Monitoring of Cure and Water Uptake in a Freeformed Epoxy Resin by an Embedded Optical Fiber

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Solid freeform fabrication has been used to produce epoxy resin parts containing embedded optical fibers. By illuminating the exterior of the part, the curing of the resin and water uptake in the cured component can be monitored in the near-infrared region. The applicability of this approach to the formation of "intelligent" materials is discussed.

Introduction

There is currently much interest in the potential for intelligent (or smart) materials with embedded sensors to detect changes in stress[1,2] or environment and, possibly, embedded actuators to allow some response to these sensed changes. A problem with this concept is that the embedded sensors are frequently large enough to disrupt the mechanical integrity of the material,[3,4] particularly by disturbing the packing of reinforcing fibers in a composite. Without spectroscopic information, optical fibers also tend to act as "universal sensors" so that it is hard to distinguish the effect of changes in, for instance, stress, temperature, or water uptake. Separately, optical fiber spectroscopy has been used to monitor curing of resins in special geometries, such as a short section of resin enclosed between two fibers in a capillary tube.[5]

If we take biological tissues, such as skin or bone, as a model for intelligent materials, we would hope to construct components containing arrays of diverse sensors which are coupled out through low-stress zones, via a trunk connection to a central processor. Until recently it was not at all clear how such components could be prepared. The developing techniques of freeforming do offer the potential for building these structures. In this paper we illustrate this approach by forming an epoxy part with an embedded fine silica fiber and show how this can monitor cure and water absorption of the resin near the surface. Rather than requiring resin enclosed in a special cell, this can be achieved with a simple fiber terminating below the resin surface, as a nerve terminates at the skin.

TGDDM (*N,N,N',N'*-tetraglycidyl-(4,4′-diaminophenyl)methane) is commercially available as MY721 from Ciba Geigy Corp. When cured with DDS (4,4′-diaminodiphenyl sulfone), it has been widely used in the aerospace industry for its high glass transition temper- ature. The curing kinetics of the resin have been studied by StJohn and George[6,7] using near-infrared spectroscopy both on bulk resin and on short sections of resin cast into a capillary cell between two aligned optical fibers. Using these methods, they followed changes in the amine bands at 6500−6800 and 5072 cm^{-1}, the epoxy bands at 8627 and 6057 cm^{-1}, and the hydroxyl band at 7000 cm^{-1}. In addition they were able to follow water uptake and desorption at 5223 cm^{-1}.[5]

For several years we have been developing a reactive extrusion freeforming system which has been used to process a range of materials from ceramics to rubbers.[8,9] This is one variant of the family of freeform fabrication methods which also includes stereolithography, solid laser sintering, fused deposition modeling, and 3-D printing.[10] The present work was carried out as a step toward incorporating optical sensors by in situ fabrication of the sensor as the part is made.

Experimental Methods

The reactive extrusion freeforming method has been described elsewhere.[9] The apparatus used in this project was a simple version based on a moving sample stage above which was suspended a 3 mL disposable syringe (Figure 1). The syringe was fitted with a 22 gauge needle (0.5 mm i.d.), cut off short. The *x*−*y* stage was an MD2 9 in. × 9 in. belt-drive system from Arrick Robotics (Hurst, TX), controlled via the printer port of a Compaq Aero computer. The piston of the syringe was driven by an Oriel (Stratford CT) "stepper mike" motor, and a second Oriel motor controlled the height of the syringe, both motors were addressed via an RS232 interface. The MD2 and syringes were controlled by a program written in Basic.

Samples were formed as square plates 20 mm × 20 mm × 5 mm. Each layer was written as a series of up-and-down sweeps with alternate layers written left-and-right. The line spacing was selected to allow neighbors to just touch. Each layer took about 60 s to write and had a thickness of about 0.2 mm.

TGDDM was as MY721 was obtained from Ciba-Geigy and blended with 27 wt % DDS (Aldrich Chemical Co.) by mixing at 60 °C. The mixed resin was hard at room temperature and was stored in a freezer. This mixture was warmed to 60 °C and blended with 15 wt % dioxane and 3 wt % of Degussa R202 hydrophobic fumed silica. The resulting mixture had the

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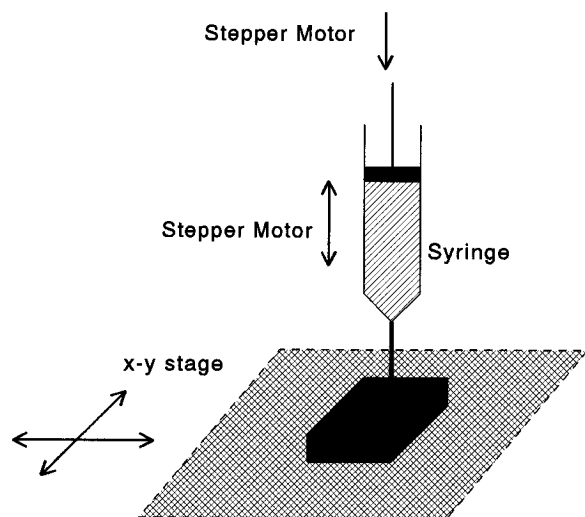
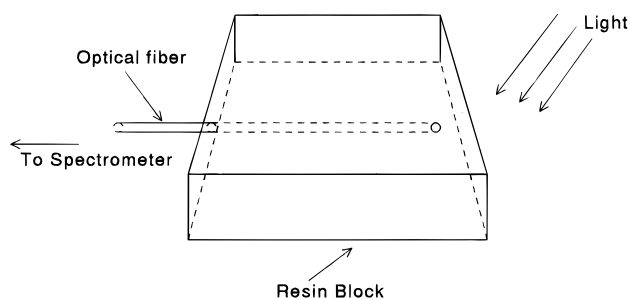**Figure 1.** Schematic diagram of the freeforming apparatus.

Figure 2. Diagram of an optical fiber embedded in a resin block.

consistency of toothpaste and would hold its shape when formed into a small cone using a spatula.

Freeforming was carried out onto a hotplate at 100 °C such that slow loss of dioxane stiffened the paste progressively. After 10 layers an optical fiber was placed across the surface of the soft resin such one end was a few millimeters from the edge and the other end extended 20 cm from the sample. Successive layers were then deposited to bury the fiber (Figure 2).

Optical fibers were Quartz et Silice PCS plastic-clad silica 600 W and a doped (low hydroxyl) silica-clad silica fiber AS200/280. Some early samples were formed containing 600 μm optical fibers but once adequate spectral intensity was attained, 200 μm fibers were used subsequently. In addition to being less mechanically disruptive, these finer fibers had fewer spectral artifacts and a low absorbance at 7000 cm^{-1}, the hydroxyl spectral region. The polymer coating was stripped from the end few millimeters of the fiber prior to embedding.

After forming, the part was precured overnight at 100 °C in an air-circulating oven to form a brittle yellow opaque solid. Subsequent full curing at 160 or 170 °C gave a brown partly transparent block.

During the full curing cycle the sample was removed at intervals for NIR spectroscopy. Water uptake was monitored also at intervals after exposure to ambient air or after immersion in water at 60 °C.

Spectra were taken on a Perkin-Elmer 2000 FT-Raman/NIR spectrometer using InGaAs and cooled InSb detectors. The laser and NIR sources were shut off. The free end of the optical fiber was carefully positioned at the focus of the Raman compartment with the sample dangling outside the compartment. The sample was placed in the beam of a Schott 150 W quartz–halogen microscope illuminator, with the heat filter removed (Figure 2). The radiation passed through about 2 mm of resin and was then collected by the embedded end of the optical fiber. Light emerging from the free end of the fiber was collected by the high-aperture optics of the Raman compartment and passed to the N-IR spectrometer.

Using a power meter (Molectron Detector Inc, PowerMax 5100) the output of full beam of the lamp was registered as 1.65 W over an area of 3 cm^2. A 600 μm fiber placed in the beam gave an output of 1.5 mW, reduced to below 0.5 mW when a sample with an embedded fiber is illuminated. Using the spectrometer in integrated energy mode over the range 8000–6000 cm^{-1} the intensity observed from a 200 μm fiber illuminated through a sample was about three-quarters of that from a bare fiber illuminated over one end by the lamp.

Spectra were run over the range 8000–5850 cm^{-1}, with resolution of 8 cm^{-1}, using an InGaAs detector. With a 200 μm fiber a 4% neutral density filter was placed in front of the sample to prevent saturation of the detector. Twenty-five scans were used to obtain the spectrum. Spectra were also run from 8000 to 4000 cm^{-1} with a cooled InSb detector using the full beam intensity, a gain of 8 and 100 scans. The lower sensitivity of this second detector did cause obvious spectral noise.

Results

Figure 3 compares spectra over the range 8000–4000 cm^{-1} for a sample precured at 100 °C and fully cured at 160 °C for 75 min. Several features may be observed from these spectra when compared with published spectral changes during the curing of bulk resin.[5] First, it is noted that the precuring reaction at 100 °C for 16 h has resulted in total consumption of primary amine since the strong combination band at 5067 cm^{-1} is absent. From the temperature dependence of the amine–epoxy reaction it is estimated that, at 100 °C, the amine should be totally consumed in about 4 h.[5] Total primary amine consumption corresponds to gelation of the resin, and the precured sample is thus a cross-linked network.

However, there is still unreacted epoxide as shown by the clearly defined band at 6057 cm^{-1} (Figure 3). The major cure reaction at 160 °C enables this epoxide to react with the secondary amine groups resulting from the earlier epoxide–primary amine reaction. The removal of secondary amine is essential to achievement of a high glass transition temperature and to lower the number of active sites for sorption of water. The sensitivity of the precured material to ambient moisture is shown by the appearance of a band due to water at 5223 cm^{-1} in the precured sample (Figure 3).

The curing reaction produces a higher crosslink density through both etherification (epoxy–hydroxyl reaction) and reaction of epoxide with secondary amines to produce tertiary amines. The first reaction produces no net increase in hydroxyl groups while the second produces both an increase in –OH and a decrease in –NH–. From the spectra in Figure 3, it can be seen that there is a growth of the –OH peak at 7000 cm^{-1} and a loss of the –NH– peak at 6600 cm^{-1}. Figure 4 shows the ratio of these peak heights as a function of curing time at 160 and 170 °C. The higher temperature gives a higher rate of crosslinking and a higher network density (lower –NH–). The solid line in Figure 4 is a fit of these data to pseudo-second-order kinetics based on the equation[11]

$$-\mathrm{d}(NH)/\mathrm{d}t = k[\mathrm{NH}][\mathrm{OH}][\mathrm{epoxy}]$$

Since the system has excess epoxide, [epoxy] was taken as constant. The line results from a straight-line fit of the data to the integrated form of the equation which yields a value of k.

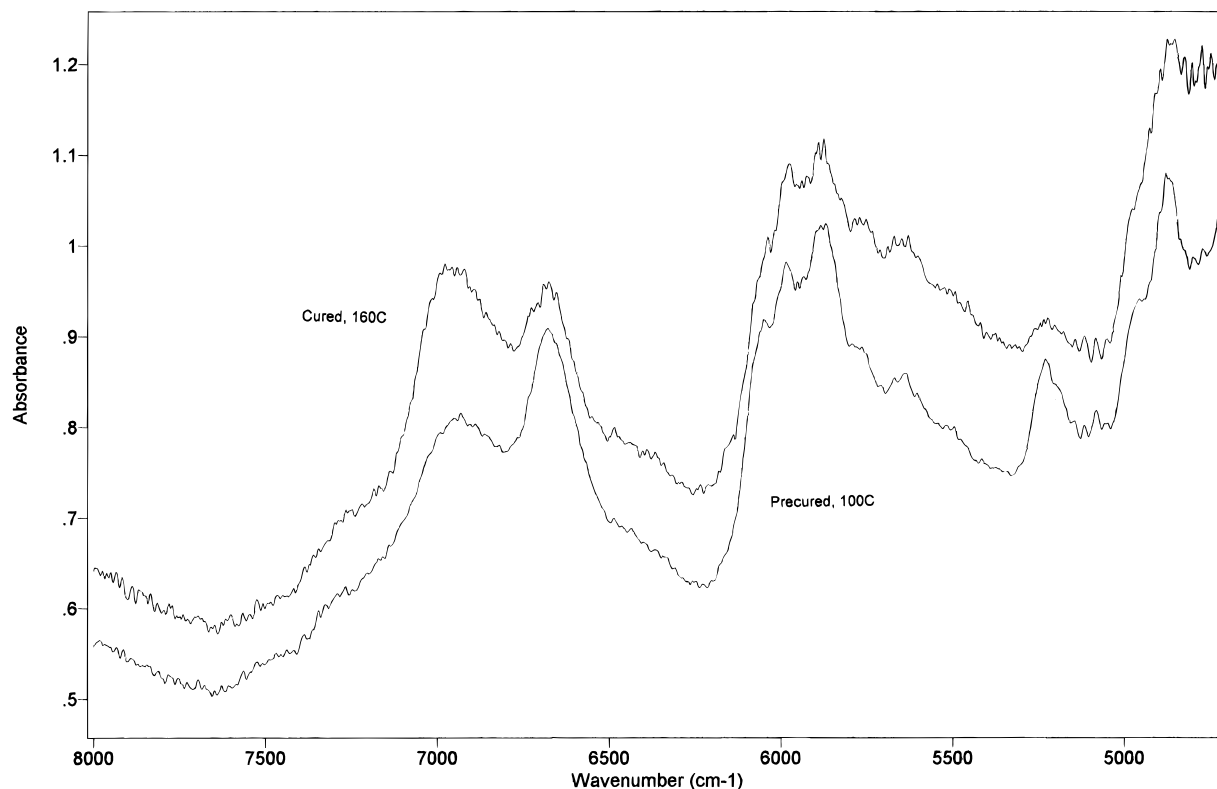(11) StJohn, N. A. Ph.D. Thesis, Queensland University of Technology, 1992.

Figure 3. Spectra of samples with different degrees of cure obtained through an embedded 200 μm fiber, 8000−4000 cm^{-1}.
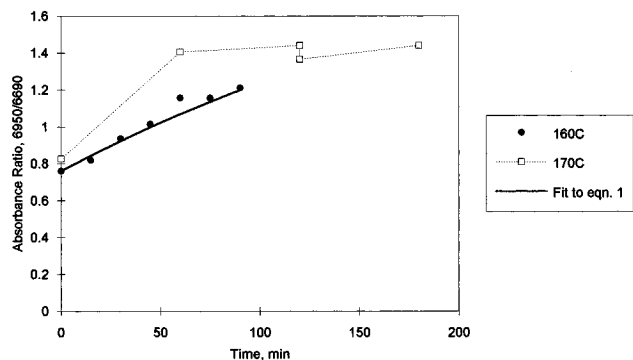

Figure 4. Peak height at 7000 cm^{-1} (−OH) compared to 6690 cm^{-1} (−NH−) vs degree of cure at 160 and 170 °C. Solid line, fitted to eq 1.

Figure 5 shows spectra of a dry sample and one soaked in water at 60 °C for 53 h. It can be seen that the water OH combination band at 5223 cm^{-1} reflects the increasing water content. Some change in the −OH peak at 7000 cm^{-1} would also be expected but the effect of added water is small compared to that of the −OH resulting from opening of the epoxy rings. As there is no contribution from alcoholic −OH groups to the peak at 5223 cm^{-1}, this may be used as a direct monitor of water uptake.

Figure 6 shows the increase in the water peak (5223 cm^{-1}) and −OH peak (7000 cm^{-1}) in comparison to the −CH< peaks at 5800−6100 cm^{-1} on uptake of water from liquid at 60 °C into a sample cured at 160 °C. These data may be analyzed for comparison with water sorption kinetics in these and similar epoxy systems. The thickness of the element, through which water uptake is measured, can be determined from the absorbance of the −CH< band at 5900 cm^{-1} in the precured sample (Figure 3) with that from a 1 cm uncured sample of MY721/DDS.[7] The effective path length is calculated to be 1.8 mm. If scattering, in the

near-infrared, by the silica particles (∼10 nm) is ignored, then the water diffusion path and optical path are similar.

The water uptake curve (Figure 6) is fitted to a Fickian diffusion model for total uptake in the first 2 mm by diffusion of water into a semiinfinite solid. The solution of Crank[12] for the concentration profile was integrated using Mathcad and fitted to the data using diffusion coefficient and infinite-time absorbance as fitting parameters. The fitted curve is shown in Figure 6. The diffusion coefficient obtained is 8×10^{-9} cm^2 s^{-1} for water diffusion at 60 °C. This compares with 10^{-9} cm^2 s^{-1} for water in TGDDM/27% DDS determined by Morgan et al. at 23 °C[13] and values of $(3-12) \times 10^{-8}$ cm^2 s^{-1} for a range of related resins at 100 °C.[14]

The estimated water uptake at saturation is 12%, which is higher than the values in the 4−6% region reported in other work but agrees with long-term weight change data on similar samples. This may reflect the absorption to the silica surface or voids in the formulation used for freeforming.

Figure 6 also shows water uptake from ambient air by a sample cured at 170 °C and then dried overnight at 100 °C. The rate of uptake should be slower at this lower temperature than at 60 °C, and the final equilibrium value is lower from room air than from liquid water, corresponding to about 2% after 100 h.

Discussion

A major concern with optical fiber sensors in composite materials is the disruption to the structure caused by the large fiber will introduce weakness. A fiber

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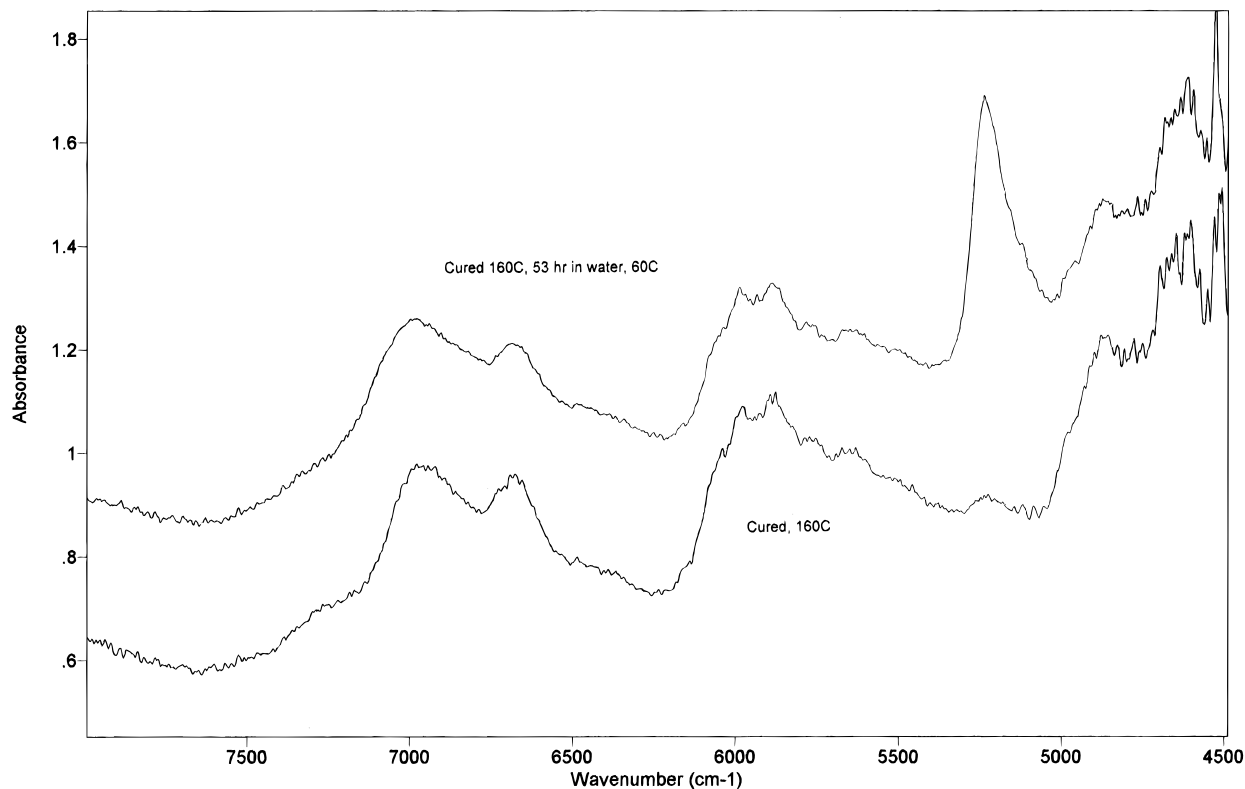(14) Bellenger, V.; Verdu, J.; Morel, E. *J. Mater. Sci.* **1989**, *24*, 63.

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Figure 5. Spectra of samples with different degrees of water uptake from water at 60 °C and from air at room temperature.
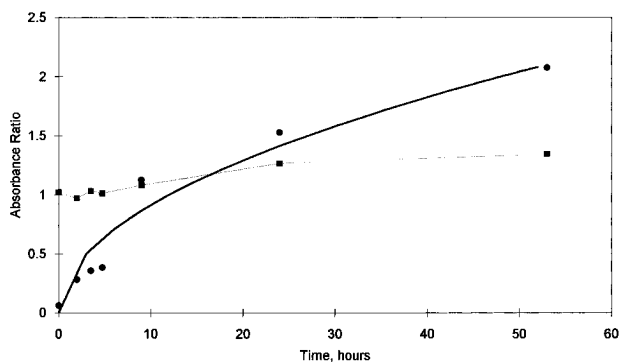

Figure 6. Rate of uptake of water followed at 7000 and 5223 cm^{-1} as a ratio to $-CH<$ at 5900 cm^{-1}. (●) Uptake from water at 60 °C. Sample cured at 160 °C. Solid line, fitted to Fickian diffusion with saturation concentration of 12% water, diffusion coefficient 8 × 10^{-9} cm^2 s^{-1}. (■) Rate of uptake of water followed at 7000 and 5223 cm^{-1} as a ratio to $-CH<$ at 5900 cm^{-1}. Uptake from ambient air at room temperature. Sample cured at 170 °C.

diameter of 10 μm would be ideal in terms of fitting easily into a composite reinforced with carbon fibers of approximately this diameter. With our system the light intensity at 5200 cm^{-1} is close to the minimum which allows reliable measurement of water, whereas the greater sensitivity of the InGaAs detector would certainly allow the fiber diameter to be reduced by a factor of 5−10. By changing from an FTIR spectrometer to a system of narrow-bandpass filters, it should be possible to achieve the 400× increase in sensitivity at 5200 cm^{-1} that would be required to use this system with small-diameter fibers.

The light input is believed to occur principally through the fiber end. The silica-filled epoxy does scatter visible light, so the embedded fiber end may be in an essentially isotropic radiation field. That part of the light which hits the end within the acceptance cone is transmitted by the fiber. We thus do not expect that the flatness of the fiber end will have much effect. Some part of the light may also enter the fiber through the short unclad section near the end. There will be conditions under which wavelength-dependent scattering will bias the spectral sensitivity, but we do not expect this to be important for the very fine silica particles used here.

An ideal optical sensor would provide the versatility of optical probes for physical and chemical sensing but would not seriously degrade the mechanical integrity of the structure. There is an interest in developing methods to make "intelligent" materials with sensing and response properties analogous to those of biological tissues. A system will then be needed to combine multiple probes and cable them to a detector system. Since freeforming methods allow parts to be made point by point, they have the potential to integrate the required complex sensing systems into composite parts.

Conclusions

A silica fiber optic has been used to detect water and monitor cure in an MY721/DDS epoxy sample. The use of an external light source illuminating the end of an embedded fiber provides a convenient source and detector geometry. Near-infrared spectroscopy provides a range of information about the state of the resin and impurity species such as water. Large components with many embedded sensors of this type could be processed by freeforming methods.