Cure Rates of Some Epoxy Systems

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Synopsis

The property changes of Epon 828 crosslinked by either diethylenetriamine or *m*-phenylenediamine at several temperatures have been studied by two *in situ* techniques. The mechanical property changes were followed by continuously monitoring the changes in the fundamental frequency of vibration during cure of a resin-coated substrate acting as a cantilever reed. The disappearance of the reactive epoxy group was followed *in situ* by continuously monitoring the absorbance of the infrared epoxide band at 915 cm.$^{-1}$. Correlation of the two techniques was accomplished by normalizing both the mechanical property and infrared data. The apparent energy of activation was calculated to be 10.4 and 11.4 kcal./mole, respectively, for the *m*-phenylenediamine and diethylenetriamine systems by the mechanical technique, and 11.0 kcal./mole for the *m*-phenylenediamine crosslinked system by the infrared technique.

INTRODUCTION

Numerous experimental techniques and results on the study of resin cure rates have been reported in the literature with emphasis on the chemical, physical, and mechanical property changes with cure time.[1–6] Most of the techniques employed are limited in their utility due to the difficulty in handling a curing resin system as it changes in state from liquid to gel to solid. The technique of employing a nonreactive substrate[5,7,8] to support the resin system while monitoring the changes in mechanical properties offers one attractive solution to the problem. Generally, these coated substrate techniques utilize a thin polymer film which prevents direct temperature monitoring of the resin system and may or may not correlate with bulk curing rates. In previous work, infrared transmittance measurements have been used to follow the chemical changes occurring in curing resin systems,[9–11] but no concerted effort has been attempted to correlate infrared cure rates with data derived from mechanical property measurements.

This paper reports the correlation of cure rate data obtained by continuous *in situ* monitoring of mechanical and spectroscopic properties at several temperatures. Close temperature control was maintained in both techniques by monitoring the temperature of the curing resins rather than the surrounding environment. These techniques provided cure data at several temperatures which yielded activation energies higher than that reported by Lewis[6] on an epoxy–diethylenetriamine system. The activation energies for the epoxy–*m*-phenylenediamine system determined by

either method showed close correlation with each other and the literature values.[12]

EXPERIMENTAL

General

Shell Epon 828 was used as the base resin in the epoxy systems studied. This is a diglycidyl ether of bisphenol A with a molecular weight of approximately 350–400. The crosslinking agents used in the curing reactions were Allied Chemical diethylenetriamine (DETA) and Eastman Kodak m-phenylenediamine (m-PLDA). To eliminate concentration errors, all identical resin samples were drawn from the same mix. Batches were made up by weighing both resin and crosslinking agent on an analytical balance to the desired concentration and then blending the two components thoroughly. The m-phenylenediamine was warmed above its melting point prior to blending with the epoxy resin to effect good mixing. Once the batch was thoroughly mixed, aliquot portions were taken and transferred to stoppered test tubes. These test tubes were immediately transferred to a cold box maintained at −40°C. for storage. Prior to the cure rate study, a stoppered test tube was removed from the cold box and allowed to rise to room temperature, the required amount of resin necessary to coat the metallic vibrating reed substrate and to prepare the infrared sample was removed, and the remainder of the mix discarded. Subsequent cure studies at various temperatures were conducted on fresh samples of the master batch following the above procedure. The advancement of the resin caused by heating it to room and cure temperatures was considered insignificant due to the brief time required to reach cure temperature, but could possibly influence the higher temperature cure rates slightly.

Infrared Cure Study

All infrared absorbance data were obtained on a Perkin-Elmer Model 13 double-beam prism spectrophotometer operated in the direct (single-beam) mode. The change in absorbance of the epoxide band at 915 cm.$^{-1}$ was monitored *in situ* by sweeping through the spectral range between 880 and 1000 cm.$^{-1}$ at regular 2-min. intervals. A modified demountable cell assembly was situated in a housing which enclosed the sample holder area of the spectrophotometer. The sample was maintained in the housing at the desired cure temperature by a regulated heater which was controlled by a thermocouple embedded in a resin reservoir in the salt plate in close proximity to the resin film. Considerable variations in cure rates were noted when the technique of embedding the thermocouple in the resin was not used. As further assurance of controlling the temperature accurately, a second thermocouple was embedded in a duplicate resin reservoir and was used to check the temperature periodically by means of a calibrated potentiometer. This control of temperature was necessary to obtain

infrared cure rates which have meaningful correlation with the mechanical cure rate data.

Demountable cells were assembled by using lead spacers between the sodium chloride disks. The thicknesses of the resin films formed were approximately 0.027 mm., as determined by the interference fringe method on the spaced cells prior to filling with the epoxy systems. The spectrophotometer was operated in the single-beam mode with fixed slit widths. The best selection of sample thicknesses and slit widths was determined experimentally to keep transmittance errors for the spectrophotometer at a minimum. The absorbance was determined by using the relationship $A = \log (1/T)$. The transmittance values used to determine absorbances were developed by using the baseline technique.[13]

The epoxy system was warmed to room temperature and introduced to the sample area in the lead spacer as well as the two resin reservoirs. Two thermocouples were inserted into the filled reservoirs, secured, and the demountable cell was assembled. The assembled cell was placed in the sample compartment and the housing put in place. The cell was heated to cure temperature, which required approximately 4 min., dependent on the cure experiment being studied. The change of the 915 cm.$^{-1}$ epoxide band was monitored at 2-min. intervals during the initial cure period and at 10 min. thereafter until no further change occurred. The region of the curve in which no further change in the 915 cm.$^{-1}$ band occurred was considered to be a 100% change in absorbance. By using the zero and 100% time values of absorbances, the per cent change in absorbance was plotted versus time. These normalized plots gave rate curves which are readily comparable to the normalized mechanical rate data.

Mechanical Technique

The changes in the mechanical properties of the curing resin were followed continuously *in situ* by use of a modified vibrating-reed technique. The vibrating-reed apparatus consists essentially of a resin- or polymer-coated metallic cantilever reed which was mounted horizontally. The coated reed was driven into its fundamental frequency of vibration by use of a mechanically linked loudspeaker head driven by a low-frequency oscillator. A pin, mounted on the free end of the cantilever reed, generates a variable amplitude sinusoidal signal as it moves in a linear variable differential transformer (LVDT). The maximum height of the signal produced by the LVDT as a function of frequency was taken as the polymer–substrate resonance frequency, from which data the cure of the polymers was followed by plotting the change of the squared fundamental frequency of vibration (ν^2) of the composite as a function of time.

The resin thickness was 0.040–0.070 in., whereas that of the supporting metallic reed was about 0.010 in. The resin system was brought to a cure temperature by two heaters controlled by a thermocouple immersed in the resin. The thickness of the polymer film influences the height of the curves, as depicted in Figure 1, but does not influence the time required to reach arbitrarily defined time points.
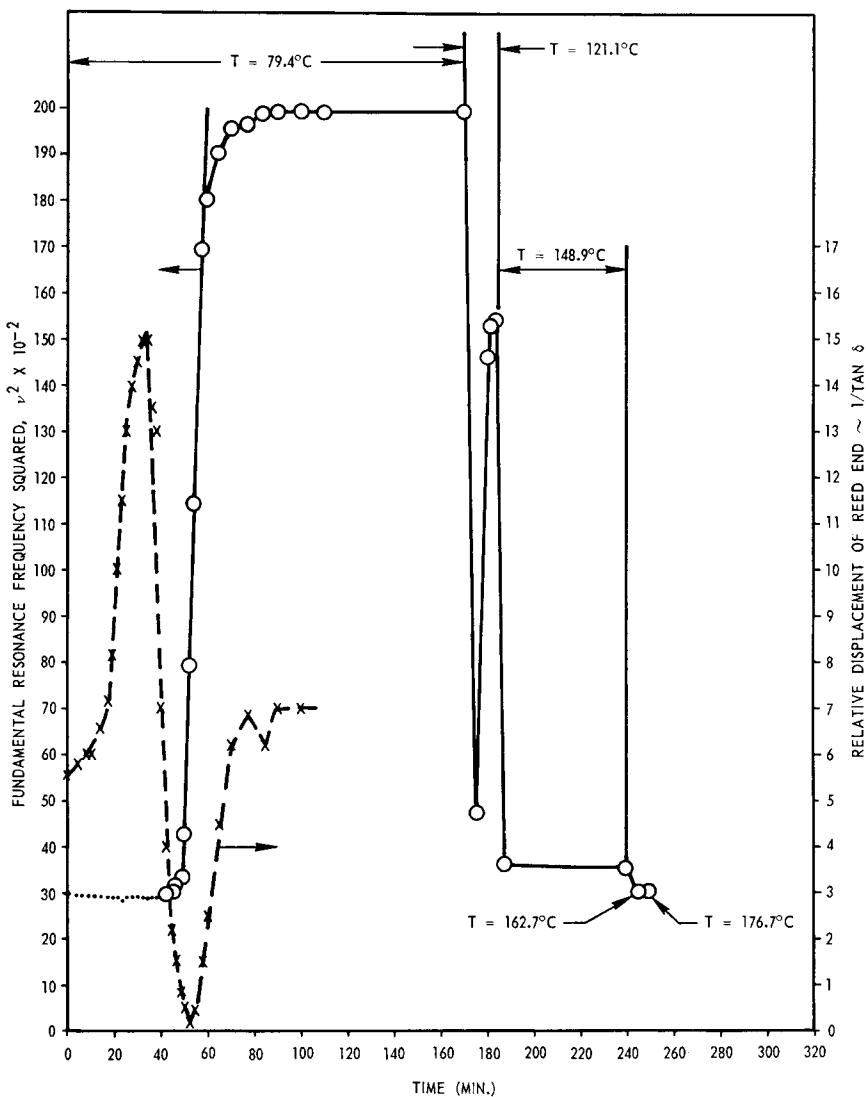
Fig. 1. Relative modulus and displacement as a function of cure time for Epon 828 with 20 phr of m-PLDA.

RESULTS AND DISCUSSION

Figure 1 depicts the results obtained as the squared fundamental frequency of vibration of a polymer-coated substrate was plotted as a function of time at a cure temperature of 79.4°C. In addition, the relative displacement of the free end of the coated reed was plotted as a function of time. This relative displacement of the reed tip is a measure of the damping behavior of the polymer as it passes through its various viscoelastic states. The relative modulus, given by $E'_{dyn} \sim A\nu^2$, was found to be constant dur-
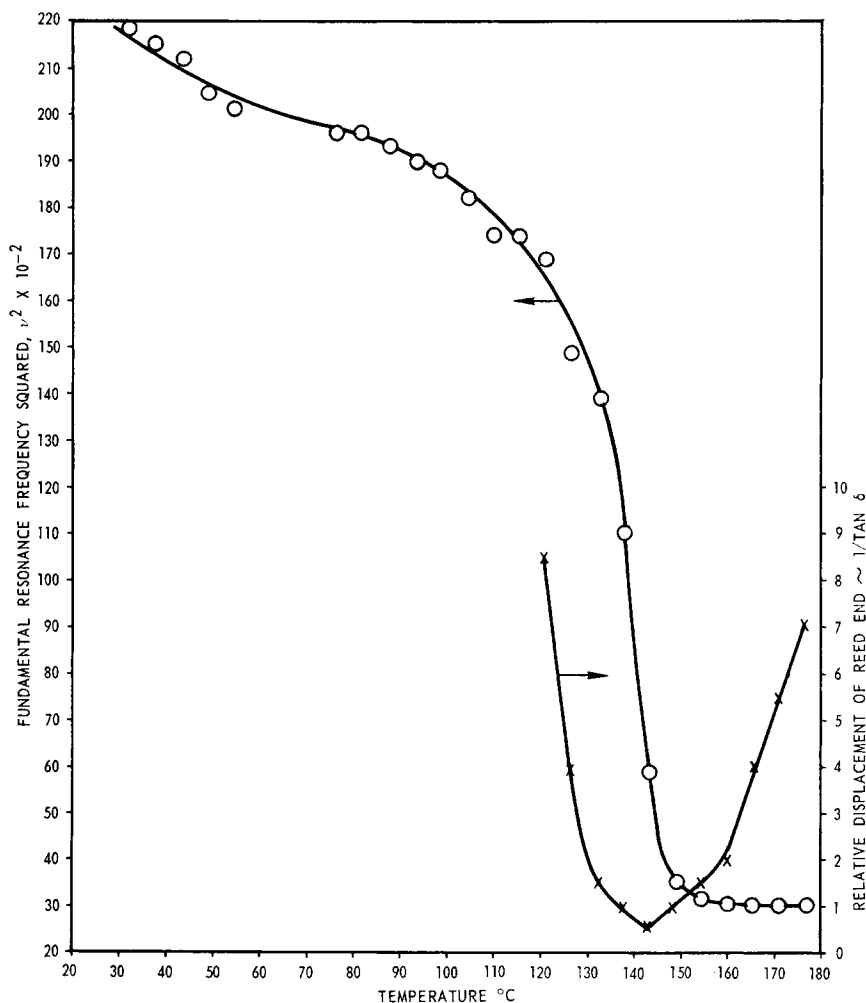
Fig. 2. Relative modulus and displacement as a function of temperature for Epon 828 with 20 phr of m-PLDA.

ing the first 40 min. of cure followed by a rapid modulus increase for the next 8 min. and finally leveling off to a constant value. From about 85 to 170 min., the apparent modulus curve was constant with time and represents 100% mechanical conversion. The zero conversion was taken as the horizontal portion of the curve from 0 to 40 min. The temperature was increased to 121.1°C. after 170 min. of cure. This temperature increase caused a rapid decrease in the apparent modulus which was followed immediately by rapid curing. These modulus movements result as the polymer passes through its glass transition temperature T_g, where $T_g <$ 121.1°C. The modulus increases due to a rapid crosslinking that forces T_g to advance such that $T_g \geq 121.1$°C.
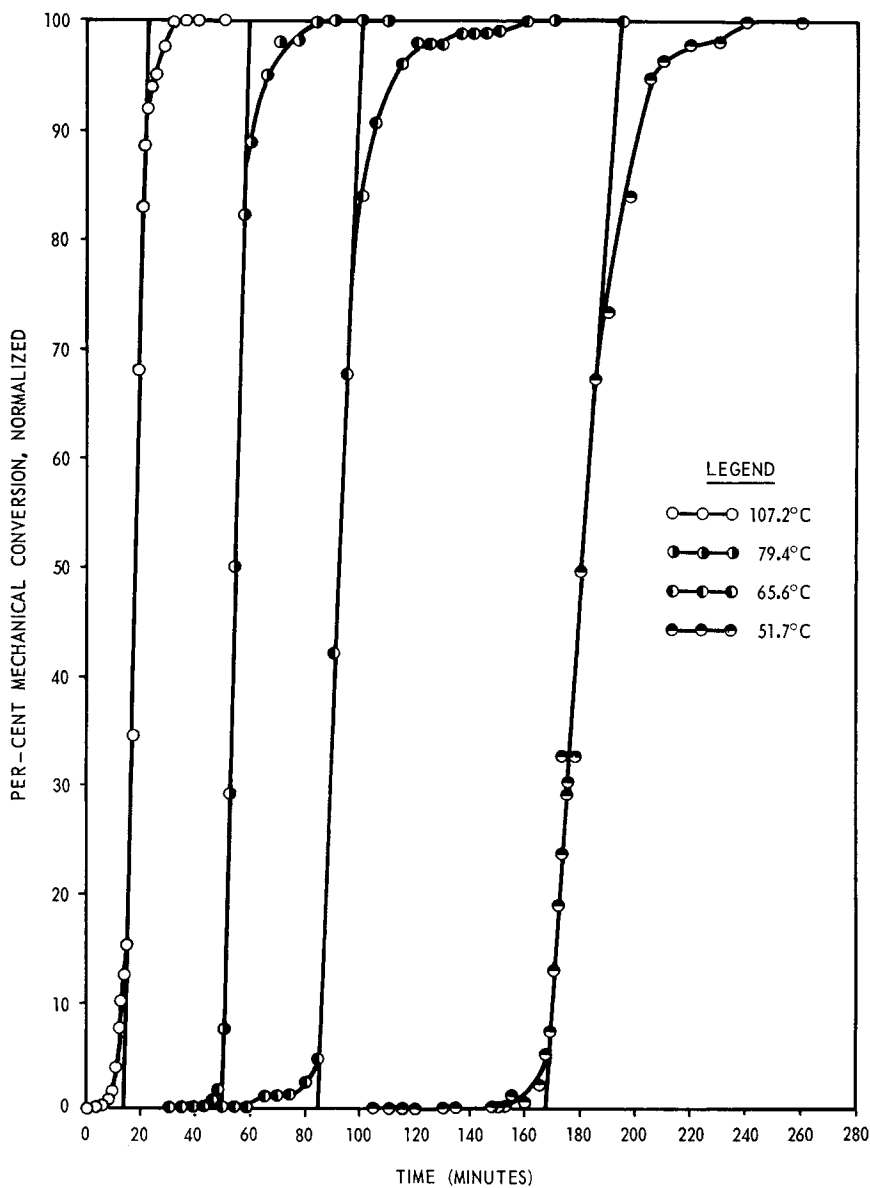
Fig. 3. Mechanical conversion as a function of time at several temperatures for Epon 828 with 20 phr m-PLDA.

This phenomenon demonstrates the effects of freezing in the polymer's segmental motion as T_g advances beyond the cure temperature. It demonstrates that, although reactive sites are available on the polymer's chain, the rate of segmental motion that allows position to be established for reactions is extremely slow in the glassy state, thus yielding an apparent constant modulus with cure time. When the cure temperature T_c is
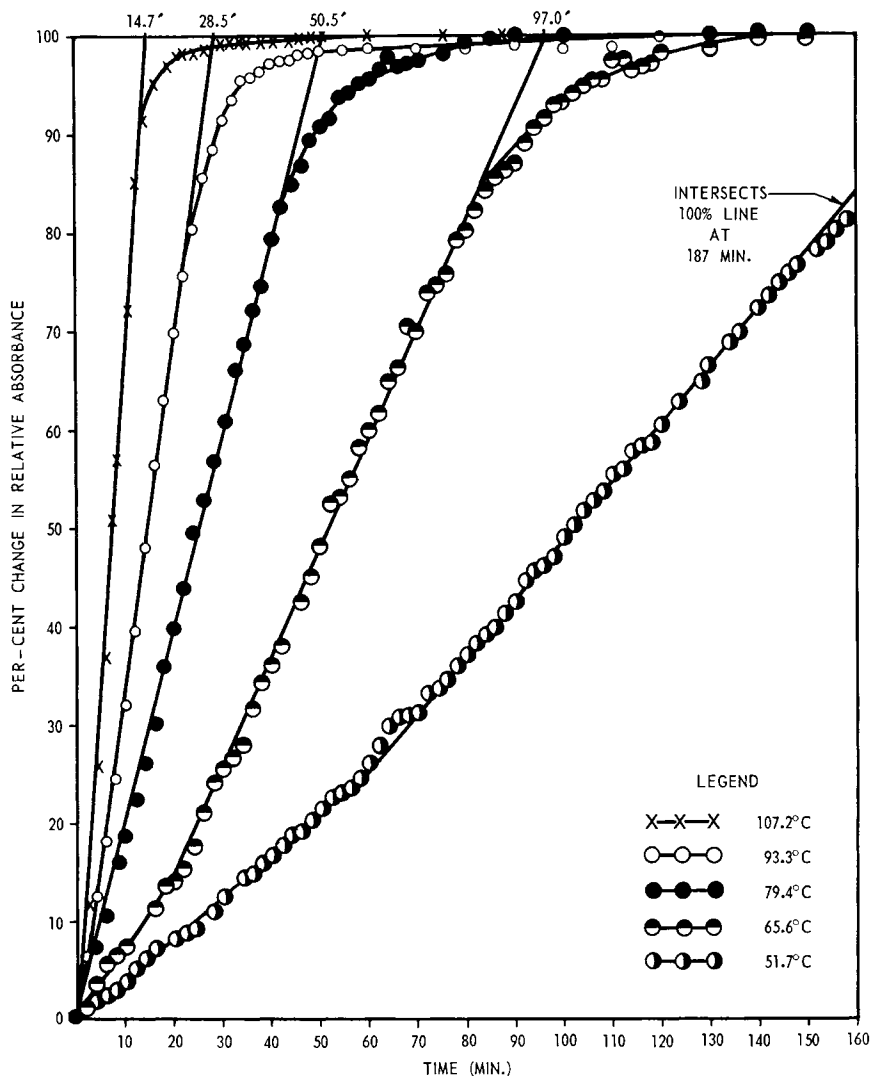
Fig. 4. Change in relative absorbance as a function of time at several temperatures for Epon 828 with 20 phr of m-PLDA.

about equal to T_g and reactive sites are available, segmental motion occurs, thus allowing further reaction. The temperature was increased to 148.9°C. after 184 min. of cure, thus causing the apparent modulus to again decrease. This temperature was held for about 50 min. with no further modulus increase. Reference to Figure 2 indicates that the polymer is now close to its rubbery temperature and any further crosslinking would not be measurable due to the relative contribution of the metal substrate, $\sim 10^{11}$ dyne/cm.^{2}, and the contribution of a rubberlike bond, $\sim 10^7$ dyne/cm.^{2}. Further temperature increases to 162.7 and 176.7°C. were made that caused the apparent modulus to reach a minimum value. The temperature of 176.7°C.

was held for approximately 2 hr. Thereafter, the temperature was lowered in about 6° increments as the relative modulus was recorded. The system was allowed to reach temperature equilibrium by holding the temperature constant for 15 min. for each data point. The T_g of this system was found to be 143°C. if the minima of the displacement curve of Figure 2 is taken as the T_g.

Referring to Figure 1, it is interesting to note that the relative damping curve exhibits a maximum at 33 min. followed by a minimum at 52 min. The minimum is associated with the cure transition temperature analogous to the glass transition temperature exhibited by this polymer as in Figure 2. The maximum at 33 min. is difficult to explain, but it was observed in each cure study that was run. Initially, the maximum was believed to be caused by the gelation of the resin. Subsequent viscosity studies indicated that the gel point was at 44 min. for this particular cure temperature and always displaced to the right of the displacement maximum for all cures studied.

Figures 3 and 4 present cure data of Epon 828 crosslinked with 20 phr of m-phenylenediamine (m-PLDA) as measured by the mechanical and infrared techniques. The mechanical property data, as measured by the change of apparent modulus with cure time, were normalized to per cent mechanical conversion in Figure 3. In addition, the infrared data have been normalized to per cent relative absorbance, as in Figure 4. It is readily apparent that three asymptotical lines may be drawn on the mechanical conversion curve at zero conversion, cure transition region, and 100% conversion. The intersections of the asymptotical lines and also the intersection of the asymptotical lines with the mechanical property curves offer convenient time parameters that may be employed to develop Arrhenius-type rate curves. We have arbitrarily chosen the intersection of the zero mechanical conversion and the cure transition asymptotes to represent a cure parameter for the mechanical technique and the intersection of the 100% change in relative absorbance and rate line asymptotes as the infrared time parameter as indicated in Figure 4. These time parameters were used to generate the Arrhenius type plot of the reciprocal of conversion time versus the reciprocal of absolute temperature shown in Figure 6. The gelation times of the curing resin system as determined by the infrared technique appear to correspond to the inflection points where the change in absorbance curves begin to deviate from the rate line asymptotes. This observation was verified independently with viscosity data generated at identical temperatures. The gelation point as determined by the mechanical technique was expected to correspond to the time when an increase in modulus was observed; however, no correlation was noted due to the relative modulus contributions of the metallic substrate and curing resin. Correlation of activation energies by the mechanical and infrared techniques may be expected if the rate parameters described are used to develop an Arrhenius plot.

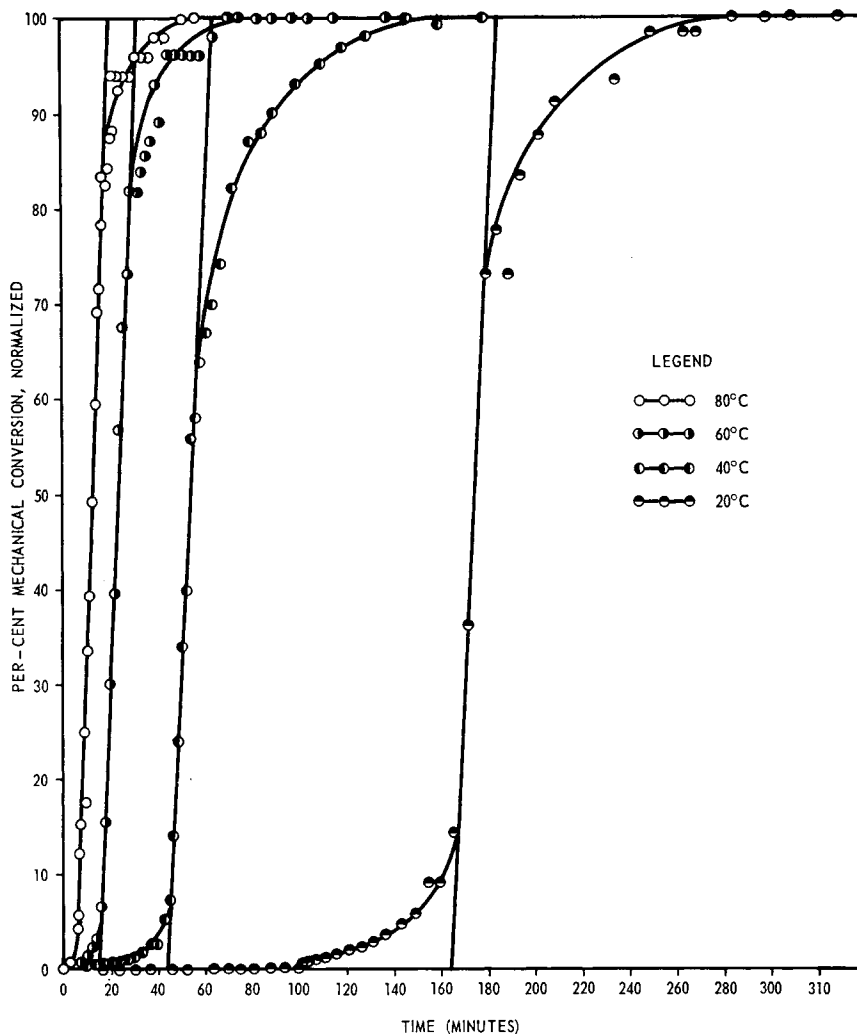Figure 5 presents cure data on Epon 828 crosslinked by 10 phr of di-

Fig. 5. Mechanical conversion as a function of time at several temperatures for Epon 828 with 10 phr of DETA.

ethylenetriamine (DETA) as measured by the mechanical vibrating-reed technique. This resin system was so chosen that a comparison of our technique and results could be made with the published data of Lewis,[5,6] who studied the curing of epoxy 828 by use of the torsional braid analysis (TBA). Lewis[6] chose the time for the damping to reach a maximum as his criterion of cure. Utilizing this parameter, he calculated an activation energy of 8.5 ± 0.7 kcal./mole for the amine epoxide reaction. The reported values for this reaction are 11–17 kcal./mole.[12]

Figure 6 presents the results of our data on the systems studied both by the infrared and mechanical techniques. We have plotted reciprocal conversion time versus reciprocal absolute temperature. The calculated
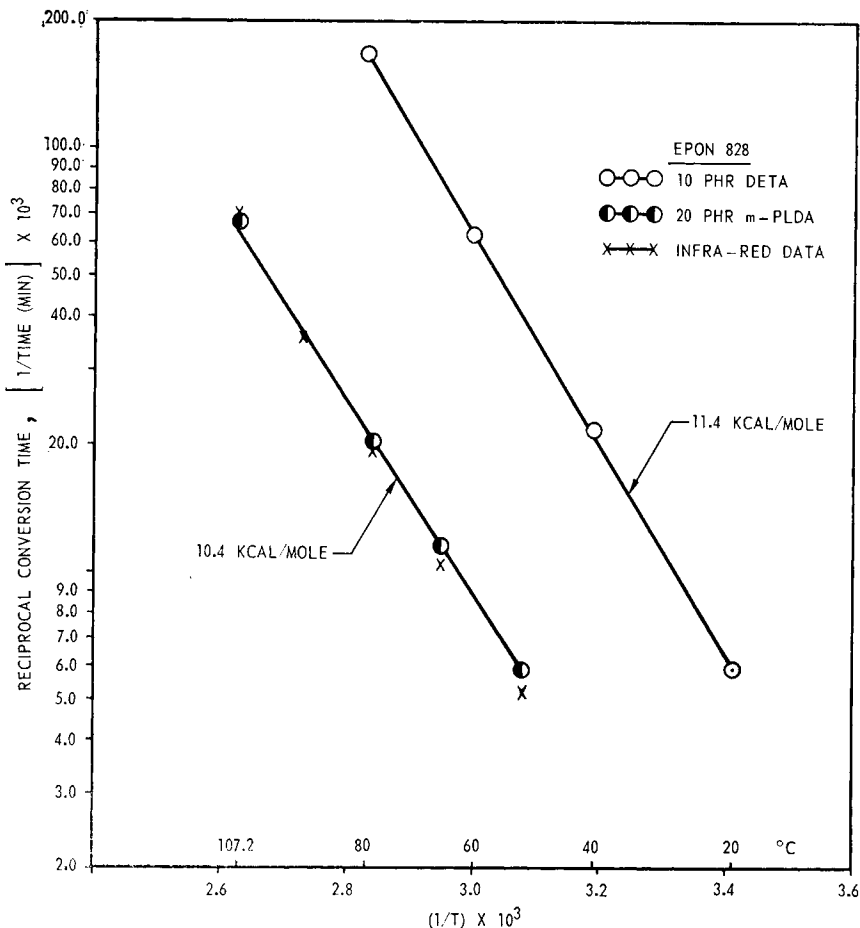
Fig. 6. Reciprocal conversion time vs. reciprocal absolute temperature.

energy of activation was found to be 11.4 kcal./mole for the epoxy–DETA system and 10.4 kcal./mole for the epoxy–m-PLDA system, as measured by the mechanical technique. The infrared data yielded an activation energy of 11.0 kcal./mole for the epoxy–m-PLDA system. We believe that the correlation of the calculated activation energies as measured by the two techniques and with the literature demonstrates the soundness of both approaches. Perhaps the fact that our results are somewhat higher than those of Lewis et al. is due to the stringent temperature control employed in this investigation. Previous work in which the thermocouple was located near the polymer film, but not in it, yielded significantly different reaction rates.

CONCLUSIONS

Two independent *in situ* techniques were utilized to obtain activation energies of the epoxy–*m*-phenylenediamine reaction. It appears that

mechanical and infrared changes measured during the cure of polymers may be correlated if the correct time parameters are chosen. Close thermal controls of the curing resin appear to be essential in obtaining reliable activation energies.

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Résumé

On a étudié, par deux techniques in situ, les variations, en fonction de la température, des propriétés de l'Epon 828 ponté par le diéthylènetriamine et la *m*-phénylènediamine. Les changements dan les propriétés mécaniques ont été suivis en mesurant continuellement la fréquence fondamentale de vibration d'un diapason constitué par un substrat enduit de résine. La disparition du groupe époxy réactionnel a été suivie in situ en mesurant de façon continue l'absorption de la bande époxy infra-rouge située à 915 cm^{-1}. On a reliés les résultats fournis par ces deux techniques en comparant les propriétés mécaniques et les résultats infra-rouge. L'énergie d'activation apparente calculée par la première méthode pour les systèmes epon 828., *m*-phénylènediamine et diéthylènetriamine sont respectivement de 10.4, 11.4 Kcal/mole. Cette énergie d'activation calculée par la méthode infra-rouge pour le système ponté par la *m*-phénylènediamine est de 11 Kcal/mole.

Zusammenfassung

Die Änderung der Eigenschaften von Diäthylentriamin- oder *m*-Phenylendiamin-vernetztem Epon 828 wurde nach zwei in situ-Verfahren bei mehreren Temperaturen untersucht. Die Änderung der mechanischen Eigenschaften wurde durch kontinuierliche Aufzeichnung der Änderung der Grundschwingungsfrequenz während der Härtung eines als Trägerstäbchen wirkenden, mit Harz überzogenen Substrats verfolgt. Das Verschwinden der reaktiven Epxoygruppe wurde in situ durch kontinuierliche Aufzeichnung der Infrarot-Epoxydbande bei 915 cm^{-1} verfolgt. Eine Korrelation der beiden Verfahren wurde durch eine Normalisierung der mechanischen und der Infrarotdaten erreicht. Die scheinbare Aktivierungsenergie wurde für die *m*-Phenylendiamin- und Diäthylenetriaminsysteme nach dem mechanischen Verfahren zu 10,4 bzw. 11,4 kcal/Mol berechnet und zu 11,0 kcal/Mol für das *m*-Phenylendiamin-vernetzte System nach dem Infrarotverfahren.