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The effect of cure on thermally stimulated discharge measurements in epoxy resin coatings

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Thermally stimulated discharge (TSD) measurements are reported as a function of the degree of cure for a series of dicyandiamide cured powder epoxy resins. Data are presented on the effects of ageing and water uptake on the TSD traces. The observed effects are interpretated in terms of the generation of traps, creation of voids and changes in the bulk conductivity on the charge mobility. The TSD data are compared with dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) observations on these systems. These studies indicate that the method is very sensitive to changes in the state of the coating and has potential as a test method for the characterization of epoxy resin coatings.

1. Introduction

In a previous paper [1] it is shown that ultrasonic attenuation and velocity changes observed during the process of cure of a powder epoxy resin could be interpretated in terms of a combination of the effects of void generation and increased crosslinking as cure proceeds. Preliminary investigations of thermally stimulated discharge (TSD) traces as a function of cure indicate that the amplitude and position of the highest temperature peak is sensitive to the extent of cure [1]. In this paper we report a systematic investigation of the effects of cure, ageing and adsorption of water on the TSD traces obtained from a series of epoxy resin powder coatings.

Many methods have been used for the determination of the extent of cure in epoxy resin coatings. The majority of the methods, whether destructive or non-destructive, are sensitive to the gel point (the early stages of crosslinking) but fail in the latter stages. However it is these later stages of cure which are believed to determine the ultimate life of a coating and will significantly alter its mechanical and dielectric properties [2, 3].

Chemical methods usually involve equilibrium swelling, sol–gel analysis and solvent tests. Equilibrium swelling measurements are usually performed above the glass transition temperature, T_g, and in the case of the dicyandiamide type of system the test procedure is likely to advance cure. Sol–gel analysis is only satisfactory for systems below their gel point, analysis of systems beyond this point being limited by the availability of suitable solvents and the extent of reaction. For high degrees of cure, long immersion times and elevated temperatures are usually required [4], making the results subject to considerable uncertainty.

Infrared analysis provides an accurate, quick test for systems which are optically transparent, but is of little use when the coating is either filled or pigmented. Even with this technique care has to be taken with interpretation, competing reactions can in certain cases complicate interpretation [5, 6].

Physically the gel point can be readily determined from the heat distortion temperature [6]. This test has inherent in it two major disadvantages: (i) the test is likely to lead to advance of

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the cure and hence will not reflect the properties of the original sample, and (ii) it is a destructive test. Other methods have been employed and include surface hardness measurements [7], resistivity [8], and differential scanning calorimetry [9]. This latter method, though destructive can provide a useful estimate of the extent of cure when used with the correct precautions. An alternative method is that of dynamic mechanical analysis (DMA) and the application of this method has been discussed by Arridge and Speake [10]. This latter method uses the difference in value of the modulus above and below the low temperature secondary mechanical transition to provide a quantitative estimate of the extent of cure. In this paper we report a study of the TSD behaviour [11] of partially and completely cured epoxy resin materials.

2. Experimental procedures

The chemistry of the epoxy resin coatings used in this study has been discussed elsewhere [1, 12, 13] and they are basically composed of an epoxy resin – diglycidyl ether of bisphenol A, a high surface area silica and dicyandiamide (dicy) as a curative. The samples used in this study were prepared from a fresh batch of powder resin (3M Scotchkote 206N), and were fabricated by spraying the powder onto a pre-heated heavy mild steel plate which had been previously coated with a polytetrafluoroethene (PTFE) spray. The resultant cured epoxy coating was detached from the metal substrate by cutting around the edge of the plate and peeling off the coating. The films generated in this way had thicknesses of between 0.1 to 1 mm, depending upon the number of passes used in the spraying and the powder through-put rate. Post-curing was achieved by heating the detached films in a pre-heated oven for a defined period.

2.1. Differential scanning calorimetry (DSC) measurements

The degree of cure was estimated by measurement of the ΔT_g of the coating [14]. Small pieces of coating were placed in the pan of a Dupont differential scanning calorimeter. The sample was first heated to 120° C for 5 min. This initial heating was performed in order to remove all traces of moisture from the film. The dry coating was then subjected to a heating rate of $5^\circ \mathrm{C}^{-1}$ and the trace recorded up to a temperature of 140° C. This trace provided the first estimate of T_{g1}. The heating above T_g is assumed to complete the cure cycle and the value of T_{g2} obtained from a subsequent scan is ascribed to that of the fully cured coating. The difference between the two values of T_g obtained is used to estimate the extent of cure. A sample with a value of ΔT_g of less than two is assumed to be completely cured, a more precise estimate of the degree of reaction is difficult with this method [14].

2.2. Dynamic mechanical analysis (DMA)

Samples of the coating cut in the form of rectangles were examined using the Dupont DMA system. From the amplitude and frequency were calculated the real and imaginary moduli as a function of temperature.

2.3. Thermally stimulated discharge (TSD) measurements

The method used for obtaining the TSD traces has been described previously [1]. The samples were used without the use of evaporated electrodes and a fresh sample was used for each experiment except where indicated otherwise. The apparatus used for the TSD measurements was also used for the estimation of the d.c. conductivity of the samples, these latter measurements being performed during the charging cycle. In these studies the charging cycle was performed at a temperature just below T_g.

3. Results

The study is subdivided into the investigation of the changes in the TSD traces which occur as a consequence of advancement of cure, the effects of change in the temperature of cure, the effects of addition of water, effects of ageing and the effects of changes in the sampling area.

3.1. Effects of changes in the sample area

As indicated above, the films used in this study were prepared by curing thin films of powder epoxy resin coated on a heavy metal plate. The plate was supported on two metal points and as a consequence of the mass and shape of the metal slab finite temperature gradients would have been created across the surface of the slab. Samples taken from different areas would have been subjected to slightly different temperature cycles. The traces obtained are presented in Fig. 1, and

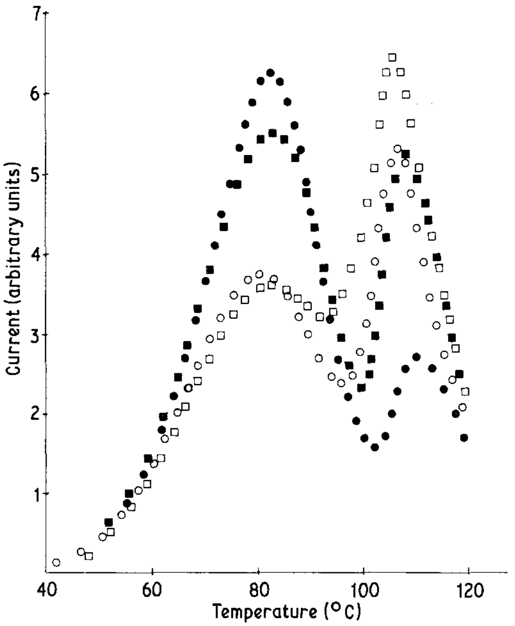

Figure 1 Variation of the TSD trace with sampling position. Film cured at 240° C for 4 min; samples taken from various areas of the same plate.

reflect differences in the state of cure at different points on the plate. It can clearly be seen that large variations in the amplitudes of the high and lower temperature peaks are observed. Integration of the area under the curve, however, indicates that this is approximately constant for a given state of cure.

3.2. Voltage dependence of the TSD traces

It has been pointed out by van Turnhout [11] that the TSD peak associated with the glass transition temperature varies linearly with the applied potential. In an attempt to assign the molecular origins of the features observed traces were obtained with various voltages (Fig. 2). In contrast to the traces normally obtained for synthetic polymers [11], these materials do not exhibit a linear voltage dependence. It is, however, found that the area under the combined peaks do vary linearly with the applied voltage.

In an attempt to establish which of the observed TSD peaks should be ascribed to the T_g process, dynamic mechanical measurements were performed (Fig. 3). Two peaks in tan δ were observed; a low temperature peak at approximately $-60°$ C ascribed to the beta process and associated with local motion of the chain, and a higher temperature peak ascribed to the glass transition process. In agreement with previous reports [15], the amplitude of the beta process decreases and the position of the glass transition moves to higher temperatures as cure proceeds.

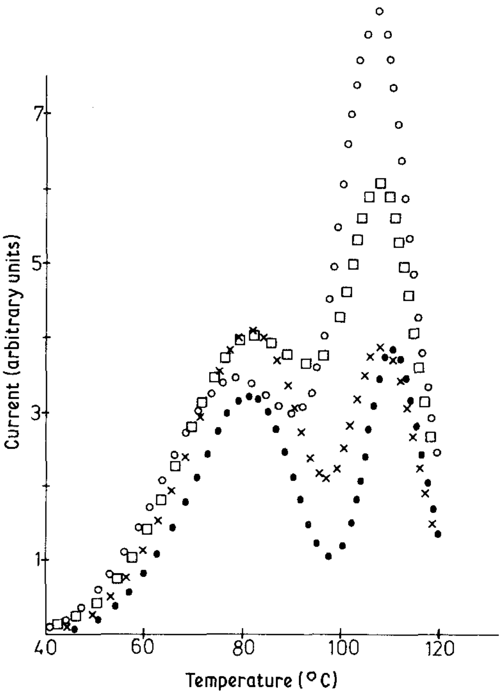

Figure 2 Variation of TSD trace with applied charging voltage. Film cured at 230° C for 3 min. Voltage used: 400 V (●), 600 V (X), 800 V (□), 1000 V (○).

3.3. Polarity of the applied voltage

The effects of cure on the shape of the TSD curves are illustrated for positive, Fig. 4, and negative, Fig. 5 polarity. The experiments were performed on a sample initially cured at 185° C for 5 min and the post cure was carried out during the polarization cycle at 100° C for 20 min. The sign of the polarization was alternated during the cure process and reflects differences in charge trapping and mobility in the resin.

3.4. Changes in the electrodes

The effect of changing the contacting electrodes are illustrated in Fig. 6. In the previous examples the electrodes were both mild steel, in the above examples one electrode was steel and the other aluminium. The differences between the traces must be ascribed to the effects of change in the contacting potential.

3.5. Effects of cure on the TSD traces

The effects of progressive cure on the TSD traces for a sample initially cured at 200° C for 1 min

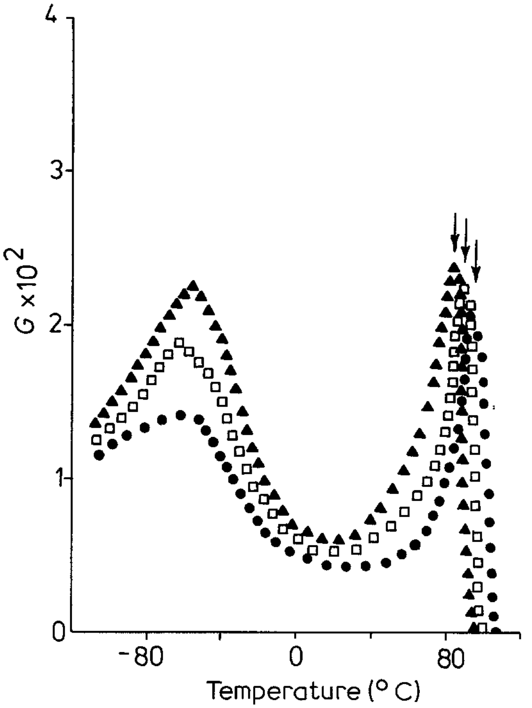

Figure 3 Temperature variation of the dynamic modulus recorded at 500 Hz. Film cured at 185° C for 5 min; post-cured at 110° C for 15 min (▲) post-cured at 110° C for 30 min (□), post-cured at 110° C for 45 min (●).

and subsequently post-cured at 120° C for 30 min between traces are illustrated in Fig. 7. As cure proceeds the lower temperature peak moves to higher temperatures and the higher temperature peak decreases in amplitude.

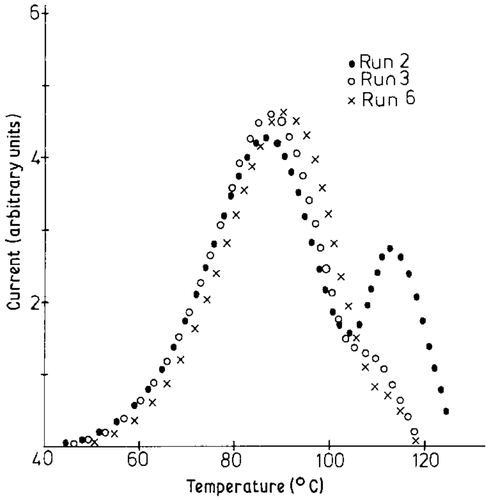

Figure 4 Epoxy resin TSD traces for cure at 185° C, positive polarity. Run 2 – post-cured at 110° C for 15 min (●), Run 3 – post-cured at 110° C for 30 min (○), Run 6 – post-cured at 110° C for 75 min (×).

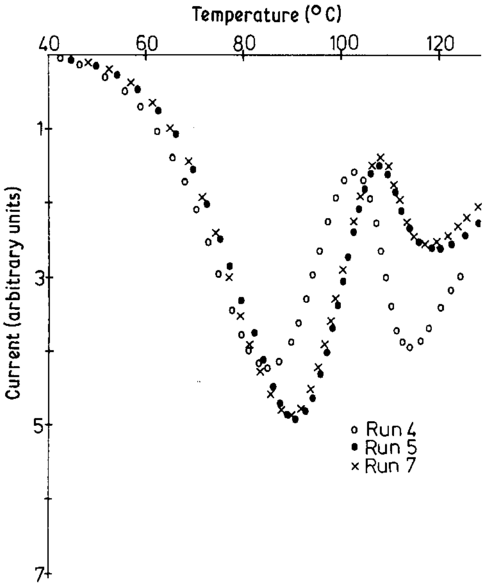

Figure 5 Epoxy resin TSD traces for cure at 185° C, negative polarity. Run 4 – post-cured at 110° C for 45 min (○), Run 5 – post-cured at 110° C for 60 min (●), Run 7 – post-cured at 110° C for 90 min (×).

3.6. Effect of water adsorption on TSD traces

The effect of water absorption is illustrated in Fig. 8. The two initial traces illustrate the curves

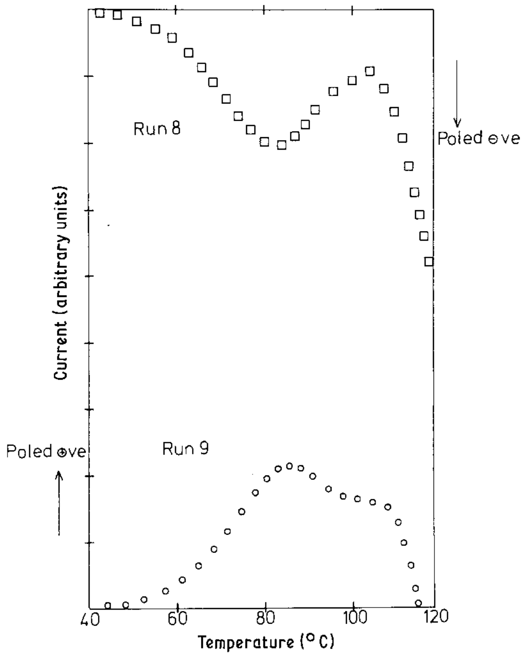

Figure 6 Epoxy resin TSD traces for cure at 185° C, effects of variation of electrodes; steel/aluminium electrodes. Run 8 – post-cured at 110° C for 105 min, negative polarity (□), Run 9 – post-cured at 110° C for 120 min, positive polarity (○).

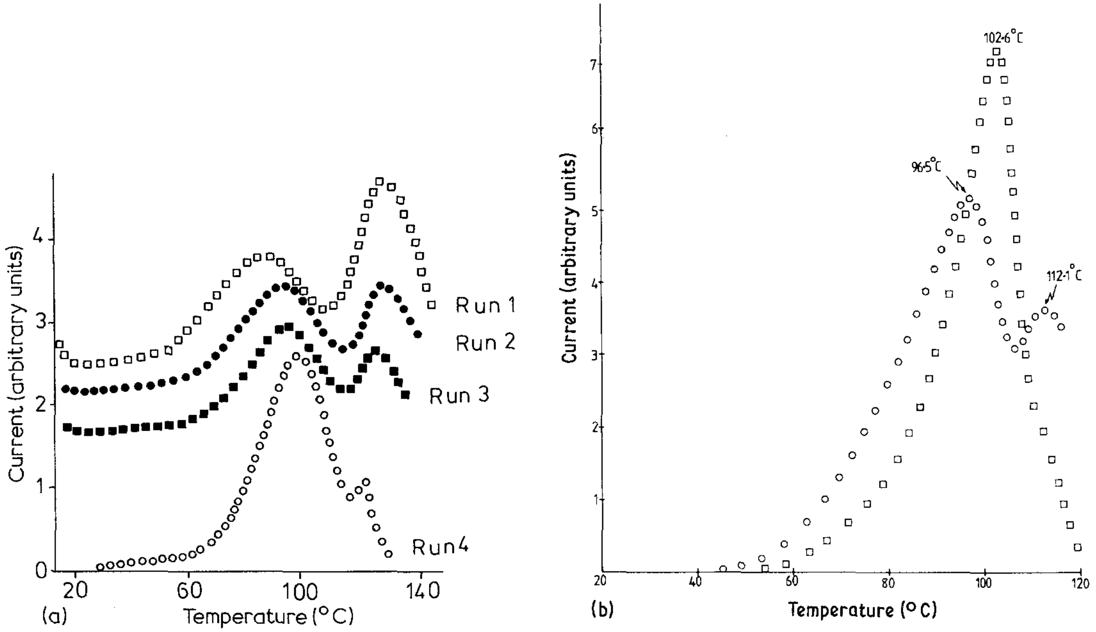

Figure 7 (a) Effect of cure on TSD traces for epoxy resins cured at 200° C for 1 min. (The traces are displaced vertically for clarity.) Run 1 – initial material (□), Run 2 – post-cured at 120° C for 30 min (•), Run 3 – post-cured at 120° C for 60 min (▪), Run 4 – post-cured at 120° C for 90 min (○). (b) Epoxy resin cured at 260° C for 10 min. Run 1 – initial trace (○), Run 2 – post-cured at 150° C for 15 h (□).

obtained for a sample obtained at 260° C and cured for 3 min and then post-cured at 150° C for 2 h. The changes observed are similar to those reported in Fig. 7. The sample was subsequently exposed to water at 100 RH for 48 h at 60° C and the trace obtained. Similar observations were performed using DMA. Both observations indicate that the glass transition peak is moved to a lower temperature as a consequence of plasticization by water and in the case of TSD the higher temperature peak increases dramatically in amplitude.

3.7. Effects of ageing on the TSD traces

Powder epoxy resin which had been stored for six months was used to fabricate films which were subsequently examined. Unlike the traces presented for fresh powder, the curing cycle for the aged power generates a different cycle of changes, Fig. 9. The effects of using a high temperature for the post-curing of the power resin are presented in Fig. 10.

4. Discussion

4.1. Assignment of the TSD peaks

As indicated above, the lower temperature TSD peak coincides closely with the drop in the modulus associated with the change from glassy to rubbery state. The fact that the amplitude of the lower temperature peak does not vary linearly with the applied voltage at first appears to be contrary to the concept that it is associated with a dipolar process [11]. We will consider this point later in this paper. The higher temperature TSD peak is assigned to space charge migration [16].

4.2. Effects of cure

The effects of cure are illustrated in Figs. 7 and 8. As reported previously [1], the d.c. conductivity was observed to decrease as cure proceeds, Fig. 11, and correlates closely with the observed decrease in the high temperature space charge peak. Correlation of this data with the ΔT_g measurements obtained from DSC studies indicate that changes are observed in the TSD traces at a point when the ΔT_g of the resin is within the uncertainty of the measurement. The TSD technique therefore, in principle, appears capable of characterizing the extent of cure in a region where most techniques have ceased to be sensitive.

4.3. Effects of water adsorption

As indicated in a recent publication [3] epoxy resins can readily take up 2 to 3% water. The water is dispersed throughout the epoxy resin both as a clustered pseudo-water-like form and also in a molecularly dispersed form. In the case

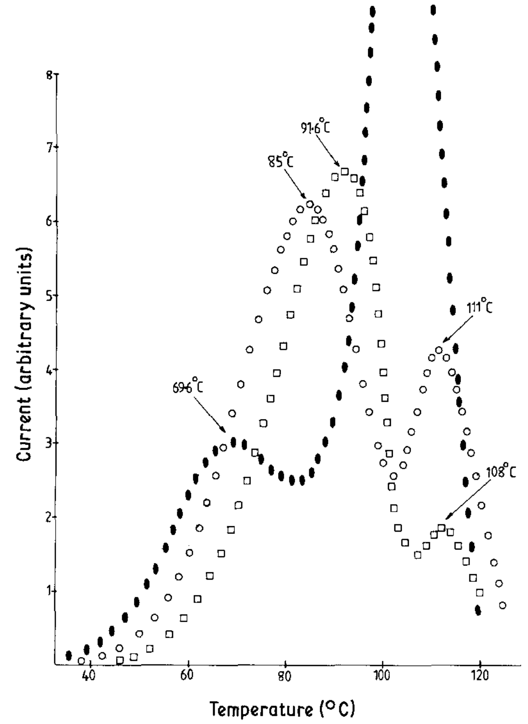

Figure 8 Effects of water adsorption on TSD traces from epoxy resins: cured at 260° C for 3 min (○), post-cured at 150° C for 2 h (□), adsorption of water for 48 h at 100 RH and 60° C (●).

of the TSD measurement, the conductivity of the film increased markedly as reflected in the large space charge peak, Fig. 8. The water, molecularly dispersed, is also capable of plasticizing the matrix as evidenced by a lowering of the TSD and DMA traces.

4.4. Effects of polarity of the TSD traces

Comparison of Figs. 4 and 5 indicate that changing the polarity of the changing voltage has very significant effects on the traces observed. The applied voltage will define the nature of the migrating charged species and these observations must be assumed to reflect the differences which result from electron and cationic species. The conduction level in the insulator will be principally determined by the contact between the metal electrode and the polymer. Changes in the nature of the charge carrier may be expected to give rise to differences in the space charge peak, but to have little effect on the dipolar process. This hypothesis is in agreement with experimental observation. The principle differences observed are associated with the space charge peak and probably reflect differences in the nature of the trapped states being observed and their population.

4.5. Ageing effects

It is well known that epoxy resins can age on storage and this process is associated with slow crosslinking of the matrix. It is interesting to note that when this powder is subsequently cured the resultant matrix does not follow the cycle observed with the freshly prepared resin and though showing an initial decrease in the

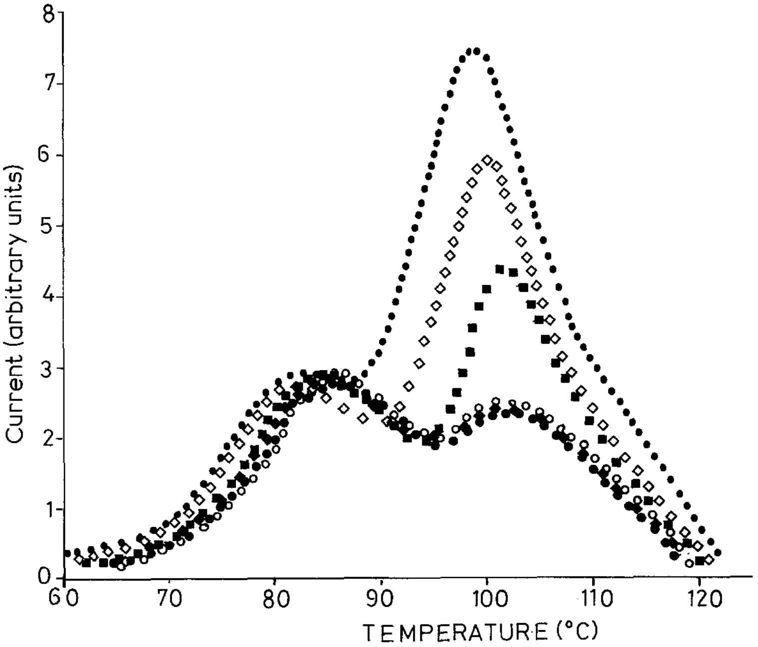

Figure 9 Effects of cure on an aged epoxy resin sample. Cure at 200° C for 2 min. • – initial trace, ◇ – post-cured at 110° C for 30 min, ▪ – post-cured at 110° C for 60 min, ○ – post-cured at 110° C for 75 min, ● – post-cured at 110° C for 90 min, ◆ – post-cured at 110° C for 180 min.

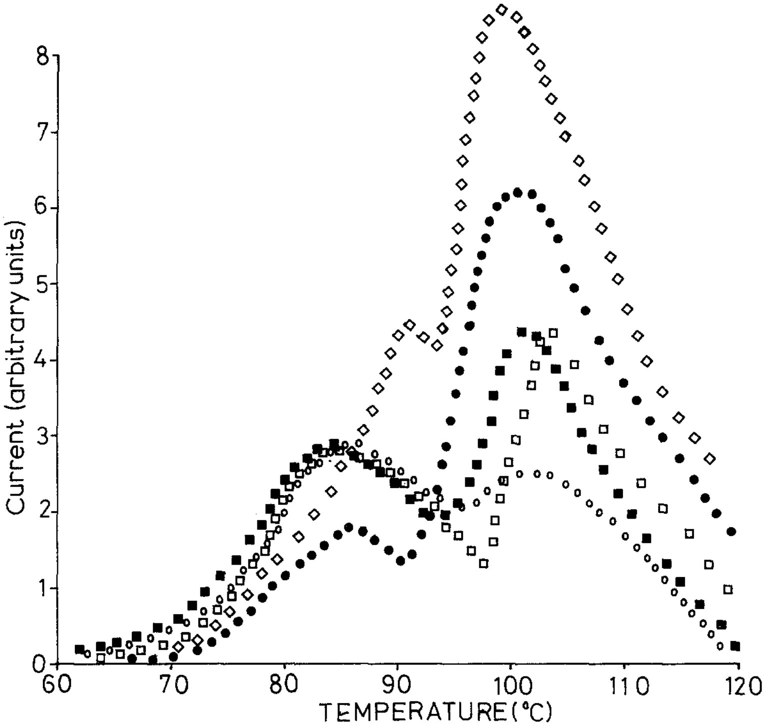

Figure 10 Effect of high temperature post-cure on epoxy resins. Cure at 200° C for 3 min. ■ – initial trace, ○ – post-cured at 150° C for 3 h, □ – post-cured at 200° C for 1 min, ● – post-cured at 200° C for 5 min, ◇ – post-cured at 200° C for 10 min.

space charge peak it is impossible to reduce it to the low levels observed with the new samples. Similarly the d.c. conductivity is not lowered to the same extent and this appears to reflect a higher level of charge carriers in this material than in the freshly prepared material. There are two probable causes of this effect. Firstly, the aged powder will have taken up moisture and this may be so trapped in the powder so as to be unable to be released on curing. Secondly, the chemistry which is known to occur can be considered to generate a number of pendant hydroxide groups which are able to generate protons. Since this same process is occurring in the "normal" cured material it is unable to explain totally the observations and we once again have to invoke adsorbed water as the most probable explanation.

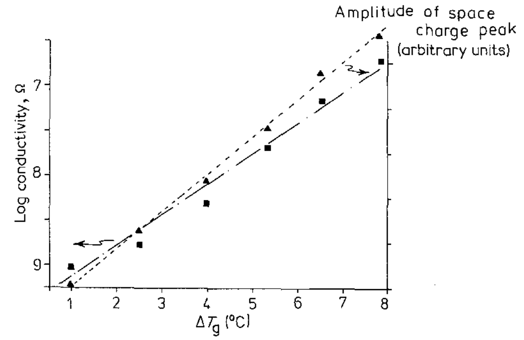

Figure 11 Correlation of the variation of the conductivity and amplitude of the space charge peak against T_g for a freshly prepared powder epoxy resin sample.

In a recent paper [17], we have reported chemical rearrangements which occur to epoxy resins when subjected to high temperature post-cures. The data presented in Fig. 10 indicate a marked increase in the conductivity as cure proceeds, in contrast to the reductions in conductivity observed in the low temperature cure. It is known that these rearrangements are likely to generate low molecular weight species which may be expected to enhance the conductivity. The increase in the conductivity as cure proceeds is consistent with rearrangement of the epoxy resin and the observation of colour changes in the films with scorching.

5. Model for TSD studies of cure in epoxy resins

To explain the effects observed in this study we will propose a model in which the epoxy resin is considered to be composed of a matrix of varying conductivity and also containing a series of trap sites. These latter can have two forms: glassy regions and voids. In a previous study we have reported that during the process of cure voids are generated. Electrically such features can act as traps for the migration of charge and lead to modifications of the conduction level in the powder, Fig. 12. Changes in the shape of the traces with the contacting electrode similarly reflect the influence of the Fermi level on the conduction level.

In order to explain the observed behaviour we propose a model for the polymer–electrode contact of the form shown in Fig. 12. The Fermi-conduction level will be defined by the nature of the metal–polymer contact. The traditional model for TSD assumes that the dielectric is homogeneous and that traps are associated with dipolar states. Heating a sample will lead to the observation of firstly a peak associated with dipolar motions and then at a higher temperature a space charge peak. The position and amplitude of the latter reflects the migration of charge through the polymer to the electrode. In the present system we assume that additional traps can occur; associated with the surface of the filler and/or the voids in the material. Their spacial distribution and depth will have a very significant effect on the position, temperature and amplitude of the space charge peak. The model is summarized in Fig. 12 and a general mathematical analysis of this system will be the subject of a future publication. Qualitatively we can, however, draw certain conclusions with regards the origins of the effects observed in the cured epoxy resin systems.

In a partially cured matrix, the void content will be low but finite and hence when heated, although the injected charges are nominally mobile at T_g, a proportion will be trapped by voids in the matrix. The variation of the applied voltage will influence the number of charges and hence the population of traps, the nature of the conduction level and the ratio of trapped to mobile charges at T_g. In normal homogeneous polymer solids, the influence of voids is not observed, and a linear dependence of the amplitude of the lower temperature peak with applied voltage is usually observed. Changes in the water content lead to changes in the nature of the traps present and hence in the magnitude of the space charge peak. The influence of voids also explains why the TSD method is so sensitive to changes in the sampling area, Fig. 1. It is known from studies of cured epoxy films that the layer next to the metal substrate can have a subsequent void content and this interfacial zone is sensitive to the maximum temperature and time associated with cure. It is probable that the marked variations in part reflect the void content. Support for this hypothesis is gained from optical examination of sections through the films [1] and also the fact that the lower temperature peak for all samples occurs in essentially the same position and hence same extent of cure.

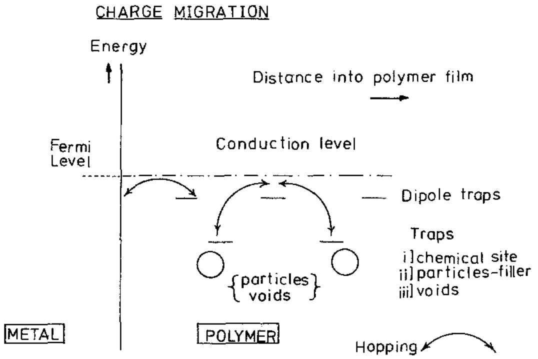

Figure 12 Model for TSD studies of epoxy resins.

In a highly cured resin the charge will be unable to penetrate into the resin to the same extent that it can in the more conductive, less well cured matrix, and as a consequence the charges released at T_g are able to flow without significant trapping at the electrodes. In the more conducting materials trapping effects are evident and indicative of the change in the mean free path of the conducting species.

6. Conclusions

It is evident that the TSD technique is capable in principle of indicating the extent of cure of powder epoxy resins. The interpretation of the data is complicated by the effects of water both in terms of changes in the conductivity of the matrix, when present at low concentrations and plasticization when present at higher concentrations. The effects of degradation and chemical rearrangement are also detectable by this method. The generation of voids during the cure process are also explicable in terms of the distribution of charge between the higher and lower temperature peaks.

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