

# Investigation of Cure in Epoxy Resins: Ultrasonic and Thermally Stimulated Current Measurements

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## Synopsis

Acoustic and thermally stimulated current measurements are reported as a function of cure for dicyanodiamide-cured epoxy resins. It is found that the acoustic propagation is dominated by the generation of voids and does not directly reflect the extent of cure. In contrast, the thermally stimulated data correlate well with conductivity data, the amplitude of the space charge peak decreasing with increasing degree of cure and the dipole peak shifting to high temperatures as predicted from DSC data. Both methods exhibit potential as NDT methods for cure in resins.

## INTRODUCTION

Epoxy resins are widely used commercially as protective coatings and also as adhesives; therefore, methods of monitoring the degree of cure of the resin are of considerable technological importance.<sup>1-4</sup> The characterization of the degree of cure relies extensively on thermal and electrical methods, both of which have limitations and are subject to misinterpretation. Electrical methods have been favored since they provide a method by which coatings can be monitored continuously and *in situ*. Much of the literature on this subject<sup>5-7</sup> is concerned with either the use of aliphatic amine- or, alternatively, boron trifluoride-catalyzed cures. In the present communication, the changes which occur during the cure of a dicyanodiamide system will be discussed. The product of this type of cure tends to be of higher modulus than the aliphatic amine-cured materials and is favored for protective coatings.

Investigations of changes in the acoustic velocity and attenuation as a consequence of cure in phenol-formaldehyde resins<sup>8</sup> indicate that the method has potential for the monitoring of cure in this system. The attenuation is observed to rise rapidly in the initial stages of cure, reaching a maximum at about 25%, and then falls as the cure proceeds toward 100%. In contrast, the velocity of sound was observed to drop initially and then to increase, reflecting changes in the high-frequency modulus as the crosslinking process proceeds. No comparable study exists on epoxy resins, and the current study will attempt to provide parallel observations against which the potential of the method can be evaluated.

A recent article on the thermally stimulated discharge of amine-cured epoxy resins<sup>9</sup> indicated that the beta relaxation associated with rotational motion of the  $-(\text{OCH}_2\text{CHOH}-\text{CH}_2-\text{NH}-$  is observed at 180 K. However, the authors

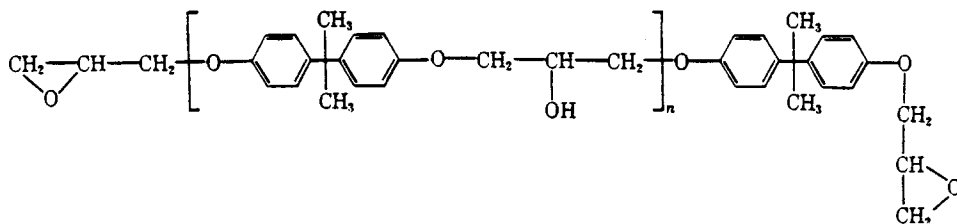
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indicated that they were unable to detect consistent changes in the relaxation behavior as a function of cure. In contrast, our study will concentrate on the way in which the higher-temperature relaxation process changes and will attempt to correlate these data with other electrical measurements and also with thermal determinations of cure in these epoxy resins.

## EXPERIMENTAL

### Materials

Two resin systems were investigated: a commercially available powder resin and a laboratory-formulated system. The commercial system was the 3M Skotchkote 206N powder coating resin which is composed of the diglycidyl ether of bisphenol A and is cured with dicyanodiamide catalyzed with 2,5-ethylmethylimidazole. The resin was cured by spray application to heavy steel plates preheated to 513 K. The extent of cure was controlled by quenching the panels in a water bath, after storing at 513 K. The second epoxy system was formulated from Epikote 2057, which was supplied by Shell Chemicals:



Epikote has an average value of  $n$  equal to 3. The resin was first ball milled to provide a powder which had a size distribution of less than  $50\ \mu\text{m}$ . The powder was then mixed with the catalyst, 4 phr of imidazole. The mixture was then heated to its melting point, mixed, and then cooled rapidly before excess cure had occurred. The resultant resin was then ball milled to provide a powder with particle size distribution below  $50\ \mu\text{m}$ . The compacted powder was then pressed in aluminum foil and cured at 433 K for 30 min. This material was postcured for a further 30 min at 438 K before use.

Epoxy resins are known to be relatively high temperature-stable materials.<sup>2</sup> Recent studies of their degradation behavior, performed in these laboratories, have indicated that temperatures in excess of 593 K are required before measurable volatiles can be detected. However, we have evidence for significant structural rearrangement of the cured resin occurring below 593 K, the threshold temperature for these latter processes being 543 K. The data presented in this paper are believed to be independent of the high-temperature rearrangement and degradation processes, and these will be discussed in a subsequent publication.

Both materials were then subjected to postcure, as will be indicated in the results and discussion section of this report. The extent of cure was determined using differential scanning calorimetry (DSC).

### Determination of Extent of Cure

The thermograms were measured using a du Pont 904 DSC. Approximately 10–15 mg of sample was ground into a powder and placed in an open aluminum pan; an empty pan of similar dimensions was used as reference. The sample was preconditioned by heating the sample from ambient to 423 K and held for a period of 1 min at a temperature in the range 423–433 K before being cooled to ambient using liquid nitrogen coolant. The first trace for the sample was then determined using a heating rate of 20 K/min, and heating was continued until a temperature of 553 K was reached.

The sample was then cooled at approximately 3 K/min and a second trace obtained. The difference in the glass transition temperature between the first and second traces is indicative of the difference between partially and fully cured resin. The quantity which is determined is  $\Delta T_g [= T_g(2) - T_g(1)]$ .

### Ultrasonic Measurements

Two methods were used: an immersion technique operating at 5 MHz<sup>10</sup> and a modified resonator method.<sup>11</sup> The resonator formed from a sandwich of two piezoelectric 5-MHz fundamental gold-coated quartz crystals and the polymer will propagate sound waves in the range 200 kHz to 5 MHz. With the samples used in this study, between four to six resonances would be detected dependent upon the thickness of the polymer sample. The immersion technique has been described in detail elsewhere.<sup>11</sup> The coupling liquids used in this experiment were water and *n*-propanol. In order to investigate acoustic velocity and attenuation to dry thin films, a modification of the acoustic resonator method was used. Instead of the conventional cell configuration, the cell illustrated in Figure 1 was used. This configuration allowed the film to be taken out of the cell and replaced without significantly changing the alignment of the crystals. The films

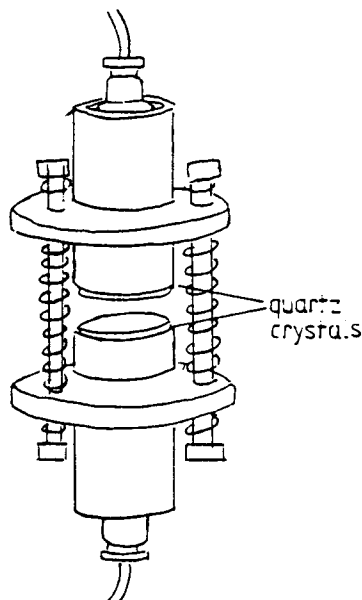
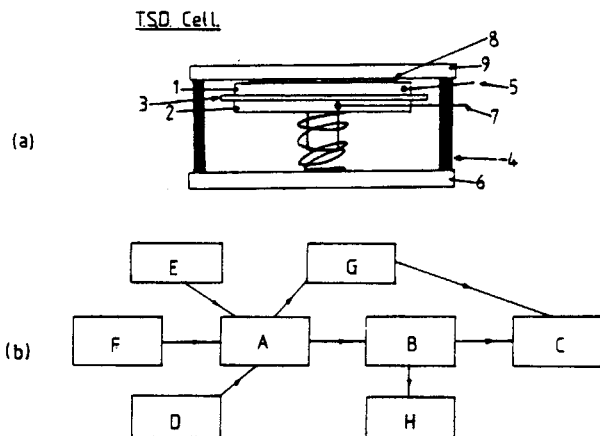


Fig. 1. Acoustic resonator cell used for the investigation of epoxy resin films.

were typically between 2 and 4 mm thick and as parallel sided as possible. The crystal is coupled to the epoxy slab by a thin liquid film. It was found that a low-molecular-weight poly(dimethylsiloxane) was unsuitable for use as a coupling medium since it tends to flow under pressure and lead to a nonreproducible bond. Hexachlorobutadiene produced a reproducible bond, but its relatively high volatility leads to a rapid deterioration of the bond. It was found that glycerol proved to be the most versatile coupling liquid, and the bonds so formed were both reproducible and stable for many hours. The peak positions were found to be reproducible to better than 1% for a series of six measurements. Attenuation measurements were performed both by measurement of the resonance width and by a direct transmission method using two quartz delay lines and glycerol as coupling liquid. In both cases, corrections were made for the effects of reflections at the coupling interface.

### Thermally Stimulated Discharge Measurements

The method used has been described elsewhere.<sup>12</sup> The apparatus was constructed from a Nordiko metal coater and allowed heating by halogen lamps, cooling from a liquid nitrogen helix, and contacting via solid copper electrodes connected ultimately to steel pole pieces. A schematic of the apparatus is presented in Figure 2. The heating program was controlled using a Type 802 temperature programmer supplied by Control and Readout Ltd. The voltage was applied using a Brandenburg variable voltage supply and was typically 1 kV/cm. The discharge current was recorded using a Keithley 602 electrometer, the output being supplied to either a twin pen recorder or stored on a PDP 11 computer.



Block diagram of TSD experiment.

Fig. 2. Diagram of apparatus used in the thermally stimulated discharge measurements. (a) 1, Upper electrode; 2, spring-loaded lower electrode; 3, sample; 4, ceramic pillars; 5, connections to electrometer; 6, lower (stainless steel) plate; 7, thermocouple; 8, poly(ethylene terephthalate) insulator; 9, upper (stainless steel) plate. (b) A, TSD cell; B, electrometer; C, two-pen recorder; D, high-voltage supply; E, temperature programmer; F, vacuum system; G, digital thermometer; H, P.D.P. 11 Minicomputer.

### Density Measurements

The densities of the solid films were determined using a flotation method, the dense liquid being carbon tetrachloride ( $1595 \text{ kg/m}^3$ ) and the lighter liquid being propanol ( $804 \text{ kg/m}^3$ ). The density of the mixture, corresponding to the point at which the film just sinks, was determined using an Anton Paar digital densimeter. The density was determined using this method to a precision of  $1 \times 10^{-1} \text{ kg/m}^3$ .

### Electrical Conductivity Measurements

The configuration used has been described in detail elsewhere<sup>13</sup> and consists of a Wayne Kerr three-terminal cell, a Keithley 642 electrometer, and a strip chart recorder. The charging voltage was applied from a stabilized Hewlett Packard low-voltage power supply and was typically 50 V.

## RESULTS AND DISCUSSION

### Acoustic Propagation Studies

**Temperature dependence of fully cured materials.** Initial measurements on the films were performed using the immersion technique with water as coupling fluid. A typical trace for the first temperature scan is shown in Figure 3(a). Subsequent attempts to repeat these data failed. As we shall see later, this can be attributed to the effects of water diffusion into the film and its effect on the subsequent acoustic relaxation and dispersion properties. The water-containing samples do not contain the distinct increase in the attenuation observed at high temperatures and exhibit a much flatter profile, Figure 3(b). Recent studies by Hartmann<sup>14</sup> on aliphatic diamine-cured epoxy resins with much lower glass transition temperatures than those of the materials can be easily detected acoustically. Using the shift parameters which he indicates on these materials would suggest that the corresponding relaxation process should be observed at approximately 413 K. The data obtained for the dry sample is therefore consistent with the data of Hartmann<sup>14</sup> on the lower  $T_g$  materials.

**Variation of acoustic properties with extent of cure.** The velocity of propagation of the fully cured and partially cured films was investigated as a function of temperature using the resonator cell, Figure 4. The velocity of both the fully cured samples and those partially cured exhibited a monotonic decrease with increasing temperature which is the type of behavior expected of a material which is below its glass transition temperature. The values of the velocity observed in the fully cured materials are similar to those reported by other workers for boron trifluoride- and amine-cured resins.<sup>15-17</sup>

An investigation of the variation of the attenuation determined at 293 K for samples cured at various temperatures and for various times was undertaken, and the results are presented in Figure 5. These data represent the average of a minimum of four samples of graded thickness for each  $\Delta T_g$  value. There is a very small increase in the attenuation with extent of cure. However, this variation is several orders of magnitude smaller than that observed in the case of phenol-formaldehyde resins.<sup>8</sup> In the former, the peak has been attributed to a shift of the main relaxation peak through the temperature-frequency window

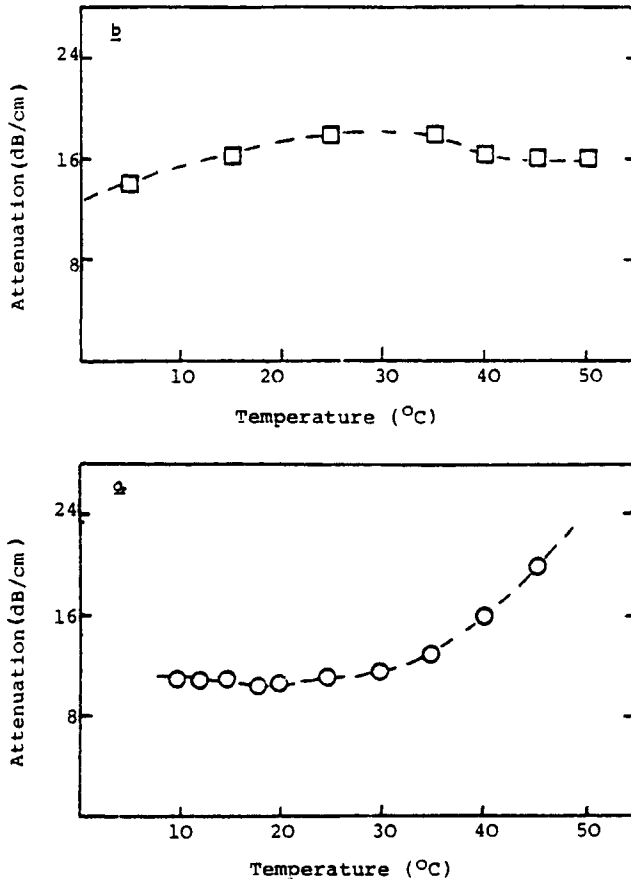


Fig. 3. Acoustic attenuation variation as a function of temperature: (a) using the immersion cell, first run; (b) subsequent investigation of a water-soaked sample.

for the acoustic experiment as a consequence of the changes in the nature of the molecular structure of the resin on curing. In the case of the epoxy resin system studied here, it is unlikely that such a parallel situation will arise. The epoxy resin is firstly a solid; and secondly, the final glass transition temperature is fairly high, ca. in excess of 372 K, determined by DSC measurements. Both factors act to preclude major relaxation features occurring in the temperature–frequency window currently used.

A parallel investigation of changes in the velocity was performed and is presented in Figures 6(a)–6(c). Cure time-vs.- $\Delta T_g$  plots were obtained for all the samples investigated. An example of the type of behavior observed is presented in Figure 6(d). The general behavior of the velocity as a function of  $\Delta T_g$  was similar for all the postcure temperatures investigated. While the shape of the variation changes with the precise cure temperature, the ultimate velocities are approximately the same and all exhibit a decrease in velocity before ultimately increasing. This behavior is inexplicable in terms of lowering of the velocity associated with the occurrence of a molecular relaxation in the frequency–temperature window being used. A parallel investigation of the variation of the density with cure, Figure 7, indicates that there is initially a decrease followed by a subsequent increase. An examination of the optical micrographs of the

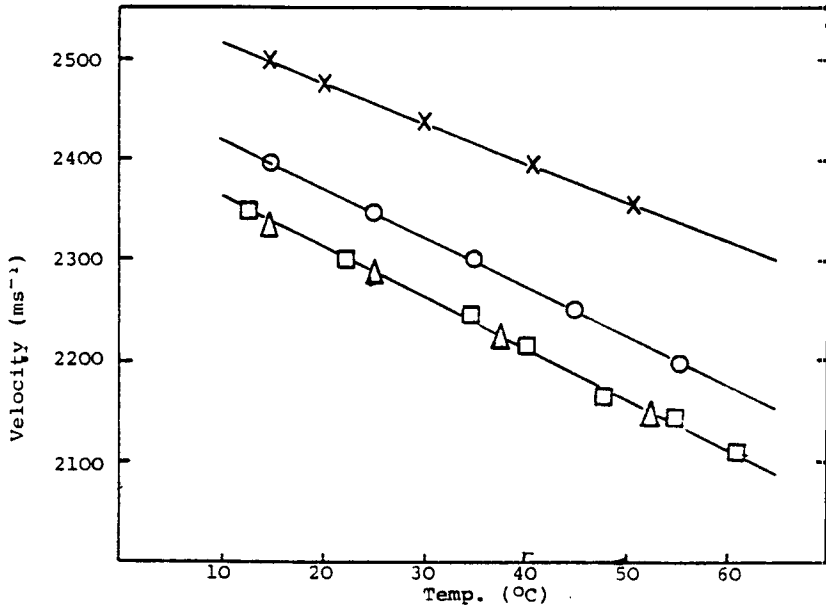


Fig. 4. Variation of the acoustic velocity with temperature for fully and partially cured samples. Sample designation: (X) 200/2; (□) 200/4; (Δ) = 200/5; (O) 200/7; where the first number indicates temperature of cure and the second number, after the slant, the time in minutes.

films, Figure 7, indicates that this decrease in the density corresponds to the generation of voids in the films. Subsequent postcure of these samples leads to a change in the distribution of such voids and size, Figure 7.

A parallel study of the variation in the thickness was undertaken using a statistically average of random samples over an area of 10 cm<sup>2</sup> measured using a micrometer. The data obtained are presented in Figure 8. The thickness measurement was repeated three times and the data presented represent the statistical average of all the measurements. The film initially contracts, then expands before finally contracting once more. A plot of the variation of the velocity against  $\Delta T_g$  indicates that the velocity falls as the cure is initiated, and

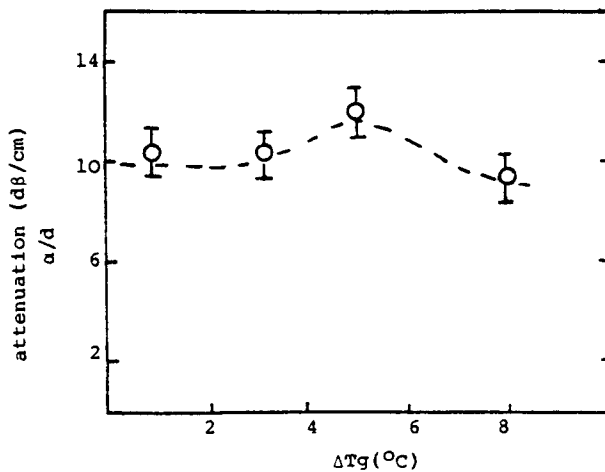


Fig. 5. Variation of the attenuation as function of the degree of cure, designated by  $\Delta T_g$ .

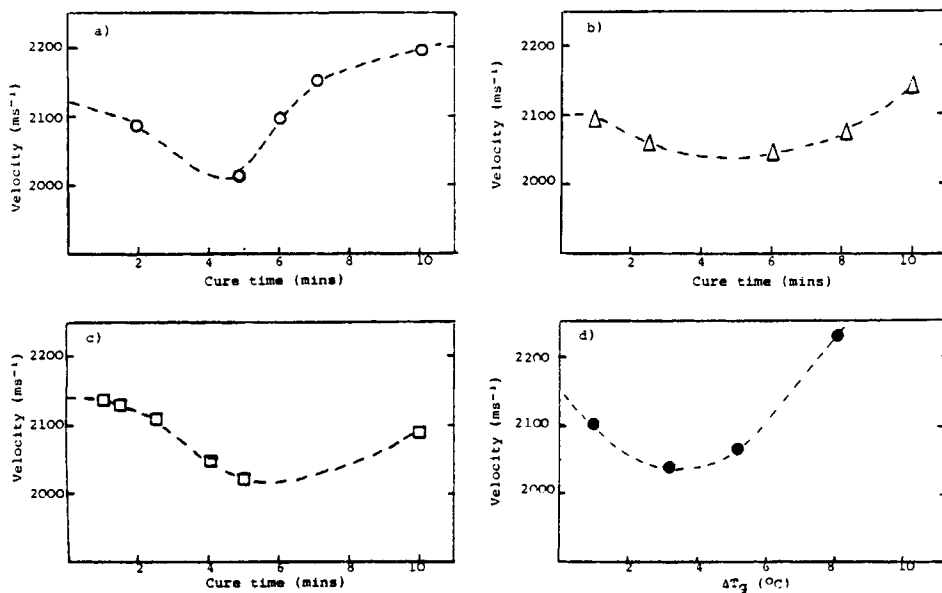


Fig. 6. Variation of the velocity as function of cure for samples subjected to different initial cure temperatures: (a) 473 K, (b) 493 K, (c) 513 K; (d) 493 K, variation of velocity with  $\Delta T_g$ .

only in the latter stages does it rise as would be expected for a material undergoing crosslinking. Comparison of these data with the variation of the density indicates that part of the explanation lies in the fact that the creation of voids will *decrease* the mean velocity, and it is only in the latter stages that this trend is counteracted by the increasing modulus associated with the crosslinking. It is probable that such effects contribute to the variation observed in phenol-formaldehyde resins<sup>8</sup> and other systems.<sup>18</sup> However, the occurrence of strong molecular relaxation processes can mask these effects.

### Electrical Investigations

**Conductivity studies.** As indicated in the introduction, conductivity measurements have been used extensively for the characterization of cure in epoxy systems. As far as the authors are aware, data on the dicyanodiamide system have not been published; and for this reason, data were collected on the samples used for the previous acoustic study. Data obtained from samples cured at various temperatures are presented in Figure 9. As the cure proceeds, the conductivity measured at 293 K decreases, indicative of the formation of the cross-linked matrix. Investigation of the variation of the conductivity as a function of temperature indicates that a marked increase is observed at approximately 323 K in certain samples, Figure 9. Such changes are characteristic of an increase in charge mobility often associated with the onset of molecular motion in the matrix. Comparison of the break point with the known beta and alpha relaxation temperatures indicates that it does not coincide with either of these features. However, a plot of log conductivity against reciprocal temperature below the break temperature does exhibit a slope (Table I), which is close to that for the reported activation of the beta process<sup>9,18</sup> determined from mechanical data and indicates that the activation energy for electrical conduction has a similar magnitude in this temperature range.



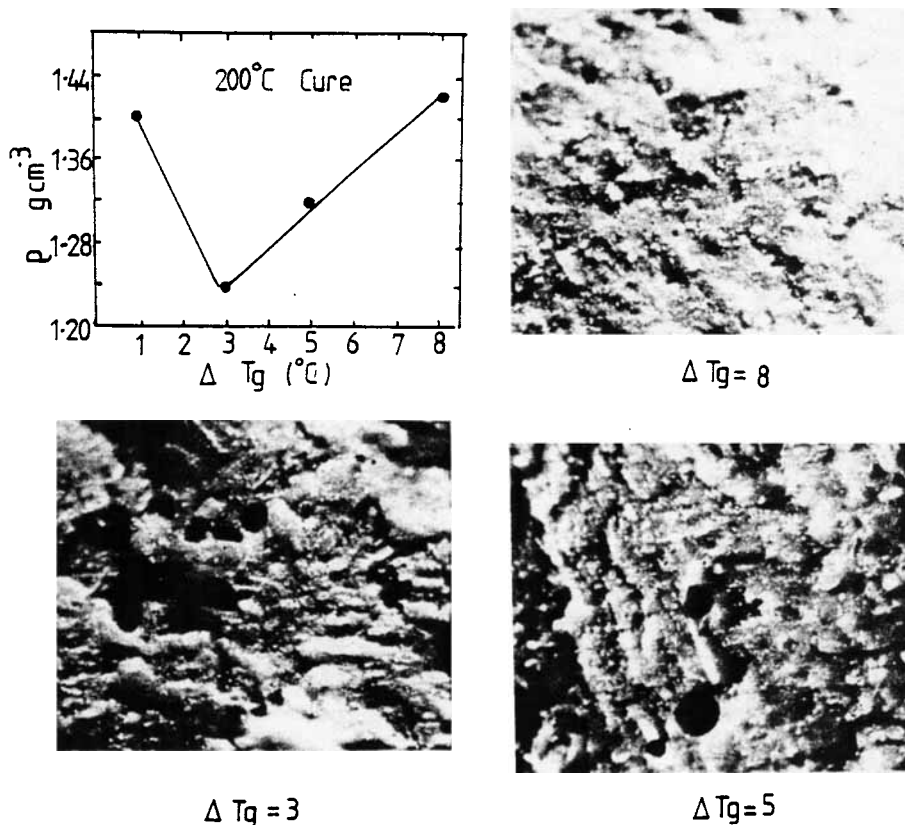


Fig. 7. Variation of density and optical micrographs as function of cure.

**Thermally stimulated current measurements.** Two peaks are observed in the thermogram of the epoxies in the temperature range 293–403 K. The lower temperature peak is assigned to the  $T_g$  by correlation with DSC measurements, while the higher temperature peak can be associated with space charge effects, Figure 10. The curves obtained as the cure proceeds were obtained by postcuring

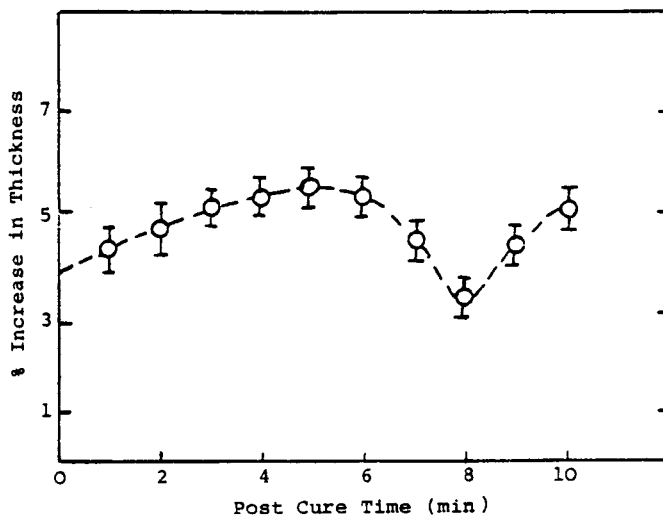


Fig. 8. Variation of thickness as function of cure time for samples cured at 473 K.

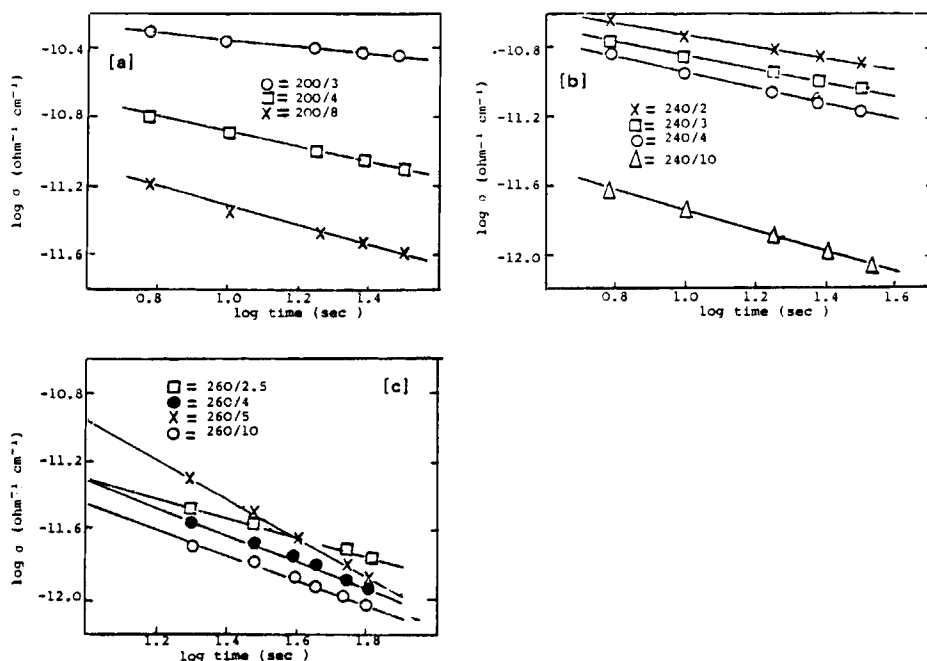


Fig. 9. Variation of the conductivity as function of time at various cure temperatures: (a) 473 K; (b) 493 K; (c) 513 K.

the films during the charging cycle. The final cure was performed by heating the film in an oven at 413 K for 1 h.

The activation energy  $E_a$  and  $\tau_0$ , the relaxation time associated with the glass transition temperature, can be derived using the approach of Grossweiner<sup>19</sup>:

$$E_a = \frac{1.3 \times 10^{-4}(T_m T_h)}{T_m - T_h} \quad (1)$$

where  $T_m$  is the peak temperature in degrees K and  $T_h$  is the temperature corresponding to the half-height of the peak on the lower-temperature side of the spectrum. Provided that the heating rate and the frequency factor are constant over the temperature range, the equation is accurate to better than 5%. The

TABLE I  
Slopes of the Variation of the Electrical Conductivity Against Reciprocal Temperature—  
Activation Energies

Cure temperature, °C	Cure time, min	$E_a$ , kJ/mol
200	3	20.5
	4	25.9
240	2	20.7
	3	19.3
	4	27.0
	10	12.2
260	2.5	20.2
	4	11.4
	10	19.5

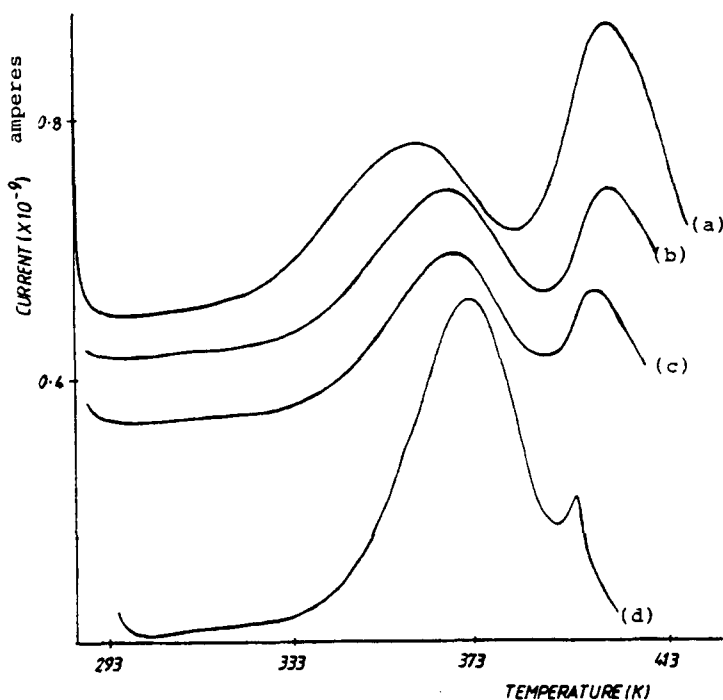


Fig. 10. Thermally stimulated current data displayed as function of cure, Skotchkote 206N: (a) film  $\Delta T_g \sim 8$  K; (b) postcured at 473 K for 30 min; (c) postcured at 473 K for 60 min; (d) postcured at 573 K for 10 min.

relaxation time can be estimated from

$$\tau_0 = \frac{kT_m}{BE_a \exp(E_a/kT)} \quad (2)$$

where  $B$  is the heating rate. Apparent activation energies (Table 2) have been calculated using eq. (1) as the cure proceeds. It is observed that the value of  $E_a$  reaches a constant value as the cure goes to 100%. Agreement between the  $T_g$  values of the fully cured system obtained by DSC and TSD are in good agreement, allowance being made for the differences in the rates of heating used in the two methods.

The space charge peak for the Skotchkote 206N, Figure 10, decreases in intensity as cure proceeds. For the Epikote 2057/imidazole cure, the space charge peak shows a parallel variation but changes sign at high temperatures. In dielectric measurements, conduction losses are found above  $T_g$ , associated with oscillatory motion of ohmic carriers in the applied ac field leading to an exponential increase of the loss with temperature. In TSD, however, the sample is

TABLE II  
Variation of the Apparent Activation Energy of the Alpha Relaxation as the Cure Proceeds, as Determined from TSD

Run No.	$\Delta T_g$	$E_a$ , kJ/mol
1	15	98.64
2	8	198.64
3	6	117.13
4	0	141.0

shortcircuited, and therefore the charges migrate under their own field. This self-motion of charges gives rise to a peak because the number of charges stored eventually becomes depleted. The activation energy for the space charge motion has been shown to agree with that for conduction above the  $T_g$ .

The TSD study indicates that in the case of Skotchkote 206N, the generation of a highly crosslinked network is also associated with a reduction in the amplitude of the space charge current, Figure 10. The matrix will also become more homogeneous as the crosslink density becomes more uniform and thus interfacial polarization will also be less prevalent. The interfacial polarization is reflected in the rate of the initial charge decay on commencement of the thermal analysis. Similar results were obtained for the Epikote 2057/imidazole system. Comparison of the change in conductivity with extent of cure, Figure 9, and also that for the space charge current, Figure 10, indicates qualitatively a correspondence of the variation of these properties with extent of cure. A more qualitative comparison is currently being undertaken to establish the basis for the similarity in these properties.

### CONCLUSIONS

In this article, we have indicated that the effect of cure on the acoustic propagation in epoxy systems is not purely one of shifting a molecular relaxation into a frequency-temperature window but also involves the effects of structural changes in the bulk. In the case of the aliphatic amine-cured epoxies with lower  $T_g$  values, one would anticipate that they would exhibit dramatic changes in the attenuation associated with motion of the relaxation through the frequency-temperature window, similar to those found in phenol-formaldehyde resins. The TSD clearly indicates that the changes in the conductivity can be observed by this method and are extremely sensitive to the extent of cure of the resin. Application of these techniques for the characterization of cure in epoxy resins are obvious and provide alternative NDT methods for application to those currently employed.

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