Near Infrared Measurements of Terminal Epoxides in Polymer Resin Systems. I. Analytical Considerations

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Synopsis

Terminal epoxides display a group specific near infrared absorption at 4532 cm^{-1}. This combination tone is reasonably free of interferences and can be employed to measure oxirane ring concentrations for epoxy coating resin systems during synthesis and crosslinking. With the use of low signal-to-noise FTIR supported by computer data manipulation, chloroform solutions of five commercially available resins were analyzed for epoxide equivalent weight and correlated with results obtained by perchloric acid titrations. The near infrared technique displays linearity for epoxy concentrations of 3.6–20.7 meq/L. Similar results were obtained via a serial concentration study, indicating that the technique is not strongly affected by matrix effects.

INTRODUCTION

Epoxy resins have been successfully employed in coatings, adhesives, and other commercial formulations. The specific physical properties of these systems are largely dependent upon the reactivity of the epoxide ring functionality on the resin molecule. To maintain these desired properties on a continual basis, it is of key importance to monitor epoxide conversion during the production stages of curing, as a function of storage time, and for quality control studies. For most resins, however, the epoxide contribution to the overall mass of the resin molecule is quite small. Curing agents and solvents may also interfere with the analysis. A near infrared spectroscopic method is reported herein that has the sensitivity and selectivity for such analyses.

Epoxide monitoring has commonly involved the titrimetric hydrohalogenation of the oxirane ring. Some early analytical methods required the heating of resins in toxic and odorous solvents, like pyridine. Although the direct hydrobromination method[1,2] is the most widely used technique, its drawbacks are numerous. The titrant is prepared by bubbling anhydrous hydrogen bromide gas through glacial acetic acid. The resulting reagent is light-sensitive, and frequent standardization is recommended. Moreover, some curing agents (e.g., amines) react with the titrant, causing serious systematic errors. The limited application and related shortcomings of more recently developed methods have been discussed elsewhere.[3,4]

Mid-infrared spectroscopic monitoring of the epoxide C—H deformation mode band at 915 cm^{-1} (10.9 μm)[5] has been generally limited to relatively small molecular systems for several reasons. Considerable band overlapping from other modes of the resin molecule reduce the ability to detect the weaker epoxy band in reacting or processed resin systems. Although solutions provide

a medium for optimum spectroscopic quantitation, this approach is restricted because solvent absorption in the 915 cm^{-1} region is commonplace. When either concentrated solution or neat film methods are used, cell pathlengths and/or film thicknesses required to keep spectral intensities within the Beers–Lambert linearity range are often comparable to the radiation wavelengths. Interference distortions within the sample are created as a result. Additional transmission losses occur at the cell/sample interfaces. The inorganic salts used as window material in the mid-infrared have refractive indices which differ greatly from the samples being measured. Considerable discussion on the effects of these optical distortions can be found in the literature.[6-8]

Near infrared spectroscopy has emerged as a promising tool for quantitation as a result of improvements in detector technology. Although bands within this region are of weak absorption, reasonable sensitivity is possible over a wide concentration range by the judicious combination of sample concentration and cell pathlength. The refractive indices of quartz and glass, window materials commonly used in the near infrared, closely match those of organic solutions thereby minimizing transmission losses and optical interference patterns. Chemical inertness also makes these materials readily cleanable and unreactive to resin samples.

Goddu and Delker[9] have reported that terminal epoxides exhibit sharp absorbances relatively free of spectral interferences in the near infrared at 2.2 and 1.65 μm (4532 and 6060 cm^{-1}). These absorptions result from overtones and/or combinations of fundamental vibrations found in the mid-infrared. Using a dispersive infrared spectrometer, Dannenburg[10] conducted a study of epoxides in solution. Sensitivity was restricted by the capabilities of instrumentation available at that time. These investigations were limited to epoxide resins with an equivalent weight less than 1000 g resin/g-eq epoxy. Concentration levels for these resins exceeded 1.0 eq/L.

In this work, Fourier-transform infrared spectrometry is used to achieve improved sensitivity over previous near infrared techniques. A mercury–cadmium–telluride detector has sufficient sensitivity in the 4600–4500 cm^{-1} region to monitor the epoxide response at 4532 cm^{-1} with an adequate signal-to-noise ratio (S/N). Coaddition of the interferograms can further diminish the inherent detector noise. Data manipulation routines can isolate the epoxide band from neighboring absorption bands to facilitate direct numeric integration. With these methods, solutions of resins with epoxide equivalent weights greater than 1000 g resin/g-eq epoxy were studied at concentration levels of meq/L.

EXPERIMENTAL

Materials. Samples of the following epoxy resins were obtained as solids from Shell Chemical Company Laboratories: Epon 1001F, Epon 1002F, Epon 1004F, Epon 1007F, and Epon 1009F. The resins, derived from Bisphenol A and epichlorohydrin, were produced by a batch process. Prior to shipment the manufacturer analyzed the samples for epoxy equivalent weight. Shell's method involved a modified version of the ASTM titration method, D1652, wherein perchloric acid is added in the presence of excess bromide.[11] Gram-equivalent values for these resin samples, given in Table I, range from 533 to

TABLE I
Computer Integrated Areas of the Terminal Epoxide Combination Band at 4532 cm^{-1} Obtained
from Spectra of Various Commercial Epoxide Resins in Chloroform (HgCdTe Detector)

Sample	Epoxide equivalent weight[a]	Titration method concn (meq/L)	IR method integrated area (a.u.)[b]
Epon 1001F	533	20.7	9.86
Epon 1002F	655	16.1	7.72
Epon 1004F	845	12.2	5.59
Epon 1007F	2195	4.81	2.43
Epon 1009F	2849	3.65	1.84

[a] Expressed as g resin/g-equivalent of epoxy; supplied by manufacturer using perchloric acid method (11).

[b] Mean of three determinations; better than 1.5% precision.

2849 g resin/g-eq epoxy. Diethanolamine was obtained from Union Carbide. Dowanal DPM, (dipropylene glycol methyl ether), was obtained from Dow Chemical. Chloroform (Burdick and Jackson), containing a hydrocarbon preservative, was used throughout this study.

Synthesis of Epoxy–Alkanolamine Diadducts. Epoxy–alkanolamine diadducts were prepared by the condensation of the various Bisphenol-A-epichlorohydrin resins with diethanolamine, according to the established procedures.[12] Typically, the synthesis involved the slow addition of the resin to the solution of diethanolamine in dipropylene glycol methyl ether (Dowanal DPM). For every epoxy equivalent a 1.1 eq of diethanolamine was used to prevent epoxy–epoxy reaction. The total concentration of the reactants in Dowanal DPM was 50 wt%. The reaction was carried out at 120°C (150°C for Epon 1009F) for 2–4 h and then maintained at 80°C overnight. Near infrared spectra were obtained for the resulting products dissolved in chloroform. Absence of the epoxide band at 4532 cm^{-1} confirmed complete reaction.

Preparation of Solutions. The solvent strength and suitable window made chloroform the solvent of choice. The solubility of higher polymer systems was assured by preparing solutions of epoxide resins at 0.01 g resin/mL. Based on the manufacturer supplied equivalent weight values, epoxy concentration levels for these solutions ranged from 3.6–20.7 meq/L. Additional samples of Epon 1001F were weighed, and solutions prepared with concentrations corresponding to those of the epoxy concentrations of the higher polymer systems. Epoxy–alkanolamine solutions were prepared as 0.025 g reaction mixture/mL chloroform solution. A glass-stoppered infrared-type quartz cylindrical cell with a 20 mm pathlength and 22 mm outer diameter was used for analysis of the solutions. The cell was rinsed with chloroform and dried prior to each use.

Instrumentation. Fourier-transform infrared (FTIR) spectra of the solutions were obtained using a Nicolet 7001 Michelson interferometer interfaced to a DEC PDP-11/60 computer. Computer acquisition and processing of interferograms and manipulation of spectra was accomplished by software developed in-house at Ford Motor Co. A broad-band HgCdTe detector and a Ge–KBr beamsplitter were used throughout the experiment. The noise
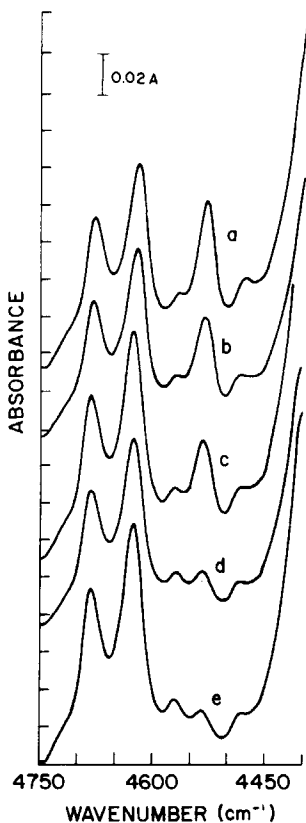
Fig. 1. Near infrared spectra of commercial epoxy resins in chloroform: (a) Epon 1001F; (b) Epon 1002F; (c) Epon 1004F; (d) Epon 1007F; (e) Epon 1009F.

contributions below the quartz transmission cutoff region were reduced by using the appropriate electronic high-pass filter. The large aperture supplied with the optical bench was used. Mirror velocity was 0.673 cm/s. Interferograms were recorded at an optical retardation equal to a resolution of 2 cm^{-1}. A spectrum of each resin in chloroform was obtained from 512 coadded interferograms. Absorbance spectra were obtained by referencing against a spectrum for chloroform. To reduce solvent-related aberrations, the chloroform spectrum was obtained from the identical batch used to prepare the solutions. The solvent spectrum was obtained in the same cell, on the same day as the sample spectrum.

RESULTS AND DISCUSSION

Epoxy absorption bands appear in the near infrared at 4532 and 6060 cm^{-1}.[9] In this study, the 4532 cm^{-1} band is preferred for quantitative use because a near total loss of signal occurs at the higher frequency for systems equipped with a Ge–KBr beamsplitter and HgCdTe detector. Near infrared spectra of Epon 1001F, Epon 1002F, Epon 1004F, Epon 1007F, and Epon 1009F are presented in Figure 1. All spectra are shown here as they appear for concentrations of approximately 0.01 g resin/mL chloroform. The epoxy

absorbance at 4532 cm^{-1} is situated well within the chloroform solvent window of 4750–4450 cm^{-1}. Bands at 4682, 4626, and 4570 cm^{-1} correspond to other polymer vibrations. Because the concentrations, based on total resin mass, were held constant for all systems within this illustration, the intensity of neighboring bands remain the same. As a result, the decrease in the epoxy absorbance at 4532 cm^{-1} can be correlated with increasing epoxide equivalent weight as shown in Table I.

The contribution of the shoulder at 4570 cm^{-1} remains a source of interference. This may cause errors when monitoring solutions of resins with very low epoxide content and high molecular weight. Spectral subtraction could be used to remove this band from the spectrum if an appropriate reference spectrum were available. The reference, in this instance, would require a molecular skeletal structure identical to the epoxy resin but without epoxide. Hence, the alkanolamine diadducts of the epoxy resins were synthesized. Near infrared spectra of Epon 1001F and its corresponding alkanolamine diadduct are presented in Figure 2. The bands at 4682, 4626, and 4570 cm^{-1} do not
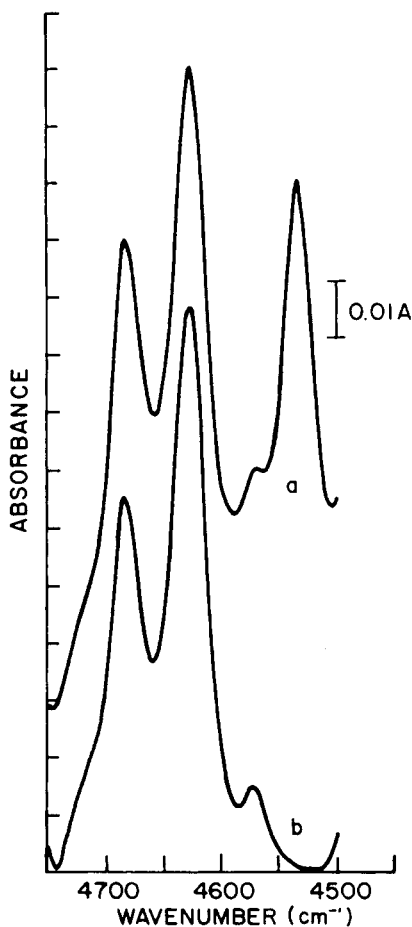

Fig. 2. Near infrared spectra of chloroform solutions of (a) Epon 1001F (21.8 meq epoxide/L) and (b) its corresponding alkanolamine diadduct (0.025 g/mL).
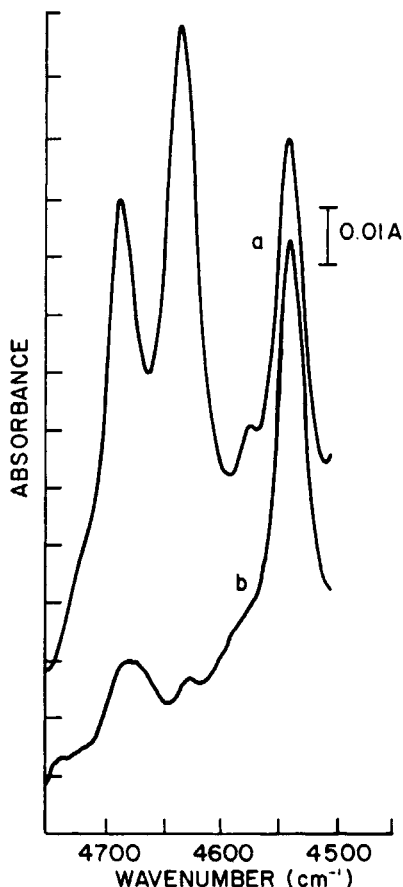
Fig. 3. Spectrum of (a) Epon 1001F (21.8 meq epoxide/L) and (b) corresponding spectrum after removal of phenyl bands by computer subtraction of the alkanolamine diadduct.

change in the diadduct reaction and are present in both spectra. The 4532 cm^{-1} band is apparent only in the epoxide, providing further evidence that it is attributable to this functionality.

Through the spectral subtraction of spectrum of the appropriate amine adduct from the spectrum of the epoxide, the epoxide band at 4532 cm^{-1} was isolated. A spectral window of 4750–4550 cm^{-1} was selected to accomplish the removal of the triad of polymer bands. In Figure 3, spectra of an epoxy resin before and after subtraction are presented. The shoulder band at 4570 cm^{-1} was clearly removed in the final spectrum. The 4532 cm^{-1} band was smoothed by a third-order polynomial function, baseline corrected, and integrated within the spectral window of 4570–4505 cm^{-1}. The spectra of the five resin systems under study were treated in this manner, and the results of the subtraction are displayed in Figure 4. Each spectrum had been independently analyzed several times to obtain a standard deviation for the data manipulation part of the method. Results are presented in Table I.

Spectra for one epoxy system, Epon 1001F, with epoxide equivalent concentrations corresponding to those of the other resins in Table I were treated in similar fashion. For these spectra, the amine adduct of Epon 1001F was used throughout the spectral subtraction procedure. Results of this concentra-
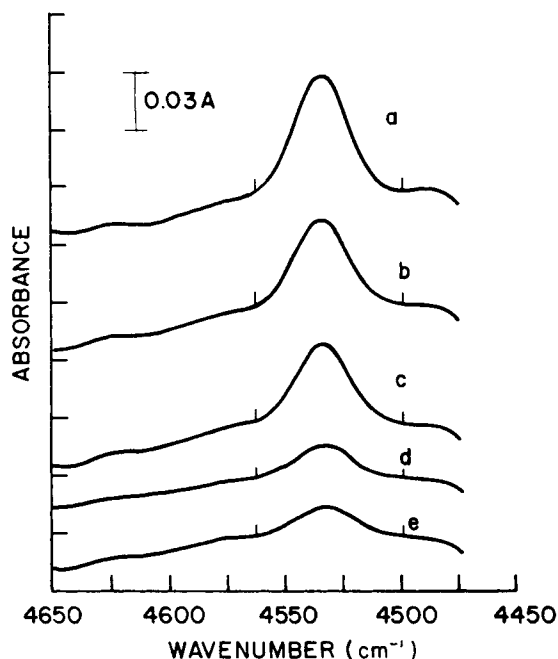
Fig. 4. Spectra of epoxide bands at 4532 cm^{-1} isolated by computer subtraction of alkanola-mine diadducts. Hash marks indicate integration endpoints: (a) Epon 1001F; (b) Epon 1002F; (c) Epon 1004F; (d) Epon 1007F; (e) Epon 1009F.

tion study are presented in Table II. In both the concentration study and the varied resin study, the standard deviation remains below 3% for concentrations approaching 3.5 meq/L in a 20 mm pathlength cell.

The mean integrated areas and corresponding epoxide concentrations found in Table I were then treated to linear least squares analysis. By this method, the five points fit a regression line of slope 0.4690 ± 0.2030 area units L/meq and a y-intercept 0.1028 ± 0.2677 area units. Data from the concentration study in Table II were similarly treated and resulted in a slope 0.4725 ± 0.0128 area units L/meq and a y-intercept 0.0068 ± 0.1681 area units. For the

TABLE II

Computer Integrated Areas of the Terminal Epoxide Band at 4532 cm^{-1} Obtained from Spectra of Varied Concentrations of Epon 1001F in Chloroform (HgCdTe Detector)

Concentration (meq/L)[a]	Integrated area (a.u.)[b]
20.7	9.74
15.4	7.24
12.8	6.20
4.38	2.08
3.84	1.76

[a] Obtained by individual weighings of Epon 1001F followed by dissolution in chloroform. Concentration values are derived from the epoxy equivalent weight supplied for the resin by the manufacturer.[11]

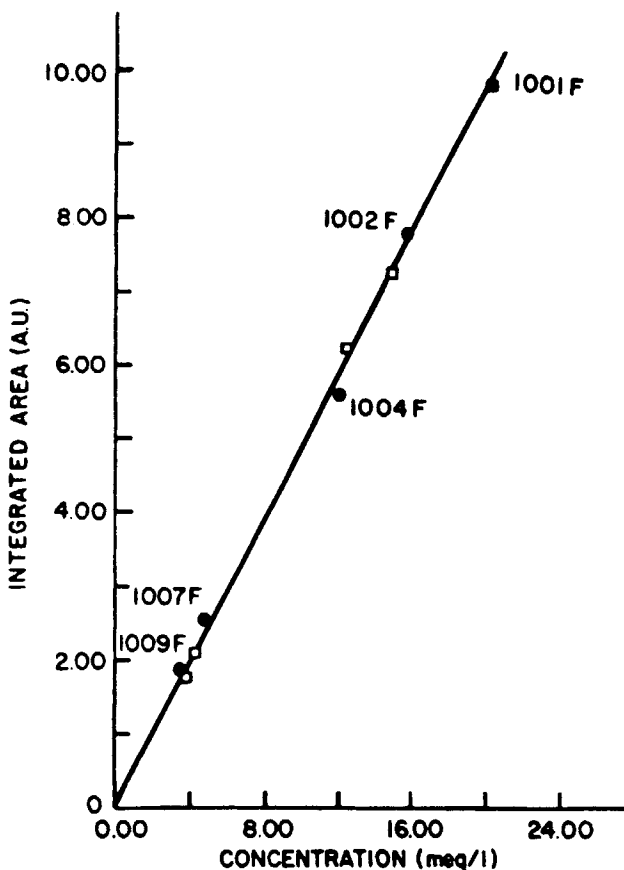[b] Mean of three determinations; better than 0.5% precision.

Fig. 5.   Response curve relating computer integrated areas of the 4532 cm^{-1} epoxide band to varied concentrations of Epon 1001F in chloroform (□) and corresponding epoxide concentrations of various Epon resins in chloroform (■, ●).

concentration study, the y-intercept more closely approached the origin than the study using a variety of resins. However, in both cases, the origin lies within one standard deviation of the intercept.

A linear regression plot was drawn from the Epon 1001F concentration study data (Fig. 5). Data from the varied resin study in Table I were also included on the plot. Concentrations for the varied resin solutions were

TABLE III

Concentration Results (meq Epoxy/L Chloroform) for Various Commercial Epoxide Resins Obtained from Perchloric Acid Titrations[11] and Near Infrared Spectroscopic Techniques

Sample	Spectroscopic method	Titrimetric method	R[a]
Epon 1002F	16.3	16.1	0.1
Epon 1004F	11.8	12.2	−0.1
Epon 1007F	5.13	4.81	0.2
Epon 1009F	3.80	3.65	0.1

[a] Residuals for the titrimetric method as a result of linear regression plot.

calculated from the equation of the line from the concentration study in Figure 5. These results are compared in Table III with the concentration values based on epoxy equivalent weights obtained by the perchloric acid titrations performed by the manufacturer.

CONCLUSIONS

In both the varied resin and the concentration studies, a linear response is found for the epoxy concentration range 3.6–20.7 meq/L chloroform in a 20 mm cell pathlength. The slopes for the two studies agree within the standard deviations. In both instances the intercepts are found at the origin within statistical limits.

Deviation from the linear regression plot, however, is greater for the varied resin study, as shown in Figure 5. Concentration values for each individual resin in this study are dependent upon equivalent weight values obtained by the perchloric titrimetric method. In the serial concentration study, however, all concentration values are based upon the single epoxy equivalent weight value for Epon 1001F. Matrix effects may contribute to this deviation in the varied resin study. Furthermore, examination of the residuals calculated for the titrimetrically derived concentrations in Table III, as related to the linear regression plot of the concentration study, display a random deviation. This suggests that minor experimental errors in the perchloric acid technique may contribute to this variation.

Several curing agents and solvents used in commercial formulations were studied for spectral interference in the epoxy band window of 4565–4500 cm^{-1}. The following displayed transparency in this region: Dowanal DPM, methyl isobutyl ketone, dioctyl phthalate, Genamide 250, and hexyl cellosolve. Thus, in contrast to their interference in titrimetric reactions, their interference in the near infrared method was negligible. Resin formulations may be analyzed by the above technique when additives demonstrate similar transparency.

The above procedure may also be extended to studies involving solid epoxy resin films. The chemical inertness of glass and quartz make these materials ideal windows to support the films for curing studies in the near infrared. Thickness-dependent interferences must be considered, however, in this instance.

The installation of a calcium fluoride beamsplitter coupled with an indium antimonide detector would expand the near infrared region to 8000 cm^{-1} to enable quantitation at higher frequencies. This combination, however, is not as commonly available as the one employed in this study.

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