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THERMALLY STIMULATED DISCHARGE CURRENT ANALYSIS OF EPOXY RESINS--ETC(U)
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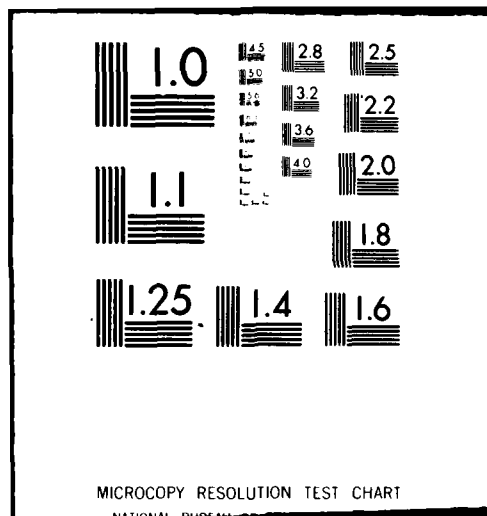
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"THERMALLY STIMULATED DISCHARGE CURRENT ANALYSIS OF EPOXY RESINS"

by

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"THERMALLY STIMULATED DISCHARGE CURRENT ANALYSIS OF EPOXY RESINS"

INTRODUCTION

Epoxy resins have been utilized as engineering materials because of their high mechanical strength, resistance to chemical attack and thermal stability. Epoxy-based fiber reinforced composites of more recent origin are also being developed and utilized as engineering structural materials, particularly in high-performance aircraft. The correspondingly more severe service requirements in these structural applications have resulted in renewed interest in the behavior of the epoxy resins themselves. Such interest is centered about their thermal and chemical stability, their adhesion characteristics, and their mechanical behavior in terms of strength, ductility, and fracture toughness.

Structural applications of epoxy resins normally are limited to temperatures below the heat distortion (or glass-transition) temperature, where these materials make very useful solids in terms of elastic modulus and strength. In addition, many epoxy resins have outstanding fracture toughness, due to their resistance to crack initiation and propagation during both static and dynamic loading conditions. High impact strength is usually related to such fracture toughness, and it has been found with other polymeric materials that this property can be associated with the existence local mode relaxation processes¹⁻⁹, such as the β or γ relaxations.

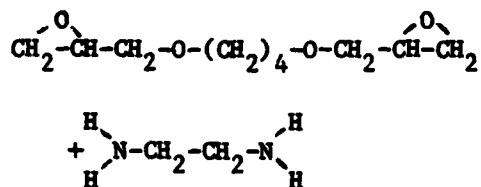
The local mode relaxations and the glass transition are being studied via thermally stimulated depolarization (TSD) current measurements. This technique is capable of determining both molecular dipole and space charge motion, and it permits the experimental resolution of complex relaxation modes because TSD corresponds to dispersion dielectric measurements made at very low frequencies, 10^{-3} Hertz. Furthermore, overlapping bands are

susceptible to resolution by the use of a peak cleaning method. In addition, the activation energy spectrum for relaxation processes can be obtained in TSD measurements by the use of a partial heating technique. This technique is also quite useful in evaluating the effect of low molecular species such as solvents or sorbed water upon relaxation processes.

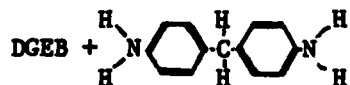
The structure and properties of epoxy resins are also dependent upon the cross-linkage molecular weight, M_c , and the density of the cross-links. The cross-link density and M_c are functions of stoichiometry and the curing process. The average degree of cross-linking can be characterized by M_c , which can be estimated from: (1) solvent swelling experiments¹⁰, (2) measurements of the glass transition temperature (T_g)^{11,12}, and (3) measurements of rubber-like elasticity above T_g ¹². The most important parameter of the polymer network is the average molecular weight, M_c , of chain segments connecting the junction points.

The epoxy resins currently under investigation are:

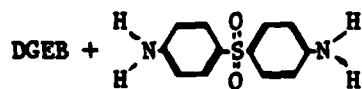
- 1) diglycidyl ether of butanediol (DGEb) plus ethylene diamine (EDA),



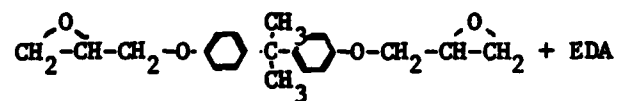
- 2) DGEb plus diaminodiphenyl methane (DDM),



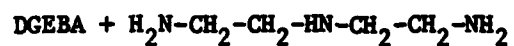
- 3) DGEb plus diaminodiphenyl sulfone (DDS),



4) diglycidyl ether of bisphenol A (DGEBA) + EDA



5) DGEBA plus diethylene triamine (DETA)



In addition to these epoxy resin systems, we have also measured the TSD spectra of DGEBA as a monomer and as a self-polymerized linear chain.

EXPERIMENTAL

The details of material preparation are cited in Table 1. The epoxy resins were molded between polished teflon plates or polyethylene-coated glass slides and cured in an inert atmosphere according to time-temperature schedules listed in Table 1. Specimens utilized in the thermally stimulated discharge (TSD) current measurements were 3.0 cm in diameter and were 0.03 to 1.0 mm thickness. Gold electrodes were vacuum evaporated onto opposite sides of the specimens to provide complete electrical contacts. Some of the TSD measurements were made on a Toyo-Seiki Electret Thermal Analyzer, while others were run on a TSD apparatus of our own design and construction¹³. The thermograms were obtained at heating rates of 2°C per minute.

Differential scanning calorimetry was performed with a Perkin-Elmer Model DSC-IB. Thermograms were obtained isothermally or at heating rates of 10°C/min. The infrared spectroscopy was done by means of a Fourier Transform Infrared Instrument, Nicolet Model 7199. Absorbance was measured as the area under the appropriate peaks with their baselines constructed as a chord tangent to the sides of the individual peaks. Dynamic-mechanical measurements were made at 11 Hz in the temperature range 25°C to 190°C using a Rheovibron Dynamic Viscoelastometer.

RESULTS AND DISCUSSION

The first epoxy system listed in Table I investigated DGEBA-EDA contains only the minimum functional groups (epoxy and amine groups) to react. The TSD thermogram for this system consists of two local mode relaxations at about 110° and 180°K and a rapid increase in current above 220°K, the onset of the glass-transition, Figure 1. When the system was not subjected to the elevated post-curing treatment at 88°C, the TSD thermogram, Figure 2, still had the two local mode relaxations but they were reduced in magnitude and may be somewhat more distributed. In addition, the temperature of the onset of the glass-transition appears to be increased by about 10°K, this is in contrast to the T_g 's listed in Table I for this system. When the molecular segment $\begin{array}{c} \text{H} \text{ H} \\ | \quad | \\ -\text{C}-\text{C}- \\ | \quad | \\ \text{H} \text{ H} \end{array}$ in the amine is replaced by the segment $\begin{array}{c} \text{H} \\ | \\ -\text{C}- \\ | \\ \text{H} \end{array}$ to form the DGEBA-DDM resin system number 2, the TSD thermograms still showed the two local mode relaxations, perhaps more distributed than in the DGEBA-EDA system and with peak temperatures increased by about 10°K, Figure 3. In addition, the onset of T_g has been increased to about 250°K. Note, however, that no additional peaks were observed in this system.

When the nonpolar methane molecular segment of the DDM amine is replaced by the sulfone polar segment to form the number 3 resin system DGEBA-DDS, the thermogram still consists of the two local mode relaxations with the onset of the glass transition now in excess of 260°K, Figure 4. The same system, when cured to a lesser extent, 88%, also showed the two local mode relaxations, Figure 5, but now they are not as distributed as in the case of the 100% cured DGEBA-DDS resin.

In the system DGEBA-EDA where the molecular segment $\begin{array}{c} \text{H} \text{ H} \text{ H} \text{ H} \\ | \quad | \quad | \quad | \\ -\text{C}-\text{C}-\text{C}-\text{C}- \\ | \quad | \quad | \quad | \\ \text{H} \text{ H} \text{ H} \text{ H} \end{array}$ in DGEBA has been replaced by the molecular segment $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}- \\ | \\ \text{CH}_3 \end{array}$, the TSD thermogram

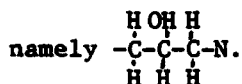
shows only one prominent local mode relaxation at 200°K, Figure 6.

The lowest temperature peak has become quite distributed and decreased in magnitude; it is now only a shoulder on the thermogram at about 140°K. The α -transition is also increased to temperatures in excess of 300°K.

In summarizing these finds, we found that the phenyl group in the epoxy resin system does not participate directly in the low temperature local mode transitions. The phenyl groups do profoundly effect the glass transition. As indicated in Table 1, the DGEBA + EDA resin system, which does not contain a phenyl group, has a T_g of -263°K(-10°C). The addition of the phenyl group to the system either via the amine part (in the system DGEBA + DDM or DGEBA-DDS) or the epoxy resin part (system DGEBA-EDA) results in an increase in T_g of 75 to 100°, the largest increase in T_g occurred when the phenyl group was in the epoxy backbone resin part of the system.

In an attempt to clarify the origin of the local mode relaxations observed in the four epoxy resin systems cited, TSD measurements were made on the epoxy resin part without the amine addition. Figure 7 shows the thermogram of unreacted DGEBA. The relaxations at 110° and 180-200°K are absent, and a new weak relaxation appears at 150°K. When DGEBA is linearly polymerized, designated DER667, only one prominent local mode relaxation appeared at 130°K, Figure 8. Since the 110°K relaxation is common to all of the epoxy resin systems, this local mode transition is most likely associated with the ether linkage. There are several reasons for arriving at this judgment. First, the DGEBA-EDA system, Figure 6, had a relaxation, as indicated by the shoulder, at 140°K, while the other systems had local mode relaxations at about 110°K. This increase from 110°K to 140°K may be due to the presence of the adjacent stiffer phenylene group which reduced the mobility of the ether linkage and thus resulted in the increase in the temperature for this relaxation in the DGEBA-EDA system. Second, the TSD thermograms of the unreacted DGEBA and the

linearly polymerized DGEBA(DER667) also displayed similar effects by the adjacent phenylene groups. In the case of DER667, the local mode relaxation was shifted to about 130°K, Figure 8, while the relaxation in DGEBA was greatly reduced in strength. The peak at 180-200°K is thought to reside in the local motion of the molecular segment created during the curing reaction,



The activation energy for the local mode relaxations was determined by applying the partial heating method^{14,15} to the epoxy resin systems. The preliminary results for two systems, DGEBA-EDA and DGEBA-DDM are shown in Figures 9 and 10 respectively. These figures clearly show that the local mode relaxations are distributed and, in addition, the change in slopes appears to suggest distributions about two local modes in DGEBA-EDA, Figure 9, and three local modes in DGEBA-DDM, Figure 10. The distributive nature of the activation process is most likely to be associated with the complexity of the molecular structure in the cross-linked epoxies.

In order to evaluate the effect of nonstoichiometry upon the cross-linking density in epoxy resins, dynamical-mechanical measurements and TSD measurements have been made on the epoxy resin system number 5, DGEBA cured with DETA. DGEBA was heated to 60°C and, after cooling to room temperature, mixed with DETA; the mole ratio of epoxide to amine and the curing conditions are listed in Table I.

Figures 11 and 12 show the temperature-dependence of the complex tensile modulus and $\tan \delta$ for the stoichiometric, the amine-rich, and the epoxide-rich systems. The peaks in E'' and $\tan \delta$ of Figures 10 and 11 are related to the glass-transition temperature, T_g . The DSC determination of T_g is also listed in Table I. In agreement with reports in the literature¹⁶, the stoichiometric system had the highest T_g . The cross-link molecular weight, M_c , can be estimated from the elastic shear modulus above T_g by the relation:

$$G = \rho RT/M_c \quad (1)$$

where ρ is the polymer density and R is the gas constant. Table 2 lists the M_c values evaluated in this way. M_c is also related to T_g by the expression:

$$M_c = 3.9 \times 10^4 / (T_g - T_{g_0}) \quad (2)$$

where T_{g_0} is the glass transition for the uncrosslinked polymers. In our case, T_{g_0} is taken as the melting temperature of DGEBA as determined from DSC measurement, i.e., 44°C . Thus, by utilizing equation 2, the validity of M_c can be ascertained by computing the T_{g_0} from the observed T_g and calculated values of M_c . As noted in Table 2, the value of T_{g_0} for the stoichiometric system is quite reasonable and lends credence to this method of determining M_c .

The relaxation strength of the glass-transition as measured by $\tan \delta$ is larger for the off-stoichiometric compositions in agreement with the literature¹⁷. The increase in magnitude of the peaks has been associated with the increase in M_c ¹⁷.

The activation energy, ΔH , for the T_g transition can be estimated from the relation¹⁶.

$$\Delta H = \left[G_R^{T_{\max}} - G_u^{T_{\max}} \right] R\pi/2 \int_0^\infty G'' d(1/T) \quad (3)$$

where $T_{\max}$ is the temperature of the maximum loss, G'_u and G'_R are the unrelaxed and relaxed shear moduli respectively, G'' is the out-of-phase component of shear modulus, and R is the gas constant. The estimated values are tabulated in Table II. The ΔH values are clearly composition-dependent and vary inversely with M_c . The distribution of the activated process can be evaluated from the relation between activation energy and width of the relaxation peak at half value, i.e.,

$$\Delta H = 2.63R(1/T_1 - 1/T_2) = 2.63R\Delta(1/T) \quad (4)$$

where T_1 and T_2 are the higher and lower temperatures for the half-value of

the G'' peak value. Comparison of the observed and calculated values of peak width in Table II clearly demonstrates the distributive nature of T_g . There is the suggestion that the distribution is greatest for the stoichiometric composition, that is to say, the system with the smallest M_c has the largest deviation of relaxation times from that of the average M_c . Others have attributed the distributed nature of T_g to the inhomogeneous structure of epoxy polymers¹⁸.

TSDC measurements of the three DGEBA-DETA epoxy systems are shown in Figure 13. In agreement with the results observed in the other epoxy systems listed in Table I, a local mode relaxation occurred at about 220°K in the stoichiometric system, while the non-stoichiometric systems both show low temperature relaxations at about 150°K. The excess amine system also had a 220°K relaxation which was not observed in the excess epoxide system. The 150°K, or γ , relaxation has also been observed in the epoxy system DGEBA cured with triethylene tetramine in dynamical-mechanical measurements¹⁶. The strength of the relaxation (peak value of $\tan \delta$) increased with degree of cure¹⁶; this complements the results discussed for Figures 1 and 2 and Figures 7 and 8. The strength of the 220°K, or β , relaxation has been correlated with the content of the hydroxy ether moiety¹⁸ $\begin{array}{c} \text{OH} \quad \text{H} \\ | \quad | \\ -\text{C}-\text{C}-\text{O}- \\ | \quad | \\ \text{H} \quad \text{H} \end{array}$; the same conclusion reached in our earlier discussion of the 220°K local mode transition. The failure to observe the β -relaxation in the excess epoxide system, Figure 13, is associated with the insufficient number of hydroxy groups formed because the number of active hydrogens in the amine is unable to complete the curing reaction and thereby cause a decrease in the number of hydroxy ether segments.

The TSD thermogram for DGEBA-DETA above 273°K is strongly dependent upon the chemical composition of the epoxy system, Figure 13. Both the stoichiometric and excess epoxide compositions have relaxation peaks at about 380°K followed by an increase in the current at the higher temperatures. The excess

epoxide sample also had a peak at about 430°K. The thermogram of the sample with the excess amine had relaxation peaks at 350°K and 380°K. The origin of the high temperature relaxations appears to be space charge because the peak temperature varied with the strength of the polarizing field, E_p , Figure 14. If the relaxations were dipolar, the peak temperature should be independent of E_p ¹⁹. Note that the low temperature portion of the thermogram, Figure 14, is invariant with E_p . This electric field-dependence of high temperature TSD peaks has been discussed previously^{20,21}. The conformity of polarization also effects the TSD thermogram. If the initial polarization, P_o , is uniform (as would not be expected to be the case for space charging), P_o should be independent of the heating rate, but as indicated in Table III, P_o is observed to depend upon the heating rate. The inhomogeneity of the internal field might, furthermore, suggest an inhomogeneous physical and/or chemical structure in the polymer. Additional arguments in support of the space charge origin of the high temperature relaxations are the variation of the current with the electrode material, Figure 15, and the variation of the thermogram with specimen thickness at a constant electric field density, Figure 16.

Elucidation of the exact molecular nature of the relaxation processes in epoxy resins is, of course, a necessary part of this research. Most valuable information is obtained experimentally from the relaxation parameters: the activation energy (ΔH), the activated volume (ΔV), and the pre-exponential factor, τ_o . While both ΔH and τ_o can be readily determined in the usual TSD experiment, the determination of ΔV requires the pressure-dependence of the TSD spectrum. A high pressure TSD cell has been designed and is currently under construction. It will provide the data from which it will be possible to determine the activated volume for the various relaxation transitions (especially those that are "local mode" in character).

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TABLE I

System(active hydrogen: epoxy group)	Mixing Condition	Mold	Curing Processing	Extent of Cure (Epoxy group reacted)	T _g , °K
1. DGEBA + EDA (1:1)	Mix both liquid components by magnetic stirrer at room temperature	Teflon plates	24 hrs. at room temperature + 6 hrs. at 88°C, 1 atm. N ₂	100	267
" " "	"	"	24 hrs. at room temperature, 1 atm. N ₂	100	260
2. DGEBA + DIM (1:1)	Dissolve DIM into DGEBA which had been heated to 100°C	"	10 hrs. 50 min. at 150°C, 1 atm. N ₂		349
3. DGEBA + DDS (1:1)	Dissolve DDS into DGEBA which had been heated to 135°C	"	8 hrs. at 150°C, 1 atm. N ₂	100	347
" " "	"	"	2 hrs. at 150°C, 1 atm. N ₂	88	312
4. DGEBA + EDA (1:1)	Mix at room temperature for 5 min.	"	5 hrs., 30 min. at room temperature + 5 hrs. at 88°C, 1 atm. N ₂		373
5. DGEBA + DETA (1:1)	Mix at room temperature	Polyethylene coated glass plate for precuring, curing + 6 hrs. teflon plate at 120°C (post-curing)	24 hrs. at room temperature		421
" " (2:1)	"	"	"		357
" " (1:2)	"	"	"		323

Table II

Characterization of DGERA cured with DETA

Mole Ratio of Active hydrogen/epoxide	T_g (°C)	T_{max} (°C)	M_c	T_{g_0} (°C)	ΔH (Kcal/mol)	$\Delta(1/T)_{obs.}$ (10^{-4}OK^{-1})	$\Delta(1/T)_{calc.}$ (10^{-4}OK^{-1})	$\frac{\Delta(1/T)_{obs.} - \Delta(1/T)_{calc.}}{\Delta(1/T)_{calc.}}$	
								$\Delta(1/T)_{obs.}$ $\Delta(1/T)_{calc.}$	$-\Delta(1/T)_{calc.}$ $\Delta(1/T)_{calc.}$
A1 1:1	148	146	372	41	176	1.01	0.3		2.4
A2 2:1	84	87	1584	62	156	0.92	0.3		2.0
A $\frac{1}{2}$ 1:2	50	70	1978	50	93	1.5	0.56		1.7

T_g = glass transition temperature, T_{g_0} = glass transition temperature of uncrosslinked polymer, T_{max} = peak temperature of imaginary part of dynamical tensile modulus (E'') at 11 Hz, M_c = molecular weight between cross links, ΔH = activation energy, $\Delta(1/T) = 1/T_1 - 1/T_2$; T_1 and T_2 are the temperatures at which E'' is at half its peak value. Curing cycle: 24 hrs. at 25°C plus 6 hrs. at 120°C.

Table III

Depolarization charge of α peak of DGEBA
cured with stoichiometric amount of DETA

Heating Rate (°C/min.)	Peak Temperature (°C)	Depolarization Charge (10^{-9} coulomb/cm ²)
1	89	1.6
2	103	1.4
3	108	0.97

Curing cycle, 24 hr. at 25°C plus 6 hr. at 120°C

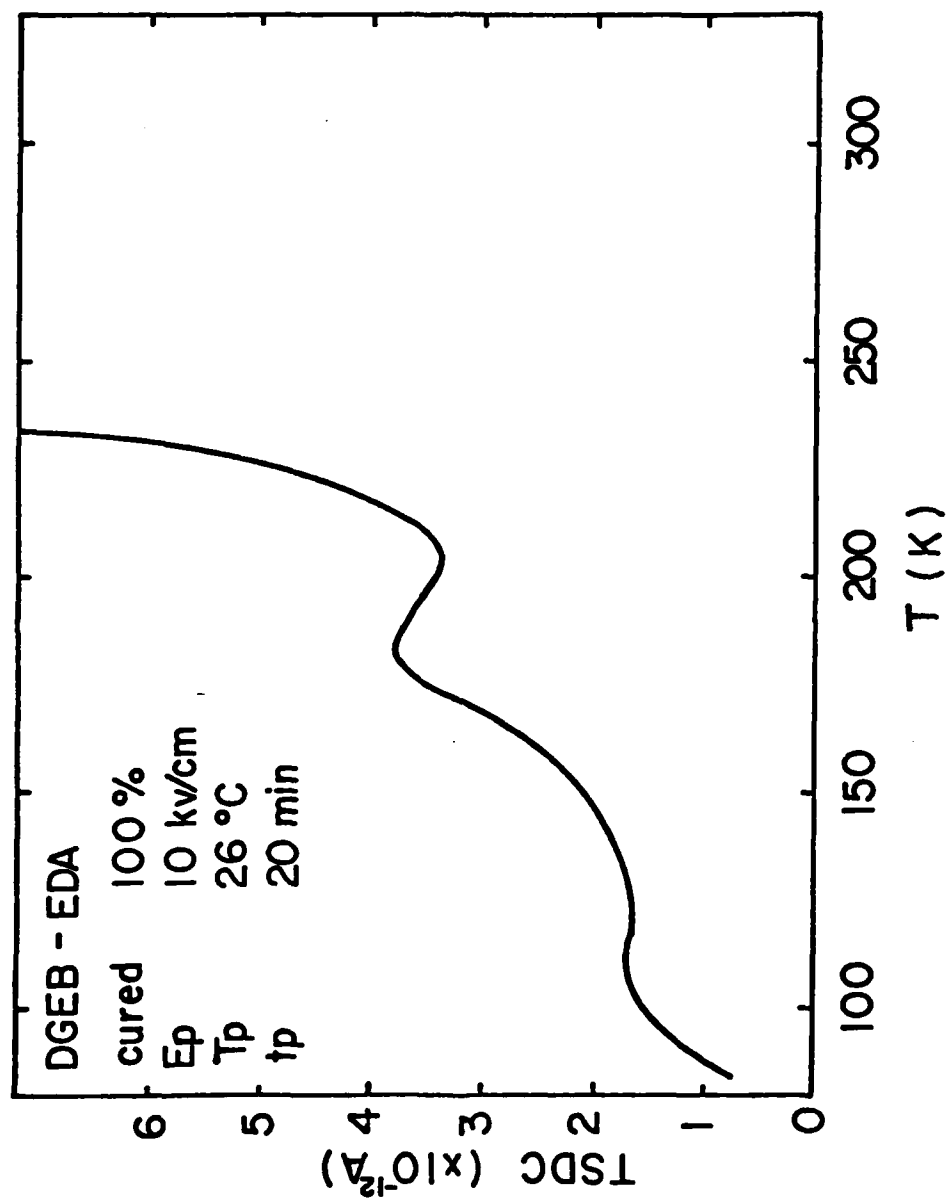


Figure 1. TSD thermogram of DGEBA + EDA Epoxy Resin cured 24 hours at 22°C plus 6 hrs. at 88°C.

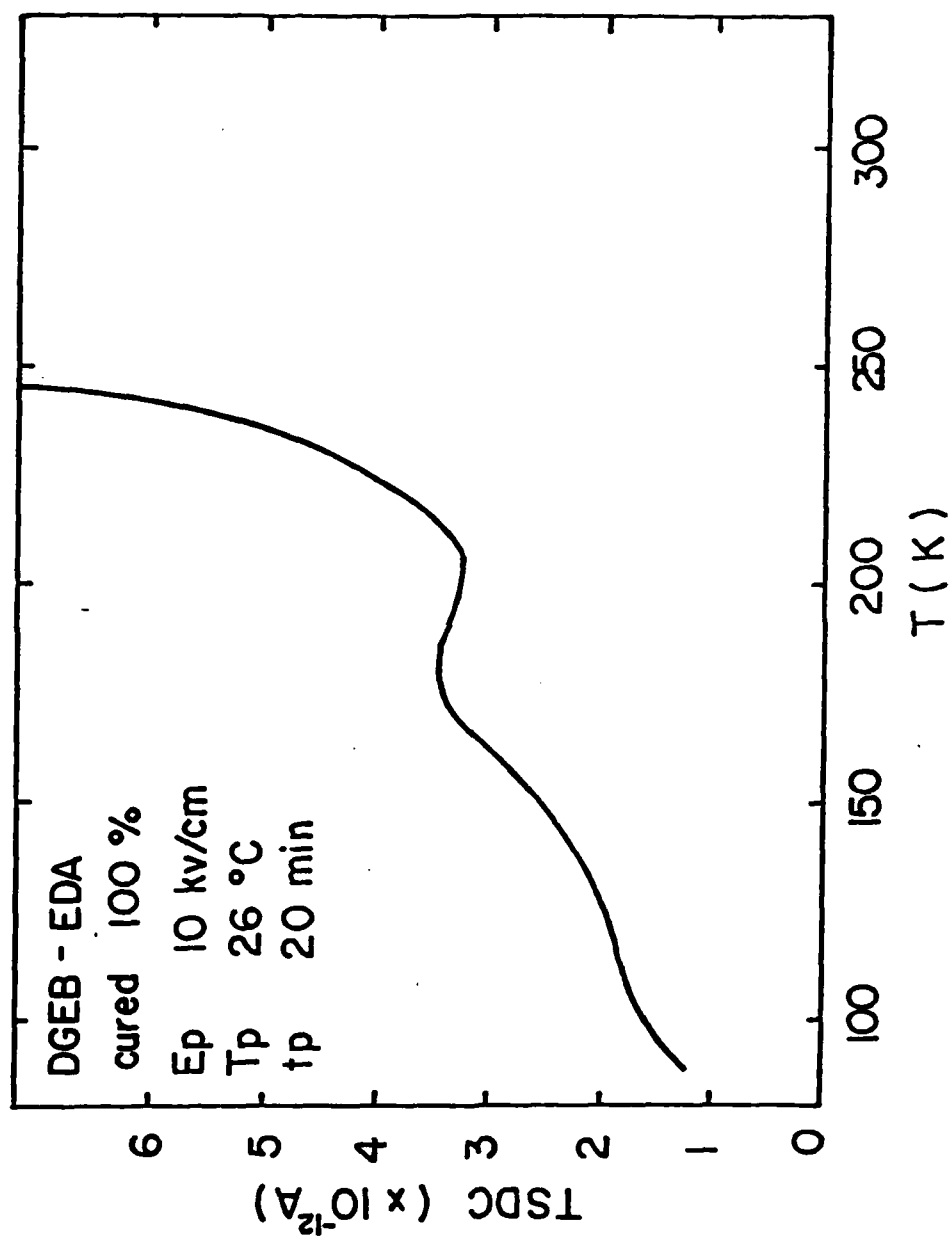


Figure 2. TSD thermogram of DGEBA + EDA Epoxy Resin cured 24 hrs. at 22°C.

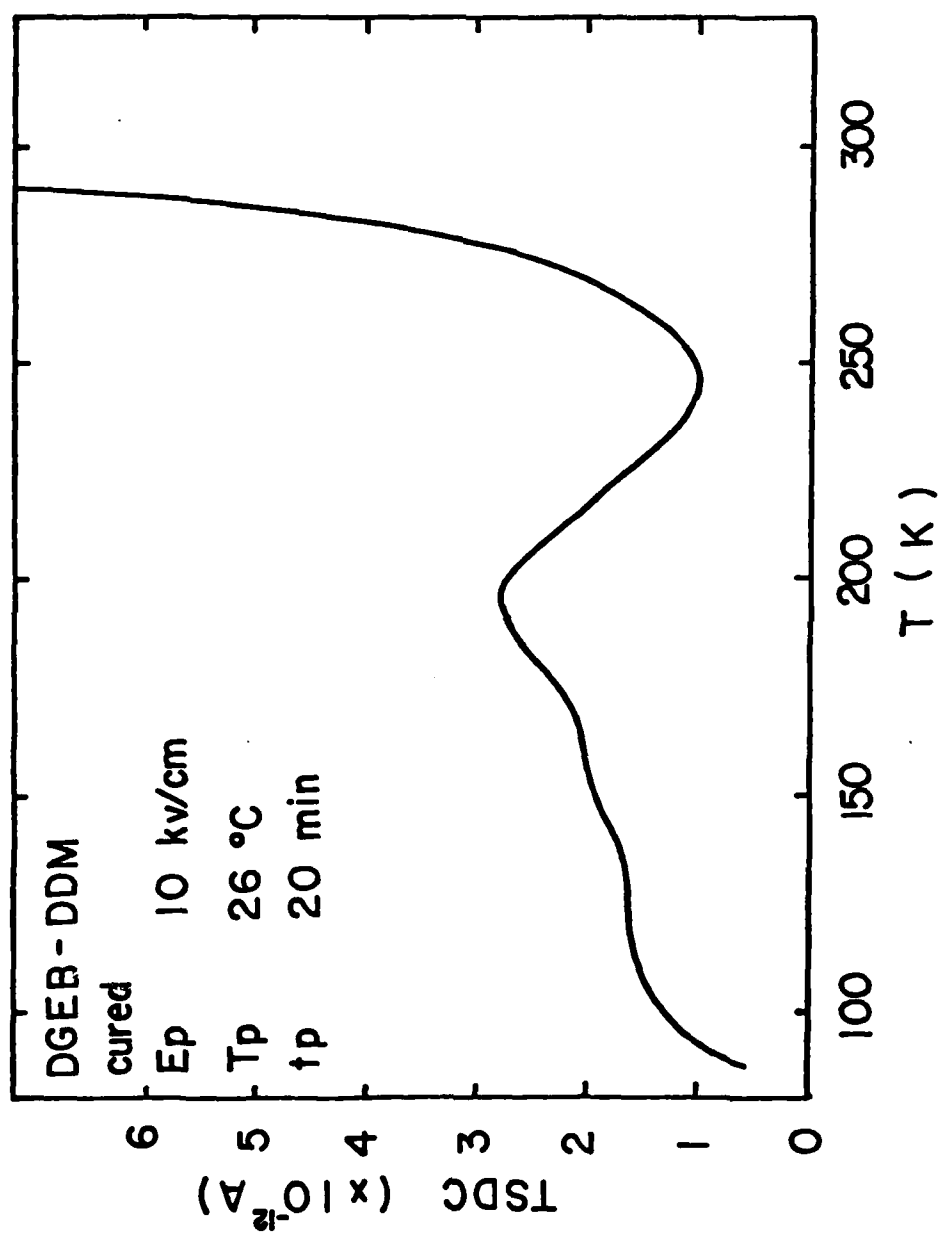


Figure 3. TSD thermogram of DGER + DDM Epoxy Resin cured -11 hrs. at 150°C.

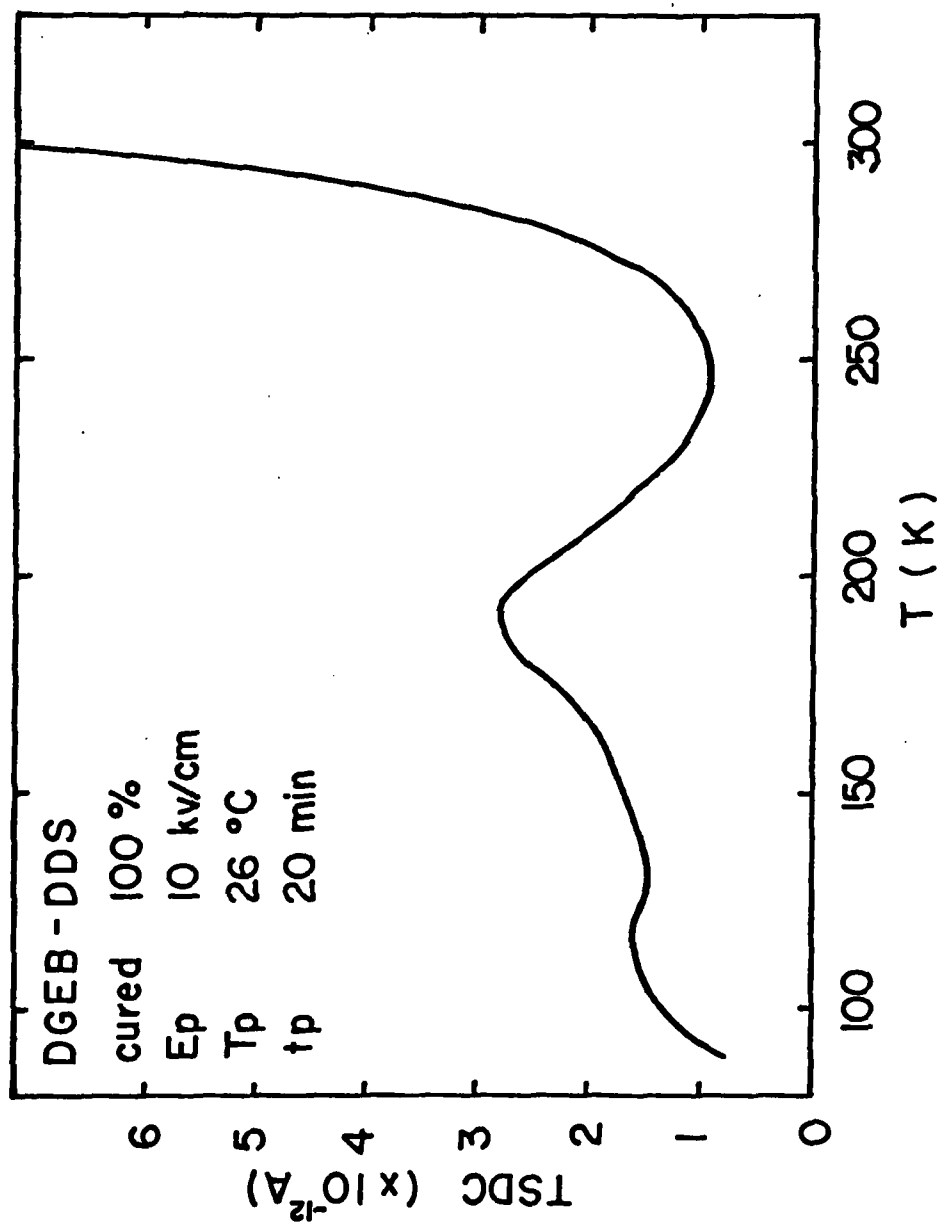


Figure 4. TSD thermogram of DGEB + DDS Epoxy Resin cured 8 hrs. at 150°C.

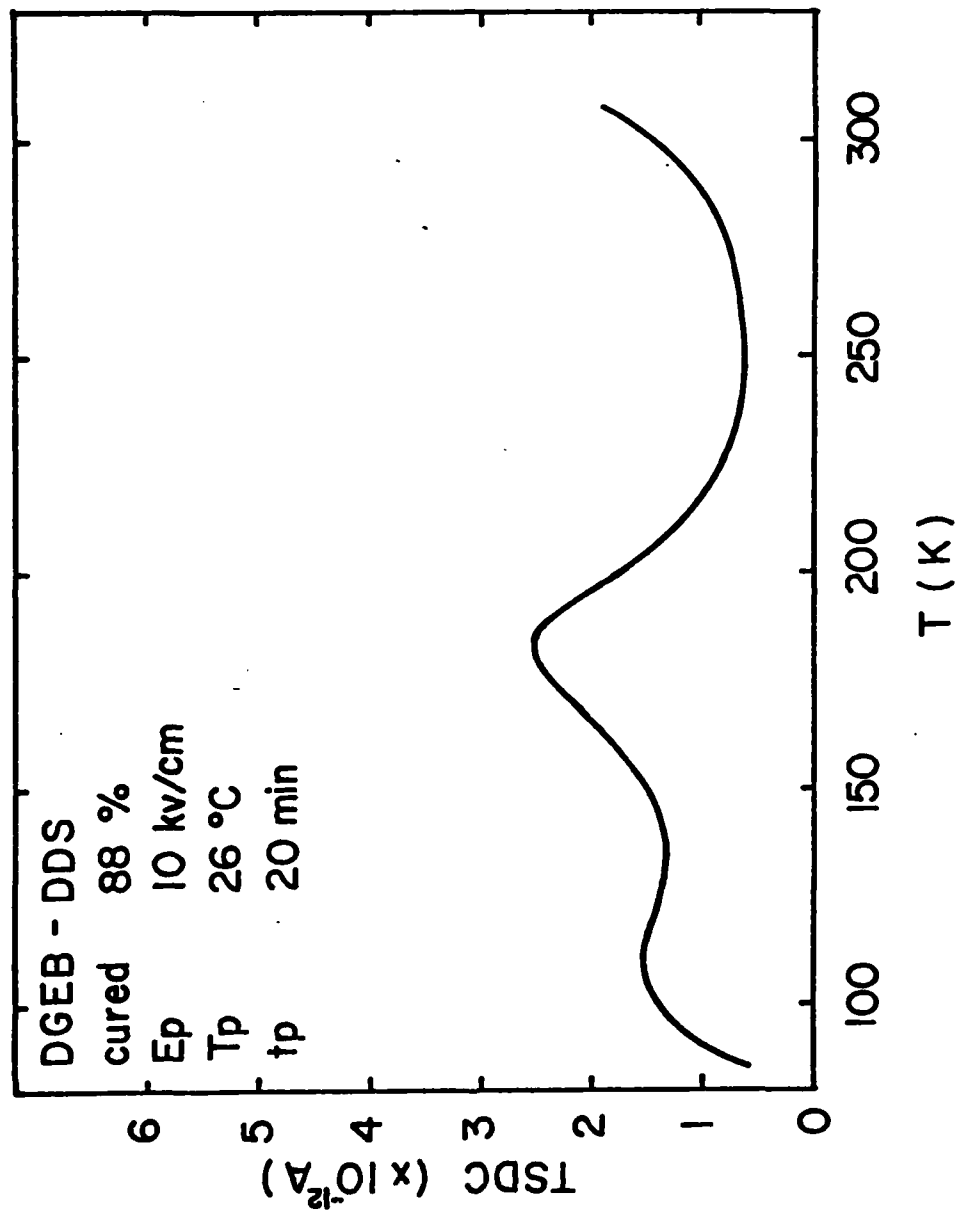


Figure 5. TSD thermogram of DGEB + DDS Epoxy Resin cured 2 hrs. at 150°C.

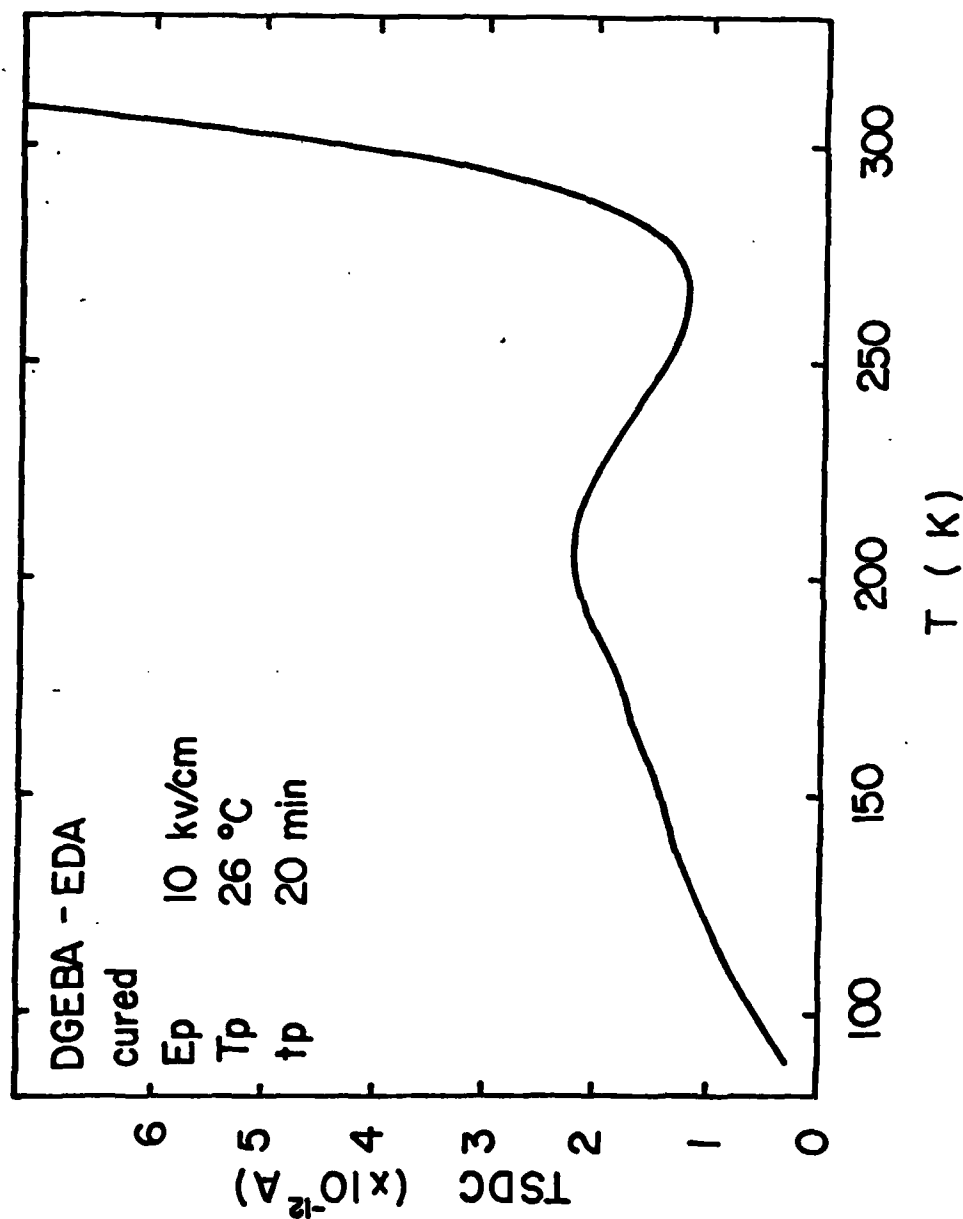


Figure 6. TSD thermogram of DGEBA + EDA Epoxy Resin cured 5 hrs. at 22°C plus 5 hrs. at 88°C.

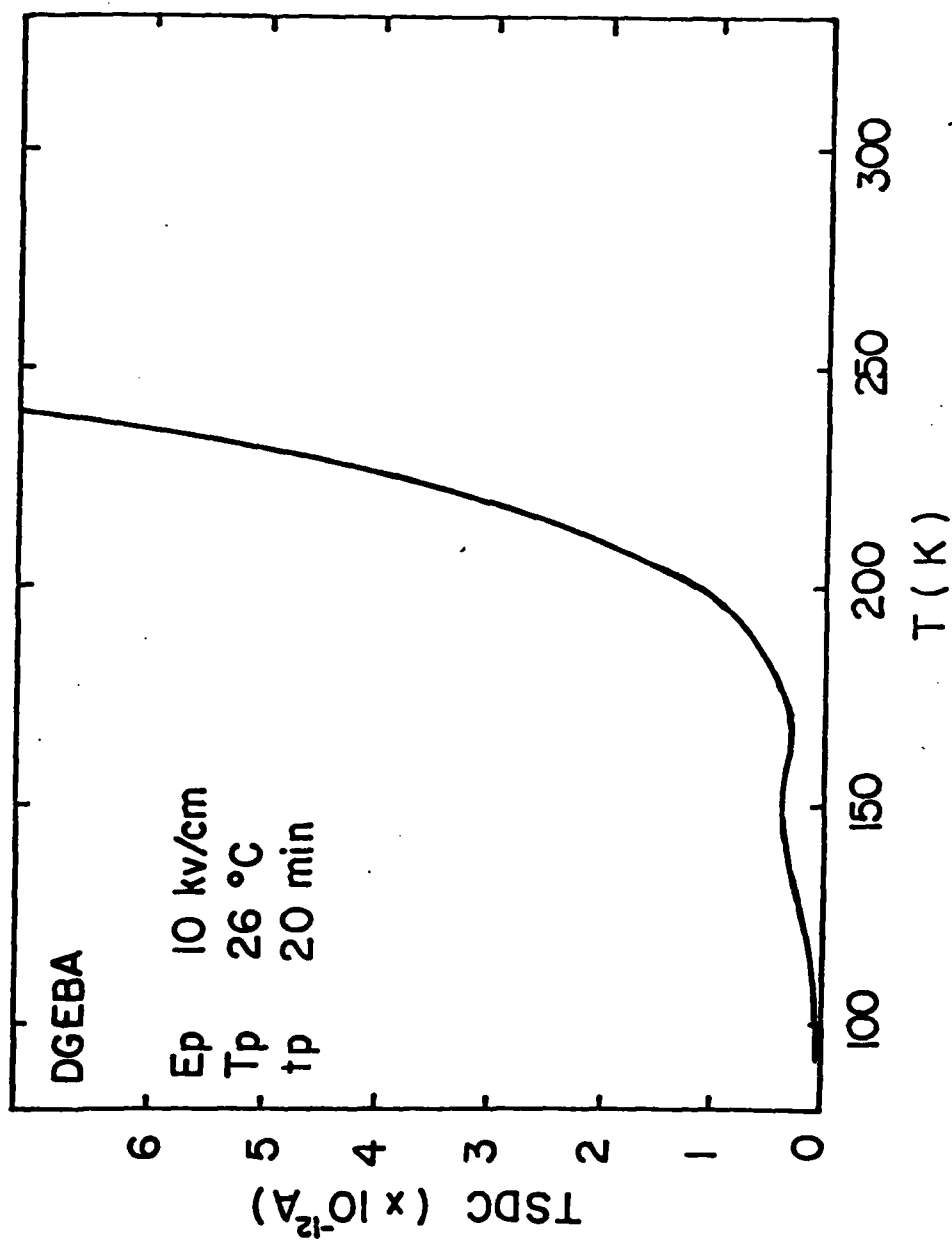


Figure 7. TSD thermogram of DGEBA monomer.

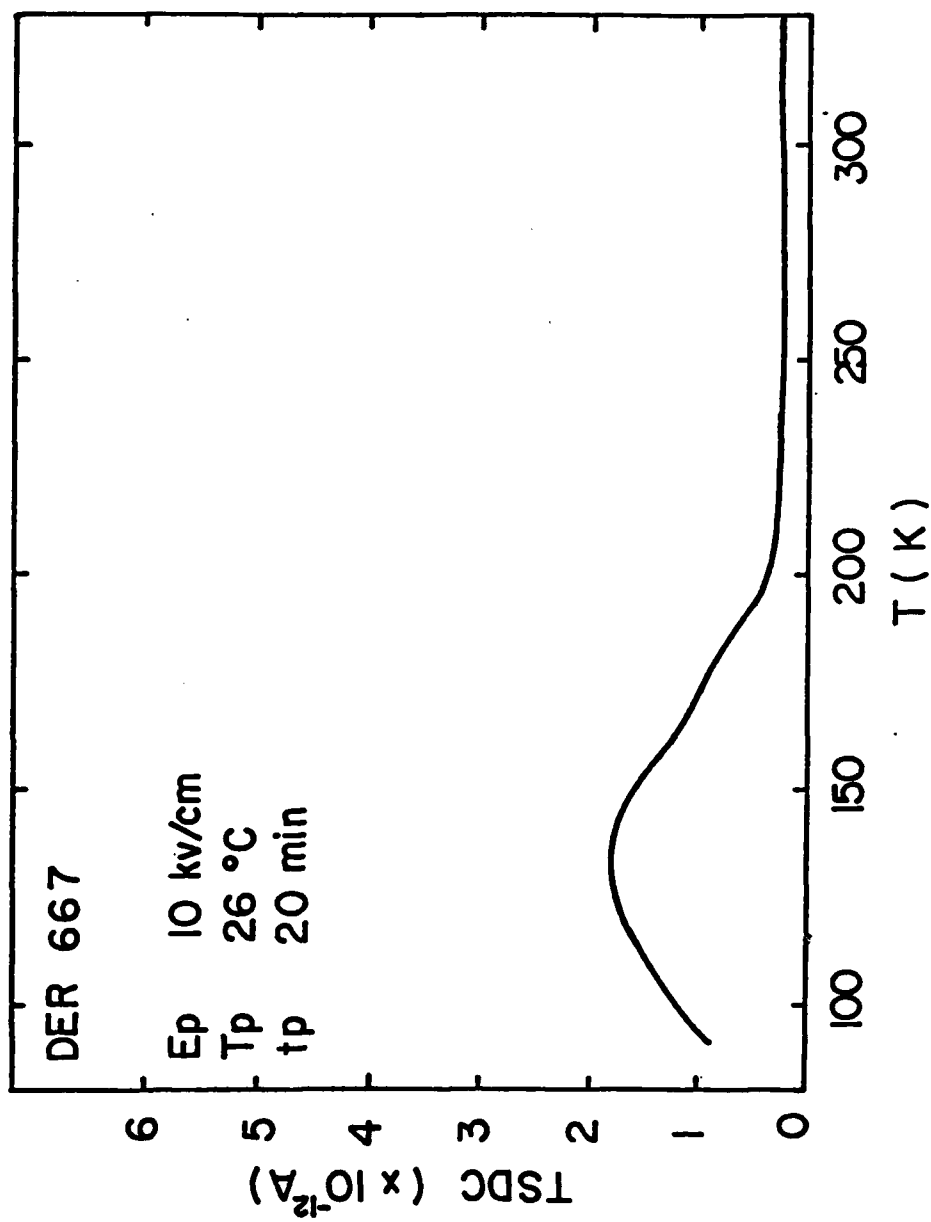


Figure 8. TSD thermogram of linearly polymerized DGEBA.

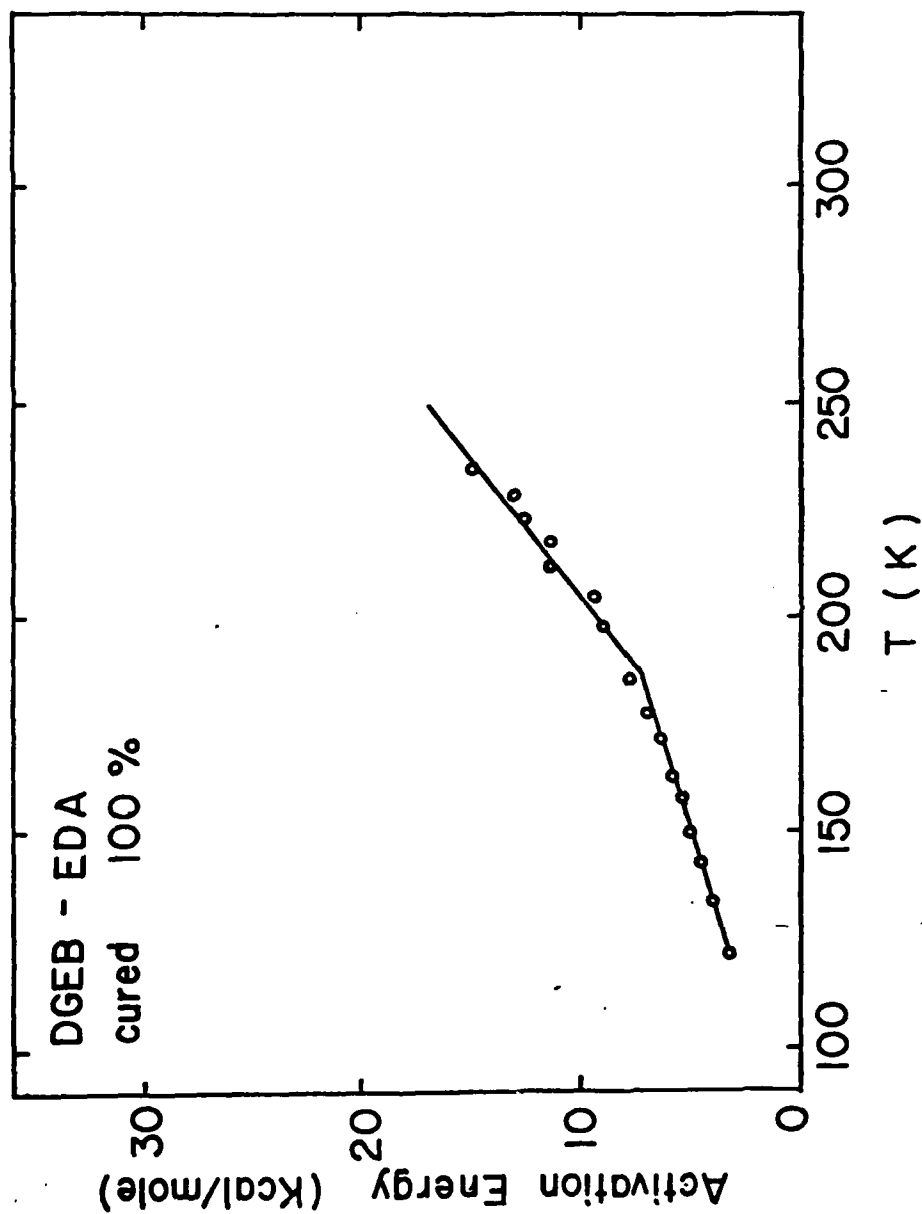


Figure 9. Activation Energy Distribution of DGEBA + EDA Epoxy Resin
cured 24 hrs. at 22°C plus 6 hrs. at 88°C.

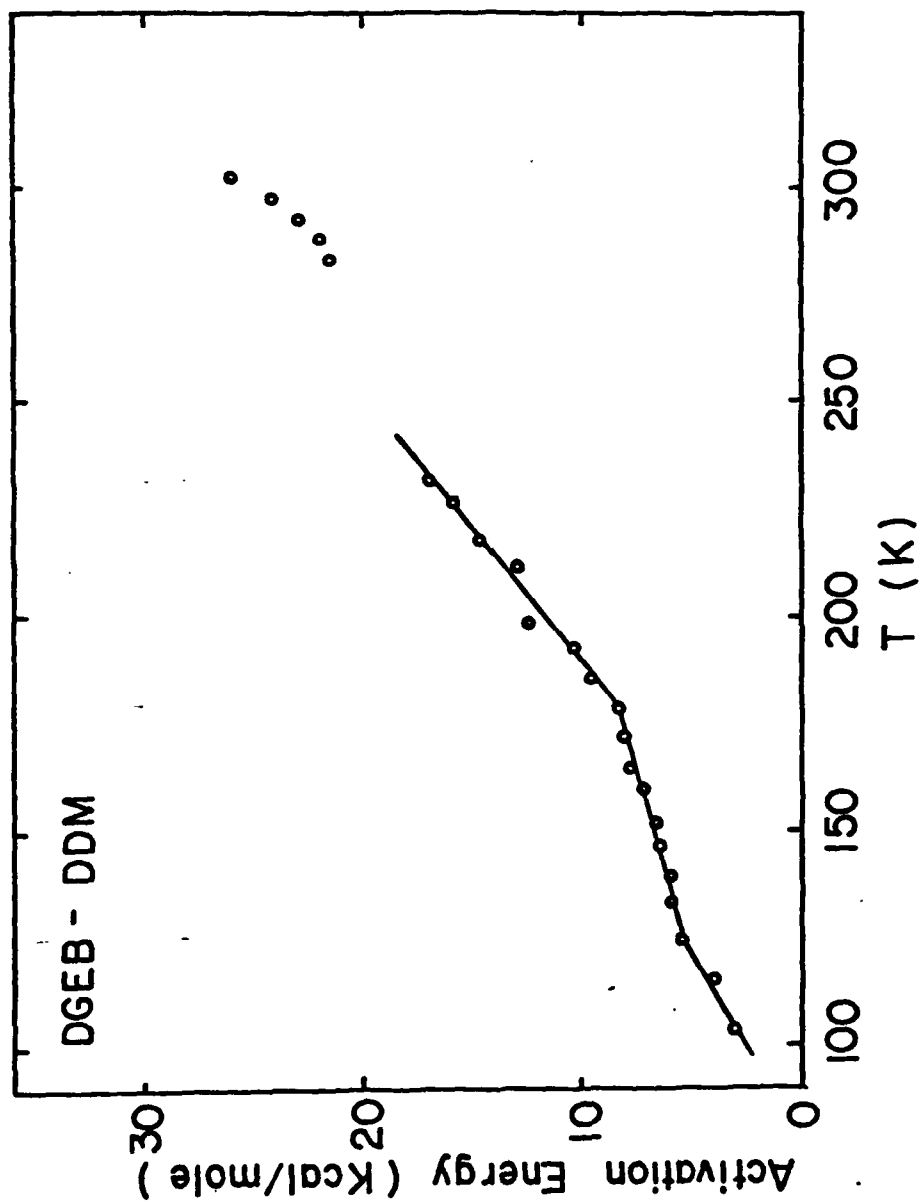


Figure 10. Activation Energy Distribution of DGEB + DDM Epoxy Resin cured 8 hrs. at 150°C.

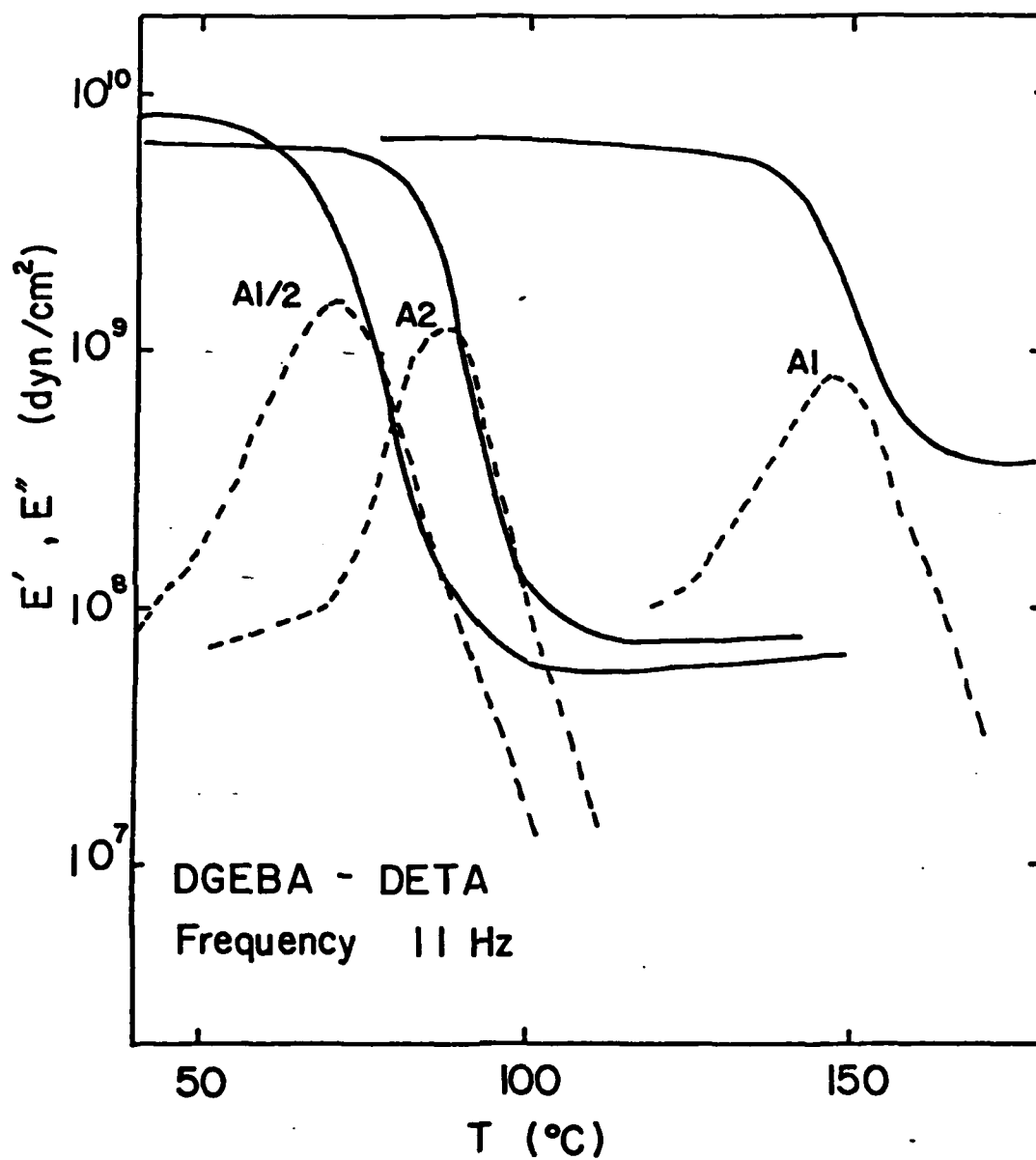


Figure 11. Temperature dependence of Dynamical Elastic Modulus
 DGEBA + DETA Epoxy Resins cured 24 hrs. at 25°C plus
 6 hrs. at 120°C. Mole Ratio of active hydrogen/epoxide
 A-1 1:1, A-1/2 1:2, A-2 2:1.

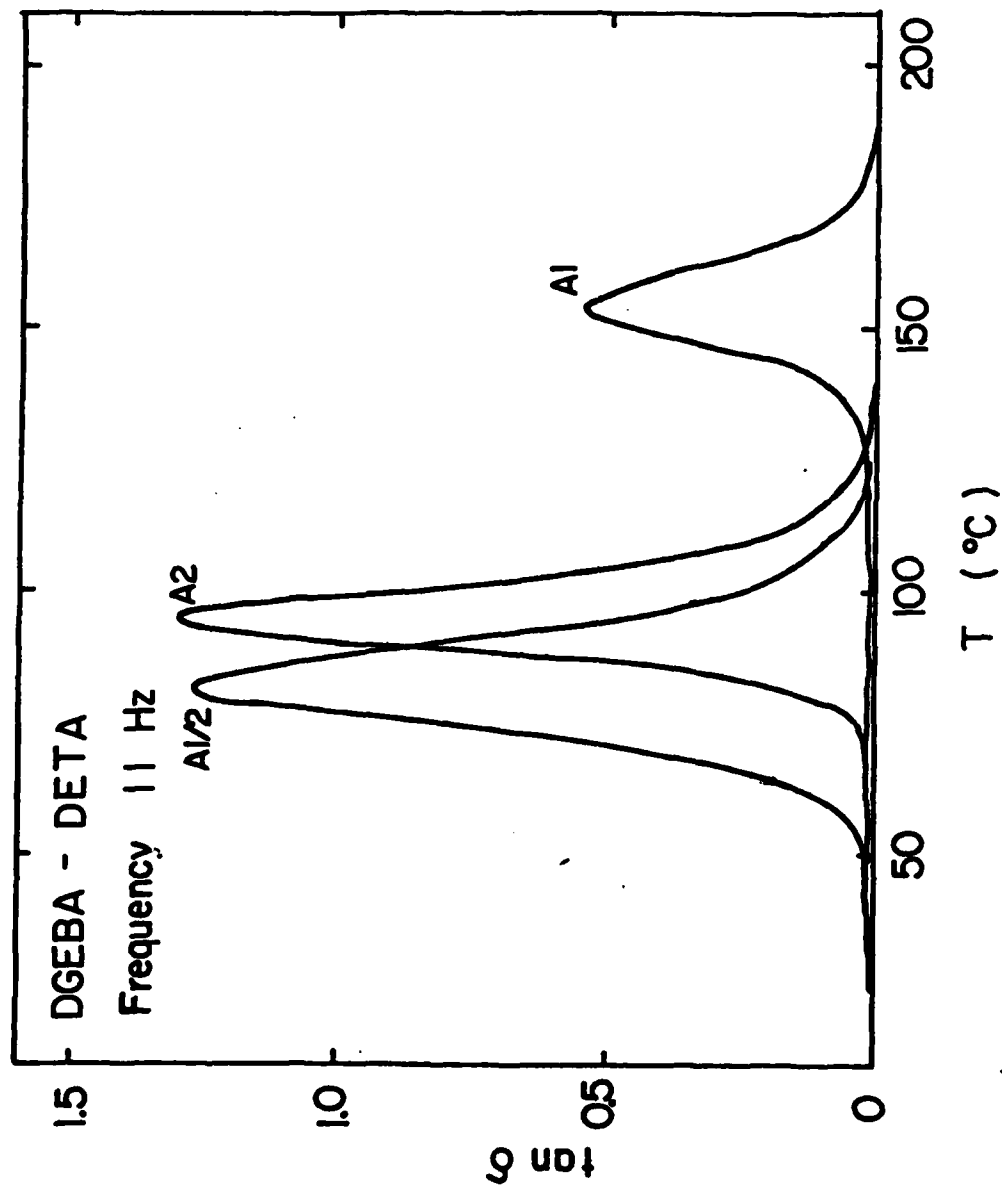


Figure 12. Temperature dependence of internal friction of DGEBA + DETA Epoxy Resins cured 24 hrs. at 25°C plus 6 hrs. at 120°C. Mole Ratio of active hydrogen/epoxide A-1 1:1, A-2 1:2, A-2 2:1.

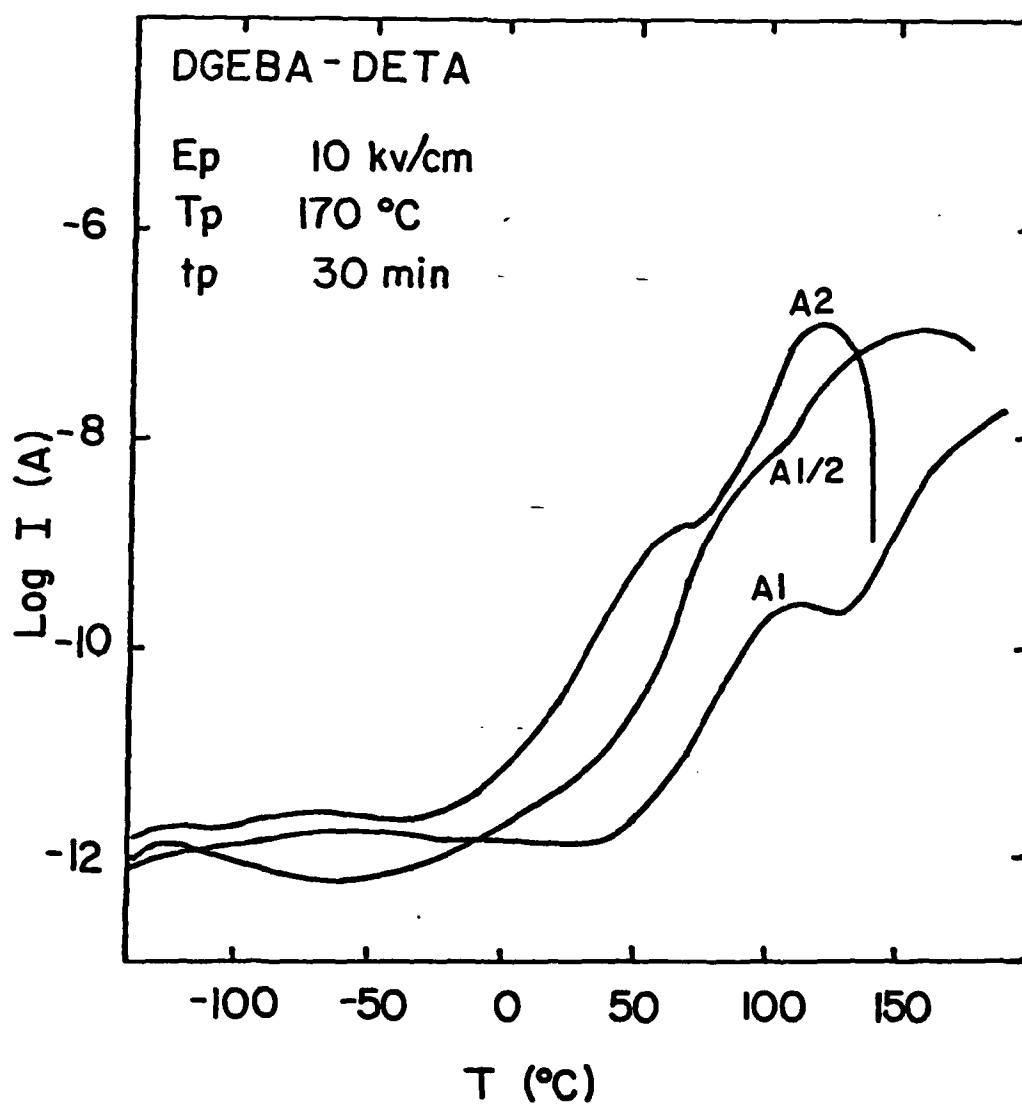
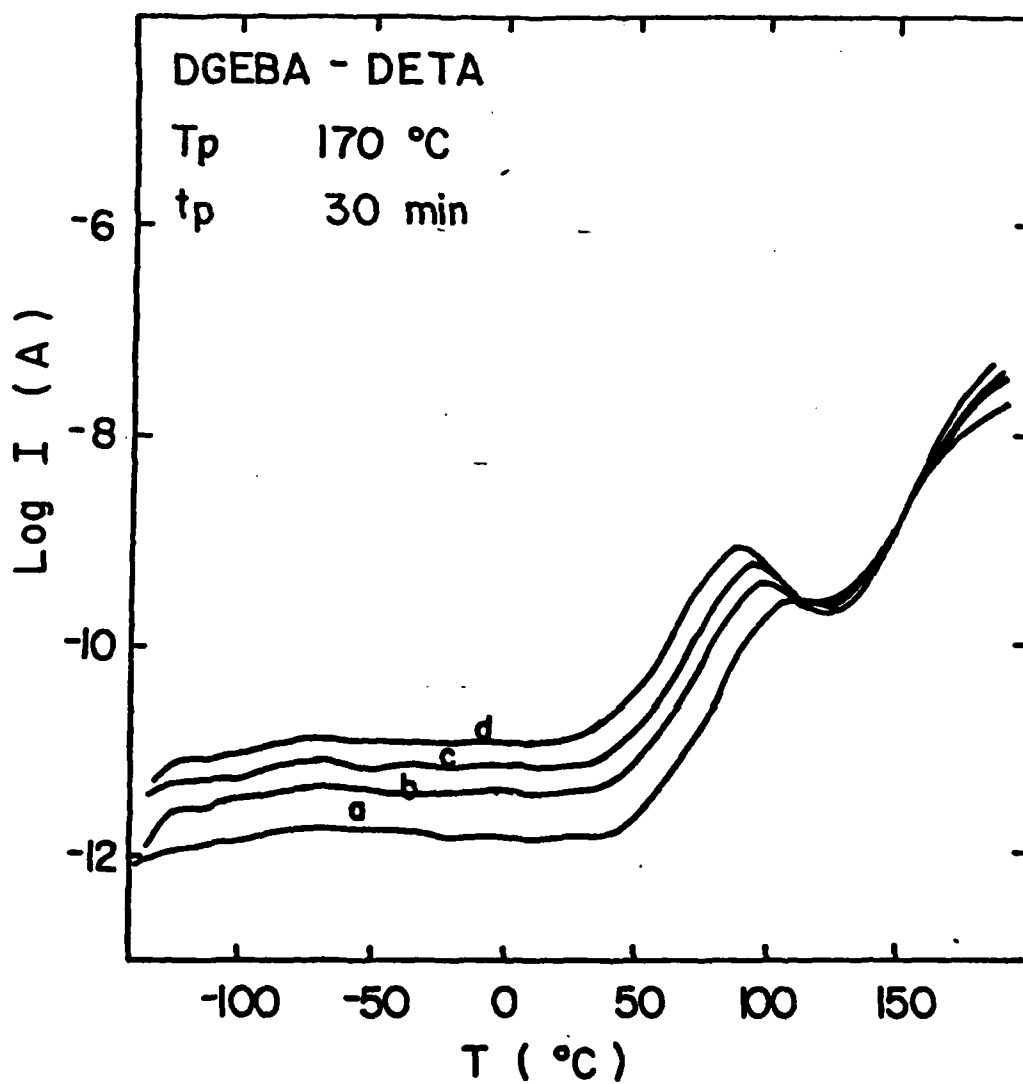


Fig. 13

Figure 13. TSD thermogram of DGEBA + DETA Epoxy Resins
Mole Ratio of active hydrogen/epoxide A-1 1:1,
A- $\frac{1}{2}$ 1:2, A-2 2:1.



T-19

Figure 14. TSD thermogram of DGEBA - DETA. Mole ratio of active hydrogen/epoxide 1:1. E , (a) = 10 kV/cm, (b) = 20 kV/cm, (c) = 40 kV/cm, and (d) = 60 kV/cm.

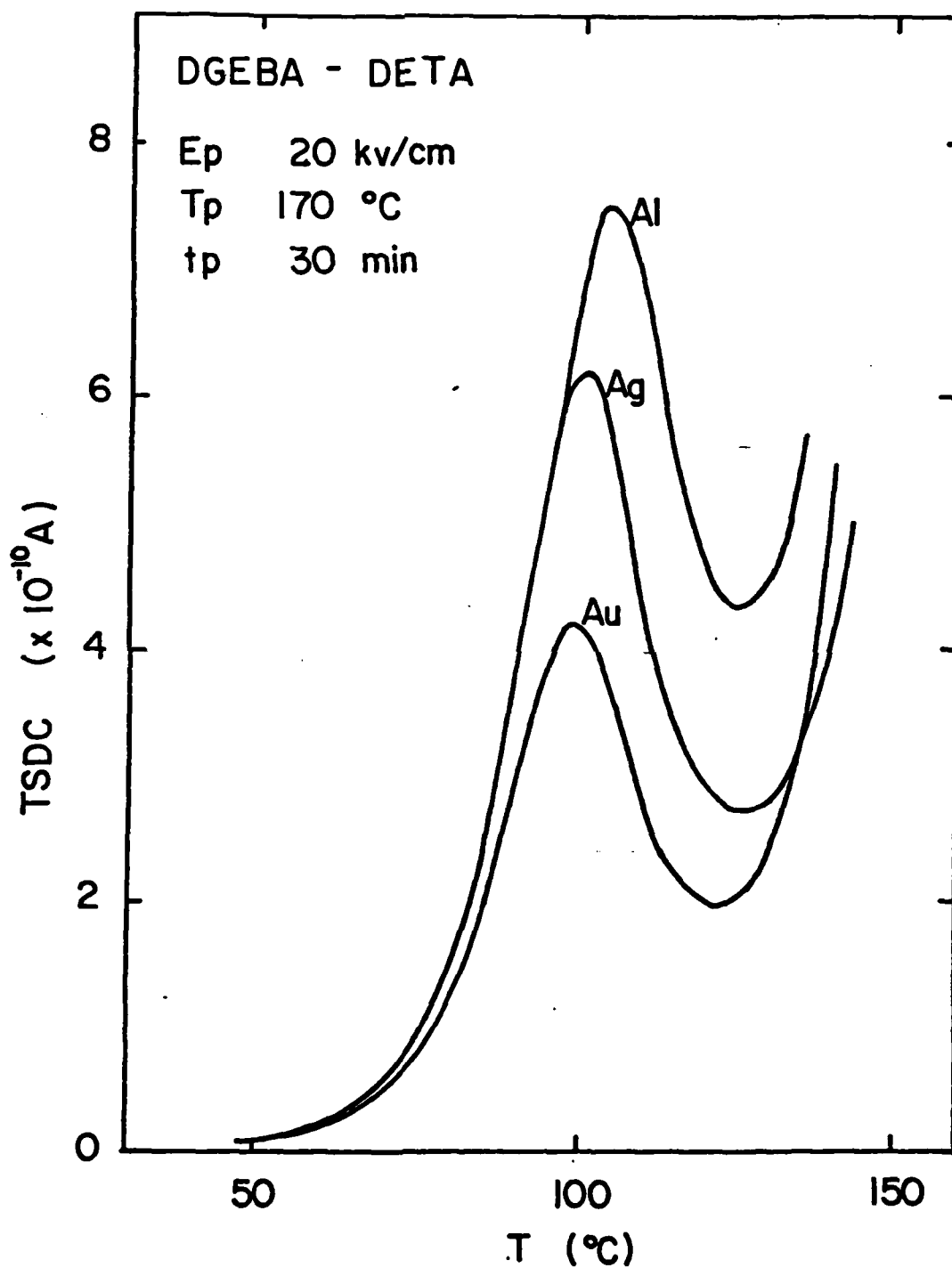


Fig. 15

Figure 15. Effect of Electrode Material on TSD thermogram of DGEBA - DETA. Mole Ratio of active hydrogen/epoxide 1:1.

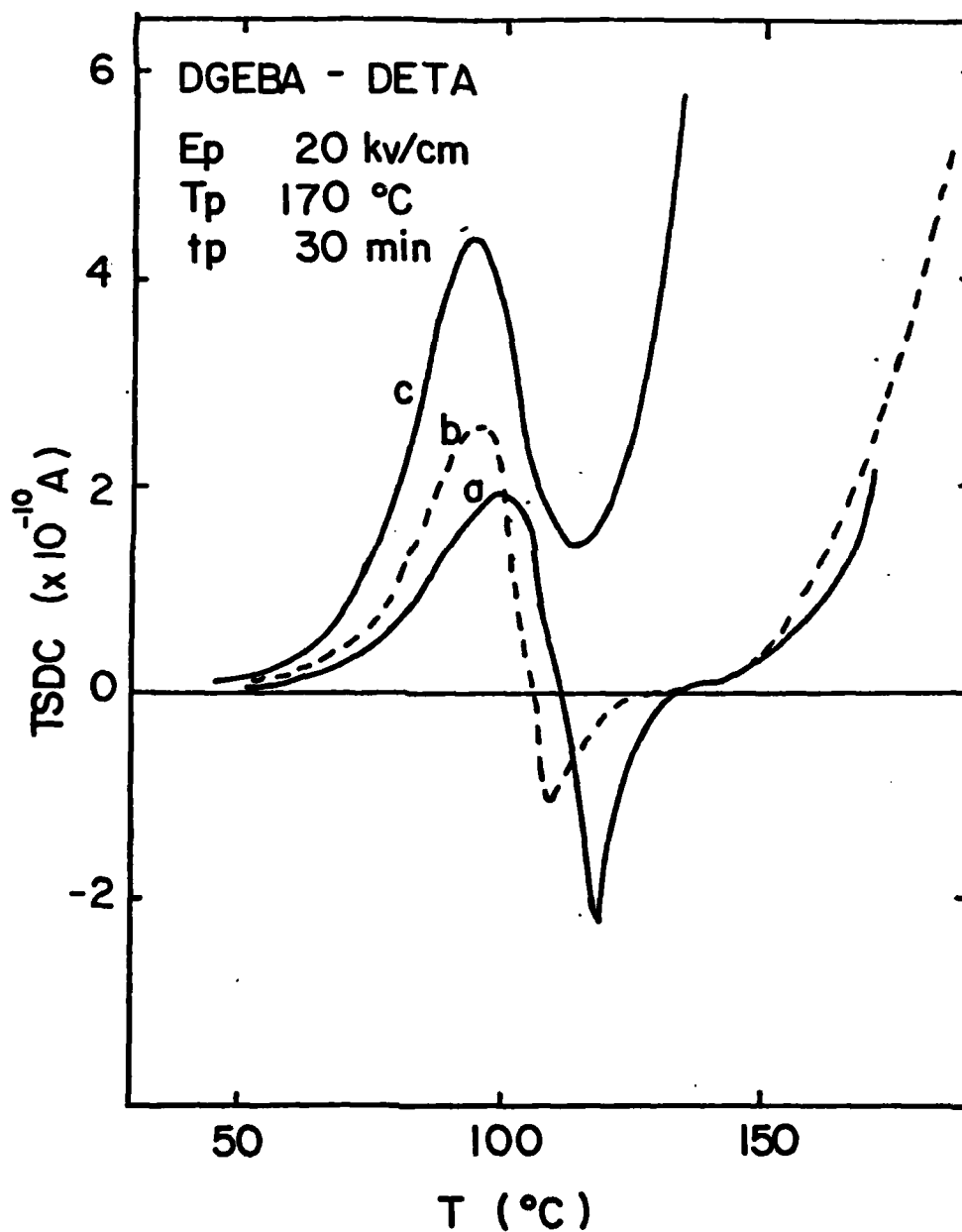


Figure 16. Effect of sample thickness on TSD thermogram of DGEBA - DETA. Mole Ratio of active hydrogen/epoxide 1:1
sample thickness (a) = 0.058 cm, (b) = 0.048 cm, and
(c) = 0.022 cm.

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