( \frac{\partial^2 s}{\partial x^2} + \frac{\partial^2 s}{\partial y^2} + \frac{\partial^2 s}{\partial z^2} \right)$$

(2)

Propagation of optical filed typically given by Non-linear Schrodinger equation as,

$$\frac{\partial E_r}{\partial z} = \frac{1}{2jk_0n_0} \nabla_r^2 E_r - j\Delta n k_0 E_r - \frac{\alpha}{2} E_r$$

(3)

is considered to simulate the propagation of hollow Gaussian beam in photopolymer medium (it is to be noted that intensity of light is, \( I = \left| E_r \right|^2 \)). \( \nabla_r^2 \), denotes the traverse Laplacian \( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \). Propagation of hollow Gaussian shaped beam in resin space is represented by first term of right hand side of Eq.3. Furthermore, second term depicts propagation of hollow Gaussian shaped beam in graded refractive index (\( \Delta n \)) medium induced in the resin. Taking a note of experimental results presented in study [26-32], the gradient change in the refractive index of resin is function of optical field and mathematically represented in Eq.4,

$$\Delta n_{(x,y,z,t)} = \Delta n_0 \left\{ 1 - \exp \left[ -\frac{1}{E_r} \int_0^t \left| E_r(t) \right|^2 dt \right] \right\}$$

(4)

The variation in refractive index which is influenced due to intensity is modelled by Eq. 4. The study depicting beam propagation under typically inhomogeneous medium is important to understand evolution of curing accurately. This inhomogeneity is typically induced because of change in refractive index. This is useful to understand evolution of shape of cured voxel in region I and region II. Photopolymerization gets started by absorption of photons, further resulting decrease in laser intensity along the propagation direction. In addition to this phenomenon, progression of curing leads to establish gradient of concentration of photoinitiator species in and around reaction zone. Further it is to be noted that this also exists in zone I and II mainly due to diffusion set because of absorption of photoinitiator species due to hollow Gaussian shaped beam. The developed concentration gradient
results in diffusion to takes place simultaneously. The physics of diffusion is captured mathematically in eq.2. Further under exposure of hollow Gaussian beam the diffusion of photoinitiator takes place in region I and II as mentioned in figure.2. The diffusion dynamics in these regions under exposure time and exposure energy doses results in different possible shapes of cured voxel. Eq. 2 depicting diffusion of photoinitiator species in combination with third or last term presented on right hand side of Eq.3 representing utilization of photoinitiator species due to reaction considers above mentioned aspects of propagation of beam. In conclusion, propagation with absorption of photoinitiator species setting dynamic concentration of photoinitiator is mainly studied.

Split beam propagation method is used to simulate the model presented by Equations 2-4. The terms representing different physics in Equation 3 converted into spectral domain for simplicity. The effect of each of the physical phenomenon on curing is considered one-by-one in solution by split beam method. Further to get computational advantage the differential equation is converted into spectral domain through Fourier transformation. Later the solution in spectral domain is converted into time domain for easy interpretation.

Table 1. The properties of the resin used in the study to understand evolution of curing under hollow Gaussian beam exposure.

| Process Parameters                                           | Symbols | Values          |
|-------------------------------------------------------------|---------|-----------------|
| Quantum efficiency of photoinitiator [10]                   | \( \phi \) | 0.1            |
| Monomer initial concentration [23]                          | M       | \( 4.46 \times 10^3 \) mol/m³  |
| Gaussian beam waist                                         | \( W_0 \) | -              |
| Hollow radius                                               | \( rh \) | -              |
| Photoinitiator initial concentration [23]                   | S       | \( 2.23 \times 10^2 \) mol/m³  |
| Concentration of dissolve oxygen [10]                       | \( O_2 \) | 1 mol/m³        |
| Molar absorptivity of photoinitiator [23]                   | \( \varepsilon \) | 20 m²/mol      |
| Threshold energy of resin (HDDA-BEE)                       | \( E_c \) | 111 mJ/cm²     |
| Diffusion coefficient of Radical [23]                       | \( D_R \) | \( 3 \times 10^{-10} \) m²/s   |
| Diffusion coefficient of Initiator [23]                     | \( D_S \) | \( 3 \times 10^{-10} \) m²/s   |
| Diffusion coefficient of Oxygen [10]                        | \( D_{O_2} \) | \( 1 \times 10^{-10} \) m²/s  |
| Propagation rate constant of reaction [10]                  | \( k_p \) | \( 0.26 \) m³/(mol·s) |
| Termination rate constant of reaction [10]                  | \( k_t \) | \( 0.39 \) m³/(mol·s) |
| Termination rate constant through oxygen inhibition [10]    | \( k_{o2} \) | \( 2 \) m³/(mol·s) |
| Refractive index of HDDA-BEE resin system [27]              | \( n_0 \) | 1.4            |
| Refractive index at saturation (complete curing) of HDDA-BEE resin system [27] | \( n_s \) | 1.414          |
| Penetration depth of HDDA-BEE resin system                  | \( D_p \) | 242            |

In this study, Hexane diol-diacyrlate (HDDA) and Benzoil Ethyl Ether (BEE) is used as a monomer and photoinitiator respectively. To solve the mathematical model some process parameters are required [13] so, these are presented in Table 1.

4. Results and Discussions

Study of unconstraint depth photopolymerization under hollow Gaussian beam is studied on UV curable photopolymer resin system. Wide range of exposure dose attained by wide variation in intensity of light and exposure time is studied by applying the solution scheme mentioned in above section. To study beam propagation, wide range of intensities to be considered. These intensities are
categorized as low intensity category for the span of 0-2500 W/m² and high intensity for span of 2500-100000 W/m². Figures 3 and 4 show the results of propagation of hollow Gaussian shaped beam obtained through simulations executed through split beam method. These results are obtained after solving mathematical model across these ranges at constant exposure time of 0.2 s. Intensity range wise categorized simulated results of beam propagation are presented in subsequent following sections. The influence of various physical phenomena mentioned in above model like diffraction attained due to formation of focusing lens, progressive change in gradient of refractive index due to intensity of beam, and simultaneously absorption coupled with diffusion of photoinitiator in region I and region II of reaction zone area is discussed. Figures 3 and 4 show beam propagation along the direction of propagation in resin system under low exposure (time of 0.2s) (refer subfigures (a) beam intensity profile at entrance face, (b) profile of refractive index along propagation axis in figures 3 and 4.)

Figure 3. Propagation of low intensity (2000 W/m²) beam along propagation axis in photopolymer resin under exposure time 0.2 s (subfigures (a) profile of beam intensity at z=0, entrance face, (b) profile of refractive index gradient in xy plane and (c) beam width)

Figure 4. Propagation of high intensity (50000 W/m²) beam along propagation axis in photopolymer resin under exposure time 0.2 s (subfigures (a) profile of beam intensity at z=0, entrance face, (b) profile of refractive index gradient in xy plane and (c) beam width)

4.1 Propagation of Low Intensity Laser Beam
As per the Eq. 4, at lower intensity, there is unnoticeable changes in the refractive index (∆n=0) as ∆n is absolutely zero. Hence, the optical effect such as focusing effect due to lens formation due to curing is found to be insignificant. Thus during beam propagation, the significant effect observed is the absorption by photoinitiator and which set diffusion of photoinitiator species in region I and II of
reaction zone. Further if exposure dose is for longer time, it provides sufficient time for photoinitiator species from inner part of reaction zone (refer region I in figure 2) to get into curing. This results in curing inner hollow part. Hence, the cured voxel under such case do not exhibit hollow voxel. Further, decrease in refractive index is observed because the absorption effect in the polymerization reaction attenuates the beam intensity. This is typically observed along the direction of propagation (see figure 3 (b)).

4.2 Propagation of High Intensity Laser Beam
Due to rapid and spontaneous change in refractive index that typically takes place at higher intensity, refractive index goes to threshold limit \( \text{ns} = 1.414 \). This result in flattened hollow Gaussian profile of the beam and will be propagated further in resin (see figure 4 (b)). In this case of high intensity Gaussian beam exposure [13], cured voxel acts as a lens. The formation of this lens due to curing further offers phenomenon of the self-focusing of light into the resin system and also the diffraction effect. In case of high degree of hollowness under hollow Gaussian beam exposure; thin cured wall thickness is obtained. The thin wall thickness results in negligible self-focusing and diffraction effect as against reported [13] rigorously under Gaussian beam exposure. Further, propagation of beam goes to a considerably large distance in resin system in comparison with the case of energy exposure with beam of low intensity (see figure 4 (c)). Dynamics of refractive index variation, along with simultaneous absorption of light and diffusion of photoinitiator in resin system is recognized to coinciding aperiodic self-focus and de-focus of beam along propagation axis of the beam.

4.3 Results and Discussions on Evolution of Cured Voxel
Due to various phenomenon as stated in above subsections, variation of cured width along the propagation axis (profile of cured voxel) of beam is anticipated to get affected due to modulations observed in the beam intensity.

Figure 5 illustrates the experimentally obtained cured voxel at high (intensity 50000 W/m² and exposure time 0.6 s for case A) and low energy dose (intensity 2500 W/m² and exposure time 0.3 s for case B). Cured voxel obtained from experiments are compared with obtained cured voxel from simulations (see figure 6). Note that only exterior profile of the voxel is compared one-to-one for case of low energy dose. Further obtained cured voxel are characterized for its depth. Except at the base of the voxel, figure 6 represents good similarity between experimental and simulated predictions from
cured profile point of view. Maximum error between simulation and experimental result is observed at the base (z=0) of the voxel. Further, study [13, 14] has shown aperiodic nature of self-focus-de-focus effect along the direction of propagation of light. This effect is not observed in unconstraint photopolymerization on exposure of hollow Gaussian shaped beam. This cured width deviation particularly at the z=0 of propagation is due to the curing model used which do not consider absorption and scattering effects due to change in graded refractive index. These assumptions in used model show wherever energy exceeds its threshold energy required for curing. Although, in actual curing process, this typically do not holds good.

Figure 7 shows the comparison of experimentally obtained cured depth characteristic with the simulation results under wider energy dose for different degree of hollowness prescribed by ratio W0/rh. Here W0 is laser beam waist and rh is the hollow radius of beam. Lesser W0/rh ratio depicts higher degree of hollowness. Overall acceptable correlation among numerically predicted and experimental cured depth characteristics is observed. Both simulations and experimental results shows the gradual deviation from Beer Lambert’s cured depth model. In figure 7, marks A and B shows curing characteristic at lower and higher degree of hollowness respectively at constant energy dose attained at ratio 3.33 and 1.667 for A and B respectively. Marks C and D in figure 8 represents the curing characteristics at same ratio 3.33 and 1.667 respectively but these ratios are achieved by varying hollow radius. Earlier study [14] has discussed the significance of diffusion responsible for variation in cured depth at these marks. Process condition at point A signifies lesser inner zone for diffusion of species (region I in figure. 2) compared to process condition at point B. Lesser the inner area for diffusion at point A results in low absorption of photon. Thus, photons of light penetrate to a larger depth for reaction compared to point B, yielding higher cured depth.

Following points are summarized based on the mathematical modelling and experimental findings presented in this work:

- Self-focusing and trapping (optical effects) of light occurs in the photo-polymerised voxel because of changes in the refractive index through progression of curing. However, the effect of self-trapping is not significant in hollow Gaussian beam exposure as compared to complete Gaussian beam exposure.
- Dynamics of photoinitiator diffusion (both from internal and external regions of hollow Gaussian beam) and optical effects governs the shape of cured profile.
- In case of delivery of light of energy dose with higher exposure time, photoinitiator molecules from internal hollow region gets consumed. This leads to progression of curing in inner part of
hollow portion. This results in completely cured voxel although exposure is of hollow Gaussian beam.

- For development of microneedle it is necessary to have progression of curing in depth direction faster than diffusion of species from inner part of Gaussian exposure zone. To have this prescribed condition, exposure dose shall consists of lower exposure time and high beam intensity and degree of hollowness.

5 Conclusion

This paper presented a study of curing and development of cured voxel (typically the profile of voxel) under exposure of hollow Gaussian shaped laser beam over sufficient large depth resin system. Various physical phenomena such as diffraction, optical effects due to intensity (hollow Gaussian Beam) induced and dependent refractive index variation, absorption of photons and simultaneous diffusion of photoinitiator in both sides of exposure zone (zone I and II) are considered in the model. Simulation results are compared with experimental results. Approximately both; experimental and numerical predictions show similar results. Thus study presents effectiveness of the proposed model to determine development of cured voxel accurately. The typical of estimated cured voxel parameters includes cured depth and outer profile depicting width. The obtained outcomes are investigated to obtain process conditions for hollow microneedle from curing. It has been observed from results that formation of hollow microneedle depends on dominance between diffusion of photoinitiator species from inner part of reaction zone of hollow beam exposure and propagation of Gaussian beam along axis for the particular intensity and exposure time. Finally study lays a process attributes for developing microneedle by controlling exposure time, beam intensity and degree of hollowness. Thus study presents a new avenue of fabrication of polymer microneedle with controlled exposure conditions of hollow Gaussian beam. Use of biocompatible UV resin may be used in fabrication process to develop microneedle to be used in various biomedical applications.

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