An Infrared Spectroscopic Investigation of the Curing Reactions of the EPON 828 / Meta-Phenylenediamine System

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Synopsis

Mid- and near-infrared (IR) spectroscopy has been used to study the curing of a bisphenol-A based epoxy resin (EPON-828) with a tetrafunctional curing agent, viz., meta-phenylenediamine (MPDA). Three different cure cycles were used in the study. Primary amine functionality was observed to react relatively rapidly; none remained after curing for 2 h at 75°C. Secondary amine functionality was exhausted in epoxy rich samples subjected to the standard cure cycle (2 h at 75°C followed by 2 h at 125°C). In samples with stoichiometric amount or higher MPDA, complete reaction of secondary amine or epoxy groups was not observed. In amine-rich samples subjected to post curing (6 h at 175°C), evidence was seen for the reaction of hydroxyl and epoxy groups, resulting in a considerable increase in the crosslink density of these samples.

INTRODUCTION

Few studies have been reported concerning the reaction(s) of diglycidyl ether of bisphenol-A type epoxy resins and meta-phenylenediamine (MPDA).[1,2] However, the epoxy–amine reaction has received considerable attention in other systems.[3-8] It is well known that primary amines can undergo nucleophilic reactions with epoxides, resulting in ring cleavage and formation of a hydroxyl and secondary amine groups[2,9] (as shown in Fig. 1). Further reaction between secondary amine and epoxy groups can also occur. Although rate studies show that primary amine reacts about twice as fast as secondary amine, in epoxy resin systems, some tertiary amine is formed almost immediately.

In some recent studies[10-13] of EPON-828 (Fig. 2) cured with different amounts of MPDA, it was observed that the samples prepared using the standard cure cycle (2 h at 75°C followed by 2 h at 125°C) were not fully cured. Post-curing for 6 h at 175°C in an argon atmosphere brought them closer to complete cure. To characterize these samples for their degree of cure and to understand the reactions occurring during the cure, mid- and near-infrared spectra of the samples were acquired, and the resulting data analyzed.

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$$H_2C\overset{\diagdown}{\underset{O}{\diagup}}CHR_1 \;+\; R_2\text{-}NH_2 \;\longrightarrow\; R_2\text{---}\underset{\underset{H}{|}}{N}\text{---}CH_2\text{---}\overset{\overset{OH}{|}}{CH}\text{---}R_1$$
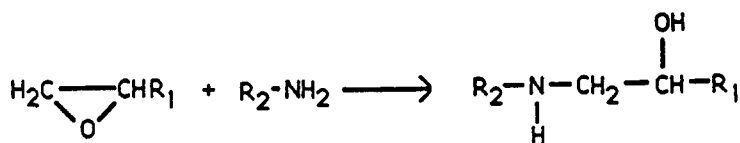
Fig. 1. General scheme for the reaction of amine groups with epoxides.

The utility of mid- and near-infrared (IR) spectroscopy for the quantitation or semi-quantitation of epoxide and hydroxyl functional groups in epoxy resins has been demonstranted.[3] Mones et al.[7] have extended the method to the quantitation of functional groups that are formed in cured films of diaminodiphenylsulfone and tetraglycidyl-4,4'-diaminodiphenylmethane. The reactions taking place during curing of films initially consisting of meta-phenylenediamine (MPDA), and epoxy resin has been studied in a crude way using near-IR spectroscopy.[1] The use of mid- and near-IR spectroscopic techniques is reported herein to study the reactions occurring during the curing cycle of films initially consisting of EPON-828 and meta-phenyl-enediamine (MPDA). Unreacted epoxide has been quantitated in films prepared from differing amounts of reactants which were subjected to different cure cycles. In addition, we followed the appearance and disappearance of hydroxyl and secondary amine functionalities which are formed as a result of the cure reactions.

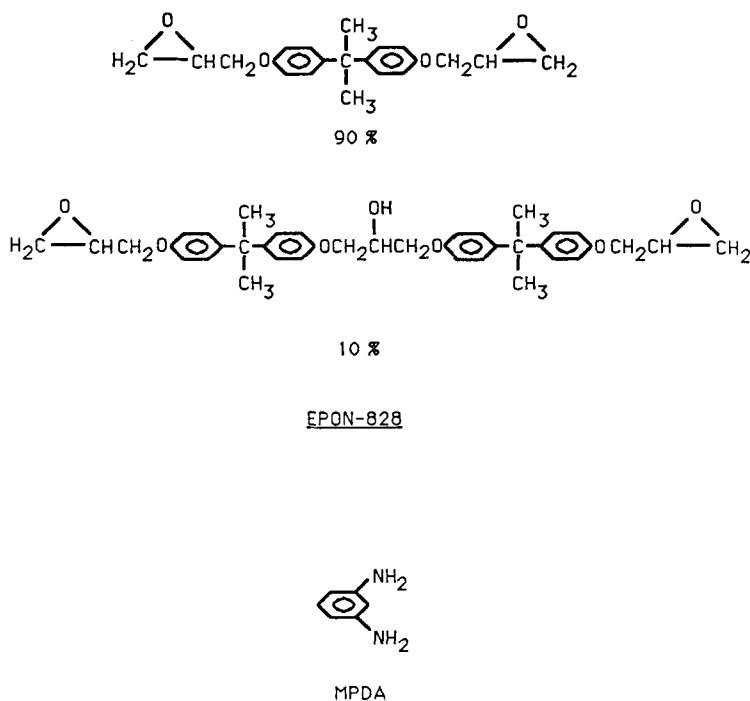90 %

10 %

EPON-828

MPDA

Fig. 2. The structures of materials utilized for this study.

EXPERIMENTAL

EPON-828 (Shell) is a diglycidyl ether of bisphenol-A-based epoxy resin (10% of the molecules in the resin have the extended structure shown in Fig. 2). MPDA is a di-primary amine. Each of these materials was kept in a cool, dry, and dark environment to preclude degradation over time. The stoichiometric amount of MPDA is 14.5 parts by weight per hundred parts of the resin (phr). In the present investigation, samples having 7.5, 10, 14.5, 20, and 25 phr (%) MPDA were prepared. The following procedure was used: The resin and curing agent were heated in separate containers at 75°C until the MPDA had melted. They were then mixed by stirring and vacuum degassed for 7 min. For near-IR studies, circular discs of 1 mm thickness and 1 cm diameter were prepared by pouring the mixture into flexible silicone mold cavities. For mid-IR investigations, two drops of the resin were placed on a CsI window, and a matching window was placed on top of it. A five cent coin was used as dead weight on the top window to thin the sample to the appropriate pathlength. Uncured samples were prepared for near-infrared data collection by dissolving the appropriate amount of meta-phenylenediamine in EPON-828, and placing the solution in a 1 mm pathlength demountable cell with CsI windows. Three curing cycles were used: (i) 75°C for 2 h, (ii) 75°C for 2 h followed by 125°C for 2 h, and (iii) 75°C for 2 h followed by 125°C for 2 h and post-cured under argon at 175°C for 6 h.

Infrared spectra from 4000 to 400 cm^{-1} were obtained using a Digilab FTS-14C/D fourier Transform infrared spectrometer with a coiled hot wire source and a TGS detector. One hundred and fifty single beam scans were collected at a 4 cm^{-1} resolution. Double precision word size and triangular apodization were used in the calculation of the spectra. The single beam spectra of the samples were ratioed against the single beam spectrum of the background, and the resulting spectra were plotted in the absorbance mode.

A Cary Model 14 spectrophotometer was used to record the near-infrared spectra in the range from 1000 to 2100 nm. A tungsten source and a PbSe detector were employed. The Model 14 is a dual beam instrument which has a resolution of 0.3 nm in the near-infrared, a photometric accuracy of 0.002 absorbance unit, and a wavelength accuracy of ± 0.4 nm.

RESULTS AND DISCUSSION

To accurately quantitate specific species in mixtures, using infrared spectroscopy, it is desirable to have an analytical band (a band which arises as a result of a vibrational mode of the functional group of interest) which is fairly strong and not overlapped with other bands. The mid-IR spectra of the EPON-828/MPDA systems studied are complicated by considerable band overlap in the regions where most of the bands which could be used as analytical bands occur. The OH and NH stretches are overlapped with one another. The NH in-plane bend is overlapped with an aromatic ring stretch of EPON-828. The tertiary amine CN stretch absorbs in a region where CH deformation modes are observed. Since EPON-828 is an ether itself, and has ether CO stretches in its spectrum, new ether CO stretches cannot be observed to be intensifying if these bonds are formed during the cure cycle. For the bands mentioned above to be observed, they would have to be strong and the
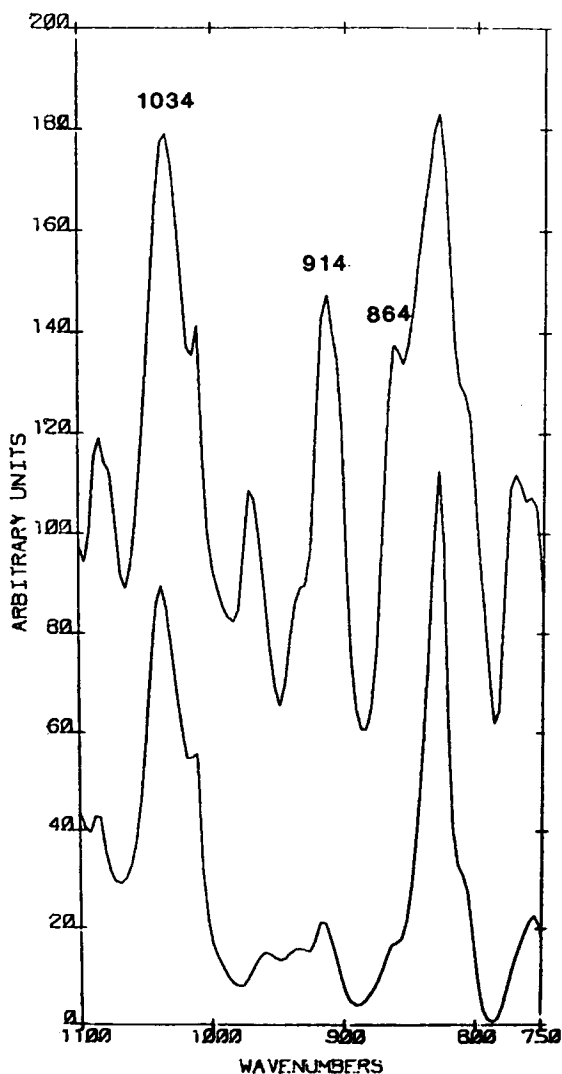
Fig. 3. The top trace is an infrared absorbance spectrum of a film initially consisting of 14.5 wt % MPDA in EPON-828. This film has been cured for 2 h at 75°C.

functional group of interest would have to be more concentrated than is the case in this system.

Shown in Figure 3 are the mid-IR spectra of a film of EPON-828 (top trace) and a film cured for 2 h at 75°C which initially consisted of EPON-828 with 14.5 wt % MPDA added. The absorbance decrease of the 914 and 864 cm^{-1} bands is consistent with the assignment of these bands to epoxide ring stretches. The intensity reduction is due to the reaction and consequent cleavage of epoxide rings of EPON-828, which results in a lowering of the concentration of epoxide ring containing molecules. The band at 914 cm^{-1} is most suitable for an epoxide analytical band. Although it is somewhat overlapped with another band, it is much less so than the 864 cm^{-1} band, and it is the best band that could be found.

To account for the pathlength differences of the films, the intensity of the 914 cm^{-1} band was ratioed to the intensity of the 1034 cm^{-1} band. The 1034 cm^{-1} band is due to an out-of-plane CH deformation of an aromatic ring. Since the aromatic rings do not participate in the reaction, the 1034 cm^{-1} band intensity should remain constant. The band intensity measurements were made by using an integration program, called INTEGRATE, which was supplied with the Digilab FTS-14C/D.

The 914 cm^{-1}/1034 cm^{-1} integrated intensity ratio of pure EPON-828 was assigned as the 100% epoxide level. For films cured with added MPDA, the integrated intensity ratio was compared to that of pure EPON-828 and the percentage of remaining (unreacted) epoxide groups were calculated.

The epoxide band at 914 cm^{-1} never completely disappeared in any of the films studied, which leads to the conclusion that the reaction between epoxy and amine (or other) groups does not go to completion. As the reaction proceeds, the increase in crosslink density raises the T_g of the crosslinked regions, and, when this equals or exceeds the cure temperature, the reactive functional groups are probably sterically hindered from reacting[10] with the epoxide rings and the reaction is quenched.

The results of the mid-IR quantitation of unreacted epoxide in films cured with MPDA is shown graphically in Figure 4. The abscissa is presented in time, but the temperatures are also ramped. From 0 to 2 h the temperature was held at 75°C, from 2 to 4 h the temperature was held at 125°C, and from 4 to 10 h the temperature was held at 175°C. Films with initial concentrations of 7.5, 10, 14.5, and 25 wt % MPDA were studied. A decrease in the percentage of unreacted epoxide groups is observed with increasing concentrations of MPDA and to a lesser extent, increasing cure temperatures and times. The final point on the 14.5 wt % curve indicates epoxide ring formation. No scenario could be envisioned where epoxide ring formation could occur, and since the analytical band is somewhat overlapped, it is believed that this increase in the percentage of unreacted epoxide is within experimental error.

Because of the complexity of the mid-IR spectra and the inability to observe isolated bands, indicating the presence of secondary amine and hydroxyl groups, it was decided to record near-IR spectra of cured and uncured films containing various concentrations of MPDA. Near-IR spectroscopy was found to be useful in quantitating hydroxyl groups in epoxy resins[3] and was used to study the cure reactions of the EPON-828/MPDA system for a very limited number of examples.[1]

The top trace in Figure 5 is the near-IR spectrum from 1000 to 2100 nm of EPON-828 with 14.5 wt % MPDA added. The spectrum was obtained on an uncured sample with a one mm pathlength. The bands at 1503 nm (6653 cm^{-1}) and 1980 nm (5051 cm^{-1}) increase in intensity with increasing concentrations of MPDA. This behavior points to the fact that these bands are MPDA absorption bands. The 1503 nm band is an overtone of the NH stretch of MDPA. The 1980 nm band is a combination of a different NH stretch and an NH in-plane deformation. The bottom trace of Figure 5 is the near-IR spectrum of a film cured for 2 h at 75°C which initially consisted of EPON-828 with 14.5 wt % MPDA added. The 1980 nm band has completely disappeared which indicates that all primary amine has reacted. The 1980 nm band was not observed in the near-IR spectra of any of the cured films which were
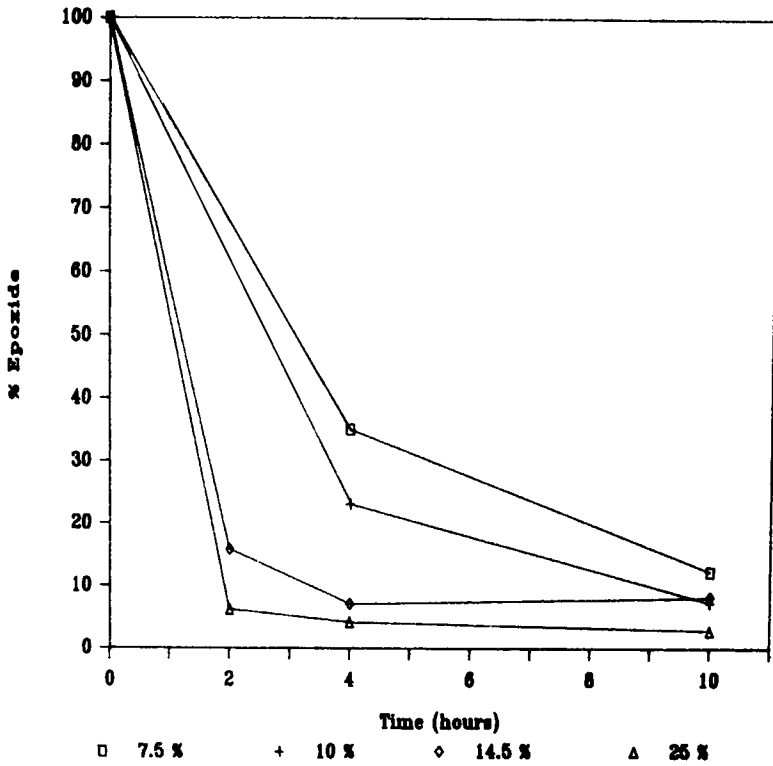
EPOXIDE

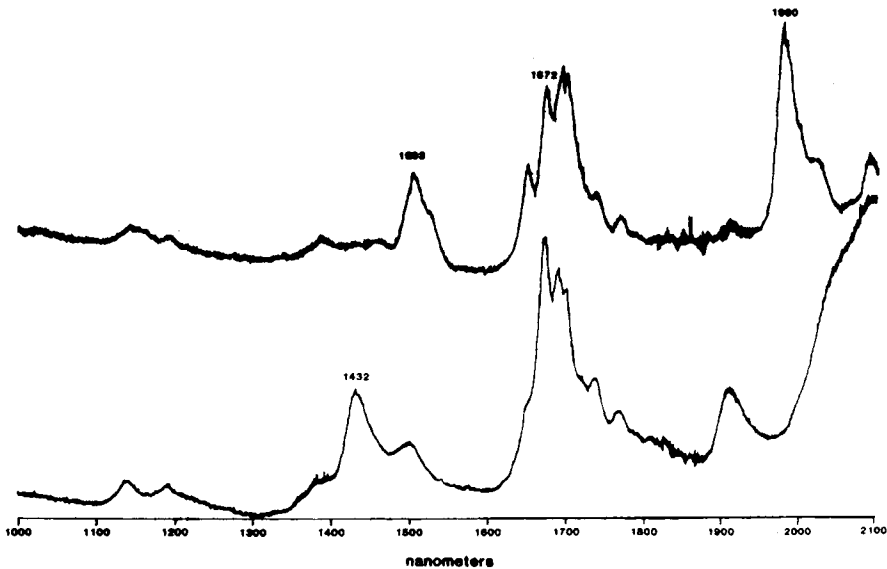Fig. 4. The effect of curing on epoxide concentration for films with 7.5, 10, 14.5, and 25 wt % MPDA.

Fig. 5. The top trace is a near-infrared absorbance spectrum of a mixture of EPON-828 and 14.5 wt % MPDA. This sample has not been cured. The bottom trace is a near-infrared absorbance spectrum of a film consisting of the same quantities of reactants but cured for 2 h at 75°C.
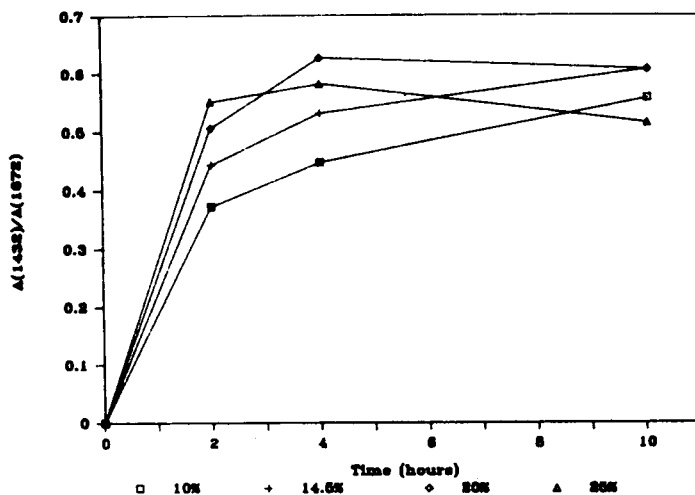
HYDROXYL

Fig. 6.   The effect of curing on the hydroxyl/aromatic absorbance ratio for films with 10, 14.5, 20, and 25 wt % MPDA.

studied. This indicates that the initial reaction of primary amine with the epoxide ring proceeds relatively rapidly and requires little heat. The 1503 nm band in the bottom trace is a secondary amine band which is accidentally degenerate with the primary amine band in the upper trace which is observed at the same wavelength. The band at 1432 nm (6983 cm^{-1}) in the bottom trace of Figure 5 is assigned to an overtone of the OH stretch. This band is observed as a result of hydroxyl formation when epoxide rings are cleaved by the amine groups of MPDA. As can be seen, the hydroxyl and secondary amine bands are sufficiently separated in the near-IR to measure their intensities. This was not the case in the mid-IR. The 1672 nm (5981 cm^{-1}) band was used to correct for pathlength differences between different samples. This band is a combination band of aromatic CH stretches and its intensity should remain constant since aromatic groups do not participate in the reaction.

The absorbance ratio of the hydroxyl band at 1432 nm and the aromatic band at 1572 nm is plotted vs. time in the curves of Figure 6. The films studied had initial MPDA concentrations of 10, 14.5, 20, and 25 wt %. Again, although the abscissa is in units of time, the temperature was ramped in the manner described earlier.

As is evident from the curves, hydroxyl concentration increases as more MPDA is added. The films with initial concentrations of 20 and 25 wt % MPDA showed hydroxyl concentration decreases as longer, hotter cures were used. This decrease in the absorbance ratio is consistent with the reaction of hydroxyl groups to form either ethers or olefins. The concentration of epoxide groups also decreases slightly, indicating that they either react with hydroxyls followed by further reaction of the hydroxyl group formed or that they dehydrate directly.[14] This behavior was also observed in a similar system.[7]

In the graph of Figure 7, the absorbance ratio of the 1503 nm band and the 1672 nm band, which is a measure of secondary amine absorbance, is plotted
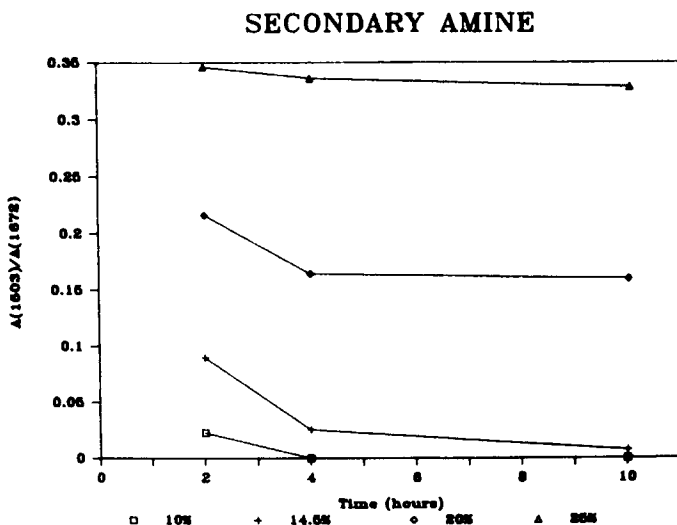
SECONDARY AMINE

Fig. 7. The effect of curing on the secondary amine/aromatic absorbance ratio for films with 10, 14.5, 20, and 25 wt % MPDA.

vs. time (temperature is ramped as before). The absorbance ratio increases with increasing initial MPDA concentration. The film having an initial 10 wt % concentration of MPDA has no observable secondary amine absorbance when it is cured for 2 h at 75°C and two additional hours at 125°C. In this film, all of the secondary amine groups have further reacted to form tertiary amine species. The films having an initial MPDA concentration of 14.5 wt % (the stoichiometric amount) yield data which show that the secondary amine groups are not completely consumed in the reaction. This data is reinforced by the data shown for the percent of unreacted epoxide (Fig. 4), which never reaches zero. For the 25 wt % initial concentration of MPDA the secondary amine/aromatic absorbance ratio stays fairly constant. As was stated above, the hydroxyl groups appear to react at this high concentration of MPDA. The secondary amine groups must be more hindered by the highly polymerized and crosslinked chains and cannot move freely to come in contact with unreacted epoxide rings.

CONCLUSION

It is concluded from the mid-IR results that epoxide groups react relatively rapidly in cured films of EPON-828/MPDA, but are never exhausted due to the lack of diffusional transport of the reactive site because of steric hindrance as the crosslinked regions approach T_g, which is close to or higher than the cure temperature.

Semi-quantitative results for the concentration of hydroxyl and secondary amine groups were obtained from near-IR spectra of cured films. The concentration of hydroxyl groups increased with increasing initial MPDA concentration, but, in the case of a film with an initial concentration of 25 wt % MPDA, the hydroxyl concentration decreased with longer, hotter cures. From this data, it is concluded that hydroxyl and epoxy groups react to form ethers

or olefins. The cured films with an initial concentration of 10 wt % MPDA showed the most complete reaction of amine groups. No secondary amine absorbance was detected in these films having longer, hotter cures. In the film initially having stoichiometric amounts of reactants, complete reaction of epoxide and secondary amine groups is not observed. The reaction of primary amine with the epoxide groups proceeds relatively rapidly as no primary amine bands were observed in the near-IR spectra of any of the cured films which were studied.

References

1. J. C. Illman, *J. Appl. Polym. Sci.*, **10**, 1519 (1966).
2. S. Sourour and M. R. Kamal, *Thermo. Chim. Acta*, **14**, 41 (1976).
3. H. Lee and K. Neville, *Handbook of Epoxy Resins*, McGraw-Hill, New York, 1967.
4. Y. Tanaka and T. F. Mika, *Epoxy Resins: Chemistry and Technology*, C. A. May and Y. Tanaka, Eds., Dekker, New York, 1973.
5. L. Schechter, J. Wynstra, and R. E. Kurjky, *Ind. Eng. Chem.*, **48**, 94 (1956).
6. T. Kakurai and T. Noguchi, *J. Soc. Org. Syn. Chem. Jpn.*, **18**, 485 (1960).
7. E. T. Mones, C. M. Walkup, J. A. Happe, and R. J. Morgan, *Proc. 14th Nat. SAMPE Tech. Conf.*, **91** (1982).
8. R. E. Smith, F. N. Larsen, and C. L. Long, *J. Appl. Poly. Sci.*, **29**, 3713 (1984).
9. R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 3rd ed., Allyn and Bacon, Boston, 1973.
10. V. B. Gupta, L. T. Drzal, W. W. Adams, and R. Omlar, *J. Mater. Sci.*, **20**, 3439 (1985).
11. V. B. Gupta, L. T. Drzal, and M. J. Rich, *J. Appl. Polym. Sci.*, **30**, 4467 (1985).
12. V. B. Gupta, L. T. Drzal, C. Y-C. Lee, and M. J. Rich, *J. Macromol. Sci. Phys.*, **B23**, 435 (1985).
13. V. B. Gupta, L. T. Drzal, C. Y-C. Lee, and M. J. Rich, *Polym. Eng. Sci.*, **25**, 812 (1985).
14. R. J. Morgan, *Advances in Polymer Science*, K. Dusek, Ed., Springer-Verlag, New York, 1985, Vol. 72, Chap. 1.