

Mid- and Near-Infrared Spectroscopic Investigations of Reactions between Phenyl Glycidyl Ether (PGE) and Aromatic Amines

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SYNOPSIS

Mid-infrared (MIR) and near-infrared (NIR) spectroscopies have been employed to examine the reactions between phenyl glycidyl ether (PGE) and five aromatic amines. Although MIR spectroscopy can effectively study the kinetics of PGE/aromatic amine cure reactions, the OH and NH stretching bands overlap and the NH in-plane bending band overlaps with an aromatic ring stretching band of PGE. This significantly reduces the utility of MIR spectroscopy for quantitative studies of PGE cure reactions. In contrast, the absorption bands of these functional groups in the NIR spectrum are well separated from the absorption bands of other functional groups. The utility of NIR spectroscopy for studying the kinetics of epoxy resin cure reactions has been clearly established. Absorbances in the NIR spectra suitable for quantitative studies of epoxy resin reaction kinetics have been identified. The ability of *in situ* NIR spectroscopy to obtain isothermal kinetic data has been demonstrated.

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INTRODUCTION

Infrared (FTIR) spectroscopy is an important tool for monitoring cure reactions of epoxy resins with hardeners. The mid-infrared (MIR) region of the spectrum typically has been utilized in such studies. For example, Morgan and Mones used MIR spectroscopy to study the cure reactions between epoxy resins and diaminodiphenyl methane.¹ The intensities of the epoxide, hydroxyl, ether, primary amine, and secondary amine absorption bands at 906, 3500, 1120, 1630, and 3410 cm^{-1} , respectively, were determined from spectral differences and correlated with cure conditions. These results were used to describe the extent and mechanism of the cure reactions.

Allen and Sanderson characterized cure reactions associated with epoxy glues using FTIR spectroscopy.² The MIR spectra of bisphenol A epichloro-

hydrin resin, an amine-based hardener, and a cured epoxy adhesive were reported; assignments for the epoxy, hydroxyl, and primary amine stretching bands were made. During cure of the epoxy adhesive, the epoxide absorptions at 915 and 862 cm^{-1} decreased in intensity and the intensity of the hydroxyl absorption at 3450 cm^{-1} increased as compared to the separate resin and hardener.

As demonstrated in the references above, the functional groups involved in epoxy resin cure reactions all have strong, characteristic frequencies in the MIR. However, the MIR spectra of epoxy resins and hardeners are very complex; isolated primary amine, secondary amine, and hydroxyl group absorption bands cannot be observed. Near-infrared (NIR) spectra often have well-isolated absorption bands for these functional groups. This is a consequence of the absorptions in the NIR resulting from overtone and combination bands. NIR spectroscopy presents several potential advantages over MIR spectroscopy for characterizing the cure reactions of epoxy resin systems, such as enhanced resolution, higher energy sources, and lower oscillator strengths.^{3,4}

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Schiering and Katon studied the reaction between diglycidyl ether of bisphenol A (DGEBA) and *m*-phenylenediamine.⁵ Both MIR and NIR spectra were used to quantify the terminal epoxide bands as well as the amine and hydroxyl groups. The band at 914 cm^{-1} in the MIR spectra was chosen for analysis of the epoxide group. The bands at 5051 , 6653 , and 6983 cm^{-1} in the NIR spectra were used to quantify primary amine, secondary amine, and hydroxyl groups, respectively.

Paputa Peck and co-workers quantified the cure of epoxy coating systems using NIR spectroscopy.⁶ The terminal epoxy group NIR absorption at 4532 cm^{-1} in these data was utilized to measure epoxy ring concentrations during synthesis and cross-linking. A linear response was found for the epoxy concentrations of various chloroform solutions (3.6 – 20.7 meq/L) using a 20 mm path-length cell.

Few kinetic studies have been reported concerning the reactions of phenyl glycidyl ether (PGE)/

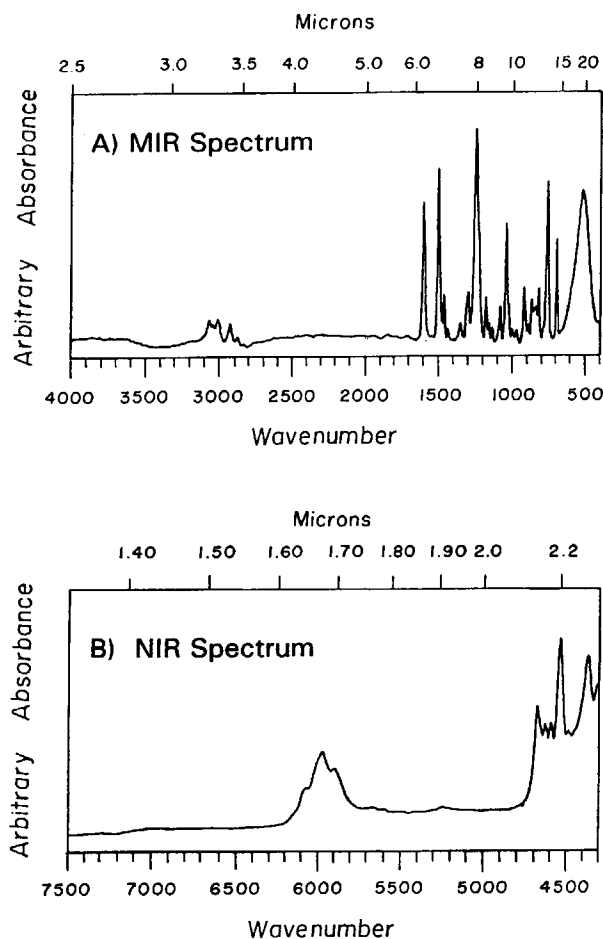


Figure 1 Infrared absorption spectra of pure PGE: (A) MIR spectrum; (B) NIR spectrum.

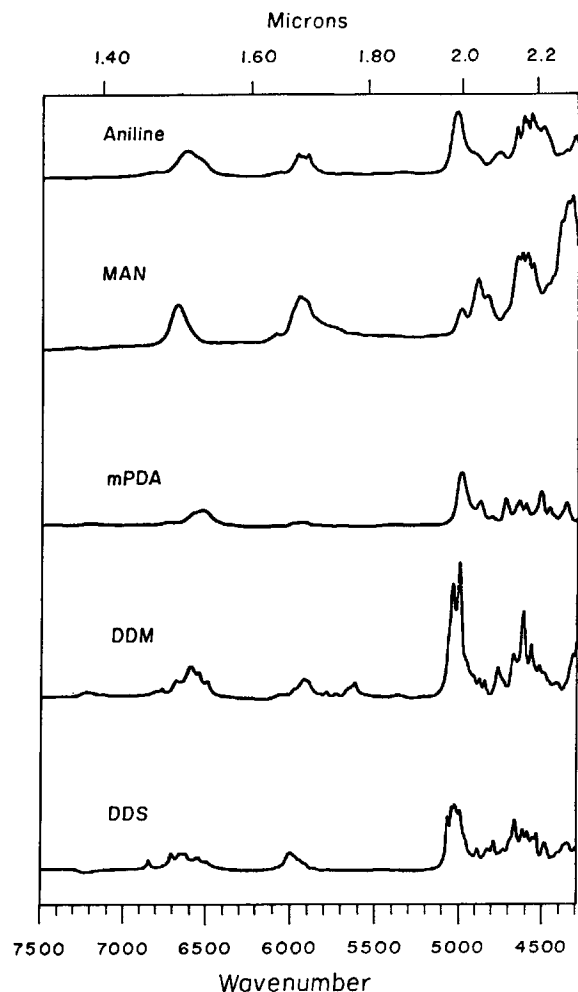


Figure 2 NIR spectra of aniline, MAN, mPDA, DDM, and DDS.

aromatic amine systems.^{7,8} However, this family of reactions is ideal for developing FTIR techniques for studying epoxy cure reactions *in situ* for several reasons. The PGE/aromatic amine systems themselves are liquid solutions. Thus, interferences from solvents can be avoided. Although the reactions that occur between PGE and aromatic amines are typical of epoxy resin cure reactions, polymerization does not occur. This greatly simplifies interpretation of the data.

Changes in the terminal epoxy, hydroxyl, and amine absorption bands upon curing PGE/aromatic amine resin systems are reported herein based upon MIR and NIR spectroscopic data. Five aromatic amines were reacted with PGE: aniline, methylaniline (MAN), *m*-phenylenediamine (mPDA), 4,4'-diaminodiphenylmethane (DDM), and 4,4'-diaminodiphenyl sulfone (DDS). Optimum peaks for

Table I MIR Characteristic Absorption Frequencies (in cm^{-1}) of PGE and Five Aromatic Amine Hardeners

	Aniline	MAN	mPDA	DDM	DDS	PGE
Primary amine NH stretch	3433		3422	3444	3456	
	3356		3343	3415	3399	
	3212		3216	3338	3367	
				3211	3333	
					3242	
Secondary amine NH stretch		3414				
Primary amine NH in-plane bending	1621		1617	1624	1632	
Terminal epoxy ring stretch						1250 916 863

quantitative analyses and for studying reaction kinetics have been identified.

EXPERIMENTAL

Sample Preparation

In the systems studied, the aromatic amine was dissolved directly into liquid PGE. The mass ratio of PGE to amine was 3:1. AN, MAN, mPDA, and DDM all easily dissolve into PGE at room temperature to form liquid solutions. DDS has only limited solubility in PGE; therefore, PGE was heated to 75°C and the DDS was added slowly with stirring.

PGE and PGE/Aromatic Amine Solutions

For MIR studies, a drop of the solution of interest was placed between two NaCl windows. For NIR investigations, a semipermanent cell was constructed by joining two NaCl crystal plates with a 0.5 mm lead spacer. Liquid was injected into the interior of the cell with a syringe.

Solid Aromatic Amines

Two procedures were followed in obtaining reference spectra of these solid aromatic amines. In the first, the solid amine was dissolved in acetone and cast as a thin film on a NaCl plate. The NaCl plate was placed in an oven at 60°C for 10 min to evaporate the acetone. None of the spectra obtained using this method gave any indication of residual acetone. In the second procedure, a thin layer of solid amine was placed on a NaCl window and the window plate was placed in an oven at a temperature slightly higher than the melting point of the amine. The molten amine then was cooled, forming a thin film on the NaCl window. None of the aromatic amines decomposed at the temperatures used in this procedure. Reference spectra were obtained using both methods.

Cured PGE Aromatic Amine Samples

PGE/aromatic amine solutions were cured at 177°C for 30 min (90 min for the PGE/DDS system) between two NaCl windows. The samples then were allowed to cool slowly to room temperature.

Table II NIR Characteristic Absorption Frequencies (in cm^{-1}) of PGE and Five Aromatic Amine Hardeners

	Aniline	MAN	mPDA	DDM	DDS	PGE
Primary amine NH overtone ^a	6641		6577	6595	6627	
Secondary amine NH overtone		6690				
Primary amine NH combination	5035		5000	5045	5028	
Terminal epoxy-ring bands						6070 4532

^a Primary amine N—H overtones have at least two overlapping peaks; only the maximum is given here.

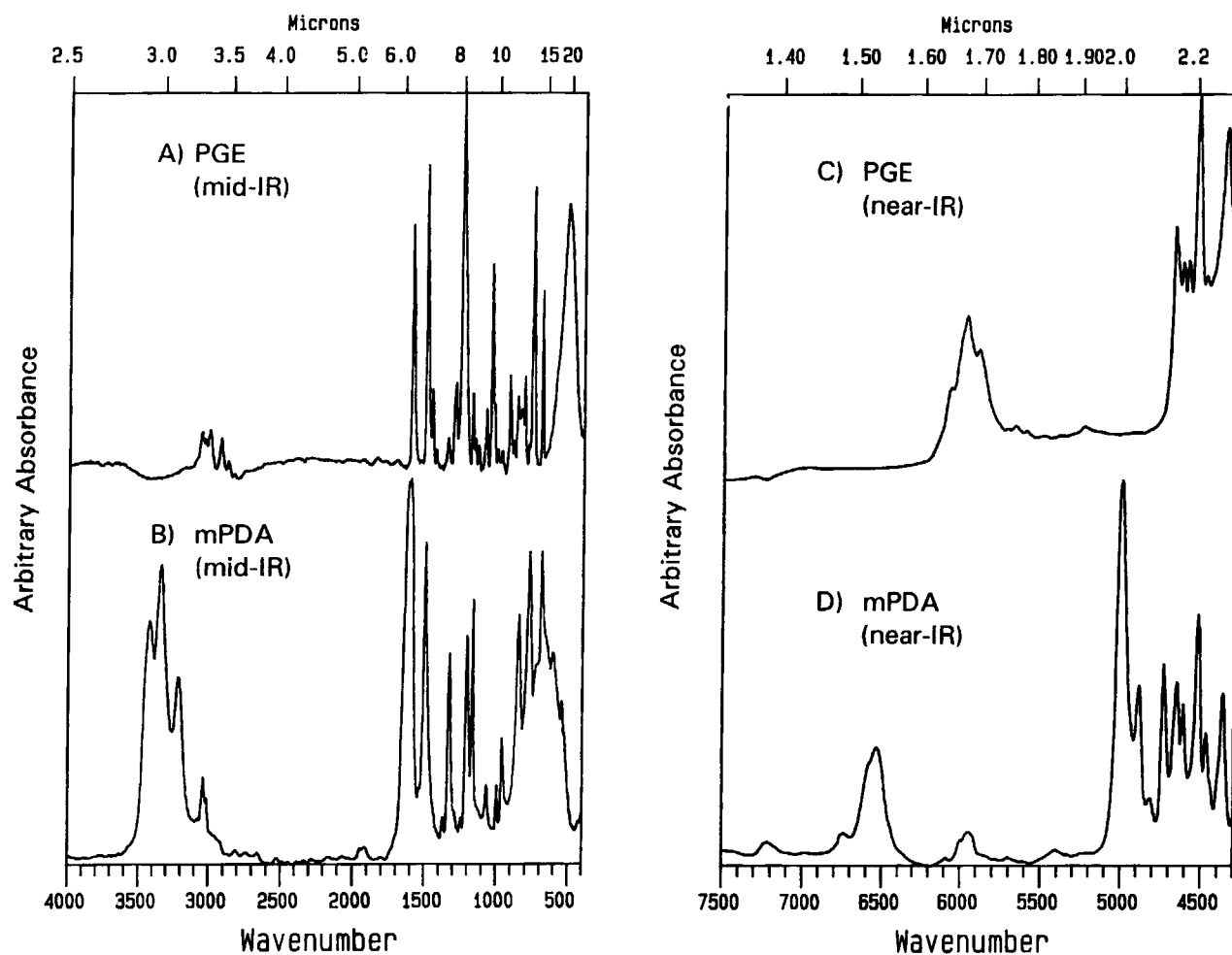


Figure 3 Spectra of PGE and mPDA: (A) MIR spectrum of PGE; (B) MIR spectrum of mPDA; (C) NIR spectrum of PGE; (D) NIR spectrum of mPDA.

FTIR Spectroscopy

All MIR spectra were obtained using a Mattson Instruments NOVA CYGNI 120 spectrometer with an MCT detector, a Ge-coated KBr beamsplitter, and a rare-earth oxide source. Sixteen scans were coadded at 4 cm^{-1} resolution. The NIR spectra were obtained using a Mattson Instruments NOVA CYGNI 120 spectrometer with a tungsten halogen source, a quartz beamsplitter, and an indium antimonide (InSb) detector. Sixty-four scans were coadded at a resolution of 8 cm^{-1} .

In situ NIR Spectroscopy

The NIR optical bench described above was used in conjunction with a Spectratech high-temperature transmission cell. A PGE/mPDA solution (having a 3:1 mass ratio) was placed in the sample cell. A background spectrum ($t = 0\text{ min}$) was obtained.

Power was applied to the heating element with data acquisition occurring at regular intervals. Absorption was measured using integrated intensities about absorption maxima. Isothermal kinetic data were recorded by observing the absorbance ratio of the epoxide combination band at 4534 cm^{-1} with the aromatic C—H overtone band at 5969 cm^{-1} . The conversion rate of the epoxide ring to a hydroxyl group is equal to the time derivative of this absorbance ratio.

The time derivative of the absorbance ratio was calculated using a 7-point Savitsky-Golay algorithm.^{9,10} The data were fit to the rate expression¹¹ below using a simplex algorithm:

$$\frac{dX_E}{dt} = (k_1 + k_2 X_E^\alpha)(1 - X_E)^\beta$$

where X_E is the conversion of epoxide resin and k_1 and k_2 are reaction rate constants.

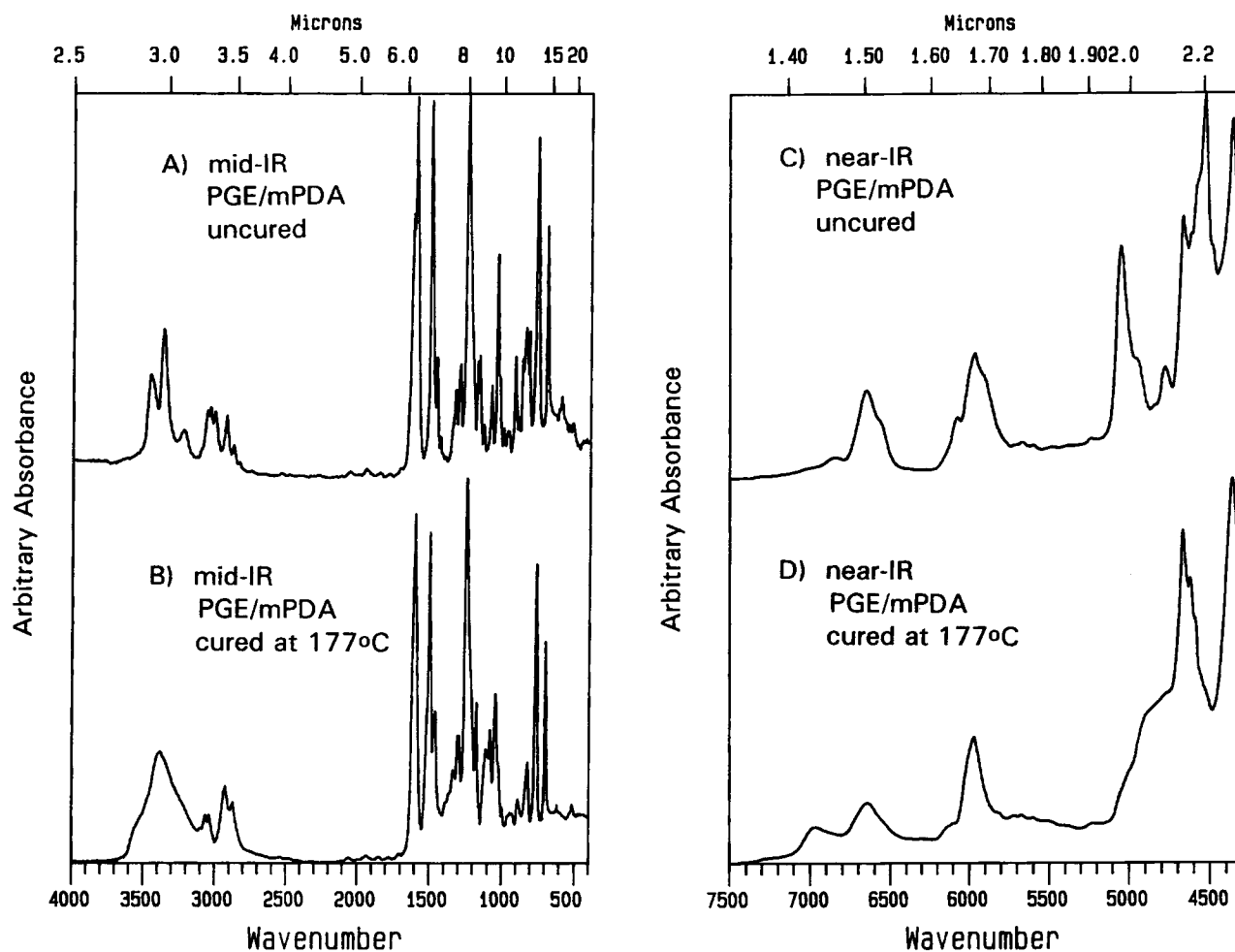


Figure 4 Spectra of the PGE/mPDA system: (A) uncured system (MIR spectrum); (B) system cured at 177°C for 30 min (MIR spectrum); (C) uncured system (NIR spectrum); (D) system following curing at 177°C for 30 min (NIR spectrum).

RESULTS

The MIR and NIR spectra of PGE are shown in Figure 1(a) and (b), respectively. The epoxy group has three characteristic absorption bands in the MIR spectrum. The band at 916 cm^{-1} is well separated from adjacent absorption bands. The bands at 1250 and 863 cm^{-1} overlap with the carbon-oxygen single-bond stretching band of the phenyl ether and an out-of-plane bending band of the aromatic ring. In the NIR spectrum, the bands at 4532 and 6070 cm^{-1} are due to the terminal epoxide group, with the sharp absorption at 4532 cm^{-1} being free of spectral interferences.

Although the MIR spectra of aniline, MAN, mPDA, DDM, and DDS are well studied,¹² the NIR spectra of these materials are not well documented. The NIR spectra of aniline, MAN, mPDA, DDM, and DDS are shown in Figure 2. The overtone vi-

brations of the amine N—H stretch appear over a range from 6577 to 6690 cm^{-1} . The bands from 5000 to 5045 cm^{-1} are combination bands of the primary N—H stretch and N—H in-plane bending.

A summary of characteristic peaks in the MIR and NIR spectra for PGE and the five aromatic amine hardening agents of interest can be found in Tables I and II, respectively.

The MIR spectrum of PGE and mPDA are shown in Figure 3(a) and (b), respectively. There is obviously a significant overlap of the absorptions; in particular, the aromatic ring stretch of PGE at 1600 cm^{-1} and the N—H in-plane bending of mPDA at 1617 cm^{-1} significantly overlap one another. Figure 3(c) and (d) are the corresponding NIR spectra for PGE and mPDA, respectively. The epoxide combination band at 4532 cm^{-1} is isolated from neighboring mPDA absorptions. The overtone and combination bands for the amine groups in mPDA are

Table III MIR and NIR Characteristic Absorption Frequencies (in cm^{-1}) for the PGE/mPDA System

	Uncured	Cured
Terminal epoxy ring stretch	863	863
	914	914
Primary amine N—H in-plane bend	1620	1620
Primary amine N—H stretches	3456	3456
	3368	3368
	3223	3222
Secondary amine N—H stretch	—	3380
O—H stretch	—	3380
Terminal epoxide ring combination	4534	4534
	5052	5052
Primary amine combination	5052	5052
Aromatic C—H overtone	5969	5969
Secondary amine overtone	—	6641
Primary amine overtone	6652	6652
O—H overtone	—	6968

now well isolated from any major contributions from PGE.

The MIR spectra of the PGE/mPDA system, both uncured and cured, are shown in Figure 4(a)

and (b), respectively. The assignments of N—H and terminal epoxide group absorptions in the MIR spectra of an uncured PGE/mPDA system are listed in Table III. It is well known that primary amines undergo nucleophilic addition reactions with epoxides, resulting in ring cleavage and the formation of a hydroxyl and a secondary amine group. Secondary amines and epoxide groups can react to form tertiary amines. These reactions have been readily observed using MIR spectroscopy both in prior literature^{1,2,7} and in the present study.

After curing at 177°C for 30 min, the absorption bands at 1620 cm^{-1} for N—H in-plane bending associated with primary amines have disappeared completely. The epoxide ring stretching absorption bands at 914 and 863 cm^{-1} have decreased. The hydroxyl and secondary amine stretching bands have appeared, overlapping over a wide region of the spectrum about 3400 cm^{-1} (Table III). Clearly, analysis of the primary amine N—H in-plane bending band (near 1620 cm^{-1}), the secondary amine N—H, and the hydroxyl stretching band (near 3400 cm^{-1}) will be difficult. Therefore, the NIR spectrum of the PGE/mPDA system was examined.

The NIR spectra of the uncured and cured PGE/mPDA system are shown in Figure 4(c) and (d).

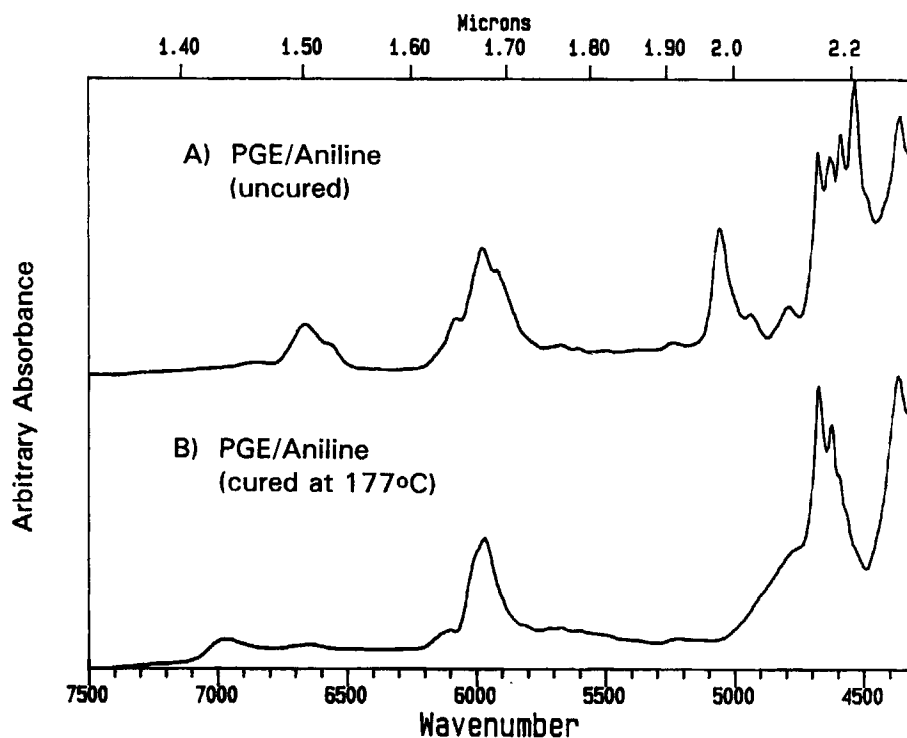


Figure 5 NIR spectra of the PGE/Aniline system: (A) uncured; (B) cured at 177°C for 30 min.

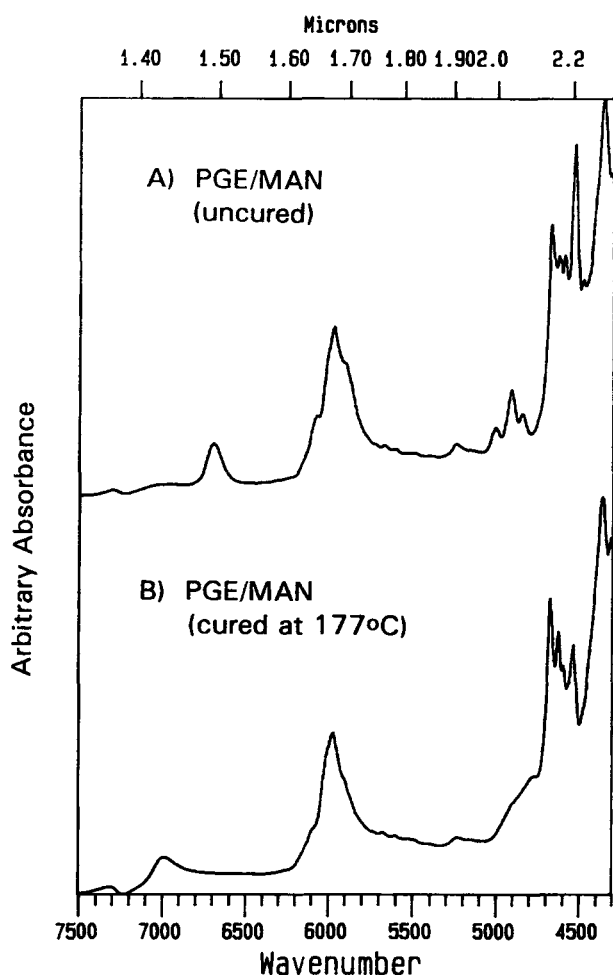


Figure 6 NIR spectra of the PGE/MAN system: (A) uncured; (B) cured at 177°C for 30 min.

The primary amine overtone and combination bands at 6652 and 5052 cm^{-1} disappear as well as the combination band associated with stretching vibrations in the terminal epoxide ring (at 4534 cm^{-1}). Secondary amine and hydroxyl group overtone bands appear at 6641 and 6968 cm^{-1} , respectively.

In Figures 5–8, the upper spectra are the NIR data for uncured PGE/aromatic amine mixtures (aniline, MAN, DDM, and DDS, respectively). The lower spectra are the NIR spectra for each of these systems following cure. After curing at 177°C, N—H combination bands characteristic of the primary amines ($\sim 5050 \text{ cm}^{-1}$) have disappeared completely. The terminal epoxide ring absorptions (near 6070 and 4532 cm^{-1}) have decreased in intensity. The secondary amine N—H overtone bands near 6650 cm^{-1} have significantly decreased in intensity, whereas hydroxyl overtone bands have appeared near 6970 cm^{-1} . The hydroxyl group and secondary amine bands are sufficiently separated in the NIR

spectra to measure their intensities without curve fitting or deconvolution of the spectra. In addition, the N—H combination ($\sim 5050 \text{ cm}^{-1}$) and terminal epoxide ($\sim 4532 \text{ cm}^{-1}$) bands are also suitable for monitoring the polymerization reactions. Summaries of the peak assignments for each of these systems, both uncured and cured, are found in Tables IV and V, respectively.

In situ NIR data for the PGE/mPDA system at 90°C are shown in Figure 9. The disappearances of the terminal epoxide ring and primary amine combination bands (4534 and 5052 cm^{-1} , respectively) are observed readily. The formation of hydroxyl groups is indicated by the appearance of the absorption at 6968 cm^{-1} .

The reaction rate (expressed as the rate of consumption of epoxide groups) is equal to the time derivative of the ratio of the intensity of the 4534 cm^{-1} absorption at any time to that of its intensity at time zero. The reaction rates thus obtained are shown as a function of time in Figure 10. These data were fit to the rate expression proposed by Ryan and Dutta.¹¹ The resulting rate equation for the consumption of epoxide groups is

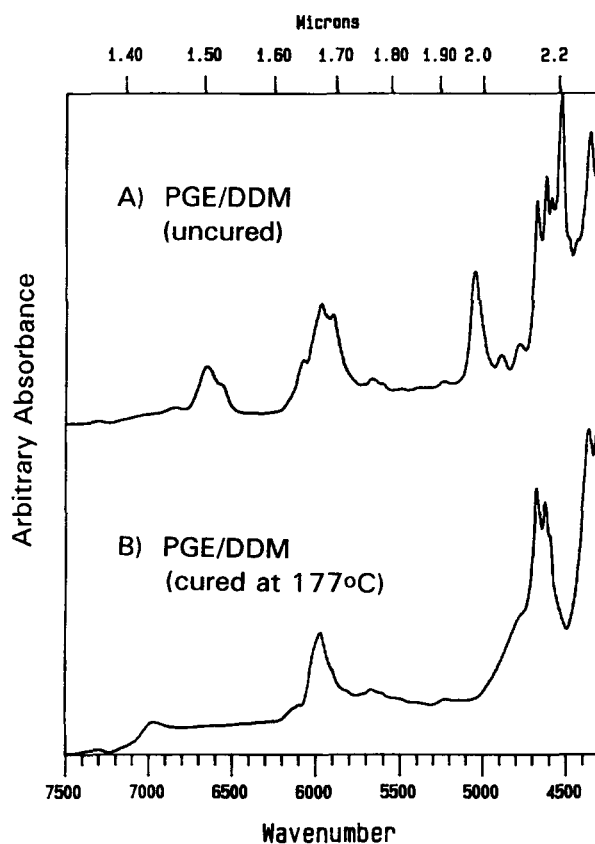


Figure 7 NIR spectra of the PGE/DDM system: (A) uncured; (B) cured at 177°C for 30 min.

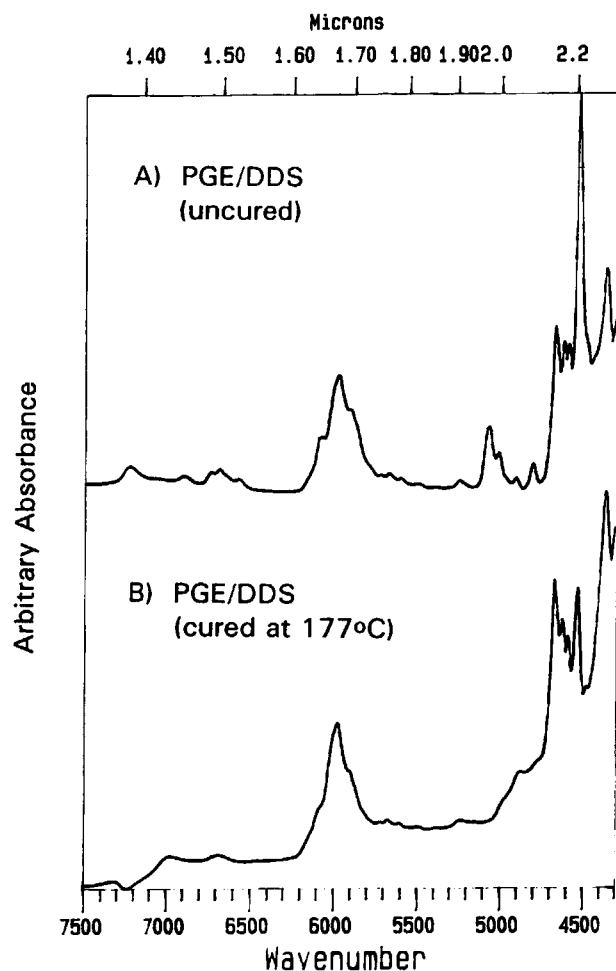


Figure 8 NIR spectra of the PGE/DDS system: (A) uncured; (B) cured at 177°C for 90 min.

$$\frac{dX_E}{dt} = [0.0243/\text{min}$$

$$+ (0.135/\text{min})X_E^{1.91}](1 - X_E)^{2.20}$$

CONCLUSIONS

In the MIR spectra of PGE/aromatic amine mixtures, the primary amine N—H in-plane bending bands (near 1620 cm^{-1}) overlap significantly with aromatic ring stretching bands (near 1600 cm^{-1}), whereas the primary amine NH combination bands (near 5050 cm^{-1}) are free of spectral interferences in the NIR spectra of these systems. The OH and secondary amine stretching bands in the cure reactions of PGE/aromatic amine systems strongly overlap in the MIR spectra (near 3400 cm^{-1}), but the associated overtone bands are well separated in the NIR (near 6970 and 6650 cm^{-1}). The terminal epoxide group ring stretching absorption (near 915 cm^{-1}) in the MIR and the terminal epoxide group combination band (near 4532 cm^{-1}) in the NIR spectra are both sufficiently separated from adjacent bands for use in monitoring cure reactions. This comparison between MIR and NIR spectra indicates that NIR spectroscopy has significant advantages in monitoring polymer cure reactions and will be a useful tool for quantitative analyses and kinetics research. *In situ* NIR spectra can be obtained that permit calculation of the reaction rates, greatly simplifying quantitative data analysis. The utility of this approach has been demonstrated by fitting data obtained for the reaction between PGE and mPDA to the rate expression proposed by Ryan and Dutta.

Table IV NIR Characteristic Absorption Frequencies (in cm^{-1}) of Uncured PGE/Aromatic Amine Mixtures

	PGE/Aniline	PGE/MAN	PGE/mPDA	PGE/DDM	PGE/DDS
Primary amine N—H overtone*	6662		6652	6650	6682
Secondary amine N—H overtone		6694			
Primary amine N—H combination	5055		5052	5047	5067
Terminal epoxy ring absorption bands	6070	6070	6076	6071	6073
	4532	4532	4534	4532	4532

* Primary amine NH overtones have at least two overlapping peaks; therefore, only the maximum is given here.

Table V NIR Characteristic Absorption Frequencies (in cm^{-1}) of Cured PGE/Aromatic Amine

	PGE/Aniline	PGE/MAN	PGE/mPDA	PGE/DDM	PGE/DDS
Primary amine N—H overtone	6662		6652	6650	6682
Primary amine N—H combination	5055		5052	5047	5067
Secondary amine NH overtone	6652	6694	6641	6613	6687
Terminal epoxy ring stretch	6070	6070	6076	6071	6073
	4532	4532	4534	4532	4532
OH stretch	6970	6984	6968	6964	6960

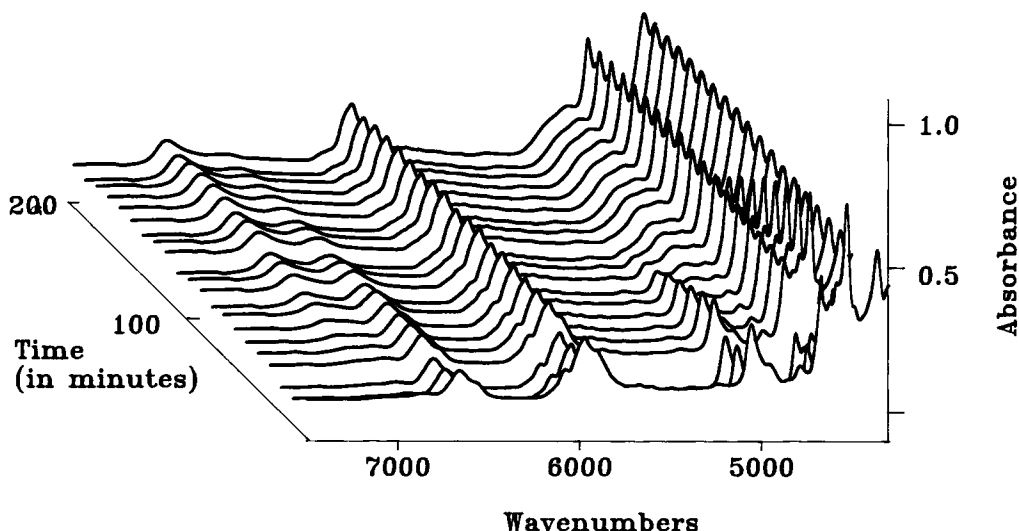


Figure 9 Isothermal (90°C) *in situ* NIR spectroscopic data for the PGE/mPDA cure reaction.

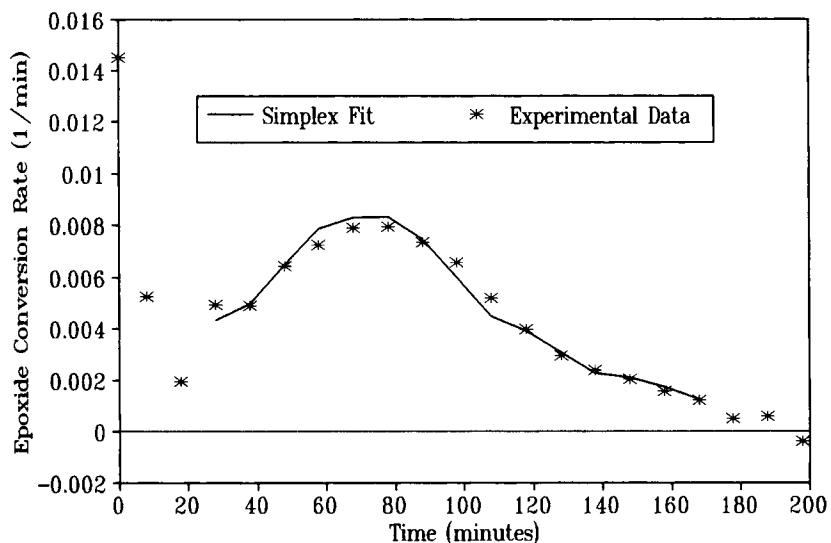


Figure 10 Conversion rates for the PGE/mPDA Reaction at 90°C: (*) experimental data; (—) best fit to data.

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