NOTES

Stereolithography with Thermosensitive Resins Using a CO_2 Laser

INTRODUCTION

Stereolithography is a powerful technique for producing three-dimensional plastic models of almost any desired geometry. In the conventional process, an ultraviolet laser source (325 nm) is used to expose the polymeric material. Thus, there is a combination of laser physics, computer-aided design, and polymer science, with a considerable emphasis on the curing process in the latter. In general, the stereolithographic apparatus (SLA) is, of necessity, a highly automated process.[1-3]

In this work, we adopted a different approach to the production of three-dimensional models, which can be called thermo-stereolithography (TSLO), in which thermosensitive resins are used in the fabrication process. A CO_2 laser is used for the selective local heating of the resins. We studied the interaction of the laser with the thermosensitive material, in particular, the high-viscosity fluid that is formed. A physical study of thermosensitive processes allows the determination of suitable characteristics for the resins and the filling materials. We present here experimental results of the production of solid layers of thickness 10^{-1}–10^{-2} mm in one, two, and three dimensions. Two plastic parts that we produced are used to illustrate the process.

EXPERIMENTAL

Sample

The thermosensitive material consists of a resin mixed with a curing agent and filling material. On the basis of their viscosity, thermosensitivity, and dimensional stability during the curing process, we chose two types of thermosensitive resins—epoxy and polyester. For each, we had to determine the appropriate filling material, compatible with the desired curing properties.[4,5] To study the infrared absorption, thin layers of the resins (0.2 mm) were obtained using a mylar substrate. Using an infrared spectrometer (400–2500 cm^{-1}), we determined for experimental purposes that the transmittance of such layers at 1000 cm^{-1} (CO_2 laser) was 12% for the epoxy and 10% for the polyester (extinction coefficient 2.8). We found that the amount of filling material and curing agent to be added to the epoxy resin was critical. There was a marked deterioration of the prototype's properties for small deviations from this amount. For epoxy resin, the chemical composition is 14% of the curing agent, with 7% pulverized silica as a filling material. In the case of polyester resin, the amount of activator to be added is about 2%, for 3% of filling material. Maintaining the correct stoichiometry of the curing and resin agents is critical to avoid noncured regions.

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Apparatus

A CW CO_2 laser (10.6 microns) with a beam waist of about 0.5 mm was used to produce the local heating at the focus of the zinc selenide (ZnSe) lens (f = 26 cm). The laser beam was directed through an off-center rotating lens (180 rpm), creating a circular path (see Fig. 1). The sample was mounted on an elevator (Z motion) support, within a vat filled with the liquid resin. A control system is used so that the sample is always just below the surface. It is also necessary to carefully control the horizontal position of the sample surface to obtain precise local heating. A resin layer, generally less than 0.1 mm, is produced in the laser focus trajectory where the resin is selectively cured. For three-dimensional modeling, multiple layers can be successively deposited (see Fig. 2).

Role of Pressure Wave

In our previous work,[6,7] we described an experimental physical model for the behavior of epoxy and polyester resins submited to a 10.6 micron laser beam. The curing process is also considered in this model. We call one of the principal deleterious experimental effects that has been considered by us the pressure wave. Controlling this effect is the key factor in obtaining localized curing.

The pressure wave is due to the localized heating produced by the focused laser. Although the laser is continuous and the sample stationary, the laser focus is in motion. Thus, there is a moving temperature gradient in the thermosensitive resin being cured. This moving gradient produces a thermal wave and a transverse pressure wave in the viscous liquid, as well as a local reduction in viscosity, a volumetric expansion, and a further heating by the curing reactions. These effects propagate as a wave,

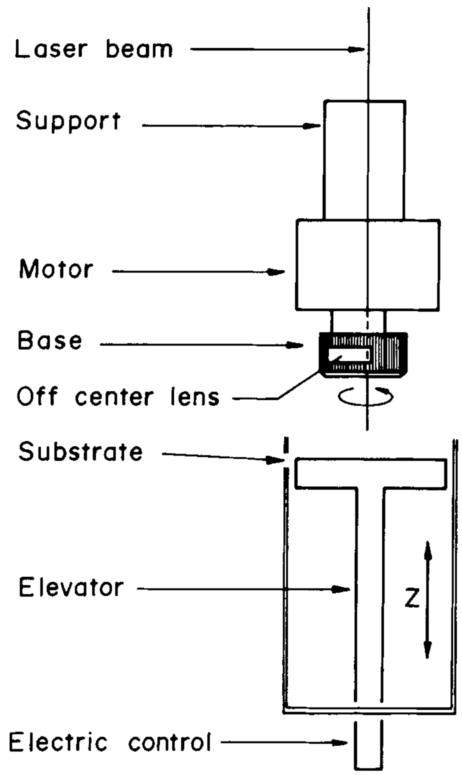

Figure 1 Illustration of system used for fabrication of three-dimensional rings.

with strong interactions among its components: pressure, reaction heat, viscosity, temperature, and density. The visible appearance of this wave is due to the pressure wave front. Under unfavorable circumstances, it looks like an expanding ring on the resin surface. These effects can be deleterious to the layer being deposited, as well as to adjacent layers. We found that the magnitude of these effects depends on the optical and thermodynamic properties of the resins, the curing agent, and the type of filling material used.

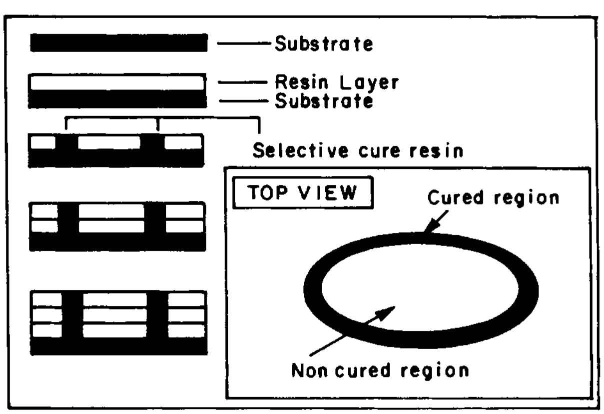

Figure 2 Method utilized for the construction of rings.

Table I Parameter Values for the Resins Used

Parameters	Epoxy	Polyester
Transmittance (%)	12	10
Thermal diffusivity (cm^2/s)	0.00022	0.00028
Thermal conductivity (mw/cmk)	0.359	0.553
Viscosity (cps)	23,000	16,000
Shrink	0	0
Filler	7% (silica)	2% (silica)
Cure agent	14% (DT)[a]	—
Activator	—	2% (DP)[b]

[a] Diethylene–triamine.
[b] Dicumyl peroxide.

In general, we conclude that the high optical absorption coefficient, low thermal diffusivity, low coefficient of volumetric expansion, high viscosity, and small thermal variation of the viscosity are desirable for the minimization of the pressure-wave effects. In Table I, we give experimental values for the important parameters, which are adequate for producing good models with a CO_2 laser at 10.6 microns for epoxy and polyester using TSLO. It is important to note that the activator agent for the polyester resin works best above room temperature and that the curing agent for the epoxy works best at room temperature. The laser heating accelerates the rate of curing. We estimate that the temperature at the focus reaches a level above 200°C.

RESULTS

Figure 3 illustrates an epoxy ring formed under different experimental conditions, but with equal laser irradiation. At the left, we show a coated substrate, but without a filling material. The two examples in the middle illustrate partially set resins, but without enough filling material, whereas the ring on the right shows the layer produced using the appropriate filling material and cure agent. The final size of the cured ring is about 15 mm of diameter. In Figure 4, we show two examples of a cylinder (1.5 cm diameter, 0.75 cm height) produced by multilayering. The cylinder on the right was built with layers 0.4 mm thick. The cylinder on the left was built with epoxy of layers 0.1 mm, with improvement in the final result. It was important to maintain constant the viscosity of the material in the vat to obtain good local curing as well as to use appropriate curing and filling materials. We note that the models obtained do not experience appreciable dimensional retraction and that the final product is firm and stable.

DISCUSSION AND CONCLUSION

We have presented the results of a low-cost method for the spatially selective solidification of liquid resins using

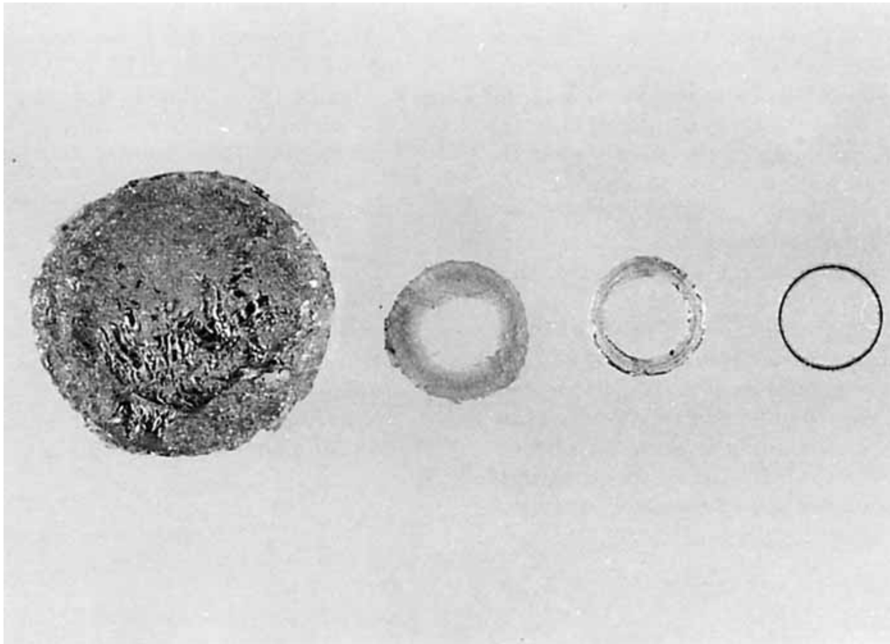

Figure 3 Epoxy rings formed under different experimental conditions for equal laser irradiation. The final size of the cured ring is about 15 mm diameter.

a CO_2 laser. The TSLO technique provides good spatial resolution and results in a product with desirable physical properties. A careful study of the thermal and pressure transients produced by the moving focus allows one to minimize the main deleterious effects. It was important to control the heating rate (laser power and rotation rate) and carefully choose materials and temperatures.

Given all the correct conditions, structures of one, two,

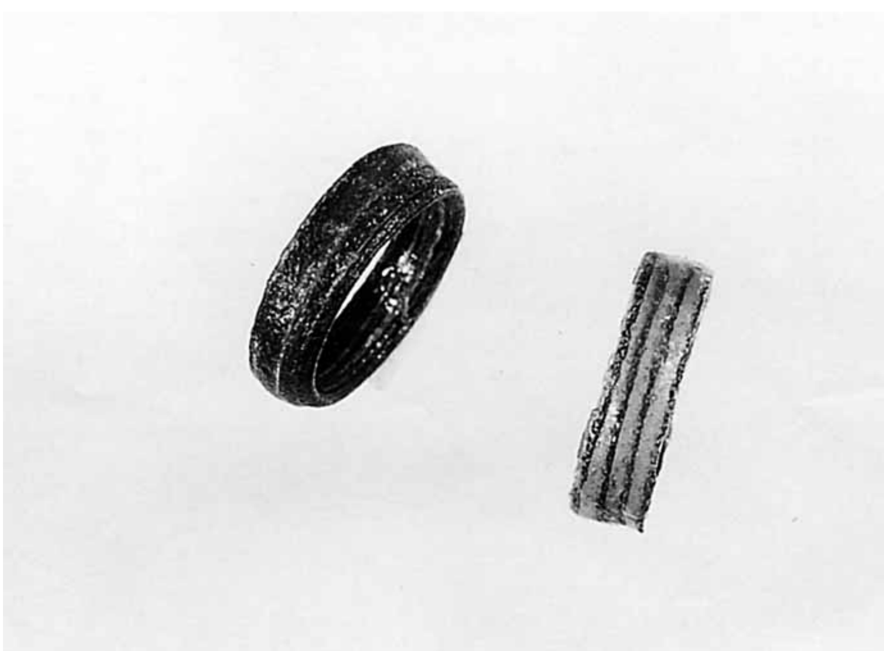

Figure 4 Epoxy multilayer final products using differents thickness 0.1 mm (left) and 0.4 mm (right).

and three dimensions were produced. To achieve good three-dimensional models, we found that a layer thickness of 0.1 mm for polyester and 0.2 mm for epoxy were good values. The final products showed no marked dimensional contraction. In the case of the epoxy with silica filler, the resin was very hard, whereas with the polyester and the same filler, the resin was pliable. The epoxy products required no postcure treatment, whereas the polyester required about 10% of the usual complementary postcure treatment. An important parameter for the fabrication of resin structures is the pot-life of the polymers. Thermoset epoxy resin with silica filler had a very short pot-life of 30 min, while the polyester pot-life is about 3–4 days. We found that a viscosity of approximately 23,000 cps gave the best results for the epoxy, whereas a viscosity of approximately 16,000 cps was the best value for the polyester. We note, however, that the high viscosity necessary may complicate the fabrication of three-dimensional structures.

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