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The study of glass transition in epoxy resin by thermally stimulated depolarization current. Compensation phenomenon

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Abstract

The pure and the cured epoxy resin was characterized by the integral and partial thermally stimulated depolarization current (TSDC) in the range of the glass transition. The function of the activation energy (E) vs. T obtained by use of the integral current curve $I_i(T_i)$ by direct transition of points I_i into E_i showed only one linear course without peculiarities. The $E(T)$ function obtained by use of a series of the partial peaks showed several linear stages. The relaxation maps (RM) were drawn and the compensation points (C) were determined. The coordinates of C's for cured resin in comparison with the pure resin indicated a decrease in motion of the moving parts in resin due to the curing. The relative numbers of the relaxing dipoles (N) vs. E were approximated. The related energy distribution width ω in the cured resin was significantly decreased. © 1997 Elsevier Science B.V.

Keywords: Activation energy distribution; Compensation phenomenon; Epoxy resin; Glass transition; Thermally stimulated current

1. Introduction

Thermally stimulated depolarization current (TSDC) measurement is the important method for the study of dipolar and ionic relaxations in dielectric materials. Due to the low equivalent frequencies (10^{-2} to 10^{-4} Hz), the method enables high resolution [1,2]. Usually, the TSDC measurements are performed by the so called integral procedure. It means that the previous polarization by use of a d.c. field (E_p) is applied in a wider temperature range from a relatively high temperature (T_p) up to the storage temperature (T_o). The obtained TSDC curves are being used for determination of the various relaxation parameters as well as for study of the distribution functions [3]. More sophisticated application of TSDC measurements is the partial TSDC analysis [4,5]. Partial technique is based on polarization within a narrow temperature window (ΔT_p) in order to isolate the narrow relaxation part [6]. In such a way a complex integral curve is divided into a series of the partial elementary curves which make possible the determination of the real distribution functions. From the practical point of view the procedure for getting an integral curve is more simple than the procedure for partial runs. Therefore, an idea of so called direct transformation of an integral TSDC curve into the distribution function without making partial measurements, seems to be very interesting [7,3]. Direct transformation is

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based on the assumption that each point of an integral curve represents the maximum of the elementary curve for the narrow group of the relaxing dipoles.

The obtained data of the elementary values for the activation energy and relaxation time enable one to construct the so called relaxation maps (RM) as well as to determine the compensation points (C). It represents a new trend in characterization of the polymer systems [8–10].

The aim of this paper was study of the epoxy resin across the glass transition by the partial measurements, with the temperature window of 5 K, in order to construct the related RM's and search for the compensation phenomena. Another intention was to check the possibility of use of the integral curves and direct transformation for determination of the activation energy distribution. The preliminary consideration of TSDC of the same resin has been published in the recent paper [11].

2. Experimental

The preparation of samples and the characterization of epoxy resin (commercial Epicote 1004 Shell with $\bar{M}_n = 1400$) was described elsewhere [11]. The measurements were performed on the pure and the cured resin. The curing was performed by addition of 7.4 wt% of dicyandiamide and by heating: 20 min at 368–373 K, 15 min at 373–413 K and 10 min at 413–423 K. The DSC curve of pure resin, obtained by heating rate of 10 K min^{-1}, showed the T_g of about 324 K. For cured resin the DSC signal was flat. The samples were 13.6 mm in diameter, 1 mm thick with silver coated brass electrodes. Other details about the sample holder were given in [12]. The procedure for integral measurements was as follows: preheating up to 380 K in the short-circuited state (s.c.s.), polarization by E_p=8 kV cm^{-1} during cooling from 338 to 288 K with the rate of 2 K min^{-1}, storage relaxation at T_o=283 K in the s.c.s. for 30 min and depolarization by heating with 5 K min^{-1}. In comparison with the previous methodology [10] the polarization was performed just during continuous cooling without constant temperature standing. It was made in order to equalize the methodology of polarization in the integral and the partial runs. The runs with the partial polarization were performed in a slightly different way: preheating up to 370 K, cooling to various ΔT_p, application of E_p=8 kV cm^{-1} during cooling of 2 K min^{-1} in the narrow temperature window of 5 K, cooling to T_o=283 K in the s.c.s. and the storage

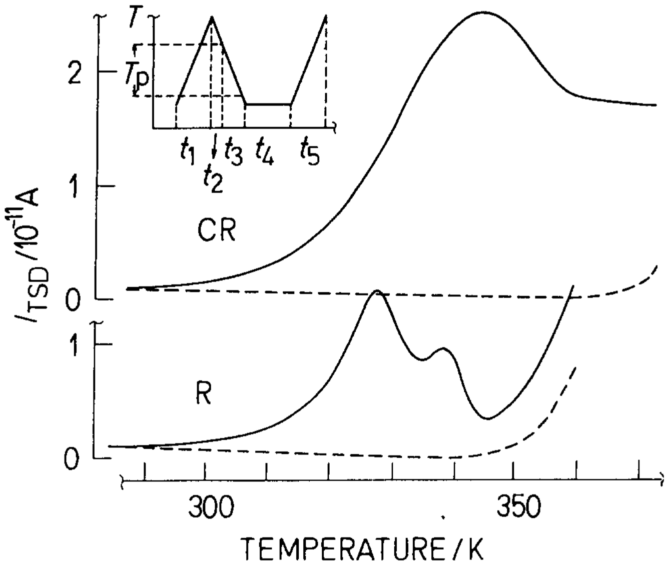

Fig. 1. Plot of TSDC versus temperature for different samples: R, epoxy resin; CR, cured resin. E_p=8 kV cm^{-1}, T_p=338–288 K. Inset: Procedure for integral measurements; t_1, time of preheating; t_2, time for stabilization of cooling rate; t_3, polarization time; t_4, storage time; t_5, heating time for current stimulation; arbitrary units.

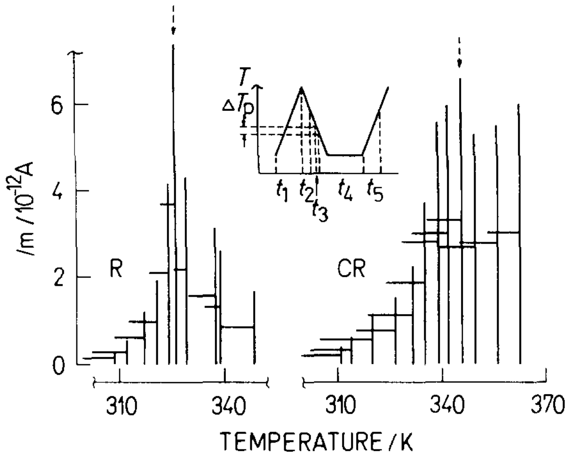

Fig. 2. Parameters of elementary peaks obtained by partial polarization. I_m, current of the peak maximum. Dashed arrows are related to the elementary peaks with maximum amplitude. Horizontal lines show half width at $I_m/2$ (low-temperature side). Inset: Procedure for partial polarization; ΔT_p, temperature interval in which the E_p takes place, equal to 5 K. Other symbols as in Fig. 1.

relaxation at T_0 in the s.c.s. The time of cooling to T_0 and the time of storage at T_0 together were 30 min. Depolarization was performed by heating at 5 K min^{-1}. The diagrams of $T(t)$ of the temperature courses, in arbitrary units, showing the methodology for integral and partial runs were drawn, as the insets, in Figs. 1 and 2. The current was measured by a Keithley 617 electrometer and the temperature was controlled by a LFE model 2012 controller.

3. Results and discussion

3.1. Integral and partial measurements

Integral curves of TSDC for pure resin (R) and for cured resin (CR), in the range of the glass transition, are shown in Fig. 1. The lower temperature peak is dipolar α peak which coincide with the glass transition while the other one is a satellite ρ peak caused by the conductive phenomenon. In comparison with the recent results [11] some increase in current and shift of the maxima occur due to the increased rate of heating for more than double. For cured resin, only one peak is observed. The dashed lines show the zero current obtained by the measurements of resin following the complete procedure, as explained in the experimental part, but without the application of E_p.

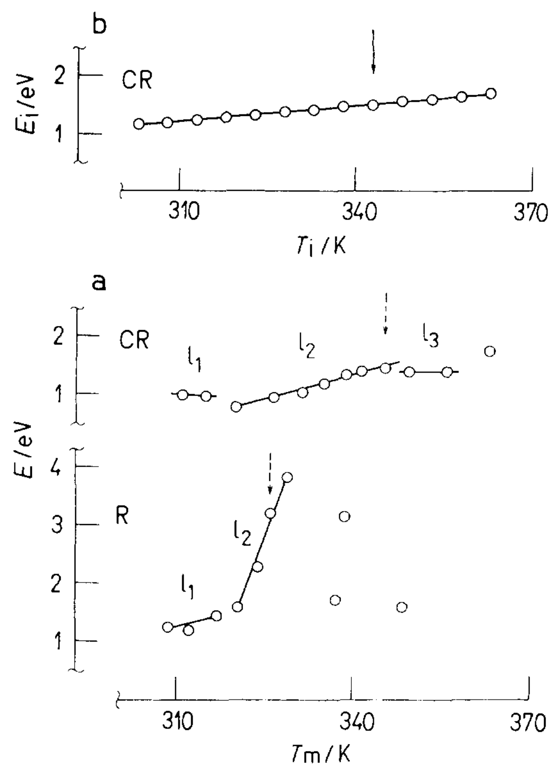

Fig. 3. (a) E versus T_m for R and CR obtained from elementary peaks: l_1, l_2 and l_3 are fitting lines. Dashed arrows are related to the elementary peaks with maximum amplitude. (b) E_i versus T_i for CR obtained by direct transformation from the integral curve in Fig. 1 CR. Arrow is related to the maximum of the integral curve.

Measurements with the partial "windowing" polarization were performed in the same temperature range as the integral measurements. Instead of one curve a series of elementary peaks were obtained. The peaks were normalized by the subtraction of the parasitic current [11]. The net values for the maximum of the elementary peaks (I_m) versus temperature and the half-widths at $I_m/2$ (low temperature side) are shown in Fig. 2. The half-widths were necessary in determination of the activation energy (E) of the elementary peaks by the Christodoulides methods [13,14,10]. The obtained E's versus temperature of the maximum (T_m) of the elementary peaks are shown in Fig. 3a. The results of E for R may be refined by two lines l_1 and l_2. As regards the results at higher temperatures, the points are very dispersed and uncertain due to the conductive processes and the refinement is impossible. In the case of CR one may consider three distinctive groups and draw the most probable lines l_1, l_2 and l_3. In further analysis the elementary *E*'s for both systems are replaced by the refined E_l's which fit the drawn lines.

One attempt was made to calculate a series of the activation energies directly from the integral curve of the cured resin. According to the literature [3] direct transformation can be performed by use of the equation

$$E_i = E_{mi}T_i^2/T_{mi}^2 \qquad (1)$$

where E_i is an elementary activation energy of any point lying on the integral curve at the related temperature T_i, E_{mi} and T_{mi} are the activation energy and temperature related to the maximum of the integral curve. E_{mi} in question is an unknown value and should be approximated. For that purpose, the refined energy of 1.49 eV related to the partial elementary peak with the maximum current of sample CR was used. The calculated E_i versus the arbitrary T_i for cured resin are shown in Fig. 3b. While comparing the $E(T_m)$ function for sample CR and the $E_i(T_i)$ function for the same sample, one can see that $E_i(T_i)$ is just a monotonous line covering the whole temperature range of investigation with the significantly reduced difference between the high and the low level of the activation energy (ΔE). Direct transformation can get just a global and reduced distribution with no fine peculiarities and it can not be a substitute for the much sophisticated methodology of the partial runs.

3.2. Compensation phenomena

The first step in determination of the compensation phenomena is the construction of the RM. RM is a set of the Arrhenius lines:

$$\ln\tau = \frac{E}{0.0862} \times \frac{10^3}{T}\ln\tau_o \qquad (2)$$

where τ is the relaxation time of an elementary peak, τ_o is the pre-exponential factor and *E* is the activation energy in eV. If the group of the Arrhenius lines converge to a single point it is called the compensation point with coordinates: compensation temperature (T_C) and compensation time (τ_c). The Arrhenius lines were drawn by use of the refined E_l as a slope and one well defined point for $\tau(T)$. The methodology for determination of the C's has been explained elsewhere [10]. The different groups of lines could be considered as caused by the different amorphous phases [15,16]. Knowing that the T_g is the temperature in which the various tendencies of motion are being unified, the T_c's might be understood as the glass transitions of the phases in question [10]. The position of C's is an indication of the molecular motion. The cooperative mobility occurs at T_c equal or close to the measured T_g with the maximum in ΔE. The shift of T_c's towards the higher temperature is the consequence of the tighter structure with the decrease in ΔE. In extreme cases the Arrhenius lines are close to be parallel with the minimum ΔE and the irrational $T_c(10^3/T{<}0)$. It is characteristic for the very hindered molecules or for the post-transition state [10,14,17].

RM's for the system R and CR are shown in Fig. 4. The numerical values are listed in Table 1. The upper

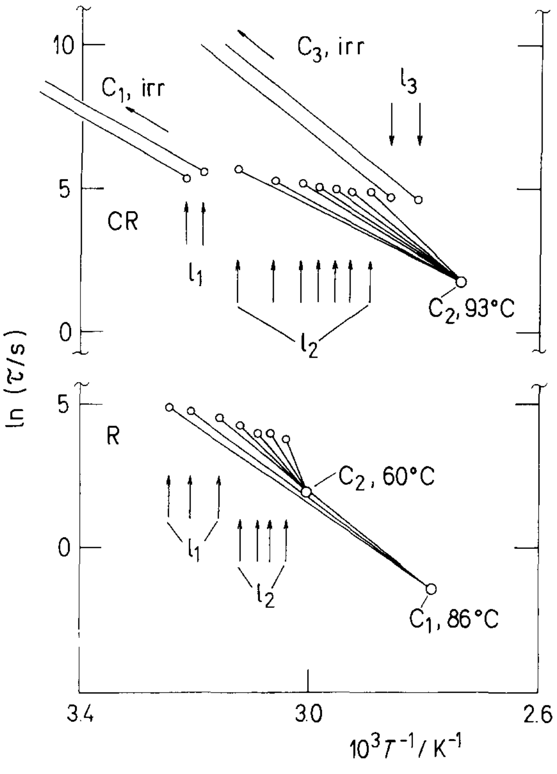

Fig. 4. Relaxation maps lnτ versus $10^3/T$ for samples R and CR: l's temperature ranges related to fitting lines in Fig. 3; C's, compensation points and the related temperatures; irr, irrational. Arrows show T_m of the elementary peaks.

Table 1
Parameters of peaks obtained by partial polarization

Sample	Range	T_m/K	(T_m-T_l)/K	E_l/eV	$\ln[\tau(T_m)/s]$	T_c/K	τ_c/s
R	l_1	308.5	9.2	1.194	4.88		
		312.0	9.8	1.276	4.74		
		317.0	8.5	1.393	4.52	358.9	0.24
	l_2	320.6	7.9	1.547	4.26		
		323.8	5.6	2.435	3.98		
		326.0	4.1	3.046	3.99		
		329.0	3.5	3.879	3.76	332.8	6.95
CR	l_1	311.0	11.6	0.991	5.36		
		314.0	12.0	0.965	5.54	irr.	
	l_2	320.0	15.2	0.776	5.70		
		326.6	13.0	0.959	5.25		
		331.6	12.6	1.098	5.18		
		335.1	11.2	1.195	5.06		
		338.9	10.3	1.301	4.98		
		341.6	10.1	1.376	4.90		
		345.6	9.8	1.487	4.89	365.8	6.04
	l_3	349.4	10.2	1.370	4.70		
		355.9	11.0	1.380	4.60	irr.	

(T_m-T_l) is equal to the half-width at $I_m/2$ (low temperature side).

points are related to $\ln\tau(T_m)$ of the elementary peaks. The l's indicate the related lines of refinements according to Fig. 3. The initial part of the relaxation in R is characterized by T_{c1} at 359 K (86°C). The following part related to l_2 with T_{c2}=333 K (60°C) shows a possible maximum in molecular motion as T_{c2} is very close to T_g. Final part was not possible to characterize because of the dispersed results for E. The initial part of the relaxation in the cured CR in comparison with the initial part in R shows an almost parallel couple of lines with the irrational T_c and a very low ΔE due to the curing. Following part related to l_2 with T_c equal to 366 K (93°C) shows a more intensive motion but still very hindered in comparison with the non-cured R. The Arrhenius lines in the final stage of CR were parallel again showing a minimum in ΔE.

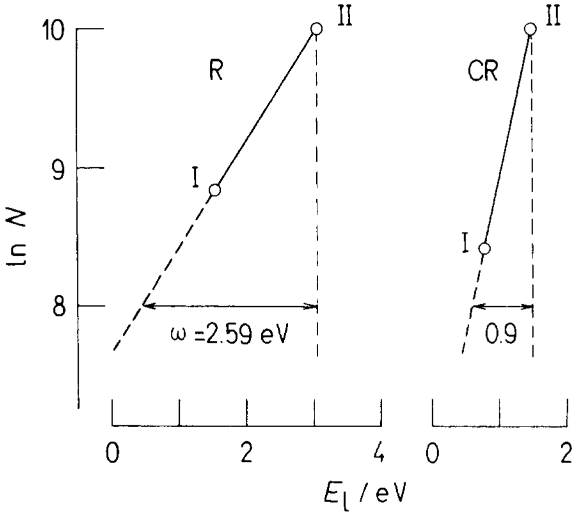

Fig. 5. Activation energy distribution for samples R and CR, related to l_2 temperature range in Fig. 3: N, approximate number of dipoles; ω distribution width at 80% of the maximum value; I, related to the minimum energy peak; II, related to the peaks with maximum amplitude.

3.3. Distribution of activation energy

Another approach in characterization of samples based on TSDC is the determination of the energy distribution function $N(E)$ [3], where N is the relative number of electric dipoles in the sample, which take part in the relaxation. A simplified method for the approximation of the energy distribution, by use of the three extreme values, has been proposed in [18]. Fig. 5 contains the $\ln N(E_l)$ approximations for the l_2 range with two extreme values for R and CR systems. N is approximated [3] by equation:

$$N = I_m \times T_m \qquad (3)$$

For determination of the points, the elementary peaks were used. I_m, T_m and E_l values are shown in Fig. 2 and Fig. 3, respectively. E_l(I) and N(I) are related to the minimum energy peaks. E_l(II) and N(II) are related to the peaks with maximum amplitude (dashed arrows in Fig. 2). All the values of ln$N$ were normalized to ln$N$(II) $= 10$. The distributions were characterized by widths, ω at heights equal to 80% of the maximum value. One can see the significant decrease in ω from 2.59 eV for R to 0.90 eV for CR due to the decreased flexibility of the constituents in the cured resin.

4. Conclusions

The integral TSDC curve across the glass transition in the temperature range from 290 to 360 K for pure epoxy resin showed a dipolar α peak and the satellite space charge ρ peak. The corresponding peak obtained with the cured resin showed only one broadened peak which was shifted towards the higher temperature. For better analysis, the partial measurements were performed. The glass transition range for pure and for cured resin was covered by 10 and 12 partial runs, respectively. Each of the partial peaks was characterized by E and $\tau(T_m)$. The analysis of the $E(T_m)$ function for pure resin showed two linear stages and for cured resin three linear stages.

The RM's for the pure resin showed two compensation points. The initial one, C_1 which was related to the start of relaxation, and the following one, C_2 which was very close to the T_g showing an actual glass transition in resin. The C_1 for the cured resin became irrational while the C_2 was shifted towards the higher temperature indicating an increase in hindering of the moving constituents due to the curing. The C_3 for the cured resin was irrational indicating extremely low ΔE and therefore a very inhibited motion.

Another characterization of the samples by the approximate distribution $N(E)$ showed that the curing essentially decreased the distribution width ω due to the decrease of flexibility in resin.

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References

[1] Van Turnhout, in G.M. Sessler(eds.), "Topics in Applied Physics" , Vol. 33, Springer, Berlin (1980).

[2] G.A. Lushcheikin "Metody Issledovaniya Elektricheskikh Svoistv Polimerov", Khimiya, Moscow (1988) pp. 118–126 (in Russian).

[3] A.L. Kovarskii, S.A. Mansimov and A.L. Buchachenko, Polymer, 27 (1986) 1014.

[4] J. Wanderschuren and J. Gasiot, in P. Bräunlich (eds.),"Topics in Applied Physics" , Vol. 37, Springer, Berlin (1979) pp. 159, 160.

[5] K. Nishinari, D. Chatain and C. Lacabanne, J. Macromol. Sci. Phys., B22 (1983) 529.

[6] C. Lacabanne, D. Chatain, J. Guillet, G. Seytre and J.F. May, J. Polym. Sci., Polym. Phys. Edn., 13 (1975) 445.

[7] G. Pfister and M.A. Abkowitz, J. Appl. Phys., 45 (1974) 1001.

[8] A. Bernes, R.F. Boyer, D. Chatain, C. Lacabanne and J.P. Ibar, in S.E. Keinath, R.L. Miller and J.K. Rieke (eds.), "Order in the Amorphous State of Polymers", Plenum, New York (1987) pp. 305–26.

[9] J.P. Ibar, Polymer Eng. Sci., 31 (1991) 1467.

[10] M. Topić, Thermochim. Acta, 285 (1996) 231.

[11] M. Topić and A. Moguš-Milanković, Polymer, 32 (1991) 2892.

[12] M. Topić, A. Moguš-Milanković and Z. Katovi, Phys. Status Solidi (A), 86 (1984) 413.

[13] C. Christodoulides, J. Phys. (D) Appl. Phys., 18 (1985) 1501.

[14] M. Topić and Z. Katović, Polymer, 35 (1994) 5536.

[15] J.P. Ibar, ACS Polym. Mater. Sci. Eng., 61 (1989) 753.

[16] A. Bernes, J.J. Martinez, D. Chatain and C. Lacabanne, J. Therm. Anal., 37 (1991) 1795.

[17] M. Topić and Z. Katović, Croat. Chem. Acta, 69 (1996) 1215.

[18] M. Topić and Z. Veksli, Polymer, 34 (1993) 2118.