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Study of resin based materials using CO_2 laser stereolithography

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We present an experimental and theoretical analysis of i.r. (thermal) sintering of thermosetting resins used for stereolithography. In the experimental work an epoxy resin was chosen. The optimum mix (which was quite critical) was composed of 10 parts (by weight), 1.4 parts diethylene triamine and 0.7 parts of silica powder. Using a differential scanning calorimeter (d.s.c.) we were able to determine reaction rates as a function of temperature as well as the enthalpy ($\Delta H \cong 368\,\mathrm{J\,g^{-1}}$) involved in the phase transition and the activation energy ($21.7 \pm 0.9\,\mathrm{kJ\,mol^{-1}}$) of the sintering process. The solution of the heat equation simulating this process was in general agreement with our previous observations of the stereolithographic results. It was also found that the minimum radius of lateral confinement was limited to ~0.3 mm due to heat conduction. The absorption depth should be approximately the same (0.2 mm in this case) at the frequency of the laser. It was also noticed that the epoxy degrades rapidly at temperatures above ~280°C. © 1997 Elsevier Science Ltd.

(Keywords: polymer; i.r. radiation; localized curing)

INTRODUCTION

In a series of papers[1–3] we have studied thermal pulse sintering of thermosetting resins. This paper is intended to provide a more profound physical basis for this process.

The use of lasers for material processing has advanced rapidly within the past few years. An example of this, which has proved to be quite important, is stereolithography, a powerful technique for producing models and prototypes in two and three dimensions[4,5].

In conventional steriolithography ultraviolet (u.v.) light (typically a Cd–He laser at 352 nm) is used to cure a photosensitive polymer in a carefully designed pattern. Using computer control of the optical and mechanical elements as well as the thermal and chemical conditions, it has proved to be possible to fabricate complex structures. The important parameters are by now well understood as are the mechanisms of u.v. curing.

In this paper we will analyse a different method for curing polymers to form desired patterns; the controlled heating of thermosetting resins. This procedure utilizes a scanning CO_2 laser system to sinter the polymer according to a predetermined program. The heat produced by the absorptions of the i.r. radiation raises the temperature of the liquified, but quite viscous, resin. This thermal pulse sinters the photosensitive polymer (in this case, an epoxy) producing a local, controlled curing. The result can be a hard, fairly tough, and well formed plastic. In the best cases the final product shows good spatial resolution with no marked contractions after the sintering and cooking. These results have been reported in ref. 1.

Although it cannot be claimed yet that this thermal process is competitive with the prevailing u.v. techniques, our method does have some advantages. The CO_2 laser is considerably cheaper than the u.v. lasers at the necessary power levels; the penetration of the beam is considerably deeper and the superior dimensional stability of the finished product eliminates the necessity of additional post-cure treatment. On the negative side there was the difficulty of preventing a mass flow from the heated region to its surroundings which sometimes ruined the prototypes.

In our previous papers[1–3] the detailed physical and chemical studies of local, thermal curing were scant. The subject of this paper is a more detailed investigation of the sintering properties of an epoxy, thermosetting resin. We present estimates of the activation energy, reaction rates and other properties as functions of temperature. We also introduce a model to describe the sintering process and treat the time dependent heat equation in cylindrical coordinates. In general, the agreement of the analysis and experiment is good.

LASER PROCESSING OF RESINS

The main advantage of using a laser is that curing may be restricted to a highly localized region. In previous work, we have presented the results of a method for spatially selective solidification of a high-viscosity region mixed with diethylene triamine and silica powder. Using a carbon dioxide (CO_2) laser, it was

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possible to form simple three-dimensional structures, with good spatial resolution[3].

Curing occurs in the epoxy sample by means of maximum cross-linkage between epoxy resin and diethylene triamine reactants. Resins typically cure (or sinter) when the temperature of the initially liquid polymer is increased between 60°C and 100°C. Thermosetting polymers are normally made from relatively low molecular weight, semi-fluid substances which become highly cross-linked when heated. The cross-linked substance which results is typically hard, and has a three-dimensional network of bonds interconnecting the polymer chain. To be able to localize curing, we found that a specific ratio of epoxy, diethylene triamine, and silica powder is required. Improper ratios of the reactants leads to the formation of low-weight molecules and results in a sample which is, at best, poorly cured.

We also determined that the amount of silica, relative to the amounts of epoxy and diethylene triamine, is critical in confining the curing process to a localized volume. Silica serves a dual purpose in the curing process. It both dilutes the reactants, and it inhibits their free movement. If the amount of silica powder is too great, the reaction is effectively blocked and no curing occurs in a reasonable time frame. If, however the proportion of silica is too small, there will be a difficulty in confining (or localizing) the cured region because the reaction occurs too rapidly in areas bordering the laser irradiated site. The formula for our sample, given near the beginning of the Experimental section, represents a balance of these competing concerns.

We have developed a simple model to describe energy flux in laser-induced curing to predict both localization and curing rates as functions of laser parameters such as power level, beam diameter, and scanning speed. First, localized curing was achieved by scanning a continuous wave (c.w.) CO_2 laser repeatedly over a circular path on the samples surface. By dividing the beam diameter $2a$ by the scanning speed v, one obtains the dwell time

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

In order to predict the effect that the laser has on curing, it was necessary 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, it was assumed that energy in the beam during the dwell time was

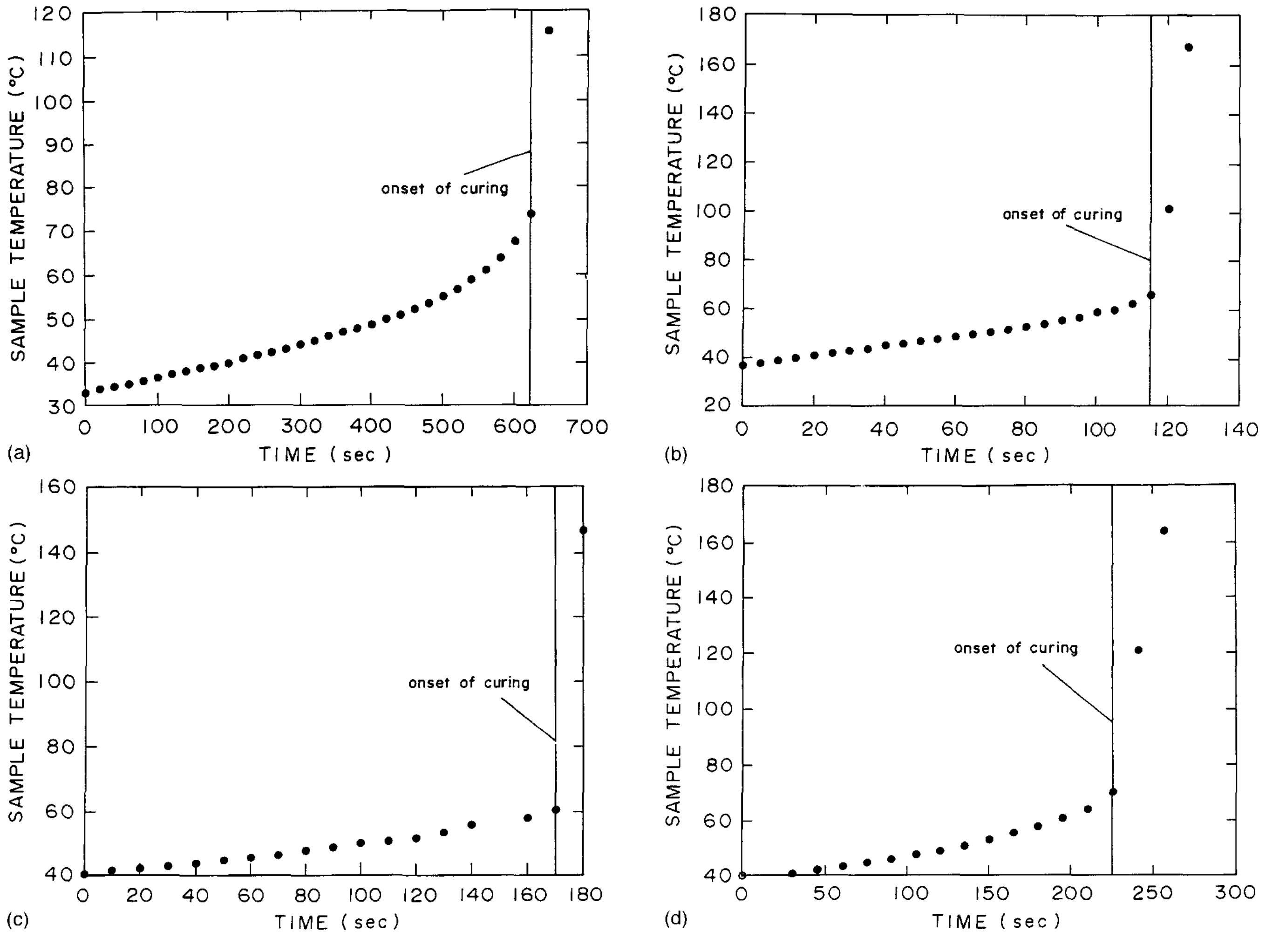

Figure 1 (a) Temperature evolution for the sample as it cured at external temperature of 44.5°C. The 'curing-point' was determined by the rapid increase in shape (denoted as the 'onset' of curing). (b) Temperature evolution for the sample as it cured at external temperature of 65°C. The 'curing point' was determined by the rapid increase in shape (denoted as the 'onset' of curing). (c) Temperature evolution for the sample as it cured at external temperature of 73°C. The 'curing point' was determined by the rapid increase in shape (denoted as the 'onset' of curing). (d) Temperature evolution for the sample as cured at external temperature of 80°C. The 'curing point' was determined by the rapid increase in shape (denoted as the 'onset' of curing)

absorbed by the sample within a distance from the surface roughly equal to the absorption depth δ. We determined the absorption depth by measuring the transmittance of an 80 μm thick sample over a wavelength range which included that of the CO_2 laser at 10.6 μm, and found to be $\delta \cong 22\,\mu$m.

We assumed that a small cylindrical volume V absorbed the energy E delivered during the dwell time, where V is given by $V = \pi a^2 \delta$. The energy deposited in volume V is the product of the c.w. laser power and the dwell time, $E_p = Pt_d$.

The approximation of the equation above is reasonable for the sample in the experiment because the absorption depth is quite small. 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 this case, it is likely that the depth of focus will be the factor which most determines the confinement of laser energy in the direction normal to the sample surface. Beyond the depth of focus, the laser energy would decrease sufficiently that curing would no longer be induced.

The rate $d\beta/dt$ at which the polymer cures (where β is the fractional conversion of the reaction) is a function of the temperature increase. The change in temperature 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

$$E_p = mC_p \Delta T \qquad (2)$$

We can calculate the mass of the heated volume using the measured mass density $\rho = 1.16\,\mathrm{g\,cm^{-3}}$. Once the curing process is described as a function of the temperature and the time, one may predict the curing behaviour as a function of laser irradiation conditions.

Since one is concerned with achieving curing in a highly localized region, it is important to have a quantitative understanding of where the laser energy is deposited and how it spreads through the polymer. 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. The other extreme is when the scanning speed is too low, we would overheat the spot, and the deposited energy would spread outward from the irradiated area thus curing a greater area than desired. There is a balance between initiating the curing process and restricting its spread to within the desired spatial boundaries. In fact, we observed such behaviour, and in this work we describe the process quantitatively.

In order to model the flow of heat in laser-induced curing, we used a finite-element approach to solve the time-dependent heat equation[6]. We assumed that each time the laser passed over a point on the epoxy surface, the irradiated volume absorbs the energy of the pulse and experiences a temperature increase of

$$\Delta T = \frac{E}{mC_p} = \frac{Pt_d}{\pi a^2 \rho C_p \delta} \qquad (3)$$

The time-dependent heat equation is

$$\nabla^2 T = \frac{1}{D}\frac{\partial T}{\partial t} - \frac{G}{K} \qquad (4)$$

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. It was 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[7]:

$$G \cong \frac{P}{\pi a^2 \delta}\exp(-r^2/a^2)\exp(-z/\delta)S(t_d) \qquad (5)$$

where $S(t_d) = 1$, $0 \leq t \leq t_d$; $S(t_d) = 0$, $t < 0$, $t > t_d$, z is the depth measured from the surface, and r is the distance from the centre of the beam.

As in previous experiments, we scanned the laser in a circular path with total travel for 2 to 10 times 2π (consequently the irradiation of a given 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 roughly 38 ms. We used these parameters in the numerical simulation which required the thermal transient constant τ is defined as $\tau = a^2/D$. D for our sample is $22.5 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$, making τ to be about 10 s for the radial transient. The Crank–Nickelson finite-difference algorithm was used to solve the heat equation with the appropriate periodic heat source term G defined above. The thermal conductivity of our epoxy sample is $K = 0.359 \times 10^{-3}\,\mathrm{mW\,cm^{-1}}$, which is close to that of air ($0.24 \times 10^{-3}\,\mathrm{mW\,cm^{-1}}$). This indicates that a significant fraction of the heat dissipation will occur into the air. It is assumed that the thermal properties K and D and the optical properties are all temperature-independent.

EXPERIMENTAL PROCEDURE

An epoxy resin was chosen on the basis of its viscosity, thermosensitivity and stability during the curing process. When heated, such polymers become a viscous fluid, and may be moulded into a desired shape. We determined by trial and error an appropriate mixture of reactants that provided the best results for localized curing. The optimum mix was composed of 10 parts (by weight) epoxy resin, 1.4 parts of diethylene triamine, and 0.7 parts of silica powder. Localized curing was achieved with a (c.w.) carbon dioxide (CO_2) laser operating at a wavelength of 10.6 μm. We focused the beam to a diameter of 0.6 mm to confine the heating of the sample to a reasonably small region.

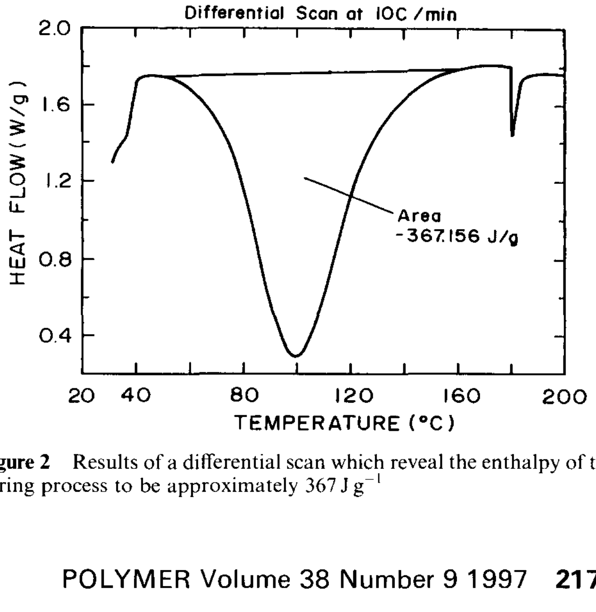

Figure 2 Results of a differential scan which reveal the enthalpy of the curing process to be approximately 367 J g^{-1}

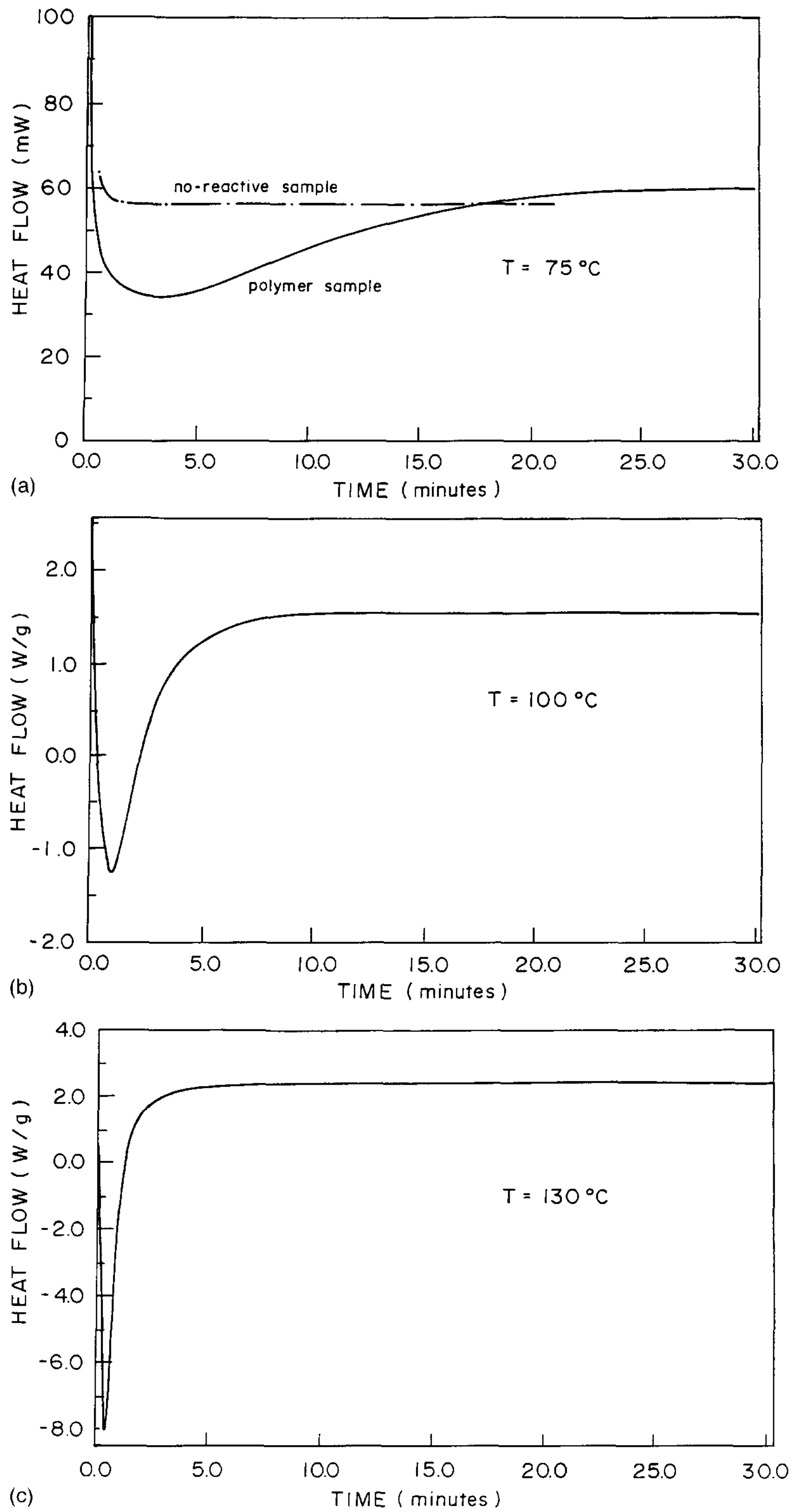

Figure 3 (a) Results of d.s.c. isothermal scan of the polymer curing process and a comparison with the heat flow to a non-reactive sample. (b) Results of d.s.c. isothermal scan of the polymer curing process at 100°C. (c) Results of d.s.c. isothermal scan of the polymer curing process at 130°C

Before attempting to explain the experimental results of localized curing, we decided first to characterize the bulk curing process. We heated a small volume of the liquid sample by placing it in a beaker wrapped in heat tape, and then monitored by a pair of parameters which would yield information on the curing process. 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 the data giving the temperature evolution of the sample was stored. Simultaneously, the transmissivity of the sample to a helium neon (HeNe) laser was monitored. 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

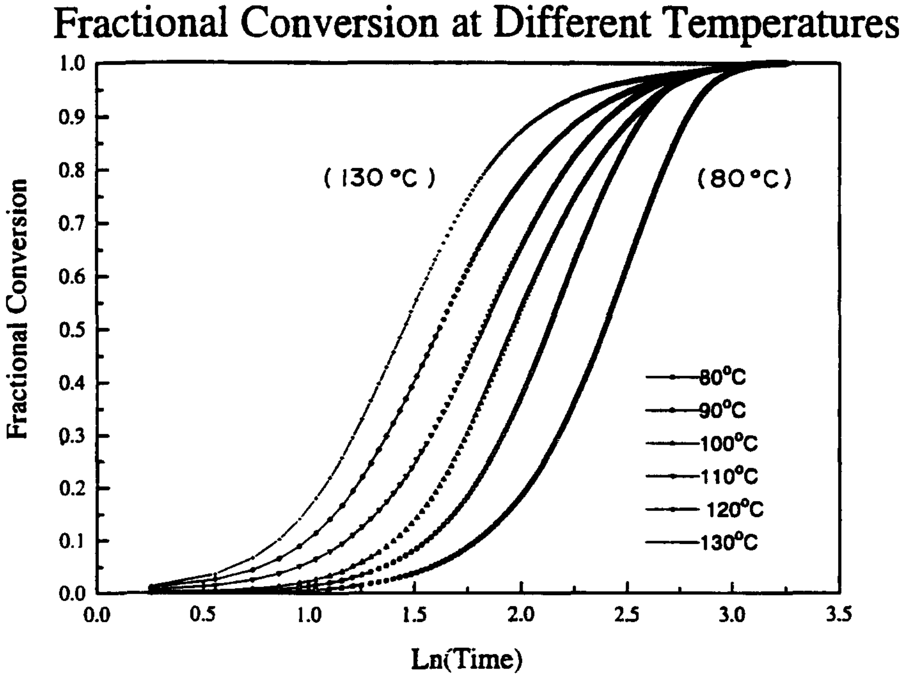

Figure 4 Plot of fractional completion of the reaction (or conversion) vs ln(t) for various temperatures ramped from 80°C to 130°C

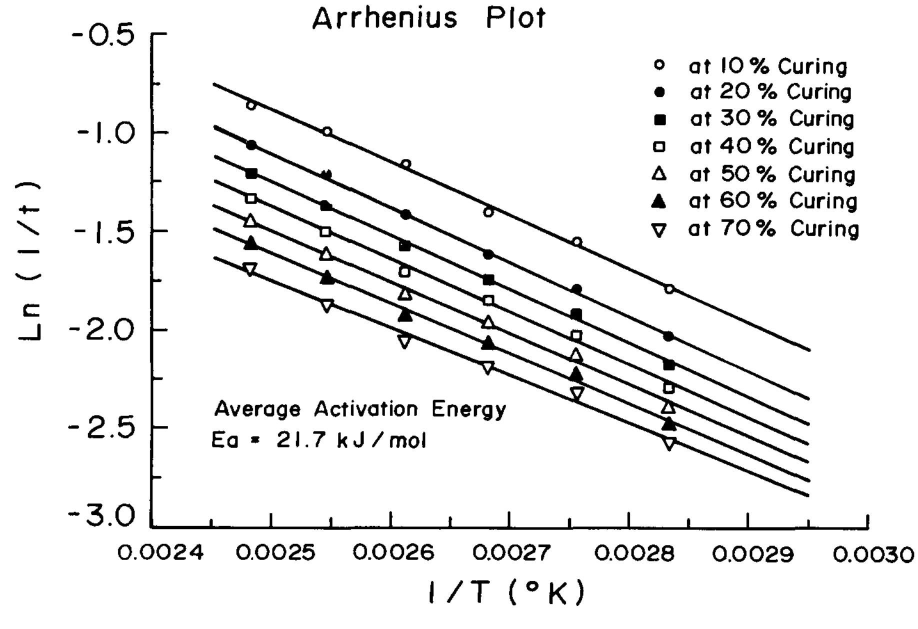

Figure 5 The Arrhenius plots of the curing process taken from results of *Figure 4*

the record of its transmissivity, it was possible to determine the rate of curing as a function of the sample temperature.

The results of the temperature evolution for different heating rates are shown in *Figures 1a–d*. Four different external temperatures were imposed on the sample, and we see the curing behaviour was noticed to be similar for each case, but as expected, the curing occurred more rapidly at higher room temperature. The results also show plainly that the reaction is exothermic. The problem with the above measurements was that it was unable to obtain an accurate value for the activation energy of the reaction, nor was it possible to define quantitatively the rate at which the reaction was occurring. In order to determine the reaction rate more accurately as a function of temperature, a standard measurement procedure was employed using a differential scanning calorimeter (Perkin-Elmer DSC-7). The d.s.c. process can plot heat flow into a small sample using either a fixed temperature or a ramped temperature. In either case, the heat flow required to maintain a certain temperature in the sample is compared to 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 the heat flow between the reactive and nonreactive samples, one finds the enthalpy of the reaction.

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

(β is the fractional conversion)

$$\frac{d\beta}{dt} = B\exp(E_A/RT) \tag{6}$$

where R is the gas constant, T is the absolute temperature, and B is a pre-exponential constant. We used a standard d.s.c. method to obtain E_A[8,9]. 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 vs time for multiple isothermal scans, each at a different room temperature, provides the necessary information to calculate the activation energy. This method is explained in detail by Wisanrakkit and Gillham[10].

RESULTS

The first tests performed with the d.s.c. made use of a linearly increasing (or scanned) temperature, where the flow of power to the sample was monitored. 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 $\Delta H \cong 367.9\,J\,g^{-1}$.

Another series of experiments involved the use of the sample in isothermal conditions. A small sample is quickly heated to a preset temperature, and maintained at that temperature for the duration of the reaction. The d.s.c. again monitors the power required to maintain a nonreactive sample at the same temperature. A typical comparison is shown in *Figures 3a–c* 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 (*Figure 3a*) quickly equilibrates, whereas the flow to the reactive epoxy sample shows the variations 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 time t. Eventually as $t \to \infty$, the energy released in the isothermal scan equals ΔH. We then associate the ratio of the energy released before τ_0 to ΔH with the fractional conversion β of reactants occurring up to time t_0.

A standard means of extracting the activation energy E_A from the d.s.c. data is to recognize that the exponential dependence of the reaction rate on E_A and T allows us to write[8,9]

$$\ln(t_{1\beta}) - \ln(t_{2\beta}) = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{7}$$

where $t_{1\beta}$ and $t_{2\beta}$ are the times required to reach a given fractional cure at two different temperatures T_1 and T_2, and R is the molar gas constant $T = 8.314\,J\,K\,mol^{-1}$. By plotting β vs $\ln(t)$, one may 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 vs $\ln(t)$ are shown together in *Figure 4*, and the corresponding Arrhenius plots are shown in *Figure 5*. The Arrhenius plots show the $\ln(t)$ vs inverse temperature, where each of the lines represents one specific fractional conversion β. The results show that the activation energy for the curing process is

$$E_A = (21.7 \pm 0.9)\,kJ\,mol^{-1}$$

Numerical simulation of heat flow in the sample induced by the laser is accomplished with the heat equation (4). Parameters relevant to an experiment previously carried out were made use of where a CO_2 laser beam scanned a circular path on the sample. The scanning speed was approximately $v = 159.2\,cm\,s^{-1}$, and the period of rotation was 35 ms. Using equation (1), we obtain a dwell time of 377 μs. The beam was focused to a $1/e$ radius of 0.3 mm, so using the absorption depth of 22.4 μm, we find that the laser energy of each dwell time was deposited in a volume of $3.3 \times 10^{-3}\,mm^3$. With the c.w. operating power of the laser at 20 W, the energy deposited per dwell time is approximately 7.6 mJ. The thickness of the sample was roughly 80 μm. Using these parameters in a finite-difference simulation of the heat equation reveals the temperature evolution at the surface of the sample, at the centre of the laser beam, as shown in *Figure 6*. We see that within a small number of pulses, the temperature at the surface of the sample is sufficiently high to ensure that curing occurs quite rapidly. We have also performed a thermogravimetric analysis of the sample which revealed that the sample begins to degrade rapidly at approximately 550 K. In any future work, it will be imperative to operate the laser so that sample does not reach this temperature. We can accomplish this goal either by reducing the power of the laser beam or by reducing the duty cycle of the pulses (i.e. increasing the period of revolution).

Figure 7a shows temperature profile across the epoxy–air interface after about three pulses, where the various curves are surfaces of constant temperature, and are useful in determining the rate at which the curing process occurs at any location in the plane. Of particular interest are the points where the temperature falls to some given fraction of its peak. *Figure 7b* shows 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, which is a pleasing result. The fact that the temperature increase is confined roughly to within a lateral radius of 0.3 mm and a depth of 0.2 mm is easily attributable to a relatively short exposure to the laser and to the low thermal conductivity of the sample. This gives us confidence that we are capable of specifying the region of curing to roughly the width of the beam.

The rise in temperature at the surface of the sample and at the centre of the laser beam was also calculated. This shows that within a relatively small number of dwell times, or scanning cycles (three or four), the epoxy was heated to a temperature that ensures rapid curing. Equation (8) is a differential equation describing the reaction rate as

$$\frac{d\beta}{dt} = A(1-\beta)^n \tag{8}$$

where A is the reaction rate constant, and n is the order of the reaction. The order of the reaction is an empirical quantity which reflects how a number of elementary chemical processes affect the overall reaction. The fractional conversion is calculated as a function of time on the basis of the temperature evolution shown in *Figure 6*. According to reaction kinetics, the order of the reaction is the power dependence on the concentration of reactants. It is generally accepted that the reaction is bimolecular, and thus of second order.

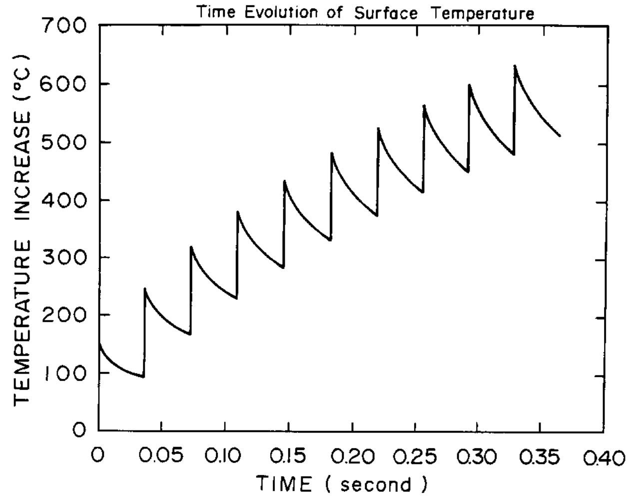

Figure 6 Evolution of the temperature at the sample over a sequence of pulses

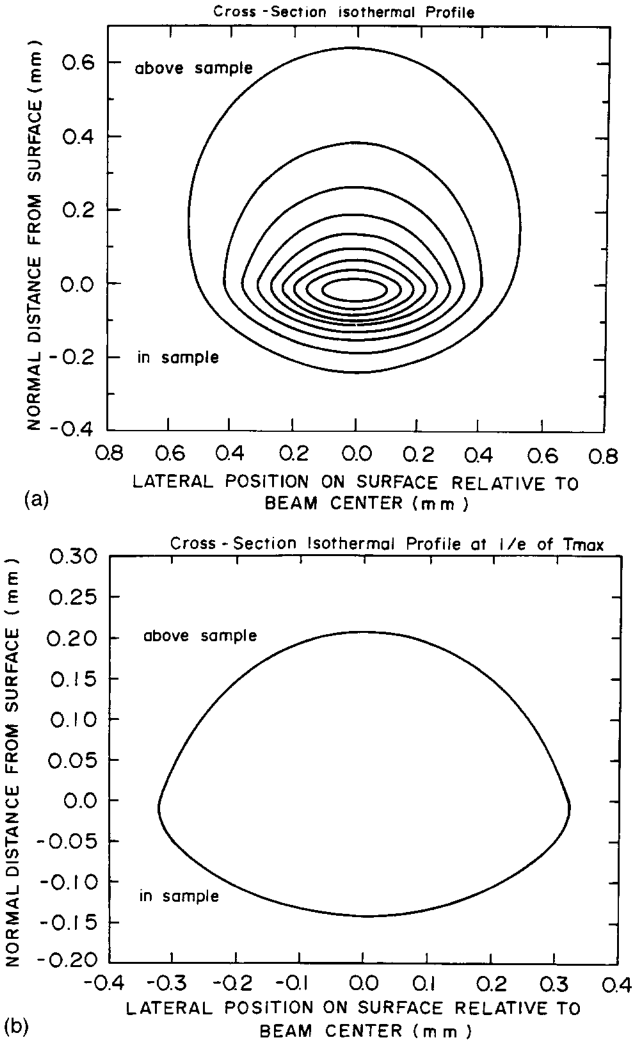

Figure 7 (a) Isotherms representing 10% increments from maximum temperature (at the centre) after 3 pulses. (b) Isotherm enclosing the region when the surface temperature is within $1/e$ of the maximum temperature

CONCLUSION

This paper has presented the results of the study of spatially-selective solidification of a semi-liquid sample composed of epoxy, diethylene triamine and silica powder, using a CO_2 laser as a localized heat source. It is believed that this is a new use of an i.r. laser for the localized curing of liquefied polymers. We have found that localizing curing occurs only for a specific composition of the sample.

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 i.r. laser curing process to other desired geometries (besides 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 likely, its material quality.

Localizing the curing process to a desired (and presumably small) region in all three dimensions requires the laser energy to be deposited in a well-defined volume, and that the heat not be conducted away by the sample to regions where it is not desired to cure the epoxy. Fortunately, we have found that our sample has a relatively low thermal conductivity, and it strongly absorbs the CO_2 laser irradiation. Both are advantageous for restricting the curing to a desired region. It was possible to show by numerical simulation that in the time required for curing to occur, it was possible to successfully confine curing laterally within roughly the diameter of the laser beam, and vertically within the absorption depth. Unfortunately, it appears that there is still enough conduction of heat so that confining curing to within the absorption depth of the surface (rather than the radius of the laser beam) is not possible.

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