

# A COMPUTER MODEL FOR LASER PHOTOPOLYMERIZATION

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## Abstract

A computer model for a laser induced photopolymerization process has been established which simulates stereolithography. The model couples irradiation, chemical reaction, and heat transfer equations to provide insights into rate processes occurring in the volume element contacted by the laser beam. Quantities predicted include the spatial variation in conversion of monomer to polymer, depletion of photoinitiator, and local variations in temperature in and around the spot contacted by the laser. This allows predictions to be made about the laser dwell time, depth penetration and uniformity of the photopolymer formed in the process.

## Introduction

One aspect of the stereolithography process that has not received much attention during initial development of the overall procedure concerns the physical and chemical changes that occur in the small zone of monomer/polymer mixture directly exposed to laser irradiation, and the rates at which these changes occur. The work described here addresses this aspect of the process.

Mathematical models have been developed for the photopolymerization process which allow computation of light intensity, absorbed light, photoinitiator concentration, monomer concentration, and temperature profiles, as functions of time, for the exposed reaction zone and surrounding monomer/polymer mixture. The model discussed here deals with the situation where the laser light spot remains stationary on the surface of the resin vat. A second model, one capable of handling the situation where the light spot moves across the surface of the resin vat in a series of small discrete steps, is being developed. Some preliminary results obtained from the moving spot model are presented to illustrate some of its capabilities.

### Mathematical Model

The mathematical model for the stationary light spot situation was developed by considering a cylindrical region of exposed material as shown in Figure 1. For this situation, where the light spot does not move with time, and the resin is spatially homogeneous, cylindrical symmetry can be assumed. This allows light intensities, concentrations and temperatures to be functions of the two spatial coordinates ( $r$  and  $z$ ) and time ( $t$ ).

The incident laser light is assumed to have a Gaussian intensity distribution

$$I(r, z, t) = I_0 e^{-2\left(\frac{r}{R}\right)^2} \quad \text{at } z=0, r \geq 0, t \geq 0 \quad (1)$$

The beam radius,  $R$ , being the value of  $r$  at which light intensity drops to  $e^{-2}$  of the peak value.

The decrease in light intensity with depth into the resin due to absorption by photoinitiator is given by

$$\frac{\partial I}{\partial z} = -\epsilon SI \quad (2)$$

with the light intensity at the surface ( $z=0$ ) given by eqn.(1). The light absorbed by photoinitiator is thus given by

$$I_a(r, z, t) = \epsilon SI. \quad (3)$$

Since photoinitiator is consumed by the photochemical initiation process, the rate of change of photoinitiator concentration can be calculated from

$$\frac{\partial S}{\partial t} = -\phi I_a \quad (4)$$

with  $S(r, z, t) = S_0$  at  $t=0, r \geq 0, z \leq D$ .

Monomer is consumed by the polymerization reaction, so the rate of change of monomer concentration can be calculated from

$$\frac{\partial M}{\partial t} = -R_p \quad (5)$$

with  $M(r, z, t) = M_0$  at  $t=0, r \geq 0, z \leq D$ .

According to Odian [1], a rate expression of the following form can be used for a photochemical polymerization process:

$$R_p = k_p M \left[ \frac{\phi I_a}{k_t} \right]^{0.5} \quad (6)$$

If an expression of this form is valid then eqn.(5) becomes

$$\frac{\partial M}{\partial t} = -k_p M \left[ \frac{\phi I_a}{k_t} \right]^{0.5} \quad (7)$$

The temperature field in the vicinity of the exposed region is given by a transient heat conduction equation with heat source term (heat generated by polymerization) [2]

$$\rho C_p \frac{\partial T}{\partial t} = k \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right] + \Delta H_p R_p \quad (8)$$

with

$$T(r, z, t) = T_0 \quad \text{at } t=0, r \geq 0, z \geq 0$$

$$\frac{\partial T}{\partial r} = 0 \quad \text{at } r=0, z \geq 0, t \geq 0$$

$$T = T_0 \quad \text{at } r \rightarrow \infty, z \geq 0, t \geq 0$$

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$$\frac{\partial T}{\partial z} = 0 \quad \text{at } z=0, r \geq 0, t \geq 0$$

The partial differential equations presented above together with the appropriate boundary and initial conditions constitute the mathematical model. It should be realized that this is a model and is an approximation to the real situation. In addition, a number of assumptions are implicit in the model formulation as presented here. Briefly these are as follows:

1. No flow of material (convection or diffusion) in any direction.
2. No optical effects (scattering, diffraction, refraction or reflection).
3. Heat generation due to heat of polymerization only.
4. Negligible heat loss from surface of monomer vat.
5. All physical and thermodynamic parameters constant.
6. Photoinitiator fragmentation products non-light-absorbing.

When considering a mathematical model for the moving spot situation, certain modifications to the model as presented above, are required. Since the moving spot situation no longer possesses cylindrical symmetry, a change to rectangular coordinates is necessary, and a

transient heat conduction equation in three spatial dimensions, x, y, and z, is required. Motion of the laser light spot is achieved simply by changing the coordinates of the light spot center on the surface of the monomer vat.

The mathematical model thus consists of a system of coupled partial differential equations of different types, the most complex of which is the parabolic, second order heat conduction equation. In order to set up numerical solution techniques for the set of equations, the infinity boundary conditions for the heat conduction equation were approximated by specifying the temperature at some finite r and z values. It has been found that values of  $r=5R$  and  $z=2D$  are adequate for the situation used to test model operation (see Figure 2). This approximation is only really valid for short times ( $<0.5$  seconds) as for longer times the boundary conditions start to influence the computed temperature values. Both Runge-Kutta and Alternating Direction Implicit methods [3, 4] were used to numerically solve the equations.

### Results and Discussion

The mathematical model presented above is general in that it can be used to model any resin system provided the appropriate physical, thermodynamic, and kinetic parameters are supplied by the user. The model was tested using physical and thermodynamic properties for a HDDA monomer, and a 15 mW laser light source. This information together with the dimensions of the exposed region, etc., is summarized in Table 1. Polymerization rate information for HDDA was obtained from a calorimetric study by Tryson and Shultz [5]. These data were used because they represented the most comprehensive available data set containing temperature dependent rate information. The data and kinetic parameters were derived experimentally by curve fitting to the 1/2-order kinetic expression of eqn.(6). Thus, in order to calculate consistent results it was necessary to use the 1/2-order rate expression in our treatment. It should be noted that mechanistically an expression that is 1st-order with respect to light intensity is most appropriate for photopolymerization of multifunctional monomers [6]. The computer model is completely general, however, and will accommodate any rate expression with appropriate rate constants.

Figures 3 and 4 are contour plots prepared from data obtained from the stationary spot model. Figure 3 illustrates how conversion of monomer to polymer varies with position for an exposure time of 0.3 seconds. The contours clearly illustrate how conical or "bullet-shaped" test-pieces would be formed by short-term exposure with a stationary laser beam. Figure 4 shows the corresponding temperature field in the vicinity of the exposed segment.

Figures 5 and 6 represent some preliminary results obtained from the moving spot model currently under development. Figure 5 shows temperature profiles along the y-axis, and how these change with time as the light spot moves in the positive y-direction. It is interesting to note that for short times ( $<0.3$  seconds) the center of the laser spot precedes the peak in the temperature distribution, whereas for longer times ( $>0.4$  seconds) the center of the spot lags behind the temperature peak. The fact that the resin is heated prior to exposure may be an important factor which could affect the nature of the polymer formed during the process. Figure 6

shows the temperature contours on the surface of the monomer vat for an exposure time of 0.3 seconds.

### Conclusion

A mathematical model for the stereolithography process has been developed and tested for a HDDA monomer reaction system and stationary laser light source. The model can be used to investigate process dynamics in slices of various thickness, with different laser light intensities, exposure times, and physical and chemical parameters. Results obtained allow prediction of laser dwell time, light depth penetration, and uniformity of polymer formed during the process. Model predictions are reasonable, but experimental verification has yet to be performed. A model for the moving spot situation is currently under development, and preliminary results obtained look promising.

### Acknowledgements

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### Nomenclature

$C_p$	heat capacity ( $J g^{-1} K^{-1}$ )
$D$	slice thickness (cm)
$I$	light intensity ( $E cm^{-2} sec^{-1}$ )
$I_a$	absorbed light ( $E cm^{-3} sec^{-1}$ )
$I_o$	peak light intensity ( $E cm^{-2} sec^{-1}$ )
$k$	thermal conductivity ( $W cm^{-1} K^{-1}$ )
$k_p$	propagation rate constant ( $l mol^{-1} sec^{-1}$ )
$k_t$	termination rate constant ( $l mol^{-1} sec^{-1}$ )
$M$	monomer concentration ( $mol l^{-1}$ )
$M_o$	initial monomer concentration ( $mol l^{-1}$ )
$r$	radial position (cm)
$R$	nominal radius of laser beam (cm)
$R_p$	polymerization rate ( $mol cm^{-3} sec^{-1}$ )
$S$	photoinitiator concentration ( $mol l^{-1}$ )
$S_o$	initial photoinitiator concentration ( $mol l^{-1}$ )
$t$	time (sec)
$T$	temperature ( $^{\circ}C$ )
$z$	depth of light penetration (cm)
$\Delta H_p$	heat of polymerization ( $J mol^{-1}$ )
$\epsilon$	molar absorptivity of photoinitiator ( $J mol^{-1}$ )
$\phi$	quantum yield for initiation
$\rho$	density ( $g cm^{-3}$ )

## References

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**Table 1.** Information and data used for test case.

<u>Item</u>	<u>Value Used</u>
Laser beam radius (R)	0.0125 cm
Slice thickness (D)	0.05 cm
Peak light intensity ( $I_0$ )	$4.81 \times 10^{-5} \text{ E cm}^{-2} \text{ sec}^{-1}$
Initial photoinitiator concentration ( $S_0$ )	$0.15 \text{ mol l}^{-1}$
Initial monomer concentration ( $M_0$ )	$3.0 \text{ mol l}^{-1}$
Initial temperature ( $T_0$ )	35°C
Molar absorptivity of photoinitiator ( $\epsilon$ )	$200 \text{ l mol}^{-1} \text{ cm}^{-1}$
Quantum yield for initiation ( $\phi$ )	0.1
Density ( $\rho$ )	$1.15 \text{ g cm}^{-3}$
Thermal conductivity (k)	$2.0 \times 10^{-3} \text{ W cm}^{-1} \text{ K}^{-1}$
Heat capacity ( $C_p$ )	$1.70 \text{ J g}^{-1} \text{ K}^{-1}$
Heat of polymerization ( $\Delta H_p$ )	$1.66 \times 10^5 \text{ J mol}^{-1}$
Polymerization rate	Data for HDDA [5]
Laser step size (moving spot)	0.00125 cm
Laser step period (moving spot)	0.025 sec

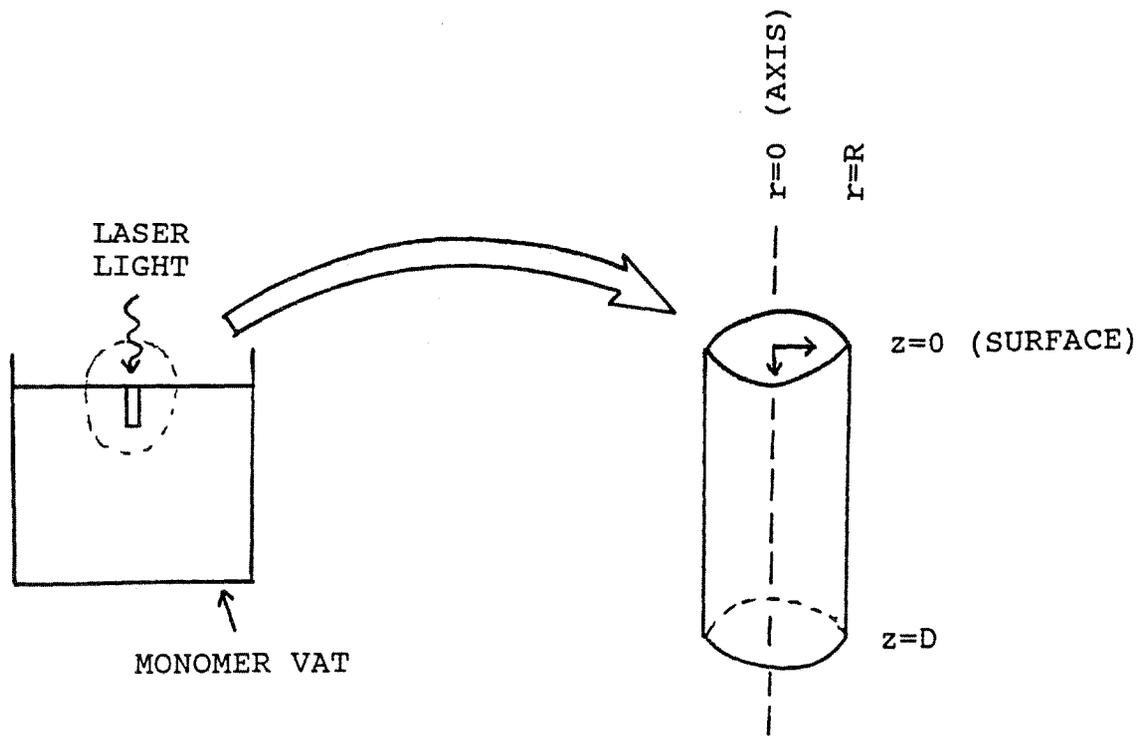


Figure 1. Cylindrical region used for development of mathematical model, showing coordinate system origin.

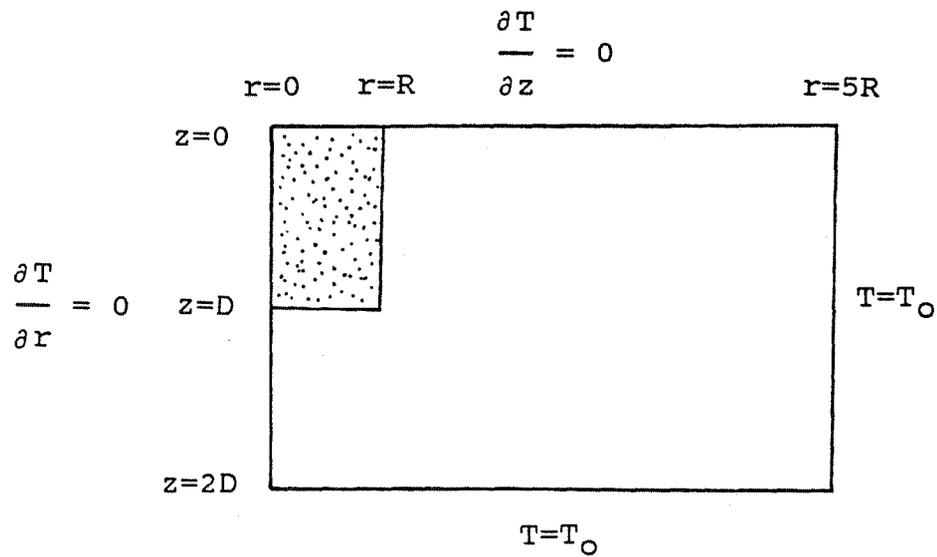


Figure 2. Finite region used for numerical solution of heat conduction equation.

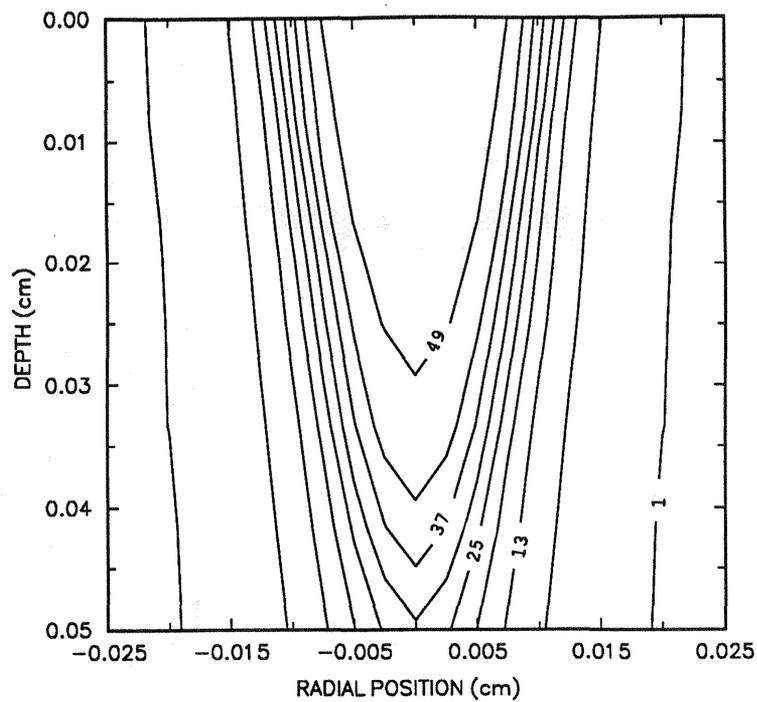


Figure 3. Contour plot showing % conversion of monomer as a function of position. Time of exposure = 0.3 seconds. Contour interval = 6%.

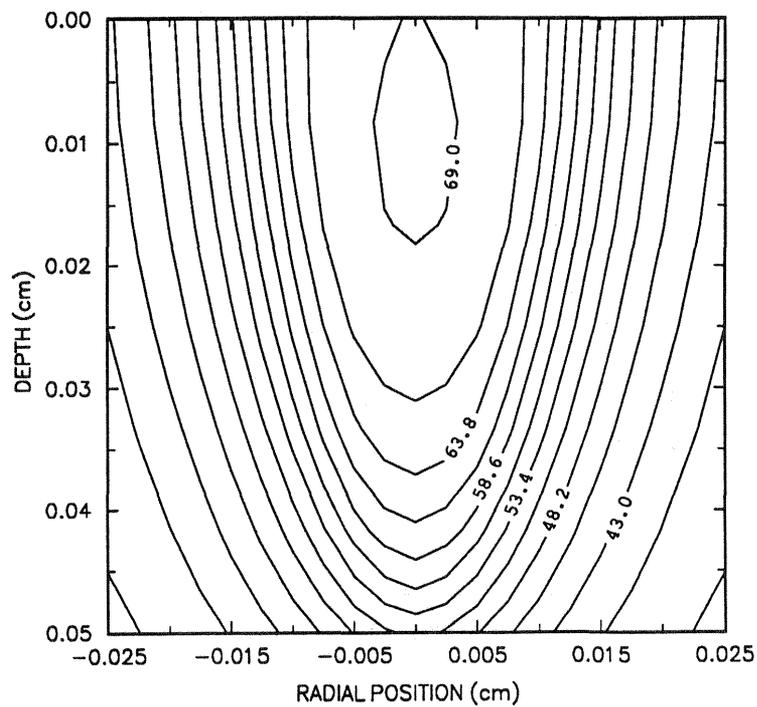


Figure 4. Contour plot showing temperature as a function of position. Time of exposure = 0.3 seconds. Contour interval = 2.6°C.

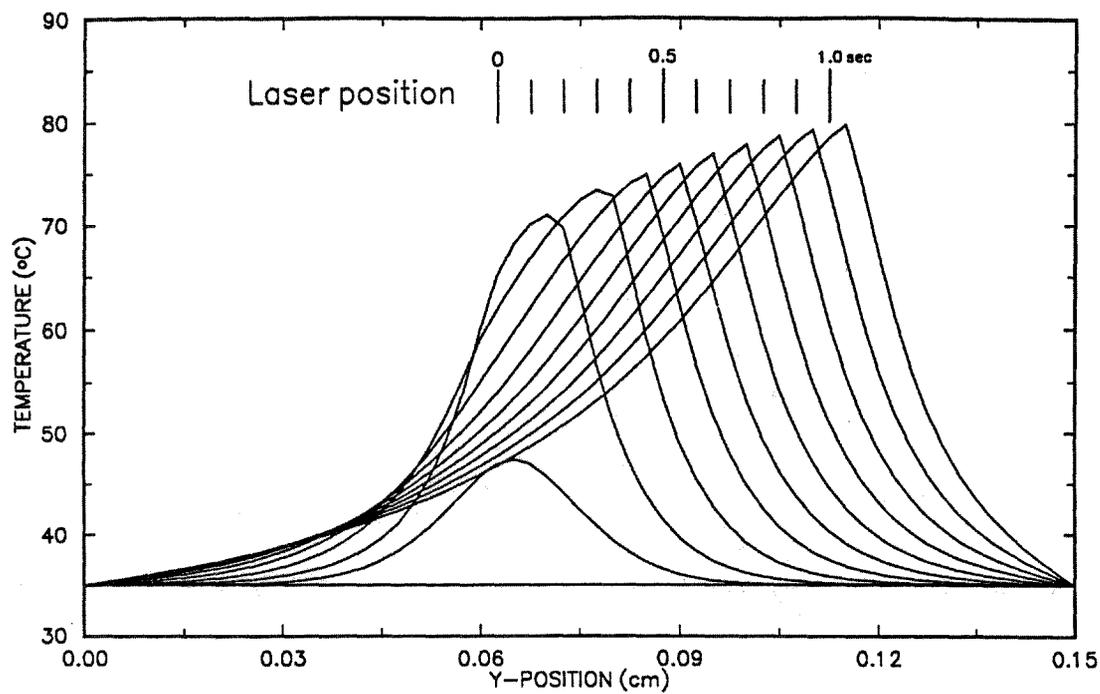


Figure 5. Temperature profiles along y-axis as obtained from moving spot model. Plot time increment = 0.1 seconds.

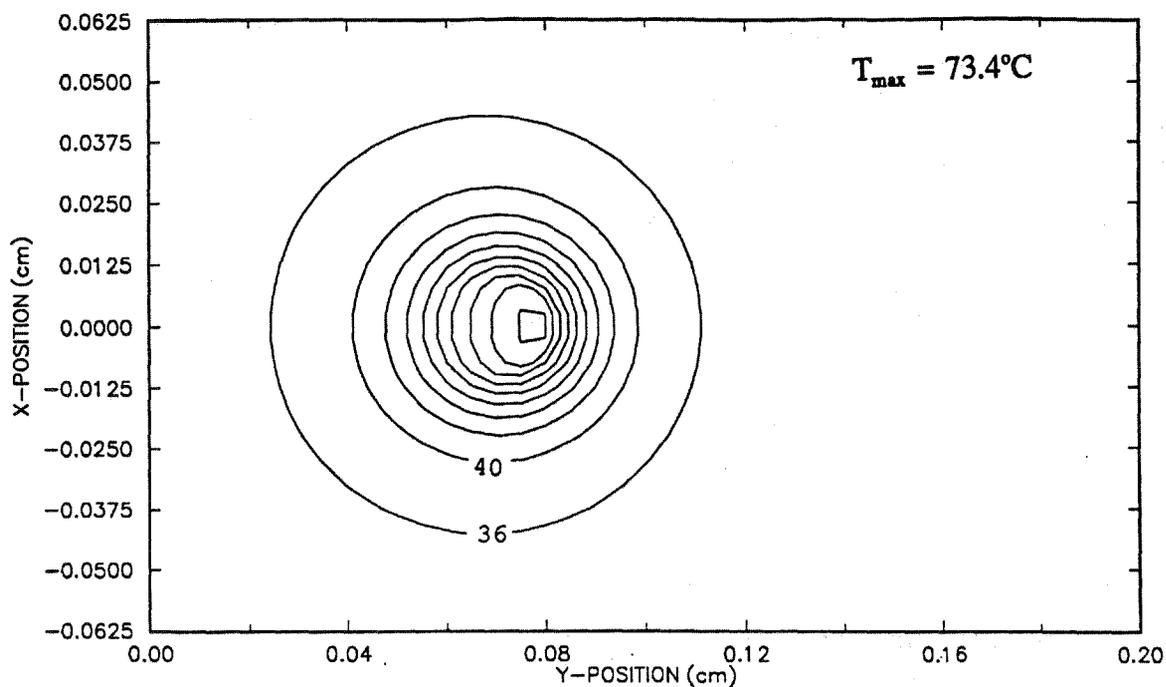


Figure 6. Contour plot showing temperature distribution on surface of monomer vat as obtained from the moving spot model. Time of exposure = 0.3 seconds. Contour interval = 4.0°C.