The study of glass transition in epoxy resin using thermally stimulated depolarization current measurements

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Analysis of the course of glass transition in epoxy resin was performed by thermally stimulated depolarization current (t.s.d.c.) measurements. The methods used were the global method, the partial heating technique and the partial polarization technique. The investigation was carried out with pure resin, with resin containing admixtures and with cured resin. The results for maximum current I_m, maximum temperature T_m and activation energy E_a of α peaks are slightly influenced by admixtures. Stepwise determination of E_a shows that the depolarization process is continuously distributed in all systems. The most pronounced changes are observed in the cured resin: I_m and T_m are increased and E_a and the width of distribution ΔE_a are significantly decreased.

(Keywords: thermally stimulated depolarization current; glass transition; epoxy resin; curing)

INTRODUCTION

The glass transition temperature, T_g, of polymers can be generally determined by continuous measurements of different physical properties *versus* temperature. The most common methods in practice are based on measurements of the specific volume, thermal properties, elasticity and deformation[1]. Observation of optical or electrical properties can also be used. The most important method for polymer dielectrics is the measurement of thermally stimulated depolarization current (t.s.d.c.)[2–5]. This method is currently used to study the dipolar and ionic relaxations in dielectrics. Low equivalent frequencies (10^{-2} to 10^{-4} Hz) enable a high resolution and thus a separation of the processes which would overlap if using the higher frequency techniques. T.s.d.c. is very useful for accurate determination of T_g[6] and more sensitive than the popular d.s.c. method[7]. A special advantage of t.s.d.c. is the possibility of performing partition of the measurements. Such a technique is known as a fractional polarization[8]. A similar procedure is the fractional polarization within a narrow temperature range followed by depolarization in order to isolate a narrow relaxation component[8,9]. Another partial analysis is the so-called partial heating technique[10,11]. Using the partition, one is able to study the distribution in the glass transition, if any. Many processes taking place in polymers, such as changes in structure, interactions due to the presence of fillers, and curing processes, might significantly influence the glass transition.

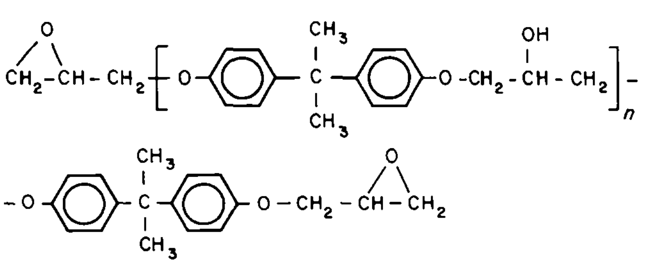
Epoxy resin was chosen as a model for study. The systems were prepared as follows.

1. Pure resin
2. Resin filled with 10 wt% non-conductive Al_2O_3, which does not possess electric dipoles in its own structure, so the dipole–dipole interactions between the resin matrix and the fillers were excluded
3. A mixture of resin with an electrically active filler possessing electric dipoles which might cause some interactions with the matrix but without chemical reaction. For this, 8 wt% dicyandiamide (DYCY) was added to the resin without curing. DYCY is commonly used as a curing agent but it does not react with epoxy below 418 K [12]
4. Epoxy resin mixed with 8 wt% DYCY, heated and cured.

The aim of this work was to study the influence of different admixtures and curing on the glass transition course in epoxy resin, analysing the distribution of activation energies by the use of various t.s.d.c. measurement techniques.

EXPERIMENTAL

Epoxy resin (see *Formula 1*) was a commercial product Epicote 1004 (Shell Chemicals Co.) with $\bar{M}_n = 1400$. G.p.c. of the resin (*Figure 1*, curve R) shows that the



Formula 1

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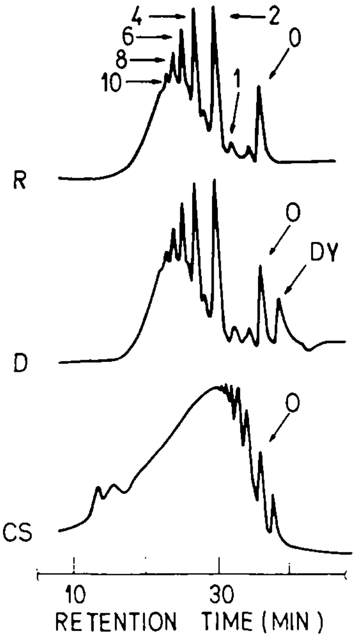

Figure 1 G.p.c. curves of the samples: R, pure resin; D, resin with addition of DYCY without curing; CS, soluble part of cured resin. Numbers represent the value of *n* in *Formula 1*. DY = peak showing DYCY

value of *n* is usually an even number, indicating that the resin was prepared from bisphenol A-diglycidilether and bisphenol A. DYCY and Al_2O_3 were analytical grade powders with non-defined particle sizes, used without further purification. The resin and the corresponding filler were mixed and finely ground in a mortar then put into a small container for t.s.d.c. measurements[13]. The container was heated up to 353 K and held at that temperature for 25 min. The contents melted and filled up the space between the silver coated brass electrodes of diameter 13.6 mm. The distance between the electrodes was 1 mm. For preparation of the cured sample the contents were heated up to 413 K and held at that temperature for 10 min. The container was placed, with the sample, in a shielded, dark cell containing dry nitrogen. Before t.s.d.c. measurements the sample was discharged by heating up to 353 K in the short-circuited state. Then the sample was polarized at temperature T_p for 20 min with a d.c. field E_p, and cooled down to room temperature under the same field conditions. The sample was then held in the short-circuited state for 30 min to clear the parasitic charge. The heating and cooling rate was 2 K min^{-1}. The current was measured by a Keithley 616 electrometer. The procedure for partial heating and partial polarization techniques will be described later.

G.p.c. characterization of the resin in the samples was performed on an apparatus consisting of a Waters 6000A pump, UGK injector and R-401 differential refractometer. Columns were Shimadzu HSG 15 and HSG 20 with 1×10^3 and 5×10^3 exclusion limit, respectively. Tetrahydrofuran was used as a solvent at a flow rate of 1 ml min^{-1}.

D.s.c. measurements were made on the Du Pont TA 900 instrument at a heating rate of 10 K min^{-1}.

RESULTS AND DISCUSSION

Characterization of samples

The characterization of samples used for t.s.d.c. measurements was performed by g.p.c. The results are presented in *Figure 1*. Curve R represents the pure resin, curve D represents the sample consisting of epoxy resin and DYCY. As the temperature during the preparation and the current measurements did not rise above 353 K, curing was not expected. One can see that the resin remains the same as in curve R, while a new peak of DYCY appears. There is no noticeable reaction between the epoxy matrix and the curing agent. Curve CS represents the soluble part of the cured resin (about 10 wt% of the sample), from which it is evident that DYCY has completely reacted. It also shows the presence of higher molecular weight products with two distinct distributions. D.s.c. curves of the samples are shown in *Figure 2*. The T_g for the pure resin in curve R is at about 324 K while T_g for the mixture of resin and DYCY in curve D appears at about 327 K. For cured resin in curve C, T_g is not observed as the d.s.c. signal obtained is flat.

T.s.d.c. measurements

The common t.s.d.c. measurements were carried out on samples polarized by $E_p = 8$ kV cm^{-1} at $T_p = 353$ K. The results are presented in *Figure 3*. According to the

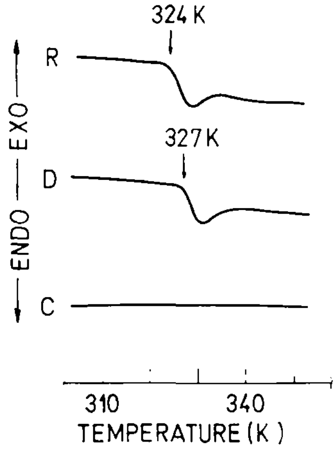

Figure 2 D.s.c. curves: R, pure resin; D, resin with DYCY without curing; C, cured resin

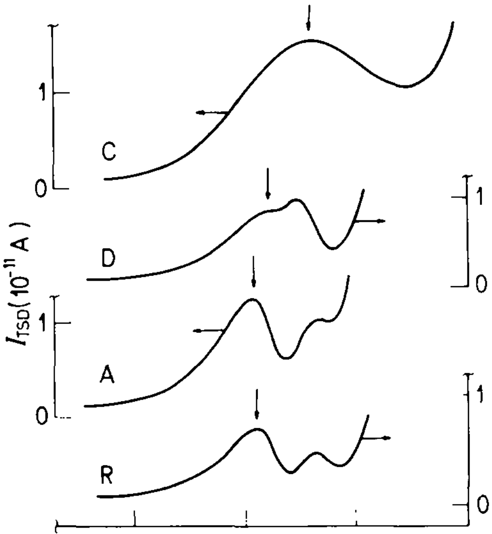

Figure 3 Thermally stimulated depolarization current, I_{TSD}, *versus* temperature for different samples: R, resin; A, resin with Al_2O_3; D, resin with DYCY; C, cured resin. $E_p = 8$ kV cm^{-1}, $T_p = 353$ K. Vertical arrows show the maximum temperature of the α peaks

d.s.c. results the lower temperature peaks are dipolar relaxation α peaks which coincide with the glass transition temperature. The higher temperature peaks are obviously the satellite space charge ρ peaks. For cured resin (*Figure 3*, curve C) only one peak appeared. Performing the experiments with a blocking electrode and with polarization at lower T_p[14,15] it was possible to obtain a peak at the same temperature. As the blocking prevents the injection of charge it means that the recorded peak is an α peak. The space charge peak was not observed separately. It is probably decreased, shifted towards the higher temperatures[16] and masked by the dominant α peak.

Comparison of the main parameters of the α peaks are presented in *Figure 4*. The maximum temperature T_m increases in the following order: Al_2O_3 doped resin (A), pure resin (R), DYCY doped resin (D) and cured resin (C). Values of T_m in A and R are practically the same. T_m in D is slightly increased. The largest increase occurs in C. The shifts in T_m are obviously the consequence of an increase in attraction between the constituents in filled resin and due to the bonding in cured resin. The tendency for the α peak to move to higher temperatures has been observed in cured epoxy resin[16] and in systems with the dipole–dipole interactions between the resin matrix and the admixtures[15].

Comparison of maximum currents I_m shows the same order of increase, with the exception of sample A, but the α peak for C is again the highest. The effect of the increased α peak in cured resin has been explained[16] as the consequence of the changed balance between the α and ρ processes. Part of the stored charge is bound by the dipolar state (compensation charge) which is released at T_g (α peak). Another part of the charge is trapped as a space charge which is subsequently released (ρ peak). In cured resin with decreased conductivity the charge cannot penetrate into the sample to the same extent as in the more conductive resin. As a consequence the compensation charge is able to flow without significant trapping. It causes an increase of α peaks and a decrease of ρ peaks. An attempt was made to calculate the relative number of dipoles taking part in depolarization phenomena using the Bucci and Fieschi equation[17]:

$$N = \frac{Q3kT_m}{SE\mu^2} \tag{1}$$

where N is the number of dipoles per volume unit, Q the released charge, k the Boltzmann constant, S the electrode area, E the electric field and μ the dipole moment. For a series of samples of epoxy resin one can assume that:

$$SE\mu^2 = \text{const.} \tag{2}$$

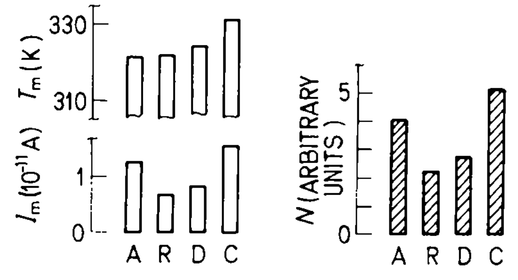

Figure 4 Main parameters related to α peaks from *Figure 3*: I_m, maximum current; T_m, maximum temperature; N, relative number of electric dipoles

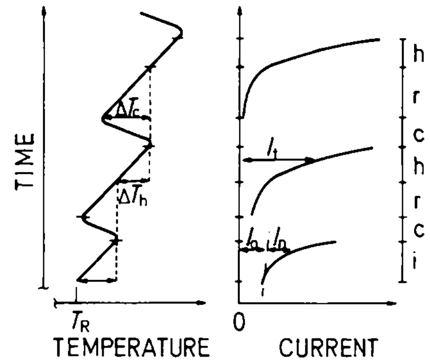

Figure 5 Diagram of the partial heating method: i, initial heating; c, cooling; r, repeated heating; h, heating for t.s.d.c. analysis; ΔT_h, temperature step in partial heating; ΔT_c, temperature step in partial cooling; I_0, background current; I_n, net current; I_t, total current; T_R, room temperature; —·—·, base line

and

$$Q \sim I_m \tag{3}$$

Thus the relative number of dipoles is given by:

$$N = I_m T_m \tag{4}$$

This approximation has been proposed and similarly derived by Kovarskii *et al.*[18]. The results for N are shown in *Figure 4*. The samples follow the same order as shown by I_m.

The t.s.d.c. curves from *Figure 3* have been used for determination of activation energy E_a of the α processes by use of the classical initial rise method[19]. Depolarization current for calculation has been taken in the temperature range 300–310 K. (The results are presented in *Figure 10* and discussed together with the other results for activation energy obtained in partitioning experiments.)

Partial heating technique

In order to perform a more thorough investigation of α relaxation the partial heating technique was carried out. The existence of masked processes is expected, particularly in sample C. The experimental procedure is explained in *Figure 5*: i denotes initial heating, c is cooling, r is repeated heating, h is new partial heating, ΔT_h is the temperature range of partial heating and ΔT_c is the temperature range of cooling. The whole run started with i followed by consecutive repeated treatments c, r and h. ΔT_h was about 5 K, and ΔT_c about 8 K. In the original description[11], after any heating the sample was cooled down to room temperature. This long cooling time was not used here in order to make the run shorter and thus decrease the possible loss of electric charge stored in the sample. The current recorded during the h treatments has been used for calculation of E_a in steps by use of the initial rise method. A serious disadvantage of this technique is the parasitic current I_0 which decreases the calculated E_a[15]. Determination of the net current I_n is impossible because the position of the base line (see *Figure 5*) is not well defined. For calculation of E_a the total current I_t, which is the sum of I_0 and I_n, has been used. At the beginning of an experiment relatively high I_0 makes the calculated E_a very inaccurate, so this result was not used. As the run proceeds I_0 decreases and E_a tends to be more accurate. However, an opposite source of error decreasing E_a appears when the calculation is performed at high levels of the depolari-

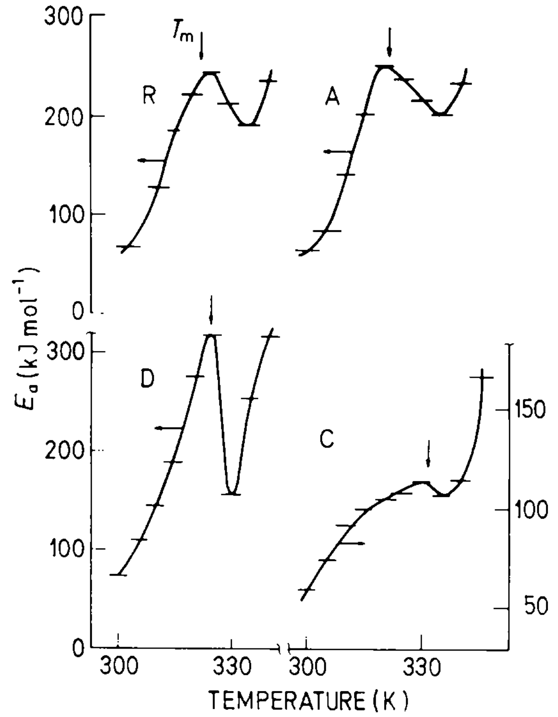

Figure 6 Activation energy, E_a, *versus* temperature obtained by partial heating. Symbols show different samples as in *Figure 3*. Vertical arrows show positions of T_m obtained in global experiments from *Figure 3*

zation peak[20]. Therefore this technique can give only qualitative information about the course of a process.

The results of E_a *versus* temperature obtained by partial heating are shown in *Figure 6*. The value of E_a increases with temperature due to the clearance of parasitic current but also due to the distribution of the α relaxation. Under the experimental conditions no levelling off was observed in the temperature range from 298 K to T_m, indicating that the processes are continuous. The results for the cured sample are distinctive: the maximum E_a achieved is significantly lower than in any other case. Processes taking place at temperatures above T_m may be influenced by conductivity phenomena and therefore are not used in characterization of the α relaxation.

Partial polarization technique

The experiments with partial polarization were carried out in the following way: (i) discharge as in common procedure; (ii) polarization at T_p for 5 min; (iii) cooling down to $T_p - 10$ K under E_p; (iv) short-circuited state at $T_p - 10$ K for 5 min to remove the parasitic charge; (v) cooling to the starting temperature in short-circuited state and commence taking measurements.

The normalized fractional t.s.d.c. curves of two characteristic samples of pure resin and cured resin are shown in *Figures 7* and *8*, respectively. The curves of the other samples are not shown but all the related results are presented and discussed in the following text. Originally, the curves obtained contained the parasitic charge which was removed graphically. The normalization is explained in the inset in *Figure 7*. The zero current (shown in inset) was determined by exponential interpolation between the points A and B[15,21]. The resolution depends upon the polarization ranges while the precision is determined by the accuracy of normalization. In comparison with the global runs the maximum current in fractional experiments for all the samples is higher. This is because the polarizations were performed in the narrow temperature range within the α events. Such polarization causes partial polarization without introducing the space charge. The decrease[16] or absence[22] of space charge (ρ peaks) usually increases the α peaks. The fractional analyses for the samples R, A and D were performed by four runs which covered the α relaxation range. The sample of cured resin C, as in the global run, shows a different behaviour (*Figure 8*). The maximum current is increased. The temperature range of the α relaxation was broadened and had to be covered by five runs. The sixth run shows the part of ρ relaxation.

Figure 9 shows the dependence of E_a on T_p for all the samples. Determination of E_a was performed for each

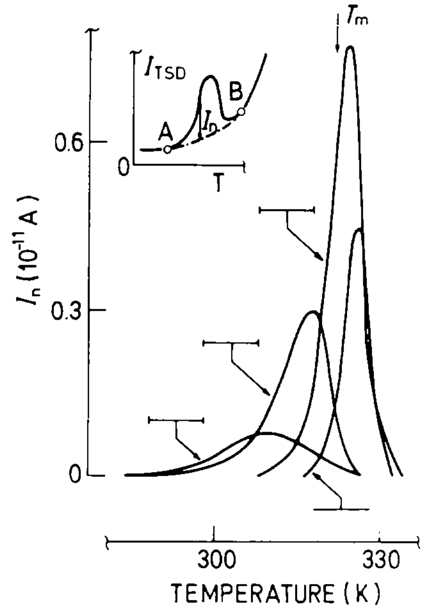

Figure 7 Normalized depolarization current, I_n, *versus* temperature, obtained by partial polarization in pure resin, $E_p = 8$ kV cm^{-1}. Horizontal lines show temperature of application of E_p. T_m, maximum temperature from global experiment. Inset: Arbitrary I_{TSD} *versus* (T) diagram showing the trend of normalization; · · ·, zero current

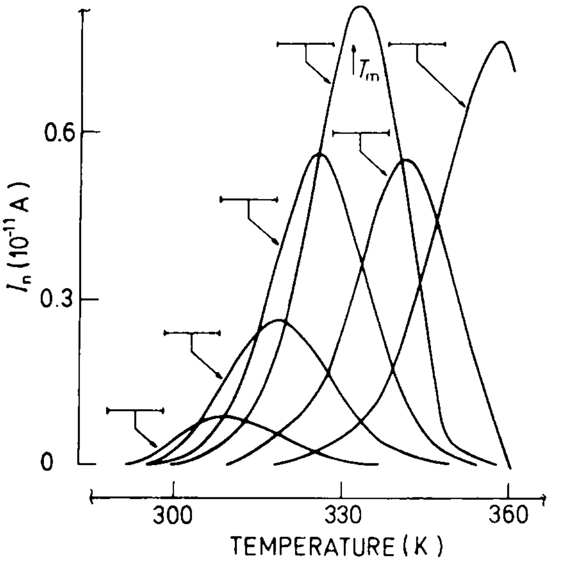

Figure 8 I_n *versus* temperature curves obtained by partial polarization in cured resin, $E_p = 8$ kV cm^{-1}. T_m, maximum temperature from global experiment

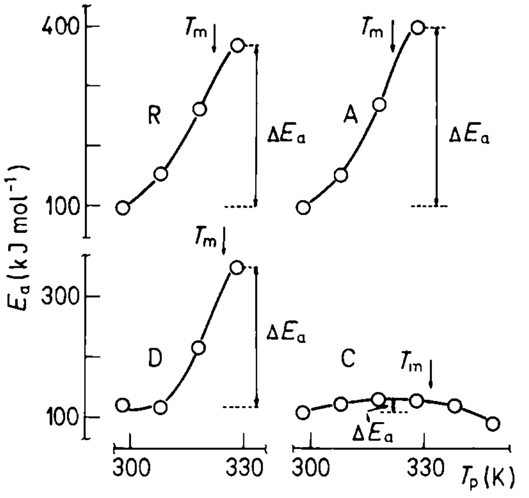

Figure 9 E_a *versus* T_p obtained by partial polarization for different samples. ΔE_a, width of activation energy; T_m, maximum temperature related to global I_{TSD} *versus* T curve

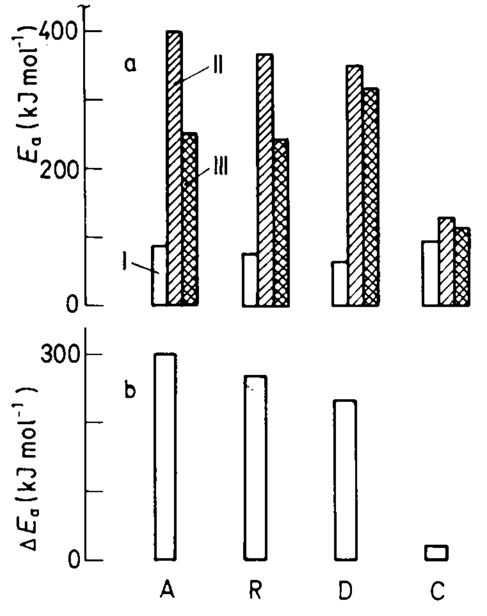

Figure 10 (a) Comparison of E_a obtained by different methods: I, initial E_a by global curves; II, maximum E_a by partial polarization; III, maximum E_a by partial heating. (b) ΔE_a, obtained by partial polarization. Symbols for samples as in *Figure 3*

normalized curve separately by use of the initial rise method. The results from *Figure 9* confirm the results obtained with the partial heating technique. The discrete phenomena are not observed. The α relaxations in all cases are continuously distributed.

Comparison of results

The results of E_a of α relaxations for all the samples obtained in different ways are presented in *Figure 10a*. The I columns show the E_a(I) which was obtained from the global t.s.d.c. curves. These values are significantly lower than the others because they are related to the beginning of the α relaxations in the region of low energy depolarization. They do not vary very much between samples. One can see that the popular initial rise method applied to global curves cannot be used for characterization of the relaxations when the distributed processes are taking place.

The II columns represent the maximum in E_a obtained in fractional polarization runs. For different samples E_a(II) decreases in the order: A, R, D, C. This is the same order of increasing T_m in global t.s.d.c. curves (*Figure 4*). Such a comparison shows that the decrease in E_a(II) is dependent upon the increase in attraction between the constituents in the samples examined. The values of E_a(II) for A, R and D vary slightly but the cured sample C with bonded molecules shows a significant drop. The curing increases the immobilization of the dipole groups which cannot be easily arranged by the action of a relatively low polarizing field. The E_p of 8 kV cm^{-1} was just sufficient to produce low energy processes of polarization. Therefore, the related depolarization has its course with low E_a. Such phenomena were observed earlier in systems with increased attraction between the constituents[15,21].

The III columns in *Figure 10a* show the maximum E_a obtained by partial heating. Values of E_a(III) are generally lower than those of E_a(II), due to the loss of charge in consecutive heating and cooling of samples and due to the other sources of error previously explained. The values of E_a(III) follow the same order of samples as the values of E_a(II) with the exception for sample D. In conclusion the results for E_a(II) are considered to be more reliable for characterization of α relaxation than those of E_a(I) and E_a(III).

Figure 10b shows the results for activation energy width, ΔE_a, in the temperature range in which the α relaxation was analysed, from 300 K up to the maximum of E_a. Values of ΔE_a are related to the fractional polarization from *Figure 9*. The addition of Al_2O_3 to the resin slightly increased ΔE_a. The addition of DYCY slightly decreased ΔE_a. The most pronounced suppression in distribution width occurred in cured resin. It is known that the distribution of relaxation time related to the glass transition is increased by the addition of a dopant or under hydrostatic pressure. The width of distribution reflects the distribution width of the order parameter[23]. Considering the results for ΔE_a in the present work one can assume that the change in ΔE_a is also a consequence of the change in ordering parameters. The systems of pure resin and of slightly doped resin are in a relatively higher ordered state than the cured system, in which the disorder is increased. The differences obtained among the ΔE_a values for various systems reflect a decrease of the distribution width of their order parameters. In short, a decrease in ΔE_a is accompanied by an increase of disorder and a decrease in flexibility of dipole groups in the systems.

CONCLUSIONS

T.s.d.c. global curves show a shift of T_m of the α peaks towards higher temperatures in the following sample order: resin with the addition of Al_2O_3 as an electrically inert material; pure resin; resin with addition of DYCY without curing for introduction of a dipole–dipole interaction between the matrix and dopant; cured resin. This order represents an increase in attraction between the constituents. The most pronounced shift occurs in the cured system.

The maximum height of the α peak as well as the maximum of the relative number of dipoles, which are involved in α relaxations, are observed in cured resin. This phenomenon was attributed to a decrease in electrical conductivity, which causes a decrease of the trapped charge and an increase of the fluent compensation charge which is released at T_g[16].

The determination of E_a was carried out using the initial rise method applied to global t.s.d.c. curves, curves obtained in partial heating and curves obtained by partial polarization. It is shown that the most reliable results are those obtained by partial polarization. The results of E_a obtained in steps in the region of glass transition show that the α relaxation processes are continuously distributed in all systems.

The maximum of E_a and the distribution width in the range of α relaxation decrease as the attractive interactions, bonding, and disorder in the systems increase. Thus, significant decreases in E_a and ΔE_a occur in cured resin.

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