

In Situ Cure Monitoring of Epoxy Resins Using Fiber-Optic Raman Spectroscopy

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SYNOPSIS

Fiber-optic Raman spectroscopy was used to monitor the curing of epoxy resins *in situ* for eventual application to polymer composite processing. A 200- μm diameter quartz fiber-optic sensor immersed in liquid resin was used to obtain Raman spectra for a concentration series of diglycidyl ether of bisphenol-A in its own reaction product with diethylamine using an 820 nm continuous-wave diode laser excitation. A Raman peak at 1240 cm^{-1} was assigned to a vibrational mode of the oxirane (epoxide) ring and its normalized intensity was found to be linearly related to the concentration of epoxide groups in the resin mixtures. Raman peaks at 1112 and 1186 cm^{-1} associated with phenyl and *gem*-dimethyl resin backbone vibrations, respectively, did not change in intensity due to the curing reaction and were used as internal references to correct the Raman spectra for intensity changes due to density fluctuations and instrumental variations during the experiments. Fiber-optic Raman spectroscopy was used to monitor the extent of reaction *in situ* for the room-temperature cure of phenyl glycidyl ether with diethylamine. The extent of reaction of the epoxide groups calculated from the Raman spectra were in excellent agreement with kinetic data from Fourier transform near-infrared absorbance measurements made under the same conditions. © 1994 John Wiley & Sons, Inc.*

INTRODUCTION

Nonflammable polymers and composites for aircraft interiors are the focus of a new FAA materials research effort. Low flammability is characteristic of thermally stable polymers such as phenolics, polyimides, and bismaleimides, but these materials can be expensive and difficult to process. Consequently, parallel development of an economical process-monitoring technology that measures both the extent of chemical reaction and temperature *in situ* will help to offset the potentially higher cost of new fire-resistant materials and facilitate their acceptance by airframe and cabin manufacturers.

Fiber-optic Raman spectroscopy is an analytical tool for remote chemical analysis¹⁻⁹ that has recently been applied to cure monitoring of thermoset polymers,¹⁰ adhesives,¹¹ and composites¹² *in situ* using miniaturized sensors. Unlike dielectric¹³⁻¹⁵ or ultra-

sonic measurements¹⁶ that sense only mechanical property changes in the curing resin, Raman spectroscopy can provide a direct measure of the chemical species concentrations during the entire cure reaction. Raman is a vibrational spectroscopy that provides the same type of chemical information as does mid-infrared spectroscopy but with the advantage of being able to utilize inexpensive, communications-grade, fused-silica optical fibers. Raman spectroscopy can also provide localized, *in situ*, temperature measurements using the same spectral information and over the same fiber-optics used for cure monitoring.¹⁰ Subsequent to monitoring the cure reaction and temperature of the composite matrix, the quartz optical fibers could be used as embedded strain or damage sensors or used for Raman spectroscopic monitoring of chemical degradation of the resin.

The Raman spectrum is measured by illuminating the sample with a laser while monitoring the inelastically scattered light at wavelengths longer than the laser wavelength (Stokes scattering) or at

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wavelengths shorter than the laser wavelength (anti-Stokes scattering). The difference in energy between the wavelength of the scattered light and the laser wavelength is equal to the energy of the Raman-active vibrational modes in the molecule. Raman spectroscopy using fiber-optics can access a large part of the vibrational spectrum from 100 cm^{-1} to beyond 4000 cm^{-1} ($100\text{--}2.5\text{ }\mu\text{m}$ wavelengths), whereas bands below 1200 cm^{-1} are not accessible using mid-infrared. Thus, the Raman scattering spectrum provides the same type of chemical information that is obtained in a mid-infrared absorption spectrum, but may be generated with any laser wavelength from ultraviolet to near-infrared. This is an advantage because the laser wavelength can be selected for maximum transmission through optical fibers. Near-infrared (NIR) and near-visible (N-Vis) diode lasers appear to be ideal as excitation sources for remote Raman spectroscopy because they are long-lived (10^4 h), highly stable, and economical and minimize sample fluorescence—important for work with dark- or amber-colored thermoset resins that are typically highly fluorescent at visible wavelengths. Thermal degradation of highly colored resins by photothermal conversion of absorbed laser light into heat is also reduced by the use of NIR and N-Vis laser sources, because even highly colored materials such as epoxies hardened with aromatic amines, polyimides, and bismaleimides have no fundamental absorbance bands in the NIR/N-Vis spectral region. Offsetting the advantages of longer wavelength lasers for fiber-optic Raman spectroscopy is the fact that Raman scattering intensity is proportional to the inverse fourth-power of the excitation wavelength, so that NIR and N-Vis lasers produce weak Raman scattering signals compared to shorter wavelength visible lasers. Recently, however, the development of tunable near-infrared laser sources, NIR and N-Vis diode lasers, NIR-sensitive CCD array detectors, Fourier transform (FT) instrumentation, and improved optical filtering technology make it possible to measure Raman scattering from curing resins using $700\text{--}1064\text{ nm}$ wavelength NIR/N-Vis laser excitation sources.^{10-12,17-19}

Fiber-optic spectroscopies other than Raman have been proposed for polymer and composite cure monitoring including mid-infrared absorbance,^{20,21} NIR absorbance,²² and ultraviolet-visible (UV-Vis) fluorescence.^{23,24} However, these spectral methods do not appear to have the combination of economy, utility, and selectivity that characterizes the Raman technique. Mid-infrared wavelengths from 2 to $15\text{ }\mu\text{m}$ are absorbed by conventional fused-silica optical fibers so that chalcogenide, heavy metal fluoride

glass, or single-crystal optical fibers are required to obtain reasonable transmission for monitoring mid-infrared spectral bands. These fibers are prohibitively expensive in long lengths and do not allow access to important absorption bands below about 1200 cm^{-1} limiting the amount of chemical information obtainable on the cure reaction. Mid-infrared transmitting optical fibers also introduce a large background in the form of fiber-absorption bands, which must be subtracted from the sample spectrum. Furthermore, mid-infrared transmitting optical fibers are brittle and exhibit large signal losses ($10\text{--}15\text{ dB/m}$), making it impossible to use lengths greater than a few meters.

Fiber-optic NIR absorbance spectroscopy is an established chemical process monitoring technique²² that has potential for thermoset polymer cure monitoring.²⁵⁻²⁸ NIR spectra contain weak absorbance bands at wavelengths between about 0.7 and $2.5\text{ }\mu\text{m}$, which are overtones or combination bands of fundamental group vibrations in the mid-infrared. The NIR spectral region is sparsely populated relative to the mid-infrared region, but certain chemical groups evolved or consumed during typical polymer curing reactions, such as the oxirane ring of epoxy resins, exhibit NIR absorbance bands that could be used for cure monitoring. Fused-silica optical fibers transmit NIR wavelengths and are small and inexpensive enough to remain embedded in the cured resin or composite.

In the UV-Vis approach to fiber-optic cure monitoring, the measured frequency shift and intensity of fluorescent tag molecules added to the reaction mixture are empirically related to the viscosity of the curing resin. UV-Vis fluorescence of tag molecules, like dielectric and ultrasonic techniques, provides only an indirect measure of the extent of chemical reaction of the thermosetting matrix during cure. Moreover, the fluorescence signal is highly susceptible to temperature variations, has no absolute intensity reference, and requires a large background correction since many epoxy monomers fluoresce with intensities comparable to the tag molecules themselves.

In previous publications,¹⁰⁻¹² changes in the fiber-optic Raman spectrum of poly(ether triamine)-cured DGEBA epoxy were used to follow the degree of cure *in situ* by assuming a linear relationship between the scattering intensity of the 1240 cm^{-1} vibrational band of the oxirane ring and the concentration of epoxide groups in the reaction mixture. Raman peaks at 1112 and 1186 cm^{-1} associated with bisphenol-A backbone vibrations of the phenyl ring and *gem*-dimethyl groups, respectively, were used in

a ratio with the 1240 cm^{-1} epoxide band to normalize the Raman spectrum for density fluctuations and instrumental variations. This normalization method is based on the assumption that, unlike the 1240 cm^{-1} epoxide band, the scattering intensity of the backbone vibrations would not change during the cure reaction and so could be used as internal standards. The objective of the present study was to calibrate the proposed Raman scattering technique for epoxy-cure monitoring using conventional NIR absorbance spectroscopy and to demonstrate quantitative fiber-optic Raman spectroscopic monitoring of model epoxy-amine curing reactions for eventual application to other thermoset resins and their fiber composites.

EXPERIMENTAL

A series of epoxide concentrations was prepared for Raman and NIR spectral measurements by diluting a high-purity diglycidyl ether of bisphenol-A (DGEBA) with a stoichiometric DGEBA-diethylamine liquid reaction product in which all of the epoxide groups had been consumed in an epoxide-secondary amine reaction. The diethylamine-endcapped DGEBA adduct was prepared by reacting 100.0 g of DGEBA (99%, Dow Chemical DER 332, epoxide equivalent weight 173 g/equiv) with 43.1 g of diethylamine (99%, Aldrich Chemical, amine hydrogen equivalent weight 73.14 g/equiv) under argon in a sealed 250 mL round-bottom flask main-

tained at 50°C . Diethylamine (DEA), a secondary aliphatic amine with only one active hydrogen, was chosen for endcapping the DGEBA to preclude cross-linking reactions leading to gelation and ensure a pourable liquid resin for mixing with pure DGEBA. The epoxide groups in the DGEBA-DEA reaction mixture were completely consumed after 48 h at 50°C as determined by the disappearance of the 4535 cm^{-1} epoxide overtone band in the NIR infrared absorbance spectrum, according to the method of Dannenburg.²⁶ The DGEBA-DEA adduct was a glassy liquid at 23°C with a density of 1.035 g/cm^3 .

The DGEBA-DEA adduct was warmed to 60°C to reduce the viscosity and mixed in 10 wt % increments with pure DGEBA to provide a series of known molar concentrations of epoxide ranging from 0.0 epoxide equiv/L for the DGEBA-DEA adduct to 6.7 epoxide equiv/L for the pure DGEBA. This approach allowed for systematic variation of the epoxide concentration while maintaining a nearly constant molar concentration of the bisphenol-A backbone, which is used as internal standard in the Raman technique. Moreover, the DGEBA/adduct blend provided a neat-liquid mixture representative of practical amine-cured epoxies. The chemical structures of DGEBA, DEA, and DGEBA-DEA adduct reaction products are shown in Figure 1.

Epoxide-amine reaction kinetics at room temperature were investigated using both Raman and NIR spectral measurements of a stoichiometric mixture of $\pm 1,2$ -epoxy-3-phenoxypropane (phenyl

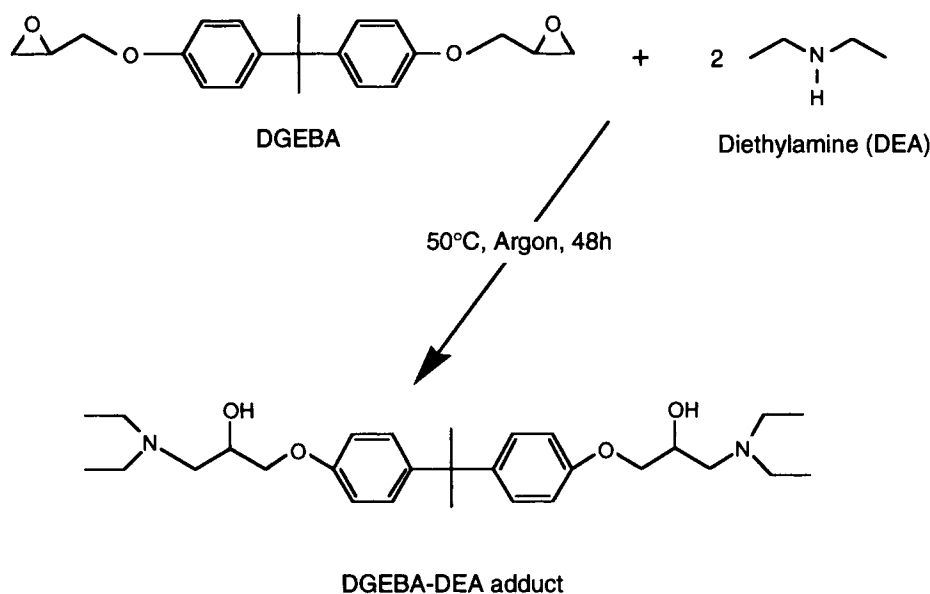


Figure 1 Reaction of DGEBA and DEA to form the DGEBA-DEA adduct.

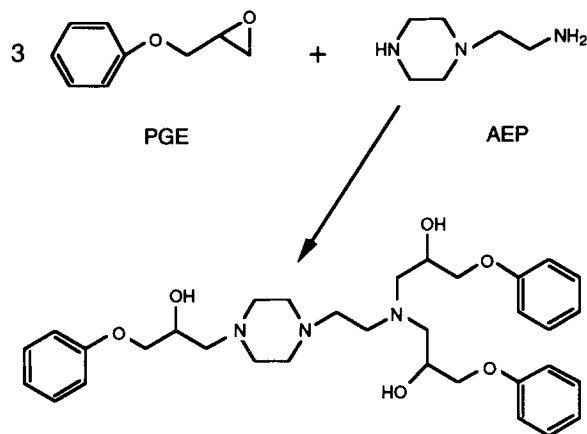


Figure 2 Chemical structure and stoichiometric reaction product of PGE and AEP.

glycidyl ether, PGE, 99%, Aldrich Chemical, epoxide equivalent weight 150.0 g/equiv) and *n*-aminoethylpiperazine (AEP, 99%, Aldrich Chemical, amine hydrogen equivalent weight 32.25 g/equiv). Reasonable room-temperature kinetics were achieved with the highly reactive cycloaliphatic primary amine, AEP, in combination with the monofunctional epoxide resin, PGE—the latter selected to preclude network formation. Reaction of the epoxide group with hydroxyl groups formed during the epoxide-amine reaction is negligible at temperatures less than about 100°C. The phenyl group of PGE provided the 1112 cm^{-1} Raman band used as an internal reference for normalizing the spectra. The

chemical structures and stoichiometric reaction product of PGE and AEP are shown in Figure 2.

The optical components used for making Raman scattering measurements are shown in Figure 3. Raman spectra were obtained at ambient temperature ($23 \pm 1^\circ\text{C}$) by immersing a dual-fiber optical probe directly into the liquid epoxy-amine mixtures contained in 30 mL polyethylene beakers. The probe consisted of two 250 μm , step-index, silica-on-silica fiber-optics (PolyMicro) that had been stripped of their polyimide jacket and adhesively bonded side-by-side into an SMA connector. Fibers were prepared by mechanical polishing of the ends with 3M Imperial lapping film, using a 0.3 μm grade film for the final polish. A stainless-steel tube was bonded over the parallel fibers and SMA connector to provide strain relief for handling and a convenient pencil-probe geometry for measurements. A GaAlAs diode laser (Spectra Diode Labs Model SDL-5412) operating at 50 mW and a wavelength of 820 nm was filtered using a 10 nm bandpass filter to remove spontaneous emission before being focused into one fiber of the probe to illuminate the sample at the probe tip. Scattered light is collected by the second fiber in the probe and travels to the spectrometer, where it is collimated as it emerges from the fiber using an $f/2$ lens before passing through an 819 nm holographic long-pass cutoff filter (Physical Optics, Inc.) to block Rayleigh scattered light. The Stokes-scattered light is then focused with a $f/4$ lens onto the slit of an image-corrected spectrograph (Chromex) containing a 600 groove/mm grating blazed

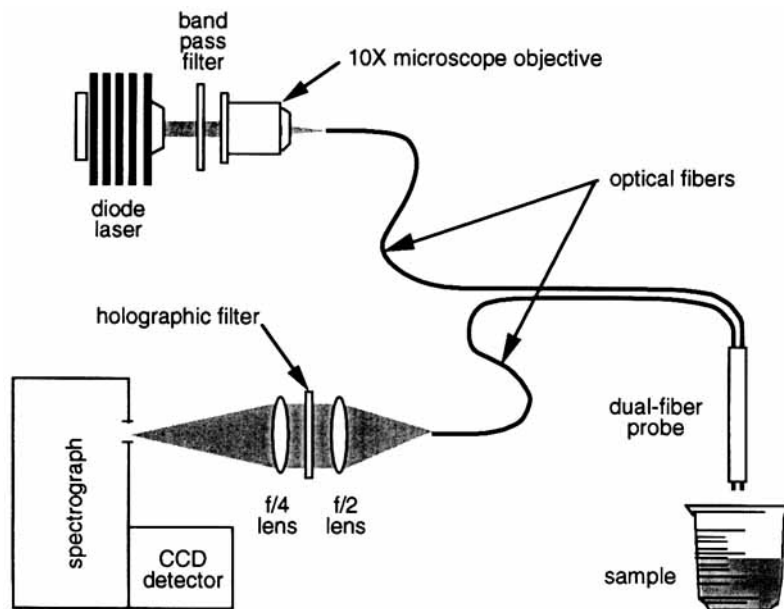


Figure 3 Experimental arrangement for fiber-optic Raman measurements.

at 750 nm and a back-illuminated charge-coupled device (CCD) imaging detector (Princeton Instruments). All spectra were obtained with 60 s exposures at a nominal 8–12 cm^{-1} resolution.

NIR and mid-infrared spectra were obtained using 64 scans at 4 cm^{-1} resolution on a Digilab FTS-40 FTIR/NIR (BioRad) instrument at $23 \pm 1^\circ\text{C}$. A 1 mm path-length, disposable Pyrex cell was used for all the NIR measurements.

RESULTS

Raman Calibration

Mid-infrared and Raman spectra for the 600–1400 cm^{-1} spectral region of the DGEBA are plotted in Figure 4. This “fingerprint” region of the vibrational spectrum consists of skeletal bending vibrations of polyatomic molecules and stretching of single bonds linking a substituent group to the remainder of the molecule. Some of the same group frequencies are active in both the mid-IR and Raman spectra of DGEBA even though the selection rules are different for these two vibrational spectroscopies. Bands that are common to both spectra include the epoxide ring stretch at 1240 cm^{-1} , the in-plane deformation of the *gem*-dimethyl group of bisphenol-A at 1186 cm^{-1} , and the C—H out-of-plane bending of the *para*-disubstituted phenyl group at 830 cm^{-1} . A strong *para*-disubstituted phenyl band at 1112 cm^{-1} is observed only in the Raman spectrum and is used

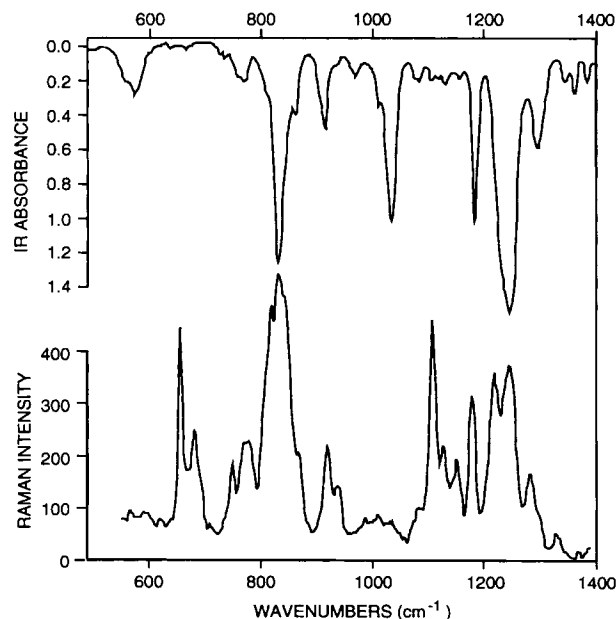


Figure 4 Raman and mid-infrared spectra of DGEBA.

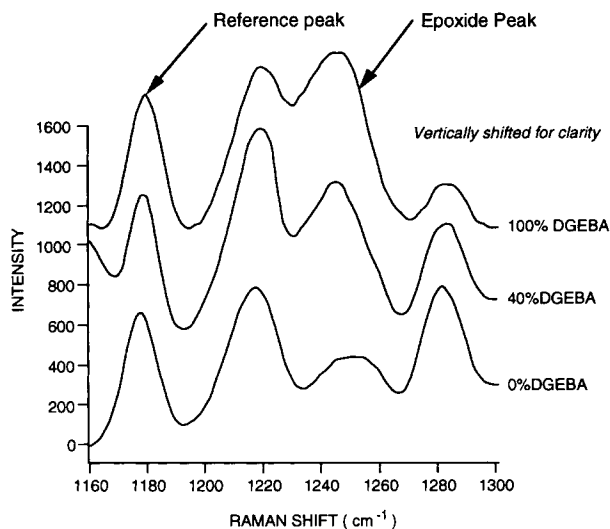


Figure 5 Fiber-optic Raman spectra for three epoxide concentrations corresponding to 100, 40, and 0% DGEBA dissolved in the DGEBA-DEA adduct.

interchangeably with the 1186 cm^{-1} band as an internal reference. In a previous publication,¹⁰ we reported the use of the 830 cm^{-1} Raman band for *in situ* temperature determination using the ratio of the Stokes and anti-Stokes intensities.

In Figure 5 are plotted Raman spectra for three epoxide concentrations corresponding to 100, 40, and 0% DGEBA dissolved in the stoichiometric DGEBA-DEA adduct (see Fig. 1). Only the 1170–1290 cm^{-1} spectral region used for cure monitoring is displayed in Figure 5 and the spectra have been vertically shifted for clarity. Raman scattering intensity was normalized to that of pure DGEBA using the 1186 cm^{-1} *gem*-dimethyl reference band as an internal standard. It is observed that the 1240 cm^{-1} epoxide ring vibration decreases in intensity but does not disappear as the epoxide concentration in the solutions goes to zero for the pure DGEBA-DEA adduct. The small residual peak at 1245 cm^{-1} observed at zero epoxide concentration and the Raman peak at 1220 cm^{-1} are thought to be due to the aromatic ether stretch and would not be expected to change in intensity during the cure reaction. The band at about 1267 cm^{-1} attributed to C—O and C—C stretching increases in intensity with decreasing epoxide concentration.

NIR absorbance spectra for the DGEBA dilution series in Figure 6 show the complete disappearance of the 4535 cm^{-1} epoxide ring overtone combination band in the DGEBA-DEA adduct (0% DGEBA), confirming complete reaction of the epoxide groups at the calculated 1 : 1 stoichiometry.

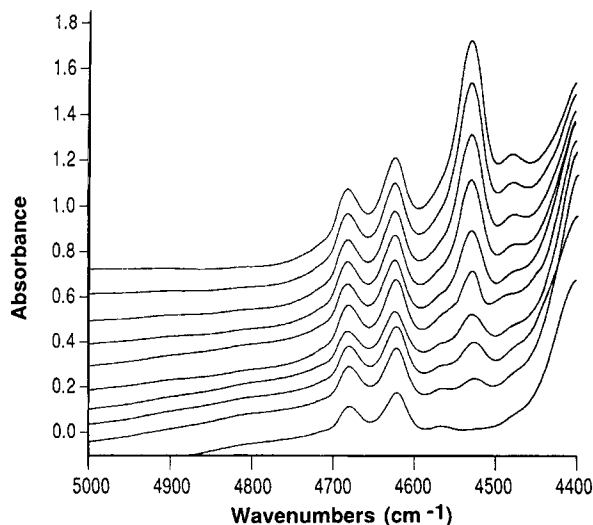


Figure 6 FT-NIR absorbance spectra of epoxide concentration series 0–100% w/w (40% spectrum omitted). Spectra vertically shifted for clarity.

Calibration curves for Raman scattering and NIR absorbance vs. epoxide concentration are shown in Figure 7. Raman response is expressed as the ratio of the $1240\text{ cm}^{-1}/1112\text{ cm}^{-1}$ peak intensities, whereas the NIR response is the corrected absorbance of a C—H overtone band of the epoxide group at 4535 cm^{-1} , according to the method of Dannenburg,²⁶ measured in a 1 mm path-length cell. Abscissa values for epoxide concentration in units of equivalents/liter were calculated from the experimentally determined epoxide equivalent weight of DGEBA (173 g/mol) and the individual weight fractions and measured densities of DGEBA ($\rho = 1.155\text{ g/cm}^3$) and the DGEBA-DEA adduct ($\rho = 1.035\text{ g/cm}^3$) by assuming volume additivity in the mixtures.

Kinetic Studies

The linear relationship between normalized Raman scattering intensity and epoxide concentration demonstrated in Figure 7 permits the degree-of-cure during the chemical reaction of PGE with AEP at room temperature to be evaluated simply from the initial, $R(0)$, instantaneous, $R(t)$, and final, $R(\infty)$, ratios of the 1240 and 1112 cm^{-1} peak intensities (I):

$$R(0) = \frac{I_{1240}(0)}{I_{1112}(0)}; \quad R(t) = \frac{I_{1240}(t)}{I_{1112}(t)}; \\ R(\infty) = \frac{I_{1240}(\infty)}{I_{1112}(\infty)} \quad (1)$$

according to

$$\alpha(t) = \frac{R(0) - R(t)}{R(0) - R(\infty)} \quad (2)$$

where $\alpha(t)$, the degree-of-cure at time, t , ranges from 0.0 to 1.0 during the cure process.

Raman spectra for the PGE-AEP stoichiometric mixture at room temperature immediately after mixing and after 29 h are shown in Figure 8. Prominent in the Raman spectra of the resin/hardener mixture are the strong, symmetric, aromatic ring stretching vibration near 1000 cm^{-1} and the in-plane hydrogen bending vibrations at about 1025 and 615 cm^{-1} characteristic of the monosubstituted aromatic PGE. Equation (2) was used to calculate the instantaneous degree-of-cure vs. time for the PGE-AEP reaction at room temperature from the ratio of the 1240 cm^{-1} epoxide band and 1000 cm^{-1} reference band of the PGE. The degree-of-cure during the PGE-AEP reaction at room temperature was also measured by NIR absorbance spectroscopy for comparison to the Raman method using eq. (2) with the corrected 4535 cm^{-1} NIR absorbance values in place of the Raman peak ratios (Fig. 9).

DISCUSSION

The Beer's law molar absorptivity at 4535 cm^{-1} ($2.205\text{ }\mu\text{m}$) of the epoxide groups in DGEBA/DGEBA-DEA adduct mixtures, determined from the slope of the NIR calibration curve (Fig. 7), is $\epsilon = 0.926\text{ L equiv}^{-1}\text{ cm}^{-1}$. This value is in excellent agreement with Dannenburg ($\epsilon = 0.934\text{ L equiv}^{-1}\text{ cm}^{-1}$) for a homologous series of DGEBA oligomers,²⁶ validating the Raman calibration scheme. The coincidence of the Raman and NIR calibration curves in Figure 7 is the result of choosing a 1 mm path length for NIR measurements and has no other physical significance. However, a 1 mm NIR path length is near optimum for neat DGEBA epoxies so that the sensitivity of the Raman technique—as indicated by the slope of the calibration curves—is comparable to NIR absorbance. The scatter in the fiber-optic Raman data about the best-fit line in Figure 7 (correlation coefficient, $r^2 = .958$) is somewhat higher than the scatter in the NIR absorbance values ($r^2 = .992$), but appears to be particular to the present fiber-optic experimental arrangement and measurement scheme. More recent epoxide calibration experiments conducted on an FT-Raman

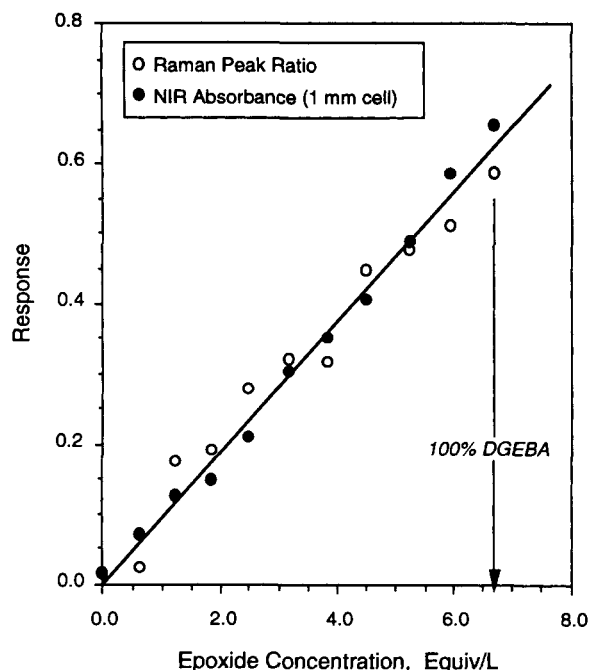


Figure 7 Raman (open circles) and NIR absorbance (solid circles) calibration curves of spectral response vs. epoxide concentration.

spectrometer at 1064 nm excitation without a fiber-optic probe indicate a correlation coefficient for Raman peak ratios that is comparable to or better than NIR absorbance.⁹

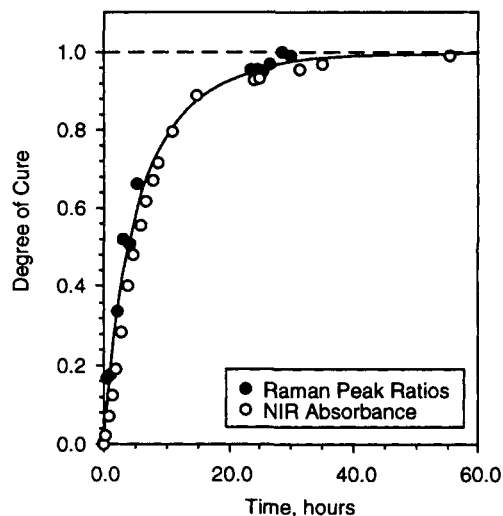


Figure 9 Comparison of fiber-optic Raman (solid circles) and NIR absorbance (open circles) method for measuring degree-of-cure vs. time during the room-temperature reaction of PGE with AEP.

CONCLUSIONS

Fiber-optic Raman spectroscopy utilizing a near-visible diode laser excitation source and a pair of 200 μm -diameter quartz optical fibers is a useful technique for remote, *in situ*, measurement of the concentration of epoxide groups in neat resin mixtures. Normalized intensity of the 1240 cm^{-1} Raman

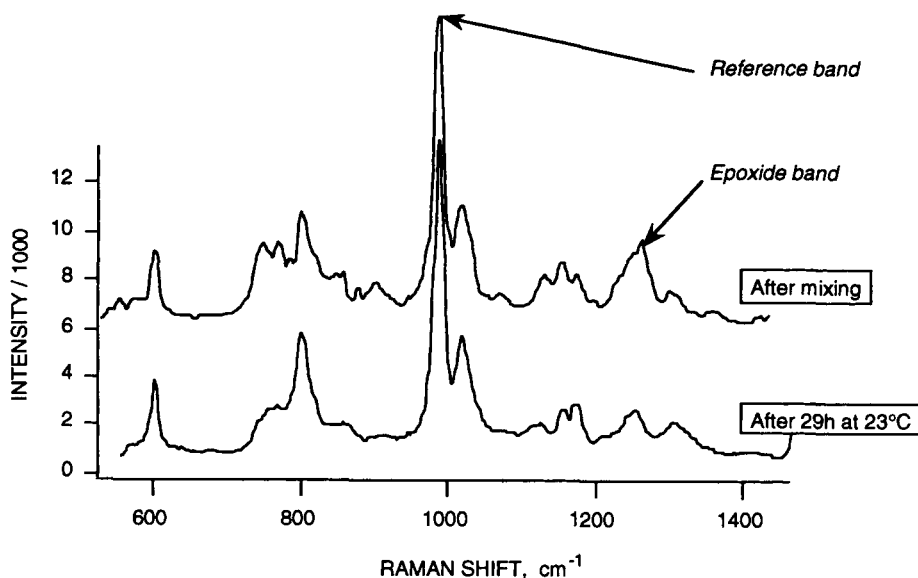


Figure 8 Raman spectra of the stoichiometric PGE and AEP mixture immediately after mixing (vertically shifted for clarity) and after 29 h at 23°C.

peak was linearly related to the molar concentration of epoxide groups in resin mixtures, providing a simple relationship for calculating the degree-of-cure in epoxies. Both fiber-optic Raman and NIR absorbance methods were used to monitor the chemical reaction of PGE with DEA and the results were in close agreement. Somewhat lower precision is indicated for the fiber-optic configuration used to obtain the Raman spectra in the present study compared to the NIR absorbance technique, although the sensitivity of the two spectroscopic methods was found to be comparable. Recent FT-Raman studies of epoxy resins, however, indicate that significant improvement in the quantitative capability of the fiber-optic Raman technique is expected with relatively simple modifications to the optical configuration. Previous publications have demonstrated that temperature can also be determined *in situ* from simultaneous Stokes and anti-Stokes Raman spectra measured over the same fiber-optics used to measure cure chemistry in the Stokes region.

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