Advances in Stereolithography: A New Experimental Technique in the Production of a Three-Dimensional Plastic Model with an Infrared Laser

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ABSTRACT: The development of a new approach for the production of three-dimensional plastic parts, called *infrared laser stereolithography*, is presented. During the experimentation, a carbon dioxide (CO_2) laser beam at 10.6 μm (infrared radiation) was focused on a sample composed of an epoxy resin, diethylene triamine (curing agent), and silica powder (filler). The CO_2 laser, adopted for cost reduction, led to no significant shrinkage, and almost no postcure treatment was required. With differential scanning calorimetry, it was possible to determine the reaction rate as a function of the temperature and the activation energy of the curing process. The solution of the heat equation, with the Ansys program simulating this process, was in general agreement with our previous observations of the stereolithography results. The experimental results of the production of solid parts layer by layer in three dimensions are presented. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2387–2394, 2004

Key words: curing of polymers; laser-induced polymers; lithography

INTRODUCTION

Stereolithography is essentially one method from a family of technologies of rapid prototyping that involve producing parts by the addition of layers of a material on top of one another to build a complete three-dimensional plastic model. The greatest benefit of using a rapid prototyping process is associated with the quick fabrication times of models and prototypes, which can eliminate 85% of the development time.[1,2]

In the stereolithography conventional process, an ultraviolet laser source (0.325 μm) is used to cure successive layers of a liquid photosensitive polymer. Therefore, the system is high-cost because of the use of an expensive ultraviolet laser.[3] In this work, a different method that can automatically construct physical models from computer-aided-design data is analyzed. This procedure uses computer control of the optical and mechanical elements as well as a scanning carbon dioxide (CO_2) laser system to cure a thermosensitive polymer according to a predetermined program. In the best cases, the final product shows good spatial resolution with no shrinkage and postcure treatment after the curing process. In general, thermosensitive polymers possess good dimensional thermal stability and can be used in household appliances, automotive parts, textile clothing treatment, electrical wiring boards, and medical and dental instruments and fillings.

The aim of this work is to study the interaction of an infrared laser with a thermosensitive polymer in which controls of the depth of heating, pulse energy, dwell time, and other thermal parameters are the principal features to be considered. Important diagnostic tests have been carried out to ascertain the performance of the laser scan head, along with effective implementation of the operating parameters. Results have shown not only that the laser parameters and stoichiometric combination of the sample compounds play important roles in the final results of the curing process but that the type of silica powder does as well. Experimental and theoretical results for the production of solid layers 0.2–0.3 mm thick in one, two, and three dimensions are presented. Differential scanning calorimetry (DSC), used to obtain the activation energy (E_A) of the curing reaction as a function of temperature and to study the rate sample behavior, including temperature changes, is discussed. Simulation by the Ansys program allows the prediction of the curing process with a time-dependent heat equation in cylindrical coordinates, and a good agreement with the preliminary experimental observations has been found.

PHYSICAL MODEL AND SIMULATION OF A LOCALIZED CURING PROCESS

In previous work,[4,5] the results of a method for the spatially selective curing of a high-viscosity resin mixed with diethylene triamine and silica powder via a CO_2 laser were presented. A simple physical model describes the energy flow deposited by the laser in terms of the operational parameters and the behavior of the resin, aiming at localized curing. The localized curing at the beginning of the experiment is achieved by the repeated scanning of a continuous-wave CO_2 laser over a circular trajectory on the sample's surface at scanning speed v. By dividing the beam diameter 2ω by v, we can obtain dwell time t_d

$$t_d = 2\omega/v \qquad (1)$$

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

As the resin is highly absorptive at the CO_2 laser wavelength (10.6 μm), it is assumed that, for t_d, nearly all the beam energy goes into the inner part of the sample at a distance from the surface equivalent to absorption depth δ. δ was determined by the measurement of the transmittance of an 80-μm-thick noncured sample at the band of the CO_2 laser emission spectrum. The value found was $\delta = 40$ μm.

It is assumed that energy E is absorbed in the small cylindrical volume V during t_d, the volume being defined as follows:

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

The energy released in V is the product of the laser power (P) and t_d:

$$E = Pt_d \qquad (3)$$

The rate $d\beta/dT$ at which the polymer cures (where β is the fractional conversion) is a function of the temperature imposed on it.

For the short irradiation times used in the previous experiments, the change in the temperature, ΔT, is directly proportional to the energy deposited through heat capacity c_p and mass m of the material contained in volume V:

TABLE I
Physical Properties Considered in the Numerical Simulation Calculations

	Thermal conductivity (W/cm K) $\times$ 10^{-3}	Thermal diffusivity (cm^2/s) $\times$ 10^{-3}	Heat capacity (J/g K)	Density (g/cm^3)
Sample	0.427	0.111	1.370	2.799
Air	0.240	201.9	1.004	0.001

TABLE II
Parameter Settings Used in the Scan Head

Description	Parameters	Function
Step size (vector)	100	Microvector size for imprinting vectors
Jump size (vector)	100	Microvector size for nonimprinting vectors
Step period (μs)	35/40	Microvector output rate
Mark delay (μs)	10	End of imprinting vector delay
Jump delay (μs)	10	End of nonimprinting vector delay
Laser on (μs)	250	Turn-on delay for laser at start of stroke
Laser off (μs)	300	Turn-off delay for laser at end of stroke

$$E_p = c_p m \Delta T, \qquad (4)$$

The mass of the heated volume may be calculated with the mass density of the sample ($\rho = 1.16$ g/cm^{-3}).

For the modeling of the heat flow in laser-induced curing, a finite-element approach to solve the time-dependent heat equation is used.[6] The thermal analysis is developed with the Ansys program. The time-dependent heat equation is

$$\rho c_p \left(\frac{\partial T}{\partial t} + \{\mathbf{v}\}^T \{\mathbf{L}\}T \right) + \{\mathbf{L}\}^T \{\mathbf{q}\} = \overset{\cdots}{q} \qquad (5)$$

where T is the temperature, t is the time, $\{\mathbf{L}\} = \left(\frac{\partial}{\partial X'}, \frac{\partial}{\partial Y'}, \frac{\partial}{\partial Z} \right)$ is the operator vector, $\{\mathbf{v}\} = (V_x, V_y, V_z)$ is the velocity vector for the transport of heat, $\{\mathbf{q}\}$ is the heat flow vector, and $\overset{\cdots}{q}$ is the heat generation for volume unity.

The numerical simulation requires the insertion of the physical properties of the basic sample composed of an epoxy resin (10 parts), diethylene triamine (1.4 parts), and silica powder (0.7 parts), as shown in Table I. It has been assumed that the physical properties are all temperature-independent.

EXPERIMENTAL

The epoxy resins (DER 383) were chosen on the basis of their viscosity, thermosensitivity, and stability during the cure process. To explain the experimental results of localized curing with the CO_2 laser, we characterized the bulk curing process. First, a small volume of the liquid sample was heated, and the temperature inside the sample as a function of time for several different external temperature was monitored. For the temperature monitoring, the voltage from a cold junction compensator was recorded with a digital
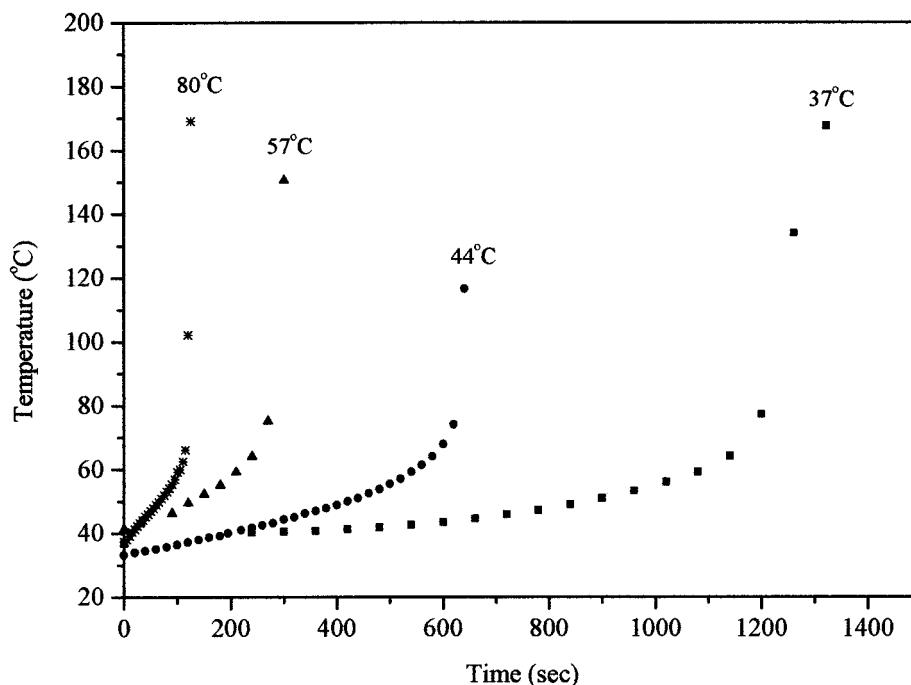
Figure 1 Evolution of the internal temperature and onset of curing.

oscilloscope, in which data on the temperature evolution of the sample were stored.

Simultaneously, the transmittance of the sample for the helium–neon (HeNe) laser was measured with a detector. Transmittance is a simple means of detecting the onset of curing in the sample because the liquid sample is relatively transmissive to the red light of the HeNe laser, becoming opaque as it cures. Through the correlation between the evolution of the sample internal temperature and the transmittance record, it is possible to determine the curing rate as a function of the sample temperature.

Figure 1 shows the temperature evolution at different heating rates. The results indicate similar behaviors for the evolution process of the curing at the different temperatures applied; however, a much faster curing response as the temperature increases can clearly be observed. The results also show plainly that the reaction is exothermic. The problem with the aforementioned measurements is that it is not possible to obtain an accurate value for E_A of the reaction, nor is it possible to define quantitatively the curing rate. To predict more accurately the rate at which the reaction occurs as a function of temperature, we have used the standard DSC method. The parameter of greatest interest in determining how the sample cures under laser radiation is E_A of the reaction.

E_A is determined with the general equation:

$$\frac{d\beta}{dt} = Ae^{-E_A/RT} \qquad (6)$$

where R is the Boltzmann constant, A is a pre-exponential constant, and T is the absolute temperature. A standard DSC method to obtain E_A has been used.[7,8]

RESULTS

With DSC tests at different temperatures, the heat flow to the sample was monitored. With isothermal scans, a small amount of the sample was heated quickly to a prescribed temperature and kept at that temperature for the duration of the reaction. A typical plot is shown in Figure 2, in which the initial increase in the heat flow represents the energy required to heat the sample to the desired temperature. The heat flow to the nonreactive alumina sample quickly was equilibrated, whereas the flow to the reactive epoxy sample was varied because of the 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 before t. Eventually, as t approaches infinity, the energy released in the isothermal scan approaches ΔH. The ratio of the energy released at t to ΔH is β of the reactants at time t.

To obtain E_A, we have used the following standard procedure:

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

where $t_{1\beta}$ and $t_{2\beta}$ are the times required to reach a given β value at two different temperatures (T_1 and T_2,
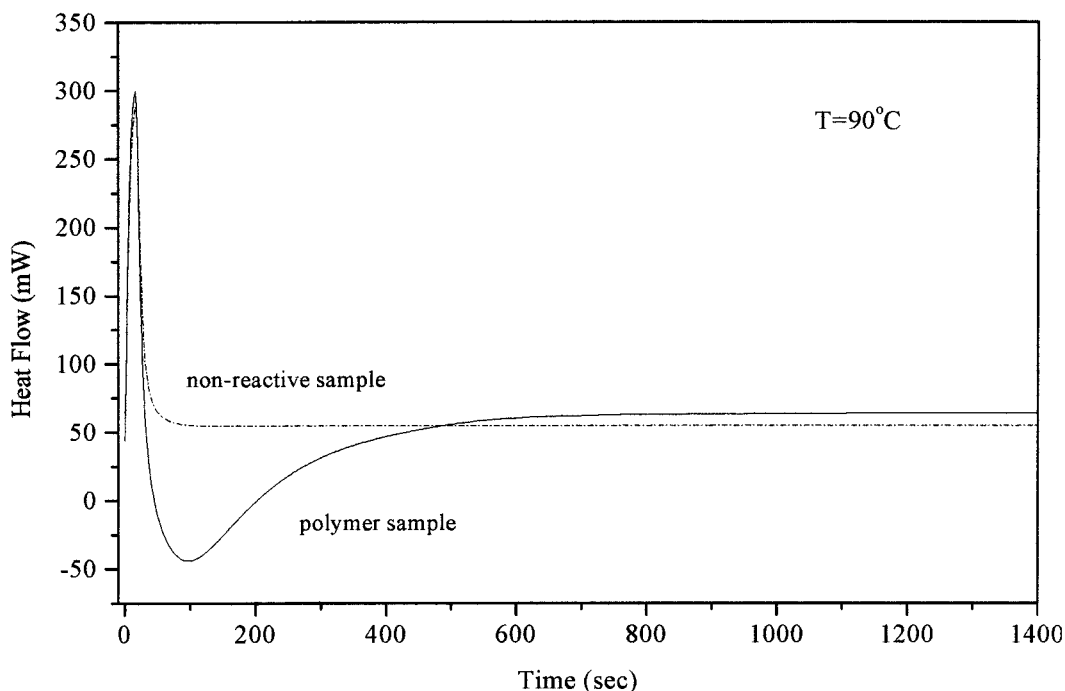
Figure 2 Results of the DSC isothermal scans of the curing process at 90°C.

respectively) and R is the molar gas constant ($R = 8.314$ J/K mol).

Several isothermal scans of the epoxy sample were performed, and the semilog plots of β versus ln t are shown in Figure 3; the corresponding Arrhenius plots are shown in Figure 4. The Arrhenius plots show $\ln(1/t)$ versus the inverse temperature; each line rep-

resents one specific β value. The results show that E_A for the curing process is 50.1 ± 0.9 kJ/mol.

The diagnostic tests of the laser scanning parameters, used to determine the localized curing in the thermosensitive process, were performed with the new experimental technique: infrared laser stereolithography consisting of a CO_2 laser (General Scan-
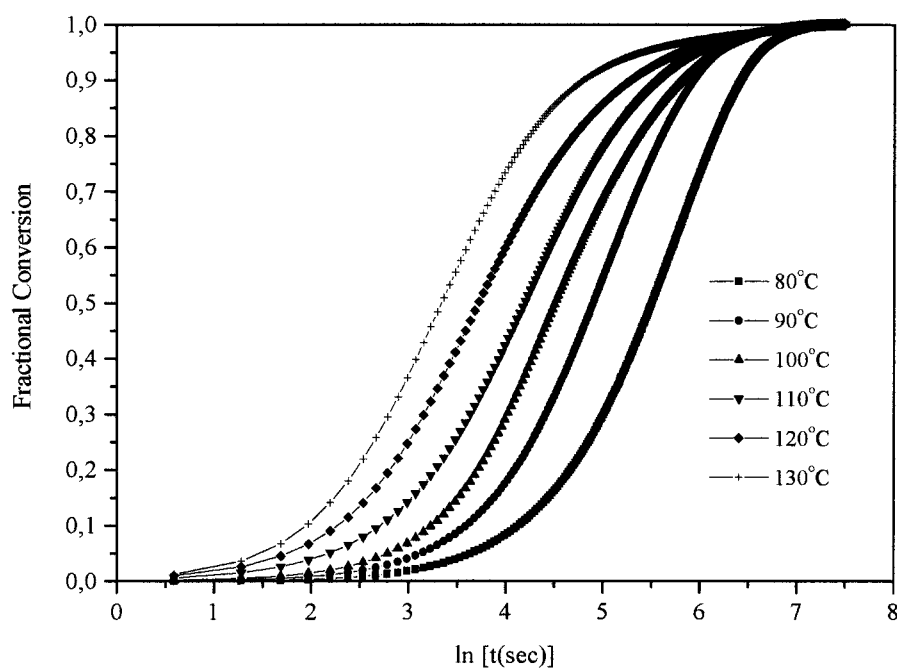

Figure 3 β of the reaction at various temperatures.
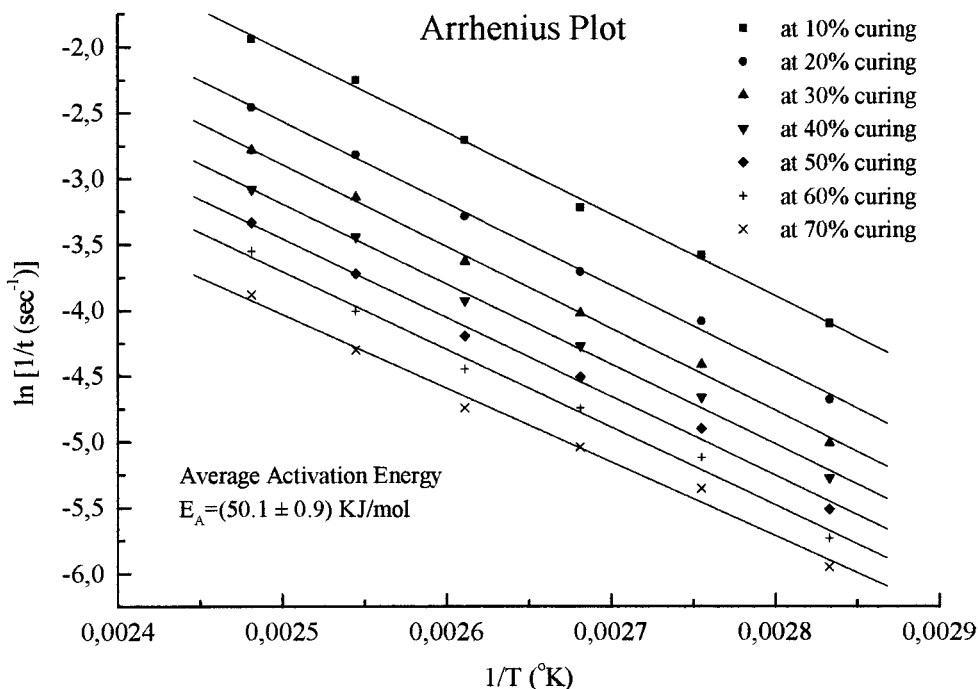
Figure 4 Arrhenius plots of the curing process (based on the results shown in Fig. 3).

ning, Inc., Boston, MA), an HPM10A optical scanning system, an elevator table, and support software. The laser beam was applied directly to the optimum sample composed of 10 parts (by weight) of the epoxy resin, 1.4 parts of diethylene triamine, and 0.7 parts of the silica powder. Localized curing by the repeated scanning of a continuous-wave CO_2 laser over a trajectory on the sample surface was achieved, t_d and the laser revolution time being varied. The relationship between t_d and the laser revolution time for single cured layers was used to determine the optimum parameters, which led to localized curing accuracy, reduced distortion, and shrinkage of the part under study. t_d, obtained with eq. (1), depended on the HPM10A optical scanning system parameters (see Table II):

$$\nu = \frac{\text{Step size}}{\text{Step period}} \times \frac{\text{Field size}}{65535} \qquad (8)$$

The constant represents the field size computer correction.[9]

In the diagnostic test (prototype A), the resulting structures did not shrink significantly after curing, and some of the physics of the parameters that affected the ability to restrict curing to a small region were examined. The results show that if the laser beam is scanned too quickly (prototypes B and C) and with several laser srevolution times, the deposited energy spreads outward from the irradiated area, 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.

The design of prototypes is initially created with three-dimensional computer-aided design, with the prototype sliced into 0.2-mm layers. The data file is then transferred from the computer to the experimental machine, which starts the production process, building the model in sliced layers, one layer at a time. The final products shown in Figure 5, obtained with CO_2 laser curing, were hard and stable, showing no significant shrinkage and requiring no postcure treatment.

To adapt the infrared laser curing process to different geometries, we must account for the effects of several experimental parameters, including P, t_d, the laser revolution time, v, the size of the laser beam, and the mixture of reactants (Table III). These parameters play important roles in the spatial resolution and lateral resolution of the obtained prototype. As shown in Table III, prototype A (circular) and prototype B (square) were constructed with the same parameters but with different values. Prototype A shows much better spatial resolution than prototype B. In prototype A, the lateral dimension of the curing confinement is 18% larger than the diameter of the laser; in prototype B, it is 58% larger than the diameter of the laser.

The numerical simulation of the heat flow in the sample induced by a laser is determined with the heat equation [eq. (5)]. The same parameters were used to
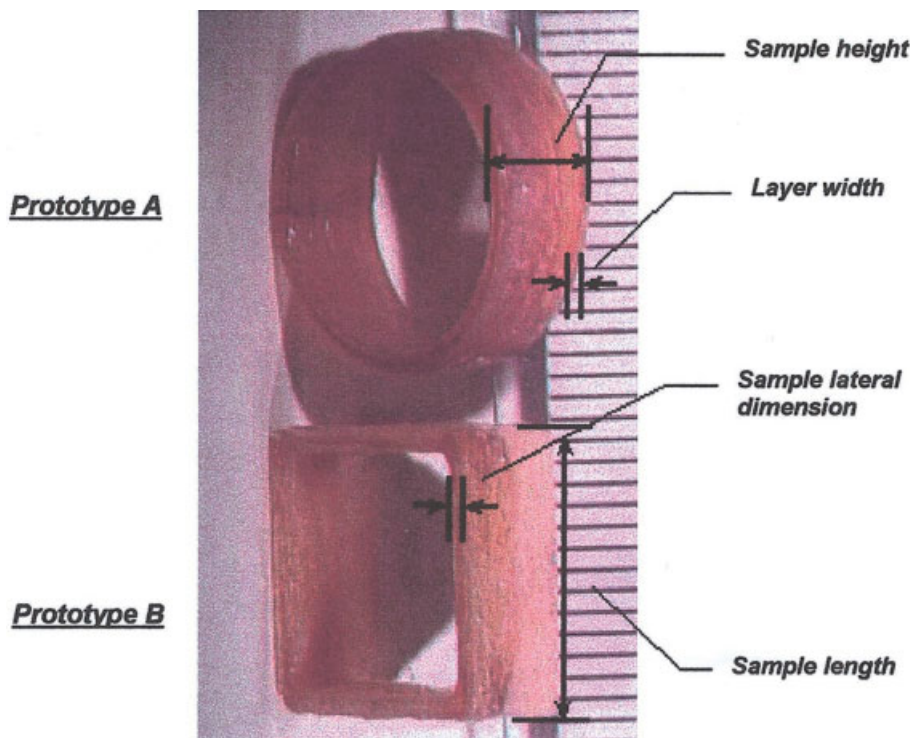
Figure 5 Layer-by-layer construction for two different geometries.

construct prototype A; a CO_2 laser beam was scanned along a circular path on the sample at an v value of 1594.5 mm/s and at a repetition rate of 35 ms. With eq. 1, with a laser beam of 0.80 mm, a t_d value of 503 μs, was obtained. With $\delta = 40$ μm, it was assumed that the laser energy of each t_d value was deposited in a volume of 20×10^{-3} mm³. With a laser operating with 20 W of power, the heat generation $\dddot{q}$ in the irradi-

ated volume was 9.95×10^5 W/cm³. With these parameters in a finite-element simulation of the heat equation, the temperature evolution on the surface of the sample for 10 laser pulses, at the center of the laser beam, is shown in Figure 6. The temperature on the surface of the sample was sufficiently high to ensure that the curing was quite rapid with a small number of pulses.

TABLE III
Diagnostic Test Involving the Stoichiometric Compositions, Laser Parameters, and Spatial Resolution

| Variable	Parameter	Value	
		Prototype A	Prototype B
CO_2 Laser ($\lambda = 10.6$ μm)	Energy $E_p = Pt_d$ (m J)	9.52	8.66
	Power P (W)	20	20
	Laser beam diameter 2ω (mm)	0.80	0.80
Scan head (stereolithography system)	Scan speed v (mm/s)	1595.4	1755.0
	Dwell time $t_d = \dfrac{2\omega}{v}$ (μs)	503	455
	Laser revolution time (x pass)	12	15
Composition (polymer)	Diglycidyl ether of bisphenol A (parts)	10	10
	Diethylene triamine [parts]	1.4	1.4
	Silica powder (parts)	0.7	0.54
	absorption depth δ (μm)	61.1	70.9
Spatial resolution (final product)	cured volume $V = \pi\omega^2\delta_1$ (mm³)	110×10^{-3}	129×10^{-3}
	Layer-by-layer width (μm)	200	200
	Lateral layer width (mm)	0.90	1.20
	Sample height (mm)	5.5	5.8
	Sample length (mm)	16.0	13.5
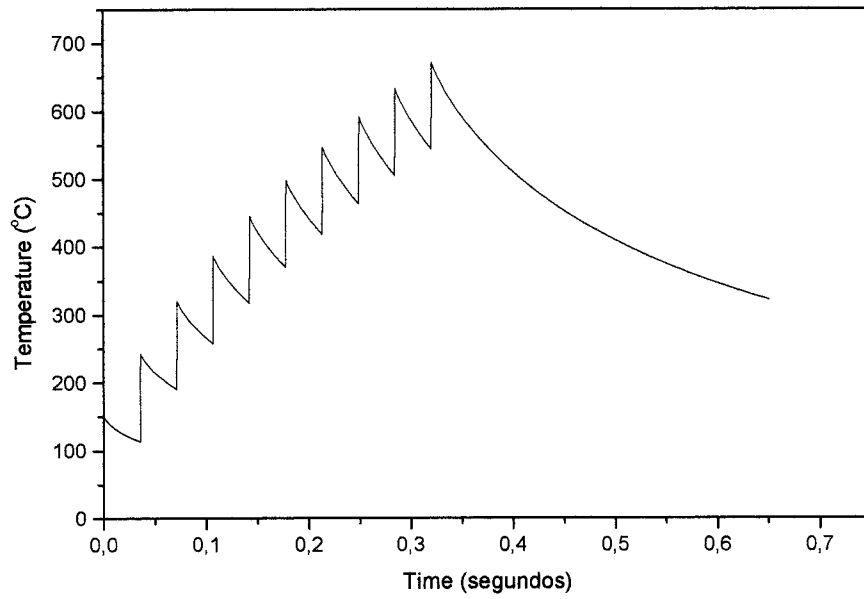
Figure 6 Evolution of the temperature during 10 laser pulses.

The Ansys program proved itself to be quite flexible in describing the complete mapping of the thermal evolution in the sample volume and in the air. In Figure 7, the spatial distribution of the temperature at the sample/air interface after 10 laser pulses is shown; the range of temperatures is indicated at the bottom.
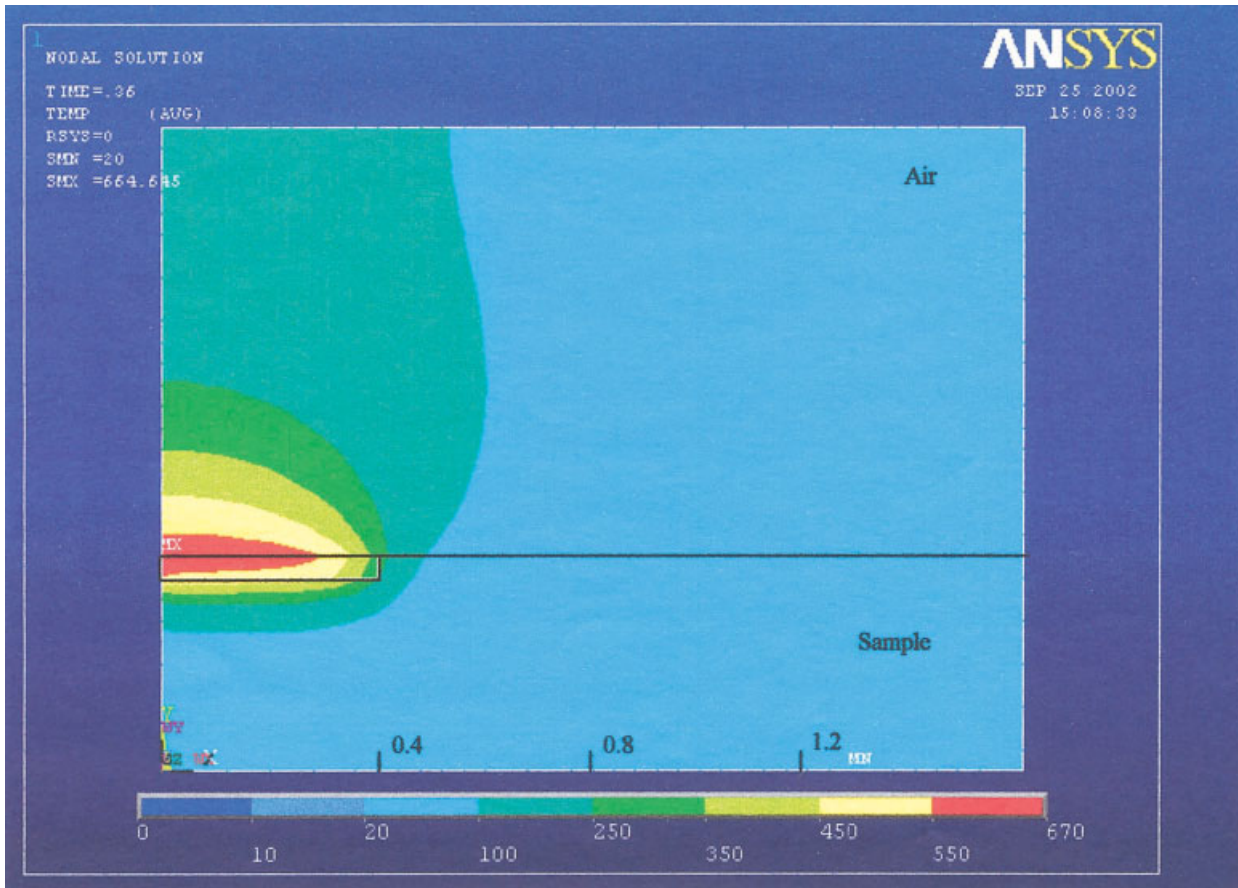

Figure 7 Isothermal profile from the maximum temperature after 10 laser pulses.
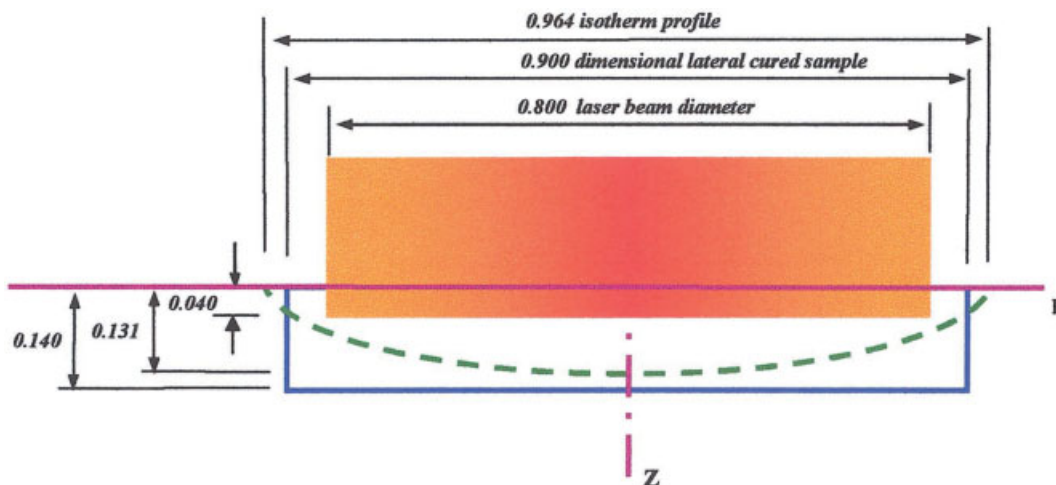
Figure 8   Results of the width and depth after curing compared with the numerical simulation and the size of the laser beam.

The isotherm of 100°C in the numerical results in Figure 7 can be associated with the experimental results in Figure 1, which show that the reaction occurred up to 80°C, and it can be assumed that this was the limit of the cured region.

It is interesting to compare the extent of the isotherm of 100°C with the size of the laser beam and the width of the experimental cure of prototype A and to note that they are nearly identical, as shown in Figure 8. The fact that the temperature rise and cured region are confined within a presumably small region in all three dimension is easily attributed to the relatively short exposure to the laser beam and to the low thermal conductivity of the sample. This shows that the curing can be confined in a volume with approximately the width of the laser beam.

CONCLUSIONS

Plastic models, built with stereolithography resins, have very good surface finishes and strength and are also translucent.

In this article, the development of a low-cost method for the localized curing of a thermosensitive polymer with a CO_2 laser has been presented. The localized curing of a viscous sample, composed of epoxy, diethylene triamine, and silica powder, with infrared laser stereolithography produces good spatial resolution and results in a product with desirable physical properties. Given the correct experimental conditions, structures of one-, two-, and three-dimensional models with a 0.2-mm layer thickness can be obtained. The final product, obtained with careful control of the laser parameters, is hard and stable, shows no marked dimensional contraction, and requires no postcure treatment.

The curing process for a desired 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 in which curing the epoxy is not desired. Fortunately, the sample that we used had relatively low thermal conductivity and strongly absorbed the CO_2 laser irradiation. Both are advantageous for restricting the curing to a desired region. The experimental cured layer and numerical simulations show that in the time required for curing, it is possible to successfully confine curing laterally within roughly the diameter of the laser beam and vertically within the absorption depth.

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