IN SITU (AUTOCLAVE) CURE MONITORING OF COMPOSITES WITH IR TRANSMITTING OPTICAL FIBERS

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INTRODUCTION

Recent research has shown that certain infrared (IR) transmitting optical fibers can be used to monitor the chemical changes that occur when a graphite fiber reinforced resin matrix is heated [1-4]. These changes are monitored as a result of the optical fiber behaving as an in situ multiple internal reflectance (MIR) cell. The optical fiber is positioned such that one end of the fiber accepts IR from a suitable source; the other end is positioned such that IR energy is focused into a suitable detector.

The genesis of this work owes itself to the efforts of Young and Chang at NASA Langley [5]. They have reported on chemical characterization of various thermosetting resins used in composites using FTIR spectroscopic techniques. Their work, conducted over the past several years, demonstrates that FTIR is an excellent and powerful tool for the characterization of advanced materials of interest to the military community. Their laboratory analysis revealed that cure cycles of these resins can be closely monitored using FTIR techniques. Of late, their work has largely concentrated on graphite fiber composites and prepregs.

The characterization of cured composites containing thermosetting resins presents a problem for infrared techniques because the material is opaque and the matrix resin is insoluble. Young solved this problem by using a diffuse reflectance technique (DRIFT). As illustrated in Fig. 1, diffuse reflectance arises from radiation penetrating into the interior of an opaque sample and re-emerging after being scattered numerous times. Since selected wavelengths are absorbed during this process, the diffuse component contains valuable optical information about the sample. Off-axis ellipsoidal mirrors collimate the reflected radiation and return it to the FTIR detector.

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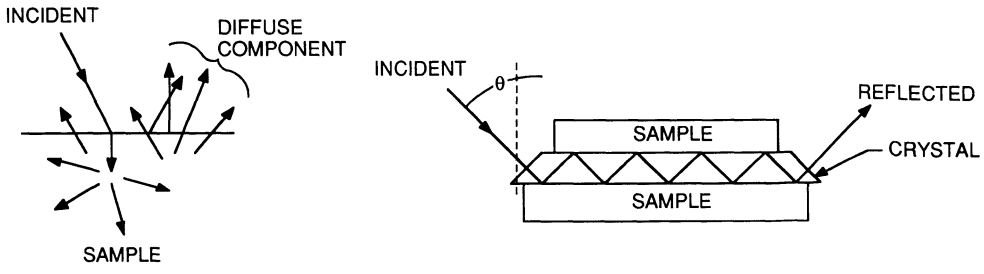

Figure 1. MIR spectroscopy.

MIR spectroscopy (Fig. 1) is a standard IR technique used for the spectroscopic measurement of highly absorbing or highly scattering materials [6]. The technique generally is referred to as evanescent wave spectroscopy when applied to optical fibers where an ensemble of reflection angles is usually present [7,8].

New optical fibers which can transmit in the IR wavelengths are currently under development. Some of these already show significant promise as a relatively low-cost method for transmiting light in the IR wavelengths of interest to the spectroscopist. A comparison of the leading candidate materials that exhibit promising characteristics in the IR wavelengths of interest and can be drawn or extruded into fibers of a length required for composite monitoring appear in Table 1.

IR fibers that have been used in previous studies consist of zirconium fluoride glass and chalcogenide glass. The HMFG fiber is the lowest loss IR optical fiber, exhibiting losses of less than 1 dB/m over a bandpass of 1 to 4.5μ wavelength. However, it also exhibits a low refractive index of ~1.51, which is close to the refractive index of most thermosetting resins. This is a potential problem of trying to use a fluoride glass as both a transmission link and as a sensor cell. The chalcogenide glass fibers, as stated earlier, have a refractive index greater than the sample medium. At this stage of development, however,

Table 1. Candidate IR Fibers

Characteristic	Chalcogenide	Fluoride	Sapphire
Core Diameter	120μ	70μ	125-250μ
Coating Thickness	90μ	-	-
Clad Thickness	-	< 2μ	-
Wavelength Range	3 to 10μ	0.5 to 4.3μ	0.2 to 4μ
	3300 - 1000 cm^{-1}	20,000 - 2325 cm^{-1}	50,000 - 2500 cm^{-1}
Attenuation	12 dB/m at 2.4μ	.02 dB/m at 2.6μ	20 dB/m at 3μ
Refractive Index	2.4	1.5	1.8
Use Temperature	250°C	250°C	> 1500 °C

they do not possess physical properties and temperature capabilities that would permit their use as an embedded IR sensor/transmission link in the autoclave environment.

Based on the above discussion, sapphire appears to be the most suitable sensor material for resin cure monitoring. Optically, sapphire is an excellent material for this application. The refractive index is well above that of the resins so that total internal reflection takes place with little light loss.

EXPERIMENTAL

The FTIR spectrometer used in this investigation consisted of a Bomem Model 110 spectrometer equipped with a liquid-nitrogen-cooled indium antimonide (InSb) detector, coupling optics, a sapphire (Saphikon, Inc.) sensor fiber, and heavy metal fluoride glass (HMFG), (Iris Fiber Optics, Inc.) optical fiber cable. The HMFG fiber cables were incorporated into the spectrometer such that a set of optics positioned the fiber end at the focal point of the incoming IR beam and another set of optics focused the exit beam back into the InSb detector. The sapphire sensor fiber was connected in between the HMFG fiber cables by means of another set of ZrFl optical fibers which were fitted with an adaptor to penetrate the autoclave. Additionally, a United-McGill Minibonder™ autoclave, rated for 700°F and 300 psig operation, with inside working dimensions of 12 in. x 12 in. x 36 in. was used. The autoclave is fitted with three additional ports for interfacing the fiber optic cable to the infrared spectrometer. An NEC APC IV personal computer (IBM AT compatible), and an FTIR data acquisition and analysis software package (SpectraCalc™, Galactic Industries) were used to obtain and analyze infrared spectra. Fig. 2 shows the above mentioned components in the desired assembly.

Lay-up of sensor fiber in laminate

Several procedures were developed for laying up the optical fiber in the laminate and connecting it to the autoclave. The most successful method is shown in Fig. 3. This configuration allows laminates up to 12 in. x 6 in. or 5 in. x 6 in. to be cured. The sensor fiber is placed in the center of the prepreg layup, parallel to the carbon fiber direction. The sensor fiber is attached with couplers to the transmission fibers. The laminate is covered with a layer each of release cloth, bleeder and breather. The fibers and the laminate are all covered with bagging, which is adhered to the tool with bagging tape (Fig. 4). The transmission fibers consist of fluoride glass fibers with a 250μ core diameter and a flexible stainless steel protective sheath. They penetrate the autoclave through a fitting designed to maintain a seal at 330 psi gauge (upper limit for autoclave) and terminate outside the autoclave to an adapter. The external fiber cables (also 250μ diameter) connect to this adapter and the fiber optic interface on the spectrometer.

The FTIR spectra were obtained over the region of 400 cm^{-1} to 5000 cm^{-1}. The transmission range of the sapphire sensor fiber, however, is limited to 2400 cm^{-1}. Therefore, spectra are displayed only between 2400 cm^{-1} and 5000 cm^{-1}. Prior to coupling the transmission cables to the autoclave connector, a

reference spectrum of the 2m HMFG optical fiber connector cables was collected over 256 scans (scan speed=1.7 scans/sec).

To date, only laminates of epoxy prepreg have been cured with the above system. Initial cure monitoring experiments were conducted with 20 layers of 0-90 prepreg layup for 10 in. (length) x 6 in. (width) and 5 in. x 6 in. parts. The epoxy prepreg was stored in the freezer at -10°C until ready for use. The sapphire sensor fiber was embedded lengthwise in the center of the laminate, parallel to the fiber direction of the layers on each side. The fiber layup and connection to the autoclave were carried out according to the procedure described above.

Prior to laying up a laminate, a sapphire sensor fiber was connected to the ZrFl transmission fibers and a spectrum of the sapphire was taken. Fig. 5 shows a transmision spectrum of the sapphire fiber (ratioed against ZrFl). After the sapphire fiber was embedded in the laminate, a spectrum of the laminate was collected at room temperature. The entire layup was evacuated and a standard cure cycle for Fiberite 934 epoxy was followed. The cure cycle is shown below:

- Heat ramp from 70°F to 350°F at 5°F/min, under 100 psi pressure
- Hold at 350°F and 100 psi for 2 hours
- Cool ramp from 350°F to 140°F at 5F/min, under 100 psi.

Simultaneously, the spectrometer computer was programmed to collect single beam spectra (64 scans). For the heat ramp phase, the spectra were obtained at 5 min intervals; during the 350°F hold phase, the spectra were obtained at 10 min intervals; and during the cool ramp, the spectra were collected at 10 min intervals. A final spectrum was collected when the laminate was at room temperature. These spectra are ratioed against the single-beam spectra of the sapphire at room temperature to obtain transmission spectra of the epoxy at various points during the cure.

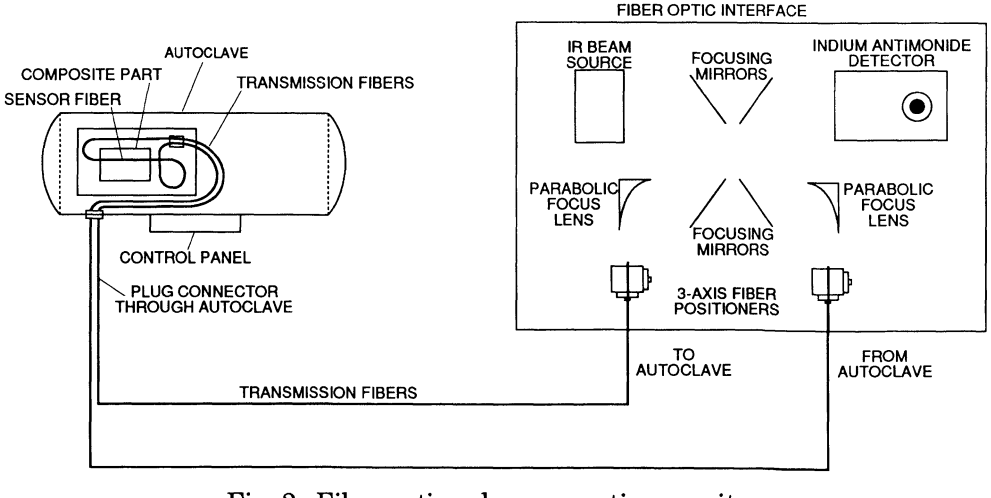

Fig. 2. Fiber optic polymer reaction monitor.

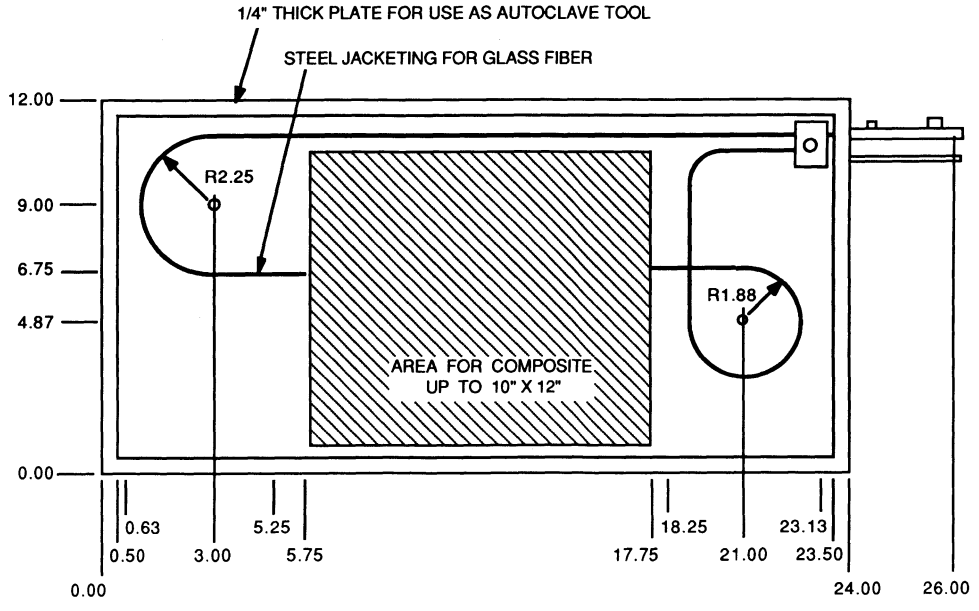

Fig. 3. Autoclave tool for laying up sensor fiber.

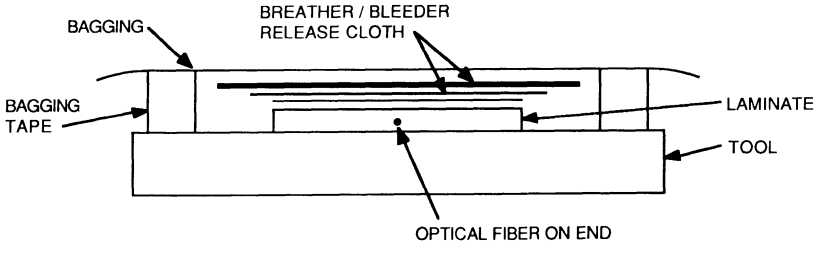

Fig. 4. Laying up of optical fiber in the laminate.

RESULTS AND DISCUSSION

The spectrum of the epoxy laminate at room temperature is shown in Fig. 6. It reveals the characteristic amine (N-H stretching mode) absorptions centered at 3372 cm^{-1} and C-H stretching modes (2900 cm^{-1}) attributable to CH_3 and CH_2 groups. Fig. 7 shows the transmission spectrum of the epoxy at 350°F. This spectrum reveals two distinct mechanisms. The first mechanism involves reaction of the epoxide ring with the amine functionality. This reaction can be followed by measuring the change in intensity at 3370 cm^{-1}, which is a signature of an amine group and the change in intensity at 3530 cm^{-1}, a signature of the hydroxyl group formed when the amine and epoxide react. This reaction occurs at relatively low temperatures. The second mechanism involves aliphatic C-H bonds. The change in intensities at 2860 cm^{-1} and 2930 cm^{-1} are indicative of subsequent cross-linking reactions which build up the epoxy network.

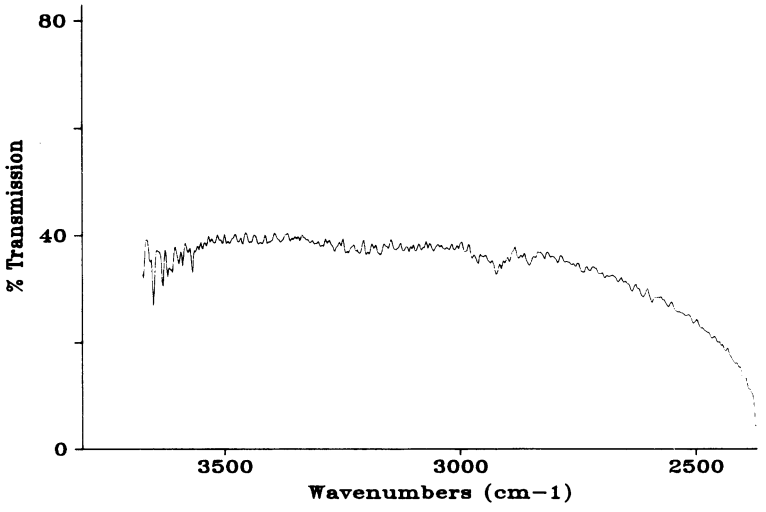

Fig. 5. Spectrum of sapphire sensor fiber.

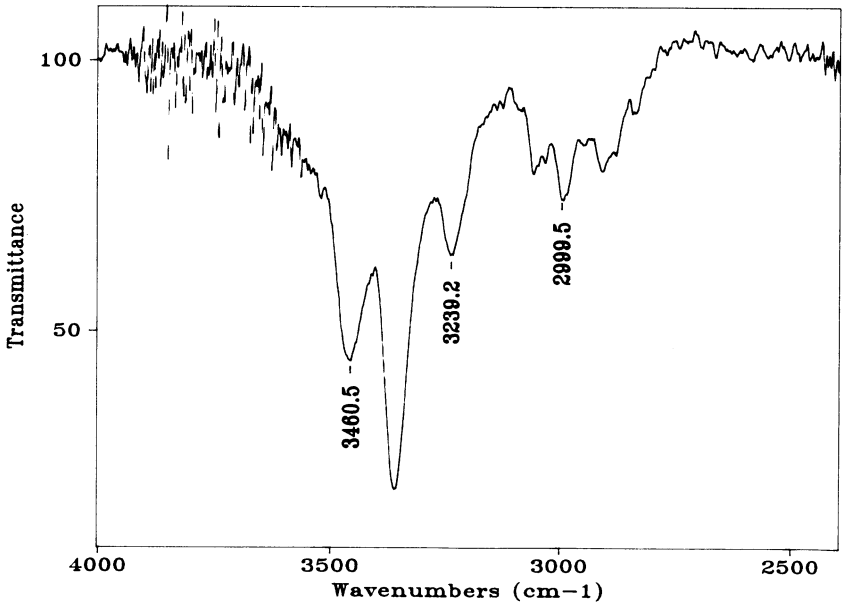

Fig. 6. Spectrum of epoxy at room temperature.

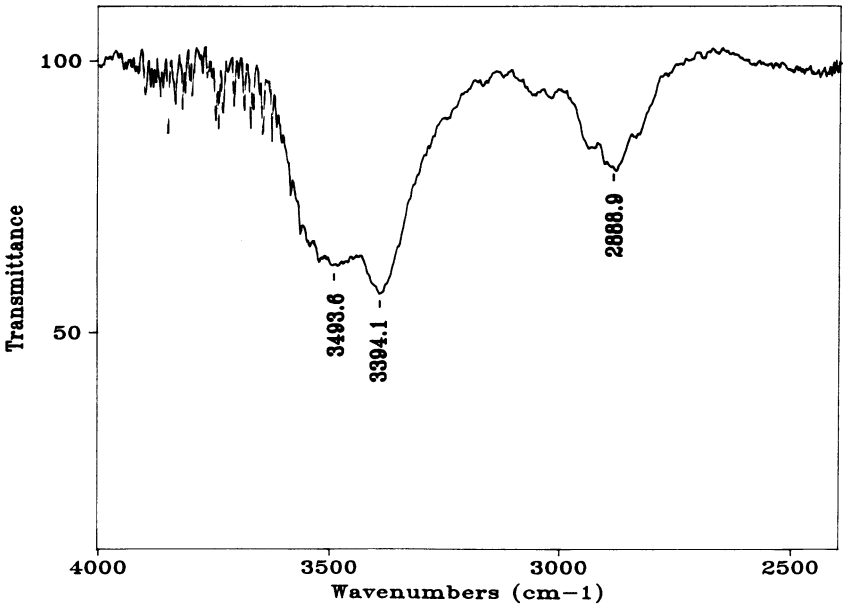

Fig. 7. Spectra of epoxy during cure at 350 °F.

To date, only complete cure cycles have been monitored. Future work will involve curing laminates to different points in the cycle. The partially and the fully cured parts will be tested. The results of the tests and the cure chemistry obtained from the spectra will be correlated in order to assess the degree of cure.

CONCLUDING REMARKS

The feasibility of using an embedded optical fiber in the autoclave curing of composites as a means of monitoring curing chemistry has been demonstrated. This technique, particularly in combination with other types of sensors, holds promise for alleviating some of the problems associated with the manufacture of advanced materials.

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