Numerical Simulation of Localized Cure of Thermosensitive Resin During Thermo Stereolithography Process (TSTL)

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Received 10 August 2005; accepted 12 February 2006
DOI 10.1002/app.24456
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this work, to analyze a type of rapid prototyping technique, a numerical model was developed that was able to simulate the heat transfer at thermosensitive polymeric material during cure by laser irradiation. The analysis was carried out as a transient thermal problem using the general-purpose finite element software ANSYS. The technique analyzed was thermal stereolithography, which uses a CO_2 laser beam to cure (solidify) thermosensitive liquid resins in a selective way to produce three-dimensional parts. In this numerical analysis, the temperature distribution at thermoset material heated by a laser irradiation and its thermal properties are investigated. This resin is a high-viscosity sample composed of epoxy resin, diethylenetriamine, and silica powder, which become highly cross-linked when irradiated by infrared laser. The localized curing becomes critical when the amount of silica and laser parameters are not appropriate. Bearing this in mind, this work intends, by applying the numerical method developed, to analyze the thermal behavior of resins in function of amount of silica and the laser radiation conditions, so that it is possible to have a knowledge on these variables so as to achieve a product with the required specifications. J Appl Polym Sci 102: 2777–2783, 2006

Key words: stereolithography; numerical simulation; localized cure; epoxy resin

INTRODUCTION

Computer-assisted technologies for product design usually comprise among their tools computer aided design, computer aided engineering (CAE), and computer aided manufacturing. CAE systems are those based on numerical methods that are able to solve a set of algebraic equations to obtain desired results in function of loading and the boundary conditions of process. CAE programs are used to calculate tensions, shifts, vibration, heat transfer, fluid flow, and other process parameters.

In this work, as a CAE tool, the ANSYS program is used to build a numerical model capable of simulating the heat transfer and the heat sink phenomena, owing to silica powder addition, during localized cure and analyze the process behavior. The model should be able to predict the temperature profile of thermosensitive material during cure in function of its physical properties as well as of the process parameters. The process analyzed is a different approach to the production of three-dimensional models, which can be called thermo stereolithography (TSTL). Traditional stereolithography apparatus builds a part by controlling an ultra violet laser beam to selectively cure photosensitive liquid resin layer by layer.[1] This novel process is a rapid prototyping technique, which uses a CO_2 laser, emitting infrared wavelength for local heating and solidification of thermosensitive material composed of epoxy resin, diethylenetriamine, and silica powder.[2]

To be able to localize cure in the sample, a specific ratio of epoxy, diethylenetriamine, and silica powder is required, together with a fine control of laser parameters, such as speed, power, and beam diameter. This work intends to present, besides the development of a numerical model, an initial study of the influence of the silica amount over the cure behavior of sample.

The amount of silica in the sample is considered in model by applying right values for its thermal physical properties that varies in function of its composition. Experimental analyses have reveled that the amount of silica, relative to the amounts of epoxy and diethylenetriamine, is critical to confining the cure process to a localized volume. Silica powder also influences other material properties.[3,4]

The proposed numerical model intends to explore this fact and help finding the optimal sample composition. Results are encouraging because they show that it is possible to confine the heating into small

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Journal of Applied Polymer Science, Vol. 102, 2777–2783 (2006)

regions, for example, on the order of the laser beam size, in three dimensions. Other process parameters should also be taken into account.

THERMO STEREOLITHOGRAPHY

Process description

Stereolithography is, essentially, one method from the family of rapid prototyping technologies that involves the curing or solidification of a liquid photosensitive polymer by applying a laser beam across its surface.[5,6] The laser beam supplies energy that induces a chemical reaction, forming a highly cross-linked polymer. Classical stereolithography process uses ultraviolet laser source to cure layers of a liquid photosensitive polymer. This work deals with a new strategy that applies an infrared laser bean (CO_2) on a thermosensitive resin to achieve localized curing. This process designated as thermo stereolithography comprises both heat and radiation effects, solving some limitations of classical stereolithography process, such as efficiency, speed, and accuracy.[7]

A TSTL apparatus, composed of a CO_2 laser, with a laser beam focused and directed through an optoelectronic system, creating a cured layer, was developed and constructed for research purposes. The sample is placed on an elevator (Z motion) support, within a platform filled with the uncured material. A computer system is used to carefully control the horizontal position of sample surface to obtain precise localized cure. The digital design is then exported by preprocessor computer aided design through a file in STL (Structure Triangular Language) format. The STL format describes the object geometry using a triangular mesh containing the x, y and z as well as the external normal coordinates. Figure 1 shows an illustration of the TSTL apparatus.

In previous work, using TSTL apparatus constructed, some diagnostic tests of the laser scanning parameters were carried out so as to obtain the localized cure in thermosensitive resins. A CW CO_2 laser (10.6 μm), with a beam waist of about 0.8 mm, was used to produce the local heating at the focus of the lens of optoelectronic system (f = 20 cm). The laser beam was applied directly to the sample over a convenient substrate (Teflon). A control system is used for scanning laser over several different trajectories on the sample surface, varying the laser speed and the laser revolution time. A thin layer of resin (0.2 mm) is produced in the laser focus trajectory where the resin is selectively cured. Figure 2 illustrates parts built under different experimental conditions.[8]

To adapt the process of localized cure, with the use of CO_2 laser, in such way to obtain plastic parts with different geometries, in addition of taking into account the proper sample composition, an effective control of the involved process parameters is necessary. Parameters to be considered are as follows: laser power, dwell time, laser revolution, scan speed, laser beam dimension, and composition and, consequently, physical properties of sample. A variation in any of the mentioned parameters may affect the process of localized cure decisively, with impact on geometry as well as on quality of final product; hence, it is important to understand their influence in the process.

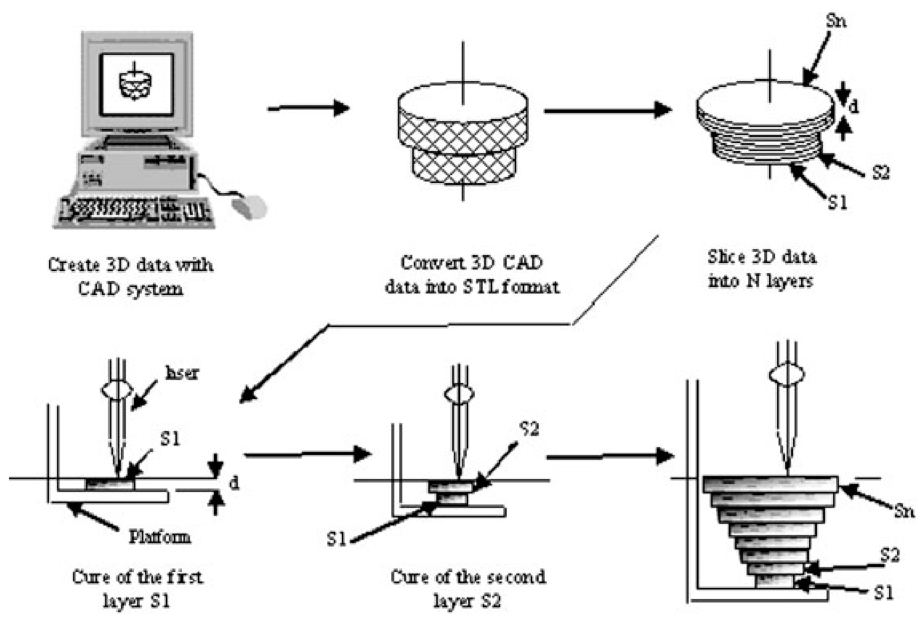

Figure 1 Illustration of STL system used for the fabrication of three-dimensional models.

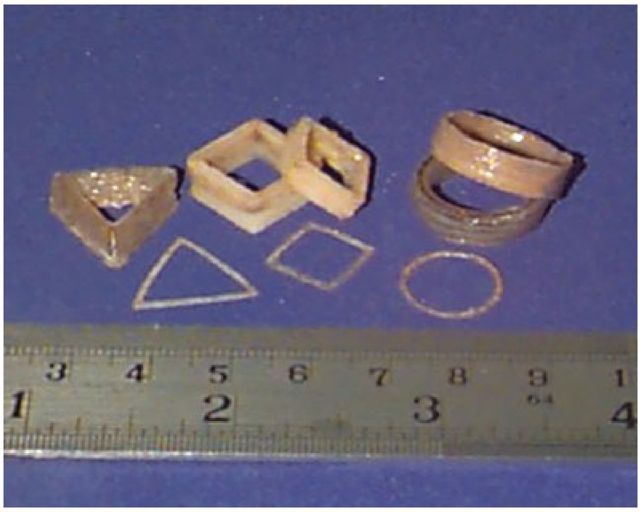

Figure 2 Multilayer parts constructed to different geometries. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Process parameters

It is important to understand the meaning of process parameters during research and development of the numerical model so that all the important phenomena taking place are considered. The dwell time (τ_d) is the average time at which any spot at sample, under the laser scanning path, is irradiated. It is obtained by dividing beam diameter (2ω) by the scanning speed (υ):

$$\tau_d = \frac{2\omega}{\upsilon} \tag{1}$$

The same spot at the sample is scanned repeatedly a number of times to ensure complete cure. The interval between scans is the time required for the laser beam to focus again, after a complete scan, at the same region, and it is related to laser trajectory and speed (υ).

To predict the effect the laser has on the cure process, it is necessary to determine how much energy was delivered to sample and over what volume the energy is distributed. Because the sample is highly absorptive for 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. The absorption depth is determined by measuring the transmittance of sample of uncured material.[9] The cylindrical volume V, which absorbs the energy provided by laser, during the dwell time τ_d, is given by:

$$V = \pi\omega^2\delta \tag{2}$$

The energy deposited in volume V is the product of the laser power and the dwell time

$$E = P\tau_d \tag{3}$$

The approximation of eq. (2) is reasonable for the sample because absorption depth, as well as dwell time, is quite short, but for larger dimensions, the spread of energy would influence this volume calculation.

The laser parameters used at the simulations are shown in Table II.

MATERIAL AND EXPERIMENTAL CHARACTERIZATION

The thermosensitive material considered in this work consists of an epoxy resin mixed with diethylenetriamine as cure agent and silica powder as filling material.

Epoxy resin (DER 383/Dow Chemical, Brazil) shows a unique combination of appropriate properties such as low shrinkage, thermosensitivity, and stability during cure. There are some liquid resins that have similar properties to epoxy; but this one seems to have a more appropriate combination of properties.[10]

Diethylenetriamine, the cure agent, is a low-viscosity liquid, fast cure, outstanding in chemical resistance.

Filler material is a nontreated silica powder, with an average size of 20 nm (L90/Cabot, Brasil), that has shown to present a decisive influence in the process of localized cure acting like a heat sink. If there is no silica in sample, the heat diffusion between reagents is too fast and the cure is not localized enough. If the amount is too large, the contact between reagents is blocked up. The aim of this work is to study the suitable amount of silica powder.

It was identified in previous experiments that the sample composition, in weight, that showed good results in term of geometries accuracy was the one with 10 parts of epoxy resin, 1.4 parts of diethylenetriamine, and 0.7 parts of silica powder. Parts were built with other amounts of silica, such as 3.5 wt %, 9.0 wt %, and no silica, and it was found that the most suitable amount is 7.0 wt %, since physical models with desired properties were obtained using this sample composition (Fig. 2). However, other compositions, not tested yet, can also be used depending upon specific applications.

To follow the process optimization, the appropriate amount of reactants compatible with the desirable localized cure properties should be determined. However, to do that is important to investigate the sample behavior in function of silica energy absorption and to study the heat sink effect and cure profiles.

The absorption depth (δ), as defined before at process parameters description, is essential for the definition of the volume of the cured region. It is known[8,9] that amount of silica influences, directly, the sample energy absorption depth, and so it follows that the amount of silica in the composition may determine the dimension of the cured volume [see eq. (2)].

To study the infrared absorption of samples in function of amount of silica, an optical characterization has been performed. The transmittance of samples with different amounts of silica powder was measured using an Infrared Spectrophotometer (Model IR-700), and an analytical solution using Beer-Lambert law [eq. (4)] was applied to estimate absorption depth (δ) values in function of silica amount.

$$I_t = I_o e^{-x/\delta} \tag{4}$$

Equation 4 represents Beer-Lambert law, where I_t/I_o is the sample transmittance and x is the sample thickness. Figure 3 shows experimental results of the absorption depth in function of the mass fraction of silica powder at samples.[11]

Considering the importance of silica, and the appropriate composition of the thermosensitive resin, it is necessary to analyze its effect over the process to obtain local cure. So, in addition to experimental results of the absorption depth, a numerical model has been developed to predict the thermal behavior of samples with different amounts of silica, during laser exposure, as well as to analyze silica amount effects over temperature distribution.

Cure occurs in thermosensitive resin by means of crosslinkage between epoxy resin and diethylenetriamine reactants and it would be incomplete if the materials proportion is not appropriate. Resins typically cure, or solidify, when heated to moderate high temperatures of approximately 80–100°C.[12] In a previous work,[8,9,13] differential scanning calorimeter was used to determine the cure temperature and reactions rate of the thermosensitive material considered in this work, and the results showed agreement with this statement. This cure temperature must be carefully observed and the process parameters handled to obtain the desired properties and geometry of final product.

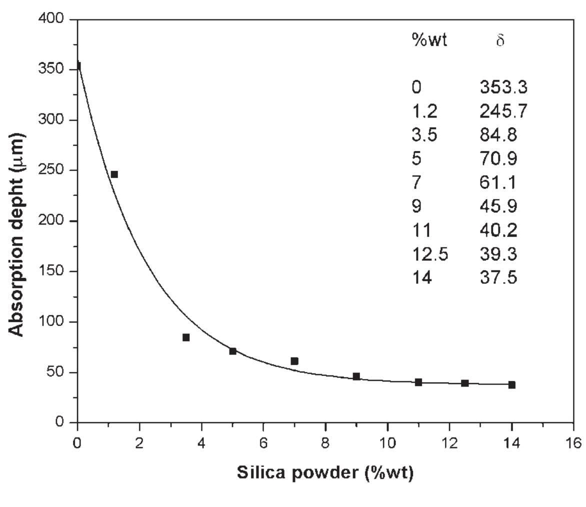

Figure 3 Absorption depth (δ) in function of silica amount at sample.

The developed numerical model is presented as follows.

NUMERICAL MODEL

A detailed deterministic model describing the main phenomena taking place in thermal cure process has been developed. It allows simulations of the temperature evolution at samples produced by a repetition rate of laser pulses, and hence to propose operational policy to optimize the process. The numerical model has been developed using ANSYS computer code, based on Finite Element Method (FEM), able to solve wide-ranging problems in engineering area. The FEM has been used by several authors[14] to solve problems of structural and fluids mechanics, diffusion problems, chemical transport, heat transfer, and phase change analysis.[15]

The main goal of FEM is to solve, numerically, complex continuous system that no analytical solution is available. FEM has also been applied to analyze different approaches of processes in rapid prototyping area.[16,17] In this work, ANSYS code is used as a tool to develop a numerical model capable of analyzing the heat transfer at thermosensitive materials during cure by laser irradiation.

The heat transfer at sample is analyzed as a conduction problem, and the laser irradiation is taking into account as a heat source at the material. The equation governing the transfer of heat can be derived from the principle of energy conservation and it can be written as eq. 5:

$$\rho c_p \left(\frac{\partial T}{\partial t} + V_x \frac{\partial T}{\partial x} + V_y \frac{\partial T}{\partial y} + V_z \frac{\partial T}{\partial z} \right) = Q + \frac{\partial}{\partial x}\left(k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y}\left(k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z}\left(k_z \frac{\partial T}{\partial z} \right) \tag{5}$$

where ρ is density, c_p is is specific heat, k is material conductivity, T is temperature, V is the transport of heat velocity, and Q is the heat generation rate per unit volume. The amount of heat due to the laser beam scanning is taken into account by adding appropriate values to heat generation term. The value of heat generation, at developed model, is considered to be a function of laser power (P) and cylindrical volume irradiated (V), as shown in eq. (6):

$$Q = \frac{P}{\pi \omega^2 \delta} \tag{6}$$

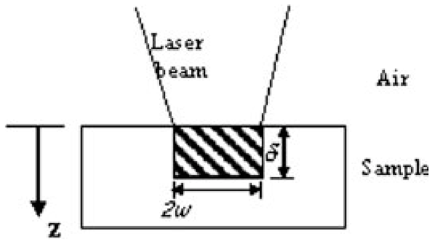

Figure 4 Representation of geometry considered in numerical model.

It has already been discussed that absorption depth (δ) depends on the amount of silica and its values have been shown in Figure 3. The geometry considered by the model represents a transversal cut of sample, in contact with air, under laser beam exposure. In the numerical model, the amount of heat in the sample due to the laser beam scanning is taken into account by the heat generation term (Q). The value of heat generation, in this model, is dependent on laser power as well as on the volume irradiated (taken as a cylindrical shape) [eq. 6]. Figure 4 shows a representation of the geometry considered and Figure 5 shows the mesh of elements.

As initial condition, it is considered ambient temperature (25°C) at the sample and air. As boundary conditions, at interface between sample and air, it is proposed a perfect contact and conduction of heat.

The thermal physical properties of samples (ρ, c_p, and k) vary according to silica amount. The thermal behavior of two samples was analyzed: one sample without silica powder (sample 1) and another sample (sample 2) with 7 wt % of silica powder in relation with the epoxy resin amount. Table I shows the physical properties of samples and the absorption depth (δ) used in each simulation. The material's properties were experimentally measured by Jardini.[18] The physical properties of air are also listed in this table.

RESULTS

The numerical model was developed to calculate the temporal and spatial variation of temperature, in a portion of the sample, during cure, considering a repetition number of laser beam scans.

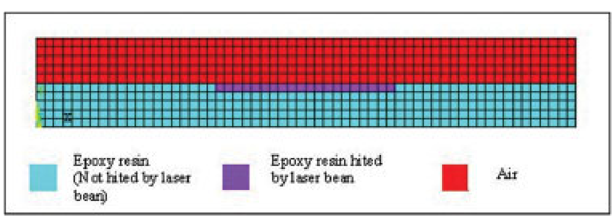

Figure 5 Mesh of elements. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Physical Properties and Absorption Depth (δ)

Samples	K (W/m K)	ρ (Kg/m^3)	c_p (J/Kg K)	δ (m)
S1—no silica	0.036	1155	1410	0.00035
S2—7% silica	0.043	2799	1384	0.00006
Air	0.026	1.16	1007	–

The results of numerical simulations show the temperature variation at samples during 10 lasers scans, and the spatial distribution of temperature after the 10 pulses for both samples. The dwell time (τ_d) and the interval between scans depend on laser scan speed. The time interval between pulses is the time required for the laser beam to focus again on the considered region of the sample after each scan, and it is related to the trajectory of laser beam that, in this case, is considered to be a circle to produce a cylindrical-shape object. Figure 6 is a representation of laser scan path and Table II shows the values of laser parameters considered.

The numerical results, depicted in Figures 7 and 8, show the temperature variation, during 10 revolutions of laser beam, for samples 1 and 2, respectively, at two different locations: at center of laser beam and at 4 μm distance from the center (beam waist). To analyze the heat diffusion of the samples with different amounts of silica, the figures show the difference of temperature (ΔT) between the two considered locations.

By looking at Figures 7 and 8 it is possible to compare the temperature behavior of the samples with and without silica. It is observed that, using different percentages of silica, significant difference of temperature variation is detected. The dynamic behavior of temperature of an irradiated area is represented by a series of temperature spikes on a constant background, with a decay time equal to the cycle time

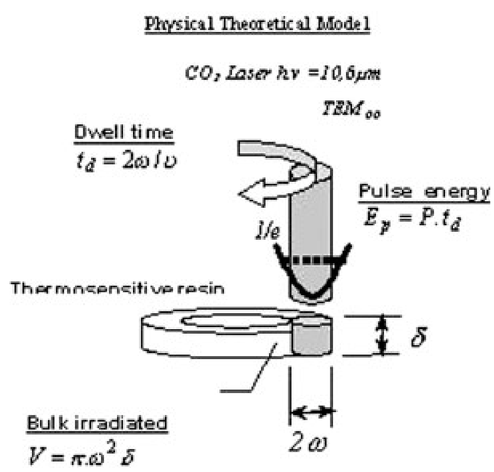

Figure 6 Representation of the trajectory of laser beam and considered parameters.

TABLE II
Scan Speed and Respective Parameters of Laser Beam Used in Simulations

Scan speed (m/s)	Dwell time (s)	Interval between pulses (s)	Laser beam power (W)
1.6	0.000502	0.035	10

(repetition rate). Because of the assumption of constant thermal properties, each temperature spike is the same, in each considered real case.

The results show a larger increase in temperature as well as a larger temperature gradient (ΔT) between the center and the waist of laser beam at sample with silica. This behavior indicates that the increase in temperature is confined in region where laser beam have reached and if the amount of silica is too small, curing is not localized. So, as it was mentioned before, silica powder acts as a heat sink agent during cure. The simulation results also depict that temperatures, at the center and at the edge of the laser beam, are enough to guarantee complete cure ($\sim$ 100°C) of all the irradiated portion of the sample, since the epoxy resin used in this work cures in the range of 80–100°C. At the center, the temperature is larger than 100°C, as it is necessary to guarantee that of the portion of sample located at the edge of the laser bean also achieve this temperature. The operating conditions described in Table II were tested and a final product with good spatial resolution was obtained without having any indication of degradation, as shown in Figure 2. Still, if other parameters, such as laser power and/or laser scan speed, were varied, it was possible to achieve the cure temperature for a small number of pulses.

One of the post processor capabilities of ANSYS code is the possibility to obtain spatial distribution of temperature at any time during process. These results are very interesting because it is possible, for example, by observing the isothermals at sample, to see the portion of material that had achieved the cure temperature after each pulse of laser and choose an optimum number of revolutions.

Figures 9 and 10 are an example of this kind of results. These Figures show temperature distribution after 10 laser pulses (samples 1 and 2, respectively) and they also show, clearly, the influence of amount of silica over the temperature behavior. The final temperature of sample 2 is 60% greater than that of sample 1, under the same lasers conditions. The gradient of temperature between the center of sample and the laser beam waist is also different for these samples. Greater ΔT indicates lower diffusivity and a localized raise of temperature; this behavior is observed for sample 2.

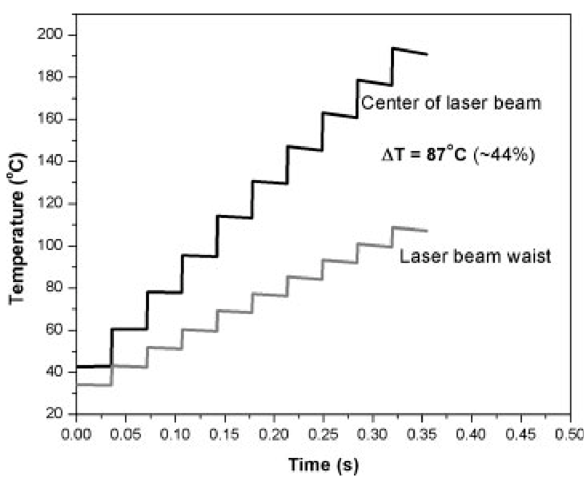

Figure 7 Temperature evolution at two points at the surface of sample 1.

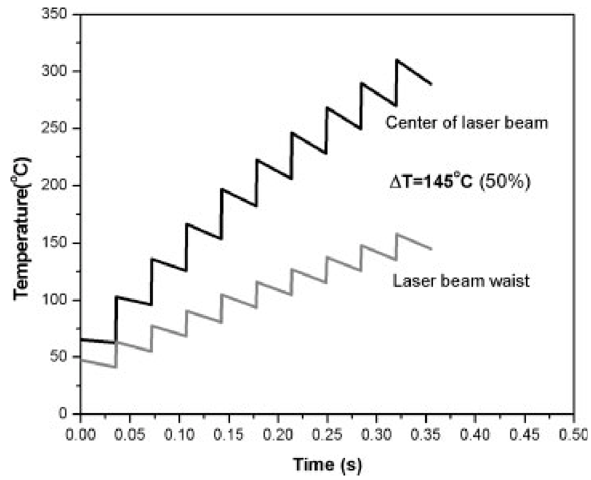

Figure 8 Temperature evolution at two points at the surface of sample 2.

CONCLUSIONS

The numerical model developed seems to be an efficient tool to study the influence of silica powder in

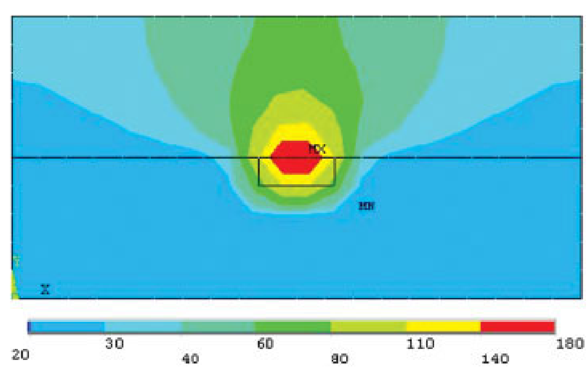

Figure 9 Cross section isothermal profile of sample 1 and air, after 10 laser pulses. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

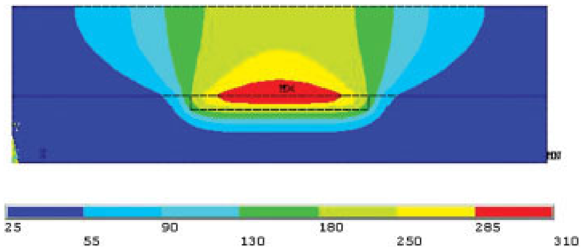

Figure 10 Cross section isothermal profile of sample 2 and air, after 10 laser pulses. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the localized cure process, as well as to continue the investigation of influence of other parameters to optimize the thermal stereolithography process. Simulations results agree, qualitatively, with experimental results that had showed how silica amount influences temperature behavior after laser exposure. The temperature behavior expected in function of sample composition has been obtained by simulations.

Simulations of thermal stereolithography process has proved to be an important tool to explore and analyze the efficiency of silica powder in the localized cure process, and to continue the investigation about other process parameters.

At this point of the analysis, the sample with 7 wt % of silica powder seems to have a very good behavior to obtain localized cure by infrared radiation with the physical model at the desired properties. A sample composed of 3.5 wt % of silica was already examined, experimentally and through simulations,[19] but did not show any improvement in the cure behavior. The amount of silica should be chosen to successfully confine curing laterally within the diameter of the laser beam. It is worth mentioning that vertically the prototype layers are mainly dependent on the absorption depth. The way as absorption varies with the amount of silica is shown in Figure 3, and it can be noted that the largest variations take place for the range of 0 up to 7 wt %. After that, smaller changes were verified but, the choice of 7.0 wt % of silica in the sample was defined, primary, in terms of the physical models obtained until this point of the research.

Numerical model has shown important results for better understanding localized cure. Thermal stereolithography process still needs to be studied and improved. Other process parameters should be analyzed and it is the objective to continue the investigation using the numerical model presented.

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