Thermal depolarization effect in phenolic resin

Malti Goel, P. S. Viswanathan and Padma Vasudevan

Centre for Biomedical Engineering, Indian Institute of Technology, New Delhi 29, India

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Electrets were prepared by polarizing phenol formaldehyde resins in the semi-cured state. Thermal depolarization characteristics of electrets of varying thickness prepared under different polarizing field, temperature and curing conditions, were studied. D.c. conductance measurements were made as a function of temperature. The activation energies (E_a) for depolarization and conductance are reported.

INTRODUCTION

Electrets are finding increasing application in several fields of technology[1]. While electret formation in many of the common thermoplastic materials has been reported, little work is available on thermosets[2,3] such as the phenolics. Since phenol–formaldehyde resins are widely used as insulating and binding materials, in particular in the electrical industry, and are known to have a good thermal stability, it was considered of interest to study electret formation in the materials.

Jux and North[3] in their work essentially on phenol–formaldehyde resin–paper laminates, reported the possibility of polarization of pure resin as well as laminates at low fields (1.7 kV/m). Warfield[4] studied the resistivity of phenolics as a function of temperature and also for several other resins as a function of the extent of curing[5] and found that resistivity (ρ) increases with duration of curing and reaches a constant maximum value in the completely cured state. Considering that the resistivity of completely cured phenolics at 298K can be as high as 10^{26} ohm cm, it was decided to polarize the samples in the semi-cured state and to study the depolarization under different conditions.

EXPERIMENTAL

Phenol formaldehyde resins were prepared by standard methods. 9.4 g of distilled phenol and 12.3 g of 37% formaldehyde (1 mol phenol:1.5 mol HCHO) were refluxed in the presence of 0.12 g of NaOH for 1.5 h to form a viscous prepolymer. This was poured into a square-shaped mica cavity on an aluminium electrode and cured at 347–349K in an oven for 12–24 h. Thus sandwiched between two aluminium electrodes, the resin filled the cavity of known dimensions (0.01 x 0.01 m^2). Sample thickness was measured using a micrometer screw.

The resistivity (ρ) of semi-cured unpolarized samples was measured at 298K to check the extent of curing. The samples chosen for polarization had ρ values in the range of 10^8–10^{10} ohm cm at 298K. Also, the resistance (R) of some unpolarized samples was determined as a function of temperature at an applied field of the order of 100–200 kV/m.

Freshly prepared samples were polarized at 329, 339 and 349K in a specially designed oven at field strengths of 50–150 kV/m for 1 h. Without removing the voltage source, the sample was cooled to room temperature in ~1 h. Thereafter the voltage source was disconnected and the sample was heated at a uniformly linear rate (~4K/min) and the depolarization current was measured as a function of time and temperature.

RESULTS

Figure 1 represents depolarization current (t.s.d.) as a function of temperature for samples polarized at 100 kV/m at different polarizing temperatures (329, 339 and 349K). The current $i_{\max}$ at the peak temperature, and hence the amount of stored charge (q), increases with polarizing temperature for a constant field of polarization. Also $T_{\max}$ shifts from 383 to 431K on increasing the temperature from 329 to 349K.

Figure 2 is a t.s.d. plot of samples polarized at 349K and at different fields (50, 100, and 130 kV/m). The sample polarized at 130 kV/m had a thickness of 2.2 x 10^{-3} m while those polarized at 50 and 100 kV/m had a thickness of approximately 1.7 x 10^{-3} m. There is an increase in the depolarization current with increase of polarizing field. At lower fields (50 kV/m) there is only one 'depolarization peak' while at higher fields there is a tendency towards formation of an additional peak below 383K.

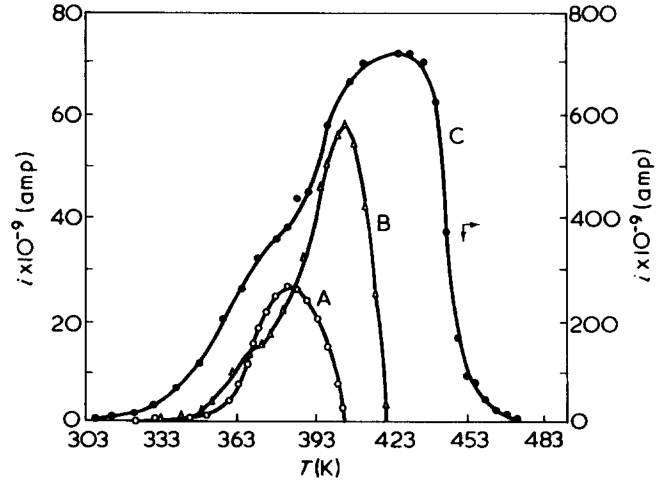

Figure 1 Effect of temperature on the 'depolarization peak' of samples polarized with 100 kV/m: A, 329K; B, 339K; C, 349K

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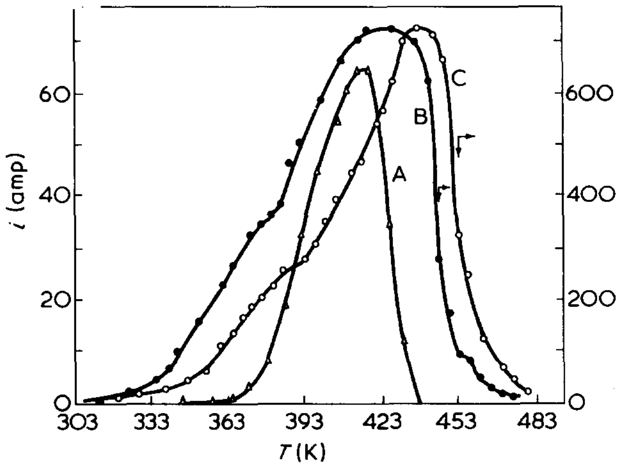

Figure 2 Effect of polarizing field on the 'depolarization peaks' of samples polarized at 349K: A, 50; B, 100; C, 130 kV/m

Figure 3 gives t.s.d. plots of samples of varying thickness (1.0×10^{-3}, 1.7×10^{-3}, 3.0×10^{-3} m) polarized at 50 kV/m and 349K. It was observed that i_{max} values decrease with increase in thickness.

Activation energy E_a has been calculated from the semi-logarithmic plots of current (i) in the initial rise of the 'depolarization peak' *versus* $1/T$. The E_a values vary slightly from sample to sample and are in the range 60 ± 10 kJ/mol (see *Table 1*).

Resistance, R, of the unpolarized samples (which were cured for 24 h) was also measured as a function of temperature. From the plots of log R *versus* $1/T$, the average activation energy for 6 samples was in the range of 80–90 kJ/mol.

DISCUSSION

Effect of curing on resistance

Fully cured phenolics are expected[4] to have ρ of the order of 10^{26} ohm cm. Warfield[5] showed that resistance can be correlated with the extent of curing; his plot of ρ *versus* $1/T$ for fully cured samples[4] indicated a transition at 398K with a reduced slope above this temperature.

We have deliberately used semi-cured samples ($\rho_{298} = 10^8$–10^{10} ohm cm) because fully cured samples could not be polarized within 1 h at low fields. For these samples the plots of log R *versus* $1/T$ are linear but no secondary transition at 398K could be observed. Probably this transition is characteristic of the highly crosslinked solids. E_a (80–90 kJ/mol) for these samples is about 3 times less than the value of 280 kJ/mol reported by Warfield for fully cured samples. Further, according to Warfield[5], the E_a values vary linearly with log ρ and, reading from this plot, a resin with resistivity of the order of 10^8–10^{10} ohm cm would have E_a 40–80 kJ/mol. Our experimental values are in agreement with this, and with those of Jux *et al.*[3]. The latter reported that E_a above 314K is 60 ± 20 kJ/mol but increases to 120 ± 20 kJ/mol below this temperature.

Effect of conditions of polarization on t.s.d.

The observed increase of i_{max} and the total charge stored, with increase of polarizing temperature as well as polarizing field (*Figures 1* and *2*) may be due to the increased mobilities of the carriers. This has also been noted for other polymers[6]. Slightly lower values of i_{max} for the sample represented by plot C in *Figure 2* may be attributed to the variation in sample thickness. As shown in *Figure 3*, i_{max} tends to decrease with increasing thickness, probably due to decrease of the net heterocharge at the surface.

Mechanisms of depolarization

Considering only the internal polarization, two of the mechanisms which are likely to be operative in the depolarization process are the relaxation of the polar groups and ionic space charge polarization. In the phenolics the relaxing dipoles are the phenolic –OH groups; there is also the possibility of the group being ionized to give H^+ and the phenolate ion. Jux *et al.*[3] reported the existence of two major relaxation processes. From their data the 'short time' process, which was independent of electrode nature and charging field, was attributed to the rotational orientation of the hydroxyl groups. Relaxation time would vary depending on the molecular environment. The 'long time' process was attributed to space charge effects arising from ionic rather than electronic charge carriers.

Our experimental data is in general agreement with the relaxation mechanisms suggested above. At low fields the peaks due to these two processes are overlapping, while at higher fields there is a tendency for separation. The E_a above 314K is 60 ± 10 kJ/mol from the initial rise method (*Table 1*).

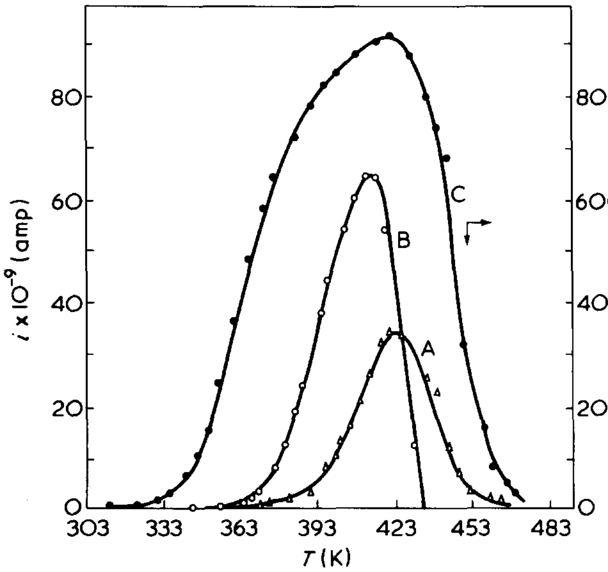

Figure 3 Effect of thickness on the 'depolarization peak' of samples polarized at 50 kV/m: A, 2.96×10^{-3}; B, 1.71×10^{-3}; C, 1.00×10^{-3} m

Table 1 Calculation of E_a values by different methods

	E_a (kJ/mol)		
Sample No.	Initial rise method ± 10 kJ/mol	First order kinetics	Second order kinetics
1	45	–	–
2	50	70	90
3	70	60	53
4	60	–	–
5	65	110	120
6	55	60	–

Kinetics of relaxation

The temperature dependence of t.s.d. cement $i(T)$, for a first order relaxation process may be expressed[8] as:

$$i(T) = -\frac{\mathrm{d}q}{\mathrm{d}t} = \omega(q - q_0) \qquad (1)$$

$$\frac{1}{\omega} = \Gamma(\tau) = \frac{\int_{t'(T)}^{\infty} i(t')\mathrm{d}t}{i(t)} \qquad (2)$$

where Γ is the dipole relaxation time.

For ionic migration (as in the case of the CaF_2 system) ω can be taken as:

$$\omega = 4\pi\sigma/\epsilon$$

where σ is the specific conductance and ϵ is the dielectric constant. However, this relationship generally does not hold for polymeric systems with conductivities in this regime. Nevertheless, it may be used as an approximation in order to show in a qualitative way the relationship between polarization and conductivity. Plots of log Γ *versus* $1/T$ would also give E_a, and the values are compiled in *Table 1.*

If the depolarization phenomenon follows second order kinetics, then:

$$i(T) = -\frac{\mathrm{d}q}{\mathrm{d}t} = \omega(q - q_0)^2 \qquad (3)$$

$$\omega = i(T)\left[\int_{t'(T)}^{\alpha} i(t')\mathrm{d}t\right]^{-2} \qquad (4)$$

ω is obtained by graphical integration of the thermal current spectrum and log ω is plotted against $1/T$. We observe that these plots are also linear. Thus with the present set of data it is difficult to decide on the order of the depolarization kinetics.

CONCLUSIONS

Electrets can be formed from thermosetting polymers such as phenolic resins, even at low fields, provided the polarization is carried out in the semi-cured state.

At least two relaxation processes, namely space charge and dipolar relaxations, seem to be operative in the case of phenolic resins.

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