Mechanisms of Carbon Dioxide Laser Stereolithography in Epoxy-Based Materials

M. A. F. SCARPARO,[1,*] Q. J. CHEN,[2] A. S. MILLER,[2] J. H. ZHANG,[3] and S. D. ALLEN[2]

[1]UNICAMP—Instituto de Fisica, D.E.Q. 13083-790, Campinas, S.P., Brasil; [2]Tulane University, 103 Stanley Thomas Hall, New Orleans, Louisiana 70118; and [3]Xavier University of Louisiana, Department of Chemistry, New Orleans, Louisiana 70125

SYNOPSIS

We present in this article the use of infrared laser radiation to achieve localized curing in thermosensitive epoxy resin compounds. In stereolithography, the objective is to cure a localized region in a material by precisely confining the laser energy to the area that is to be cured. Industry already uses ultraviolet laser radiation at 352 nm to fabricate three-dimensional structures. Via infrared laser curing, we demonstrate the viability of a completely thermal localized curing process. In our experiment, we have focused the beam from a carbon dioxide (CO_2) laser onto a sample composed of epoxy resin, diethylene triamine, and silica powder. Such resins typically cure, or solidify, when heated to moderately high temperatures, and our results show that we can confine the heating of the material, and, therefore, its curing in all three dimensions. We present a physical and a chemical model to describe the process and measure the curing rate as a function of temperature. In order to model the flow of heat in our sample as a result of infrared laser irradiation, we solved the time-dependent heat equation in cylindrical coordinates using the Crank-Nicholson finite-difference method. The results allow us to predict the curing behavior of the sample as a function of laser irradiation conditions, and we find good agreement with our preliminary experimental observations. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High-power CO_2 clasers are used in a wide variety of material-processing applications. Stereolithography, a powerful means of producing three-dimensional models or prototypes, is one such application which has not been significantly explored. Conventional stereolithography uses ultraviolet (UV) lasers, typically operated at a wavelength of 352 nm, to cure photosensitive polymers with computer control of the direction and power of the laser beam to build up a desired three-dimensional shape.[1,2] The process relies on photosensitive polymers, the chemical structure of which is affected by the absorption of high-energy (UV) photons. Organic photochemistry is a well-established science, and so the process of UV stereolithography is relatively well understood.

Infrared (IR) radiation gives rise to the vibrational and rotational excitation of organic molecules. The high intensity of IR laser sources provides the opportunity to control key parameters such as heating time and spatial confinement of heating, so that thermal effects in organic materials may be better localized and characterized. We believe that the application of IR laser radiation to thermosensitive materials such as resins may provide a novel, reliable, and cost-effective means of manufacturing industrial prototypes.

It has been reported in the mainstream press, for example, that the automobile industry plans to incorporate new lightweight materials into automobiles.[3] The material considerations are so heavily in favor of the new composites that they outweigh their higher cost. An ultralight test car was recently built by General Motors; its performance in terms of acceleration and top speed compares favorably with that of a top-of-the-line BMW and does so with only a 111 horsepower engine and an average fuel effi-

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ciency of 62 miles/gallon. Laboratory results for other lightweight cars are even more encouraging.

These same composites, so important to next-generation automobile technology, can be modeled and built by stereolithography. Design modification and fabrication of new parts or molds would be reduced to software changes. We believe that stereolithography has the potential to become a critical industrial technology.

LASER PROCESSING OF RESINS

The main advantage of using a laser to cure a resin is that curing may be restricted to a highly localized region. In previous work, we presented the results of a method for spatially selective solidification of a high-viscosity resin mixed with diethylene triamine and silica powder.[4] Using a carbon dioxide (CO_2) laser, we were able to form simple three-dimensional structures, with good spatial resolution ($\sim 100 \, \mu m$) from the liquid. The resulting structures did not shrink significantly after curing.

Thermo-resins typically cure, or solidify, when heated to moderately high temperatures, between 60 and 100°C. In this work, we have examined some of the physics and chemistry of the process, with an emphasis on understanding the parameters which most affect our ability to restrict or localize curing to a small region. We have examined the behavior of our resin mixture on heating to different temperatures for different times. Our results are encouraging because they show that we can effectively confine the heating of the material and, therefore, its curing to small regions, on the order of the laser beam size, in three dimensions.

We present physical and chemical models to describe the localized curing process and measure the curing rate as a function of applied temperature. We also solve the time-dependent heat equation in cylindrical coordinates using the Crank-Nicholson finite-difference method to allow us to predict the curing behavior of the resin as a function of laser irradiation conditions.[5] By means of differential scanning calorimetry (DSC), we have obtained the activation energy of the curing reaction. There is good agreement between the calculated and observed behavior of the resin.

CHEMICAL MODEL OF THE LOCALIZED CURING PROCESS

Curing occurs in our epoxy sample by means of crosslinkage between epoxy resin and diethylene triamine reactants. Thermosetting polymers are normally made from relatively low-molecular-weight, semifluid substances, which become highly crosslinked when heated. The crosslinked substance which results is typically hard, infusible, and insoluble and has a three-dimensional network of bonds interconnecting the polymer chain. To be able to localize curing in our sample, we found that a specific ratio of epoxy, diethylene triamine, and silica powder is required. Improper ratios of the reactants lead to the formation of low-molecular-weight molecules and result in a sample which is either poorly cured or completely uncured.

We found that the amount of silica, relative to the amounts of epoxy and diethylene triamine, is critical to confining the curing process to a localized volume. If the amount of silica is too small, curing is not localized. Conversely, if the amount of silica is too large, the sample does not cure properly. The formula for our sample represents a balance between these competing concerns. Because the thermal conductivity of silica (11.3 mW/cm K) is much greater than that of uncured epoxy (0.359 mW/cm K), it appears that the silica acts as a heat sink to localize laser heating and limit the reaction volume.

A PHYSICAL MODEL FOR LASER-INDUCED LOCALIZED CURING

We have constructed a simple model to describe the flow of energy in laser-induced curing, so that we may predict both localization and curing rates as a function of laser parameters such as power, beam diameter, and scanning speed. In our initial experiments, we achieved localized curing by scanning a continuous wave (cw) CO_2 laser repeatedly over a circular path on the sample's surface with a scan speed v. By dividing the beam diameter 2ω by the scanning speed, one obtains the dwell time,

$$t_d = \frac{2\omega}{v} \qquad (1)$$

which is the average time any spot on the laser scanning path is irradiated.

In order to predict the effect that the laser has on curing, we had to determine how much energy was delivered to the sample and over what volume that energy was distributed. Because the sample is highly absorptive at the CO_2 laser wavelength, nearly all of the energy in the beam during the dwell time is absorbed by the sample within a distance from the surface equal to the absorption depth δ. We de-

termined the absorption depth by measuring the transmittance of an 85-μm-thick sample of uncured material over a wavelength range which included that of the CO_2 laser at 10.6 μm and found that δ = 37 μm. We assumed that a small cylindrical volume V absorbed an energy E during the dwell time, where V is given by

$$V = \pi\omega^2\delta \qquad (2)$$

and ω is the $1/e$ radius of the laser beam. The energy deposited in volume V is the product of the cw laser power and the dwell time

$$E_p = Pt_d. \qquad (3)$$

The approximation of eq. (2) is reasonable for the sample in our experiment because the absorption depth is quite short. When working with a material which does not absorb the laser energy as strongly, the absorption depth may exceed the depth of focus of the laser beam. For such low-absorption cases, it is likely that the depth of focus will be the factor which best determines the confinement of laser energy in the direction normal to the sample surface.

The rate $d\beta/dt$ at which the polymer cures (where β is the fractional extent of the reaction) is a function of the temperature imposed on it. For the short irradiation times utilized in the previous experiments, the change in temperature, ΔT, is directly proportional to the energy deposited through the heat capacity C_P and the mass m of material contained in the volume V according to

$$E = mC_P\Delta T. \qquad (4)$$

We can calculate the mass of the heated volume using the mass density $\rho = 1.16$ g/cm³. Once the curing process is described as a function of temperature and time, we may predict the curing behavior as a function of laser irradiation conditions.

We are concerned with achieving curing in a highly localized region, so it is critical to have a quantitative understanding of where the laser energy is deposited and how it spreads through the polymer. Intuitively, we expect that if the laser is scanned too quickly over the sample, we may not achieve curing at all because any one spot does not absorb sufficient energy to initiate curing. When the scanning speed is too slow, the deposited energy would spread outward from the irradiated area and a larger area than desired would be cured. There is a balance between initiating the curing process and restricting its spread to within the desired spatial boundaries.

In fact, we observed such behavior, and in the following, we describe the process quantitatively.

TEMPERATURE CALCULATION FOR LASER-INDUCED HEATING OF THE POLYMER

In order to model the flow of heat in laser-induced curing, we used a finite-difference approach to solve the time-dependent heat equation. We assumed that each time the laser passes over a point on the epoxy surface, the irradiated volume absorbs the energy of the pulse and experiences a temperature increase. The time-dependent heat equation is

$$\nabla^2 T = \frac{1}{D}\frac{\partial T}{\partial t} - \frac{G}{K} \qquad (5)$$

where D is the thermal diffusivity of the sample, K is the thermal conductivity, and G describes the rate at which heat is delivered from the laser.[6] We then assumed that energy is delivered proportionally to the Gaussian intensity profile of the laser beam, which allows us to express the source term G as

$$G = \left(\frac{\alpha P}{\pi\omega^2}\right)\exp\left(-\frac{r^2}{\omega^2} - \frac{|z|}{\delta}\right) \qquad (6)$$

where r is the distance from the center of the beam, z is the depth from the surface of the sample, δ is the absorption depth, P is the power input, and α is the absorption coefficient. We also assume that this G is valid during the dwell time t_d, so that

$$t \in (0, t_d).$$

Because in our previous experiments we scanned the laser in a circular path over the sample, irradiation of any point was periodic. The scanning speed and size of the circular path were such that the period was approximately 35 ms and the dwell time was 0.6 ms for a beam diameter of 1 mm, the parameters used in our numerical simulation. The radial and axial thermal transient constant τ is defined as

$$\tau = \frac{d^2}{D} \qquad (7)$$

where D for our sample is 22.5×10^{-5} cm²/sec and d is the appropriate characteristic length, making τ about 10 s for the radial transient ($d = w = 500$ μm) and about 100 ms for the axial transient ($d = \delta$

= 37 μm). We used the Crank-Nicholson finite-difference algorithm to solve the heat equation with the appropriate periodic heat source term G defined above. The thermal conductivity of our epoxy sample is close to that of air (0.24 mw/cm K). This indicates that a significant fraction of the heat dissipation will occur into the air.

We assumed that the thermal properties, K and D, and the optical properties, δ and R (the surface reflectivity $\sim$ 5%), are all temperature independent; we ignore the silica and the change in the optical and thermal properties of the sample as it cures. To simplify the solution of the problem, we assumed that the edge of the sample is sufficiently far from the area of laser irradiation that the source term looks like a point source of heat. The implication is that for large r,

$$\frac{\partial T}{\partial r} = -\frac{Tr}{r^2 + z^2} \tag{8a}$$

and $\tag{8b}$

$$\frac{\partial T}{\partial z} = -\frac{Tz}{r^2 + z^2}$$

and that at the air-sample interface

$$K_{air}\frac{\partial T}{\partial z} = K_{sample}\frac{\partial T}{\partial z}. \tag{9}$$

EXPERIMENTAL PROCEDURE

We chose an epoxy resin on the basis of its viscosity, thermosensitivity, and stability during the curing process. When heated, such polymers become a soft viscous fluid and may be molded into a desired shape. We determined by trial and error an appropriate mixture of reactants that provided the best results for localized curing. The optimal sample was composed of 10 parts (by weight) epoxy resin, 1.4 parts diethylene triamine, and 0.7 parts silica powder.

Before attempting to explain the experimental results of localized curing, we characterized the bulk curing process. We heated a small volume of the liquid sample by placing it in a beaker wrapped in heat tape. First, we monitored the temperature inside the sample as a function of time for several different ambient temperatures. The voltage from a cold junction compensator was fed into a digital oscilloscope where we stored the temperature evolution of the sample. Simultaneously, we monitored the transmissivity of the sample with a helium neon

(HeNe) laser. Transmissivity is a simple means of detecting the onset of curing in the sample, since the liquid sample is relatively transmissive to the red light of the HeNe laser but becomes opaque after it solidifies. By correlating the evolution of the internal temperature of the sample with the record of its transmissivity, we were able to determine the rate of curing as a function of the temperature imposed on the sample.

The results of the temperature evolution for different heating rates are shown in Figure 1. We imposed six different external temperatures on the sample, and we see that the curing behavior is similar for each case; however, as expected, the curing occurs much more rapidly with a higher imposed temperature. The results also show plainly that the reaction is exothermic. In order to predict more accurately the rate at which the reaction occurs as a function of temperature and to calculate the activation energy of the reaction, we undertook a standard measurement procedure using a DSC (Perkin-Elmer DSC-7). The DSC can plot heat flow into a small sample for either a fixed temperature or a ramped temperature. In either case, the heat flow required to maintain a certain temperature ($\pm$ 0.5°C) in the sample is compared with the heat flow into a nonreactive alumina sample. Therefore, as the reaction proceeds in the reactive sample, one may easily determine whether the reaction is endothermic or exothermic. By integrating the difference in heat flow between the reactive and nonreactive samples, one finds the enthalpy of the reaction.

The parameter of greatest interest to us in determining how the sample cures under laser irradiation is the activation energy E_A of the reaction. The rate of the reaction $d\beta/dt$ is an exponential function of temperature given by

$$\frac{d\beta}{dt} = Ke^{E_A/kT}, \tag{10}$$

where k is the Boltzmann's constant, T is the absolute temperature, and K is a preexponential constant. We used a standard DSC method to obtain E_A. The fraction of the reaction completed at any time is assumed to be the ratio of the heat released by the reaction to the total heat released by the completed reaction (the enthalpy ΔH). Plotting the fractional conversion β versus time for multiple isothermal scans, each at a different temperature, provides the necessary information to calculate the activation energy.
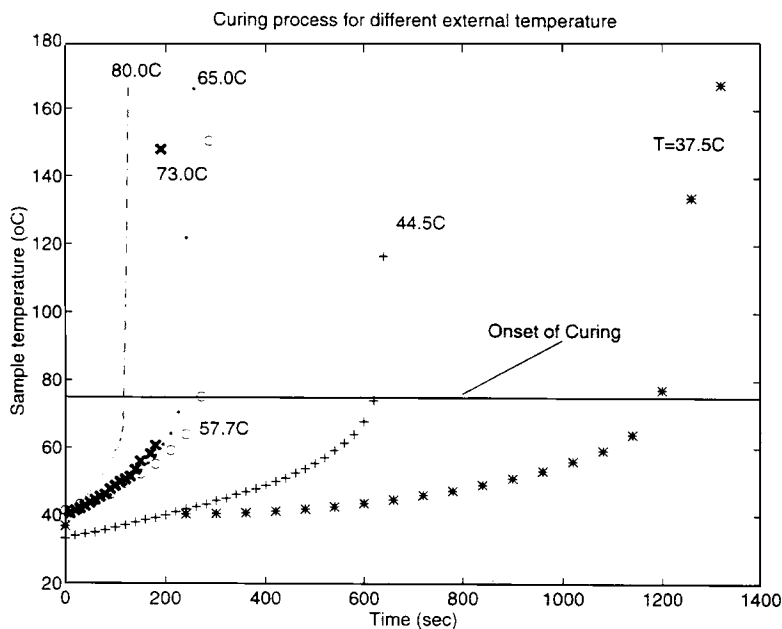
Figure 1 Temperature evolution for the sample as it cured for different heating rates. The point where the sample cured as noted by simple visual inspection is noted as the "onset of curing."

RESULTS

The first tests performed with the DSC used a linearly increasing (or scanned) temperature, where we monitored the flow of power to the sample. The average value obtained for the enthalpy of the reaction over several differential temperature scans (an example of which is shown in Figure 2) is ΔH = (65.5 ± 1) kJ/mol. We also utilized isothermal scans, where a small amount of the sample is heated
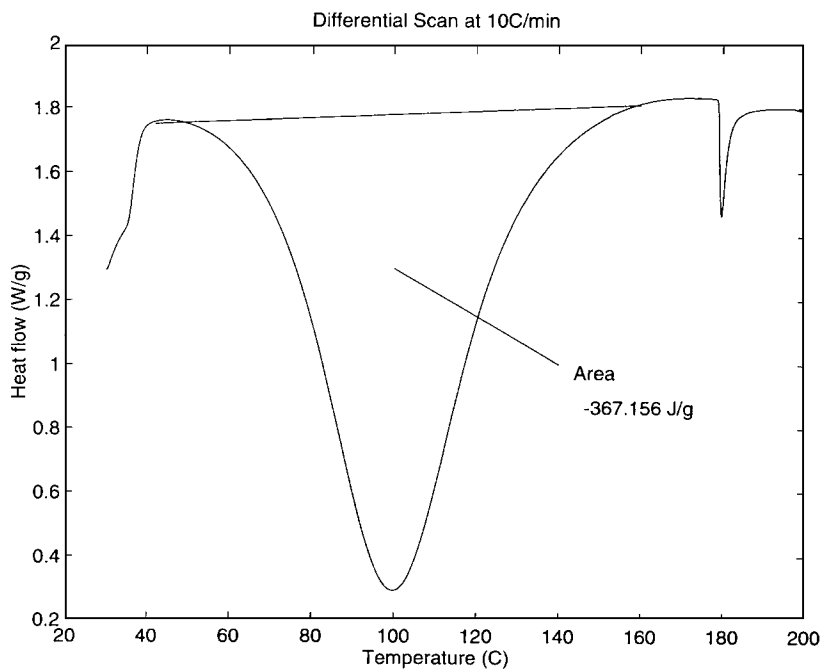
Figure 2 Results of differential scan which reveal the enthalpy of the curing process to be approximately 367 J/g.

quickly to a prescribed temperature and maintained at that temperature for the duration of the reaction. A typical plot is shown in Figure 3, where the initial increase in power flow represents the energy required to heat the sample to the desired temperature. The power flow to the nonreactive alumina sample quickly equilibrates, whereas the flow to the reactive epoxy sample shows the variation induced by heat released in its curing process. Integrating the difference of the two curves from time $t = 0$ s to t gives the amount of energy released by the reaction prior to t. As $t \rightarrow \infty$, the energy released in the isothermal scan approaches ΔH. The ratio of the energy released at t to ΔH is the fractional conversion β of reactants at time t.

One standard means of extracting the activation energy E_A from the DSC data is to recognize that the exponential dependence of the reaction rate on E_A and T allows us to write[7][9]

$$\ln(t_{1\beta}) - \ln(t_{2\beta}) = \frac{E_A}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (11)$$

where $t_{1\beta}$ and $t_{2\beta}$ are the times required to reach a given fractional conversion at two different temperatures T_1 and T_2 and R is the molar gas constant ($R = 8.314$ J/K-mol). By plotting β versus $\ln(t)$, we can find the difference in time required to reach a given conversion β for different temperatures, and

the above equation may then be solved for the activation energy. We have performed several isothermal scans of the epoxy sample, and the semilog plots of β versus $\ln(t)$ are shown together in Figure 4. The corresponding Arrhenius plots are shown in Figure 5, where each of the lines represents one specific fractional conversion β. The results show that the activation energy for the curing process is $E_A = (50.1 \pm 0.9)$ kJ/mol.

Numerical simulation of heat flow in the sample induced by the laser is accomplished with the heat equation [eq. (5)]. We used parameters relevant to an experiment that we carried out previously[4] where we scanned a CO_2 laser beam around a circular path on the sample, with a scanning speed $v = 160$ cm/s. From eq. (1), we obtain a dwell time of 0.6 ms, for a beam focused to a $1/e$ radius of 0.5 mm. Using an absorption depth of 37 μm, we assumed that the laser energy of each dwell time was deposited in a volume of 29×10^{-3} mm^3. With a cw operating power of 20 W, the energy deposited per dwell time is approximately 13 mJ. The thickness of the uncured sample for each layer of the cylinder grown by stereolithography was 80–100 μm. Using the above parameters in the finite-difference simulation of the heat equation yields the temperature evolution in time at any one spot under the center of the scanning beam on the surface of the sample (Fig. 6). Because of the low thermal conductivity
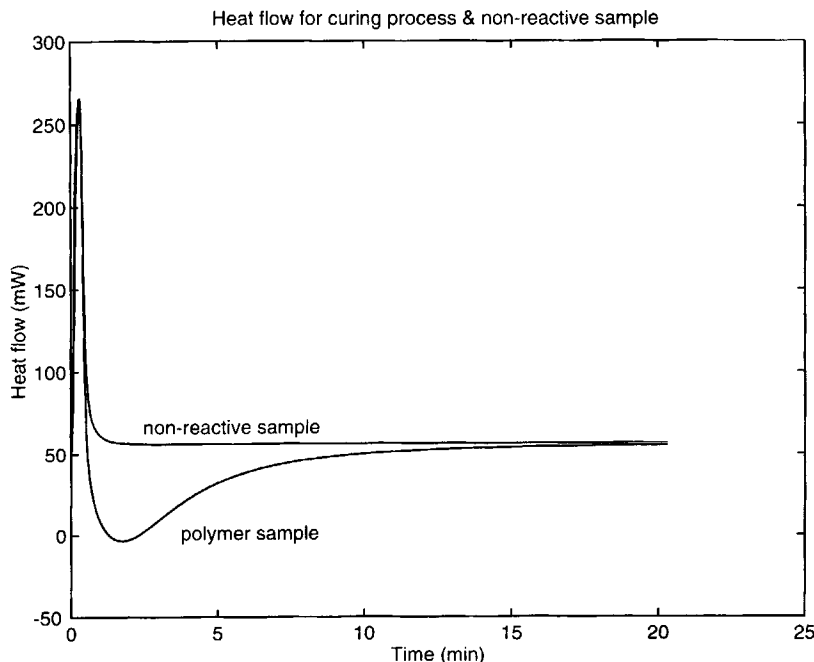

Figure 3   Results of DSC isothermal scan of the polymer-curing process and comparison with the heat flow into a nonreactive sample at 90°C.
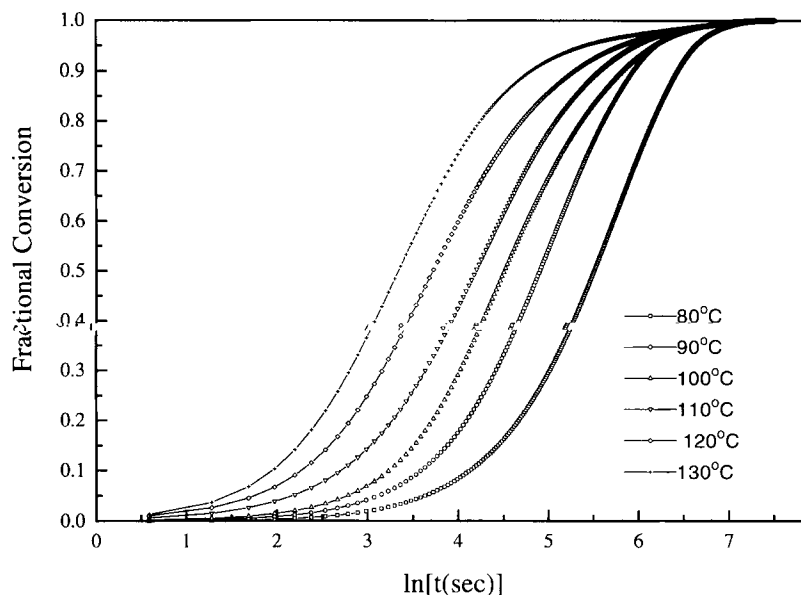
Figure 4 Plot of fractional completion of the reaction (or conversion) versus $\ln(t)$ for various temperatures.

of the sample, each irradiation of the site results in an essentially adiabatic rise in the temperature which does not decay to ambient between irradiations.

As the total ΔT increases, however, the $1/e$ decay time decreases, varying from 225 ms for the first heating cycle to 35 ms for the seventh. At steady state, the temporal behavior of the temperature of an irradiated site would be a series of temperature spikes on a constant background with a decay time

equal to the cycle time. Because of the simplifying assumption of temperature-independent thermal properties, each adiabatic temperature spike is the same. For our experimental conditions, $\Delta T_{adiabatic}$ = 253 K from eq. (4), while the time-dependent calculation yields $\Delta T_{finite\ difference}$ = 260 K. As shown in Figure 6, the temperature at the surface of the sample is sufficiently high to ensure that curing occurs quite rapidly within a small number of pulses. Although curing would take approximately 12 s at the
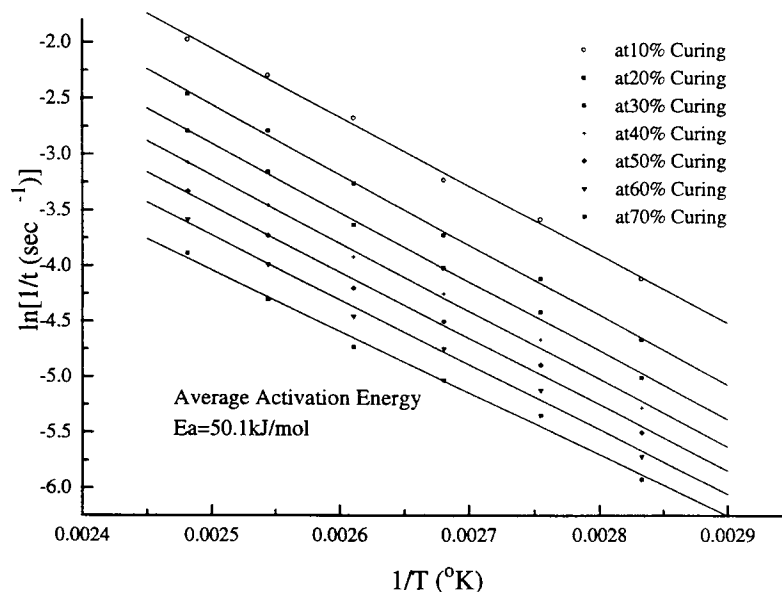

Figure 5 The Arrhenius plots of the curing process taken from the results of Figure 4.
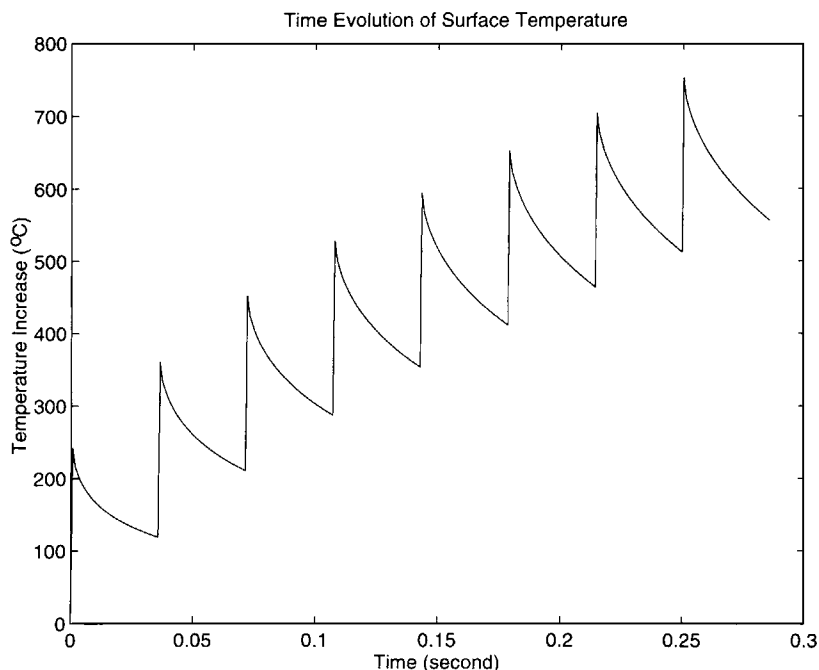
Figure 6   Evolution of the temperature of the sample over a sequence of revolutions.

average temperature during the first pulse, according to the Arrhenius plot of Figure 5, by the sixth pulse ($T_{average}$ = 888 K), curing is complete within a few tens of milliseconds.

The challenge is to maintain the temperature of the sample at a temperature that results in a rapid curing without significant sample degradation. We performed a thermogravimetric analysis which showed that degradation occurs in a few minutes above 550 K. The temperature calculation indicates that the sample does exceed the degradation limit but only for very short times. Optimization of the process will involve determining irradiation conditions, i.e., power, spot size and dwell time, such that the sample cures rapidly but does not degrade. Simply lowering the power and decreasing the scan speed would accomplish this goal but would result in larger cured areas because of thermal diffusion, thereby worsening the process resolution.

Figure 7(a) shows a temperature profile across the epoxy-air interface after about seven pulses, where the various curves are surfaces of constant temperature. Such plots are useful in determining the rate at which the curing process occurs at any location in the plane. Of particular interest is where the temperature falls to some given fraction of its peak. In Figure 7(b), we show the isotherm for 1/ e of T_{max}. It is interesting to compare the extent of the isotherm with the size of the laser beam and to note that they are nearly identical. The fact that

the temperature increase is confined roughly to within a lateral radius of 0.6 mm and a depth of 0.30 mm is easily attributable to the relatively short exposure to the laser and the low thermal conductivity of the sample. This gives us confidence that we are capable of confining the cured sample to a volume with lateral dimensions defined approximately by the width of the beam.

We also calculated the rise in temperature at the surface of the sample and at the center of the laser beam. We were able to show that, within a relatively small number of revolutions or scanning cycles (three or four), the epoxy was heated to a temperature that ensures rapid curing. The Arrhenius plot of Figure 5 shows the reaction time as a function of temperature, and Figure 6 shows the temporal evolution of the temperature on the sample surface. It is straightforward to establish an upper limit on the amount of time required to cure the sample. Referring to Figure 6, we see that during the 35 ms between the first and second pulses, the temperature is at least 140°C above room temperature. This means that the reaction will proceed at least as fast as Figure 5 would indicate for 413 K, which corresponds to approximately 39 s. Only a small amount of the reaction is complete during the 35 ms period between pulses. Between the second and third pulses, however, the temperature remains above 473 K, and the corresponding reaction time is 7 s. Still, not much of the reaction is completed
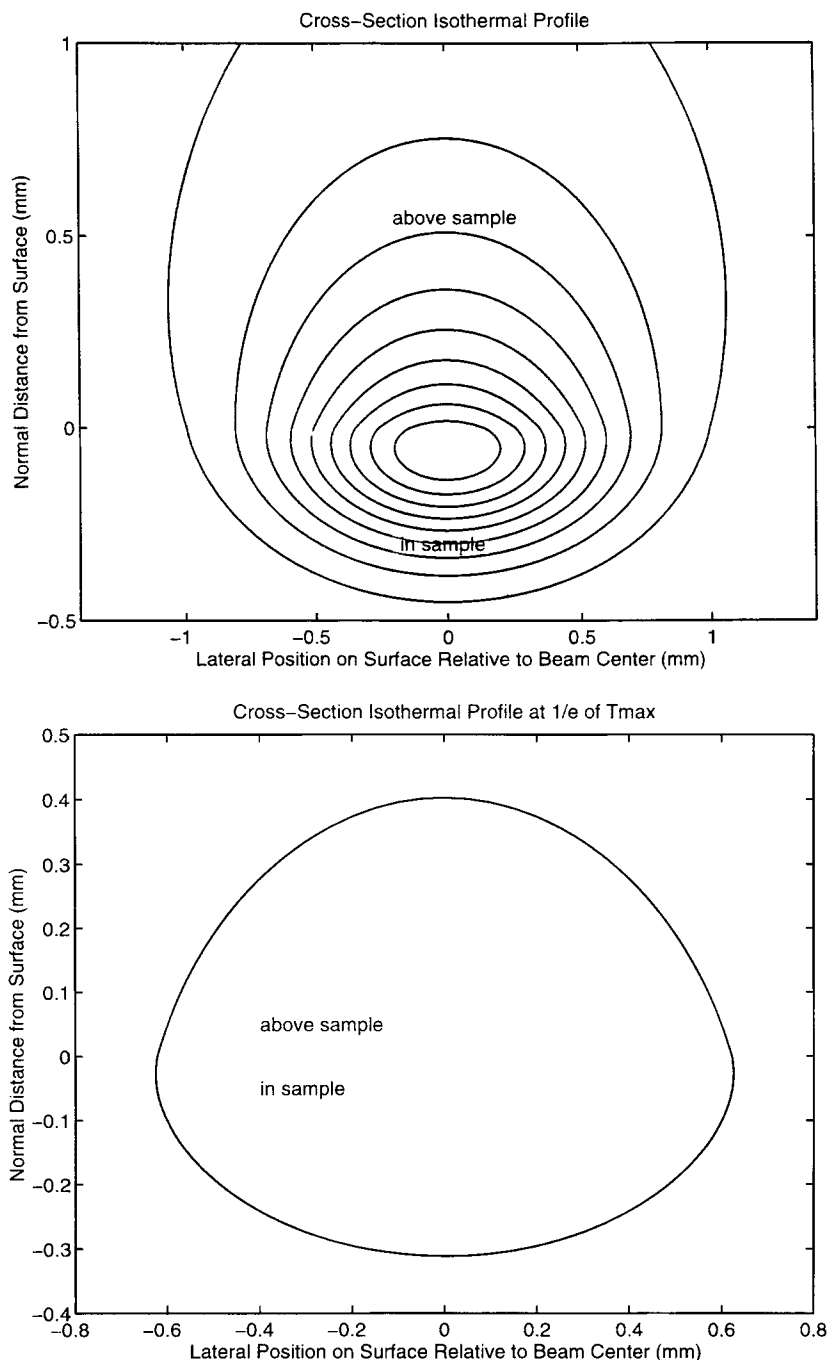
Figure 7   (a) Isotherms representing 10% increments from maximum temperature (at the center) after seven revolutions. (b) Isotherm enclosing the region where the surface temperature is within $1/e$ of the maximum temperature.

during the second revolution, but if we repeat this process, it is apparent that soon the reaction time will approach the period of revolution. We may then reasonably assume that the reaction is complete, which occurs for our sample at approximately seven pulses.

CONCLUSION

We have presented the results of our study of the spatially selective solidification of a semiliquid sample composed of epoxy, diethylene triamine, and silica powder, using a CO_2 laser as a localized heat

source. We believe that this is a novel use of an infrared laser as a localized heat source in a polymer material system. We have found that localized curing occurs only for a specific composition of the sample and that the final product obtained with CO_2 laser curing is hard and stable, showing no significant shrinkage and requiring no postcure treatment. With smaller CO_2 laser beam sizes, the technique should be capable of producing structures with a lateral spatial resolution of tens of micrometers. Depth resolution will be determined by the thickness of the uncured liquid layer and the sample absorbtion depth. In fact, a single-layer ring was produced with a ring width of 100 μm using the much larger beam diameter of our initial experimental conditions.

When we cured our sample, we scanned the laser beam across the surface of the sample in a circular path at a certain speed. In order to adapt the infrared laser curing process to geometries other than a thin ring, one must account for the effect of several experimental parameters, including laser power, dwell time or pulse duration, scanning frequency and speed, size of the laser beam, thermal conductivity of the sample, and the mixture of reactants. Variations in any of the above parameters will affect both the geometry of the cured sample and its material quality.

Localizing the curing process to a desired (presumably small) region in all three dimensions requires that the laser energy be deposited in a well-defined volume and that the heat not be conducted away by the sample to regions where we do not wish to cure the epoxy. Because our sample has a relatively low thermal conductivity and is strongly absorptive of the CO_2 laser irradiation, curing is restricted to a desired region. We were able to show by numerical simulation that, in the time required for curing to occur, we can successfully confine curing laterally to less than or equal to the diameter of the laser beam and vertically to less than twice the absorption depth.

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