A Study of Reaction Kinetics by Near-Infrared Spectroscopy. 2. Comparison with Dielectric Spectroscopy of Model and Multifunctional Epoxy/Amine Systems

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ABSTRACT: An investigation of the kinetics of two non-polymer-forming epoxy/amine model systems and a polymer-forming multifunctional epoxy/amine formulation was carried out by dielectric and near-infrared (near-IR) spectroscopy. Dielectric measurements were performed in the frequency range where polarization by charge migration is the dominant mechanism and the extent of reaction was calculated from the measured variation in impedance during reactions. Near-IR spectroscopy was carried out in the frequency range between 7100 and 4000 cm^{-1}, and the extent of reaction was evaluated from the changes in the characteristic absorption peaks. Kinetic results determined by dielectric and near-IR spectroscopy were in excellent agreement for all systems investigated.

I. Introduction

In-situ real time monitoring of physical and chemical changes in polymer-forming and non-polymer-forming materials is an area of vigorous research activity of both fundamental and applied nature. The information collected in-situ by sensors is used for real time quantitative evaluation of fundamental changes in the system parameters, which are selected and designed to guide the process along an optimum path.

Two techniques have been identified, for reasons given below, as particularly attractive for probing in-situ the chemical and physical changes during processing of reactive organic materials: near-infrared (near-IR) spectroscopy and dielectric spectroscopy. A comprehensive account of the use of near-IR spectroscopy for monitoring of reaction kinetics in a model epoxy/amine system is given in the first part of this paper. With regard to in-situ real time monitoring of reactive processes, the major advantage of the near-IR frequency range is that it can be transmitted through silica type optical fibers, which are inexpensive and readily available. The major advantage of dielectric spectroscopy, on the other hand, is its remarkably broad frequency range, between 10^{-5} and 10^{11} Hz, which enables one to focus upon a desired frequency interval and relate the observed dielectric response to specific polarization mechanisms and the corresponding physical phenomena. The literature on dielectric behavior of polymers has been accumulated in several books and key reviews.[1-10] The application of dielectric measurements to in-situ real time monitoring of processing of polymers and composites has been recently reviewed by our group.[11]

A combined use of near-IR and dielectric spectroscopy is of particular interest in monitoring of reactive processes because, together, these two techniques enable one to simultaneously generate complementary information about chemical changes (from near-IR) and physical changes (from dielectric spectroscopy) associated with various phenomena that occur during processing, including gelation, vitrification, crystallization, and various relaxations. A development of the hitherto unavailable fundamental correlations between near-IR and dielectric results with the corresponding chemical and physical changes in the medium on a molecular level is the long-range goal of our current research. The principal objective of this study, which represents the first step in that direction, is to evaluate and compare the reaction kinetics of two non-polymer-forming epoxy/amine model systems and a polymer-forming multifunctional epoxy/amine formulation, using near-IR and dielectric spectroscopy.

II. Experimental Section

Materials. Two non-polymer-forming epoxy/amine model systems were used in this investigation. The first system consisted of 1,2-epoxy-3-phenoxypropane, also known as phenyl glycidyl ether or PGE, and aniline. The second system consisted of PGE and *N*-methylaniline. All model compounds were supplied by Aldrich. The multifunctional formulation was composed of diglycidyl ether of Bisphenol A (DGEBA) epoxy resin (Epon 825, courtesy of Shell Chemical Co.) and 4,4′-methylenedianiline (MDA) curing agent (Aldrich).

Sample Preparation. The stoichiometric amounts of epoxy group and amine hydrogen (2:1 in PGE/aniline, 1:1 in PGE/*N*-methylaniline, and 2:1 in DGEBA/MDA) were mixed at room temperature, heated until a clear mixture was obtained, and tested immediately under isothermal conditions at a series of selected temperatures in the range between 80 and 130 °C.

Techniques. A. Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) was performed using the Nicolet Magna-IR system 750 spectrometer. A detailed description of the experimental procedure is given in part 1 of this paper. For analysis of the multifunctional formulation, the heated cell was modified by introduction of a disposable sample compartment. A leak-proof cuvette was assembled from two glass plates (high-purity silica) measuring 22 × 22 mm. The cuvette was placed inside the heated cell and the resin formulation injected with a syringe.

B. Dielectric Spectroscopy. Dielectric measurements were performed on a Hewlett-Packard Model 4284A Precision

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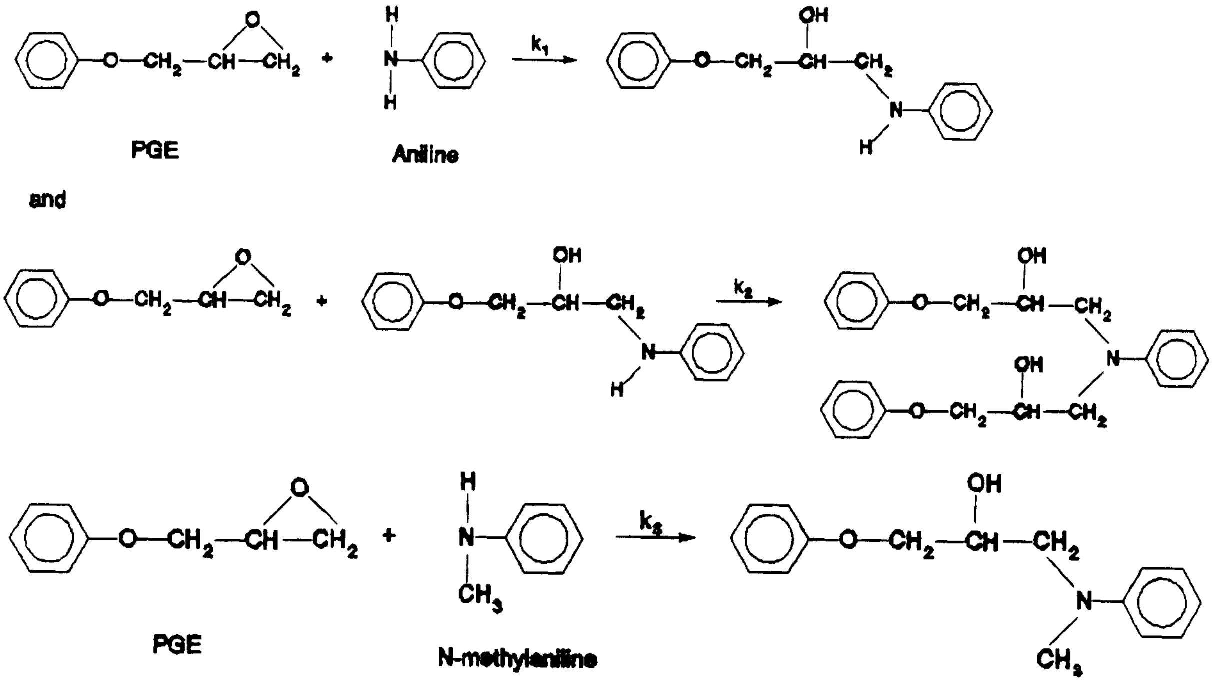


Figure 1. Chemical reactions in PGE/aniline and PGE/*N*-methylaniline systems.

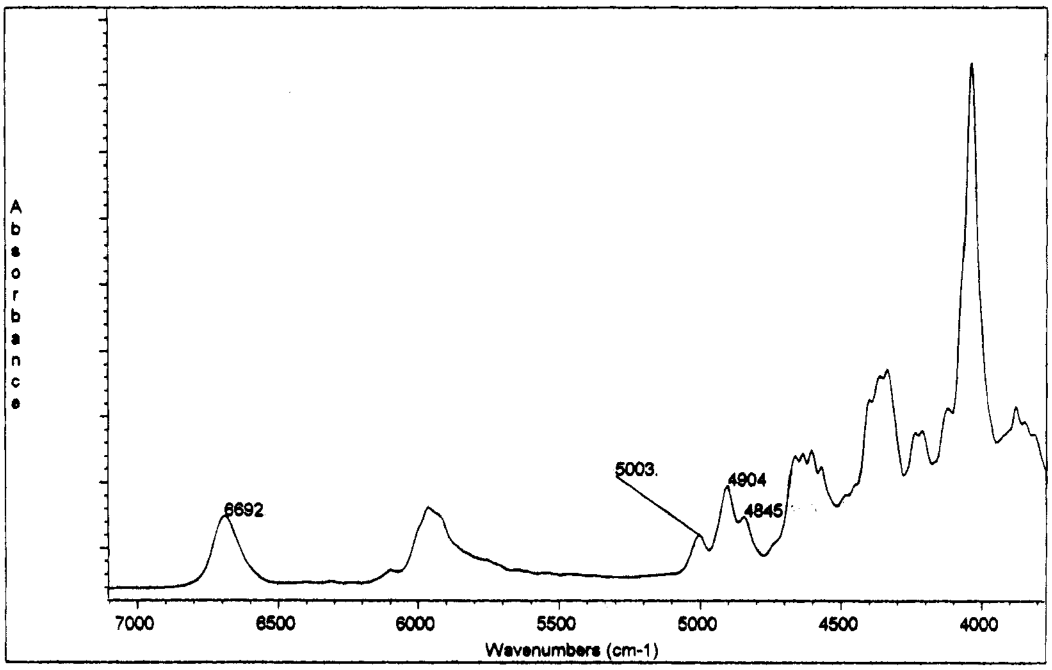


Figure 2. Near-IR spectrum of *N*-methylaniline.

LCR Meter, operable in the frequency range from 20 Hz to 1 MHz. The low limit levels of voltage and current of the test signal are 5 mV and 5 mA, respectively. Our equipment was modified by the addition of a temperature-controlled chamber and was interfaced to peripherals via National Instrument's IEEE 488.2 bus. At each frequency, a low-voltage ac excitation wave was applied to the metallic electrodes and the overall impedance measured. The excitation frequency was varied from the maximum of 10^6 Hz to a minimum value that depended on the time and temperature of the measurement. Ten frequencies were swept in each measurement. For each reaction time, five steps were taken at each of the 10 frequencies. The time required to complete the frequency sweep depended on the lowest value of frequency (f_{min}) employed during the run. The time scale of the experiment was negligible in comparison with the time scale of the changes in the reactive system; hence, each measurement could be taken to represent an isostructural state. The measuring cell consisted of two glass slides separated by a 1.6-mm-thick Teflon shim. Thin aluminum electrodes, with surface areas of 4 cm^2, were placed on each glass plate. The cell constant, $K = S/L$, was equal to 25. The same temperature control described in the NIR section was applied here. During tests, the cell was vertically held to allow for resin shrinkage (less than 2%) without altering the distance between electrodes, and hence avoiding its effect on the measurement.

C. High-Performance Liquid Chromatography (HPLC). High-performance liquid chromatography (HPLC) was utilized as a complementary tool in generating supporting evidence. The analysis was performed on a Perkin-Elmer LCI laboratory computing integrator equipped with a reverse C18 column. Gradient elution of the acetonitrile–water mixture was utilized at a constant flow rate of 2 mL/min for about 20 min. Further details of the experimental procedure are given elsewhere.[12]

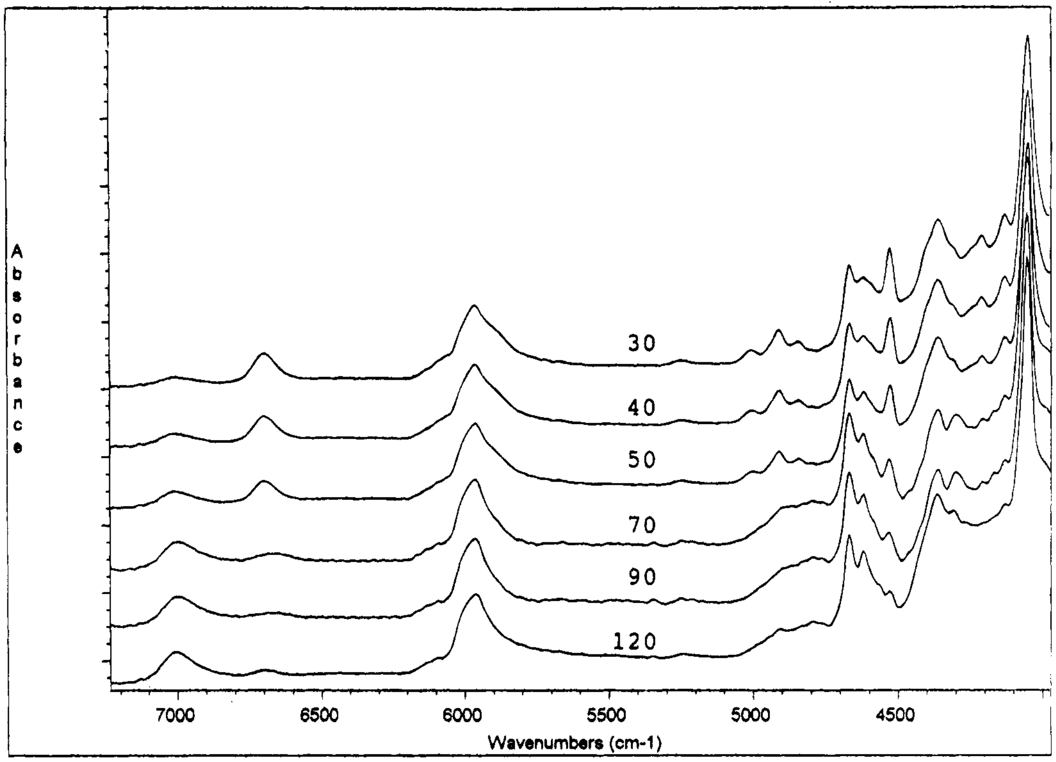


Figure 3. Near-IR spectra of a PGE/*N*-methylaniline system during reaction at 115 °C, with reaction time as a parameter.

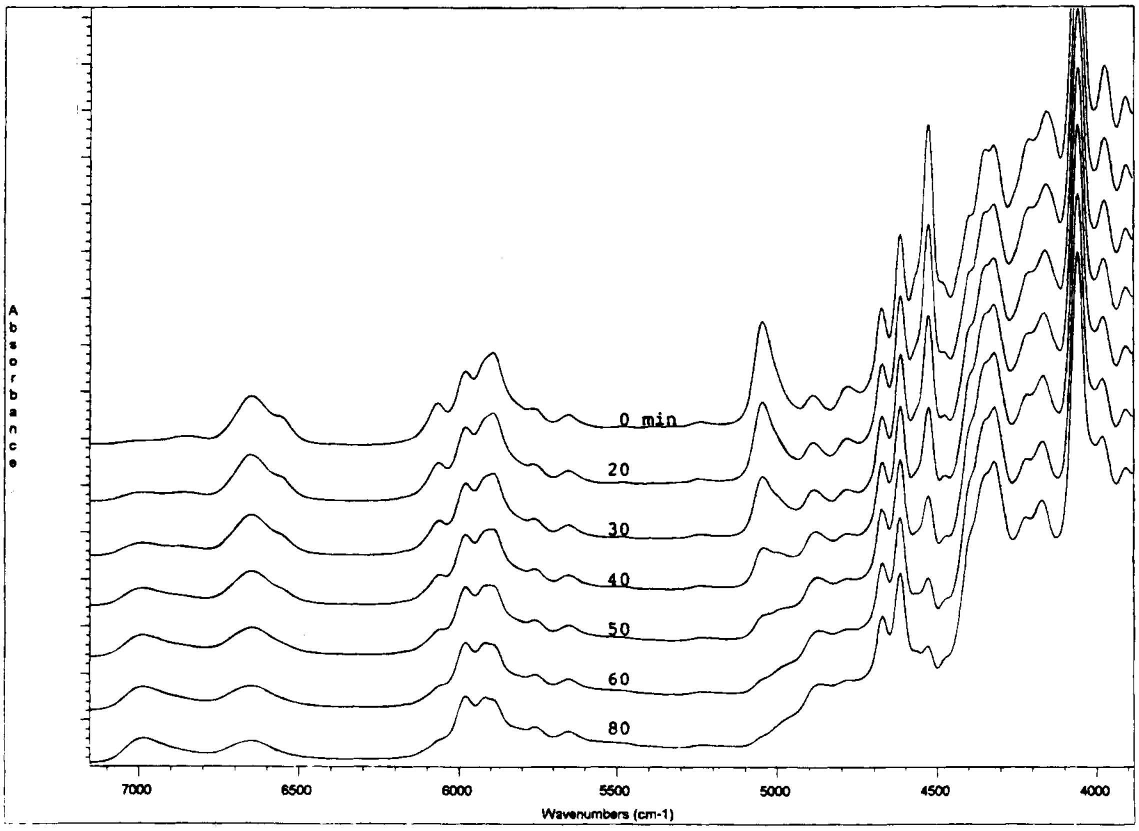


Figure 4. Near-IR spectra of a DGEBA/MDA system during reaction at 90 °C, with reaction time as a parameter.

III. Results and Discussion

The presentation of results is divided into five sections. The first section contains a brief reference to reaction schemes. An account of the location and origin of near-IR band assignments and a description of evaluation of kinetic results from near-IR spectra are given in section 2. Kinetic analyses based on impedance spectroscopy and HPLC measurements are described in sections 3 and 4, respectively. A comparative evaluation of kinetic results for all systems by different techniques is given in section 5.

1. Reaction Schemes. The reactions between PGE and aniline, and PGE and *N*-methylaniline, are shown schematically in Figure 1. The epoxy group reacts with

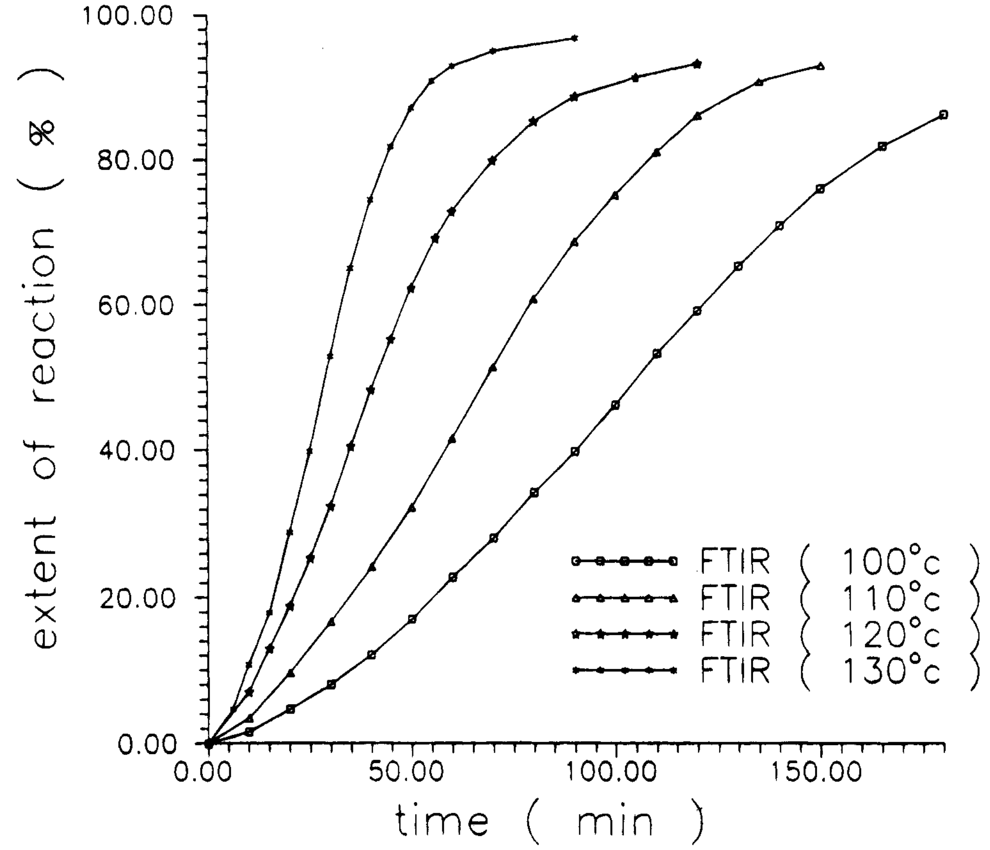


Figure 5. Extent of reaction as a function of time, with temperature as a parameter, for a PGE/*N*-methylaniline system.

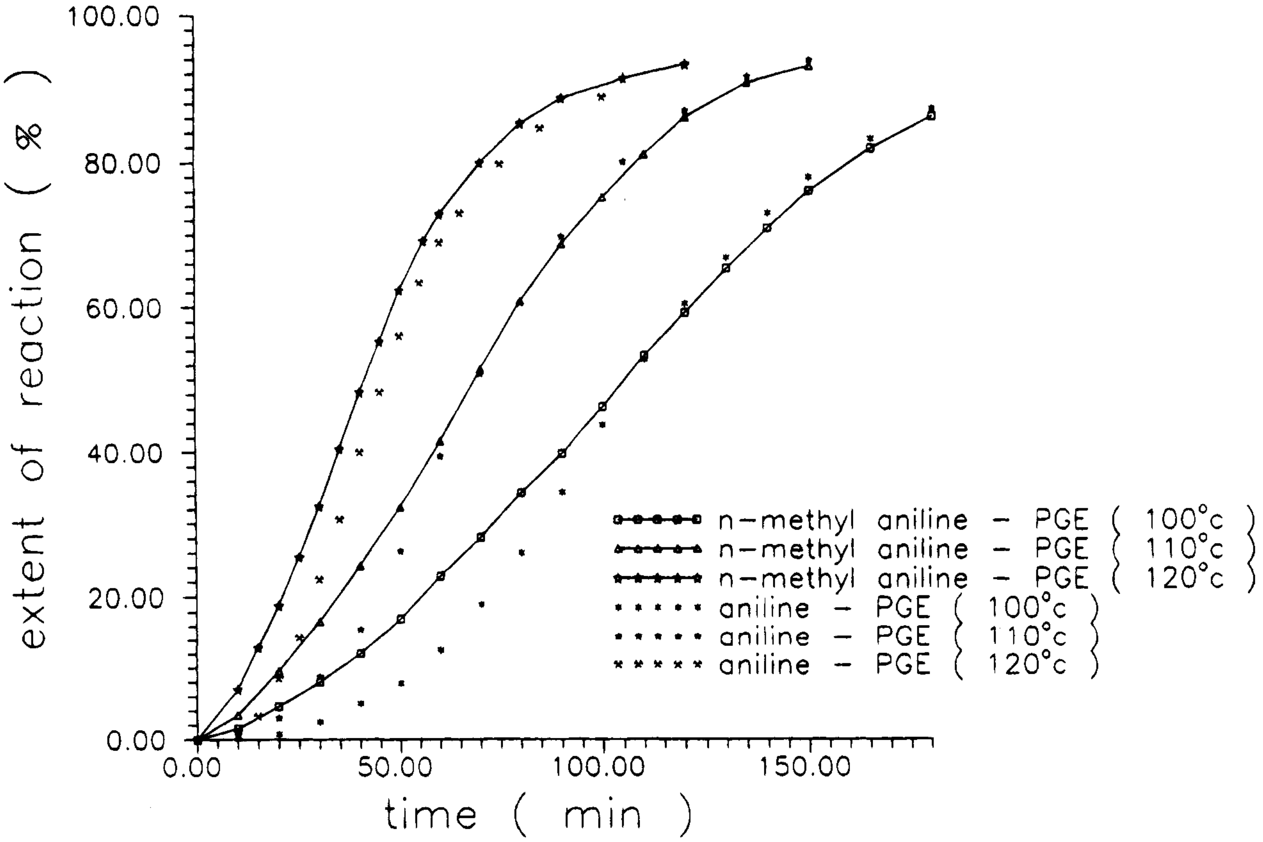


Figure 6. Comparison of extent of reaction in PGE/aniline and PGE/*N*-methylaniline systems at several temperatures.

a primary amine to form a secondary amine which, in turn, reacts with another epoxy to form a tertiary amine. The reaction schemes of Figure 1 are intended only as an illustration of the events that occur on the molecular level; the exact mechanism and the chemorheological aspects of epoxy/amine reactions, both in model systems and in multifunctional formulations, have been studied extensively over the years (e.g., ref 12 and

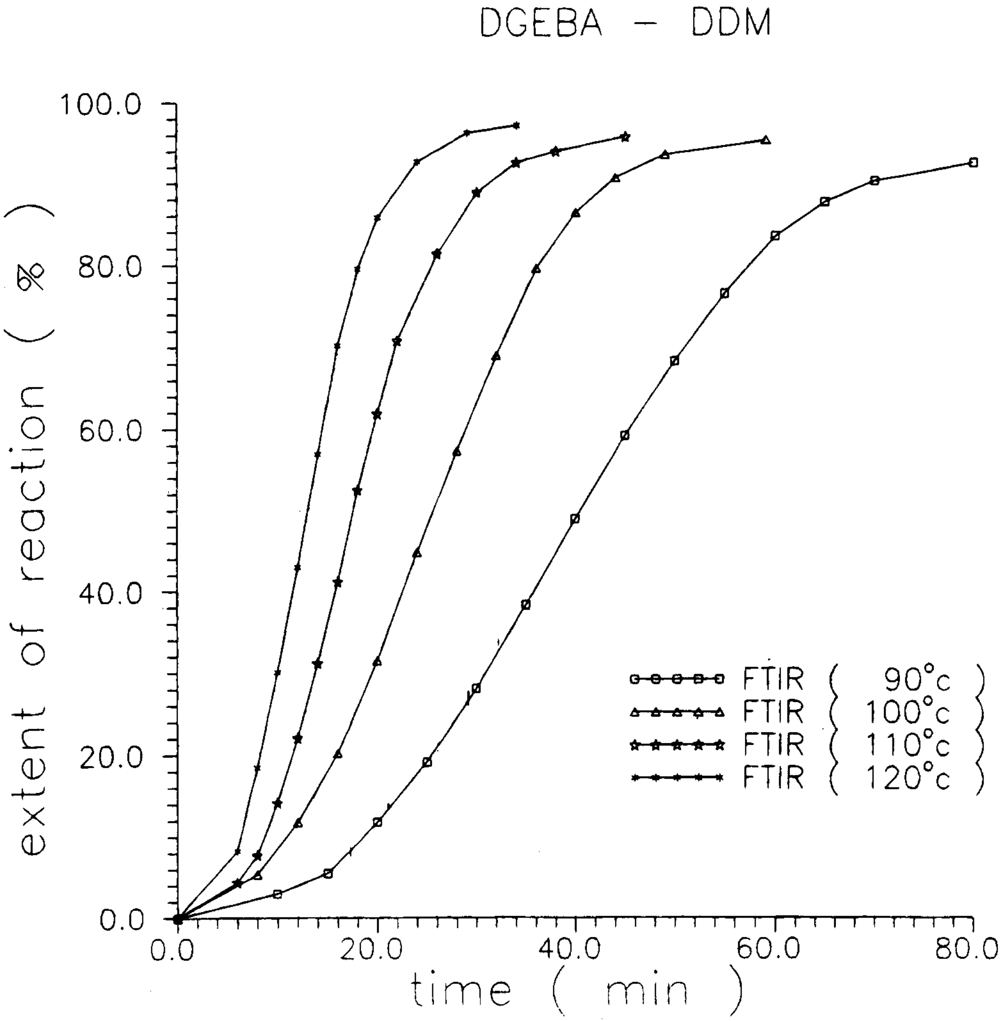


Figure 7. Extent of reaction as a function of time, with temperature as a parameter, for the DGEBA/MDA system.

references therein) and will not be discussed here. The choice of epoxy/amine systems was based upon the lack of evolution of small molecules during reaction and our considerable experience with the chemorheological behavior of this generic group of materials.

2. Evaluation of Reaction Kinetics from near-IR Spectra. A comprehensive account of the origin, location, and shifts of all major peaks during PGE/aniline reactions in the near-IR spectral range between 4000 and 7100 cm^{-1} was given in the first part of this paper. The trends displayed by major peaks of relevance in epoxy/amine reactions were also evident in PGE/*N*-methylaniline spectra: a decrease in epoxy absorption (4530 and 6080 cm^{-1}); a decrease in amine absorption (5056 and 6670 cm^{-1}); an increase in hydroxyl absorption (7000 and 4800–4900 cm^{-1}). The peak at 4530 cm^{-1} was again used for quantitative analysis of the disappearance of epoxy groups. Various reference peaks were tried, and the most reproducible results were obtained using the peak due to the C–H stretching vibration of the benzene ring at 4673 cm^{-1}. Figure 2 shows a spectrum of *N*-methylaniline, which differs from that of aniline principally by the location of N–H absorption bands. Secondary amines are characterized by a single absorption peak at ca. 6700 cm^{-1} due to N–H stretching vibrations. The combination band peaks in secondary amines appear as a three-neck crown in the region between approximately 4850 and 5000 cm^{-1}. The disappearance of these peaks is of the first-order kinetically, which supports the hypothesis of their secondary amine origin. A detailed kinetic study was performed, but only its major findings are briefly stated below. The peak at 5005 cm^{-1} was found to vary analogously to the epoxy peak at 4530 cm^{-1}, and hence it could be used to follow the reaction kinetics. The peak at 6700 cm^{-1} was characterized by a curious increase in absorption intensity during the initial stage of reaction, while, simultaneously, the epoxy peak decreased by about 12%. Beyond that point, however, the two peaks continued to decrease at identical rates. A series of spectra taken at various times during PGE/*N*-methylaniline reaction at 115 °C are shown in Figure 3. Equally systematic and reproducible changes were observed in a multifunctional system, as exemplified by a series of spectra generated during cure at 90 °C and shown in Figure 4. Non-polymer-forming and polymer-forming systems contain basically the same functional groups, and their spectra appear almost identical. A slight difference in the "fingerprint" region and around 6000 cm^{-1} is believed to be due to the variations in architecture involving –CH, –CH$_2$, and –CH$_3$ groups. Only two peaks were present in the PGE/aniline system and absent in the multifunctional formulation; at 4586 and 4300 cm^{-1}.

The extent of reaction (α) at any time *t* is calculated from the initial areas of epoxy and reference peaks, $A_{e,0}$ and $A_{r,0}$, respectively, and their corresponding values at time *t*, $A_{e,t}$ and $A_{r,t}$, according to the following equation:

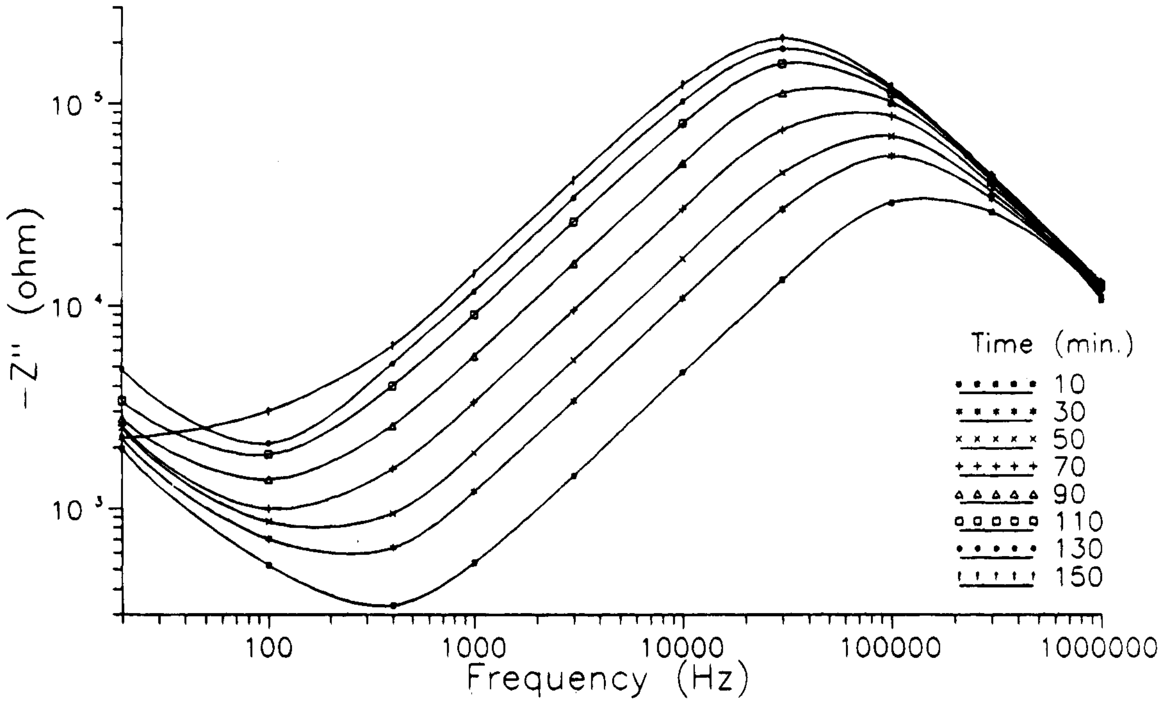


Figure 8. Imaginary impedance as a function of frequency for PGE/*N*-methylaniline reacted at 110 °C, with reaction time as a parameter.

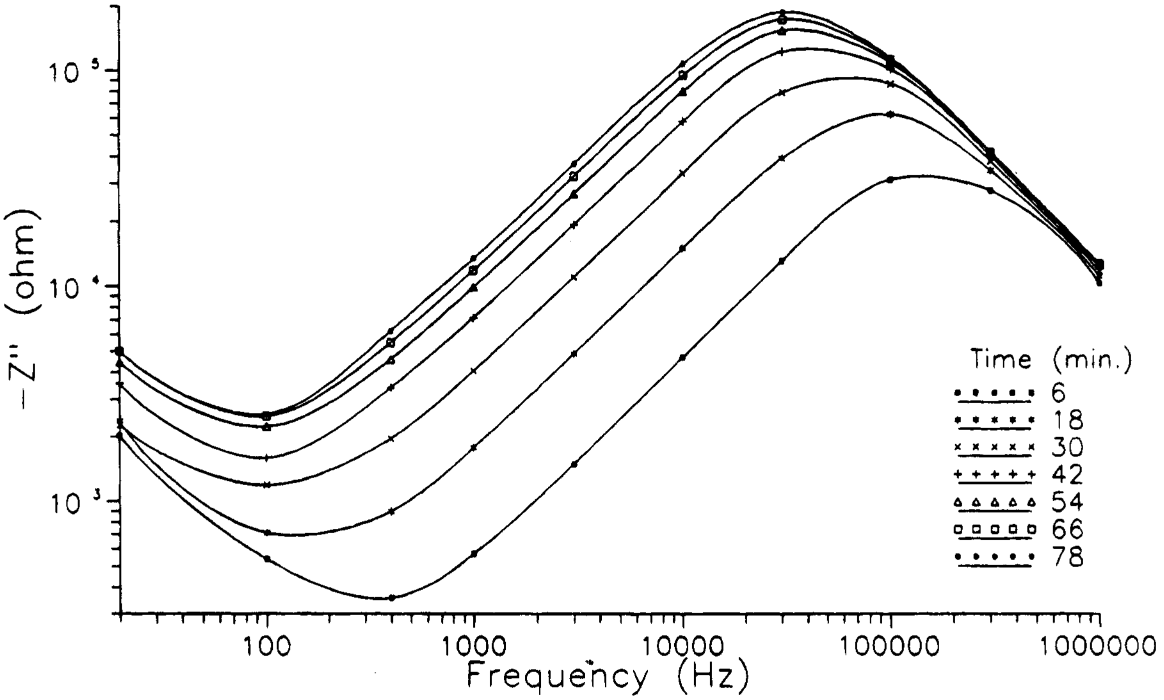
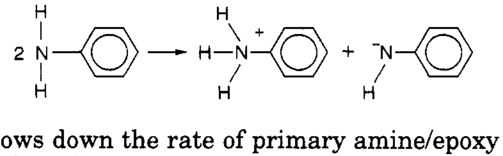


Figure 9. Imaginary impedance as a function of frequency for PGE/*N*-methylaniline reacted at 130 °C, with reaction time as a parameter.

$$\alpha = 1 - [(A_{e,t})(A_{r,0})]/[(A_{e,0})(A_{r,t})] \qquad (1)$$

Extent of reaction as a function of time, with temperature as a parameter, for PGE/*N*-methylaniline systems, is plotted in Figure 5. Results for PGE/aniline and PGE/*N*-methylaniline are replotted together in Figure 6, to facilitate direct comparison between the reaction kinetics of these two systems. An interesting and intuitively unexpected observation concerns the faster initial rate of reaction in the PGE/*N*-methylaniline system, which contains only secondary amines from the onset of reactions. However, beyond approximately 30% conversion, the PGE/aniline reaction rate becomes faster than that of PGE/*N*-methylaniline, allowing the extents of reaction of these two systems to become commensurate. One possible cause for the observed difference in the initial rate could be traced to the autoprotonization of aniline, which proceeds according to the scheme:



(2)

and slows down the rate of primary amine/epoxy reaction. This effect diminishes with decreasing concentra-

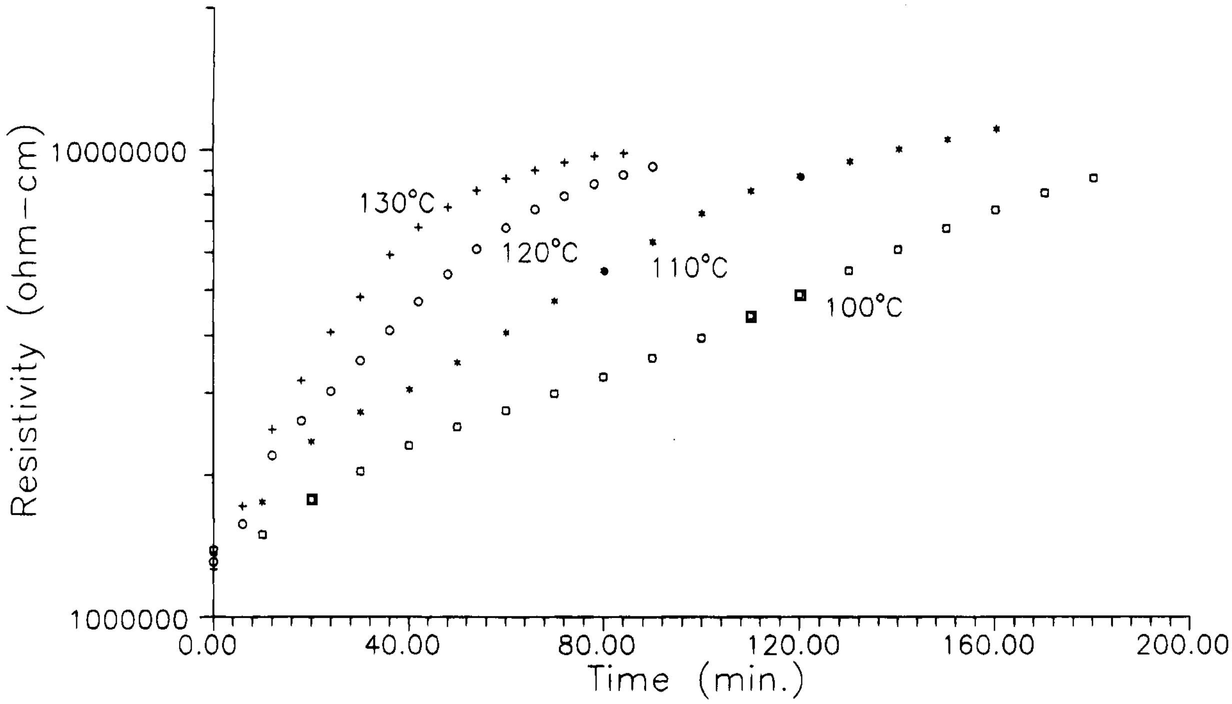


Figure 10. Resistivity as a function of time, with temperature as a parameter, for a PGE/*N*-methylaniline system.

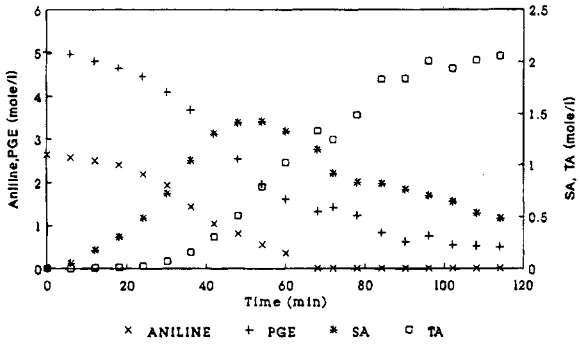


Figure 11. Concentration of various groups as a function of time during PGE/aniline reaction at 120 °C.

tion of primary amine during reaction and with increasing temperature. The likelihood of aniline autoprotonization decreases above 30% conversion to the point where the reactivity of aniline exceeds that of *N*-methylaniline, primarily as the result of steric hindrance due to the methyl group on the latter. Extent of reaction as a function of time, with temperature as a parameter, for multifunctional formulation (DGEBA/MDA), is shown in Figure 7.

3. Evaluation of Reaction Kinetics from Dielectric Spectra. Our methodology here was based on the use of real and imaginary components of impedance to monitor the progress of reactions. Changes in impedance measured herein were representative of the variation in the contribution of migrating charges to the overall polarization and were modeled using equivalent circuitry. Details of our experimental and analytical methodologies are presented elsewhere[13-16] and are only highlighted below. Migration of extrinsic and/or intrinsic charges is a dissipative process which is modeled by the resistance. A single resistance that encompasses the dissipative contribution of all migrating charges, extrinsic and/or intrinsic alike, is sufficient in the model because the dissipative contributions due to electrode polarization and dipolar relaxations fall outside the experimental frequency range utilized in this study. The single capacitance, on the other hand, measures the overall ability of the dielectric material to store energy in the form of electric field. Thus an R–C parallel circuit, its simplicity notwithstanding, represents an adequate phenomenological model of the dielectric response of our systems at those frequencies.

By expressing impedance (Z^*) in terms of its real (Z') and imaginary (Z'') components, we obtain:

$$Z = Z' = jZ'' \tag{3}$$

$$Z^* = [1/R + j\omega C]^{-1} \tag{4a}$$

$$Z' = \frac{R}{1 + \omega^2 C^2 R^2} \tag{4b}$$

$$Z'' = \frac{\omega C R^2}{1 + \omega^2 C^2 R^2} \tag{4c}$$

Quantitative evaluation of the circuit parameters can be carried out by different routes. The method outlined below is based on the use of imaginary impedance to calculate resistance, and from it resistivity (or conductivity), at any time during reaction. Other methods are based on the Nyquist and Bode plots, and their use in monitoring the progress of epoxy/amine reactions has been discussed in another work by our group.[16] Taking a derivative of Z'' (eq 4c) with respect to angular frequency, we get:

$$\frac{dZ''}{d\omega} = \frac{C R_p^{\,2}\,(1 - \omega^2 R_p^{\,2} C^2)}{(1 + \omega^2 R_p^{\,2} C^2)} = 0 \tag{5}$$

where subscript "p" denotes a parallel R–C circuit. Equation 5 is equal to zero when the following condition is met:

$$\omega = 1/R_p C \tag{6}$$

By combining eqs 5 and 6, we obtain:

$$Z''_{\max} = R_p/2 \tag{7}$$

and thus the unknown resistance, R_p, is obtained directly from $Z''_{\max}$.

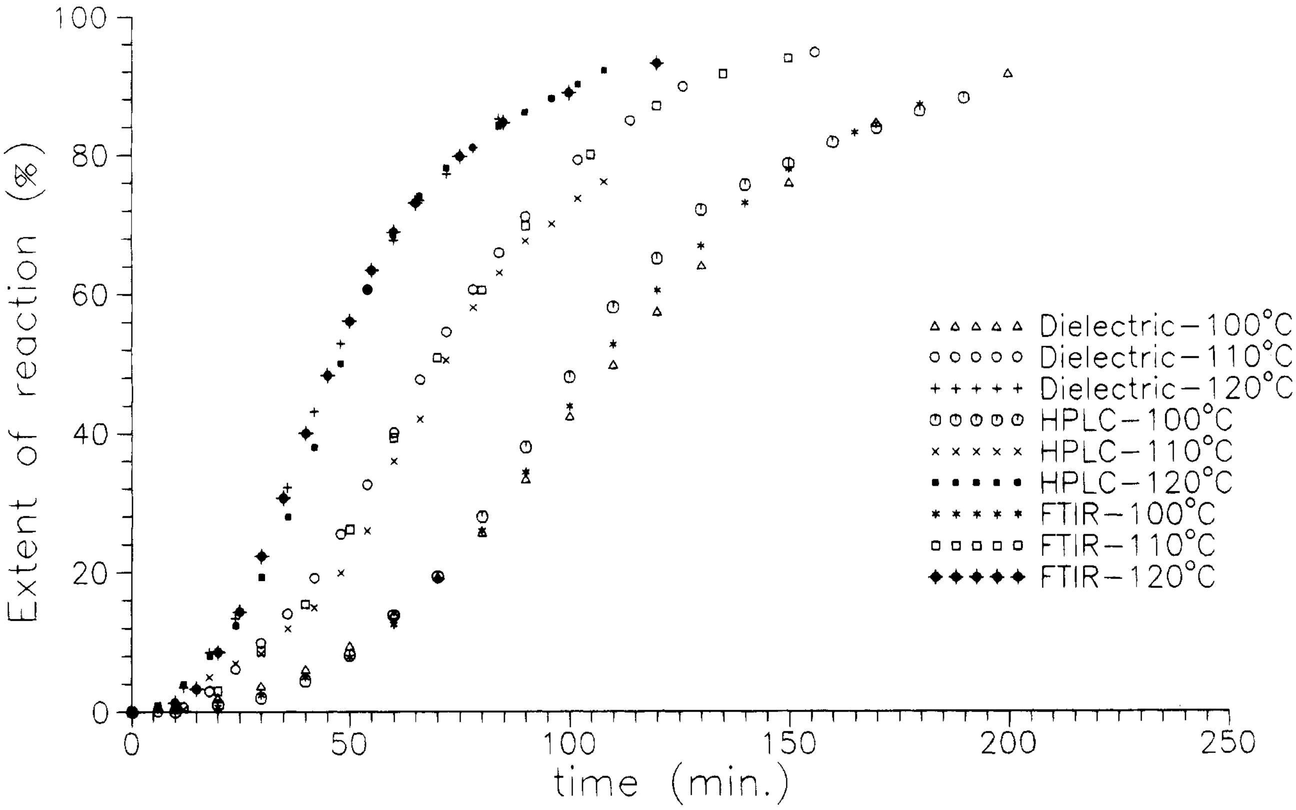


Figure 12. Comparison of extent of reaction as a function of time in a PGE/aniline system at several temperatures, calculated from dielectric, near-IR, and HPLC measurements.

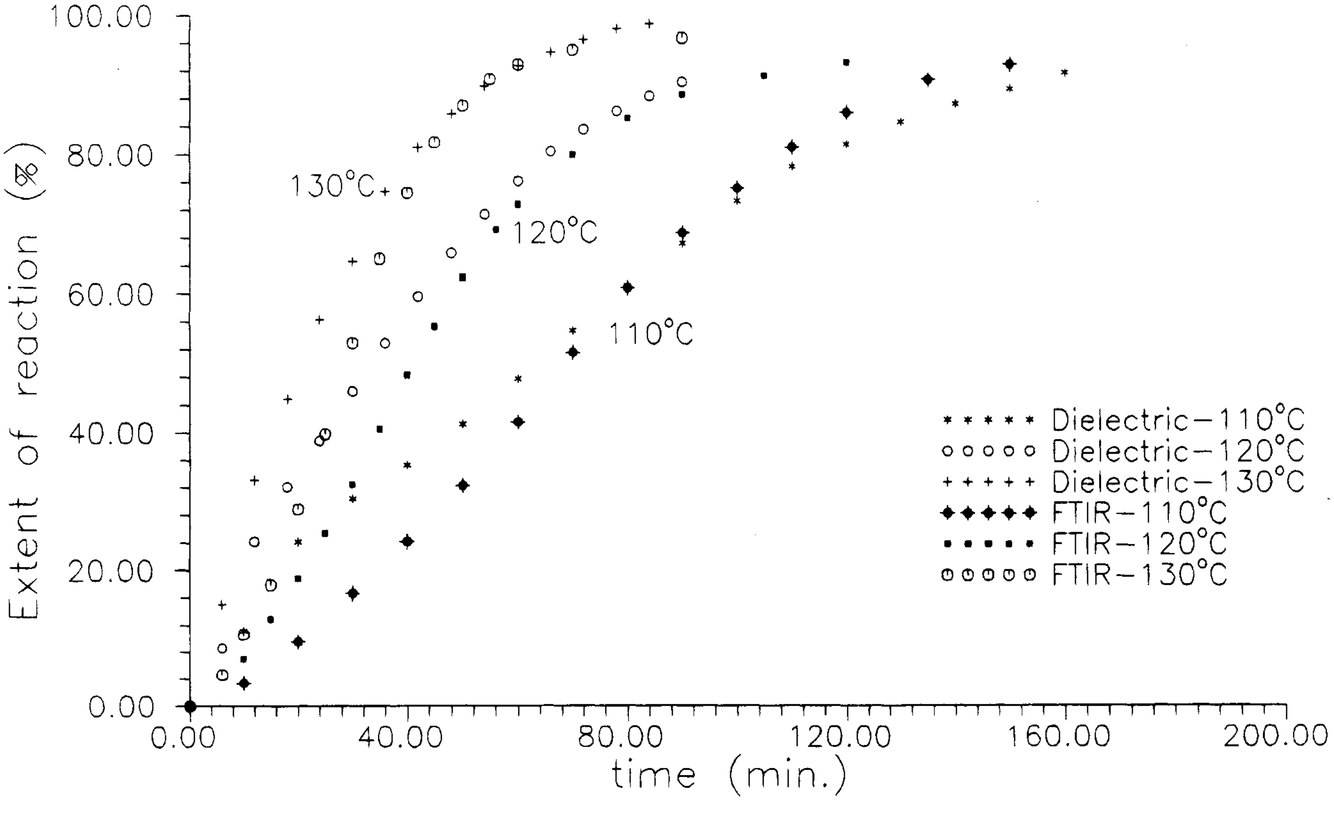


Figure 13. Comparison of extent of reaction as a function of time in a PGE/*N*-methylaniline system at several temperatures, calculated from dielectric and near-IR measurements.

Examples of plots of imaginary impedance as a function of frequency, with reaction time as a parameter, for PGE/*N*-methylaniline reaction at 110 and 130 °C, appear in Figures 8 and 9, respectively. Analogous results were obtained at other temperatures and in other systems, including the PGE/aniline system and the multifunctional DGEBA/MDA formulation. The most striking features of all plots of the type shown in Figures 8 and 9 are the systematic variation of characteristic parameters and a superb reproducibility of the

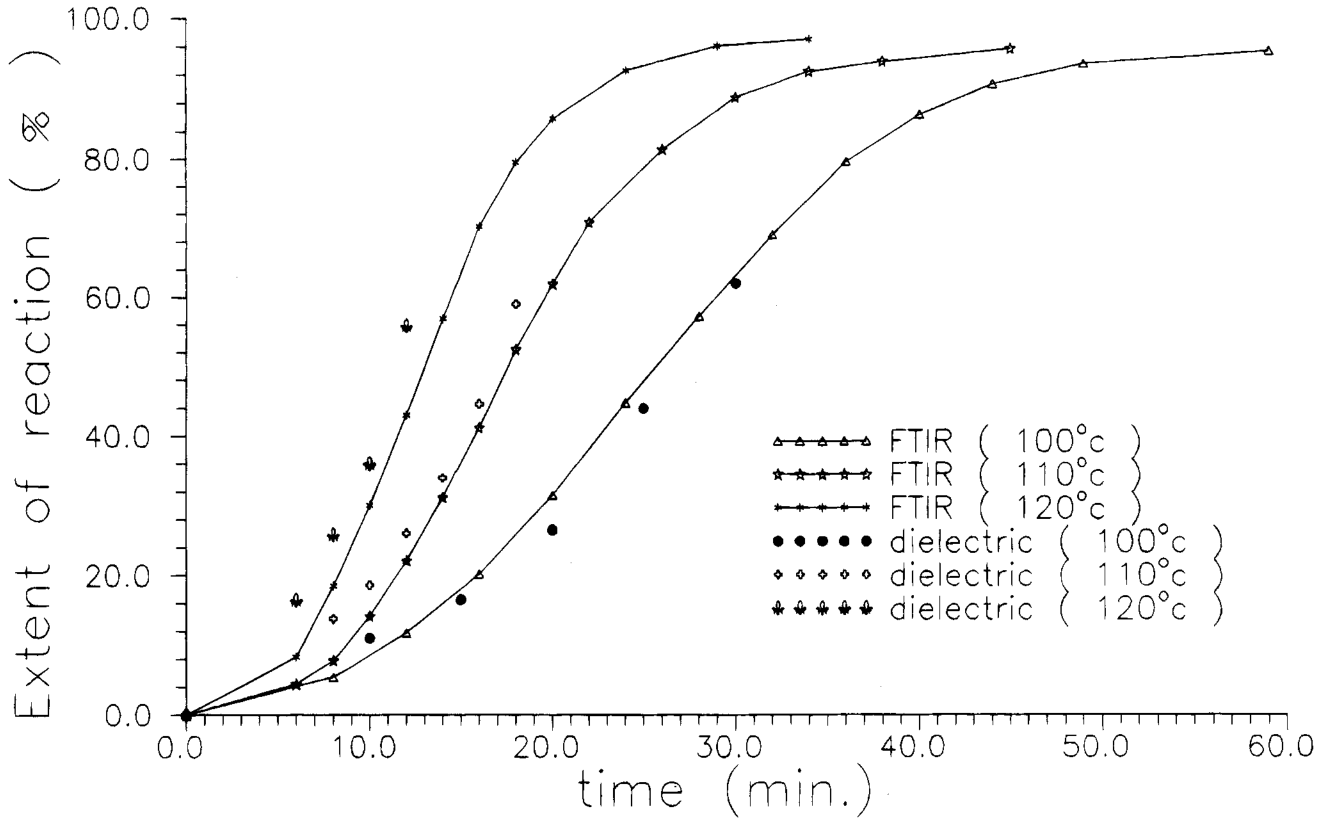


Figure 14. Comparison of extent of reaction as a function of time in a DGEBA/MDA system at several temperatures, calculated from dielectric and near-IR measurements.

measured data.

Once resistance is determined, the apparent resistivity (ϱ) and/or conductivity (σ) due to migrating charges can be calculated from the following equation:

$$\sigma = 1/\varrho = L/R_pS \qquad (8)$$

where $S/L = K$ denotes the cell constant.

An S-shaped resistivity curve was observed at each temperature, characterized by an initial increase in resistivity and the subsequent leveling off to an asymptotic value. An example is shown in Figure 10, where the calculated resistivity of a PGE/*N*-methylaniline system is plotted as a function of reaction time, with temperature as a parameter. The observed trend in resistivity was qualitatively similar to that of extent of reaction, suggesting a correlation between these two parameters. For calculation of extent of reaction from dielectric data we have selected an equation first reported by Keinle and Race[17] and later successfully utilized by Nass and Seferis,[18] and by our group,[14,15] which is of the following general form:

$$\frac{\alpha}{\alpha_m} = \frac{\log \varrho - \log \varrho_0}{\log \varrho_m - \log \varrho_0} \qquad (9)$$

where α_m depicts the maximum (limiting) extent of reaction attainable at a given temperature in a multifunctional system due to vitrification.[19]

4. Evaluation of Reaction Kinetics from HPLC. A typical result of HPLC analysis of PGE/aniline reaction is shown in Figure 11, where concentrations of PGE, aniline, secondary amine (SA), and tertiary amine (TA) are plotted as a function of reaction time at 120 °C. Analogous results were generated at other temperatures. The reproducibility of data was high, the accuracy was further verified by titration, and the deviation in mass balances calculated throughout the reaction never exceeded 5%. The extent of reaction was calculated from the measured concentration and was expressed in terms of the disappearance of epoxy groups.

5. Comparison of Reaction Kinetics by Different Methods. A comprehensive summary of the values of extent of reaction calculated from the data obtained by different experimental methods is presented in Figures 12–14. Dielectric, near-IR, and HPLC results for PGE/aniline reaction at 100, 110, and 120 °C are displayed in Figure 12; dielectric and near-IR results for PGE/*N*-methylaniline reaction at 100, 110, 120, and 130 °C are plotted in Figure 13; and dielectric and near-IR results for DGEBA/MDA cure at 100, 110, and 120 °C are shown in Figure 14. The observed agreement between the results generated by different techniques for a PGE/aniline system (Figure 12) is remarkable! The results for PGE/*N*-methylaniline (Figure 13) show good agreement but are not superimposable. We emphasize, however, that although both normalized extents of reaction must vary from zero to 1 and display the same general trend, they need not be identical since the molecular origin of the two measurements is different. Correlations between dielectric and spectroscopic measurements on a molecular level are, in fact, a major objective of our current research. Another source of discrepancy between the results of different techniques is the variation (however slight) in the thermal history between near-IR and dielectric samples. For instance, a variation as small as ±1 °C in reaching and maintaining the isothermal conditions was found to have a noticeable effect on the kinetics. The same is true for the multifunctional DGEBA/MDA system, depicted in Figure 14, where good agreement was observed between dielectric and near-IR results. Here, dielectric extent of reaction was reported only up to approximately 60% cure, above which the imaginary impedance exceeds the high limiting value of the instrument and hence cannot be experimentally determined. A specially constructed impedance adaptor which allows impedance measurements until the completion of cure has been constructured in our laboratory and its utilization in monitoring cure through gelation and vitrification of bifunctional and tetrafunctional epoxy/amine system has been described in other papers from our group.[14,15]

There are two additional points brought out by this study that deserve further attention. First, near-IR spectroscopy and HPLC measure the chemical state of the matter and as such are conducive to elucidation of reaction mechanisms and development of mechanistic reaction models. The almost identical outcome of kinetic analysis by dielectric measurements indicates that the dielectric response is driven by the same underlying molecular mechanism. At present, however, the nature of the measured dielectric parameters remains phenomenological, as we lack a fundamental understanding of the dielectric response on a molecular level.

Second, the accuracy of calculated results depends critically on the reproducibility and reliability of data which, as alluded to earlier in the text, places a premium on the experimental precision. In that context, we believe that impedance is the most versatile diagnostic tool for real time monitoring of reactive processes by dielectric measurements. FT near-IR spectroscopy is an equally attractive method capable of highly accurate quantitative evaluation of the progress of reaction. FT near-IR spectroscopy appears preferable to FT mid-IR spectroscopy for monitoring the disappearance of epoxy groups during reactions, as discussed in the first part of the paper, and is expected to gain rapidly in popularity as a major process monitoring tool, owing to its compatibility with silica type optical fibers.

IV. Conclusions

We have carried out an investigation of reaction kinetics of two non-polymer-forming epoxy/amine model systems and a thermosetting multifunctional epoxy/amine formulation, using near-infrared (near-IR) spectroscopy and impedance spectroscopy. Characteristic NIR absorption peaks were identified for all systems and used to evaluate the reaction kinetics. Dielectric measurements were carried out under identical processing conditions in the frequency range between 20 Hz and 1 MHz. Extents of reaction calculated from near-IR and dielectric measurements for each system were contrasted and found to be in excellent agreement. That finding was further corroborated by HPLC data. It was concluded that the measured dielectric response, its phenomenological nature notwithstanding, can be used to follow the progress of reactions. It is suggested that a molecular basis of the dielectric response could be further elucidated by seeking correlations with the fundamental molecular events as revealed by near-IR spectroscopy. A combined use of near-IR and dielectric measurements to monitor chemical and physical changes in reactive media offers an attractive approach to insitu real time process control.

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