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Original Scientific Paper

Compensation Phenomena in β Relaxation of Novolac Phenol-Formaldehyde Resin. Influence of Water

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A novolac phenol-formaldehyde resin was investigated by thermally stimulated depolarization current using the integral and partial measurements in the temperature range from 137 K to 270 K. Two broadened peaks assigned as β_1 and β_2 appeared at about 160 K and 190 K. The influence of water was investigated. The analysis of the activation energy, E_a *vs.* T, and the search for compensation phenomena were performed. Three different regions in relaxations were distinguished and the related compensation temperatures (T_c) were determined. Contamination with water increases the polarizability, decreases the structure differences and relieves the motions in resin. The influence of water was discussed in the terms of the shifts of T_c's. All the motions were attributed to the rotation of the phenyl rings with different surrounding structures.

INTRODUCTION

The characterization of novolac phenol-formaldehyde (NPF) resin by measurements of thermally stimulated depolarization currents (TSDC) was performed in 1978 and 1980.[1,2] The dipolar α relaxation at 320 K and the space charge ρ relaxation at 334 K were described in 1984.[3] The investigation of NPF by TSDC in a lower temperature range has been recently described.[4] The integral measurements showed two broadened peaks β_1 and β_2 with maximum current at 158 K and 187 K, respectively. The application of the

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partial polarization technique[5] in the range from 145 K to 210 K and the analysis of the relaxation map[6] made it possible to distinguish three groups of processes. Only one group was considered as a free relaxation with the compensation point, T_c close to the related glass transition temperature, T_g. Other groups showed the irrational T_c's ($10^3/T_c < 0$) and a very narrow width in activation energy, ΔE_a due to the inhibited motions. All the processes were supposed to be related to the motions of the phenyl rings around the methylene links. The investigation was performed with the resin of $\overline{M}_n = 603$. The samples were prepared, stored and measured under relatively dry conditions. Therefore, it was of interest to study the influence of water on the properties of the resin.

Hydrogen bonding in NPF with and without water molecules plays a significant role in forming the structure of novolacs.[7] Resin itself, without water forms non planar and coiled chains of novolac molecules due to the hydrogen bonding. The strength of hydrogen bonding increases with the interpolation of water. Therefore the novolac resin after drying at temperatures around 150 °C still contains appreciable amount of water even up to 2%. On the other hand, novolac resin in the powder form left in 100% of relative humidity at room temperature readily absorbs water with transformation in a viscous liquid phase.[8]

The aim of this work was to perform the TSDC measurements in β range of NPF resin on samples with different content of water.

EXPERIMENTAL

Novolac resin was prepared according to the general procedure.[9] The reactants were analytical grade with phenol to formaldehyde mole ratio 1 : 0.80, and oxalic acid 1% based on phenol charged.[4] Average molecular weight, $\overline{M}_n$ determined by GPC was 603, sample B. GPC was carried out as described elsewhere.[10,4] The resin was kept relatively dry in a desiccator over P_2O_5 unless otherwise stated. The resin was melted between the two silver coated brass electrodes with diameter of 13.6 mm and distance of 1 mm. The TSDC measurements were carried out in a dark cell filled with dry nitrogen. The polarization was performed by electric field, E_P = 20 kV/cm at temperature, T_P for 20 min. Partial polarization was performed by E_P = 10 kV/cm for 10 min at different T_P, cooling to $T_P - 5$ K under E_P for about 5 min and cooling to the storage temperature, T_o at 127 K in the short-circuited state. The heating rate was 2 K/min. Other details elsewhere.[4]

RESULTS AND DISCUSSION

Integral TSDC measurements

Integral TSDC measurements, sometimes called total or global, are the runs with prolonged polarization over the entire temperature range from T_P

to T_0. Such experiments were carried out on samples of NPF with different amounts of water in the range from 137 to 270 K. The curves with two broadened peaks β_1 and β_2 are shown in Figure 1. The small and nonreproducible peaks at the end of curves are caused by the discharge of teflon spacers in the sample cell. Curve B is related to the primary prepared batch of resin. The run was performed under relatively dry condition. Curve B' was obtained with the same resin but the cell for sample holding was, instead of dry nitrogen, filled up by air of about 60% of relative humidity at room temperature. For the curve B" the resin as the powder before melting was kept under 100% of relative humidity for 12 hours and the measurement

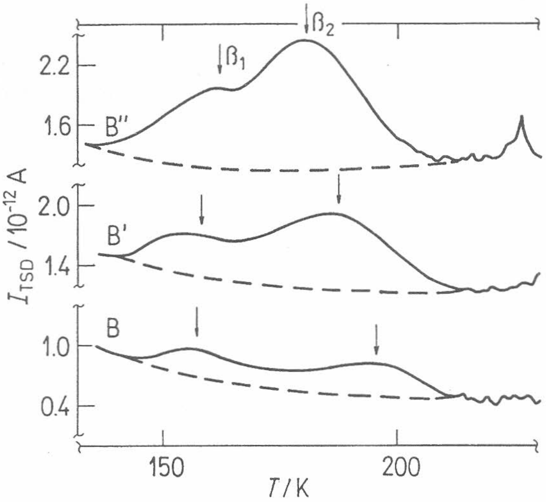

Figure 1. Thermally stimulated depolarization current I_{TSD} *vs.* T of samples with different content of water: (B) relatively dry, (B') exposed to 60% of relative humidity at 298 K, (B") exposed to 100% of humidity. E_p = 20 kV/cm, T_p = 303 K.

was performed in the cell with air as in the case for B'. The weight increase in B' due to the water absorption was about 0.4 wt% while in B" about 4 wt%. In order to consider the net depolarization current the parasitic zero current had to be approximated and subtracted from the total current. The zero current (dashed lines in Figure 1) was approximated by use of the runs with the polarized empty cell.[4] By comparison of the curves one can see that the water significantly influenced TSDC. Depolarization current increases with the increase of water content. The other effect is the shift of the peaks maxima. The effect seems to be related to a decrease of differences in the resin structure.

Partial polarization

A better way for characterization of the relaxation processes is the application of the partial polarization technique. The polarization field is applied within a narrow temperature window followed by short-circuit for isolation of a narrow relaxation part.[5] The results for samples with different amount of water are given in Figure 2. The vertical lines represent the maximum net current I_m, and the corresponding temperature T_m, of the elementary peaks obtained by the partial polarization. The results for resin sample B have been already published.[4] The comparison of results for B, B' and B'' show, that maximum peaks in the β_2 region (dashed arrows) significantly increase with the increase of the water content and shift towards the lower temperatures. The similar influence of water was observed in the solid amylose. The effect was attributed to the plasticizing action of the loosely bound water. The peak disappeared after dehydration.[11] However, it does not mean that the peak is caused by water molecules themselves but the hydrogen bonded water molecules increase the dipole moments of the moving parts in resin. In such a way the water acts as a marker which make the motions in resin easier to be observed.

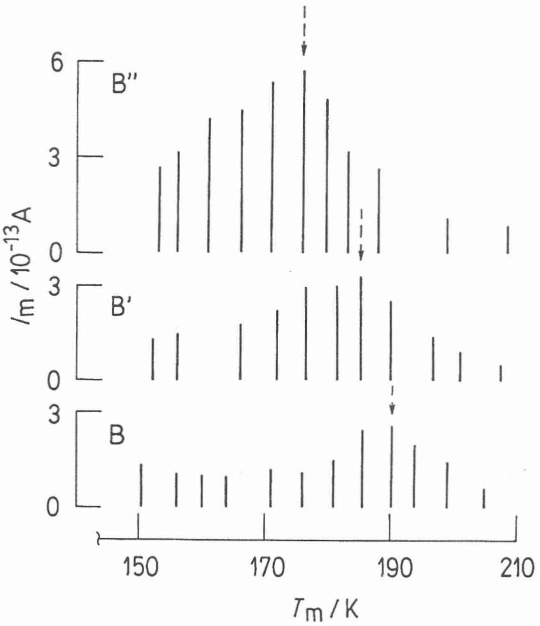

Figure 2. Parameters of the elementary peaks obtained by partial polarization for samples with different content of water. Dashed arrows are related to the maximum amplitude peaks in β_2 range. Symbols of samples as in Figure 1.

Figure 3 contains the results for the activation energy of the elementary peaks for samples B, B' and B". E_a was determined by the Christodoulides method[12] by use of the equation:

$$E_a = \frac{T_1 T_m}{7940\,(T_m - T_1)} - \frac{T_1}{14866} \tag{1}$$

where T_1 is the temperature related to $I_m/2$ (low temperature side) and T_m is the temperature of the peak maximum. It is considered that the Christodoulides method is more accurate and more practical especially for the small peaks, than the well known initial rise method. All the results for E_a were divided into three distinctive groups and presented by the most probably lines l_1, l_2 and l_3. The first group is related to the β_1 region, the second group is related to the initial part of β_2 and the third group corresponds to the final part of β_2. The dashed arrows show the points related to the maximum peaks. For further analysis and calculations the elementary values E_a will be corrected to fit the l_1, l_2 and l_3 lines. E_a in the β_1 range for resin B, as already described,[4] slightly increases with temperature. The difference between the maximum and the minimum E_a, ΔE_a was very narrow and equal to 0.013 eV. The mean energy, $\overline{E}_a$ for β_1 was 0.52 eV.

The change of E_a *vs.* T in the β_1 range for other samples is difficult to discuss due to the small number and high dispersion of points. However, one can say that ΔE_a for β_1 generally is very narrow. E_a in the starting and the final parts of β_2 increases with temperature for all the samples, but the slopes for l_3 in comparison with the slopes for l_2 are more or less reduced. The presence of water decrease the difference between the slopes. The comparison of $\overline{E}_a$ and ΔE_a for all the ranges and samples is given in Table I. The data are based to the corrected E_a's against the fitting lines. One can see that the differences between the $\overline{E}_a$ for β_1 and β_2 in all the cases are less than 0.1 eV. It supports a proposition that the both peaks are caused by the same motions, *e.g.* the rotation of the phenyl rings around the methylene links.[4]

TABLE I

Mean activation energy.
All the E_a values were obtained from the fitting lines.

Range		B		B'		B"	
		$\overline{E}_a$ / eV	ΔE_a / eV	$\overline{E}_a$ / eV	ΔE_a / eV	$\overline{E}_a$ / eV	ΔE_a / eV
β_1	l_1	0.515	0.013	0.473	0.004	0.449	0.025
β_2	l_2	0.485	0.107	0.502	0.064	0.487	0.087
	l_3	0.523	0.012	0.531	0.084	0.548	0.076

Compensation Phenomena

In order to study the compensation phenomena it is necessary to determine the Arrhenius line for each of the elementary peaks according the equation:

$$\ln \tau = \ln \tau_o + E_a/kT \tag{2}$$

where τ is the relaxation time, τ_o is the pre-exponential factor and k is the Boltzmann constant. The collection of Arrhenius lines called the relaxation map (RM) shows the relation between the relaxation behaviour of the elementary peaks. The compensation phenomenon is the case when the lines gather and converge to a point called the compensation point at the compensation temperature, T_c and compensation time, τ_c. The existence of several compensation points are due to the separate ordering of motion in the amorphous state.[13] For analysis whether or not a compensation exists the elementary parameters have to obey the so called compensation line relation:[14]

$$\ln \tau_o = -E_a \times (1/kT_c) + \ln \tau_c \tag{3}$$

$\ln \tau_o$ of an elementary peak can be calculated according to:

$$\ln \tau_o = \ln \tau(T_m) - E_a/kT_m \tag{4}$$

and

$$\tau(T_m) = Q(T_m)/I_m \tag{5}$$

where $\tau(T_m)$, $Q(T_m)$ and I_m are the relaxation time, residual charge and current at temperature of the elementary peak maximum. For E_a the corrected data fitting l_2 and l_3 lines are used. Knowing the values for $\ln \tau_o(E_a)$ it is possible to draw the points in Figure 4. One can see that the points completely fit the lines showing the existence of the compensation phenomena. The drawn lines d_2 are related to the initial parts of β_2 while d_3 is related to the final parts of β_2. The results for β_1 region are omitted due to the uncertainty of E_a for B' and B'' samples. The drawn lines give all the data about compensation. Intercept is equal to $\ln \tau_c$ while the negative slope is equal to $1/kT_c$. The abscissa projection shows ΔE_a of the related relaxation regions. In system with more than one compensation points the distance between the compensation lines and compensation points, show the differences between the regions, domains or phases[13] *i.e.* differences in structure. The calculated compensation parameters are listed in Table II.

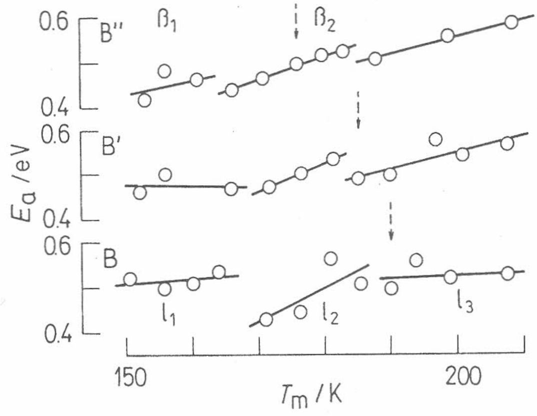

Figure 3. E_a *vs.* T_m for elementary peaks related to Figure 2: (l_1), (l_2) and (l_3) fitting lines.

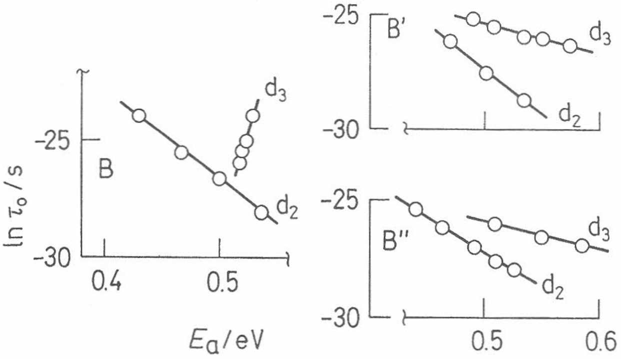

Figure 4. Compensation diagram ln τ *vs.* E_a for samples with different content of water: (d_2) related to initial part of β2, (d_3) related to final part of β2. Symbols of samples as in Figure 1.

TABLE II

Compensation parameters for resin with different amount of water

Range	B		B'		B''	
	T_c/K	τ_c/s	T_c/K	τ_c/s	T_c/K	τ_c/s
d_2	308	4.3×10^{-4}	298	3.7×10^{-4}	388	4.9×10^{-6}
d_3	–67[a]	5.1×10^{-5}	908	5.7×10^{-9}	975	2.2×10^{-9}

[a] Irrational result

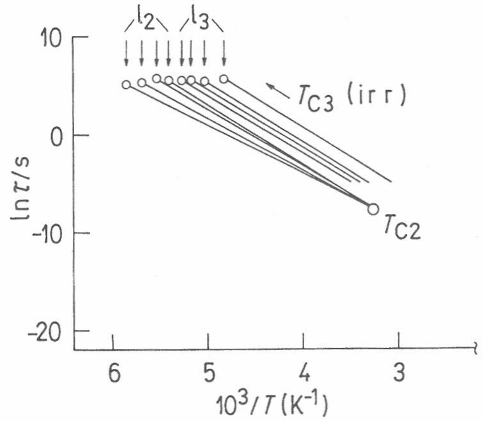

Figure 5. Relaxation map (RM), ln τ *vs.* $10^3/T$ for sample B. l's, temperature regions related to fitting lines in Figure 3; T_c's, compensation points. Vertical arrows show T_m of the elementary peaks. (irr) irrational.

In order to get a direct insight into the compensation phenomena the RM's are drawn in Figure 5, 6 and 7. According to the original Lacabanne method[6] the Arrhenius lines can be obtained by use of the τ(T) course for each of the elementary peaks. In our case the same lines were obtained by one point and a slope because of the available refined activation energy. The upper points are related to T_m and ln $\tau(T_m)$. The temperature regions are marked as the fitting lines in $E_a(T_m)$ function (Figure 3). The most charac-

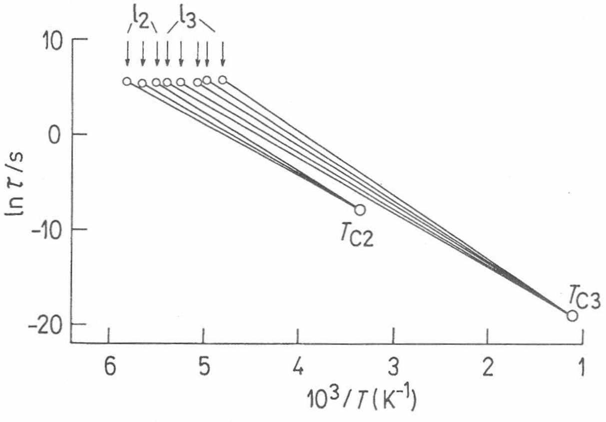

Figure 6. RM for sample B'.

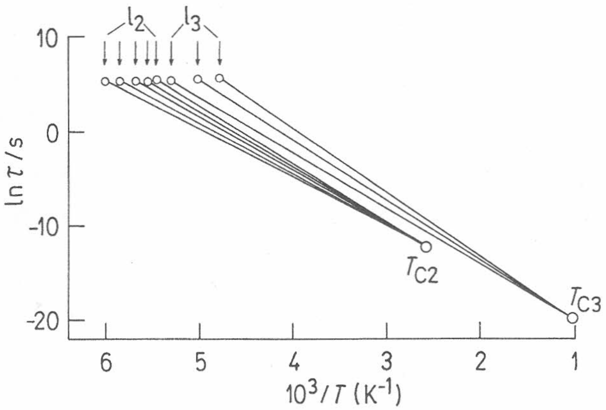

Figure 7. RM for sample B".

teristic for the resin is the compensation in the region l_2. The related T_{c2} for the so-called dry resin sample B is equal to 308 K. It is only 26 K below T_g[4] which is a good coincidence. The relaxation in this region with the tendency to achieve T_g is in fact a free relaxation and could be a micro start of the glass transition at some local level.[4] After a critical increase of motion, the balance occurred due to the interaction with the surrounded structure. Therefore, the free motion in the region l_2 turns into the inhibited motion l_3 with the irrational T_{c3}. Let us discuss the situation of samples B' and B" with addition of water. T_{c2} for B' and B" shows a shift in comparison to sample B up to 80 K for B" which means that the water influence is moderate. However, in the region l_3 the influence of water is significant. T_{c3} is shifted from the irrational –67 K for B to 908 K and 975 K for B' and B", respectively. Knowing that the irrational T_c is an indication of a rigid structure and process with extremely low ΔE_a one can suppose that the change from irrational to rational T_c is due to the changes in structure which become more flexible and more uniform. Another comparison of RM's for B' and B" shows that the distance between T_{c2} and T_{c3} decreases with the increase of water content but not adequately. The decrease is rather small in relation to the increase of water. It shows some kind of saturation in the water influence. As regards the values for T_{c3} in B' and B" they are too big and exceed the thermal stability of the usual polymers. Generally, a question arises about the position of the T_c's in comparison to T_g. That problem could be solved mathematically by introducing an additional activation energy in l_3 region which would move the T_c's at the level of T_g. The simulated energy in question could be an indication of the internal interference to molecular motions which occurred at the temperature of investigated relaxation.[15]

CONCLUSIONS

The analysis of NPF resin by integral and partial measurements in β temperature range from 137 K to 270 K shows two current peaks β_1 and β_2 with maxima at about 160 K and 190 K, respectively.

The presence of water increases the dipole moments of the moving parts and therefore increases the polarizability of resin. The maxima of peaks are shifted each to other. Analyzing the results for $E_a(T)$ and ln τ_o (E_a), based on the partial measurements, it is possible to distinguish three different relaxation regions. The first region related to β_1 peaks show a narrow ΔE_a due to the very inhibited motions. The second region related to the starting part of β_2 represents the relaxations with the T_c not very far from T_g with a moderate influence of water. The third region related to the final part of β_2 represents the relaxation steps very sensitive to the water content which relieve motions. $\overline{E}_a$ of all the regions for resin with different amount of water do not differ more than 0.1 eV. It is proposed that all the relaxations are caused by the unique motion of the phenyl rings around the methylene links with different surrounding structures.

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SAŽETAK

Kompenzacijske pojave u β relaksaciji novolačne fenol-formaldehidne smole. Utjecaj vode

Mladen Topić i Zvonimir Katović

Novolačna fenol-formaldehidna smola istraživana je metodom termalno stimulirane depolarizacije, integralno i parcijalno, u području od 137 K do 270 K. Dva proširena maksimuma β_1 i β_2 pojavljuju se na oko 160 K i 190 K. Obavljena je analiza raspodjele aktivacijske energije E_a, u odnosu na T. Ustanovljena su tri relaksacijska područja i određene temperature izjednačenja (kompenzacijske točke), T_c. Prisutnost vode povećava polarizabilnost, smanjuje razlike u strukturi i olakšava gibanja u smoli. Utjecaj vode razmatra se u svjetlu pomaka T_c. Sva uočena gibanja pripisana su rotaciji fenilnih prstenova do kojih dolazi u različitim strukturnim okruženjima.