Investigation of β relaxation in novolac phenol–formaldehyde resin by use of thermally stimulated depolarization current

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The β relaxations of novolac phenol–formaldehyde (NPF) resin were investigated by whole and partial thermally stimulated depolarization current (t.s.d.c.) measurements in the temperature region from 137 to 270 K. The whole measurements showed two peaks with maximum current at 158 and 187 K, respectively. The peaks obtained by partial polarization were characterized by the activation energy (E_a) and relaxation time at the temperature of the peak maximum. The relaxation map and the compensation diagram were drawn. The mean E_a for both relaxations is 0.51 eV. The initial part of β_2 obeys the compensation law with $T_c = 308$ K, 26 K below T_g. The appearance of extremely low convergence of the Arrhenius lines and thus irrational compensation points due to the narrow width of the activation energy (ΔE_a) were discussed. The relaxations are supposed to be caused by the motions of the phenyl rings around the methylene links.

(Keywords: novolac phenol–formaldehyde; β relaxation; t.s.d.c. measurements)

INTRODUCTION

The measurement of the thermally stimulated depolarization current (t.s.d.c.) is one of the very important methods for the study of dipolar and ionic relaxations in dielectric polymers. A special feature is the possibility of performing the measurements in steps. There are two well known methods for partitioning. Very convenient for quick investigation is the so-called partial heating technique[1–3]. More accurate is partial polarization. A review has been given by Vanderschueren and Gasiot[4] for the period from 1972 to 1977. A distinguished technique is polarization within a narrow temperature window followed by depolarization in order to isolate a narrow relaxation component[5]. It has become very popular for the investigation of the distribution of activation energy and relaxation time *versus* temperature[3,6–14]. This enables the investigation of compensation phenomena, giving an additional dimension to the characterization of polymer materials. The elementary peaks obtained by the partial analysis are usually considered as a collection of Arrhenius lines called the relaxation map. Each line is given by:

$$\ln \tau = \ln \tau_0 + E_a/kT \qquad (1)$$

where τ is the relaxation time related to an elementary peak, τ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant. The compensation phenomenon is the case when the lines are converging to one point at compensation temperature (T_c) and compensation time (τ_c). The converging lines obey the compensation law[15]:

$$\ln \tau = \ln \tau_c + E_a(T^{-1} - T_c^{-1})/k \qquad (2)$$

In order to check whether or not a group of isolated peaks obey the compensation law, the ratios between ln τ_0 and E_a defined by equation (1) have to fit the compensation line[15]:

$$\ln \tau_0 = -E_a \times (1/kT_c) + \ln \tau_c \qquad (3)$$

In systems with more than one compensation point, each of the compensation lines shows a separate order of motion or may indicate a separate phase. The more distant the compensation lines are, the greater is the phase segregation. The compensation phenomena show the distribution of the order parameters, indicating the property structure of the amorphous state[12].

The t.s.d.c. measurements for characterization of novolac phenol–formaldehyde (NPF) resin were performed in 1978 and 1980[16,17]. The dipolar α relaxation at 320 K, the space-charge ρ relaxation at 334 K[18] and a small peak at 296 K[19] were described. The aim of this work was to study the relaxation of NPF in the β temperature region by use of t.s.d.c. measurements and by the application of partial polarization.

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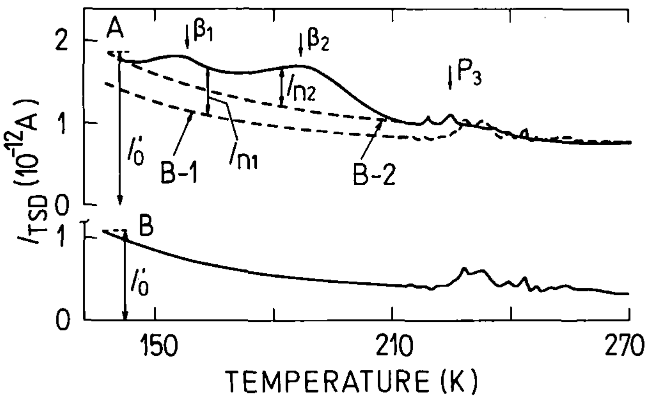

Figure 1 Plot of t.s.d.c. *versus* temperature for (A) NPF resin and (B) sample cell without resin: β_1, β_2, dipolar relaxations; P_3, discharge caused by the cell; B-1, B-2, approximated zero current; I_{n1}, I_{n2}, related net current; I_0', initial zero current

EXPERIMENTAL

NPF resin was prepared by condensing phenol with formaldehyde at a mole ratio of 1:0.80 using oxalic acid as catalyst[18]. The $\bar{M}_n$ of the prepared batch determined by g.p.c. was 603. The procedure is described elsewhere[3]. As a standard, a mixture of 2,2'-, 2,4'- and 4,4'-dihydroxybiphenylmethane was used. T_g determined by d.s.c. was 334 K. The resin was melted between two silver-coated brass electrodes with diameter of 13.6 mm and separation of 1 mm. The samples were placed in a dark cell filled with dry nitrogen. The measurements were performed in the following way: polarization by an electric field $E_p = 20$ kV cm^{-1} at $T_p = 303$ K for 20 min, cooling to the storage temperature (T_0) under E_p (rate 2–3 K min^{-1}), relaxation at T_0 in the short-circuited state (s.c.s.) for 30 min and depolarization by heating (2 K min^{-1}). The measurements with partial polarization were modified in the following way: $E_p = 10$ kV cm^{-1} for 10 min, cooling to $T_p - 5$ K under E_p for ~5 min, cooling to T_0 and relaxation at T_0 in the s.c.s. for 30 min. For the lower-temperature peaks, T_0 was 127 K; and for the higher-temperature peaks, T_0 was 143 K. The current was measured by a Keithley 616 electrometer.

RESULTS AND DISCUSSION

T.s.d.c. measurements

Curve A in *Figure 1* represents the t.s.d.c. in the temperature range from 137 to 270 K. Curve B is the zero current obtained with the empty cell, without resin, polarized in the same way. Curve A consists of two peaks, labelled β_1 and β_2, and a group of small irreproducible peaks P_3. As P_3 also appears in curve B, it is not caused by the resin. P_3 is attributed to the discharge of the small Teflon spacers inserted in the sample holder[18]. In order to consider the net current caused by the β_1 and β_2 relaxations, the zero current has to be well defined and subtracted from curve A. The depolarization current B represents only a part of the total zero or parasitic current and cannot be used for simple subtraction. One can see that the so-called initial parasitic current $(I_0')^{20}$ is much smaller in curve B than in curve A. Curve B can only be used as an approximation of the zero line. Two possible approximations were applied. The first one was performed by the translation of B into the position B-1 to fit the end of curve A, giving the net current I_{n1}. The second approximation was the translation and small rotation of B into the position B-2 to fit the beginning of β_1 and the end of β_2, giving the net current I_{n2}.

The analysis of the depolarization current is given in *Figure 2*, showing the logarithm of the net current as a function of $10^3/T$. Curve A is related to I_{n1} while curve B is related to I_{n2} from *Figure 1*. In spite of the zero current, two straight lines corresponding to β_1 and β_2 peaks are obtained. According to this observation, it seems that two unique processes are in operation. The calculation of $E_a\beta_1$ and $E_a\beta_2$ by the initial-rise method gives uncertain results depending upon the approximation of the zero current. The results for E_a are shown in the inset in *Figure 2*.

Partial polarization

As shown in the previous section, the usual whole measurements can be used only as preliminary ones. The proper characterization of small and distributed peaks with a relatively high level of parasitic current has to be performed by partial analysis. The approximation of the zero line of the partial peaks can be realized with much more certainty[3].

Figure 3 shows the results of partial measurements. The temperature range from 145 to 210 K is covered by 12 elementary peaks. For practical reasons, each peak is represented by the maximum height (I_m) and by the half-width at $I_m/2$ (low-temperature side). Small arrows show the maximum of the β_1 and β_2 peak obtained in whole measurements. For determination of E_a for elementary peaks, instead of the initial-rise method, the Christodoulides[21] equation was used:

$$E_a = \frac{T_1 T_m}{7940(T_m - T_1)} - \frac{T_1}{14866} \qquad (4)$$

where T_1 is the temperature related to $I_m/2$ (low-temperature side) and T_m is the temperature of the peak

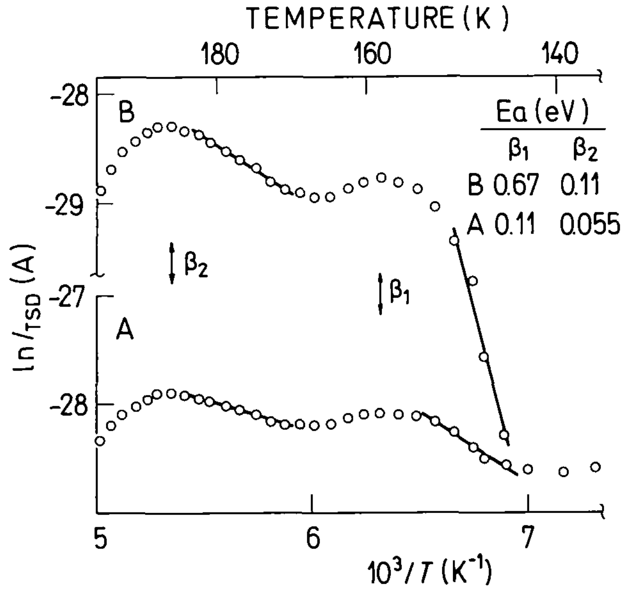

Figure 2 Plot of ln t.s.d.c. *versus* $10^3/T$: (A) related to I_{n1}; (B) related to I_{n2}. The arrows β_1 and β_2 correspond to the maximum current of the peaks in *Figure 1*; E_a is the activation energy

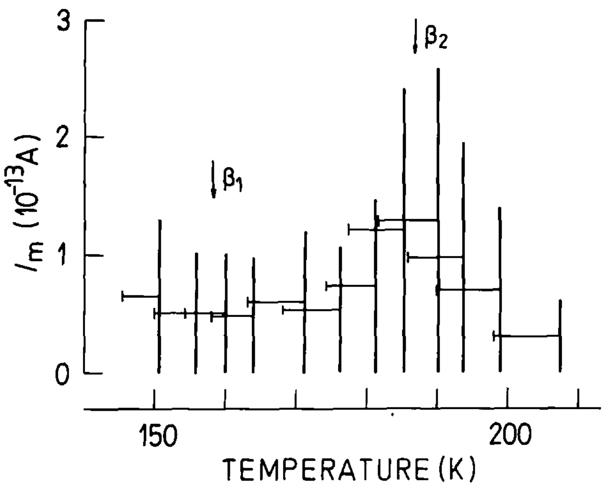

Figure 3 Parameters of peaks obtained by partial polarization. Horizontal lines show half-width at $I_m/2$ (low-temperature side)

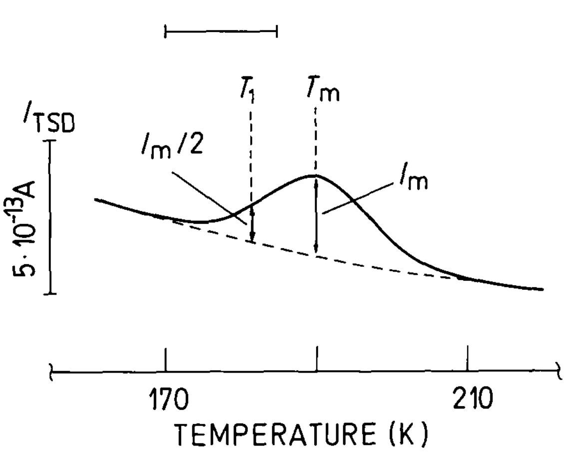

Figure 4 Plot of t.s.d.c. *versus* T, showing one of the elementary peaks obtained by partial polarization: I_m, maximum current; T_m, temperature of the peak maximum; T_1, temperature related to $I_m/2$. Horizontal line shows the temperature region of E_p application

maximum. This way of determining E_a is more accurate and more practicable, especially in the case of small peaks. One of the elementary peaks obtained by polarization in the 185–170 K range is shown in *Figure 4*. The recorded T_m of the peak is slightly shifted towards higher temperature in relation to the temperature of the applied polarization. This is because the polarization was performed at constant temperature, while T_m was recorded during the heating procedure[14]. The calculated E_a represents the mean value of E_a for the $T_m - T_1$ range. Taking into consideration that the peak is obtained in a relatively narrow temperature range, one may approximate E_a as a unique value for the entire elementary peak.

The results for E_a *versus* T_m of the elementary peaks are presented in *Figure 5*. The arrows show the T_m of the whole measurements. In the β_1 range, E_a increases slightly with T_m. The two next points at 171 and 176 K show a decrease of E_a. This is an indication of the low energy level at the beginning of the new process β_2. In spite of the dispersion of the results, it is possible to distinguish two temperature ranges in β_2. In the first one, E_a increases with temperature (the initial four points) until the maximum of β_2 is reached. Then E_a also increases with temperature, but the slope is reduced (the next four points). This agrees with the fact that in polymers the experimental dependence of E_a on T_m of partial t.s.d. is close to parabolic[22]. In order to allow further analysis, the dispersed E_a values are corrected to fit the most probable lines l_1 for β_1 as well as l_2 and l_3 for β_2 (*Table 1*).

The search for compensation phenomena

An attempt was made to analyse the partial peaks of β relaxation in NPF by drawing the relaxation map. Each of the Arrhenius lines was determined by two independent measurements. The results are shown in *Figure 6*. The upper points are related to T_m of the elementary peaks. The corresponding values for τ were obtained experimentally according to the equation:

$$\tau(T_m) = Q(T_m)/I_m \qquad (5)$$

where $\tau(T_m)$, $Q(T_m)$ and I_m are the relaxation time, residual charge and current at the temperature of the peak maximum, respectively. The slopes were determined by the corrected values of E_a. The first four lines related to β_1 are almost parallel. The group of lines from the initial range of β_2 show the compensation phenomenon. The final group of lines related to the saturated range of β_2 seem to be parallel as in the case of β_1.

A better insight into the results is obtained from the compensation diagram (*Figure 7*). The lines drawn according to equation (3) give all the necessary data about the compensation. The intercept is equal to ln τ_c, while the negative slope is equal to $1/kT_c$. Also, the projection onto the abscissa shows ΔE_a of the relaxation process.

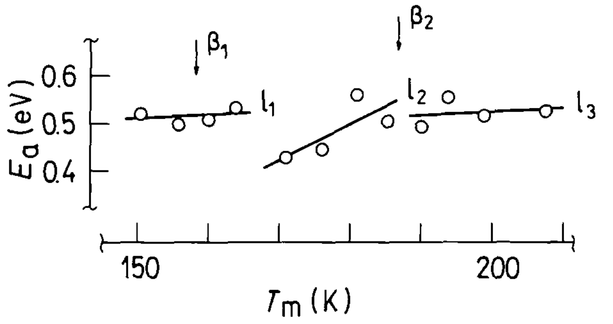

Figure 5 E_a *versus* T_m related to *Figure 3*: l_1, l_2 and l_3 are fitting lines

Table 1 Parameters of peaks obtained by partial polarization

Range	T_1 (K)	T_m (K)	E_a (eV) corrected	ln[$\tau(T_m)$ (s)]	ln[τ_0 (s)]
β_1	145	151	0.508	5.229	−33.900
	150	156	0.513	5.033	−33.154
	154	160	0.517	5.417	−32.009
	158	164	0.521	5.666	−31.190
β_2	163	171	0.430	5.209	−23.924
	168	176	0.468	5.334	−25.504
	174	181	0.505	5.716	−26.623
	177	185	0.537	5.529	−28.050
	182	190	0.517	5.550	−25.998
	186	194	0.520	5.623	−25.499
	190	199	0.524	5.456	−25.092
	198	208	0.529	5.703	−23.877

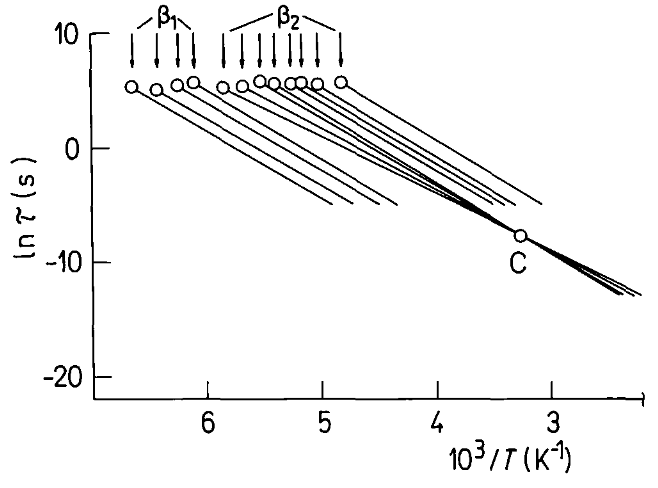

Figure 6 Relaxation map, ln τ *versus* $10^3/T$. C is the compensation point. Arrows correspond to T_m of the elementary peaks

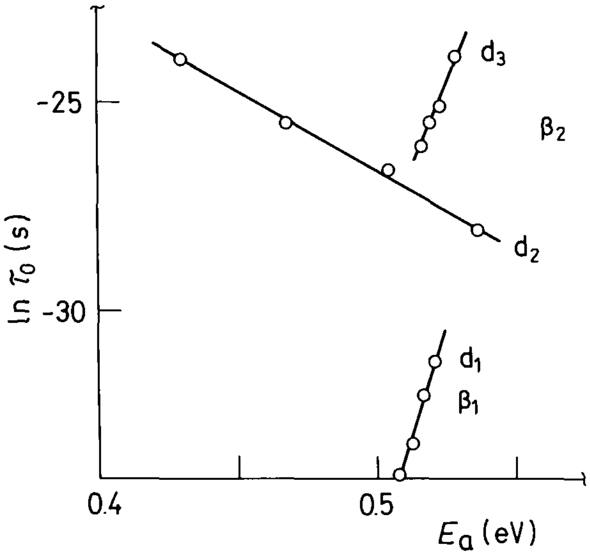

Figure 7 Compensation diagram, ln τ_0 *versus* E_a: d_1 is related to β_1; d_2 is related to initial part of β_2; d_3 is related to end part of β_2

The initial range of β_2, line d_2, obeys the compensation law with $T_c = 308$ K and $\tau_c = 4.26 \times 10^{-4}$ s. It is interesting that the points of β_1 and the saturated part of β_2 also fit the compensation lines d_1 and d_3. This means that convergence of the lines exists in the relaxation map but the compensation points are very far away. The calculated values of $10^3/T_c$ are smaller than zero, which is irrational. One can see that the convergence of the Arrhenius lines and the position of T_c depend on ΔE_a of the relaxation process. The higher is T_c, the lower is the convergence and thus ΔE_a. Therefore, the irrational result for T_c is an indication that the extremely narrow ΔE_a is in question. A narrow ΔE_a, however, is the characteristic of rigid systems[3,14].

The obtained definite T_c is relatively close to T_g, only 26 K below. The T_c obtained by the relaxation map usually appears at temperatures higher than T_g, and this was attributed to the kinetic aspect of the transition[8]. The shift of T_c should also be dependent upon the experimental conditions and the methods applied. Anyway the relaxation in question has to be put in context with the cooperative motions at T_g. The initial part of β_2 shows an undisturbed relaxation. However, as the motions increase, the interaction with the environment increases, too. As a result, a new inhibited balance occurs with significantly lower ΔE_a. In fact, β_2 is a micro start of the glass transition at some local level, which is being limited by the rigidity of the whole. As regards β_1 the experiments show only the inhibited part of the process with the narrow ΔE_a.

The relaxations described are caused by the motion of polar groups. Ionic migrations are excluded, as E_a is smaller than 0.6 eV[23]. The motion of OH requires only ~0.06 eV[7]. Therefore, the relaxations are supposed to be mainly caused by micro motions of the phenyl rings around the methylene links. Further research is in progress.

CONCLUSIONS

The t.s.d.c. curve obtained in the temperature range from 137 to 270 K showed two peaks at temperatures $T_m(\beta_1) = 158$ K and $T_m(\beta_2) = 187$ K. In preliminary analysis performed by plotting the logarithm of the current *versus* $10^3/T$, two straight lines indicated that two distinguishable and unique processes were in operation.

A better insight was obtained by partial polarization. The whole region was covered by 12 separate runs. Each of the obtained partial peaks was characterized by E_a and τ. The value of E_a was determined by the Christodoulides method, which gave the mean E_a for the $T_m - T_1$ range, where T_1 is the temperature at $I_m/2$ (low-temperature side), and τ was determined at T_m. This enables the relaxation map and the compensation diagram to be drawn. β_1 was considered in terms of partial peaks in the range from 151 to 164 K. The value $E_a\beta_1$ increased slightly with temperature. The mean value was 0.52 eV. $\Delta E_a\beta_1$ was very narrow and was equal to 0.013 eV. The corresponding Arrhenius lines were almost parallel, giving an irrational T_c very far away ($10^3/T_c < 0$). β_2 was considered in two parts. The initial range obeyed the compensation law with T_c at 308 K, 26 K below T_g. The end part showed a saturation in E_a *versus* T_m due to the interactions with the surrounding structure. T_c was very far away again. The mean E_a for all the partial peaks of β_2 was 0.51 eV.

The relaxations observed are dipolar by nature and could be caused by micro motions of the phenyl rings around the methylene bridges. Low convergence of the Arrhenius lines with irrational compensation points is the consequence of the inhibited motions and the extremely narrow ΔE_a.

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