

Thermally Stimulated Depolarization Current Studies on PC/PTBF Blends

A. K. KALKAR,^{1,*} SHANKAR KUNDAGOL,¹ SURESH CHAND,² and SUBHAS CHANDRA²

¹Physics Division, Department of Chemical Technology, University of Bombay, Matunga, Bombay 400 019, India, and
²National Physical Laboratory, New Delhi 110 012, India

SYNOPSIS

Thermally stimulated depolarization current (TSDC) studies have been carried out on blends of polycarbonate (PC) and poly (*p*-*t*-butyl phenolformaldehyde) (PTBF) using electric poling at temperatures ranging from 348°K to 383°K. The PC/PTBF blends poled at identical electric field (E_p) and temperature (T_p) exhibit a continuous distribution of polarizability (in general, in the range 300°K to 450°K) with a blend composition dependent single peak (T_M). With increasing E_p and T_p , the TSDC peak of a blend shifts toward higher temperature with increasing peak current (I_M) and charge (Q) associated with the peak. The effects of polarization field and temperature indicate that the polarization in the blend system is due to induced dipole formation. The activation energy decreases with increasing PTBF content in the blend, indicating shallow traps in PC/PTBF electret. The present blend electrets, however, comparative to its two components PC and PTBF, store more charge but decay faster. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Phenol formaldehyde class of resins are important thermosetting materials. Due to their polarizable —OH groups, the electrets of such resins are of interest. Few studies of dielectric properties of these resins have been reported.¹⁻³ The early work¹ concludes that the dielectric properties of these materials, apart from the molecular structure, very much depend on the materials in which these are reinforced. Often, the specified electrical properties of such reinforced electrical insulating sheets are altered, or deteriorate due to nonprotection of resin from humidity and environmental temperature fluctuations. Therefore, an investigation of electret properties of protective reinforced resins will be interesting and useful. This may be achieved by blending a dielectric resin with an engineering plastic. Such a blending will be effective in controlling the polarization and charge-storage ability by adjusting the weight proportions of the two compo-

nents in the blend. Such electrets probably may be comparatively more stable.

Polycarbonate (PC), an engineering plastic, is known for its toughness and moisture resistance. PC has a glass transition temperature (T_g) at $418 \pm 2^\circ\text{K}$. It is assumed that the blending of electret forming resin with PC may yield a stable family electret.

With this in view, a systematic study to understand electret formation mechanisms in PC/poly (*p*-*t*-butyl phenolformaldehyde) (PC/PTBF) blends have been undertaken using thermally stimulated depolarization current (TSDC) technique. This technique has been successfully explored to understand the mechanisms of formation, distribution, and decay of charges in polymers^{4,5} and polymer blends.⁶⁻¹¹ The present paper discusses the electret formation mechanisms in polyblends of PC and PTBF.

Our earlier study¹² has shown that PC/PTBF blends belong to the crystalline/compatible class. The system is miscible in the larger bulk amorphous phase at all compositions with low order induced PC crystallization. In the range -150° to $+55^\circ\text{C}$, the PC/PTBF blend system with low PTBF content

* To whom correspondence should be addressed.

exhibits better dynamic response, indicating improved mechanical properties to PC.

EXPERIMENTAL

PC (molecular weight 40,000) was obtained from General Electric Company. Poly(p-tertiary butyl phenolformaldehyde) (PTBF) was synthesized in the Plastic Division of this department. The molecular weight was evaluated using vapor pressure. Osmometry was 1,500–1,600; T_g was $324 \pm 2^\circ\text{K}$.

Optically clear blend films of thickness $60 \mu\text{m}$ were prepared by blending PC and PTBF in different weight proportions by solution casting technique using methylene dichloride as a solvent. The solution thus prepared was then poured onto a thoroughly cleaned, optically planed glass plate which was floating on mercury. Evaporation of the solvent was carried out at room temperature for 12 h. To remove all traces of solvent, the films were vacuum-dried (10^{-3} torr) for another 12 h and then annealed at a temperature 5°K less than its T_g for 30 min.¹² Films with different PC/PTBF blend proportions (90 : 10), (80 : 20), (70 : 30), (60 : 40), and (50 : 50) were prepared and are designated as B1, B2, B3, B4, and B5, respectively. The films with $> 50\%$ of PTBF content are highly brittle and difficult to handle.

Vacuum-deposited (10^{-3} torr) electrodes were deposited with suitable masks on the blend films, to form a metal-polymer-metal sandwich structure by thermal evaporation of spectroscopically pure aluminium. The configuration of top and bottom electrodes gave a square sandwich structure of 1 cm^2 crossover area. Further contacts were made by bonding copper leads to the metal films by means of air-drying type silver paint.

Thermoelectrets were prepared by employing time-temperature and time-field schemes. The sample was heated to an elevated temperature (T_p), usually $< T_g$, by which permanent dipoles and free charges were mobilized. When the constant temperature was achieved, say, at time t_1 , the electric field (E_p) was applied, which causes an alignment of the permanent dipoles and a drift of free charges towards the electrodes. After a certain time, say, at t_2 , while the poling field (E_p) is still on, the charge sample was cooled down to room temperature (T_r), up to time t_3 , by which time most of the permanent dipoles and charges were frozen. After switching off the field (E_p) at time t_3 , most of the charge stored at T_p was retained. Thus, the charging process was completed in time t_p (which was from time t_1 to t_3). To eliminate the accumulated electric charges

caused by the applied field during polarization, the electrodes were short-circuited for 30 min.

The TSD current was monitored as a function of temperature with a Keithley electrometer (Keithley model 610C) by heating the sample at a constant heating rate of 0.33°K/s , which ensured a high resolution of the spectra. The temperature of the sample was measured with a calibrated copper-constantan thermocouple. Various characteristic TSDC thermograms were obtained for the blends and the two individual polymers.

RESULTS AND DISCUSSION

Although the charge-storage and its relaxation studies in PC and PTBF have been reported extensively in the literature,^{1-3,13-20} we preferred to characterize our samples for their charge storage behavior using TSDC technique. The analysis of these results is also reported here; this facilitate comparative studies in PC/PTBF blends.

Figures 1 and 2 show the TSDC spectra of pure PTBF for various E_p and T_p , respectively. The two peaks at temperatures around 322°K and 336°K are observed. The peak current associated with 322°K

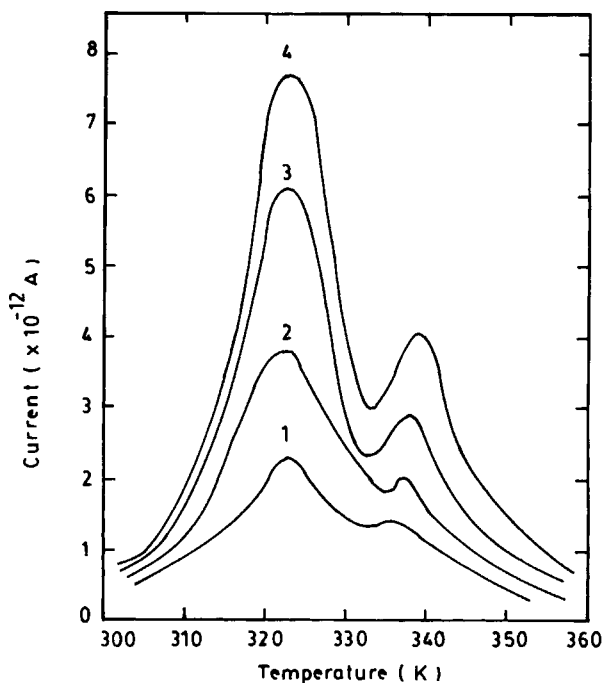


Figure 1 TSD spectra of PTBF films poled at $T_p = 323^\circ\text{K}$ for $t_p = 3.0 \times 10^3$ s with different poling fields (E_p); curves 1-4 correspond to $E_p = 1.7 \times 10^4$, 3.3×10^4 , 5.8×10^4 , and 7.5×10^4 V/cm, respectively.

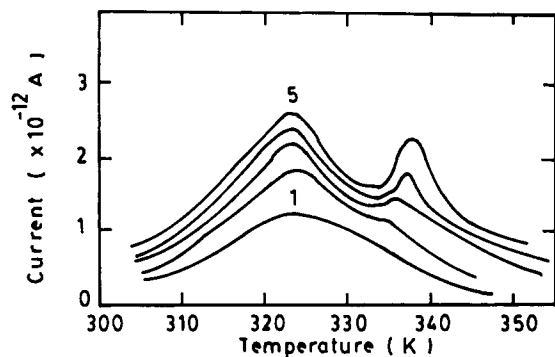


Figure 2 TSD spectra of PTBF films poled at $E_p = 1.7 \times 10^4$ V/cm for $t_p = 3.0 \times 10^3$ s with different poling temperatures (T_p); curves 1-5 correspond to T_p of 303, 313, 323, 328, and 333°K, respectively.

shows a linear dependence on E_p , but is independent of poling temperature T_p . This is attributed to the consequence of the dipole relaxation. The other peak at 336°K, however, with increasing both E_p and T_p , shifts toward higher temperature with an enhancement in T_M and Q . This suggests that the 336°K peak originates due to the discharge of the traps in the bulk material. These observed results are in agreement with an earlier reported work.¹⁹

TSDC spectra of pure PC films (Figs. 3 and 4) show two well-resolved peaks centered around 350°K and 420°K, with 0.62 eV and 1.10 eV activation energies, respectively. It is observed that the magnitude of current maxima, I_M , and charge associated, Q , with 350 K peak increases linearly with

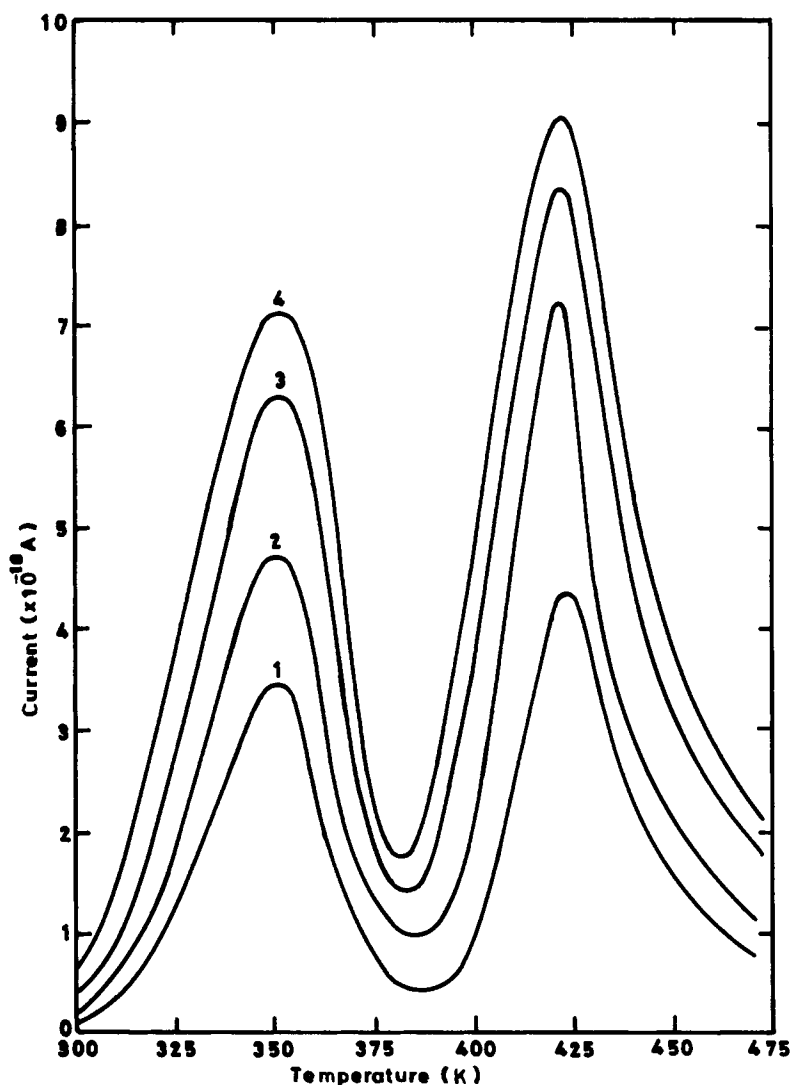


Figure 3 TSD spectra of PC films poled at $T_p = 323^\circ\text{K}$ for $t_p = 3.0 \times 10^3$ s with different poling fields (E_p); curves 1-4 correspond to $E_p = 1.7 \times 10^4$, 3.3×10^4 , 5.8×10^4 , and 7.5×10^4 V/cm, respectively.

increase in E_p , whereas for 420°K peak it increases nonlinearly. However, with increasing poling temperature, T_p , both peaks shift toward higher temperature. The magnitude of current maxima as well as charge for both peaks increases with an increase in T_p . It is also observed that with increasing poling time, t_p , both peaks shift to higher temperature with enhanced peak current and charge associated with them.

These observations and their analysis indicate that the 350 K peak originates due to the depolarization of aligned dipoles of the PC main chain,²¹ whereas the 420°K peak may be due to the detrapping of charge carriers.^{5,22} However, for both peaks,

there exists a distribution of relaxation times and activation energies.^{21,23}

TSD spectra of blends B1, B2, B3, B4, and B5 polarized with $E_p = 5.0 \times 10^4$ V/cm at $T_p = 348^\circ\text{K}$ for $t_p = 3.6 \times 10^3$ sec are shown in Figure 5.

It is interesting to note that the TSD spectra of the blends differ significantly from that of PC and PTBF. Composition-dependent single peak in the temperature range 403–377°K has been observed in each case. It is observed that with increasing PTBF content in the blend, the peak temperature T_M shifts toward lower temperature. The I_M and Q associated with the peak increases with increasing PTBF content.

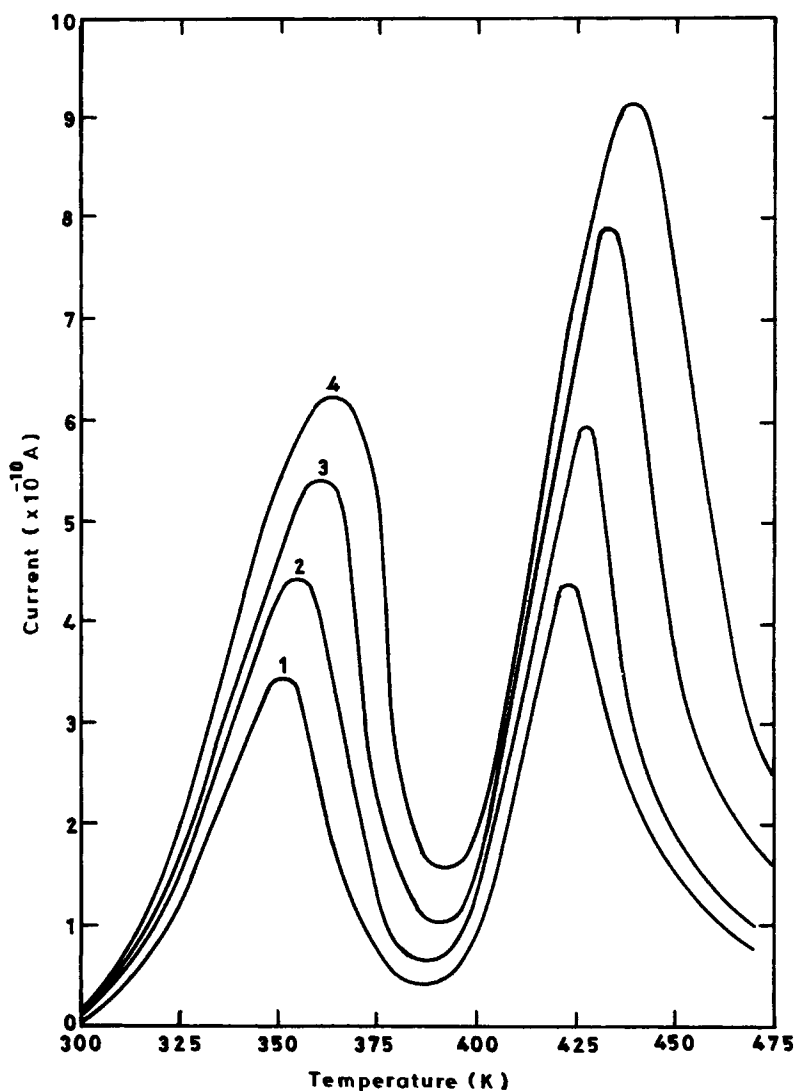


Figure 4 TSD spectra of PC films poled at $E_p = 1.7 \times 10^4$ V/cm for $t_p = 3.0 \times 10^3$ s with different poling temperatures (T_p); curves 1–4 correspond to T_p of 323, 343, 363, and 393°K, respectively.

The polarizing field dependent TSD spectra of blends B1, B2, B3, B4, and B5 polarized with field varying from 5.0×10^4 V/cm to 1.0×10^5 V/cm at $T_p = 348^\circ\text{K}$ for $t_p = 3.6 \times 10^3$ s have been recorded. The representative spectral curves for blends B1 and B5 are reproduced in Figure 6. The single peak centered around 403°K has been observed in each case. Both I_M and Q associated with the peak increase linearly with an increase in polarizing field (Fig. 7). The activation energy for each curve of Figure 1 has been evaluated by applying the initial rise method of Garlick and Gibson.²⁴ Semilogarithmic plots of $\log I$ versus I/T (Fig. 8) give a straight line whose slope gives the value of activation energy, which, in

the present case, decreases with increasing PTBF content in the blend. The relaxation time parameters such as τ_0 (relaxation time at infinite time at infinite temperature), τ_M (relaxation time for maximum current), and τ_{300} (relaxation time at room temperature) have been evaluated using these values of activation energy, and are summarized in Table I.

The typical TSD spectra of blends B1, B2, B3, B4, and B5 polarized at a constant field of 5.0×10^4 V/cm for $t_p = 3.6 \times 10^3$ s, but with varying poling temperatures ranging from 348°K to 383°K , have been recorded. The typical TSD curves for B1 and B5 are reproduced in Figure 9. It is seen that in each case, a single peak has been observed which shifts

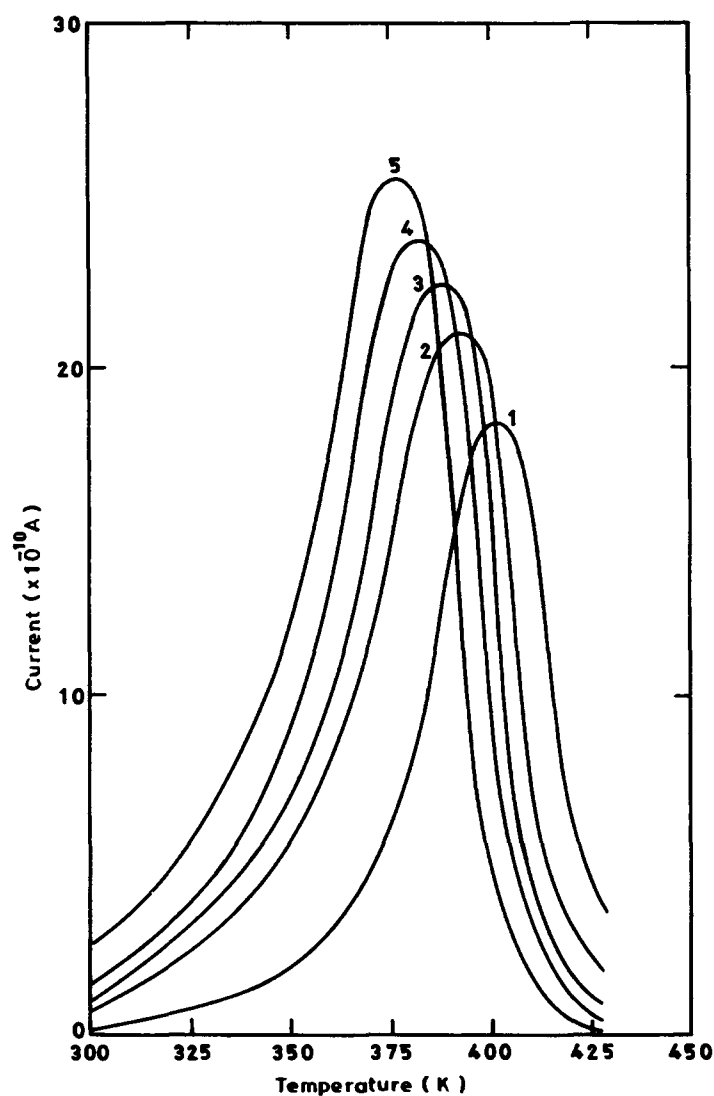


Figure 5 TSD spectra of PC/PTBF blend film polarized at $E_p = 5.0 \times 10^4$ V/cm, $T_p = 348^\circ\text{K}$, and $t_p = 3.6 \times 10^3$ s; curves 1-5 correspond to blends B1, B2, B3, B4, and B5, respectively.

toward higher temperatures with an increase in T_p . Both I_M and Q associated with the peak increase with the increase in T_p .

Dipole orientation and trapping of charge carriers generated in the bulk as well as injected from the electrodes are the mechanisms responsible for electret formation. The trapping of charges can take place at various trapping sites—surface states of the polymer, polymer interfaces, chain foldings, and molecular disorder.^{4,5}

TSD spectra of PC/PTBF blends polarized under the identical conditions of $E_p = 5.0 \times 10^4$ V/cm, $T_p = 348^\circ\text{K}$, and $t_p = 3.6 \times 10^3$ s but for different weight proportion of PTBF are shown in Figure 5. As mentioned earlier, the peak temperature, T_M , of blends shifts toward lower temperature with increasing PTBF content in the blend. It is well-established from our earlier work¹² that the low molecular weight PTBF acts as a plasticizer in PC/PTBF

blends. This creates enhanced free volume which subsequently results in a decrement in trapping sites. Apart from this, PTBF also induces low-order crystallization in PC in blends.¹² This introduces interphase boundaries in the bulk amorphous blend materials, creating additional trapping sites. However, competitively, the former dominates the latter; thus, T_M shifts toward the lower temperature side.

Field dependent TSD spectra of blends (Fig. 6) exhibits that peak current I_M shows a linear dependence of E_p (Fig. 7), but peak temperature T_M was almost unaffected by E_p . The linear dependence of I_M on E_p is suggestive of dipolar polarization.⁵ It seems that during polarization, the charge carriers get trapped in the trapping sites, which subsequently lead to formation of induced dipoles of PC and PTBF, the two strong polar components of the blend. In addition to these dipoles, the interaction of PC and PTBF through attractive electrostatic

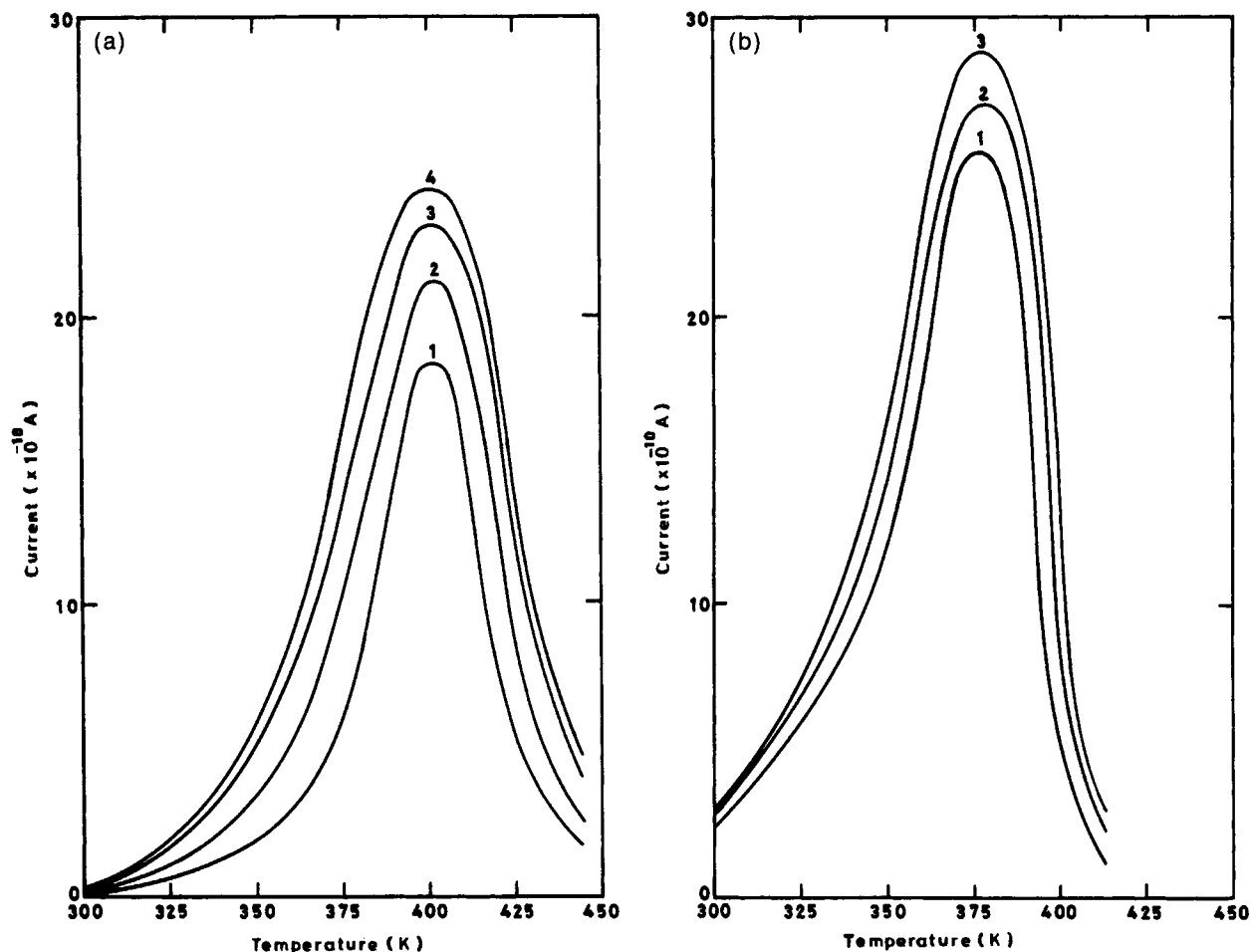


Figure 6 Effect of E_p on TSD spectra of (a) B1 and (b) B5 polarized at $T_p = 348^\circ\text{K}$ for $t_p = 3.6 \times 10^3$ s; curves (a) 1-4 and (b) 1-3 correspond to E_p of 5.0×10^4 , 6.7×10^4 , 8.3×10^4 , and 9.2×10^4 V/cm, respectively.

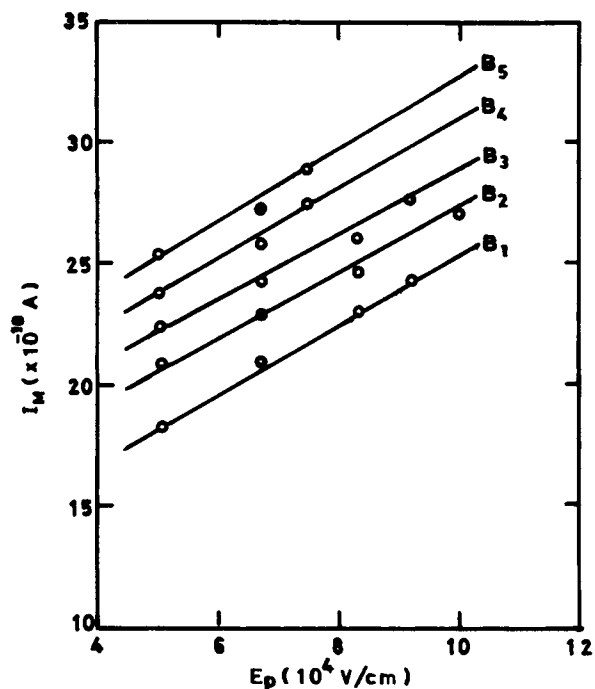


Figure 7 Plots of I_M vs. E_p for B1, B2, B3, B4, and B5 blends.

forces leads to the formation of ionic dipoles ($\text{OH} + \text{CO} \rightarrow \text{OH}^+ \text{CO}^-$) held together by electrostatic forces. These dipoles in the blends become oriented with the field. Moreover, the values of activation energy for blends (Table I) are much higher than what is expected for the local disorientation of PC side-chains.²⁵

From the TSDC thermograms, it is evident that however the charge stored in the blend electret increases with increasing PTBF content, the charge decay is faster. The observed peak in the present blend system is broad, which indicates the trapping of dipole-charge carriers in trapping centers distributed over a wide energy range with trap depths ranging from 0.35 eV to 0.71 eV. The effective mo-

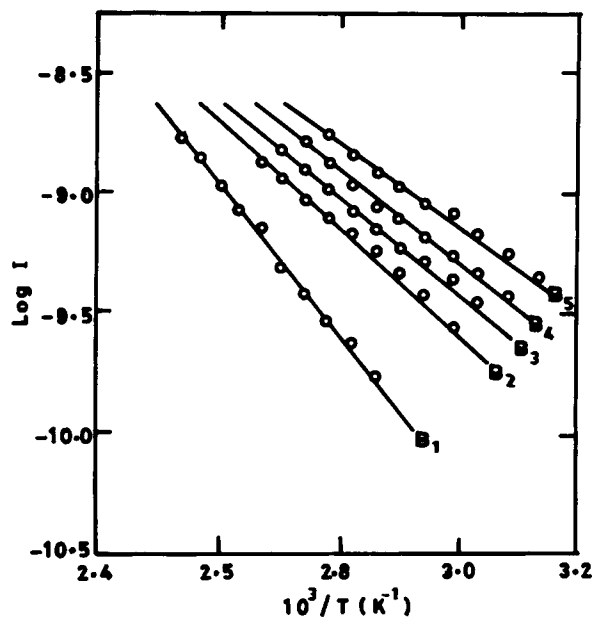


Figure 8 Plots of $\log I$ vs. $\frac{1}{T}$ for B1, B2, B3, B4, and B5 blends.

bility of carrier transport is by progressive composition-dependent created shallow traps in blends, resulting in the fast decay.

CONCLUSIONS

Blending seems to be effective in controlling the polarization and charge storage phenomena by adjusting the weight proportions of the two polymers in polymer electrets.

In a PC/PTBF blend, the TSDC peak shifts toward higher temperatures with increasing poling field (E_p) and poling temperature (T_p). The magnitude of the charge associated with the TSDC peak increases with the increase in E_p and T_p . However,

Table I Depolarization Kinetics Data Calculated by the Initial Rise Method for PC-PTBF Blend Films of Thickness 60 μm Polarized at $E_p = 5.0 \times 10^4$ V/cm, $T_p = 348^\circ\text{K}$, and $t_p = 3.6 \times 10^3$

Blend (Fig. 1)	T_M ($^\circ\text{K}$)	I_M ($\times 10^{-9}$ A)	Q ($\times 10^{-7}$ C)	E (eV)	τ_0 (s)	τ_M ($\times 10$ s)	τ_{300} (s)	T_g ($^\circ\text{K}$)
B1	403	1.82	5.72	0.71	7.94×10^{-8}	5.97	6.67×10^4	387
B2	394	2.09	7.96	0.46	1.11×10^{-4}	8.77	5.8×10^3	377
B3	389	2.22	8.34	0.42	3.42×10^{-4}	9.40	3.87×10^3	373
B4	383	2.37	8.96	0.40	5.24×10^{-4}	9.54	2.73×10^3	371
B5	377	2.55	9.72	0.35	2.20×10^{-3}	10.61	1.66×10^3	362

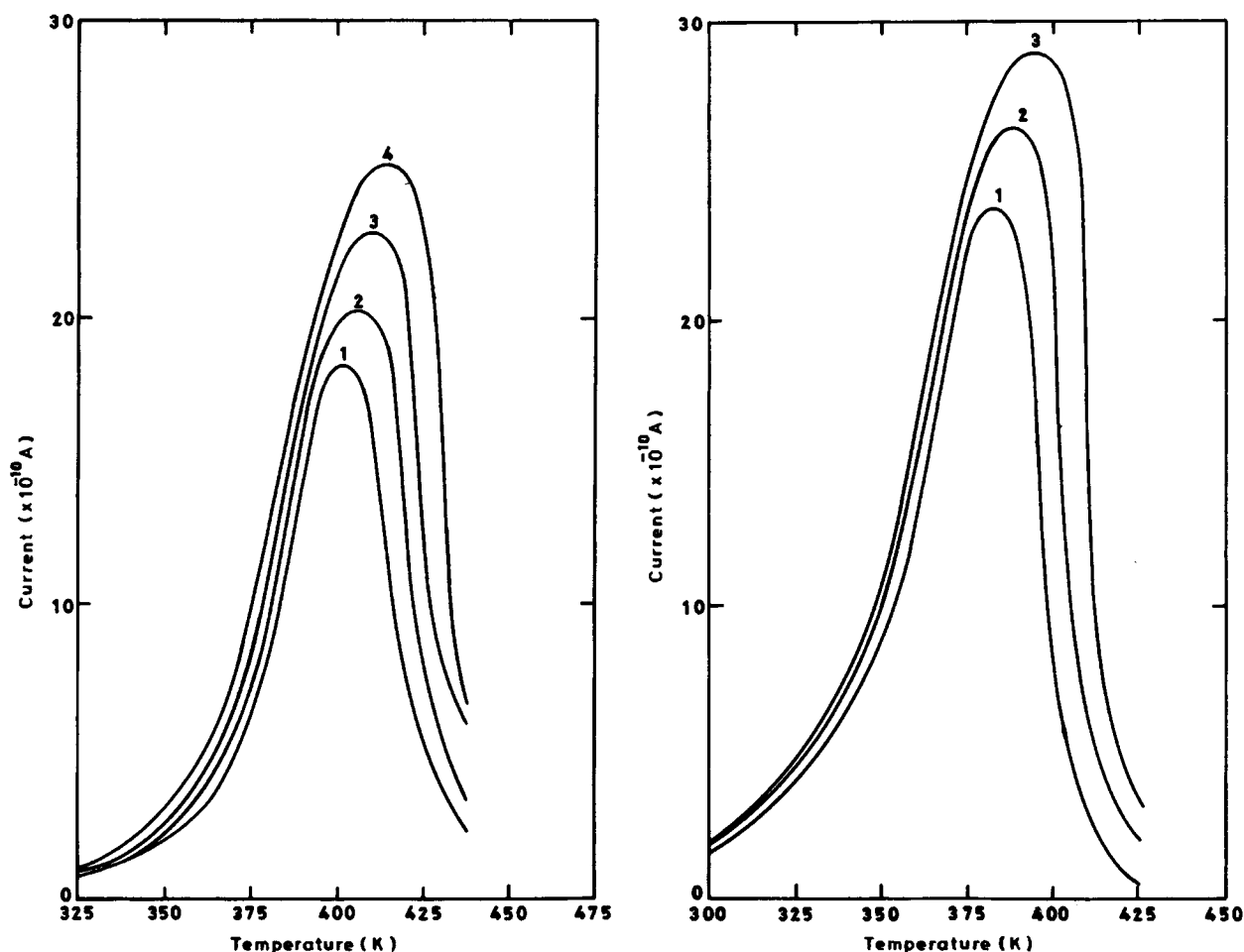


Figure 9 Effect of T_p on TSD spectra of (a) B1 and (b) B5 polarized at $E_p = 5.0 \times 10^4$ V/cm for $t_p = 3.6 \times 10^3$ s; curves 1-4 (a) and 1-3 (b) correspond to 348, 358, 370, and 383°K, respectively.

with increasing PTBF content in the PC/PTBF blend, the TSDC peak shifts toward lower temperatures. This has been attributed to changed composition-dependent blend morphology, which ultimately decreases the activation energy and thus creates shallow traps in PC/PTBF electret.

The present PC/PTBF electrets, comparative to its two components (PC and PTBF), store more charge, but decay faster.

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