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Use of thermally stimulated discharge measurements for the investigation of cure and characterization of thermoset–epoxy resins systems

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Thermally stimulated discharge (TSD) measurements have been used to monitor the cure in thermoset resins and this paper attempts a critical assessment of its application to epoxy resin systems. These studies show that, whilst the method can be used for monitoring cure, there are problems concerned with the detailed interpretation of the TSD data. The observed TSD peaks are complex and associated with charge migration coupled with dipolar reorientation. Data for a wide range of systems and conditions used in cure are discussed.

1. Introduction

Application of the thermally stimulated discharge (TSD) method to the characterization of cure in thermoset resins has been discussed previously [1–5]. A large number of methods exist for the investigation of the process of cure up to gelation; however, obtaining information beyond this point is more difficult [6–10]. The TSD method, in principle, allows investigation of the process which occurs after gelation and before vitrification and as such is an attractive complement to rheological-based methods for the study of cure. Infrared analysis, using fast Fourier transform (FTIR) techniques [11], allows quantitative study of reaction in the initial stages of cure and correlates well with rheological [12] and dielectric [13, 14] measurements.

In order to be able to apply correctly the TSD method it is important to understand, at a fundamental level, the nature of the processes producing the observed peaks. In general, three molecular processes can give rise to peaks when a polymer electret is heated. Firstly, dipoles polarized into a preferred orientation on poling are unlocked with the release of a complementary charge from the electrode surface. Secondly, charges trapped at interfaces as a result of heterogeneity in the matrix, migrate either to the electrodes or to oppositely charged centres within the polymer and lead to a diminution of the stored charge. Finally, ionic conduction within the sample will discharge electrode space charges and leads to large currents being detected in the external circuit. Quantitative analysis of the dipolar process has been reported in a large number of polymer systems and allows identification of the molecular processes responsible for the TSD peaks. Energetic data obtained from the analysis of such peaks compares well with those obtained from other methods. In this paper, the TSD method is used for the characterization of cure for a series of epoxy resin systems.

2. Experimental procedure

2.1. Materials

Two grades of the diglycidyl ether of bisphenol A (DGEBA) were used; Ciba Geigy, MY750, and Shell, Epon 828, which both have a n value of zero [14]. Cure was achieved using various hardeners: 4,4'-diamino diphenylmethane (DDM, Ciba Geigy HY972), triethylenetetramine (TETA, BDH Chemicals), and methyl bicyclohept-5-ene-2,3-dicarboxylic anhydride (NMA, Fischer). The anhydride cure required use of the catalyst benzyldimethylamine (BDMA, Ciba Geigy). The conditions used for cure are summarized in Table I. The composition of the epoxy-hardner was calculated in terms of a ratio (p.h.r.); DGEBA equivalent of 176 (i.e. 372/2) and, for instance, in the case of TETA with six active hydrogens, the stoichiometric ratio is 14 p.h.r. (parts per hundred parts of resin) based on one N–H per epoxide group. A sample of polyethylene terephthalate, (PET) commercial grade Mylar was obtained from Du Pont.

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TABLE I Cure schedules for various resin systems

Cure system	Temperature cycle
DGEBA-Shell Epon 828: DDM-HT972 flake	3 h at 373 K 2 h at 398 K 4 h at 448 K
DGEBA, Shell Epon 828: (93 p.h.r.) NMA catalysed with 1 p.p.m. BDMA	4 h at 373 K 8 h at 433 K
DGEBA-Ciba Geigy MY750: 14 p.h.r. TETA	20 min at 343 K 500 min at 423 K
DEGBA-Ciba Geigy MY750: TETA (variable)	1 day at 353 K 6 days at 373 K

2.2. Thermally stimulated discharge (TSD) measurements

The method used, Fig. 1, has been described previously; samples were prepared in a circular brass mould, placed on top of a glass plate coated with a mould release agent, Rocol MRS advanced non-silicon dry film spray, and, if necessary, heated until gelation occurs. Samples, in the form of flat discs, were placed between the upper and lower electrodes, in a parallel plate configuration. The first step in the polarization cycle involved heating the sample to a predetermined poling temperature, T_p, greater than T_g, and poling using a high-voltage supply (Keithley Instrument 240A, high voltage supply). The electric field, E_p, typically of the order of $500\ \mathrm{V\,cm^{-1}}$, was applied for a time, t_p, of 15 min; after which the sample was rapidly cooled to room temperature with liquid nitrogen, whilst the field was maintained. Once at room temperature, the voltage was removed and the sample (electret) was reheated to T_p at $3\ \mathrm{K\,min^{-1}}$. The discharge current was measured using a Keithley Instrument 610C solid state electrometer. Simultaneously, the temperature and discharge current were recorded on a Cole–Palmer dual trace chart recorder. For the cure studies, the poling time corresponds effectively to the cure time. To assist in the analysis of the TSD spectra, peak cleaning [15, 16], and theoretical fitting [17–19] were used.

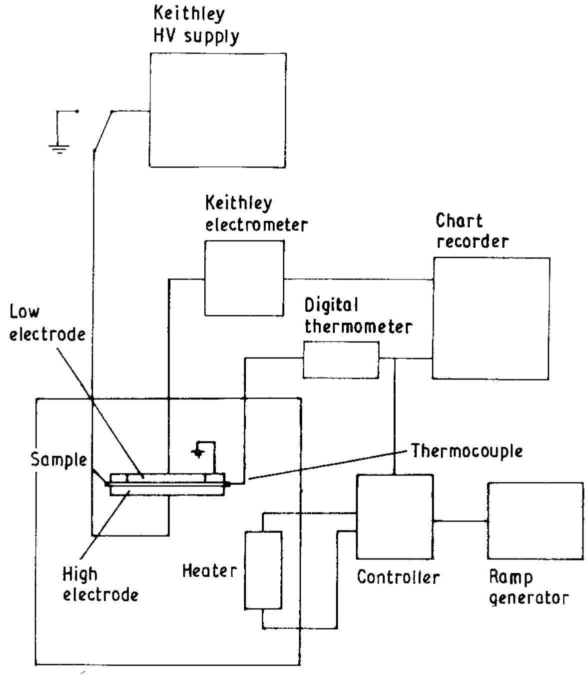

Figure 1 Schematic diagram of the TSD apparatus used for the study.

3. Results and discussion

3.1. Calibration of equipment using polyethylene terephthalate

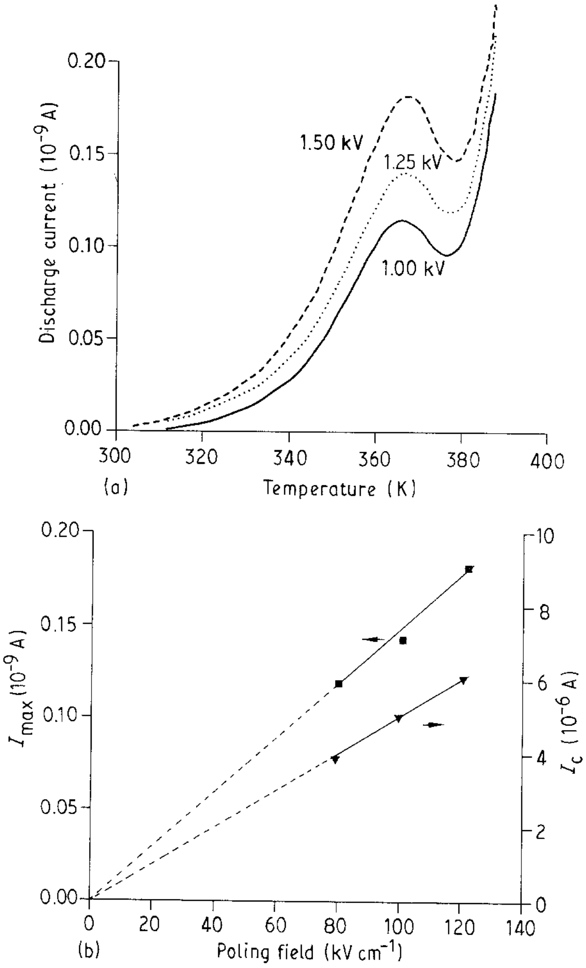

Figure 2 (a) TSD traces for polyethylene terephthalate (——) 1 kV, (···) 1.25 kV, (— — —) 1.5 kV. (b) Variation of the maximum current and poling current with field.

To calibrate the apparatus and check the hypothesis of a linear dependence of amplitude of the TSD peak on the applied voltage for dipolar peaks is observed, a study of polyethylene terephthalate (PET) was carried out (Fig. 2a,b). The area under the curves obtained as a function of applied voltage, Fig. 2b, may be expressed by

$$\int_0^\infty (\mathrm{TSD})\,\mathrm{d}t = \frac{N\mu_p^2 E_p}{3kT_p} = \Delta\varepsilon' E_p \qquad (1)$$

where E_p is the applied voltage, μ_p the dipole moment, N Avagadro's number, k is Boltzmann's number, T_p is the poling temperature, and $(\mathrm{TSD})\mathrm{d}t$ is the area under the peak. If the process is purely dipolar in nature, then the area will vary linearly with voltage (Fig. 2b). Using Equation 1, a value of the dielectric increment,

$\Delta\varepsilon'$, for the α process measured at 365 K is 1.08. This value compares well with literature values obtained by conventional dielectric measurements which lie between 0.75 and 1.8; the precise value depending upon the degree of crystallinity of the polymer. The shape of the TSD peak and its associated activation energy is a function of the degree of crystallinity of the material. The activation energy, E_a, can be calculated using the approach of Grossweiner [19]

$$E_a = \frac{1.51kT_mT_h}{T_mT_h} \tag{2}$$

where T_m is the temperature of the peak maximum, T_h is the temperature corresponding to the half height of the peak on its lower side. This approach has been applied successfully to the study of polymethyl methacrylate [20] and in the case of PET gave values of between 64 and 84 kJ mol^{-1}. Both these values are significantly higher than the value of 44 kJ mol^{-1} reported by Illers and Breur from a combination of dielectric and mechanical relaxation measurements [21]. The origins of the discrepancy probably lie in the assumptions implicit in independent dipolar reorientation; however, the observed peak does clearly correspond to a simple dipolar reorientation process [22, 23].

3.2. Analysis of DGEBA/DDM fully cured material

A fully cured sample of DEGBA/DDM was prepared, Table I, and TSD traces were obtained for samples poled at 402 K and 10^6 V m^{-1} for 30 s and 15 min, respectively, Fig. 3. The poling time, t_p, does influence both T_{max} and I_{max}, the maximum peak discharge current, so a poling time of 15 min was used in these studies. The T_g of the sample, measured by DMA, was 433 K, which is in good agreement with the literature value of 444 K [24], which is approximately 40 K higher than the temperature of the peak maximum of 390–394 K. Analysis of the peaks shape gives values of between 84.8 kJ mol^{-1} (initial rise method) [18] and 120 kJ mol^{-1} (Grossweiner analysis [19]) with $\Delta\varepsilon'$ increments of 63.6 and 69.3. The value of $\Delta\varepsilon'$ is considerably higher than that for a simple dipolar reorientation process and implies that the peak is not purely a simple dipolar process.

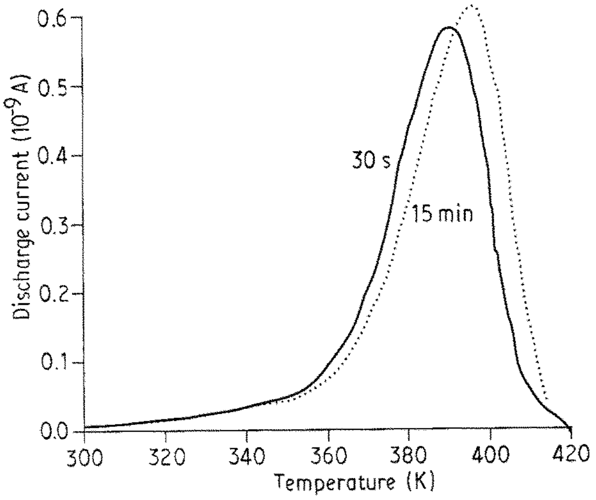

Figure 3 TSD analysis of the effect of poling times on the shape of the traces for DGEBA/DDM. (——) 30 s, (···) 15 min.

3.3. Analysis of DGEBA/NMA

A sample of DGEBA/NMA was cured with BDMA, Table I, and TSC traces were measured, Fig. 4a. The shape and form of the curve was similar to that found for DGEBA/DDM, the peak occurring at 400 K, whereas DMA measurements of T_g indicate a value of 423 K. There is once again a significant difference between the value of T_g, measured using TSD and DMA. Analysis of the TSD curve gave a $\Delta\varepsilon'$ value of 43.0 and an E_a of between 135 and 216 kJ mol^{-1}. These values are significantly higher than would be expected for the T_g process. A second study, using thermal cleaning, in which the heating process was stopped at 404 K (the peak maximum) and then depolarized for 10 min and cooled to room temperature. On reheating, Fig. 4b, a small peak located at 416 K was observed close to the value of T_g obtained using DMA. A value of $\Delta\varepsilon'$ of 1.09, in agreement with that reported by Daly *et al.* [24], is close in magnitude to that observed from conventional dielectric measurements. This study supports the idea that the initially observed peak is complex and not associated with a simple dipolar reorientation process.

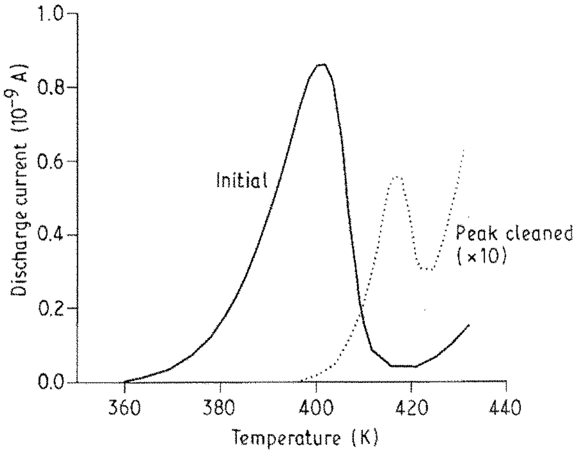

Figure 4 TSD traces for DGEBA/NMA. (——) Initial scan of the sample polarized at 433 K, (···) scan after thermal cleaning at 404 K current axis × 10 A.

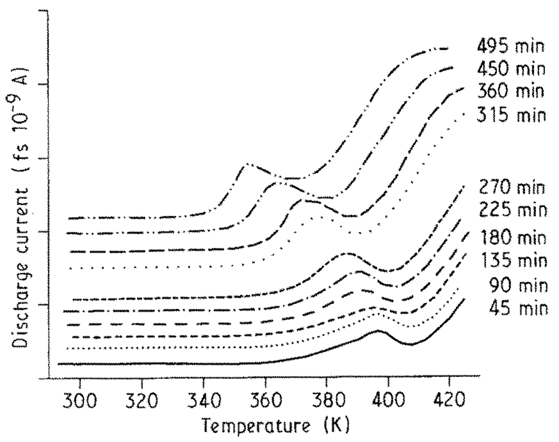

Figure 5 TSD traces for DGEBA/TETA initially cured at 343 K for 20 min, then post cured at 423 K.

TABLE II Values of T_g obtained for DGEBA/TETA

Cure schedule	Glass transition temperature, T_g (K)	Method	Reference
48 h at 373 K	383	DSC	25
48 h at 373 K	413	tanδ	25
1 day at 353 K + 6 days at 373 K	415	DSC	26
20 min at 343 K + 16 h at 403 K	411	DMA	27
2 h at 333 K + 17 h at 373 K	395	DMA	27

3.4. Analysis of DGEBA/TETA system

A 14 p.h.r. stoichiometry was used, Table I, in this part of the study. An initially gelled sample obtained by curing at 343 K for 20 min was poled at 423 K, for successive periods of 45 min. After each period, the sample was cooled to room temperature, discharged and then the electret depolarized by heating to the poling temperature, Fig. 5. A peak was observed at 350 K on the first heating cycle and then progressively shifted to 398 K on successive cycles, indicative of the increase of T_g as cure proceeds. The higher temperature space charge peak decreases in amplitude as cure proceeds. Values of E_a, between 91 and 290 kJ mol^{-1} and dielectric increment of $\Delta\varepsilon'$ of 190–310 were obtained. The former is rather lower than expected for a T_g process and the latter is much higher than for a dipolar process. Values of T_g, obtained by other workers [25–27] using a variety of techniques are summarized in Table II.

Repeating the study using a lower cure temperature, 403 K, produced a material with similar properties to those obtained using the higher cure temperature, Table II, but avoided complications associated with chain scission and rearrangement implicit in the higher cure temperature [28]. Selected traces illustrating the overall variation of the position and shape of the peak as cure proceeded are shown in Fig. 6a,b. As cure proceeds so the initial peak develops a shoulder (Fig. 6a). Thermal peak cleaning at 361 K indicates an underlying peak at 375 K which is observed as a shoulder in the original trace, Fig. 6b. Analysis of the higher temperature peak obtained after peak cleaning indicates a dielectric increment, $\Delta\varepsilon'$, of 1.9–2.1, compared with a value of between 2.4 and 5.3, for the original peak. The corresponding activation energies were 107 and 128 kJ mol^{-1}.

Similar studies were carried out at 403 and 423 K, as the post-cure temperature and in each case the amplitude of the higher temperature peak became more apparent, Fig. 7a–c.

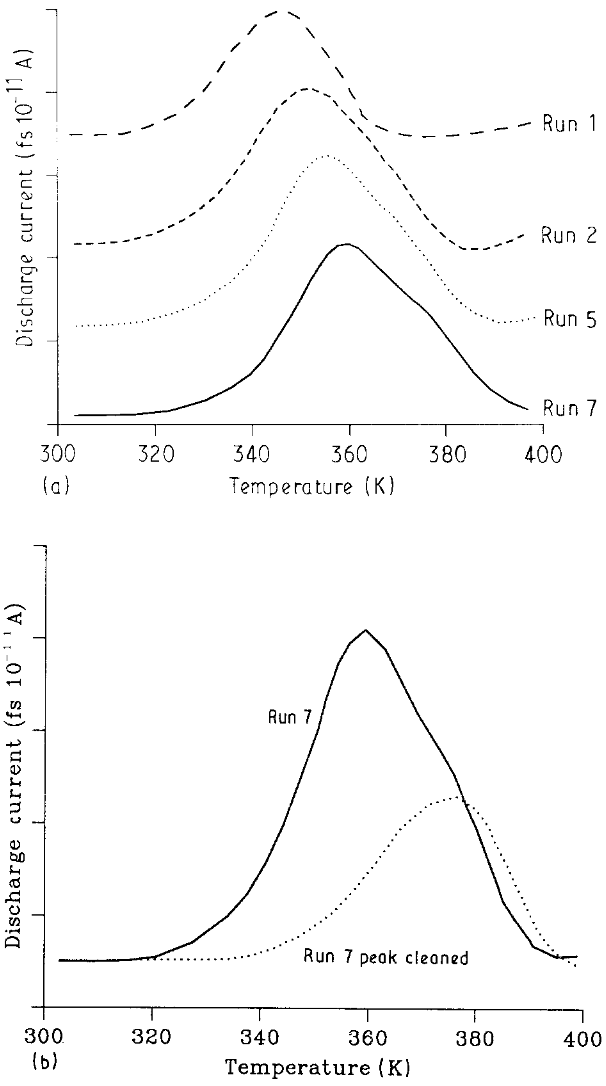

Figure 6 TSD traces for DGEBA/TETA initially cured at 343 K for 20 min, then post-cured at 403 K. (a) Changes of peak on progress of cure, (b) thermal cleaning of run 7 by depolarization at 361 K.

3.5. Degradation of DGEBA/TETA

Rearrangement of the epoxy structure leading to the development of a distinct orange coloration occurs if the sample is heated to temperatures in excess of 423 K [28]. The scission of the chain structure leads to formation of dangling ends within the matrix and these can act as internal plasticizers. Using poling temperatures of 373, 403 and 423 K, indicates that there are no significant changes in either the shape or magnitude of the observed peak and that degradation has little or no effect on the observed TSD peaks.

3.6. Analysis of DGEBA/DDM/EPPHAA

Use of epoxy fortifiers and, in particular, the use of the reaction product of 1,2-epoxy-3-phenoxypropane (EPP) with 4-hydroxy-acetanilide (HAA) has been reported previously [29]. The EPPHAA was incorporated at a level of 30 p.h.r. and has the effect of increasing the modulus and toughness of the material, presumably through the effects of internal plasticization. TSD data, Fig. 8, indicate that EPPHAA does not significantly affect the shape or form of the TSD traces, although analysis of the peak indicates substantial differences from that of the unmodified resin, Table III. As anticipated, incorporation of internal plasticizing elements lowers the activation energy and temperature of peak maximum, as well as the value of $\Delta\varepsilon'$. Lowering of the latter is the reverse of what would be expected for a plasticization process.

3.7. Influence of variation of stoichiometric ratio of DEGBA/TETA

A series of samples of DEGBA:TETA were cured, Table I, and TSD traces obtained, Fig. 9. Multiple peaks and shoulders, Table IV, were observed and to understand the TSD traces it is important to appreciate the complexity of the chemical processes occurring. The primary amine group in TETA, is significantly more reactive than the secondary and hence the initial reaction product may be a *linear* thermoplastic polymer. Subsequent cure converts this initial reaction product into a cross-linked matrix. It has been pointed out by various workers that in the early stages of cure the reaction mixture may become heterogeneous. Increasing the amine content will reduce the requirement for complete reaction of all six active amine groups of the TETA hardener. This will lead to the creation of a more open, porous structure; where the partially unreacted amines plasticize the system, leading to an increase in the free volume and a reduction in the T_g. For very high amine contents, a thermoplastic material is observed which undergoes densification and shift of the TSD peak to higher temperatures. The very high amine content materials exhibit a marked space charge peak which is larger than for the analogous low-content systems. This observation may be attributed to the high concentration of excess (i.e. non-reacted) amine groups, and also the presence of quaternized centres (generated through interaction of the tertiary amines with protons) which can assist in the charge migration. The complexity of these processes, exemplified in the case of the 30 p.h.r. system, where three separate relaxation peaks are observed, reflects the different degrees of charge and dipolar mobility along with the existence of facile charge migration as observed by the amplified space charge peak. It must be stressed that some caution must be used in the interpretation of absolute peak amplitudes, due to the sample thickness varying slightly from sample to sample.

Carfugna *et al.* [26] and Kontou *et al.* [25] have carried out a similar study using DSC and DMA, and the observed T_g for the 14 p.h.r. ratio was attributed to a homogeneous cross-linked density. For higher and lower p.h.r. ratios, lower T_g values were obtained, in agreement with the data presented for 4.8 and 30.0 p.h.r. Carfugna *et al.* [26] suggested that this reduction in T_g for p.h.r.s greater than the stoichiometric ratio was due to plasticization produced by the amine. Kontou *et al.* [25] disagreed, pointing out that the changes in modulus were too large to be the result of plasticization as a result of such a small excess of amine. Mijovic and Tsay [29] believe that higher concentrations of curing agent lead to excessive intranodular rather than the internodular matrix reactions. The net result is an increase in the effective free volume of the internodular matrix. A large excess in the curing agent results in plasticization, and reduces the T_g.

3.8. Concept of a nodular morphology

The DEGBA group, has a *chevron* type structure because of the bridging dimethyl substituted methylene group. Neighbouring molecules can adopt either a close or open packed structure dependent upon the relative orientation of adjacent phenyl groups, leading to a densified or open structure. Recent NMR data [30–32] indicate that the phenyl groups within the analogous polymer system (polycarbonate) are able to undergo facile interchange and the process of densification and antiplasticization can be associated with restriction of the motion of the phenyl groups. Dynamic changes associated with changes in the orientation of neighbouring ring structures, occur well below T_g and are separated from the β relaxation process. The glass transition process involves cooperative rotational motion of a number of chain elements and reflects extensive chain motion within the matrix. The *chevron* structures are capable of clustering into small groups and locking the motion of the chains.

The TSD peaks are consistent with short-range motions, allowing charge migration over a limited range and occurring below T_g. The charge migration coupled process dominates the TSD and swamps the dipolar reorientation process associated with T_g, which is revealed on peak cleaning.

Electron microscopic studies have suggested that cured epoxy resins consist of relatively small regions of highly cross-linked three-dimensional agglomerates embedded in a surrounding matrix of a more open structure [33]. Aspbury and Phillips [34] have reported observing regions of the order of 10 nm diameter assigned to these nodular regions. Kenyon and Neilsen [33] reported observing double peaks in DMA analysis attributed to the heterogeneous nature of the network. Evidence for a heterogeneous struc-

TABLE III Comparison of DGEBA/DDM with DGEBA/DDM/EPPHAA

Physical property	Resin system	
	DGEBA/DDM	DGEBA/DDM/EPPHAA
TSD (location of peak maximum) (K)	392	360
Activation energy, E_a (kJ mol^{-1})		
(i) initial curve method	85.4	69.7
(ii) Grossweiner's method	117.6	109.6
Dielectric increment, $\Delta\varepsilon'$	66.5	30.2

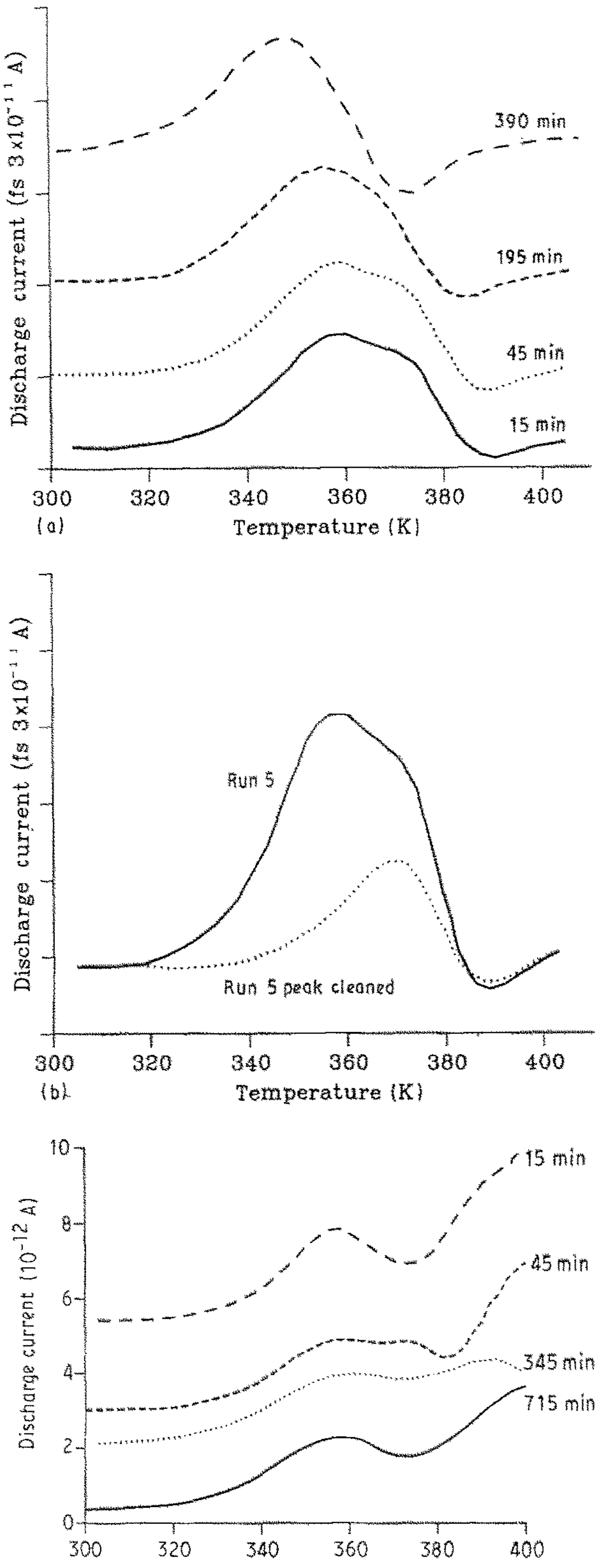

Figure 7 TSD traces for DGEBA/TETA post-cured at 403 and 423 K. (a) Initially cured at 333 K for 20 min, then post-cured at 403 K, (b) thermal cleaning at 360 K for run 5, (c) initially cured at 333 K for 40 min, then post-cured at 423 K.

ture has been obtained from examination of fracture surfaces, the average size from these measurements being 25–35 nm [36] and cracks proceed around the nodules which correspond to regions of high cross-link density. The concept of nodular morphology, which has only recently gained wide acceptance, is not such a novel idea, and was originally suggested by Houwink in 1936 [37].

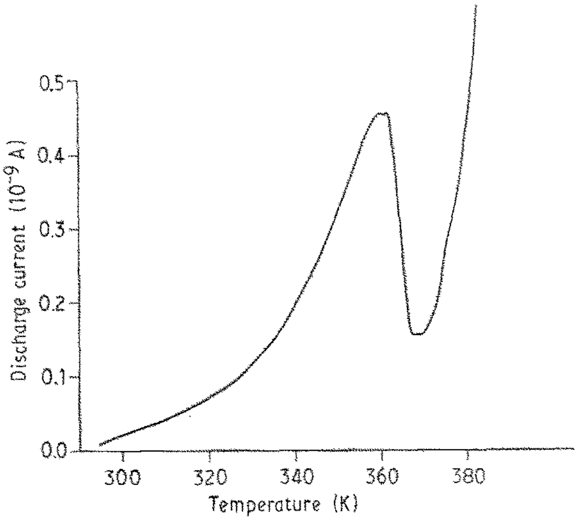

Figure 8 TSD trace for DGEBA/DDM/EPPHAAA.

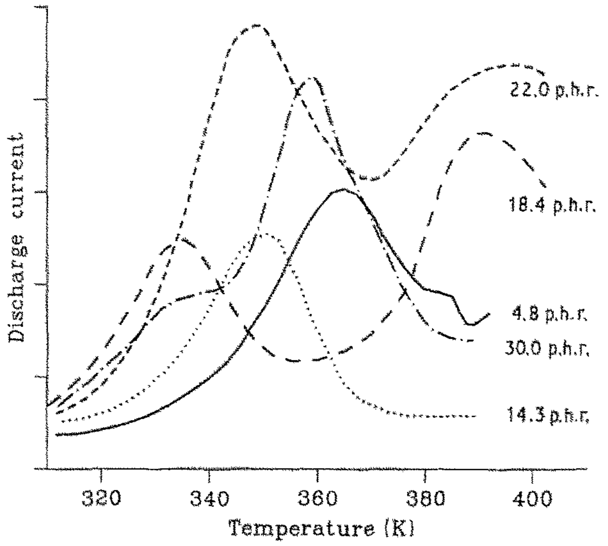

Figure 9 Variation of TSD traces with hardener:resin ratio; TETA:DGEBA.

TABLE IV Analysis of TSD curves with variable TETA:DEGBA content

Content of TETA (p.h.r.)	Location of peak maximum, T_m (K)	Location of peak maximum after cleaning
4.8	365 and 385 (sh.)	385
14.3	350	363
18.4	349 and 363 (sh.)	396
22.0	334 and 391	
30.0	349, 358 and 398	

4. Conclusions

TSD studies can be used to probe changes which occur in a thermoset polymer system; however, the nature of the observed peak is clearly very complex. It is, however, clear that the process observed is more complex than would appear at first sight. The TSD peak is attributed to short-scale migration of charge assisted by local motions of the polymer chain. The high-temperature peak, revealed on thermal cleaning is correctly associated with the T_g process. Multiplicity of the peaks observed under certain conditions of cure are consistent with the generation of a nodular morphology within the thermoset in the early stages of cure and complement electron microscopic observations of changes in the network structure.

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