Thermally Stimulated Discharge Current study of PMMA:PVP blends

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ABSTRACT : *Thermally stimulated discharge current (TSDC) method was used to study the dielectric relaxation phenomena in pure Polymethyl methacrylate (PMMA), Polyvinyl pyrrolidone (PVP) and their blends films of approximately 50 μm in thickness, measured at 60 ^{o}C as a function of poling fields (50, 70, 90, and 110 kV/cm) and weight ratios (100:0, 95:05, 90:10, 85:15, 80:20 and 0:100). The relaxation processes for PMMA and PVP shows two peaks observed at around 90 ± 5 and 150 ± 5 ^{o}C but in the blend samples the first peak disappears and only one peak can be seen at higher temperature range 155 ± 10 ^{o}C. The first peak is α-peak which is due to micro-Brownian motion of the main chain segments and the higher temperature ρ-peak is due to space charge near the electrodes. It was found that the order of current increases with increase in weight percent of PVP in PMMA and the main reason is the formation of phase between PVP and PMMA. A decrease in activation energy observed with the increase in polarizing fields and weight % composition. This suggests that peak is not due to a discrete level having a single relaxation but is a complex one having distributed activation energies.*

KEYWORDS: *Polymethyl methacrylate; Polyvinyl pyrrolidone; Thermally*

I. INTRODUCTION

A lot of work has already been done on the thermally stimulated discharge (TSD) current of polymer electrets in order to gain insight into the mechanism of charge carrier generation, trapping, and other related relaxation processes involved in the electret formation (1). The characteristic peaks due to dipolar reorientation or detrapping of charge carriers-observed in a TSD thermogram-give an idea about the activation energy, relaxation time, and trap distribution (2). TSD has also been successfully used in the study of copolymers and polymers implanted with impurities (3, 4), but very little work has been done on the polymer blends.The technique has shown that for improving charge storage properties of polymers and obtaining strong and stable electrets, a better understanding of the structural or morphological details and dynamical properties of the polymers is required on both molecular and super molecular levels (5). It has been reported that the electret state in a polymer can be produced not only by conventional methods, but also by bringing about some structural changes in the electret forming materials (6). Investigations concerning the dependence of electrical properties on structure are, however, presently very sparse. Appropriate model systems are required to obtain definite conclusions. Multicomponent polymers, especially blends of two chemically different polymers that are partially compatible, comprise such model systems.

Polymethyl methacrylate (PMMA) is a branched amorphous and polar thermoplastic with ester group (COOCH$_3$) and methyl group (CH$_3$) as its two side groups. The methyl group (CH$_3$) may be located on the same side of the polymer chain alternate regularly or alternate at random. PVP powder is white, stable, hygroscopic and water soluble. It forms complexes with many substances. Coated PVP solution forms brittle, clear, and glassy films. It has plenty of applications like additives, adhesives, agriculture; coatings; cosmetics; medical devices; pharmaceuticals.Thus it is interesting to check how polymer behaves when two polymers are blended, which can give new insight on the electrical properties of new polymer blend. The obtained results are then discussed and conclusions are formulated based on the existing theories.

II. EXPERIMENTAL

The polymers used in are Polymethyl methacrylate (PMMA) and Circular specimen of average thickness 50 μm were obtained from the solution grown PMMA : PVP blends of various wt% ratio, 100:00, 95:00, 90:10, 85:15,80:20, and 00:100. The pure and blend films were obtained by dissolving various weight percentage of PMMA and PVP in a common solvent i.e., Benzene. The solution was continuously stirred for about 2 hours by means of a teflon coated magnetic which was at an temperature of 60 ^{o}C to ensure

homogenous mixing of both the solvents. Then this homogenous solution was slowly poured on a plane and cleaned glass plate kept in a mercury pool which was kept at an elevated temperature of about 60 °C in a thermostat. While pouring the solution it was insured that no air bubble should be there in films. Thereafter the solvent was allowed to evapourate inside the oven for about 24 hours. The films from glass plates were slowly removed with help of sharp edge blade or knife.The samples were, sandwiched between two aluminium electrodes and kept in the sample holder which was placed in a temperature controlled oven. The upper electrode was given a positive potential through a high voltage power supply while the lower electrode was grounded. The temperature of the specimen was raised to the desired value (T_p) and the temperature was maintained for half an hour. After this the power supply was turned on and the desired polarizing voltage (V_p) was applied for 30 minutes. It was then allowed to attain room temperature with the polarizing field. The total time of polarization was thus adjusted to be 1 hr 30 mins in each case. The field was then removed and the thermoelectret was then short circuited at room temperature for 5 minutes to remove the frictional and stray surface charges.

For TSDC measurement, the sample was short circuited through an electrometer and was reheated at a linear heating rate of 3 °C/min. The depolarization current was recorded at regular temperature intervals using an Electrometer EA815 ECIL India. For the present investigation thermoelectrets were prepared at constant polarization temperature 60 °C with polarizing fields of 50, 70, 90 and 110 kV/cm. The different samples prepared were pure PMMA, PVP and their polyblends in different weight ratios i.e. 95:5, 90:10, 85:15 and 80:20 (in PMMA : PVP combinations), and are designated as P_1, P_2, P_3, P_4, P_5 and P_6 respectively.

III.   RESULT AND DISCUSSION:

Thermally stimulated depolarization current (TSDC) spectra for P_1, P_2, P_3, P_4, P_5 and P_6 samples polarized with poling field 50, 70, 90, and 110 kV at constant temperature 60 °C are shown in Figures 1 – 6, respectively.   The TSDC spectra for pure PMMA samples (Figure 1) exhibit two well resolved peaks designated as α and ρ respectively, in the ascending temperature. The low temperature peak observed at 90 ± 5°C in the TSDC thermogram of PMMA can be considered to arise due to relaxation process associated with the micro-brownian motion of the main chain segments near the T_g of the polymer. The second peak observed at 160 ± 10 °C was found to correspond to an activation energy value of 0.31 eV. The peak height increases almost linearly with an increase in forming field. As the temperature is increased more and more dipoles are rendered free, which are oriented by the field. Hence, the peak position must shift towards higher temperature side as is observed in the present case. This peak indicates that there is a build-up of space charge near the electrodes and hence this peak may be designated as the space charge ρ-peak.The TSDC thermograms of PVP (Figure 2) electrets also show two well resolved peaks at 95 ± 5°C and 155 ± 5°C. The first peak (α) is attributed to disorientation of polar side groups. The polar side group pyrrolidone ring in PVP has carbonyl group of double bond.

This group is attached to the main chain with an amide bond. Here the pyrrolidone group may have different possible orientations/rotations with respect to the main chain of the polymer and thus a distributed energy is associated with TSDC results. The value of activation energy (E) associated with this peak is found to be 0.51 ± 0.13 eV and is related to disorientation of polar groups of PVP. The second peak (ρ) is associated with the primary relaxation process which occurred in the temperature range 155 ± 5 °C of glass transition of PVP. The value of E calculated for ρ-peak is found to be of the order of 1.03 ± 0.16 eV which suggests the possibility of ionic processes (7), and is related to charge carriers of ionic nature. PVP exhibits the properties of solid free radical, probably at the temperature of the phase transition. Hence, the ionic and other charges may certainly be present during polarization of the sample. In PVP the different charge/ions are due to the presence of different active groups (8). All types of dissociated ions are possible including opposite charge carriers, at T_g. The releasing of the carriers/ions from the polarized state seems to be possible at the ρ-peak temperature. The structure also gets loosened to some extent, in this way, all types of charge carriers are released giving rise to a peak (ρ) in higher temperature region. This is in agreement with the earlier finding (9).

TSDC thermograms for polyblends P_3, P_4, P_5 and P_6 represent single peak around 140-180°C (Figures 3-6). For all polyblend samples initially current was of higher order and show decaying nature in temperature scale, after a particular temperature a sharp peak is found. The thermograms of the variation in peak current with poling field for various samples are shown in inset of the corresponding TSDC thermogram. The order of current in polyblend samples was higher as compared to pure polymer samples. There is no appreciable shift in the positions of two peaks for various polarizing fields (In reality there is small shift both ways right and left which is due change in the relative magnitudes of the various peaks as the polarizing field increases). For the ρ-peak the current is higher than for α peak. The height of current peaks is found to rise in magnitude with the increase in polarizing field.

The electrification of the polymers takes place due to one or more than one of the following mechanisms operative simultaneously when it is subjected to dynamical, mechanical or thermal treatment with or without static electric fields. The mechanisms are (i) Space charge injected into the dielectric by surface breakdown between the dielectric and the electrode, (ii) Space charge injected from the electrodes, (iii) Space charge caused by migration of charge carriers over macroscopic distances, (iv) Electronic or ionic dipoles caused by migration of charge over microscopic distances, and (v) Orientation of permanent dipoles.

Application of an electric field always produces a small movement of charges within the atoms of a dielectric, displacing the negative electronic cloud relative to the positive nucleus and thus temporarily generating a small dipole moment and a consequent atomic or deformational polarization. This effect occurs within very short times, its time scale cannot be changed from outside. Thus, its influence on the persistent polarization of the electrets can be disregarded. Many dielectrics, including polymers, contain molecules that have an electric moment. An applied field tends to align these elementary dipoles along its own direction and thus produce an electric moment of the whole body giving rise to dipole polarization essentially volume effect. Under the influence of electric field the irregularly distributed dipoles of side chains are oriented in a certain direction. Thermal activation at a constant rate causes the release of charges giving a peak at the site of maximum release of charge. The increase in current magnitude with electric field may be attributed to the increase in mobility of charge carriers.Generally, polymers contain a small number of free charge carriers, i.e. ions, electrons or both (10). During electret formation, the carriers move comparatively free in the direction of the applied field over microscopic distances before they fall into deep traps from which they can be released only on receiving sufficient energy.

Dipole orientation is strongly temperature dependent; at high temperature the force opposing rotation are lessened. Thus, a high degree of polarization can be achieved in a short time by application of an electric field at high temperature. If the dielectric is cooled and the field removed only after a low temperature has again been reached, dipoles return to the original disordered state very slowly because rotation is hindered by strong viscous forces. The polarization is thus frozen-in. A similar behavior is found in the case of space charge and interfacial polarization. The mobility of charge carriers is very low at room temperature but increases strongly with temperature. Thus, the previous reasoning applies here too. Space charge clouds and charges accumulated along interfaces can be frozen-in.

The temperature dependence of the dipole orientation can be differed from the motion of excess charges. The later will confirm closely to that of ohmic conduction from which the charges often originated. In particular we may expect the current maxima for dipole reorientation to occur at lower temperature than that of the excess charge motion. The first process requires only a rotational motion of molecular groups whereas the latter process involves a motion of molecular groups (ions) over macroscopic distances. The activation energy predicted theoretically for the relaxation process resulting from the local twisting of the main chain or the orientation of the side groups in a polymer is about 0.2eV (11). The relaxation process associated with the peak is the orientation of the side groups and or local twisting of the main chain. The charges may also be injected from electrodes into the polymer film. It is only at temperatures above the glass transition of the polymer that the molecular chains are sufficiently agitated to release the charges stored in them.

One of the arguments advocated for distinguishing a dipolar polarization and space charge polarization is based on the field dependence of the TSDC properties (i.e. the peak current, peak temperature and charge released). The linear dependence of charge on polarization field strength is a characteristic of dipolar origin whereas, in the case of space charge polarization the peak current and charge released will show a non-linear variation with polarizing field strengths. For a dipolar peak the peak temperature will be independent of polarizing field strength and polarizing temperature whereas, the peak temperature depends on the poling field and temperatures of the space charge polarization. In the segments, mobility may be increased after the complete phase transition and thus the possibility of injection of charge carrier near the electrodes and their drift to be possible by self motion of charge carriers/ions above T_g range. Above T_g of the polymer, a sudden change in its volume may occur and thus structural rearrangements of chains (segments) may be possible due to sufficient mobility of segments. The detrapping mechanism at higher temperature may be possible and the charge carriers may get trapped to some deeper traps levels which are available for trapping.

The activation energy is observed to decrease with the increase in polarizing fields and weight% composition. This suggests that peak is not due to a discrete level having a single relaxation but is a complex one having distributed activation energies. Furthermore, as the polarizing fields increases, the barrier height of the traps in which the charges are found is lowered accounting for the observed decreases of the activation energy with increasing field. Blending has been found to influence the TSDC behavior considerably. The peak in the higher field region suggests that it may be contributed both by electronic and ionic processes arising in the bulk and injected from the electrodes which are subjected to higher field. It is not a simple process but a

complicated one of Maxwell- Wegner type (12). Alternatively, it may be due to distribution in relaxation times, when the rotational masses of the dipoles are not equal. The TSDC peak in the present case is, however, most likely to be a function of distribution in relaxation times, because the peak occurs near the T_g of the polymers, where the side groups move in unison with the main chain. Because the distribution of dipoles in the amorphous phase is most likely to be random, it may be expected that this is a complex process involving both distribution of the activation energy and relaxation times (13). It was found that magnitude of current increases with different weight % of PVP in PMMA matrix. It is expected that the number of shallow traps with small detrapping time is considered to increase with increasing weight of PVP hence the total amount of space charge will be relatively greater at low temperature charged samples with weight % PVP than the samples with small weight % PVP charge at the same temperature. This may also be attributed to an increased orientational effect owing to more available free volume due to plasticization effect. Plasticization causes loosening of the structure and provides greater mobility to charge carriers resulting in the increase of peak current (14).

The observed dependence of peak current on forming field (E_p) indicates that trapped charge carriers leading to formation of space charge may also be responsible to a considerable extent for TSDC and may mask the dipole reorientation process. The non linear variation of in some cases with forming field is understandable because at higher temperature the number of thermally liberated and injected charge carriers is expected to increase which ultimately get trapped and frozen in during subsequent cooling.

Considering the effects of various parameters in pure and polyblend we conclude that the polarization is due to trapping of the bulk charges, produced charges as well as the electrode injected charges in the deeper traps and their subsequent alignment due to the step field. It is also possible that polymers contains a high number of impurity molecules prior to field treatment and these molecules are dissociated into various ionic species by a combination of the high internal and external fields. The charge trapping in a polymer takes place at the molecular main chain, the side chain and at the interface of crystalline and amorphous regions of the polymer (15). The high field applied during electret formation may also produce some additional trapping sites. The charge released from these traps occurs because of the thermal excitation and motion of molecular chain that causes the lowering of trap depth. The released charge can recombine, retrapped in trapping sites or may get discharged at the electrodes. The chances of retrapping of the released charge are high in a polymer having a large number of trapping sites and it is expected that the discharge will give complex TSC spectra with broad peaks indicating a distribution of activation energies. The peak observed in the thermograms is not due to single relaxation but seems to be complex and may arise due to the release of the frozen dipoles by their cooperative motion with adjoining segments of the main polymer chain.

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Figure 1 : TSDC thermogram for PMMA samples poled at 60 ^{o}C with different poling fields (i.e. 50, 70, 90 and 110 kV/cm).
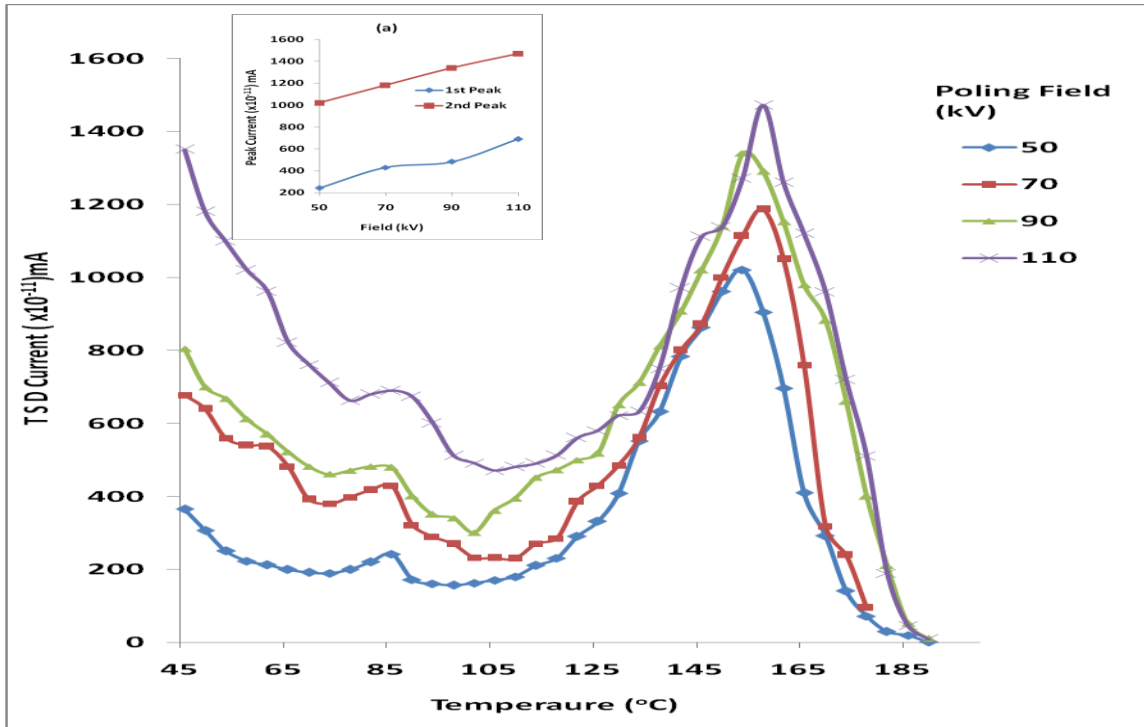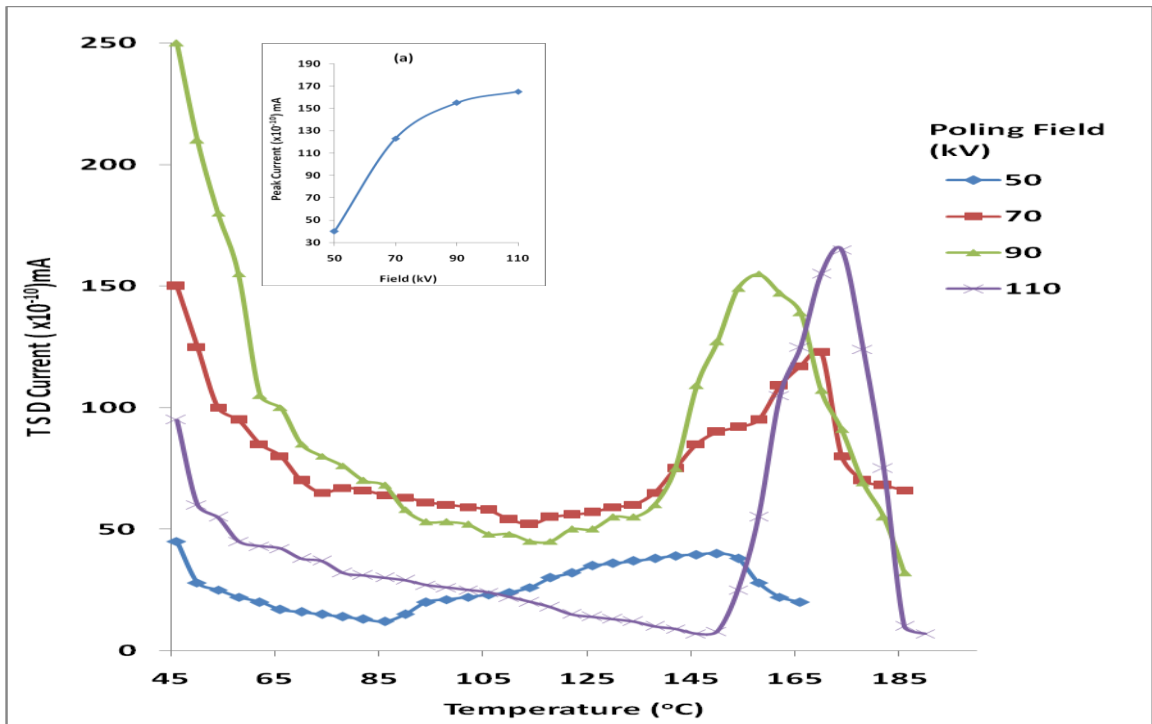

Figure 2 : TSDC thermogram for PVP samples poled at 60 ^{o}C with different poling fields (i.e. 50,

70, 90 and 110 kV/cm).

Figure 3 : TSDC thermograms for 95:05 polyblend samples poled at 60 °C with different poling fields (i.e. 50, 70, 90 and 110 kV/cm).
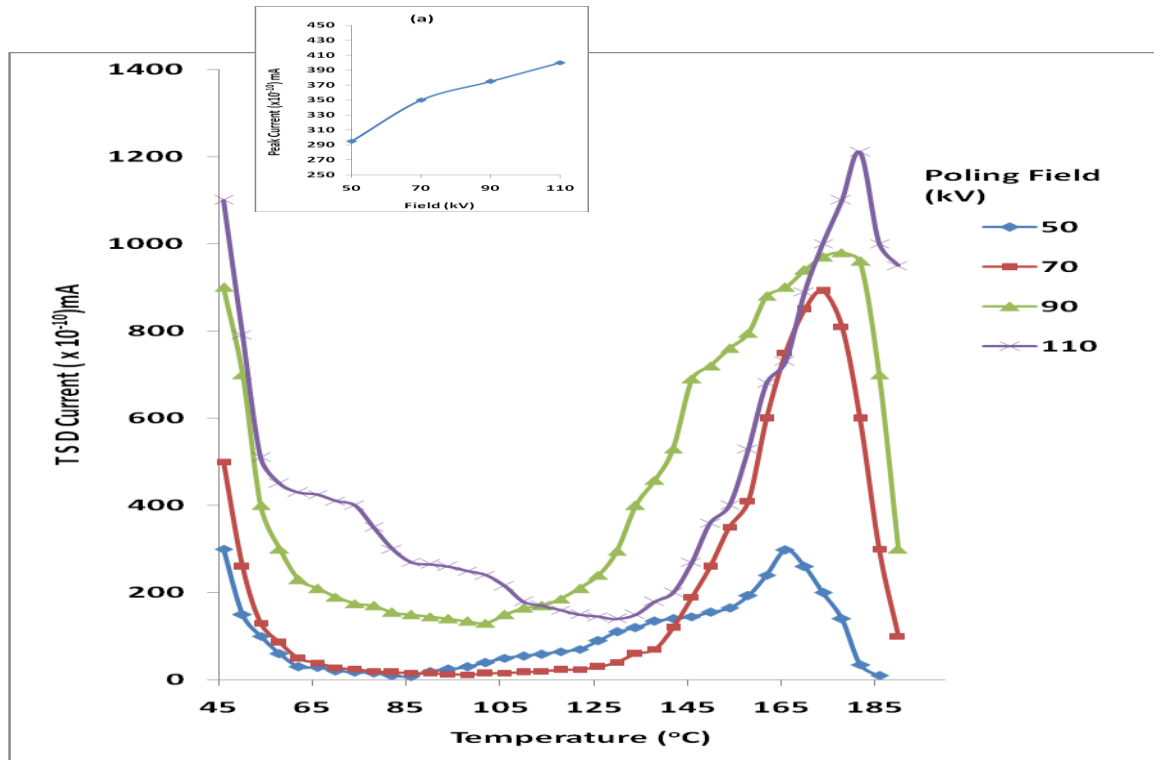

Figure 4 : TSDC thermograms for 90:10 polyblend samples poled at 60 °C with different poling fields (i.e. 50, 70, 90 and 110 kV/cm).
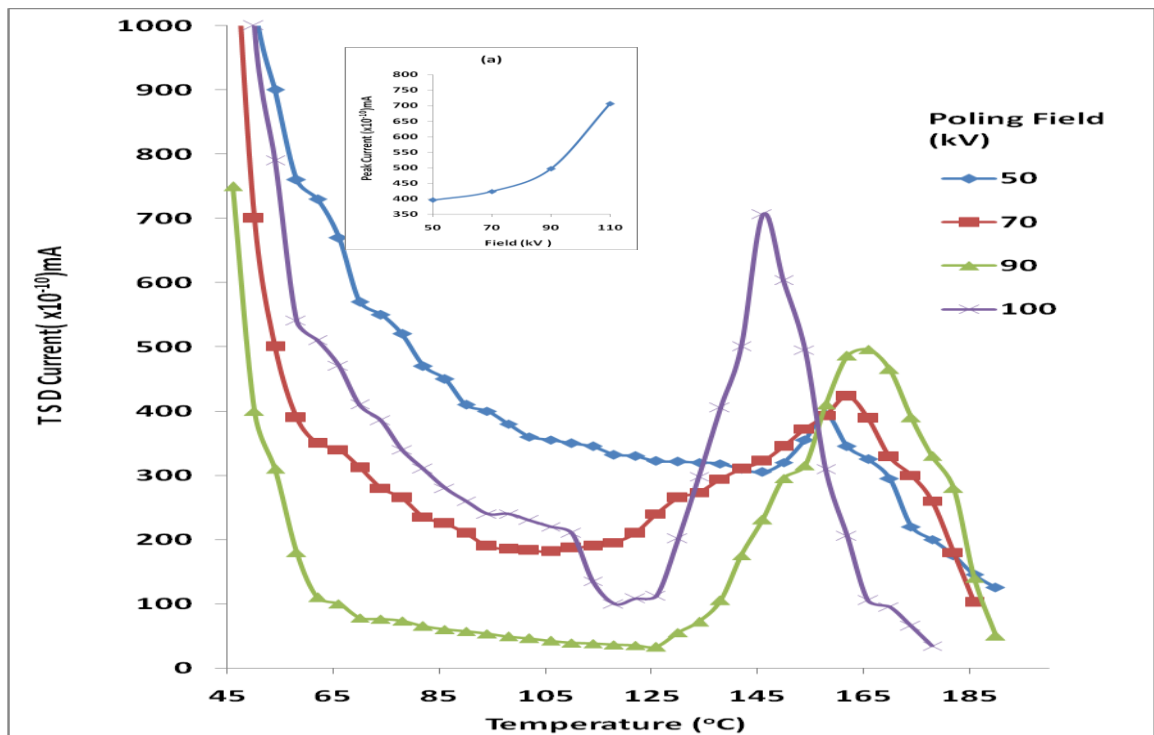
Figure 5 : TSDC thermograms for 85:15 polyblend samples poled at 60 °C with different poling fields (i.e. 50, 70, 90 and 110 kV/cm).
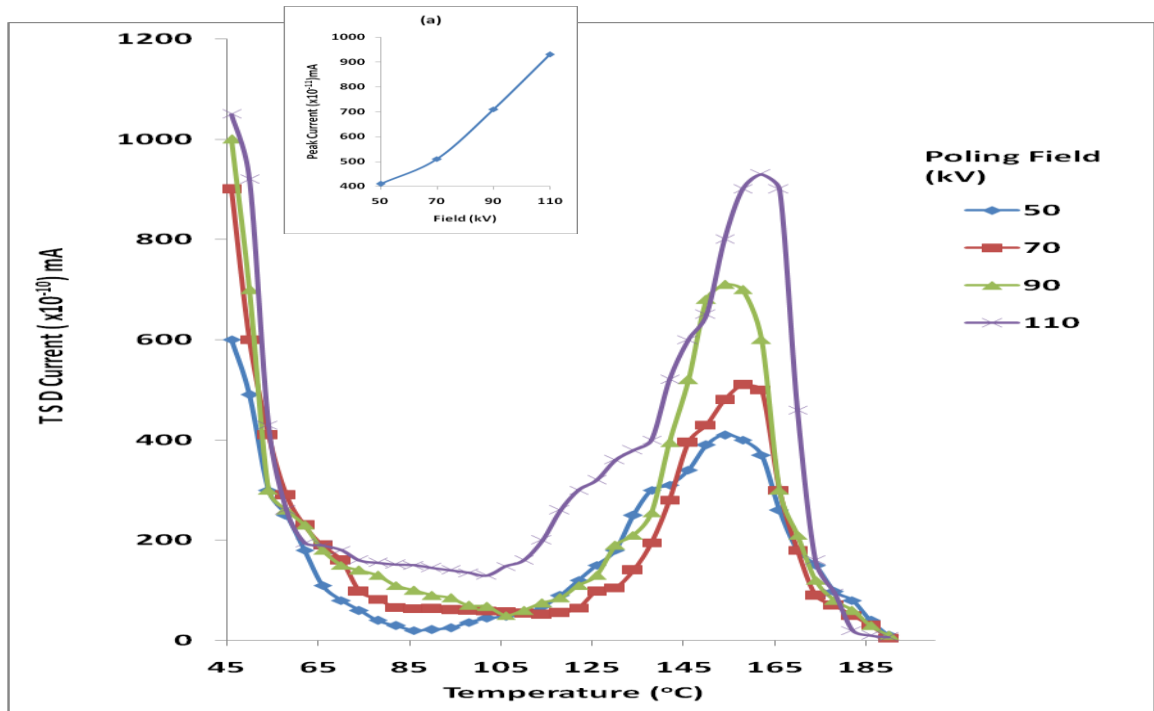

Figure 6 : TSDC thermograms for 80:20 polyblend samples poled at 60 °C with different poling fields (i.e. 50, 70, 90 and 110 kV/cm).