Real-Time Monitoring of the Cure Reaction of a TGDDM/DDS Epoxy Resin Using Fiber Optic FT-IR

G. A. GEORGE, P. COLE-CLARKE, N. ST. JOHN, and G. FRIEND*

Department of Chemistry, University of Queensland, St. Lucia 4067, Australia

SYNOPSIS

The feasibility of using remote FT-IR spectroscopy to monitor the gelation reaction of an epoxy resin used in advanced composite materials has been studied. The commercial epoxy resins MY720 and MY721, consisting mostly of tetraglycidyl 4,4'-diaminodiphenyl methane (TGDDM) were cured with diaminodiphenylsulfone (DDS) in a microcapillary cell connected to an FT-IR spectrometer by single silica fiber optics. By operating in the near-IR, direct measurement of the consumption of epoxide and primary amine and growth in hydroxyl groups was possible. It was found that the primary amine band at 5067 cm^{-1} was the most sensitive for rapid and accurate real-time monitoring of the cure reaction up to gelation. The temperature dependence of amine consumption from 135 to 180°C gave an activation energy of 70 kJ mol^{-1} for the cure reaction in agreement with DSC. Several artefacts involved in using fiber optic FT-IR in this way have been identified.

INTRODUCTION

Epoxy resins based on tetraglycidyl 4,4'-diaminodiphenylmethane (TGDDM) reacted with 4,4'-diaminodiphenylsulphone (DDS) are widely used in advanced composite materials.[1] The resin is frequently incorporated with the fiber in a pre-impregnated form (prepreg) to facilitate lay-up prior to the cure reaction which occurs at elevated temperature and pressure in an industrial autoclave.[2] The successful cure process[3] for a fiber reinforced composite involves: (i) the physical process of fiber wet-out by the resin and desorption of volatiles, both of which prevent the formation of voids and enable consolidation of the many plies of prepreg and (ii) the chemical crosslinking reaction which transforms the resin from a liquid through a gelled rubber to a glass at the cure temperature. The physical process is controlled by the pressure and the resin viscosity which is continually changing as the crosslinking reaction proceeds. If the pressure is applied when the viscosity of the resin is too low, then the resin will be lost from the composite. If the viscosity is too high then incomplete wet-out, poor consolidation, and void formation will occur.[3]

The appropriate pressure–temperature–time cycle is established from laboratory measurements of the temperature–time–transformation curves of the resin (TTT diagrams[4]). This cycle may be used for composite processing provided the composition or cure kinetics of the resin do not vary greatly from batch to batch. However, it has been found that variations of up to 30% in the thermal properties of a commercial, catalyzed TGDDM–DDS prepreg may occur both within and between batches,[1] suggesting wide variation in the cure kinetics. The reliance on a fixed cure cycle is not possible when the cure kinetics may be variable and it has been suggested that real-time process control should enable more reliable composite fabrication under autoclave conditions.[5,6]

Apart from embedded thermocouples to monitor the cure exotherm, the only other commonly reported techniques for monitoring the viscosity changes during the process cycle involve the dielectric properties of dc conductivity or ac phase lag.[7,8] A recent development in this area is the use of a

* Present address: Department of Primary Industries, Yeerongpilly, 4105, Australia.

Journal of Applied Polymer Science, Vol. 42, 643–657 (1991)
 CCC 0021-8995/91/030643-15$04.00

charge–flow transistor with temperature compensation, as a microdielectric monitor.[9,10] The use of such dielectric monitoring in closed-loop process control has been demonstrated, but has been shown to be subject to error if the rheological properties of the resin deviate from the expected limits.[8] The measurement of dielectric properties of the curing resin in the noisy electrical environment of an industrial autoclave may also be subject to substantial interference. For this reason, alternative techniques based on fiber optics have been actively researched.[6,11,12] While several of these rely on viscosity-dependent luminescence to monitor the changes in the rheological properties of the resin during cure, there are uncertainties in those techniques relying on absolute emission intensities because of possible quenching processes.

It has recently been demonstrated that fiber optic probes may be coupled to an FT-IR spectrometer to enable near infrared absorbance and reflectance spectra to be collected remote from the instrument.[13-15] This offers the possibility of measuring the extent of conversion of the epoxy resin in real-time throughout the process cycle. This would provide the most appropriate information for process control, as a direct measure of the cure kinetics may be obtained from the infrared spectrum of either the epoxide or the amine curing agent.[1]

There are, however, several important requirements which must be met before the fiber optic method can be applied in this way. First, it must be established that a band in a region of the spectrum transmitted by the optical fiber is varying systematically throughout the critical gelation region of the epoxy resin. Quantitative relationships must then be established between band intensities and concentration. The simplest relation is direct proportionality (i.e., Beer's Law) but if there are several overlapping bands, as occurs in both the mid- and near-infrared regions, this may not occur over a wide concentration range. The infrared band analysis for extent of conversion through the fiber optic must also produce the same kinetic relation as has been obtained from calorimetric[1,16] and viscometric[17] measurements up to the gel point and be amenable to real-time display for process control.

Because of the spectral cut-off of the silica used in most commercial optical fibers, most studies of remote fiber optic FT-IR have been restricted to the near IR region of the spectrum.[13,14] In this region, the strongest absorption bands arise from overtones and combinations of fundamental C—H, O—H, and N—H vibrations, because of the large anharmonicity of those vibrations involving the light hydrogen atom. This has the advantage that the spectrum is considerably simplified compared to the usual mid-IR region. In addition, as the bands are much weaker than the fundamental, quite long path lengths of up to 10 mm of material may be measured. Conventional near-IR absorption spectroscopy has been used for some time for the determination of epoxy equivalent weight and hydroxyl number of commercial resins.[18,19] More recently, semi-quantitative analysis of the near IR bands due to —OH and —NH groups of cured Epon 828-MPDA samples has been used to assess the cure cycle.[20] However, there has been no reported study of epoxy resin cure kinetics in real-time.

A significant recent advance in the development of fiber optic FT-IR is the availability of mid-IR transmitting chalcogenide glass fibers.[15] When coupled to an FT-IR with a high-sensitivity MCT detector, it was shown possible to obtain spectra between 3250 cm^{-1} and 1250 cm^{-1}. This enabled a study to be made of the cure reaction of a thermoplastic polyimide (LARC-TPI) by removing some of the fiber cladding to enable it to form an internal reflection (ATR) element.[15] However, this cannot be readily used for an epoxy system as the fiber is opaque in the region of the oxirane fundamental (910 cm^{-1}) although the primary and secondary amine stretching bands at 3300 to 3500 cm^{-1} should be accessible for amine-cured epoxy resins. Other problems noted in using the chalcogenide glass fibers were the high loss of 10 to 15 dB per meter, which set an upper limit of around 3 m for the fiber length, as well as difficulty in establishing a baseline in the mid-IR because of overlapping bands. These limitations together with the present high cost of mid-IR optical fibers have left the near-IR region as the most appropriate for researching the use of fiber optic FT-IR for real-time monitoring of the cure reaction of epoxy resins.

In this paper, we wish to describe simple methods by which silica fiber optics of several different diameters may be coupled to a commercial FT-IR spectrometer to enable the spectra of TGDDM/DDS epoxy resins to be collected remote from the instrument during cure. The spectra obtained in this way have been analyzed in detail and the artefacts introduced by the fiber optics are described. Analytically useful bands are recognized and used to monitor the critical gelation reaction of the resin under a simulated cure cycle. FT-IR software which enables a real-time display of the extent of reaction is also described.

EXPERIMENTAL

Materials

The formulations used in this study were prepared from the commercial tetraglycidyl 4,4′-diaminodiphenylmethane (TGDDM)-based epoxy resins MY720 and MY721 (both from Ciba-Geigy) and the hardener 4,4′-diaminodiphenylsulfone (DDS) as the commercial grade HT976 from Ciba-Geigy and laboratory reagent grade from Sigma Chemical Co.

Formulations containing from 17 to 37% by weight DDS were prepared by first preheating the resin to 110°C. The hardener was then slowly added to the resin with stirring and heating continued over 5 min at 100 to 120°C to produce a clear mixture. This was immediately cooled and stored in a freezer prior to the studies of curing. Material unused four weeks after preparation was discarded.

Coupling Fiber Optics to the FT-IR Spectrometer

Two methods were employed for coupling single plastic clad silica (PCS) optical fibers (Quartz et Silice PCS 600 W and 1000 W) of diameter 600 μm and 1000 μm to a Mattson Sirius 100 FT-IR spectrometer. The Mattson FT-IR was configured to operate in the near IR from 11,000 cm^{-1} to 4000 cm^{-1} by having a 20 W tungsten quartz–halogen lamp, a quartz beam splitter, and an Indium Antimonide (InSb) photovoltaic detector operating at 77 K.

The first method involved no alteration to the internal optics of the instrument and was used for preliminary studies. As shown in Figure 1, the cell compartment was fitted with the standard Universal Optical Stage and sample holder for microbeam transmission measurements. This provided a converging beam with a numerical aperture of 0.49 compared to the numerical aperture of the fiber optic of 0.4. Thus, by mounting the end of a freshly cleaved fiber optic in the microbeam transmittance holder at the focal point (by sliding it through a fine hole drilled in a rubber plug) it was possible to launch the interferometer beam into a fiber optic, several meters in length. The returning fiber optic was slipped through a second hole in the rubber plug, but from the opposite side (Fig. 1). Radiation emerging from this fiber will be off-axis and in a different plane compared to the launching fiber, and it is necessary to adjust the universal stage to collect the radiation and transfer it to the detector. This was achieved by adjusting the collimating mirror in the X–Y plane. While gross positioning of the fiber optic and the gathering mirrors could be achieved

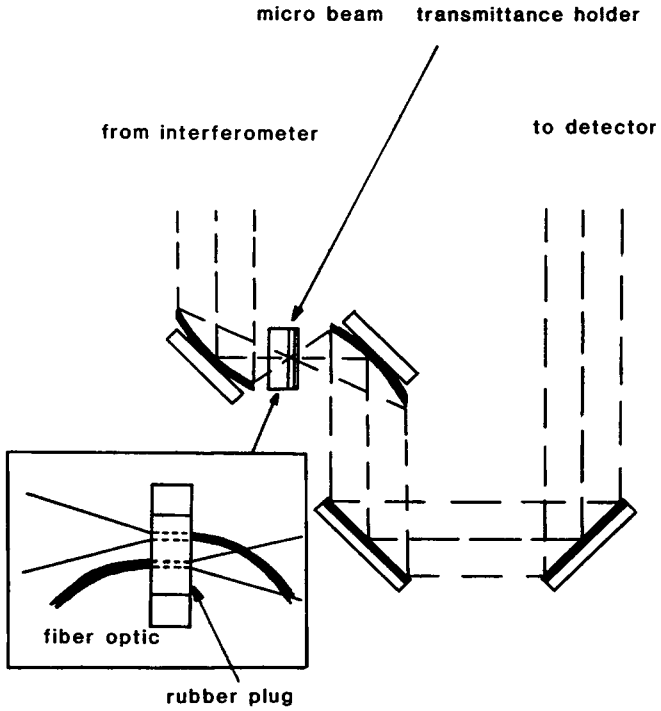


Figure 1 FT-IR sample compartment arrangement using adjustable mirrors from the universal stage and showing a detail of the fiber optic mounting method.

using the visible image of the tungsten lamp, final adjustment was made on the peak interferogram voltage.

A second optical arrangement provided superior energy throughput and thus improved signal-to-noise in the fiber optic spectra. This involved using the identical collimating mirror and mounting method for the launching fiber optic, but positioning the returning fiber optic immediately in front of the InSb detector by using an *X–Y–Z* positioner. As shown in Figure 2, the radiation from the returning fiber is focused on the detector element by an Oriel fiber optic focusing beam probe. This reduces the number of reflecting surfaces with a resultant increase in energy throughput and a greater speed of data acquisition.

To obtain the spectral transmission properties of the fiber optic, a background spectrum was collected with the microbeam transmittance holder empty and the normal optical path. A continuous loop of PCS fiber was then mounted and the spectrum obtained.

For the collection of spectra of epoxy resins, the PCS fiber optic (typical length 2 m) was cleaved in the middle and the outer protective polymer coating removed for a distance of 1 cm from each end. These two ends were then slipped into a capillary glass tube of internal diameter slightly greater than the external diameter of the clad fiber core, to make a variable path length micro-cell. Radiation emerging from the fiber core was reflected along the cell and gathered by the second optical fiber to be returned to the detector. The capillary cell, silvered to increase the energy throughput, was filled with the resin-hardener mixture at 100°C. The cell was placed in a brass block fitted with a platinum resistance thermometer which was used to regulate a hotplate through a proportional controller and programmer. Temperature equilibration typically took 2–3 min at the beginning of each run. Spectra were collected either manually at selected time intervals during cure or continuously using the software described later. Spectra were collected using 32 scans at 4 cm^{-1} resolution.

RESULTS AND DISCUSSION

Spectral Transmission of Optical Fibers and Capillary Cell

A study was made of the transmission properties of the fibers and cell to determine if any spectral artefacts were introduced during the cure reaction. Figure 3 shows the spectral transmission properties

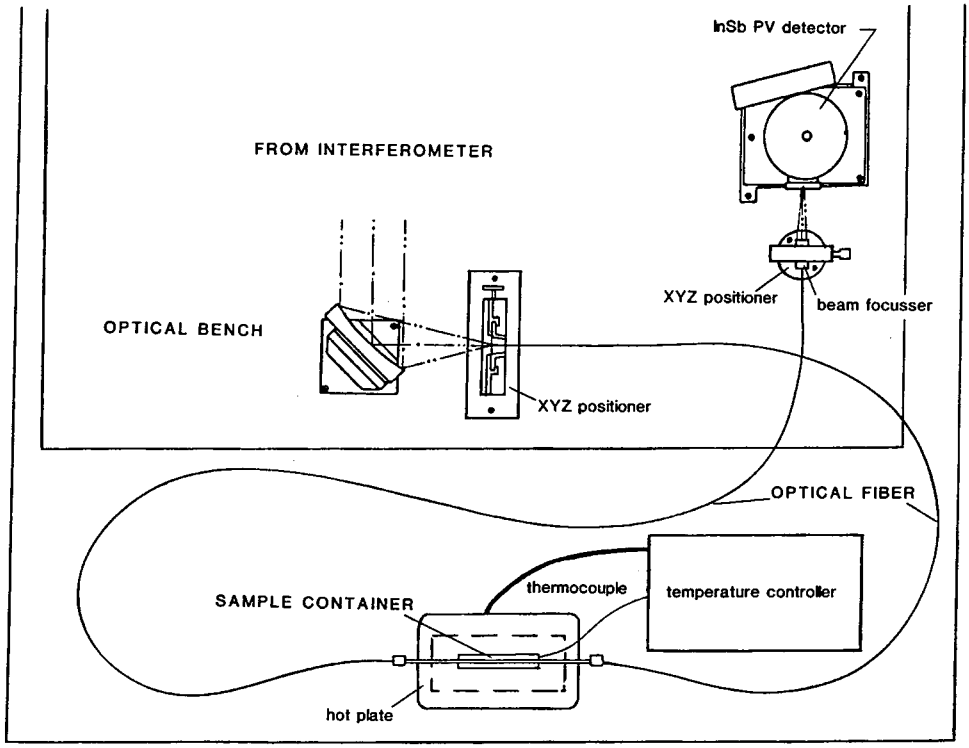


Figure 2 FT-IR modification for achieving high spectral S/N through fiber optics coupled to an externally heated microcapillary cell.

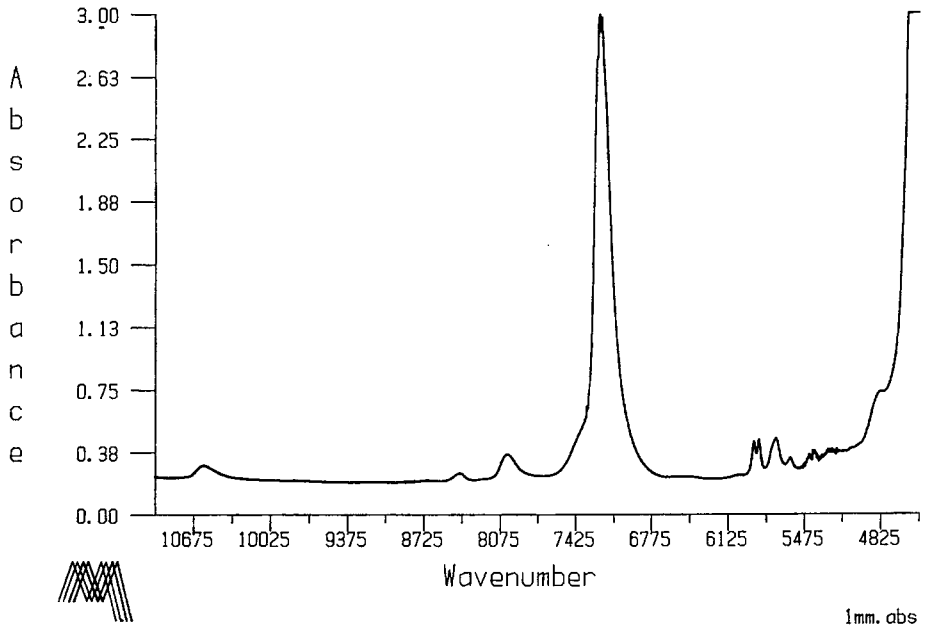


Figure 3 Near IR spectrum of a 2 m length of single PCS 1000 W optical fiber.

of a 2 m continuous loop of PCS 1000 W fiber collected using the method described above. It should be noted that the ordinate scale is not a direct measure of the attenuation of the fiber, as is achieved using a technique such as the cutback method in which a length of fiber is removed without altering the optical launch conditions.[21] The principal feature of the spectrum is the strong band at 7100 cm^{-1} which arises from the first overtone of the —OH fundamental vibration at 3540 cm^{-1} of Si—OH which is intrinsic to the silica.[22] Only by using a low hydroxyl content fiber can this band be eliminated from the spectrum.[13,14] In spite of this strong absorption, there is a wide area of the near-IR spectrum which is available for study of the epoxy resin cure reaction. Figure 4 shows the spectral transmission

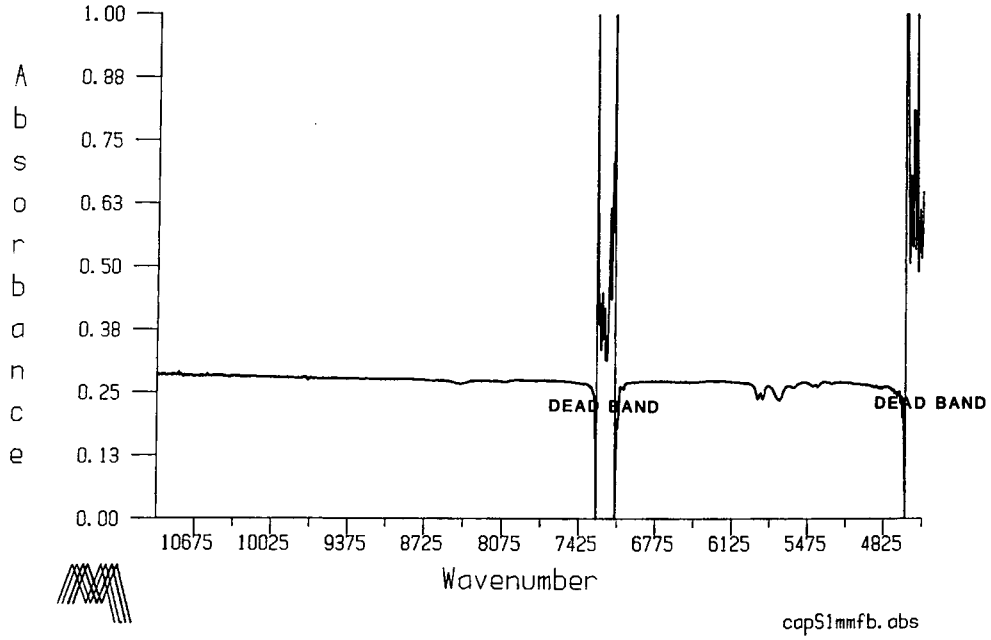


Figure 4 Near IR spectrum of the fiber optic and capillary cell, showing the dead bands around 7000 cm^{-1} and the negative peaks due to the fiber cladding.

of the capillary cell referenced to the spectrum of a continuous PCS fiber loop, and the useful spectral regions are from the fiber spectral cut off at 4700 cm^{-1} to 7050 cm^{-1} and 7350 cm^{-1} to 11,000 cm^{-1}. The width of the —OH dead band will increase with the length of the fiber[13] and it is necessary to determine the maximum fiber length as well as the possible artefacts which may limit accurate spectrophotometry.

When Figure 4 is examined, it is found that there are negative bands around 5400 cm^{-1} to 6000 cm^{-1} and around 8400 cm^{-1}. From Figure 3 it is seen that these correspond to absorption bands in the silica fiber optic that are not attributable to Si—OH absorptions. Fredericks et al[20] also reported these bands in spectra of 600 μm PCS fibers but did not comment on their origin. They are not observed from multimode fibers which do not have a plastic clad-

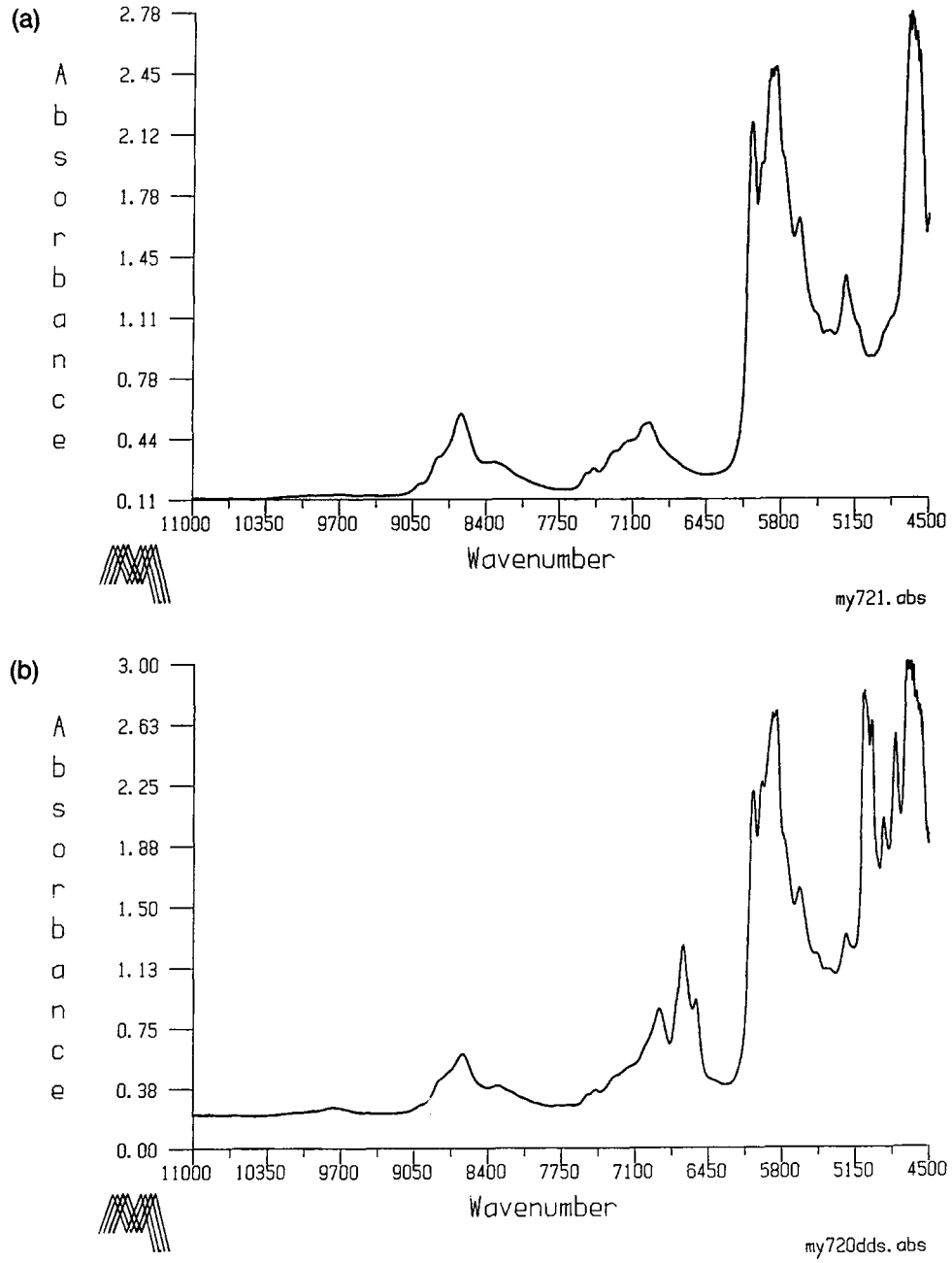


Figure 5 (a) Near IR spectrum of MY721 in a 1 cm cuvette. (b) Near IR spectrum of MY720 and 20 wt % DDS in a 1 cm cuvette.

ding.[21,22] The origin of these bands was investigated more closely as they coincide with several analytically useful bands in epoxy resins. A band analysis has shown that the absorption region corresponds to that of the methyl group first and second overtone and combination bands.[23] Since the bands appear negative in the fiber optic–capillary cell spectrum this implies that the absorption is stronger in the background spectrum of a single, uncut 2 m length of fiber optic than when the fiber was cut, some of the cladding removed, and inserted in a capillary cell. This implies that the bands originate from the methyl groups of the silicone cladding material. Since transmission of radiation within the cladding itself is unimportant in PCS fibers,[21] the band must arise by the transmitted radiation, which is undergoing total internal reflection at the silica core-silicone cladding interface, being attenuated through penetration of the evanescent wave into the silicone cladding at each reflection. From the measured absorbance of 0.15 for 1 m of fiber at 5950 cm^{-1} and the reported molar absorptivity[24] of the methyl group at this wavenumber of 0.1 $dm^3\ mol^{-1}\ cm^{-1}$, an equivalent path length of 500 μm is calculated. From the calculated penetration depth as a function of angle of incidence, and the number of reflections per meter for each angle, this path length corresponds to an incident angle of 76° which is close to the launch angle of 75.1° as given by the numerical aperture of 0.4 for the fiber optic. It is therefore considered that those modes near the critical angle are responsible for the appearance of the negative bands in the background spectrum of the capillary cell (Fig. 4). Of particular concern is the observation that the absorbance of these cladding bands changes when the epoxy resin is placed in the cell.

Near IR Absorption Spectrum of TGDDM/DDS

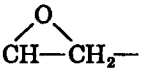
Figure 5(a) shows the near IR absorption spectrum of the neat epoxy resin MY721 in a 1 cm cuvette. Figure 5(b) shows that obtained from MY720 with 20% by weight of DDS dissolved in the resin. The main spectral bands of interest in the cure reaction and their assignments are summarized in Table 1. These assignments are in general agreement with those previously reported.[18,24,25] No difference was observed between spectra of MY720, MY721, and purified TGDDM.

The near IR spectrum of the neat TGDDM epoxy resin in a 6 mm capillary cell, collected through 2 m of PCS fiber optic is shown in Figure 6(a). The spectrum shows good signal-to-noise and the main differences between it and the cuvette spectrum [Fig. 5(a)] are in the dead band around 7200 cm^{-1} and the cut off at 4600 cm^{-1}. However, when TGDDM/DDS mixture is run, particularly at a shorter path length in the cell [Fig. 6(b)] the spectrum appears to be significantly different from that obtained in the cuvette [Fig. 5(b)]. From a comparison of Figure 6(b) with Figure 5(b), the following points are noted:

1. The epoxy band at 8627 cm^{-1} and the primary amine bands at 6684, 6578, and 5067 cm^{-1} are well clear of the deadbands due to the fiber absorption and suitable for quantitative analysis.
2. The spectrum contains a series of negative bands [arrowed in Figure 6(b)] at 8420 cm^{-1} and in the region 5920 cm^{-1} to 5410 cm^{-1}. This is the region that negative bands were noted in Figure 4 for the blank capillary cell–fiber optic spectrum.

These negative bands were attributed to attenuated total reflection at the silica fiber-cladding interface and should therefore correspond to the absorption spectrum of the siloxane group in the silicone cladding. This was confirmed by comparison with a near IR spectrum of a model siloxane compound (octa methylcyclo-tetra siloxane). The absorption peaks coincide exactly with the negative bands. The increased intensity of the bands when the epoxy resin is in the capillary cell is believed to arise from the change in refractive index, leading to a different angle of exit from the capillary cell. This results in a decreased attenuation at the fiber core–silicone cladding interface compared to the back-

Table I Band Assignments from Near-IR Spectrum of TGDDM/DDS

Observed Band cm^{-1}	Assignment
10191	—OH overtone
9763	—NH_2, —NH overtone
8627	 overtone
6970	—OH overtone
6684	—NH_2, NH overtone
6578	—NH_2 overtone
6060	Aromatic —CH overtone
5882	—CH, —CH_2 overtone
5232	—CH, —CH_2 overtone
5067	—NH_2 combination
4897	—OH combination

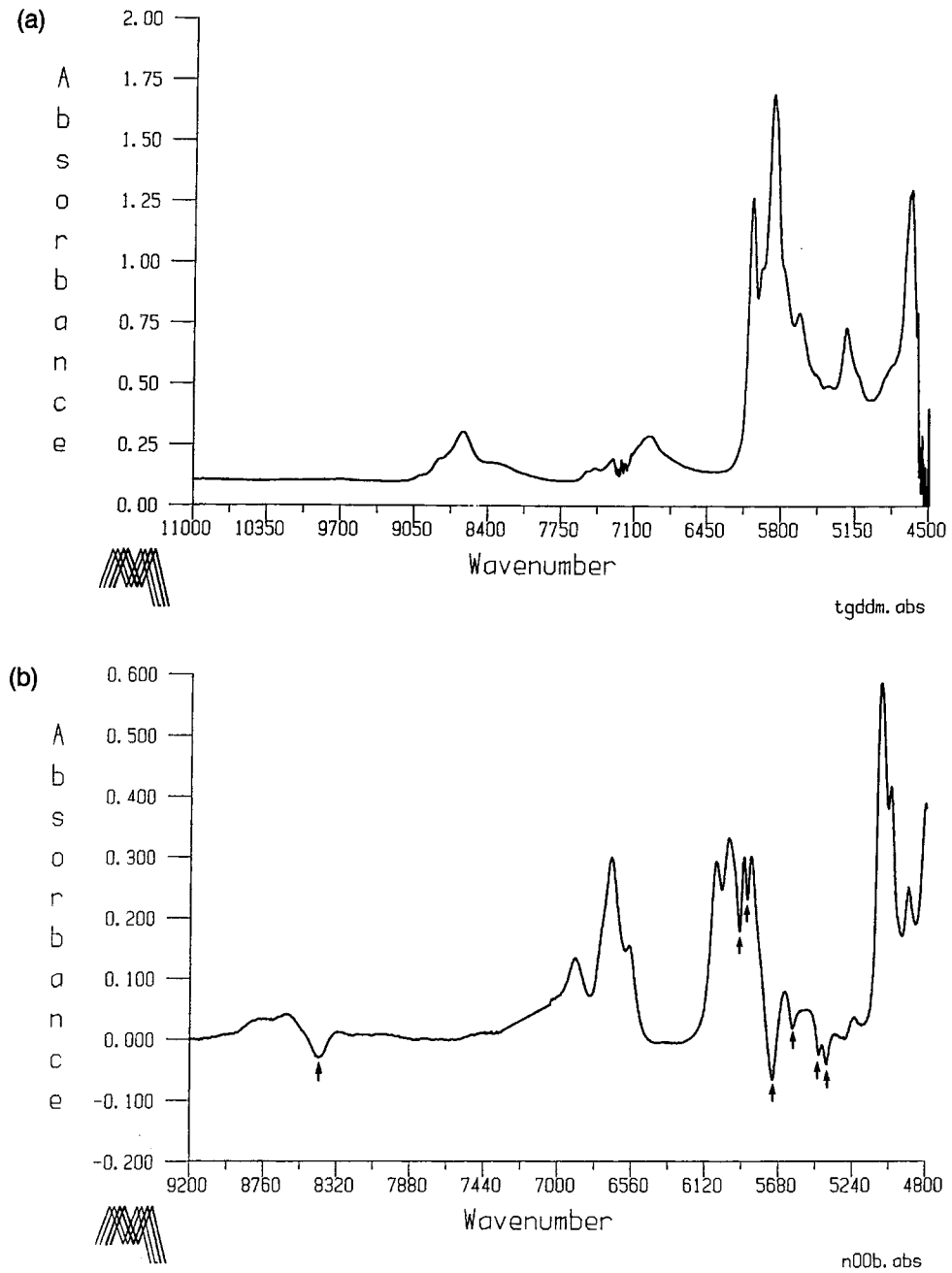


Figure 6 (a) Remote Near IR spectrum of TGDDM in a 6 mm capillary cell. The fiber optic length was 2 m. (b) Remote Near IR spectrum of MY720 and 37% DDS in a 2 mm capillary cell. The negative bands due to the cladding are indicated. (The large dead band at 7000 cm^{-1} has been deleted.)

ground, so the negative band intensity increases. The magnitude of this effect is 0.025 absorbance units per meter which is of significance for analysis of weak absorption bands in this region. The effect may be minimized by collimating the radiation through the sample cell, and totally eliminated by using an optical fiber with a doped fused silica cladding so that interfering siloxane bands are not observed. This is shown in Figure 7 in which the near IR spectrum of MY720 with 17% DDS was obtained in a capillary cell fitted with a 200 μm fluorine-doped silica fiber (Quartz et Silica AS 200/280A). The spectrum is comparable in quality to the cuvette spectrum [Fig. 5(b)] with the absence of a deadband around 7000 cm^{-1}, due to the low hydroxyl content of the fiber. However, the signal-to-noise is signifi-

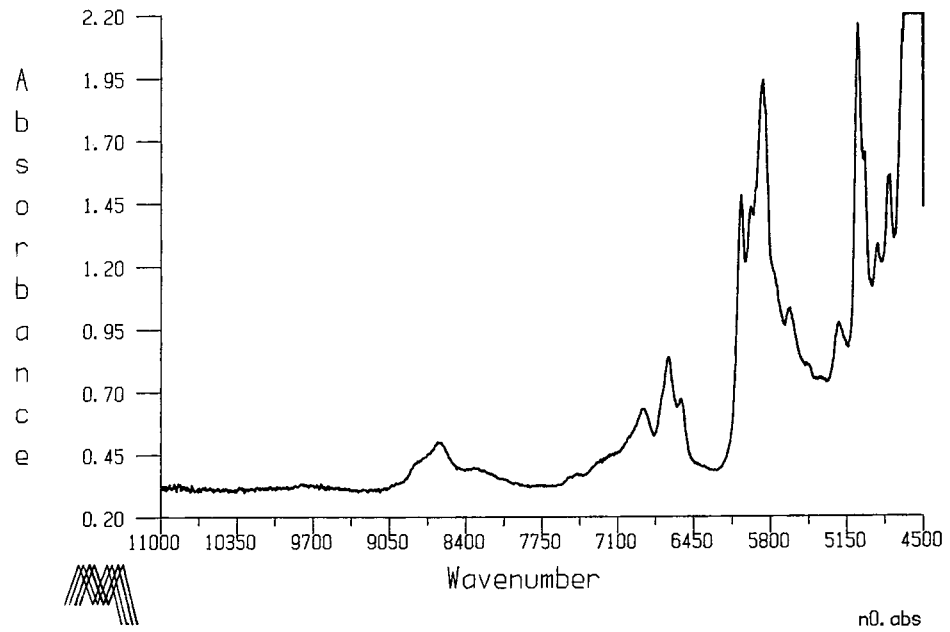


Figure 7 Near IR spectrum of MY720 with 17 wt % DDS using a 200 μm silica fiber with a fluorine-doped silica cladding. Note the absence of both negative bands and the hydroxyl dead band.

cantly lower than from the 600 μm and 1000 μm fibers and, as will be shown below, the PCS fiber is free from artefacts in the major region for monitoring the cure of the TGDDM/DDS resin system, and has been found satisfactory for these studies.

Changes to the Near IR Spectrum in the Early Stage of Cure

Figure 8 shows overlaid spectra of MY721 with 37% DDS obtained in the PCS fiber optic capillary cell before cure and after 28 min at 160°C. The main features are: (i) a decrease in the epoxy band at 8627 cm^{-1}; (ii) a decrease in the primary amine bands at 6684, 6578, and 5067 cm^{-1}; (iii) an increase in the hydroxyl bands at 6970 cm^{-1} and 4897 cm^{-1}; (iv) an increase in the baseline absorbance which is most apparent in regions away from band maxima and some changes in CH_2 bands around 6000 cm^{-1} are also observed; and (v) an epoxy band at 6100 cm^{-1} which requires deconvolution in order to be studied.

Epoxy Group Consumption

The epoxy group has been successfully analyzed[18,19] in the near IR at 4535 cm^{-1} and at 8627 cm^{-1}. The first band is beyond the cut off of the fiber optic, and the second band is shown in more detail in Figure 9. This corresponds to the second overtone of a CH stretching frequency of the epoxy. The absorption band is broad, and is clearly the sum of several bands. By applying Fourier self-deconvolution it is possible to discern six or seven overlapping bands (Fig. 9). It is possible to follow the epoxy group consumption by plotting the height of the strongest peak during the cure reaction, assuming that Beer's Law is obeyed. This is shown in Figure 10 for the cure of MY721 with 27% DDS at a temperature of 177°C. This shows a sigmoidal decrease in absorbance with cure time. The gel time for this formulation at 177°C has been measured by viscometry as 23 min, so the deviation from linearity could result from the onset of diffusion control in the gelled resin. Because of the low molar absorptivity of the epoxy band at this wave number, long path lengths are required. In addition, the presence of a negative band at 8430 cm^{-1} due to the siloxane attenuated absorption in the fiber (Fig. 3) may introduce an uncertainty in applying Beer's Law to the epoxy band maximum. For these reasons, this region of the spectrum is less suitable for monitoring the cure reaction than the primary amine region described in the following section.

Primary Amine Consumption During Cure

Several overtone and combination bands of NH_2 stretching and bending vibrations are observed in the near IR spectrum of the TGDDM/DDS resin

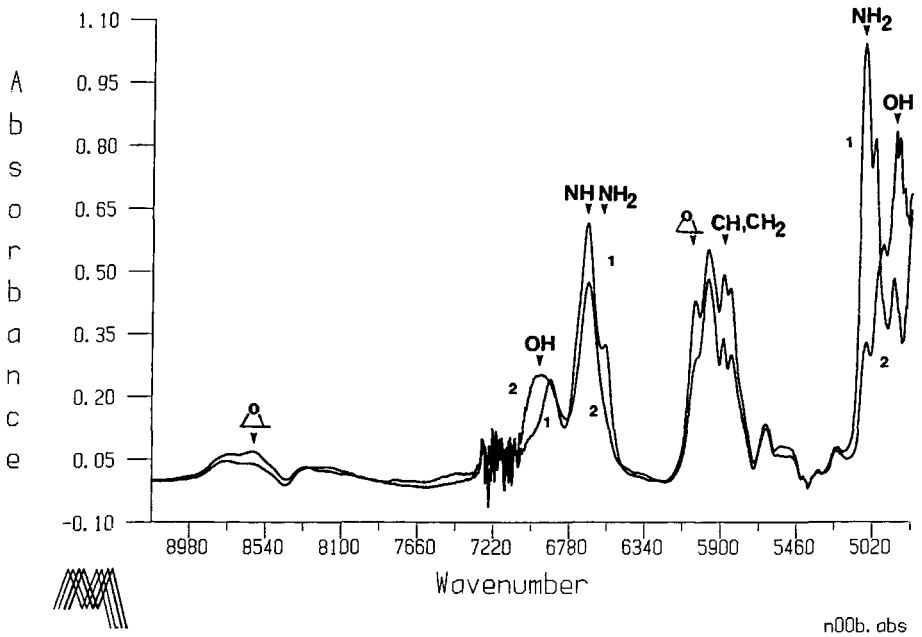


Figure 8 Overlaid spectra of MY721 with 37% DDS. *1:* before cure and *2:* after heating at 177°C for 28 min. The functional groups which change on cure are marked.

mix. The most intense and analytically useful bands are the combination band at 5067 cm^{-1} and overtone bands at 6578 cm^{-1} and 6684 cm^{-1}, corresponding to symmetric and asymmetric stretching vibrations respectively. This last band is reported[25] to be degenerate with a secondary amine band, and, as discussed below, is not as useful for monitoring changes in the primary amine group concentration during the early stages of cure as are the other bands.

Figure 11 shows the primary amine combination region for MY721 and 27% DDS cured at 177°C and it is seen that there is rapid consumption of primary

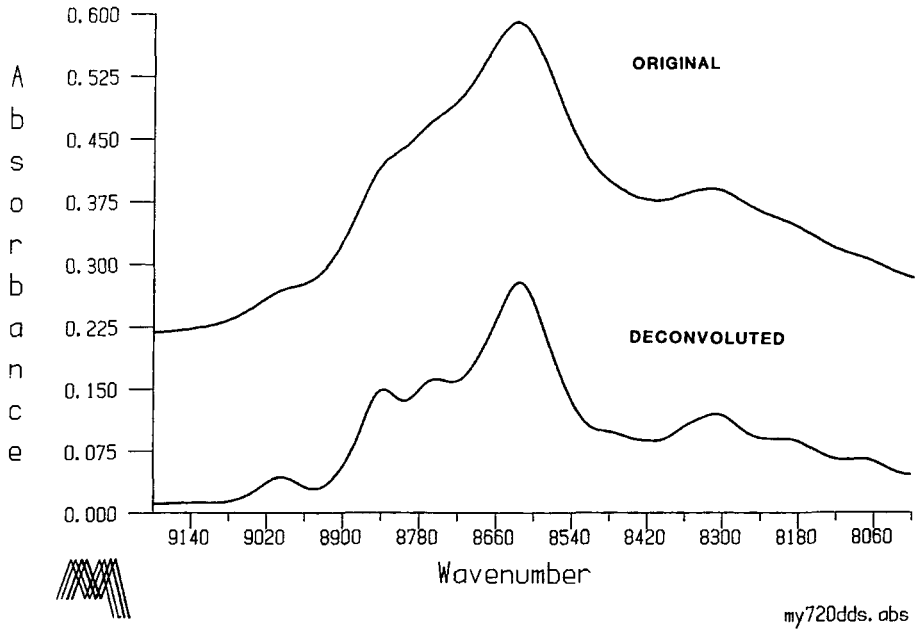


Figure 9 Near IR spectrum of the epoxy absorption region of MY720 showing the spectral resolution enhancement after Fourier self-deconvolution.

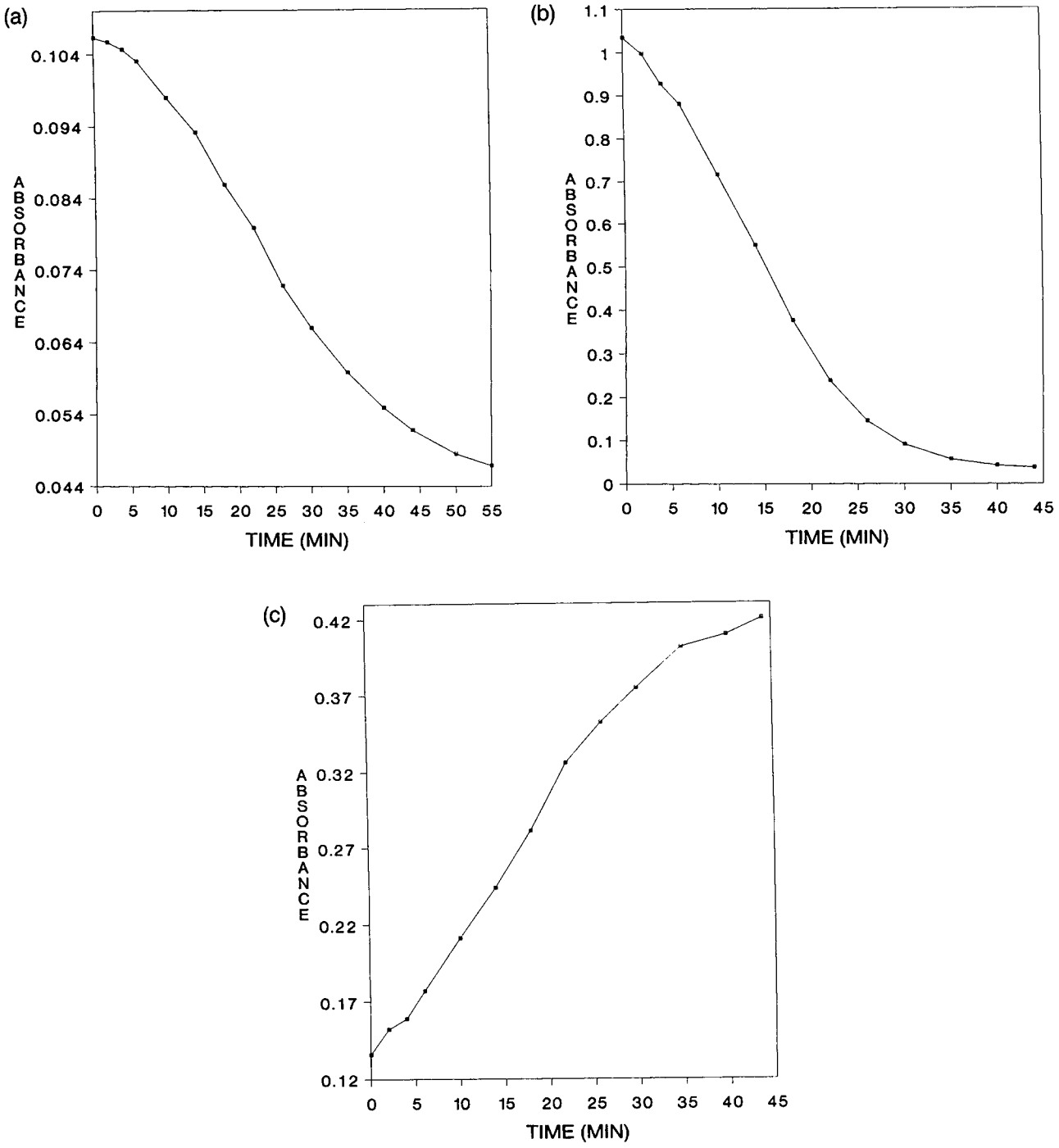


Figure 10 Plots of change in absorbance from MY721 with 27% DDS with time of heating at 177°C. (a) Decrease in epoxy absorbance (8627 cm^{-1}). (b) Decrease in primary amine absorbance (5067 cm^{-1}). (c) Growth in hydroxyl absorbance (6970 cm^{-1}).

amine in the early stages of cure. The most significant feature is the appearance of the isosbestic point at 4980 cm^{-1}. This indicates that there is a direct relationship between the disappearance of the primary amine and the appearance of the hydroxyl group at 4897 cm^{-1}, and that Beer's Law is obeyed in this region. A plot of the change in absorbance at 5067 cm^{-1} during cure is shown in Figure 10(b).

The amine overtone region is shown in more detail in Figure 12(a) for different times during cure.

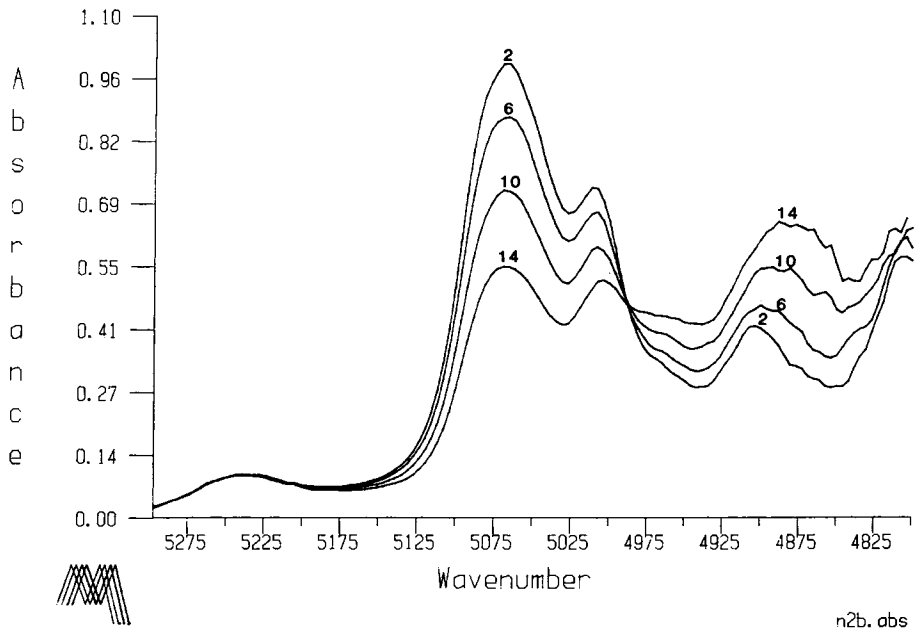


Figure 11 Overlaid spectra showing decrease in primary amine band (5067 cm^{-1}) and growth of hydroxyl band (4897 cm^{-1}) from MY721 with 27% DDS during cure at 177°C. The cure time in minutes is marked on the curves.

The band at 6678 cm^{-1} corresponds to primary and secondary amine bands which are degenerate. Spectral changes of this band are therefore expected to be more complex during cure since the reaction of a primary amine with an epoxide produces a secondary amine, so this band will consist of a component which is decreasing and another which increases. This has been studied more closely by using Fourier self-convolution as shown in Figure 12(b). It is now possible to resolve the primary amine bands into three separate components, of which the central band decreases more slowly on cure. This is clearly due to the growth of secondary amine.

While this region is rich in spectral information, the requirement to deconvolute the bands precludes using it for cure monitoring. In addition, as shown in Figure 12(a), there is a large baseline shift occurring during cure. This may be an instrumental artefact of the capillary cell due to the change in refractive index, as cure of the resin proceeds. Alternatively, a new species may be appearing, such as a hydrogen bonded hydroxyl group as discussed below.

Growth of Hydroxyl Group Absorbance During Cure

Figures 11 and 12(a) show the increase in absorbance of bands at 4900 and 6970 cm^{-1} respectively, due to hydroxyl groups from the opening of the oxirane ring during cure. The band at 6970 cm^{-1} has been studied in some detail[19,20] and is due to the first overtone of the OH stretching vibration. From a comparison of the growth in this band and the build-up of the baseline from 6200 cm^{-1} to 6500 cm^{-1} there is strong evidence that there is also a broad underlying species being formed as cure proceeds. Bellenger et al[26] have studied hydrogen bonding in amine crosslinked epoxies in the mid-IR and identified intermolecular OH . . . OH and OH . . . N chelation among the bond types which contribute to band broadening to lower energy. In a study[27] of the near IR spectrum of the OH group in model compounds and polyamides, the hydrogen bonded species form a weak, broad band between 5800 cm^{-1} and 6900 cm^{-1}. The free OH occurs at 6970 cm^{-1} and is more intense than the hydrogen bonded species in the first overtone, presumably due to the greater anharmonicity. For example, the ratio of the molar absorptivity of free to hydrogen bonded OH increases from 0.13 in the mid-IR to 3.8 in the near-IR.[27] The difference in anharmonicity also explains the greater separation between the observed[27] peak maxima in the near IR than would be expected by extrapolation from the mid-IR spectrum.[26] It is therefore believed that a major contribution to the baseline shift which is observed during cure (Fig. 12) is the build up of a hydrogen bonded hydroxyl group from the ring opening of the epoxy.

The band at 4900 cm^{-1} results from a combina-

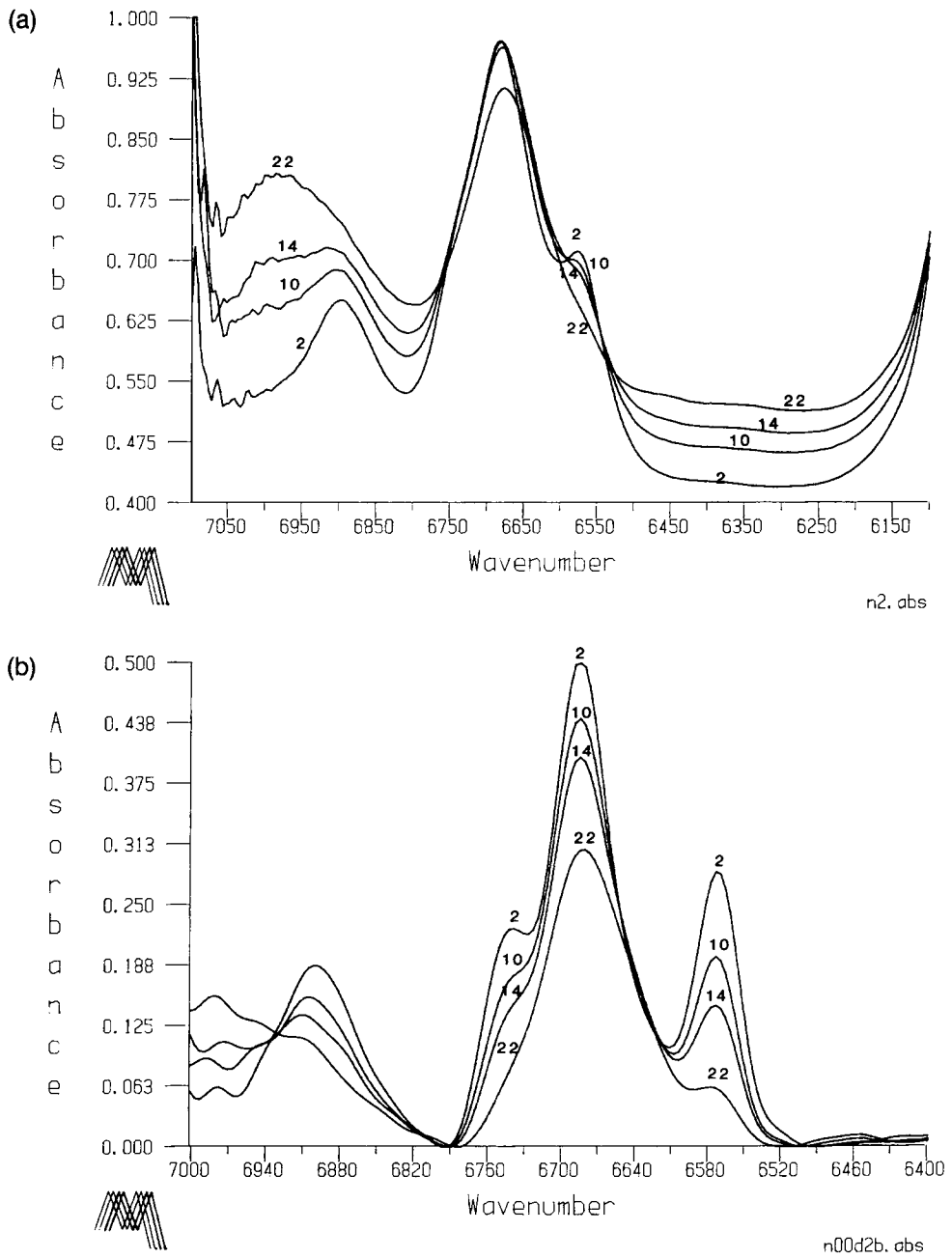


Figure 12 (a) Overlaid spectra in the amine overtone region (6684 cm^{-1}) and hydroxyl overtone region (6970 cm^{-1}) from MY720 with 27% DDS during cure at 177°C for the times indicated (min). Note the baseline shift accompanying cure. (b) Spectral resolution enhancement of the amine overtone region by Fourier self-deconvolution of the spectra shown in (a). The cure time in minutes is marked.

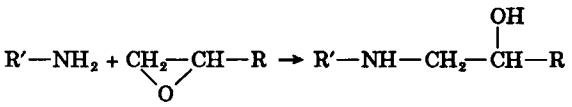
tion of the —OH stretching and bending modes. As cure proceeds, the maximum shifts to lower wave number, but the shift is only ~ 40 cm^{-1} up to gelation. This is consistent with the increased likelihood of intermolecular hydrogen bonding. A more detailed analysis is not possible as the signal-to-noise quality of the spectrum deteriorates as the spectral cutoff of the fiber optic is approached.

Figure 10(c) shows the kinetic curve for growth of hydroxyl absorbance at 6970 cm^{-1}. Because of the poor S/N as discussed above and the uncertain effect of hydrogen bonding on the absorbance, this is not considered appropriate for monitoring the cure reaction. It should also be noted that any increase in the length of fiber will result in a progressive overlap of the spectrum by the fiber bands.

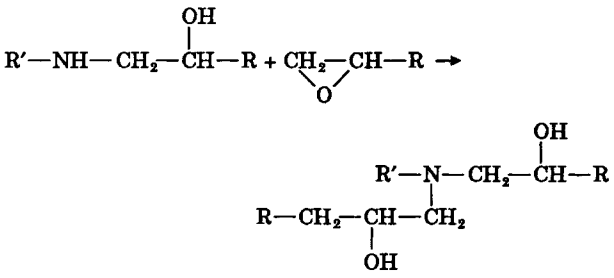
Correlation of Spectral Changes With Curing Mechanism

The curing reaction of TGDDM/DDS has been studied in detail by FT-IR spectroscopy in the mid-IR, NMR, and thermal analysis.[1] These changes have, to a limited extent, been related to the rheological properties of the resin as the crosslinked network forms. It is important to determine if the near IR spectral changes reported here are consistent with the presently accepted mechanism for the cure reaction up to gelation. The possible functional group reactions are as follows.

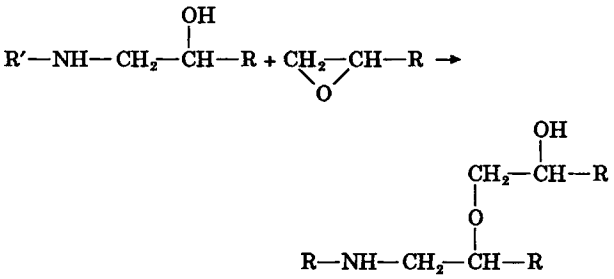
(i) Primary amine–epoxy addition



(ii) Secondary amine–epoxy addition



(iii) Hydroxyl–epoxy etherification



From Figure 10 it may be seen that the dominant reaction in the early stage of cure at 177°C is the consumption of primary amine. Both the epoxy and primary amine absorbance decrease linearly with time up to around 25 min, after which the resin is gelled, so diffusion control of the chemical reactions then dominates the kinetics. However, the primary amine is 85% reacted up to this point compared to an extent of reaction of only 35% for the epoxide. Morgan[1] has noted that the primary amine–epoxide cure reaction is dominant up to the gelation region and governs the rate at which the viscosity of the resin increases with temperature and time. From the deconvoluted spectra of Figure 12(b) it is possible to see the growth of secondary amine accompanying this reaction as a band broadening, but it is not possible to obtain direct evidence for reaction (ii) in the early stages of cure. Again, Morgan[1] has reported that the rate constants for the reaction of secondary amines and hydroxyl groups with epoxides are 10 times lower than for the primary amine–epoxide reaction, and reactions (ii) and (iii) are important only at higher cure temperatures and longer reaction times.

From the temperature dependence of the slopes of the primary amine absorbance–cure time plots, we have determined an activation energy of 70 kJ mol^{-1} over the range 135 to 180°C. This may be compared with values of 50 to 63 kJ mol^{-1} by dielectric spectroscopy and 67 to 71 kJ mol^{-1} by differential scanning calorimetry.[16] The agreement among the methods is quite good considering the sensitivity of the kinetics of the cure reaction to trace impurities and hydrolysis products.

Real-Time Cure Monitoring by Near IR FT-IR

The development of any method for real-time monitoring of epoxy resin cure up to gelation requires a simple output which is an unambiguous measurement of the extent of reaction throughout the early stage of the cure cycle. From the results described above, we consider the primary amine absorption band at 5067 cm^{-1} to be the most suitable. A particular advantage is that this band clearly obeys Beer's Law over a wide range of conversion and it is therefore possible to use band height alone as a measure of amine concentration.

The use of an FT-IR spectrometer affords high photometric accuracy and rapid spectral acquisition. In addition, the data analysis capability and powerful software of the system may be exploited to produce analytical information suitable for real-time process control. We have developed a UNIX C-shell program for the Mattson Sirius spectrometer which collects and analyzes the near IR spectra and gives successive real-time displays. This uses the standard GC-IR software to collect spectra continuously in the UNIX background mode while the analysis and display occurs in the foreground.

The analysis consists of measuring the absorbance at two specified wave numbers—one corresponding to the changing amine peak at 5067 cm^{-1} and the other to an invariant CH band. The choice of reference band is complicated by the negative bands resulting from the PCS fiber optic, but it is seen from Figure 8 that the band at 5660 cm^{-1} ap-

pears invariant. The absorbance ratio is then calculated and plotted on a VDU terminal as a function of cure time. The full overlaid spectra may be displayed on a second terminal. The time resolution of the display is set by the combination of the resolution and number of scans (typically 4 cm^{-1} and 32 scans). When the time taken to process the interferograms and calculate the ratio and display the result is added, the typical time between data points is 60 sec. For cure reactions studied here with gel times ranging from 20 min to several hours this is a suitable rate of data acquisition. For very fast reactions the spectral range may be restricted and single scans used to acquire data points.

CONCLUSIONS

The cure of TGDDM/DDS epoxy resins has been studied by using a microcapillary cell and silica fiber optics coupled to a remote FT-IR spectrometer operating in the near-IR. The spectral range available for analysis was limited by the strong absorption by hydroxyl groups in the fiber as well as the appearance of negative bands attributed to the siloxane cladding on the fiber. These occurred in the $-CH$ and $-CH_2$ regions and arose from modes near the critical angle which change path length through the cell as refractive index changes. However, the spectra were obtained with a high signal-to-noise and over a sufficient wavelength range to enable band assignment. Fourier self-deconvolution enabled resolution enhancement in the epoxide overtone region and in the primary and secondary amine overtone region. From a comparison of the changes in the functional groups with time of cure, i.e., loss of epoxide, loss of primary amine and growth of hydroxyl, it was considered that the primary amine band at 5067 cm^{-1} was the most appropriate for rapid, sensitive, and accurate real-time monitoring of the resin cure up to the gel point. The temperature dependence of the kinetics of primary amine consumption gave an activation energy of 70 kJ mol^{-1} from 135 to 180°C, in agreement with DSC. A software package has enabled real-time plots of the extent of cure of the resin from remote FT-IR spectra, so demonstrating the feasibility of the technique for process control in epoxy resin composite fabrication.

The financial assistance of the Australian Research Council and the Defence Science and Technology Organization is gratefully acknowledged.

REFERENCES

1. R. J. Morgan, *Advances in Polym. Sci.*, **72,** 1 (1985).
2. M. Molyneux, *Composites,* **14,** 87 (1983).
3. J. L. Kardos, M. P. Dudukovic, and R. Dave, *Advances in Polym. Sci.*, **80,** 101 (1986).
4. J. B. Enns and J. K. Gillham, *J. Appl. Polym. Sci.*, **28,** 2227 (1983).
5. D. H. Kaelble, *Am. Chem. Soc. Org. Coat. Appl. Polym. Sci. Proc.*, **47,** 630 (1982).
6. B. Fanconi, F. Wang, and R. Lowry, *Rev. Progr. Quant. NDE,* **6B,** 1287 (1987).
7. Y. A. Tajima, *Polym. Composites,* **3,** 162 (1982).
8. W. E. Baumgartner and T. Ricker, *SAMPE J.*, **19,** 6 (1983).
9. S. D. Senturia, N. F. Sheppard, S. Y. Poh, and H. R. Appelman, *Polym. Eng. Sci.*, **21,** 113 (1981).
10. S. D. Senturia, N. F. Sheppard, H. L. Lee, and S. B. Marshall, *SAMPE J.*, **19,** 22 (1983).
11. R. L. Levy, *Polym. Mater. Sci. Eng.*, **50,** 124 (1984).
12. G. A. George, *Materials Forum,* **9,** 224 (1986).
13. D. Archibald, L. T. Lin, and D. E. Honigs, *Appl. Spectrosc.*, **42,** 468 (1988).
14. D. Archibald, C. E. Miller, L. T. Lin, and D. E. Honigs, *Appl. Spectrosc.*, **42,** 1549 (1988).
15. (a) D. A. C. Compton, S. L. Hill, N. A. Wright, M. A. Druy, J. Piche, W. A. Stevenson, and D. W. Vidrine, *Appl. Spectrosc.*, **42,** 972 (1988).
    (b) P. R. Young, M. A. Druy, W. A. Stevenson, and D. A. C. Compton, *SAMPE J.*, **25,** 11 (1989).
16. E. B. Stark, J. C. Seferis, A. Apicella, and L. Nicolais, *Thermochim. Act.*, **77,** 19 (1988).
17. A. Apicella, P. Masi, and L. Nicolais, *Rheol. Act.*, **23,** 291 (1984).
18. H. Dannenberg, SPE Transactions, **78,** Jan (1963).
19. H. Lee and K. Neville, *Handbook of Epoxy Resins,* McGraw-Hill, NY, 1967, p. 4-1.
20. D. W. Schering, J. E. Katon, L. T. Drzal, and V. B. Gupta, *J. Appl. Polym. Sci.*, **34,** 2367 (1987).
21. P. M. Fredericks, P. J. Samson, and A. D. Stuart, *Appl. Spectrosc.*, **41,** 327 (1987).
22. W. R. X. Frank, W. Goertz, and H. H. Belz, *Appl. Spectrosc.*, **41,** 323 (1987).
23. G. Lucazeau and C. Sandorfy, *Can. J. Chem.*, **48,** 3694 (1970).
24. R. F. Goddu and D. A. Delker, *Anal. Chem.*, **32,** 140 (1960).
25. K. Whetsel, W. Roberson, and M. W. Krell, *Anal. Chem.*, **30,** 1594, 1598 (1958).
26. V. Bellenger, J. Verdu, J. Francillette, P. Hoarau, and E. Morel, *Polymer,* **28,** 1079 (1987).
27. W. A. P. Luck and W. Ditter, *J. Mol. Struct.*, **1,** 261 (1967/8).

Received November 3, 1989
Accepted April 17, 1990