

# Study of polarization and relaxation phenomena of polyblend films of poly(vinyl chloride) and poly(methyl methacrylate)

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MS received 14 July 2010; revised 12 August 2011

**Abstract.** Thermally stimulated discharge current (TSDC) studies were carried out on pure poly(methyl methacrylate), poly(vinyl chloride) and polyblends (of various weight ratios, 100:0, 90:10, 80:20 and 70:30) as a function of polarizing fields at constant temperature, to study the polarization and relaxation phenomena in them. For PVC and different blends a peak around 140–180 °C and for PMMA two peaks at around 95 and 165 °C were observed. No regular variation in peak position for PMMA and blends was observed. The various TSDC parameters i.e. activation energy, charge released and relaxation times were calculated. In the blend samples it is suggested that the chains are so entangled that in the total polarization the dipolar contribution is less and the observed polarization seems to be mainly due to the formation of induced dipoles and an increase in free volume and mobility of charge carriers due to a plasticization effect.

**Keywords.** Poly(methyl methacrylate); poly(vinyl chloride); thermally stimulated discharge current; induced dipole polarization; dipolar and space charge mechanism; plasticization effect.

## 1. Introduction

The interpretation of charge storage and transport behaviour in polymers is not an easy task; this becomes still more difficult due to complexity of polymer relaxations which is further magnified in blends by their complex morphology. Blends are the model system to understand structure–property relationship. It has been found that a suitable combination of isothermal and non-isothermal techniques can be useful for consistent interpretation of charge storage behaviour and structure–property relationship in polymers, their blends and composites.

One of the many experimental techniques which can be used to study molecular motions in solid materials is thermally stimulated depolarization current (TSDC) (Turnhout 1975, 1980; Braunlich 1979). TSDC is now a well-known technique for investigating the various mechanisms in electrets formation and also the phenomenon of charge storage in electrets. TSDC studies on polymers have shown that electret properties are very sensitive to the structure of the materials forming electrets. Thermally stimulated discharge (TSD) is a conventional technique for investigation of charge storage and transport processes in high resistivity materials and devices. For the standard TSD experiment, which is comparable to a dielectric loss measurement, the low equivalent frequency ( $\approx 10^{-3}$  Hz) and high sensitivity (ability to detect dipole concentration (Fillard and Turnhout 1974;

Soares De Campos 1977; Braunlich 1979) of  $10^{15}$  dipoles per  $\text{cm}^3$ ) make TSD quite useful for the study of amorphous relaxations in polymers and their crystallizable blends.

Poly(vinyl chloride) (PVC) is one of the most important, commercially used polymer because it is a high electrical and chemical resistant polymer and has the ability to get mixed with others to produce other compounds which have a wide range of physical and chemical properties. PVC is a polar polymer having a density of 1.332, melting temperature of 212 °C and glass transition temperature,  $T_g$ , of 80 °C. Poly(methyl methacrylate) (PMMA) is a hard, rigid, transparent polymer, which has good outdoor weatherability and is more impact resistant than glass (Waghmare *et al* 2007). PMMA is a versatile polymer showing plenty of applications. PMMA has good optical clarity and light transmittance. PMMA is strongly polar and mostly amorphous in character, having a density of 1.17–1.20, melting temperature of 140 °C and glass transition temperature,  $T_g$ , of 120 °C. Hence, the polymers differ in their dynamical as well as structural properties. Blends of these two polymers are expected to yield strong and long-lived electrets useful for industrial applications. Both PVC and PMMA are rigid polymers but by blending PVC with PMMA make the resultant blend soft and open to more uses and applications.

However, the role of various polarization processes and their relative contribution to the electret state of the polymers is not yet fully understood. Particularly, the space charge relaxation mechanism and the details of trap structure (including the trap distribution in energy and also over the volume of the polymer) are still to be well understood.

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The main aim of the present paper is to yield valuable information about the molecular interactions and the extent of mixing in polymer blends (Pillai *et al* 1981; Seanor 1982; Sekar *et al* 1985; Tripathi *et al* 1988). The electrets prepared from a polymer blend have better charge storage properties than homopolymers. Polymer blends are homogenous systems and the possibility of charge storage at the trapping sites introduced by the grain boundaries of individual component is higher in them. In the present paper charge storage phenomena and effect of stress fields on poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and their blends were investigated using TSDC technique.

## 2. Experimental

The polymers used in the present investigation, poly(vinyl chloride) (PVC) (in powdered form) and poly(methyl methacrylate) (PMMA) (in granular form), for the preparation of samples were obtained from Glaxo Laboratory, Mumbai. Polymer blends were prepared by simply dissolving the PVC and PMMA in required weight proportions, in a common solvent, dimethyl formamide (DMF), AR grade, supplied by E Merck, India, Ltd., Mumbai. The solution was continuously stirred for 60 min using teflon coated magnetic stirrer and heated at 50 °C during stirring to obtain a homogeneous solution. This solution was then poured on clean glass plates floating on a mercury pool kept in a dust free non-vacuum oven at a constant temperature,  $T = 35$  °C, for 24 h to remove all traces of the solvent. Great care was taken to avoid air bubbles during setting of the polymer solution on the glass plates. The films were then detached carefully from the glass plate using a sharp edge knife or blade (Khare and Pal 2010).

The different polymer samples prepared were pure PVC and PMMA, 90:10 (PVC:PMMA), 80:20 (PVC:PMMA) and 70:30 (PVC:PMMA). The pure PVC, PMMA, 90:10, 80:20 and 70:30 polyblend samples are designated as  $P_1$ ,  $P_2$ ,  $P_3$ ,  $P_4$  and  $P_5$ , respectively. With further increase of PMMA, the samples became brittle and handling was difficult; hence, we restricted our studies only to the above mentioned ratios.

The prepared film samples were sandwiched between aluminum electrodes inside an oven and heated to a predetermined polarization temperature,  $T_p$ . After achieving thermal equilibrium, a d.c. field, i.e. polarization field,  $E_p$ , was applied for 90 min. The sample was then cooled to room temperature under the applied field. The field was then removed and sample short circuited to remove stray charges. The thermoelectret obtained was reheated at the rate of 3 °C per min and the depolarization current was recorded using a Keithley Electrometer (610°C). The depolarization kinetic data, i.e. activation energy ( $E$ ), charge released and relaxation time were calculated and are listed in table 1. The activation energy was evaluated using the Arrhenius equation

$$= \sigma_0 \exp(-E/kT),$$

where  $\sigma_0$  is a constant;  $E$  the activation energy;  $T$  the absolute temperature and  $k$  the Boltzmann constant.

## 3. Results and discussion

TSDC spectra for the samples polarized with poling fields 45, 65, 85 and 105 kV at 80 °C, respectively are shown in figures 1–4. Figure 1 shows TSDC spectra for pure PVC sample, exhibiting single sharp peak at around 140–150 °C. Initially, the current was of the higher order and decays with temperature for a particular span. Figure 2 shows dependence of TSDC behaviour for pure PMMA on polarizing fields; it is characterized by two well-resolved peaks, designated as  $\alpha$  and  $\rho$ , positioned at around 95 and 165 °C. Figure 3 represents TSDC thermograms for polyblends  $P_3$ ,  $P_4$  and  $P_5$ ; they exhibit a single well-resolved peak at around 145–180 °C. The order of magnitude of the current was higher compared to individual polymer. In general, the peak current increases with increase in poling fields. The peaks shift towards higher temperature side for pure samples and for blends the position of the peaks was found to be independent of the poling fields.

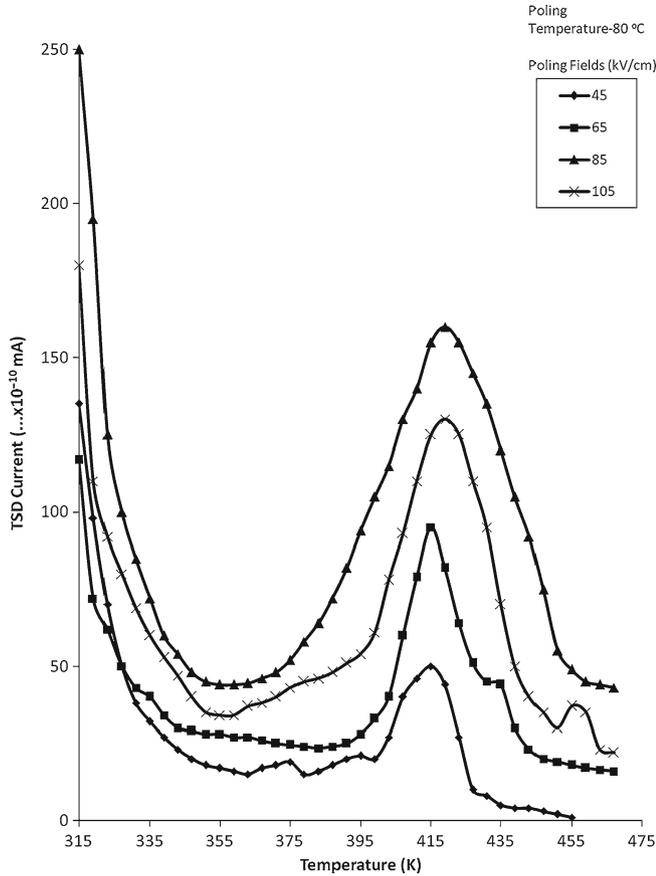
Depending upon the nature of the polymer, the polarization in a polymer can be attained by various mechanisms such as the orientation or the dipoles, trapping of the charge carriers at microscopic distances (Maxwell–Wagner effect) and space charge polarization i.e. trapping of charge carriers at macroscopic distances (Vanderschueven and Gasiot 1979). Any one or more processes can contribute to the polarization. Thus the net polarization of an electret is generally due to the aligned dipoles and space charges (makes an electret non-neutral). However, before the formation of electret the polymer is neutral and contains free charges. When electric field is applied current is observed in the circuit, hence polymer contains free charges. The charges present in the electret do not contribute to the total polarization but they are responsible only for conduction current which varies linearly with the field and *vice versa* in TSD current due to space charges which will not vary linearly.

PVC is an amorphous polymer which shows three relaxations designated as  $\alpha$ ,  $\beta$  and  $\alpha'$  (Jain *et al* 1973; Gupta *et al* 1978). The  $\alpha$ -relaxation corresponds to the glass transition temperature,  $T_g$ , and arises due to the large segmental motion. The second one,  $\beta$ -relaxation, occurring at low temperatures has been attributed to rotation of side groups. The third relaxation  $\alpha'$  is reported to occur at temperatures well above  $T_g$  and may be due to the charge pile up at the electrodes (Mahendru *et al* 1983).

PMMA is also an amorphous and polar thermoplastic with an ester group ( $\text{COOCH}_3$ ) and methyl group ( $\text{CH}_3$ ) as its two side groups. The methyl group ( $\text{CH}_3$ ) may be located on the same side of the polymer chain, alternate regularly or alternate at random, relaxation phenomenon in PMMA have been studied extensively and three peaks have been reported in pure PMMA, known as  $\beta$ ,  $\alpha$  and  $\rho$  (Turnhout 1975). The hindered local motion of side groups below the glass–rubber transition temperatures gives rise to the  $\beta$ -relaxation peak. The cooperative motion of ester side groups with the main chain manifests itself at and near the glass transition temperature in the form of  $\alpha$ -peak.  $\rho$  peak is due to space charges.

**Table 1.** TSDC parameters of pure and polyblend thermoelectrets.

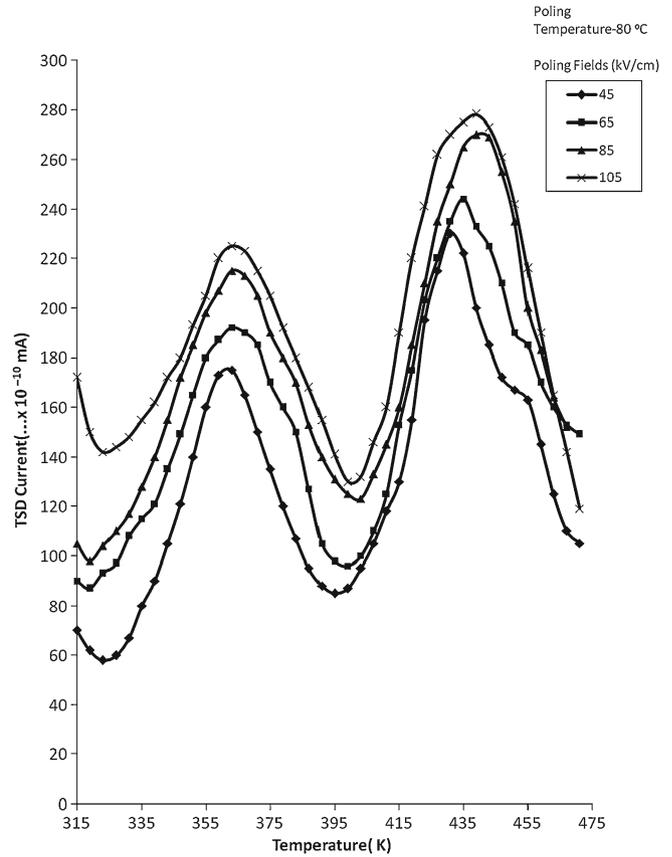
Thermoelectret	Poling temperature (°C)	Poling field (kV)	Peak position (°C)		Peak current (mA)		Activation energy (eV)		Charge released (Coul)	Relaxation time (s)
			1st	2nd	1st	2nd	1st	2nd		
PVC ( $P_1$ )	80	45	142	-	$50 \times 10^{-10}$	-	0.386	-	$3.57 \times 10^{-10}$	$8.80 \times 10^{-3}$
		65	142	-	$95 \times 10^{-10}$	-	0.377	-	$4.27 \times 10^{-9}$	$7.98 \times 10^{-4}$
		85	146	-	$160 \times 10^{-10}$	-	0.363	-	$5.84 \times 10^{-8}$	$8.78 \times 10^{-5}$
		105	146	-	$130 \times 10^{-10}$	-	0.361	-	$7.82 \times 10^{-8}$	$7.56 \times 10^{-6}$
PMMA ( $P_2$ )	80	45	90	158	$175 \times 10^{-10}$	$230 \times 10^{-10}$	0.297	0.350	$2.76 \times 10^{-8}$	$1.80 \times 10^{-4}$
		65	94	162	$192 \times 10^{-10}$	$244 \times 10^{-10}$	0.279	0.348	$3.42 \times 10^{-8}$	$2.75 \times 10^{-5}$
		85	94	166	$215 \times 10^{-10}$	$270 \times 10^{-10}$	0.272	0.344	$2.41 \times 10^{-8}$	$3.50 \times 10^{-6}$
		105	90	166	$225 \times 10^{-10}$	$278 \times 10^{-10}$	0.268	0.330	$6.70 \times 10^{-8}$	$4.23 \times 10^{-7}$
Polyblends 90:10 ( $P_3$ )	80	45	166	-	$79 \times 10^{-9}$	-	0.577	-	$1.45 \times 10^{-8}$	$6.88 \times 10^{-5}$
		65	166	-	$99 \times 10^{-9}$	-	0.572	-	$2.8 \times 10^{-8}$	$5.43 \times 10^{-6}$
		85	158	-	$235 \times 10^{-9}$	-	0.568	-	$8.98 \times 10^{-8}$	$6.77 \times 10^{-7}$
		105	158	-	$160 \times 10^{-9}$	-	0.551	-	$9.88 \times 10^{-8}$	$7.09 \times 10^{-8}$
80:20 ( $P_4$ )	80	45	154	-	$80 \times 10^{-9}$	-	0.574	-	$2.65 \times 10^{-7}$	$5.44 \times 10^{-5}$
		65	162	-	$120 \times 10^{-9}$	-	0.567	-	$4.09 \times 10^{-7}$	$6.86 \times 10^{-6}$
		85	146	-	$230 \times 10^{-9}$	-	0.556	-	$4.64 \times 10^{-7}$	$7.90 \times 10^{-7}$
		105	158	-	$280 \times 10^{-9}$	-	0.552	-	$6.97 \times 10^{-7}$	$5.20 \times 10^{-8}$
70:30 ( $P_5$ )	80	45	170	-	$180 \times 10^{-9}$	-	0.599	-	$6.27 \times 10^{-7}$	$4.36 \times 10^{-5}$
		65	154	-	$185 \times 10^{-9}$	-	0.576	-	$6.86 \times 10^{-7}$	$5.68 \times 10^{-6}$
		85	178	-	$427 \times 10^{-9}$	-	0.572	-	$9.34 \times 10^{-7}$	$6.47 \times 10^{-7}$
		105	182	-	$507 \times 10^{-9}$	-	0.566	-	$9.84 \times 10^{-7}$	$7.53 \times 10^{-8}$



**Figure 1.** TSD current vs temperature plots for PVC samples poled at 80 °C with different poling fields (i.e. 45, 65, 85 and 105 kV).

TSD current spectra for pure PVC sample shows a single peak at around 140–150 °C which can be related to  $\alpha$ -relaxation peak because peak temperature does not vary (linear dependence) with change in polarizing field; this indicates that the peak may be due to dipolar relaxation but  $\alpha$ -relaxation occurs at glass transition temperature and this peak is well above this temperature, so this possibility is completely ruled out. This peak can be clearly related to  $\alpha'$ -relaxation which occurs due to space charges accumulated near electrodes. TSD current for pure PMMA is characterized by two well-resolved peaks which can be clearly designated as  $\alpha$  and  $\rho$  because they are positioned at around 95 °C and 165 °C in which former is near to glass transition temperature which can be due to dipolar relaxation and latter due to space charge formation.

TSD current recorded in the present investigation was characterized by a single peak for the blends located in the temperature interval 145–180 °C. The observed peak exhibits no regular shift in position or height with applied field. Consequently, the peak observed in the present investigation, in view of its proximity of  $T_g$  of the polymer PVC (Matsuoka and Ishida 1966; Clark 1967), and its independence on polarizing field may be considered primarily due to space charge  $\alpha'$ -relaxation of PVC.

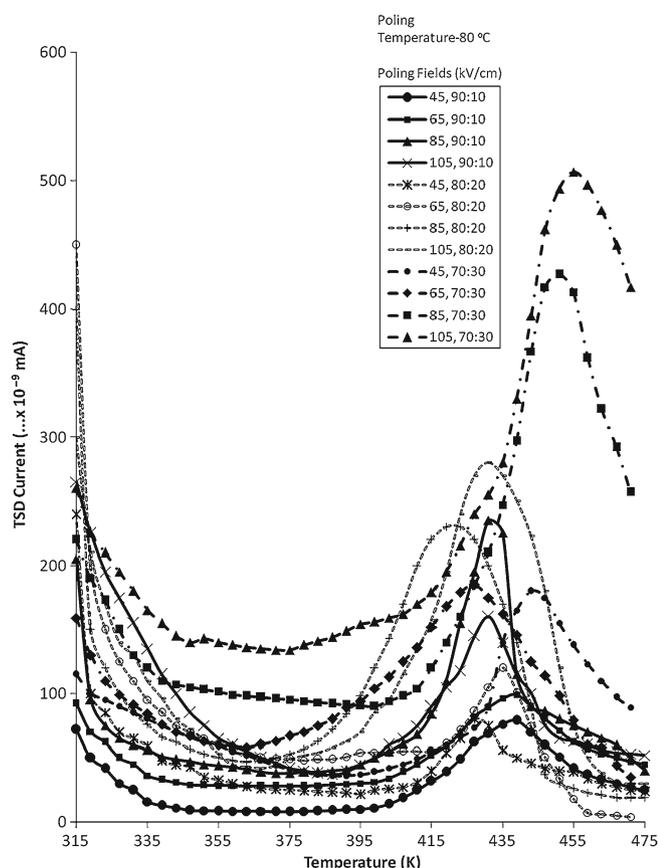


**Figure 2.** TSD current vs temperature plots for PMMA samples poled at 80 °C with different poling fields (i.e. 45, 65, 85 and 105 kV).

When phase transition competes, the segmental mobility is increased resulting in possibility of charge carrier near the electrodes. Their drift becomes easy by self motion above this phase transition i.e.  $T_g$ . After  $T_g$ , structural rearrangement or chain segments becomes easier due to increase in its free volume. A de-trapping mechanism at higher temperature may be possible and the charge carriers may become trapped at some deeper trap levels which are available for trapping (Khare and Pal 2010).

In pure PVC, PMMA and polyblend samples, we can observe that the initial value of current is high and this high value of all TSD current spectra suggests that there is another relaxation below the room temperature. This low temperature peak can be attributed to  $\beta$ -relaxation which is not observed in present case because the measurements are carried out above room temperature (>30 °C).

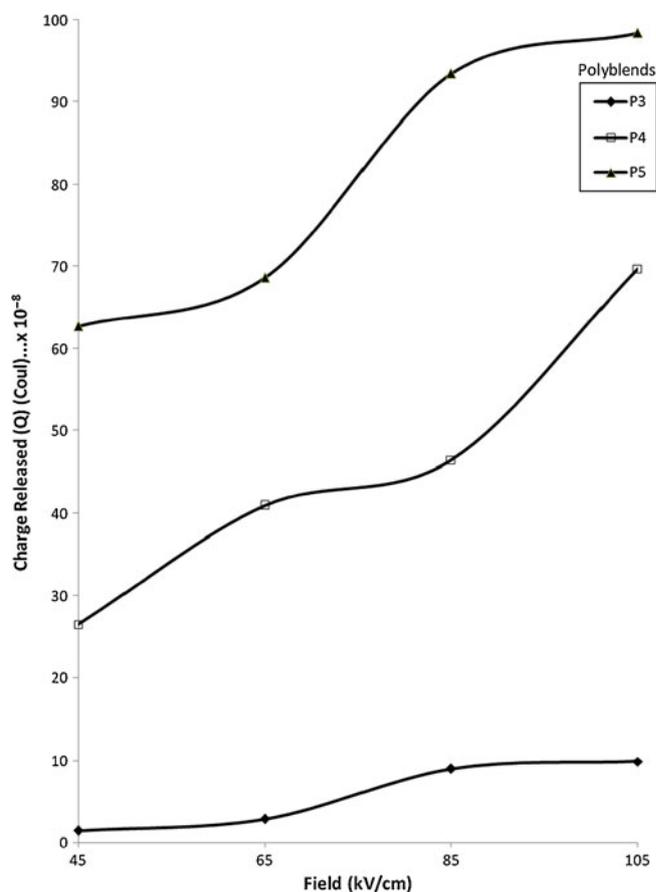
The calculated activation energy value range from 0.26–0.38 for pure samples and 0.553–0.598 for blend samples. TSD current spectra of the blend of PVC and PMMA show a single peak in its spectrum. The charge associated with the TSDC peak was found to vary nonlinearly with the poling field (figure 4). So we can say that observed peak is composite in nature and may be due to the contribution of trapped charge carriers forming a space charge. Hence, this peak may exhibit characteristics of both dipolar as well as space charge



**Figure 3.** TSD current vs temperature plots for PVC:PMMA blend samples (90:10, 80:20 and 70:30) poled at 80 °C with different poling fields (i.e. 45, 65, 85 and 105 kV).

behaviour. The activation energy values seem too high to be assigned to dipolar orientation and space charge alone. We can observe easily from the TSD spectra of the blend samples that the magnitude of the current increases as the PMMA content is increased in PVC. Due to the inclusion of the PMMA in the PVC a heterogeneous structure is formed and we can say that a plasticization effect (Khare *et al* 1993) is produced and due to this effect loosening of the structure, greater mobility of charge carriers, free volume and intermolecular interaction can happen which increases the value of current. It appears that the enhancement in free volume and molecular mobility brought about plasticization competitively dominates the polarization process. In the PVC and PMMA blend matrices two phases can exist because of the carrier conductivity in different phases and these carriers can get trapped at the inter-phase boundaries.

The induced dipole orientation can also play an important role in net polarization in the electret. These induced dipoles come into existence due to trapping of both positive and negative charge carriers in the deep traps present in material due to structural defects, chain motions, presence of impurities, etc. When an external electric field is applied, these induced dipoles align themselves in the field direction and help in induced dipole polarization in the polyblend (Pillai *et al*



**Figure 4.** Charge released vs field for different blend samples (i.e. 90:10, 80:20 and 70:30).

1981). It also appears that, on blending, due to increase in intermolecular interaction, the dipoles are entangled in such a way that the contribution of orientation of dipoles towards the polarization of the sample in the presence of an applied field becomes insignificant. It is also possible that contribution of permanent dipole of the host material is masked due to induced dipoles. PVC and PMMA are polar polymers, so when their blend is made the dipoles of the polar compound become so constrained under the field, they either do not orient or their contribution to the total polarization is almost negligible as compared to the contribution of induced dipoles, which are formed in the bulk by the deep trapping of charge carriers. Hence the de-polarization thermograms represent the characteristics of both dipolar reorientation and space charge neutralization. The value of activation energy is high, this may be taken as an indication of induced dipole formation because in the case of induced dipoles the energy required to disorient them and subsequently release charge carriers from the trapping sites is expected to be high (Khare and Srivastava 1992; Khare *et al* 1999). Hence it can be said that the mechanism responsible for the peak is characterized by not only discrete level of activation energy having a single relaxation time, but also a complex process having a continuous spectrum of activation energy and relaxation times.

As the polarizing field increases, the barrier height of the traps in which the charges are found is lowered, accounting for the observed decrease of the activation energy with increasing field. Distribution of relaxation time in polymers arises due to the different size and shape of the polar groups/dipoles orientated during polarization. Table 1 shows that the relaxation time decreases with poling field. This can be explained from the fact that the relaxation phenomenon is due to the internal friction of the polymer which depends exponentially on temperature. The time lag corresponding to the motions of permanent dipoles (ions, free and trapped charges) changes markedly with field. Heating accelerates the molecular motion, thereby decreasing the time lag, which is the relaxation time.

#### 4. Conclusions

The analysis of TSD spectra of pure and polyblend samples shows that the peaks obtained are due to space charge accumulation and induced dipole formation caused by plasticization effect in blends. Increase in polarizing field decreases the activation energy because the barrier height is lowered. The total polarization is dominated by space charge and induced dipole formation.

#### References

- Braunlich P 1979 *Thermally stimulated relaxations in solids: Topics in applied physics* (Berlin: Springer) p. 37
- Clark J E 1967 *Polym. Eng. Sci.* **7** 137
- Fillard J P and Turnhout J V 1974 *Thermally stimulated process in solids: New prospects* (Amsterdam: Elsevier)
- Gupta N, Jain P K and Mahendru P C 1978 *J. Chem. Phys.* **69** 1785
- Jain K, Rastogi A C and Chopra K L 1973 *Phys. Status Solidi (a)* **20** 167
- Khare P K and Srivastava A P 1992 *Indian J. Pure Appl. Phys.* **30** 102
- Khare P K and Pal A 2010 *J. Electrostat.* **68** 328
- Khare P K, Gaur M S and Srivastava A P 1993 *Indian J. Pure Appl. Phys.* **31** 102
- Khare P K, Keller J M and Datt S C 1999 *Bull. Mater. Sci.* **22** 109
- Mahendru P C, Chand S and Kumar N 1983 *Thin Solid Films* **105** 103
- Matsuoka S and Ishida Y 1966 *J. Polym. Sci. C* **14** 247
- Pillai P K C, Narula G K, Tripathi A K and Mendiratta R G 1981 *Phys. Status Solidi (a)* **67** 649
- Seanor D A 1982 *Electrical conduction in polymers*, in *Electrical properties of polymers* (New York: Academic Press) ch. 1
- Sekar R, Tripathi A K, Goel T C and Pillai P K C 1985 *IEEE Proc. on 5th international symposium of electrets* (West Germany: Heidelberg) p. 181
- Soares De Campos M 1977 *International symposium on electrets and dielectrics* (Rio de Janeiro: Academia Brasileira de Ciencias)
- Tripathi A, Tripathi A K and Pillai P K C 1988 *J. Appl. Phys.* **64** 2031
- Turnhout J V 1975 *Thermally stimulated discharge of polymer electrets* (Amsterdam: Elsevier)
- Turnhout J V 1980 *Topics in applied physics*, (ed.) G M Sessler (Berlin: Springer-Verlag) **Vol. 33**, p. 81
- Vanderschueven J and Gasiot J 1979 *Thermally stimulated relaxation in solids: Topics in applied physics* (Berlin: Springer-Verlag)
- Waghmare R V, Belsare N G, Raghuvanshi F C and Shilaskar S N 2007 *Bull. Mater. Sci.* **30** 167