Thermally Stimulated Discharge Current Studies on Low-Temperature Relaxation in Epoxy Resin

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Synopsis

Thermally stimulated discharge current (TSDC) analysis has been used to characterize the low-temperature (100–300 K) molecular relaxation processes (β relaxation) of an epoxy resin. Experiments were performed on a resin system composed chiefly of tetraglycidyl-4,4′-diaminodiphenylmethane and diaminodiphenyl sulfone (TGDDM/DDS). Polarization of the epoxy resin appears to be due to preferential orientations of dipoles in the temperature range studied. The broad β-dispersion peak exhibits considerable "structure," and it promises to prove rich in information related to polarization and relaxation processes in the epoxy resins. It is seen that TSDC can reveal clearly the differences between the degree of curing for epoxy resins. Temperature dependence of a mean activation energy calculated from the discharging processes reveals several temperature ranges over which common molecular relaxation events are probably occurring.

INTRODUCTION

Epoxy resins have such attractive properties, high mechanical strength, high chemical resistance, and high temperature stability that they have been put to practical use[1–4] for over two decades. The recent development of superior epoxy resin formulations has expanded the use of such resins in fiber-reinforced composites. This has permitted the evolution of new kinds of composite engineering materials for advanced structural applications, including high-performance aircraft.[5] The corresponding more severe service requirements of such applications raise new questions about the behavior of the epoxy resin itself in such composite materials. This includes stability of the resins, adhesion of the resin to reinforcing fibers, and crack initiation and propagation characteristics. In the present study, we focus on one of these advanced epoxy resin systems, Hercules 3501-6, which is primarily tetraglycidyl-4,4′-diaminodiphenylmethane epoxy cured with diaminodiphenyl sulfone (TGDDM/DDS).

The epoxy resins find structural applications normally below their heat distortion or glass transition temperature. In addition to stiffness and mechanical strength, an important mechanical property of epoxy resins is toughness, which gives rise to good impact strength. This high-impact strength has been attributed to the existence of low-temperature molecular motions,[1] as revealed by the β relaxation. Although the β relaxation of epoxy resins has been studied by dynamic mechanical measurement,[5–8] the mechanisms or molecular structure responsible for this relaxation are not yet well resolved. A relatively new method, thermally stimulated discharge current (TSDC) analysis, has been shown[9–13] to be an effective way to investigate relaxation processes. This is because it is usually sensitive to very small amplitude effects and because it is capable of re-

Journal of Applied Polymer Science, Vol. 25, 1355–1363 (1980)
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solving individual relaxation processes from each other. Therefore, the TSDC analysis was chosen to study the β relaxation of epoxy resin.

EXPERIMENTAL

Premixed TGDDM/DDS (tetraglycidyl-4,4′-diaminodiphenylmethane/diaminodiphenyl sulfone) epoxy resin (Hercules 3501-6) was supplied by the McDonnell Aircraft Co., McDonnell Douglas Corp., St. Louis, MO, and was continuously stored below −44°C. Chemical compositions of resins used in this study are summarized in Table I; detailed characterization of such Hercules 3501-6 resin systems has been reported previously.[14] Specimens were prepared by casting resin between preheated, metallographically polished Teflon plates. Thicknesses can be varied in the range of 0.005–1 mm by suitable selection of spacers. Cure conditions chosen for the epoxy specimens studied are shown in Table I.

The determination of percent conversion in cured epoxide resin was carried out by using a Fourier transform infrared instrument (Nicolet model 7199) and differential scanning calorimetry (Perkin–Elmer model DSC-1B). Specimens used for FTIR measurements had thicknesses in the range of 0.1–0.005 mm.

TSDC analyses were done with a Toyo-Seiki Electret thermal analyzer (obtained through the Atlas Electric Devices Company, Chicago, IL 60613). Specimens used for these experiments were between 2 and 3 cm in diameter and had thicknesses in the range of 0.1–0.5 mm. Gold metal electrodes[9,15] were vacuum evaporated onto the top and bottom surfaces of these specimens. Specimens were usually polarized with an electric field (E_p) of 18 kV/cm at a temperature (T_p) of 298 K. TSDC thermograms were obtained at a heating rate of 2°C/min.

TABLE I
Initial Composition, Cure Condition and Cure Extent of Epoxy Resin

Composition	Cure condition °C	Cure condition hr	Percent conversion	Code
Standard[a]: 100 phr TGDDM, 44 phr DDS				A
	140	1.5	34.8	A_{11}
	140	5.0	58.0	A_{12}
	158	2.0	52.7	A_{21}
	181	2.0	93.4	A_{31}
	181	8.0	94.2	A_{33}
	181	12.0	94.0	A_{34}
+10% DDS[a]: 100 phr TGDDM, 48.4 phr DDS				B
	140	2.0	37.0	B_{11}
	140	5.0	57.0	B_{12}
	181	2.0	92.0	B_{31}
−20% DDS[a]: 100 phr TGDDM, 35.2 phr DDS				E
	140	2 hr	26.1	E_{11}
	140	5 hr	40.0	E_{12}

[a] Also includes 16 phr epoxide no. 2, 15 phr epoxide no. 3, and 2 phr BF_3 (catalyst).

RESULTS AND DISCUSSION

The Origin of TSDC Peaks at Low Temperature

In general, the β-relaxation process occurs within the 100–300 K temperature range. Previous workers,[8,16–19] using dynamic mechanical and dielectric techniques to study this relaxation, have attributed it to motions of flexible side groups or to the crankshaft motions of methylene sequences in the polymer backbone. Because there are dipolar parts in the TGDDM/DDS epoxy resin, a dielectric effect is expected to be detectable by using TSDC analysis. The expression for TSDC owing to relaxation of dipole polarization is given as follows[9,20]:

$$\mathrm{TSDC} = I(T) = \frac{N\mu^2 E_p}{3kT_p}\left[\left(\tau_0 \exp\left\{\frac{H}{kT}\right\}\right)^{-1} \exp\left\{\int_{T_0}^{T}\left(b\tau_0 \exp\left\{\frac{H}{kT}\right\}\right)^{-1} dT\right\}\right] \tag{1}$$

and the total charge lost during heating from T_0 to T is given as

$$Q = \frac{1}{b}\int_{T_0}^{T} I(T)dT \tag{2}$$

where T is temperature, T_0 is starting temperature, $I(T)$ is thermally stimulated discharge current released after heating from T_0 to T, b is heating rate, N is number of dipoles per unit volume, μ is dipole moment of these dipoles, k is Boltzmann's constant, τ is relaxation time ($= \tau_0 \exp\{H/k\mathrm{T}\}$), τ_0 is preexponential factor, H is activation energy, and E_p is electrical field used in polarizing the specimen.

According to eqs. (1) and (2), both TSDC and total charge released (Q) because of dipole polarization must be directly proportional to E_p. Figure 1 gives an example of this predicted relationship. It has been found that the maximum TSDC peak temperature $T_{\max}$ owing to dipole polarization does not depend on T_p so long as $T_p > T_{\max}$,[10,21,22] as shown in Figure 2.

Alternatively, one might consider that TSDC in this temperature range arises from motion of excess charges.[10] However, Jonscher et al.[23] reported that the activation energy associated with migration of ions over microscopic distances in amorphous materials, as determined by dielectric measurements, is 0.6–0.8 eV or higher. Arridge[24] reported that the activation energies of the β-relaxation process of epoxy resin are in the range of 0.8 eV (18 kcal/mole) or less, depending on the extent of curing. Values in the range of 0.2–0.6 eV were obtained in the study reported here using the "partial heating method." More data and discussion on the partial heating technique will be presented later. This result, then, suggests that polarization of epoxy resins at low temperatures is due to dipole polarization.

The Effect of Curing on the Low-Temperature Relaxations

The standard formulation of the Hercules resins, Resin A, has been studied as a function of curing condition. The effect of time and temperature on curing, as seen in TSDC thermograms, is shown in Figures 3 and 4, respectively. One notices that as the state of cure increases, the following features are manifested:

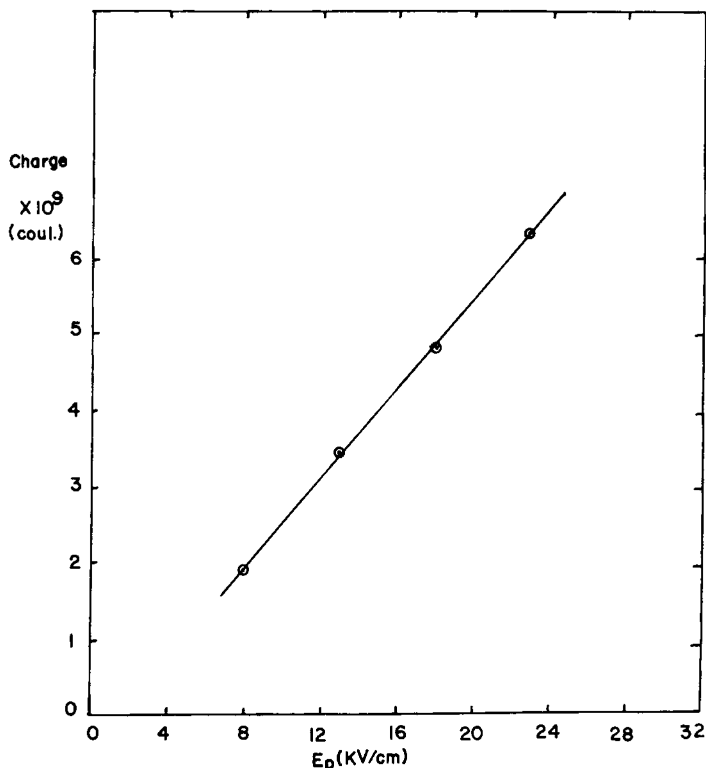

Fig. 1. Total charge released to external circuit vs. polarizing field for epoxy resin B_{31}.

(1) the area under a TSDC peak increases, (2) the height of a TSDC peak increases, and (3) the temperature at which maximum TSDC occurs, T_{max}, shifts to higher values. Results (1) and (2) are to be expected because chain segments are created as a direct result of the polymerization reaction.[8,16,24–26] Because such chain segments are thought to be the origin of this TSDC peak, its strength should rise as the concentration of chain segments grows. Result (3) may be due to the following facts.[24] For an incompletely cured resin network, many epoxy and curing agent molecules have reacted at only one or two functional groups,

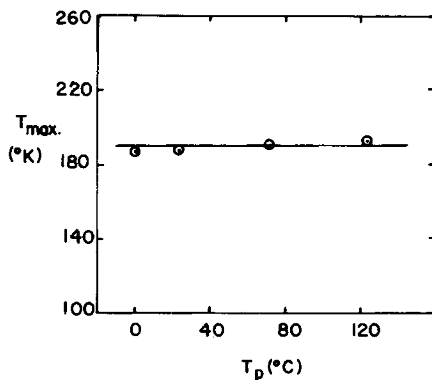

Fig. 2. Relation between TSDC peak temperature T_{max} and polarizing temperature T_p for epoxy resin A_{12}.

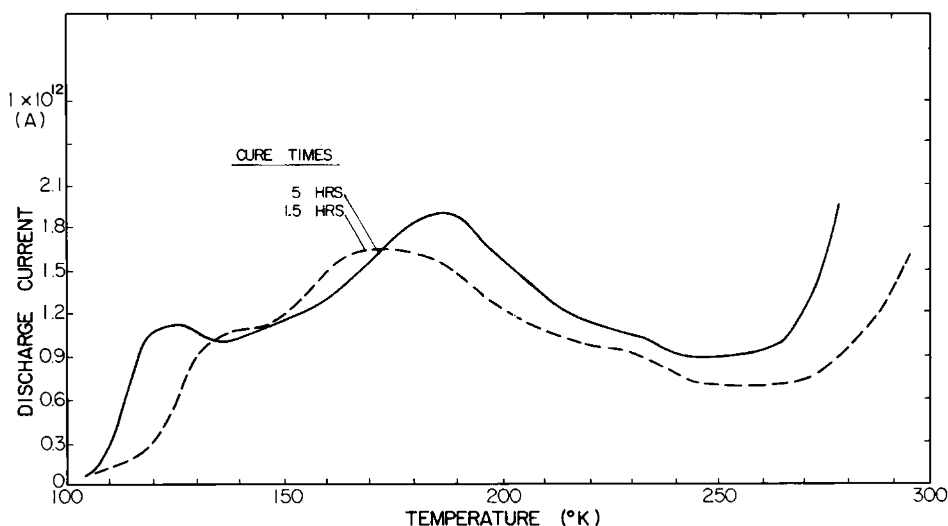

Fig. 3. Cure time effect at 140°C on TSDC thermogram, using epoxy resin A (standard formulation).

so that the flexibility of mobile segments is not influenced by neighboring segments. However, as the degree of curing nears completion, the density of linkages between chain segments becomes sufficient to cause their mobility to begin to be restricted. It follows that the temperature at which such segments can exhibit their relaxational motions would rise as cure approaches completion.

Similar analyses have been performed for epoxy resins B and E, and these results are shown in Figures 5 and 6. Again, it is seen that TSDC thermograms do reveal a systematic change with the extent of cure.

The TSDC thermogram in Figure 7 shows the effect of time on high-temperature (181°C) curing. Polymerization of epoxy resins at this temperature creates

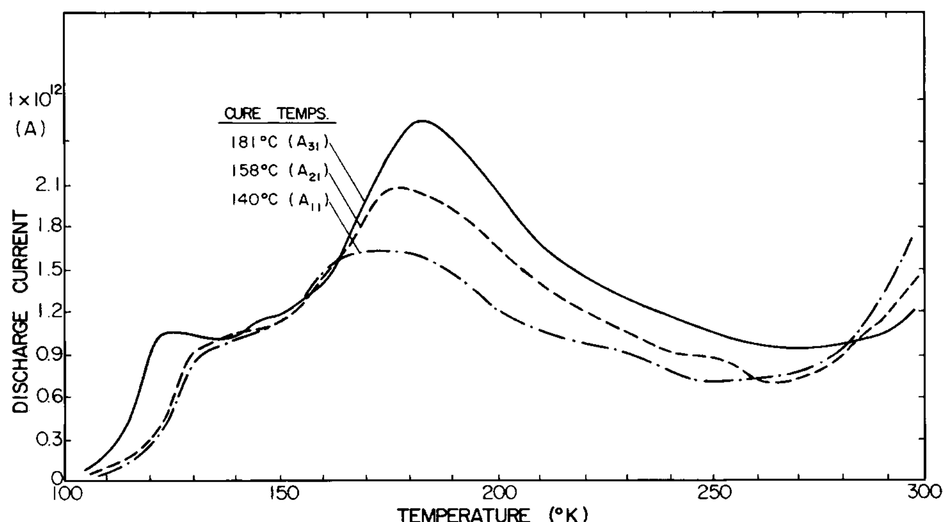

Fig. 4. Cure temperature effect on TSDC thermograms, using epoxy resin A (standard formulation) cured for short times.

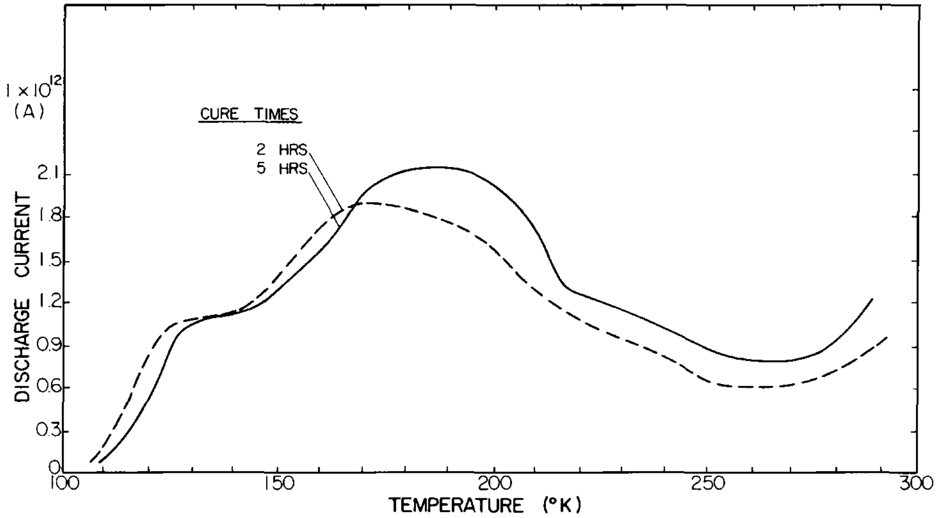

Fig. 5. Cure time effect at 140°C on TSDC thermograms, using epoxy resin B (10% excess curing agent).

macromolecular networks sufficiently complete so that the material may actually have vitrified. In such a case, curing reactions are probably strongly diffusion controlled,[5,24,27] and the network building reaction rate ought to be extremely slow. In fact, it is seen from FTIR analysis (Table I) that the polymerization reaction itself changes very little with cure time carried beyond several hours. The decrease of peak value after the prolonged curing period may be associated with the onset of degradation[20,23] caused by oxidation and chain scission of resin. One possible implication of this observation on postcuring treatment is that it may cause more damage to the specimen than improvement through any further increase in network development. Therefore, it is necessary to find for each system that curing condition which will achieve maximum mechanical properties

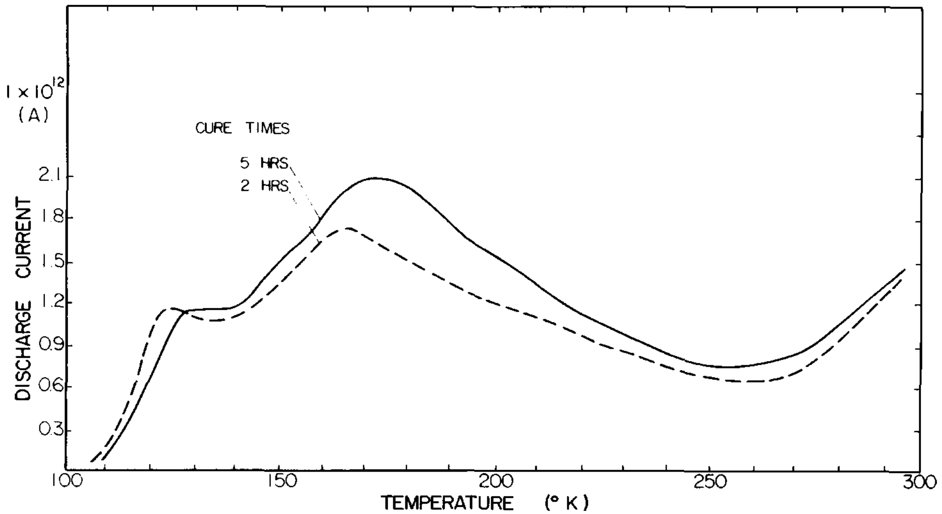

Fig. 6. Cure time effect at 140°C on TSDC thermograms, using epoxy resin E (20% deficient in curing agent).

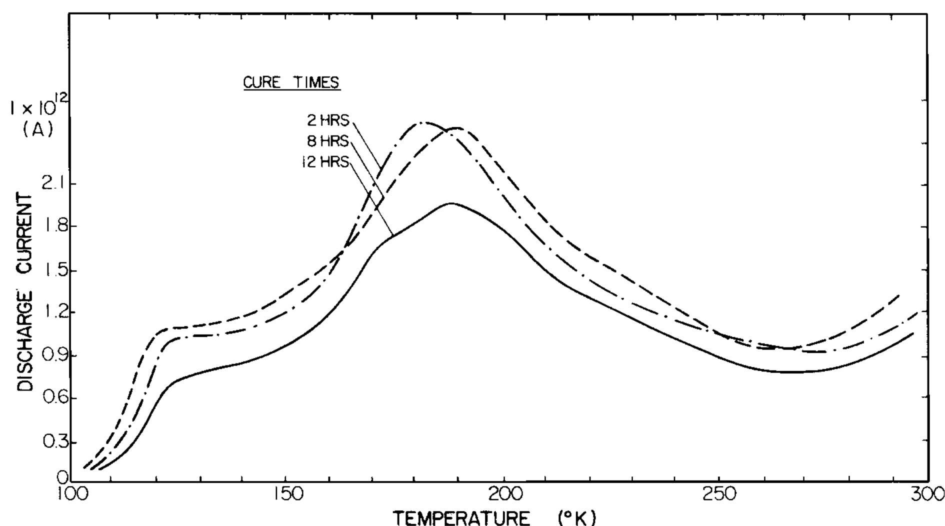

Fig. 7. Cure time effects as high temperature (181°C) on TSDC thermograms from epoxy resin A (standard formulation).

for whatever are the intended purposes for that resin. The above data show that extent of cure can be detected as a systematic change in TSDC thermogram, so TSDC can serve as a curing monitor for epoxy systems. Further study along these lines is anticipated.

Activation Energy of the β-Relaxation in Epoxy Resins

In order to resolve the individual dipolar peak from the broad β-relaxation peak and make specific molecular process assignments to each component of the peak, a partial heating method was applied.[12] This method involves the sequential heating of an initially polarized specimen to progressively higher temperatures and then cooling the specimen between each heating step. The discharge current is recorded during each heating step. A plot of ln I, where I is discharge current, versus reciprocal temperature reveals a linear relationship which suggests an application of Arrhenius or Eyring reaction rate theory and facilitates the determination of the activation energy over a small temperature interval. The activation energy–temperature spectrum is shown in Figures 8 and 9. One notes that this activation energy spectrum contains several temperature ranges over which the discharge processes are controlled by common activation energies. This suggests that some specific kinds of molecular events, or motions, may be the discharge rate-limiting steps throughout each of these particular temperature ranges.

In general, there are three activation energy plateaus observed in these figures. The plateau in the temperature range 120–150 K is fairly insensitive to the degree of curing and formulation, but the upper two activation energy plateaus do reflect changes in the state of cure. The assignment of specific molecular processes to the individual peaks is not possible at the present time. The molecular structures involved with the β-relaxation processes and the correlation of mechanical properties on this particular effect of activation energy will be the subject of the future research.

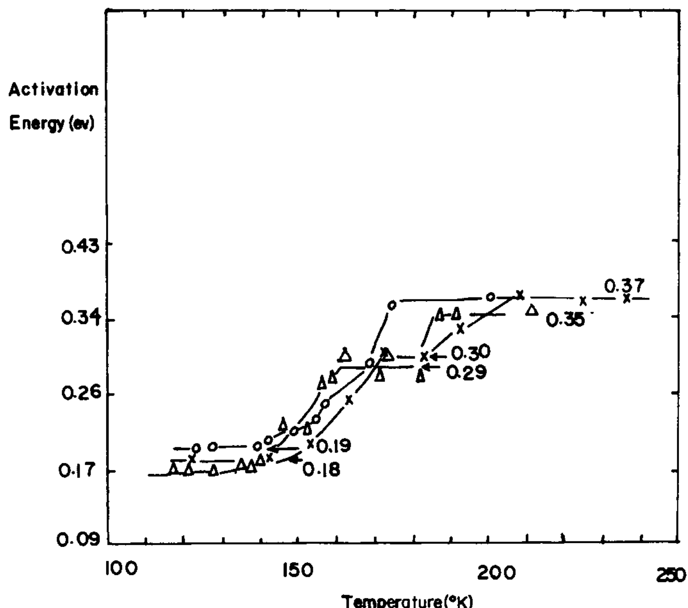

Fig. 8. Activation energy vs. TSD temperature for epoxy resins, cured at different temperatures, A_{11} (— X — X), 140°C; A_{21} (— O — O), 158°C; and A_{31} (— Δ — Δ), 181°C.

CONCLUSIONS

The TSDC technique has been found to be a very powerful tool for monitoring the extent of curing and investigating molecular structure of epoxy resin.

The polarization of epoxy resin in the temperature range of 100–300 K is be-

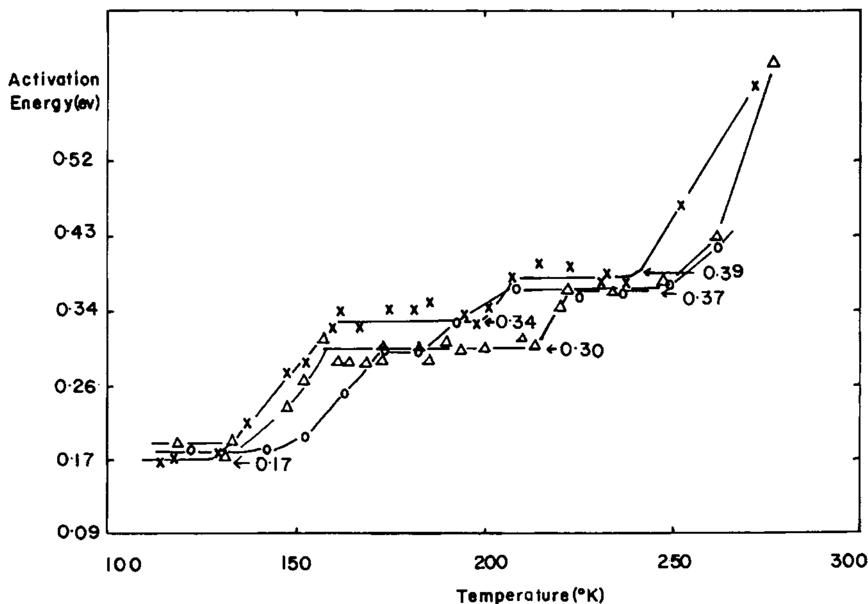

Fig. 9. Activation energy vs. TSD temperature for epoxy resins of different formulations, A_{11} (— O — O), B_{11} (— X — X), and E_{11} (— Δ — Δ).

lieved to be due to partial orientation of dipoles. The TSDC thermogram of epoxy resin showed that the β-relaxation peak is broad and rich in the information on polarization and relaxation processes.

Several individual relaxation processes can be resolved from the broad β-relaxation peak by the application of the partial heating method, and the activation energies of those individual processes that comprise the β peak have been calculated.

The authors wish to express their appreciation of the generous support of this research by the Chemistry Branch of the Office of Naval Research. Facilities for some of this research were made available by the Materials Research Center of Northwestern University (NSF-MRL program Grant DMR 76-80847).

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Received July 16, 1979
Revised November 2, 1979