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Thermally stimulated discharge current studies on PMMA–PVAc blends

R. SEKAR, ANITA TRIPATHI, T. C. GOEL, P. K. C. PILLAI
Electret and Optoelectronics Laboratory, Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Thermally stimulated discharge current (TSDC) studies have been carried out on blends of polymethyl methacrylate (PMMA) and polyvinyl acetate (PVA). The effects of polarization temperature and field on the TSDC peaks of polyblends indicate that the polarization in the polyblends is due to charge-carrier trapping in deep traps which leads to induced dipole formation. The results of a.c. dielectric bridge measurements are also compared with the TSDC results. The dielectric relaxation parameters are also reported.

1. Introduction

The thermally stimulated discharge current (TSDC) method has been used successfully to study the various mechanisms of polarization and also charge storage phenomena in polymer electrets [1]. This technique has shown that the characteristics of electrets are very sensitive to the structure of the electret-forming material [2–4]. Therefore, the TSDC study of polymer blends is likely to give valuable information about the molecular interaction and the extent of mixing between the two individual components. Polymer blends are heterogeneous mixtures, and the possibility of charge-carrier trapping at the trapping sites created by the grain boundaries of the individual polymers will be higher in such blends [5, 6].

Krause [7] carried out a comparative study of results reported by different workers on polymethyl methacrylate (PMMA) and polyvinyl acetate (PVAc) blends and found the results quite ambiguous. Schneier [8–11] proved experimentally that these two polymers would form a compatible system. However, though the mechanical properties of these polyblends have been reported [10, 11] so far no work has been reported regarding the dielectric relaxation mechanism in them. This present work has been carried out so as to understand electret formation mechanisms in polyblends of $\text{PMMA}_x\text{–PVAc}_{(100-x)}$ where x is 0, 10, 20, 50, 80, 90 and 100 wt %. A.c. dielectric bridge measurements at a fixed frequency of 1 kHz at different temperatures are also carried out to compare with the TSDC results.

2. Experimental procedure

PMMA (low molecular density) and PVA (molecular weight 500 000) were obtained from BDH (England) and Polysciences, Inc. (USA), respectively. Polymer

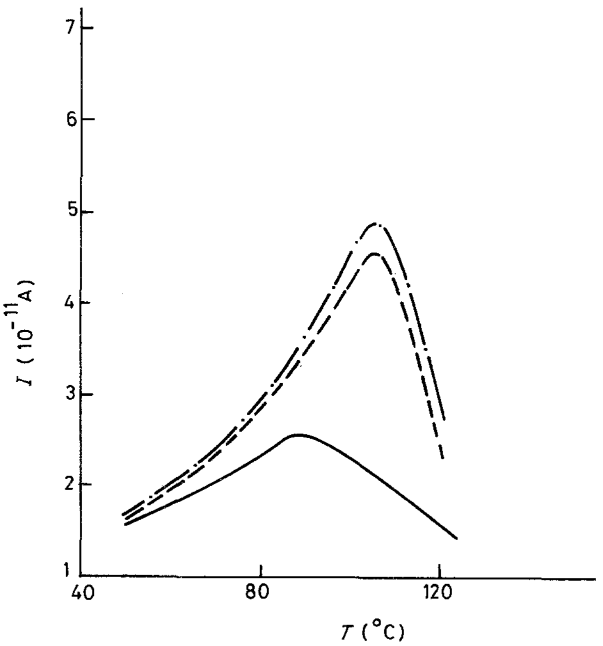

Figure 1 Effect of T_p on TSDC spectra of PMMA at E_p = 90 kV cm^{-1}: (——) 80° C, (– – –) 100° C, (–·–) 120° C.

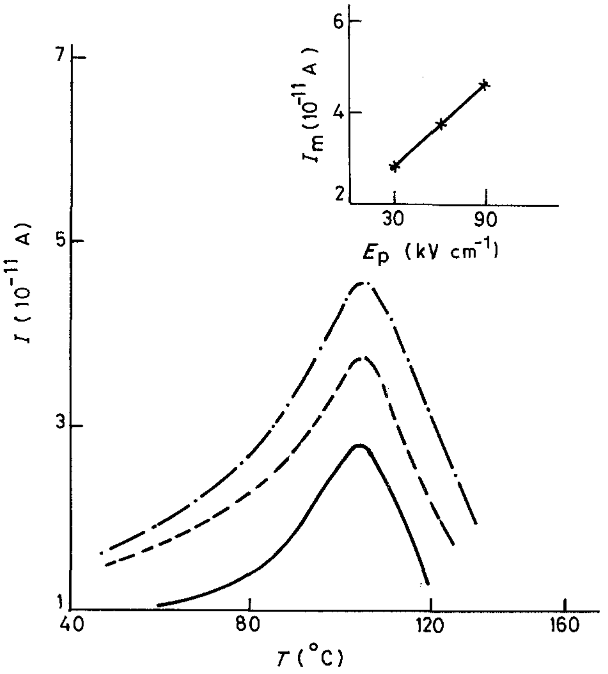

Figure 2 Effect of E_p on TSDC spectra of PMMA at T_p = 100° C: (——) 30 kV cm^{-1}, (– – –) 60 kV cm^{-1}, (–·–) 90 kV cm^{-1}.

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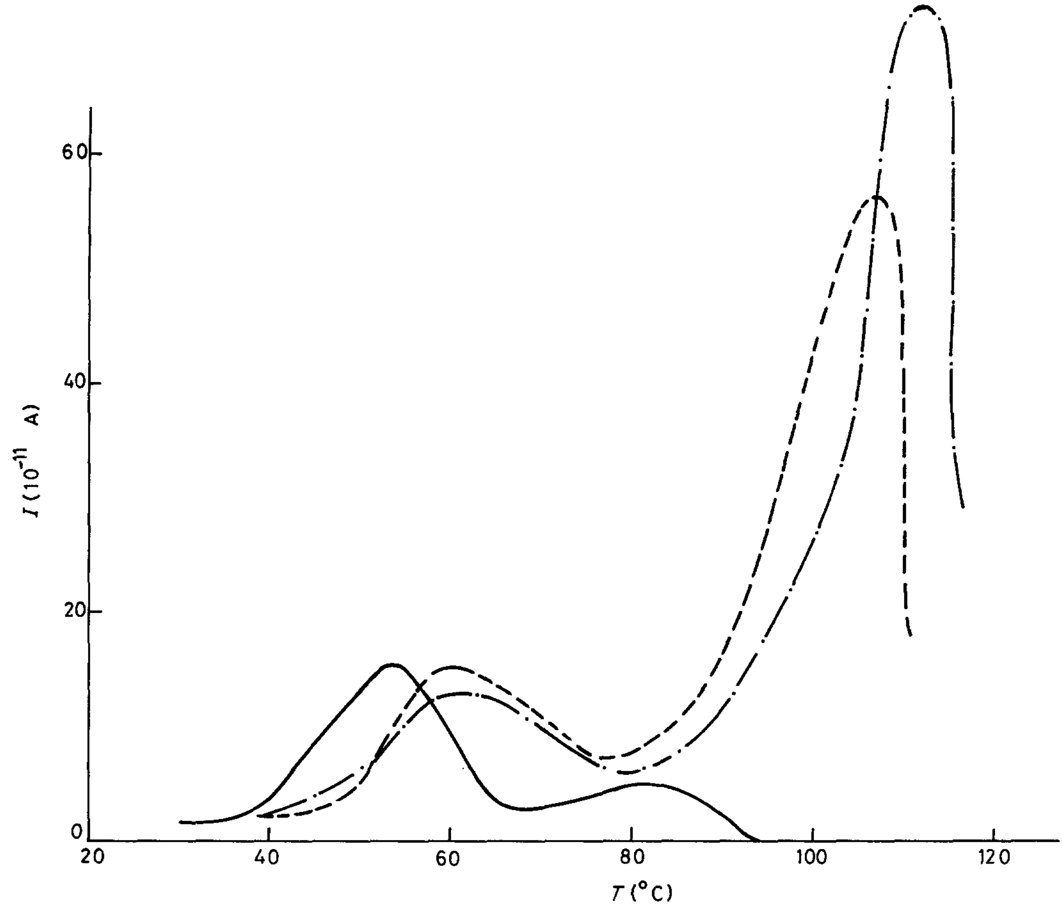

Figure 3 Effect of T_p on TSDC spectra of PVAc at E_p = 100 kV cm^{-1}: (——) 40° C, (– – –) 70° C, (–·–) 100° C.

blends were prepared by dissolving these polymers in the required weight proportion in a common solvent of chloroform. Films were cast on glass plates and allowed to dry in a saturated atmosphere of chloroform for 24 h and later they were kept in an oven maintained at 50° C for 48 h to remove all traces of the solvent. Films obtained by this technique were cut into 2 cm × 2 cm segments for our studies.

Polyblends of PMMA and PVAc in the weight proportions 90:10, 80:20, 50:50, 20:80 and 10:90, designated as PB1, PB2, PB3, PB4 and PB5, respectively, were studied along with the two individual poly-

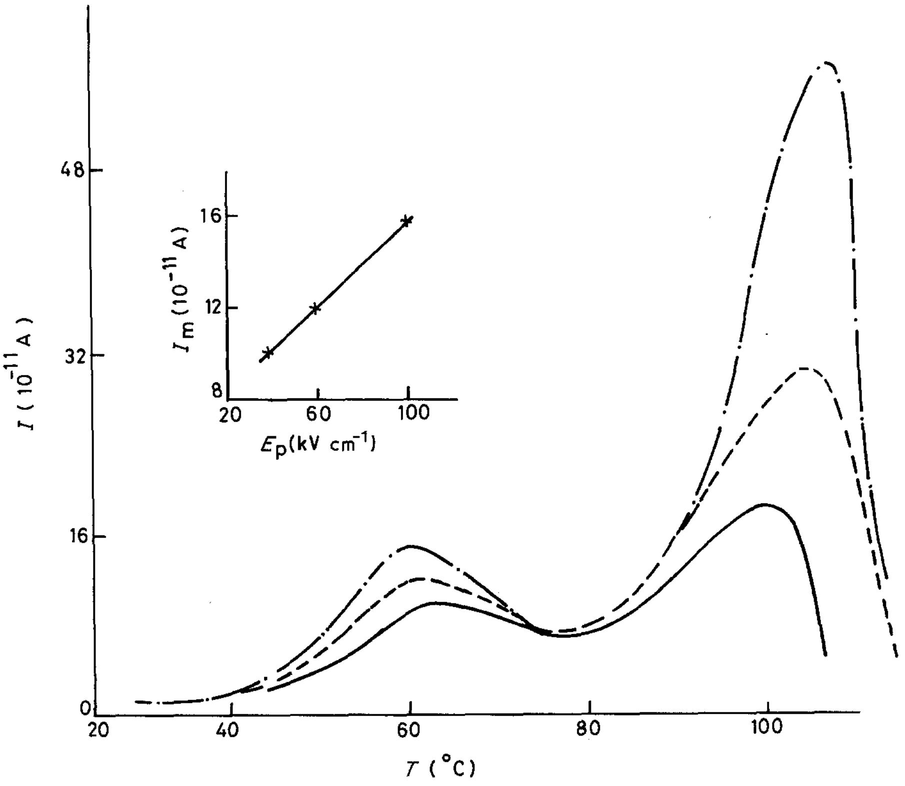

Figure 4 Effect of E_p on TSDC spectra of PVAc at T_p = 70° C: (——) 30 kV cm^{-1}, (– – –) 60 kV cm^{-1}, (–·–) 100 kV cm^{-1}.

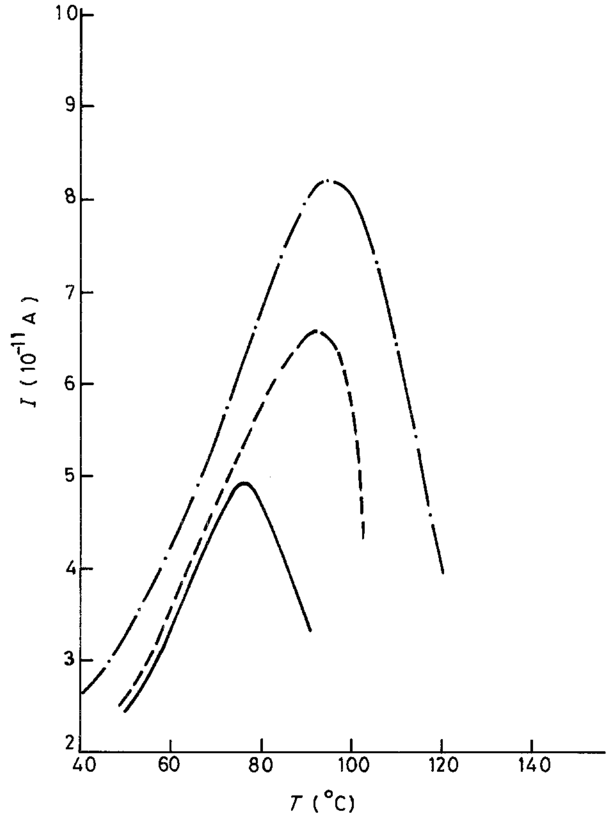

Figure 5 Effect of T_p on TSDC spectra of PB1 at $E_p = 100\,\mathrm{kV\,cm^{-1}}$: (——) 60° C, (– – –) 80° C, (–.–) 100° C.

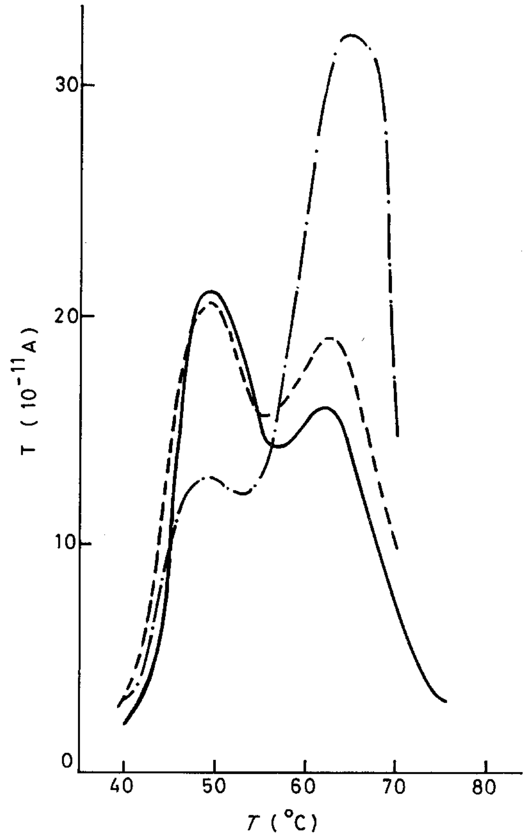

Figure 7 Effect of T_p on TSDC spectra of PB5 at $E_p = 60\,\mathrm{kV\,cm^{-1}}$: (——) 50° C, (– – –) 70° C, (–.–) 80° C.

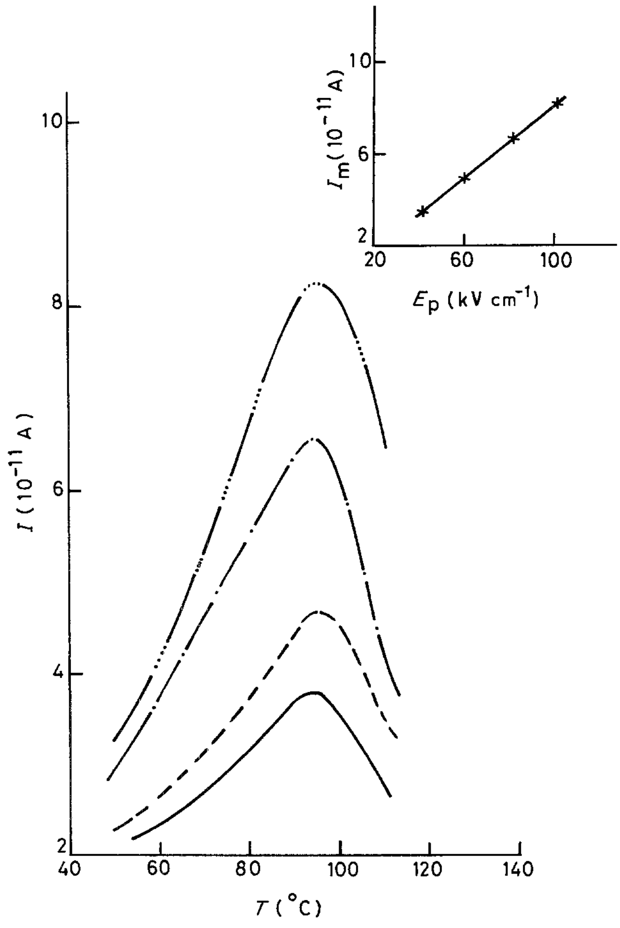

Figure 6 Effect of E_p on TSDC spectra of PB1 at $T_p = 100°\mathrm{C}$: (——) $30\,\mathrm{kV\,cm^{-1}}$, (– – –) $60\,\mathrm{kV\,cm^{-1}}$, (–.–) $90\,\mathrm{kV\,cm^{-1}}$, (–.....–) $100\,\mathrm{kV\,cm^{-1}}$.

mers. Aluminium electrodes were vacuum-deposited on both sides of the films on an area of 1.5 cm × 1.5 cm.

Thermoelectrets were prepared by heating the samples to a predetermined polarization temperature T_p, and then a d.c. field E_p was applied for a known time t_p. The sample was then cooled down to room temperature under the d.c. field. The field was then reduced to zero and the sample was short-circuited for 30 min in order to eliminate rapid discharge due to stray charges. The TSD current was then monitored with a sensitive electrometer (Keithley Model 610 C) by heating the sample at a constant rate. Most of the TSDC measurements were carried out at a heating rate of 3° C $\mathrm{min^{-1}}$. This rate ensured a good resolution of the spectrum and gave current values sufficiently high to make the background current negligible.

The dielectric measurements were carried out with a fixed frequency of 1 kHz at various fixed temperatures, with the help of Hewlett-Packard LF impedance analyser (Model 4192 A).

3. Results and discussion

Polarization in a solid dielectric can be produced by dipolar orientation and trapping of charge carriers generated in the bulk as well as injected from the electrodes. The trapping sites originate from the surface states of the polymer, polymer interfaces, chain foldings, molecular disorder and impurities in the material [12]. In addition, in a polyblend (which is a heterogeneous mixture) an interfacial or Maxwell–Wagner type of polarization will also contribute significantly [5, 6].

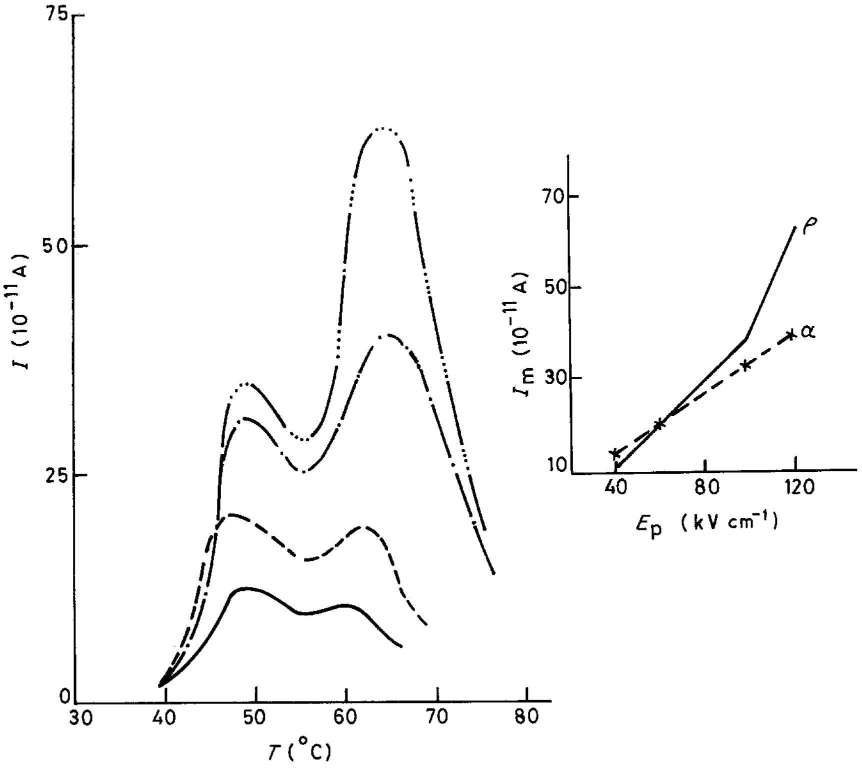

Figure 8 Effect of E_p on TSDC spectra of PB5 at T_p = 80° C: (——) 40 kV cm^{-1}, (– – –) 60 kV cm^{-1}, (–·–) 100 kV cm^{-1}, (–·····–) 120 kV cm^{-1}.

TSDC spectra of PMMA for various polarization temperatures T_p and fields E_p are shown in Figs 1 and 2, respectively. The peak temperature T_m becomes independent of T_p for polarization temperatures around and above T_g (T_g for PMMA is 105° C). The shift in peak temperature with T_p is indicative of a distribution in relaxation times [1]. For a single relaxation process T_m remains unaltered and the peak current I_m increases initially with T_p; it then saturates for higher T_p. In a distribution relaxation process, at low T_p not all the slow dipoles are activated and T_m occurs at a low temperature. As the polarization temperature is increased more and more slow dipoles are activated, which results in the shifting of the peak temperature and current. Once all the dipoles are activated an increase in the polarization temperature will show saturation in peak current and temperature. The saturation of peak current I_m with T_p and its linear dependence on E_p (inset of Fig. 2) is suggestive of dipolar orientation [1]. The observed results are in agreement with the earlier results of Kryszewski *et al.* [13]. However, no space-charge polarization has been observed as observed by Van Turnhout [1].

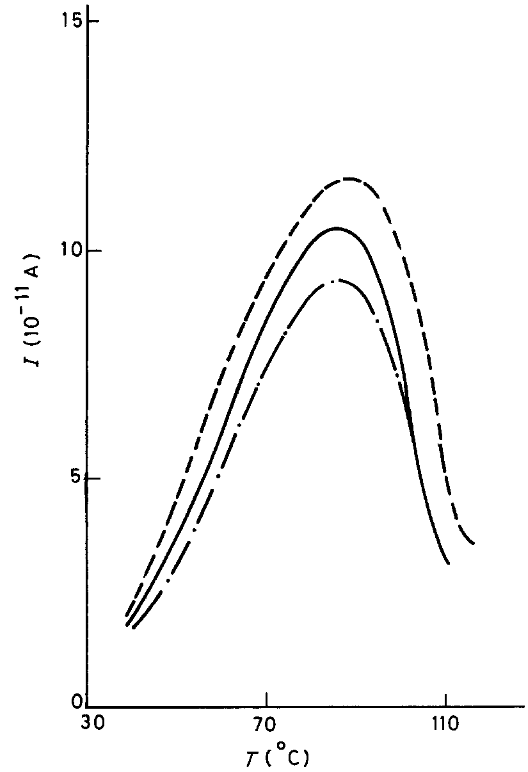

Figure 9 Effect of T_p on TSDC spectra of PB2 at E_p = 100 kV cm^{-1}: (——) 80° C, (– – –) 90° C, (–·–) 100° C.

Figs 3 and 4 show the TSDC spectra of pure PVAc for various T_p and E_p, respectively. Two peaks are observed: one around 55° C (α peak) and the other at 90° C (ϱ peak). The temperature of the α peak is independent of T_p and its peak current shows a linear dependence on E_p (inset of Fig. 4) and it can, therefore, be attributed to the relaxation of PVAc dipoles. The intensity of ϱ peak, however, increases along with a shift towards high temperature with both T_p and E_p, and the peak current varies non-linearly with E_p (inset of Fig. 4). This suggests that it is due to space-charge polarization.

The TSDC spectra of polyblends PB1, PB2, PB3, PB4 and PB5 for various T_p and E_p are shown in Figs 5 to 14.

The nature of the TSDC spectra of PB1 and PB5 resembles that of PMMA and PVAc, respectively. In PB1, the peak temperature T_m has been shifted towards the low temperature side (Figs 5 and 6) which may be attributed to the increase in free volume of PMMA because of blending with PVAc. In PB5 (Figs 7 and 8) the temperature of the α peak remains unaltered whereas the ϱ peak is observed at a lower temperature (70° C) compared to pure PVAc (95° C). Furthermore, Vanderschurren [14] has shown that the

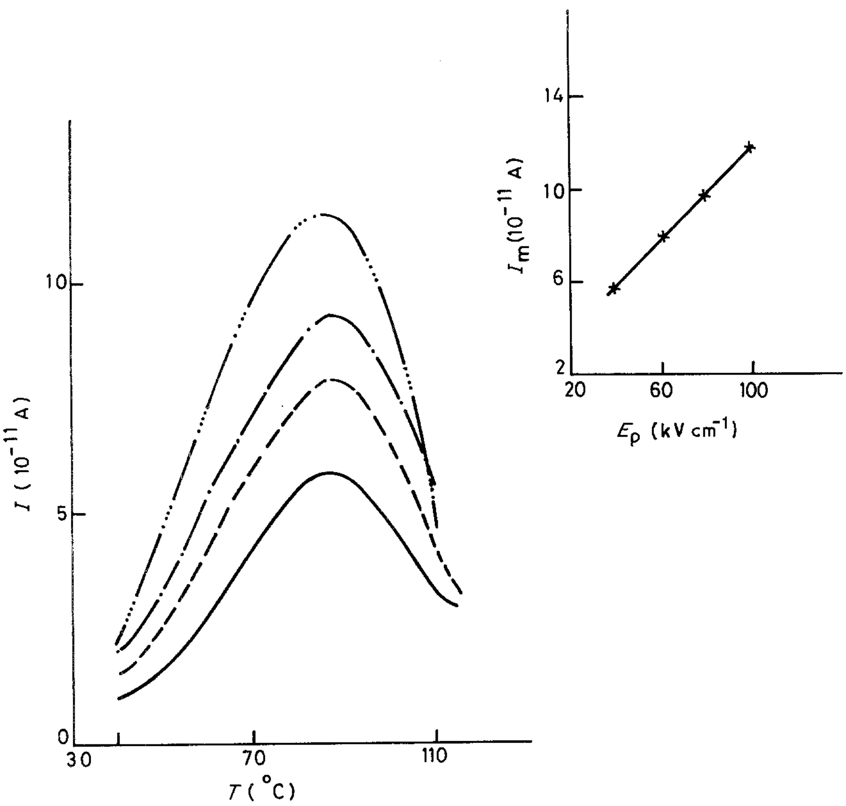

Figure 10 Effect of E_p on TSDC spectra of PB2 at T_p = 80° C: (——) 40 kV cm^{-1}, (– – –) 60 kV cm^{-1}, (–·–) 80 kV cm^{-1}, (–·····–) 100 kV cm^{-1}.

peak due to space-charge polarization is very sensitive and its properties (such as shape, position and amplitude) will be affected even if a small percentage of dopants like low molecular weight additives or plasticizers is added to the material under investigation. In this case, the shift of the ϱ peak towards low temperature may be due to the effect of blending.

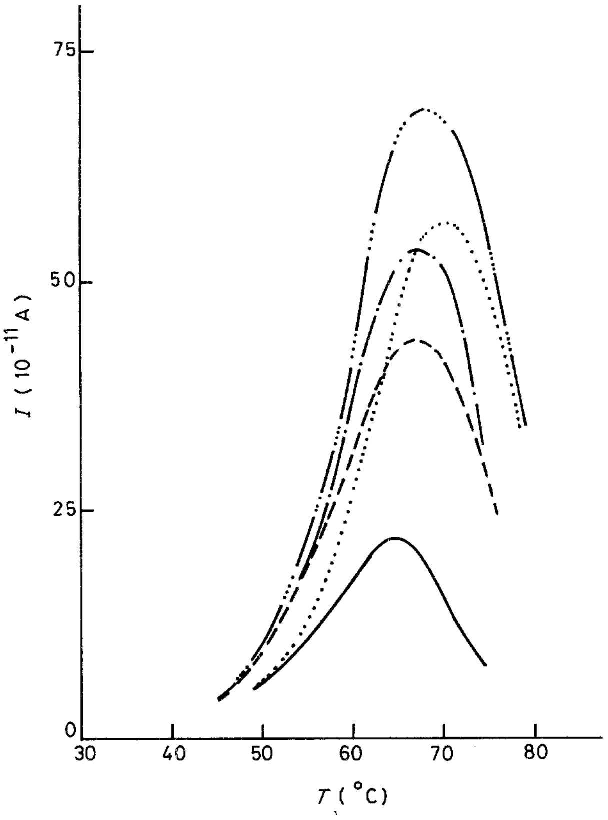

Figure 11 Effect of T_p on TSDC spectra of PB3 at E_p = 100 kV cm^{-1}: (——) 50° C, (– – –) 60° C, (–·–) 70° C, (–·····–) 80° C, (···) 100° C.

As the weight proportion of any one of the polymers is reduced further the nature of the TSDC spectra of the polyblends deviates from those of the parent polymers. The TSDC spectra of PB2, PB3 and PB4 are quite similar and these results show that

(i) these three polyblends have yielded only one peak and the peak temperatures of PB2, PB3 and PB4 are 80, 68 and 60° C, respectively;

(ii) the peak current I_m decreases for higher polarization temperatures (Figs 9, 11 and 13);

(iii) I_m shows a linear dependence on E_p up to 100 kV cm^{-1} and shows saturation above this field (insets of Figs 10, 12 and 14);

(iv) with decreasing PMMA content in the polyblend the peak temperature shifts to the lower temperature side.

The linear dependence of peak current I_m on E_p is suggestive of dipolar polarization, whereas its saturation with E_p is indicative of space-charge polarization [12]. The decrease in peak current I_m is also indicative of space-charge polarization. The possible explanation for this type of behaviour is induced dipole formation [5]. It seems that in the polyblends during polarization, both types of charge carriers are getting trapped in the trapping sites created by the phase boundaries of the individual polymers. These trapped charge carriers led to the formation of induced dipoles which will subsequently get oriented with the field.

The observation of a single peak may be due to the fact that either the dipolar contribution is small or it is getting masked by the space charge polarization. The lowering of peak temperature at higher polarization temperatures may be due to neutrality of charge carriers (a) with their image charges and (b) with their counterparts in the bulk [12], and due to a decrease in trapping sites because of increased molecular motion at higher temperatures [15].

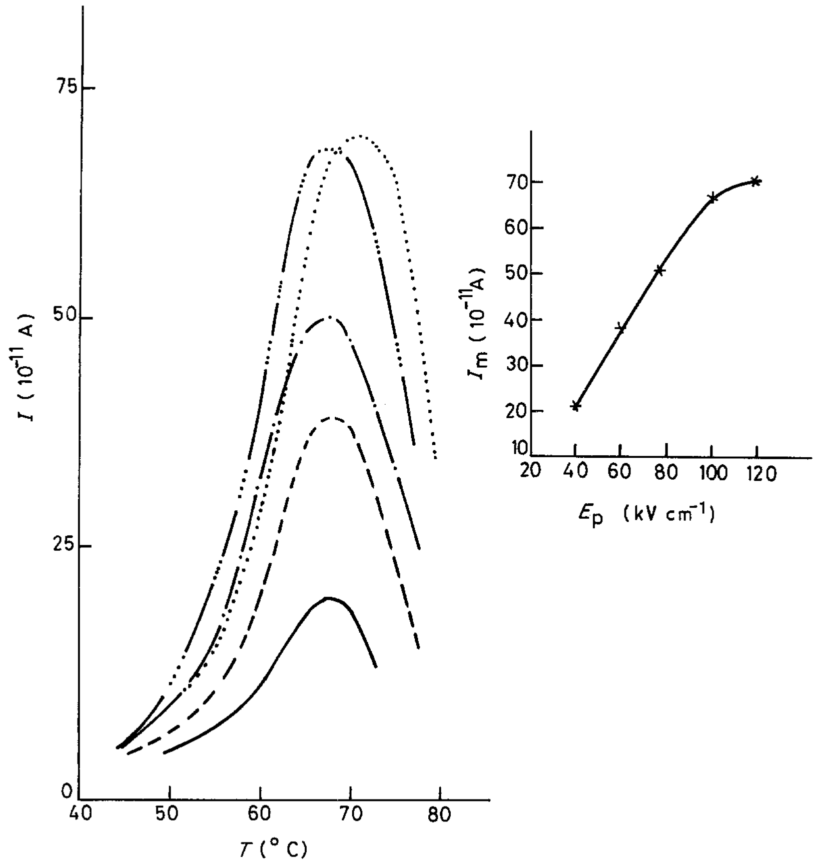

Figure 12 Effect of E_p on TSDC spectra of PB3 at T_p = 80° C: (——) 40 kV cm^{-1}, (- - -) 60 kV cm^{-1}, (-·-) 80 kV cm^{-1}, (-·····-) 100 kV cm^{-1}, (···) 120 kV cm^{-1}.

The decrease in peak temperature with decreasing PMMA content in the polyblend may be due to the internal plasticization that is taking place between the two polymers when they are blended. This is in agreement with a.c. dielectric bridge measurements, carried out at 1 kHz at different temperatures, which has also shown (Fig. 15) a single relaxation peak which shifts towards lower temperature with decreasing PMMA content.

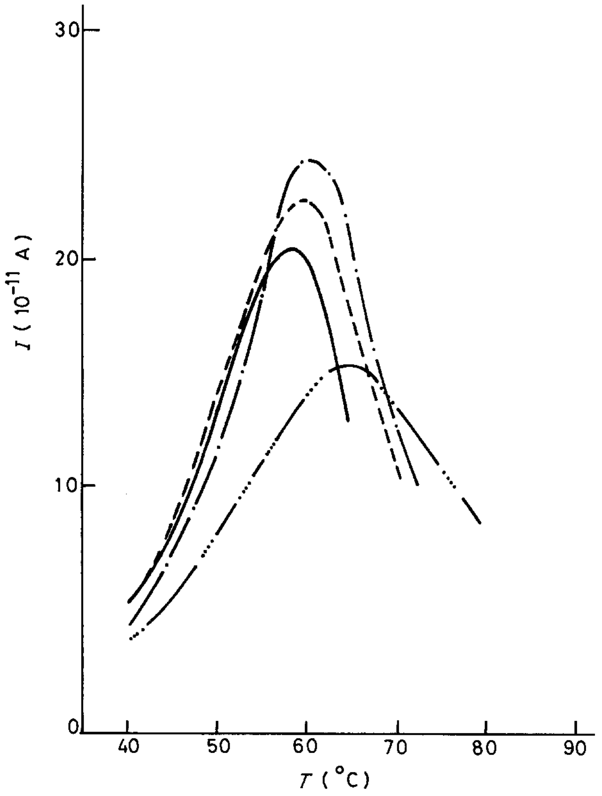

Figure 13 Effect of T_p on TSDC spectra of PB4 at E_p = 100 kV cm^{-1}: (——) 50° C, (– – –) 60° C, (–·–) 80° C, (–·····–) 100° C.

Fig. 16 shows a comparison of polarization between different polyblends. It is clear from this figure that PB3 shows a maximum polarization whereas its dielectric constant and loss factor lie intermediate to those of PMMA and PVAc (Fig. 15). The higher polarization in PB3 may be due to an increase in the trapping sites created by the grain boundaries and polymer interfaces of individual polymers, which seems to be higher in PB3 than in the other polyblends. The dielectric relaxation parameters of activation energy, calculated by the initial rise method [16] (not shown), and relaxation times are given in Table I.

4. Conclusion

Blending seem to be effective in controlling the polarization, dielectric constant, loss factor, relaxation temperature, etc., by adjusting the weight proportions of the two polymers.

TABLE I Dielectric relaxation parameters of polyblends

Sample	Activation energy, E (eV)	Relaxation time (sec)	
		τ_0	τ_{T_m}
PMMA	0.19	19.10×10^{-2}	64.80
PB1	0.21	2.50×10^{-2}	18.68
PB2	0.31	5.51×10^{-4}	12.01
PB3	1.28	2.99×10^{-19}	2.60
PB4	0.70	4.90×10^{-10}	4.83
PVAc	0.74 (α)	2.78×10^{-11}	4.30
	0.91 (ρ)	3.41×10^{-12}	4.51

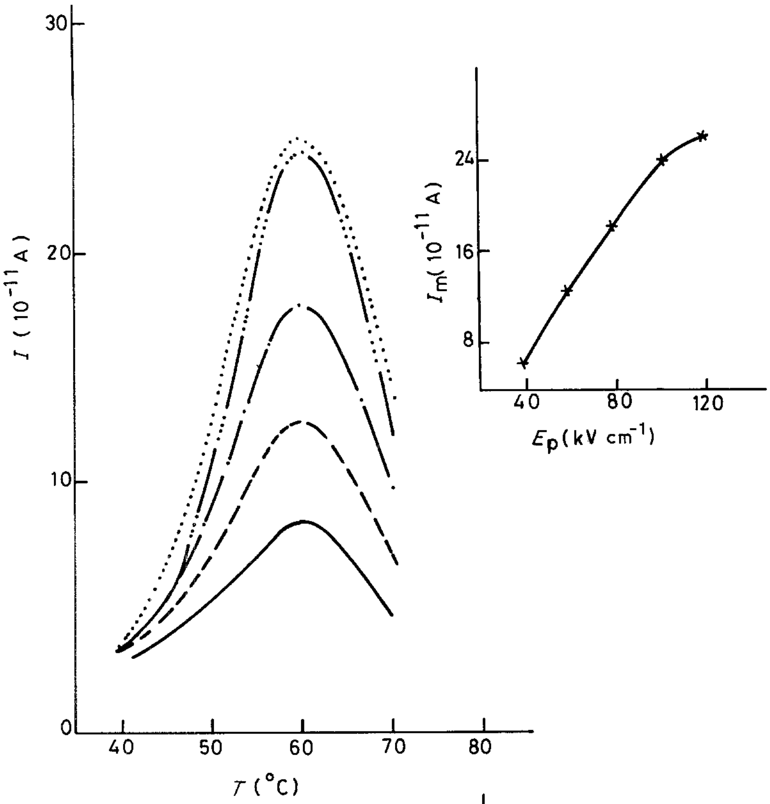

Figure 14 Effect of E_p on TSDC spectra of PB4 at T_p = 80° C: (——) 40 kV cm^{-1}, (– – –) 60 kV cm^{-1}, (–·–) 80 kV cm^{-1}, (–·····–) 100 kV cm^{-1}, (···) 120 kV cm^{-1}.

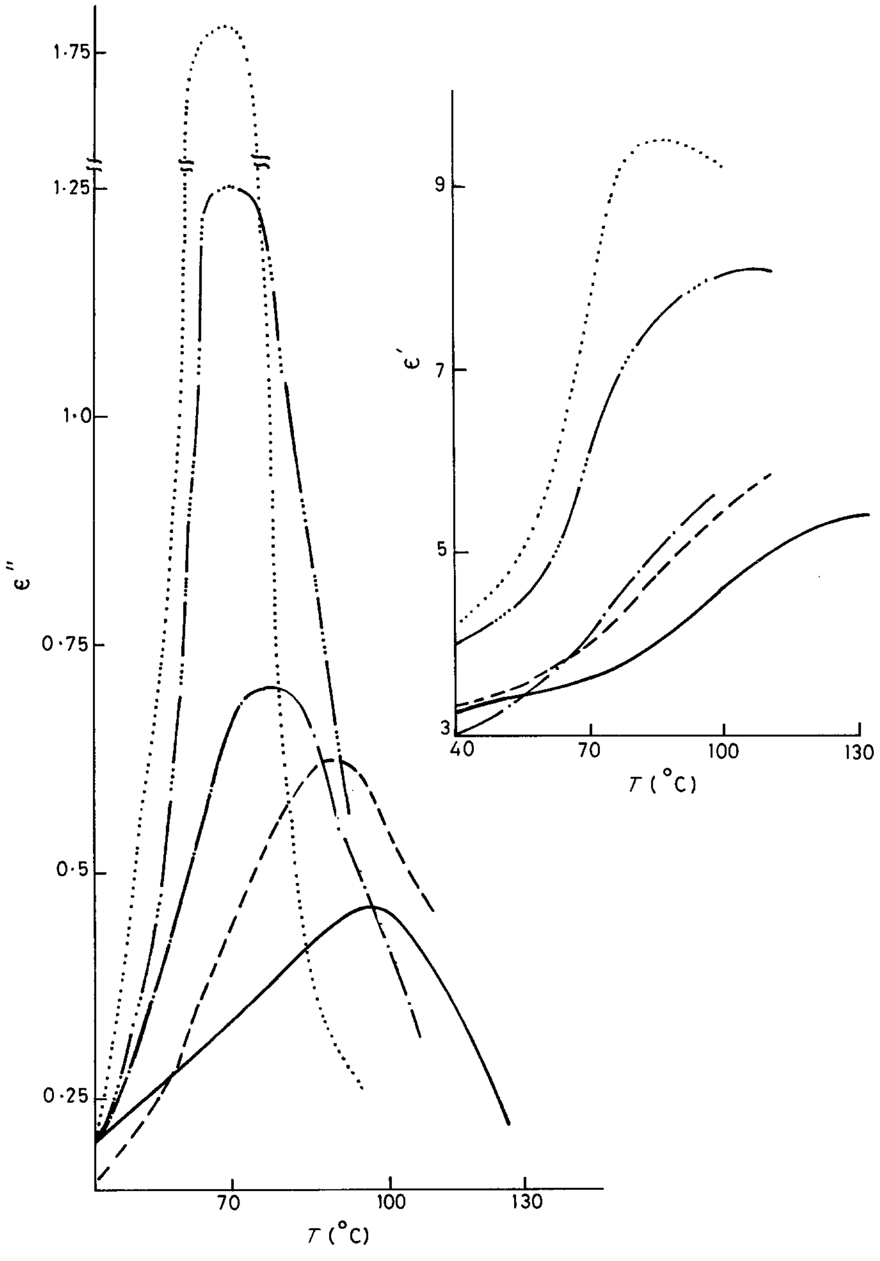

Figure 15 Variation of dielectric constant, ε′, and loss factor, ε″, with temperature at 1 kHz: (——) PMMA, (– – –) PB2, (–·–) PB3, (–·····–) PB4, (···) PVAc.

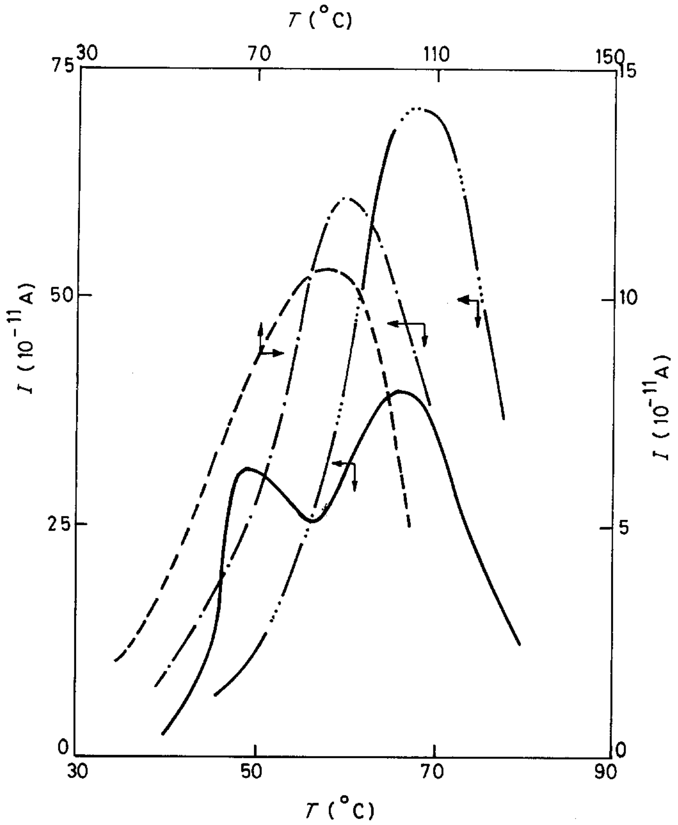

Figure 16 Comparison of polarization in different polyblends for $T_p = 80°C$, $E_p = 100\,kV\,cm^{-1}$: (——) PB5, (– – –) PB2, (–·–) PB4, (–·····–) PB3. Curve (c) is magnified two times.

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