INVESTIGATION OF MECHANISMS RESPONSIBLE FOR OBSERVED BROAD DIELECTRIC RELAXATION AND COMPATIBILITY OF POLYSULFONE- POLYVINYLIDENEFLUORIDE BLENDS

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Abstract : Short circuit thermally stimulated depolarization current measurement techniques has been employed to investigate the dielectric relaxation behavior of PSF: PVDF blends. The samples taken were blends of composition PSF: PVDF:: 80:20; 85:15; 90:10 and 95:05 percent by weight. Bimetallized samples were polarized at different temperatures 60, 75, 90 and 115^0C with various fields 100, 150, 200 and $250kVcm^{-1}$. The short circuit TSDC thermograms of the electrets thus obtained were recorded by reheating the sample in short at a linear rate of $3^0C/min$. The thermograms were characterized by a high value of initial current, a low temperature peak around $75-80^0C$ and a prominent broad peak in the temperature interval 130 to 160^0C. The open circuit thermograms were recorded on bimetallized electrets in a similar way by introducing an air gap between collecting electrode and the electrets. The open-circuit thermograms were characterized by a current of positive polarity with a peak in the temperature interval $150-160^0C$.A comparison of short circuit thermograms with the open circuit thermograms revealed that the peaks observed in the TSDC thermograms are caused primarily by motion of excess charges. The two polymers are found to form compatible blend in the studied composition range.

IndexTerms – PSF, PVDF, TSDC, Glass- Transition Temperature (T_g), Activation Energy
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I. INTRODUCTION

In recent years considerable attention has been shown to the study of polymeric blends [1-9]. Polymer blends are mixture of at least two macromolecular species, polymer and/or copolymers. The name blend is given to a system only when the minor component content exceeds 2wt%. Blending provides a simple, efficient and economical means of meeting requirements for new materials for applications in various areas. A proper selection and combination of polymeric components in an appropriate ratio might result in a material with optimal properties for specific applications in microelectronics and engineering. A remarkable broad spectrum property can often be achieved by blending. This includes mostly processability, thermal stability, micro-mechanical strength, stiffness etc.

It has been recognized that the useful physical properties of polymers depend not only on the chemical structure but also on their supermolecular organization [1-7]. Polymers are characterized by a large number of intermediate stages of ordered arrangement of chains i. e. the existence of various levels of supermolecular organization which intervene between the crystalline and completely amorphous phases. Studies on polymeric blends, is therefore, important from the point of view of understanding morphology- property relationship or properties in relation to the crystalline and amorphous content of the polymer. The morphology of a polymer blend can be tailored and it is, therefore, possible to achieve a host of properties which can not possibly be obtained by homopolymers alone.

Many techniques including thermal analysis and scattering methods have been used to look at microscopic and macroscopic phenomena with regard to morphology, crystallization and interfacial properties. TSDC is a powerful technique with sensitively comparable to dynamic mechanical and dielectric loss measurements. For the standard TSDC experiment which is comparable to a dielectric loss measurement the low equivalent frequency ($\approx 10^{-3}$Hz) and high sensitivity makes TSDC very useful for the study of amorphous relaxations in blends. Further, for semicrystalline materials, the low equivalent frequency offers one additional advantage. The glass transition temperature T_g is shifted to low temperature and the glass transition of the purely amorphous phase can be studied without inducing crystallization [8].

Many polymeric blends have been found and reported over the last few decades. Polymeric blends of Polysulfone (PSF) and Polyvinyledene fluoride (PVDF) is one such important blends. Polysulfone are a class of amorphous engineering polymers with excellent thermal, mechanical, chemical and hydrolytic stability, though it is hydrophobic. The polymer has been a material of interest for researchers for many decades [9-17].

PVDF on the other hand is a semicrystalline polymer which has drawn both scientific and technological attention because of its useful piezo-and pyro-electric properties. It is also one of the rarest polymers that exhibits diverse crystalline forms having at least five phases namely α, β, γ, δ and ε [18-19].

Electrical behavior of polymeric blends of PSF and PVDF containing higher percentage of PVDF has been investigated by saxena *et al*. [20-22]. They have attributed the observed polarization behavior primarily to induced dipoles. It, however, appears that the mechanism responsible for the relaxation behavior of such blends is not completely understood. Further, such studies on these blends are still sparse [20-22]. A detailed investigation on the polymeric blends of these two polymers giving particular attention to the blends containing low percentage of PVDF has, therefore, been undertaken with the view to understand the fundamental origin of relaxations in the amorphous polymer PSF in general, and to understand the morphology-property relationship, in particular, by blending it with the semicrystalline polymer PVDF.

II. METHODOLOGY

The commercial PSF (*UDEL P1700 PSF granuals*) and PVDF (*Solef 1015 PVDF Powder*) used for the present study were procured from Solvay Corp. Ltd, Belgium and supplied by Redox Ltd. (India). The weight-average molecular weight of PVDF is 2, 61, 000 and that of PSF is 66, 000. The samples for the present investigation were prepared by the solution cast technique. The solution of particular concentration was prepared by dissolving the two polymers PSF and PVDF in different weight ratios in their common solvent N, N, Dimethyl formamide (DMF) at 80^0C. This solution was then poured on clean glass plates floating on a mercury pool kept in a dust free oven at a constant temperature, $T = 80^0$C, and a time of for 5 hr was given to yield blend films which was then peeled off from the glass plate . Blend samples of thickness approximately 15 -25 µm and of wt% compositions PSF: PVDF:: 80:20; 85:15; 90:10 and 95:05 designated as PB1, PB2, PB3 and PB4 respectively, were prepared. Polymers and the chemicals were used as supplied without any further purification. For TSDC measurements samples were polarized with fields of E_P = 100, 150, 200 and 250kVcm^{-1} at temperatures T_P = 60, 75, 90 and 115^0C. After polarizing for 45 min at the desired temperature, the sample was cooled to room temperature in the presence of field. The total time of polarization was adjusted to be 1. 5 hr in each case. The TSDC in short circuit of the samples thus charged were obtained by reheating the samples at linear rate of approximately 3^0Cmin^{-1} and the depolarization current was measured by means of a sensitive electrometer Keithley Electrometer (610 C). For open circuit TSDC measurement an air gap of 0.6 mm was introduced between upper electrode and the bimetallized electrets surface using taflon ring spacers.

III. RESULTS
(A) Short Circuit TSDC's
3.1   Effect of Poling Temperature

Typical TSDC thermograms for PB1 and PB3 samples polarized with a field of E_P = 250kVcm^{-1} at various temperatures are shown in Figure 1 and 2. The thermograms, in general, exhibit a well define broad peak between 130 to 150^0C; a small hump is also observed in some cases centered around 100^0C. The thermograms for PB3 samples polarized at T_P = 115^0C exhibit a low temperature second peak around 75 - 80^0C. Such thermograms are characterized by a high value of initial current. A shift in high temperature peak position is observed with increase in polarizing temperature though it is not very clear; however, the magnitude of TSD current as well as peak current, in general, is clearly found to increase with the increase in polarizing temperature.
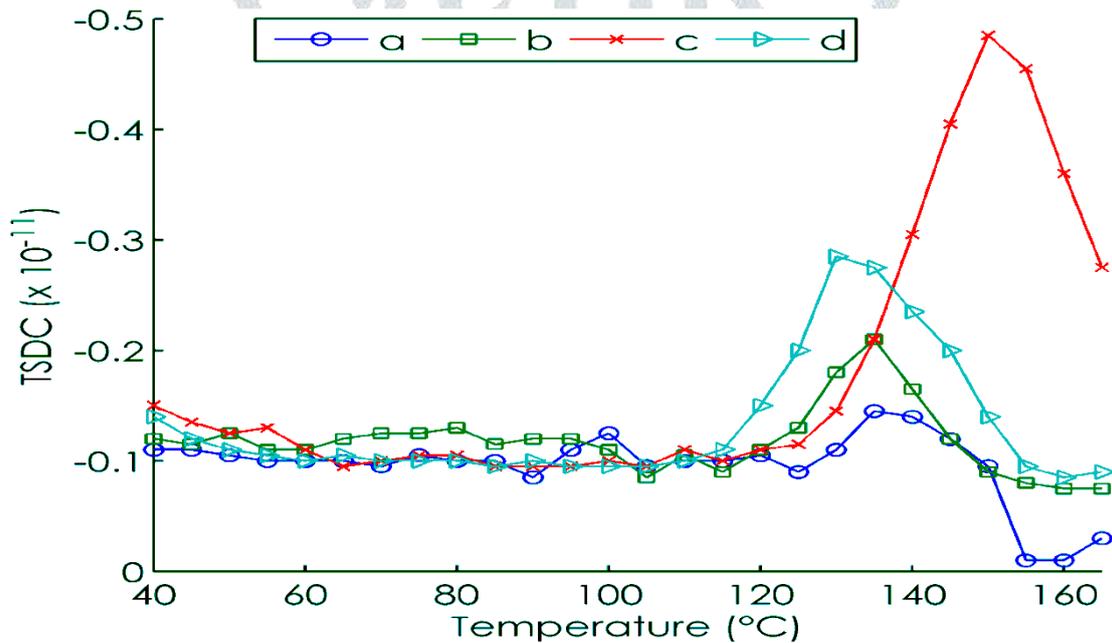

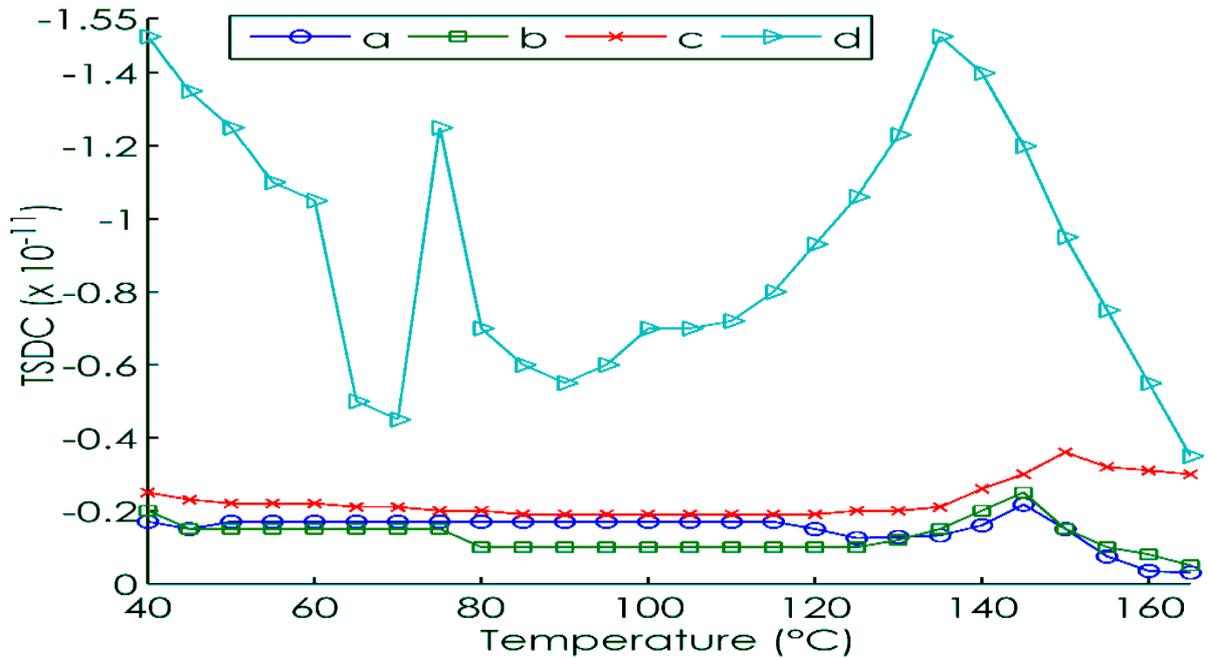**Figure 1** Effect of T_P on TSDC thermograms of PB1 at E_P =250kVcm^{-1}: (a) 60^0C (b) 75^0C (c) 90^0C (d) 115^0C

Figure 2 Effect of T_P on TSDC thermograms of PB3 at $E_P = 250kVcm^{-1}$: (a) 60^0C (b) 75^0C (c) 90^0C (d) 115^0C

3.2   Effect of Poling Field

The field dependence of the PSF: PVDF blend was investigated by TSDC thermograms for PB1 samples polarized at temperature 115^0C with various fields 100, 150, 200 and $250kVcm^{-1}$. The thermograms exhibit complex field dependence. It is evident from the Figure 3 that the thermograms exhibit a well resolved broad peak between 130 to 160^0C. Further, TSDC curves are characterized by a high value of initial current. The peak position is independent of the polarizing field. However, the TSD current as well as the peak current initially decreases with increase in the polarizing field, then increases for high values of polarizing field but finally again decreases for still higher values of polarizing field.
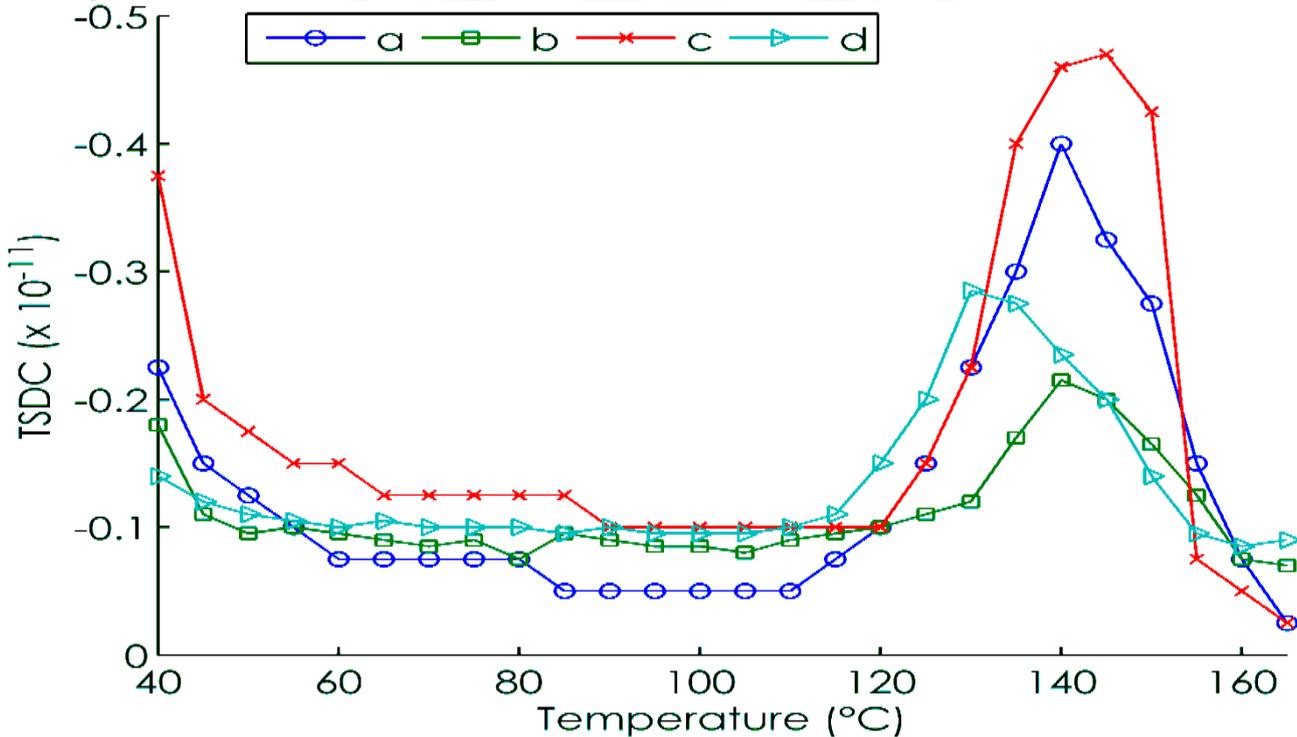

Figure 3 Effect of E_P on TSDC thermograms of PB1 at $T_P = 115^0C$: (a) $100kVcm^{-1}$ (b) $150kVcm^{-1}$ (c) $200kVcm^{-1}$ (d) $250kVcm^{-1}$
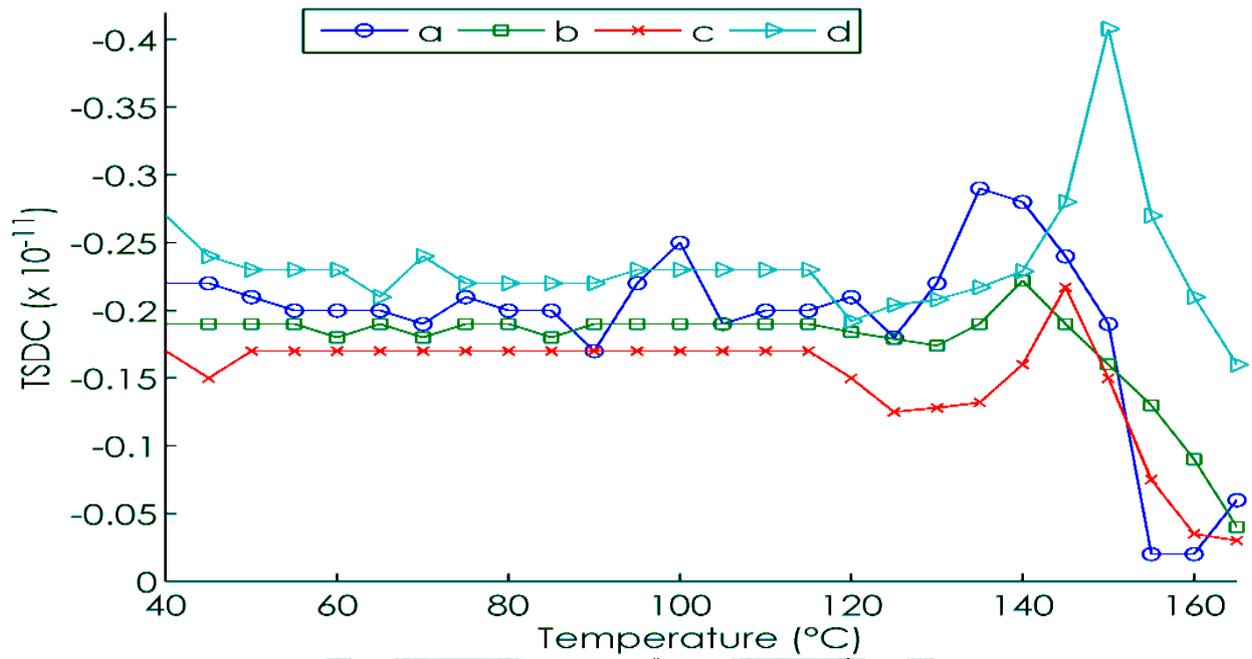
Figure 4 Effect of wt% on TSDC thermograms for $T_P=60^0C$, $E_P=250kVcm^{-1}$: (a) PB1 (b) PB2 (c) PB3 (d) PB4

3.3　Effect of Wt% Composition of the Blend

Figure 4-6 shows the TSDC thermograms for PSF: PVDF blends with various wt % compositions and polarized with a field of $E_P =$ $250kVcm^{-1}$ at temperatures $T_P = 60$, 90 and 115^0C. The TSD current as well as peak current exhibit composition dependence. For low polarizing temperatures TSD current as well as peak current decreases with increase of PVDF content in blend. For moderate temperatures TSD current and the peak current increase with the PVDF content. However, for samples polarized with very high polarizing temperatures the current increases with increase in the PVDF content but shows decrease for high wt% content of PVDF in the blend. The thermograms thus exhibit complex field dependence.
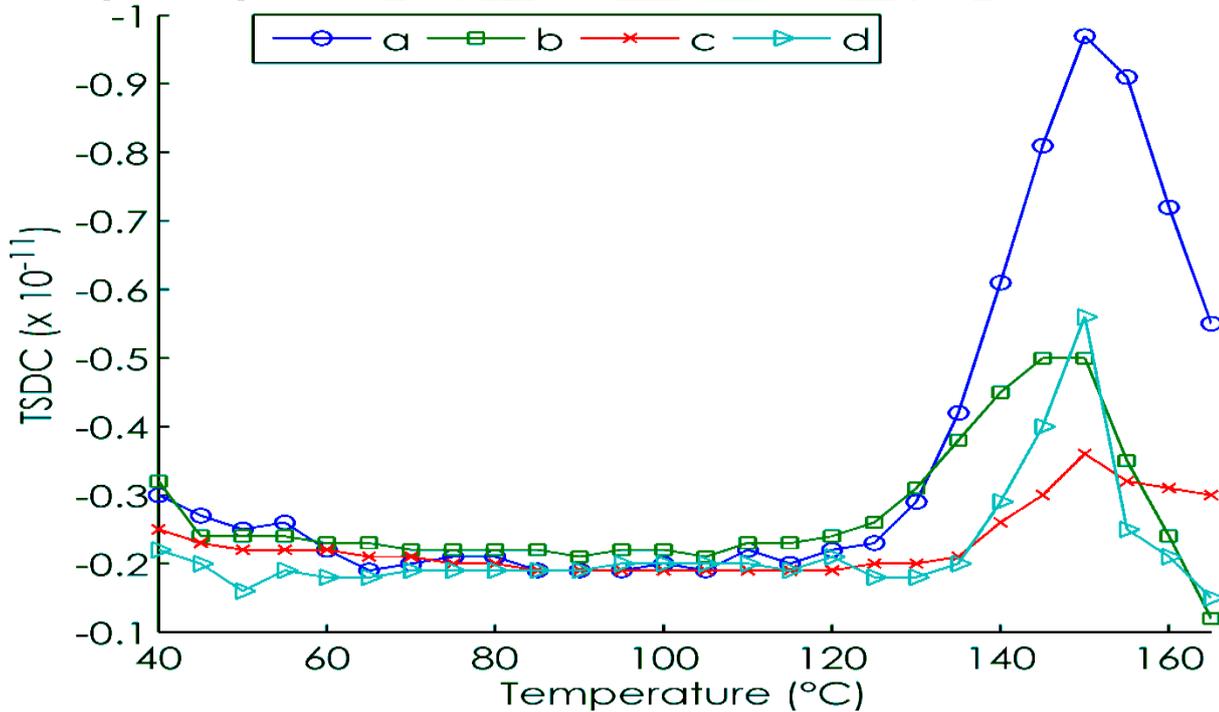

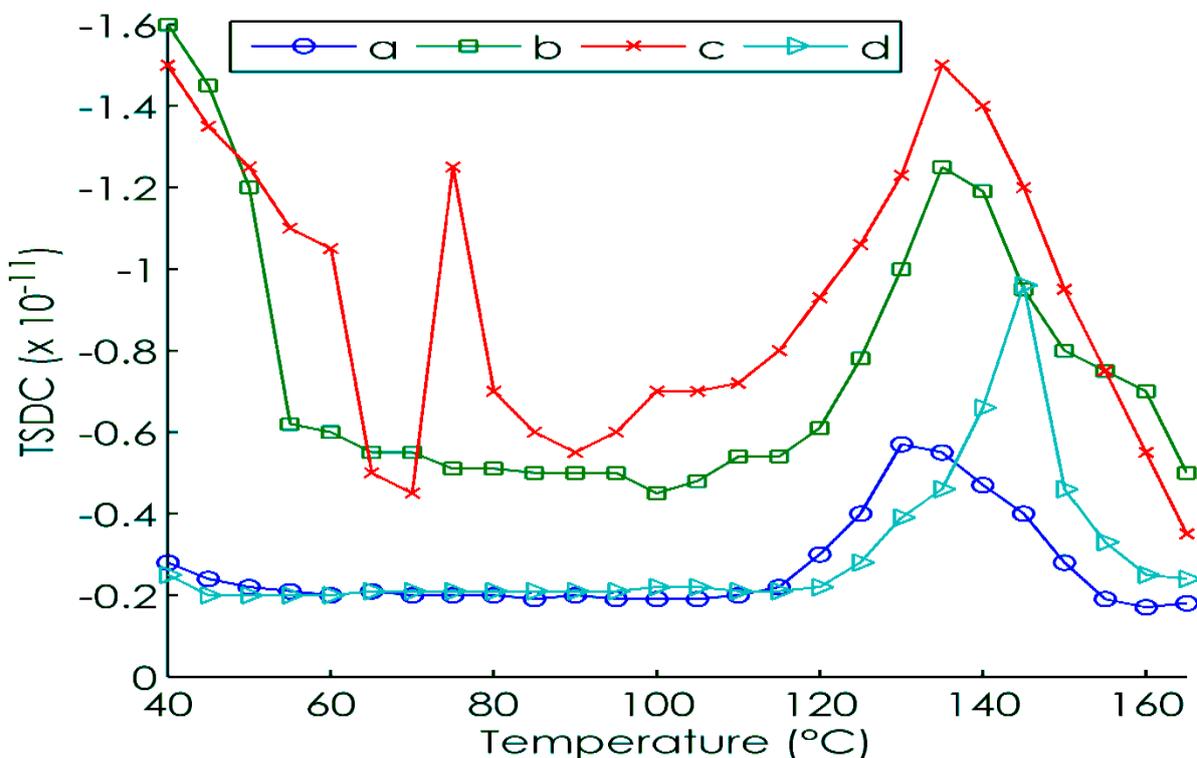**Figure 5** Effect of wt% on TSDC thermograms for $T_P=90^0C$, $E_P=250kVcm^{-1}$: (a) PB1 (b) PB2 (c) PB3 (d) PB4

Figure 6 Effect of wt% on TSDC thermograms for $T_P=115^0C$, $E_P=250kVcm^{-1}$: (a) PB1 (b) PB2 (c) PB3 (d) PB4

3.4 Calculation of Activation Energy

The activation energy values associated with the high temperature peak for various blends have been calculated using the initial rise method of Garlick and Gibson [23] and are listed in Table 1. The activation energy is, in general, found to decrease with increase of PVDF content in the blend; except for PB1 blend for which it is found to increase.

**Table 1** Activation energy for different blend composition at $250kVcm^{-1}$ poling field

Blend Composition	Poling Temperature(°C)	Activation energy(eV)
PB1	60	0.66
	90	0.96
	115	0.84
PB2	60	0.34
	90	0.48
	115	0.50
PB3	60	0.73
	90	0.52
	115	0.35
PB4	60	0.86
	90	1.01
	115	0.77

(B) Open- Circuit TSDC's

Figure 7-8 exhibits the open circuit TSDC thermograms for PB1 samples. For comparison the corresponding short circuit thermograms for such blends have been combined with the open circuit thermograms.

3.5 Effect of Poling Temperature

Figure 7 shows the open circuit TSDC thermograms for PB1 samples polarizing with a field of $250kVcm^{-1}$ at a various temperatures. The curves are characterized by a positive current flowing in a direction opposite to the short-circuit current throughout the TSDC cycle characterized with a peak located in the temperature interval $130\text{-}160^0C$.
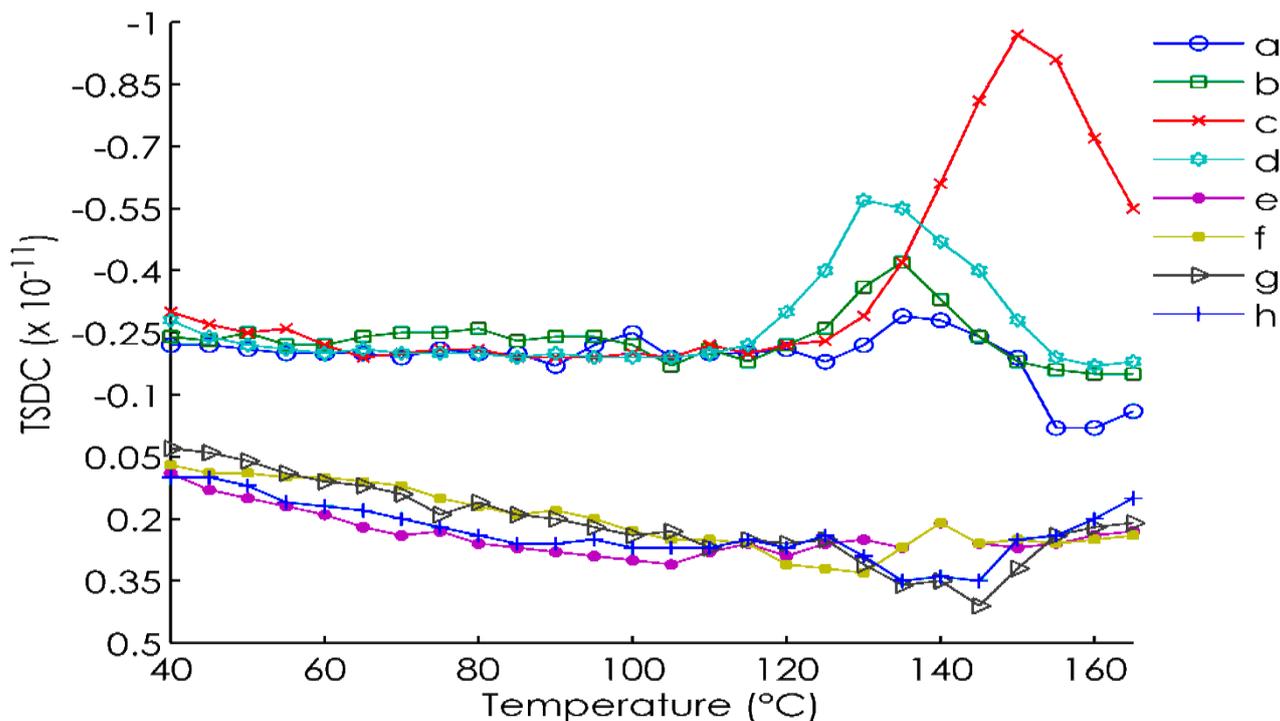
Figure 7 Effect of T_P on TSDC (Short and open circuit mode) thermograms of PB1 at E_P =250kVcm^{-1}: for short circuit mode (a) 60^{0}C (b) 75^{0}C (c) 90^{0}C (d) 115^{0}C; for open circuit mode (e) 60^{0}C (f) 75^{0}C (g) 90^{0}C (h) 115^{0}C

3.6 Effect of Poling Field

The field dependence of the open-circuit TSDC thermograms has been depicted by Fig. 8 for PB1 samples polarized with various fields at the polarizing temperature 115^{0}C. A positive current has been observed characterized with a peak in the temperature range 130-150^{0}C. No clear dependence of the open circuit TSD current in the polarizing field has been observed.
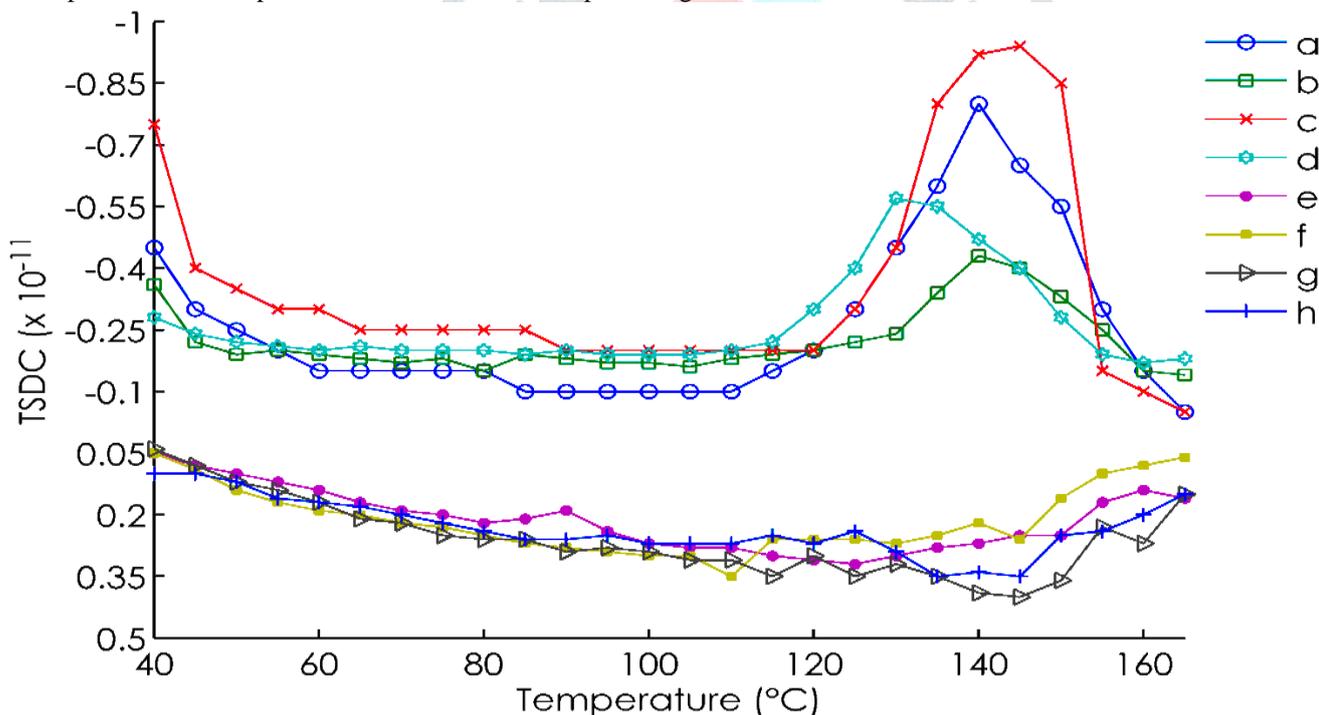
Figure 8 Effect of E_P on TSDC(Short and open circuit mode) thermograms of PB1 at T_P =115^{0}C : for short circuit mode (a) 100kVcm^{-1} (b) 150kVcm^{-1} (c) 200kVcm^{-1} (d) 250kVcm^{-1} ; for open circuit mode (e) 100kVcm^{-1} (f) 150kVcm^{-1} (g) 200kVcm^{-1} (h) 250kVcm^{-1}

IV. DISSCUSSION

   Persistent polarization in thermally charged specimen arise due to various mechanisms , the important among which are dipolar polarization, space charge polarization and translation and trapping of charge carrier at microscopic distances or accumulation near the electrodes and interfacial or Maxwell Wagner effect that is trapping of charge carrier at phase boundaries. The charge originated in TSDC due to dipole orientation or trapping of charges in defects or dislocation sites is known to give rise to uniform polarization which is heterocharge. On the other hand, space charge built up by migration of ions over microscopic distances gives a non uniform heterocharge, whereas trapped injected space charge results in a non- uniform homo -or hetero-charge, depending upon the work function of the metal electrode.

   In the present investigation, the thermally stimulated discharge current is found to flow in the directions opposite to the charging current; thus process involving hetero- charge formation are mainly responsible for polarization in the blends.

Relaxation processes in the polymer are related to molecular motions of the amorphous and /or crystalline chains. It is well known that most of the amorphous polymers exhibit a secondary β-process and a principal- or an α-relaxation located at lower frequencies or higher temperatures then the β-relaxation. By dynamic mechanical relaxation studies two relaxations have been reported in PSF; an α-relaxation at temperatures above 156^0C, and a β-relaxation appearing at lower temperatures [9-10].

The β-relaxation reported in PSF is characterized by a loss maxima at about -43^0C [9-12]. This relaxation has been ascribed to rotational movement of adsorbed water molecules bound to polar groups along the polymer chains. The TSDC cycle in the present case has been carried out at temperature above the room temperature ($≈30^0$C) which is much above the temperature of β-relaxation of PSF. Nevertheless, the high value of initial current observed in all the thermograms does point towards the existence of atleast one relaxation peak at some temperature below 30^0C.

The α-relaxation in PSF characterized by a rapid increase of the mechanical loss with increasing temperature typical for the mechanical relaxation effects correspond to the onset of large scale molecular motions. It has, therefore, been associated with the T_g, the transition from the glassy state to the rubbery state ($≈176^0$C) where large free volume is available for such motions.

The short circuit TSDC thermograms in the present investigations are characterized by a well resolved peak in the temperature range 130-160^0C. The peak exhibits the characteristics of dipolar behaviour in the sense that as the polarizing temperature is increased the peak height is increased and the peak temperature, in general, shifts towards the high temperature side. As the temperature is increased an increasing number of dipoles are oriented and as a result during charging more and more subpolarizations are filled. During depolarization the magnitude of peak TSDC is, therefore, increased and the peak is expected to shift towards the high temperature side. This peak appearing in the temperature range 130-160^0C at first sight, therefore, primarily be ascribed to the onset of dipolar orientation processes in the blend. However, it has to be noted that the polarizing temperature used in the present investigation are considerably low than the T_g of PSF and the blend, therefore, it seems unlikely that the above peak originates due to dipolar reorientation alone; some other processes may also be operative.

The broadness of the peak may be explained in terms of distribution of relaxation times. This distribution may arise from the difference in the natural frequency or the activation energy of the dipole groups [24]. In case of polymers this is more likely to arise from the difference in the natural frequency because these peaks are associated with glass rubber transition where the polar side groups move in unison with parts of the main chains differing in mass [25].

From the various curves it is evident that in addition to the high temperature peak observed in the temperature range 130-160^0C, a small hump is also observed around 100^0C and in the case of PB3 sample charged at 115^0C with a field of 250kVcm^{-1}, a well defined peak is observed around 75^0C. Further, the TSD current, in general, is also increased with PVDF blending. Relaxation processes in the crystalline polymer are related to molecular motion of amorphous and /or crystalline chains. The peak occurring at 75-80^0C and the small hump around 100^0C may be attributed to $α_c$ -dipole relaxations in the crystalline phase of PVDF [17-18]. This relaxation has been observed by several workers in phase II (non- polar) PVDF[17-18]. It has been reported earlier that the PVDF crystals in solvent cast films are mainly phase II [7].

The peak ascribed to α –relaxation in PSF may also have some contribution from relaxations in PVDF. Polymer PVDF is a semicrystalline polymer consisting or lamellae crystals and amorphous regions. The amorphous regions reside mostly between the crystalline lamellae. Sasabe *et al* [26] have reported the possibility of an additional peak in the frequency interval below the $α_c$ relaxation and at high temperatures. They have assigned it to an interfacial polarization at crystalline amorphous boundaries or to the rubbery flow of polymer chains. Similar relaxation at low frequency and high temperatures have also been observed in the other polymers viz (PET)[27] , PMMA[28], Nylone[29] all of which have been attributed to a charge build-up at the interfaces in the bulk or close to the electrode dielectric interface. Thus, the contribution to the α - peak of PSF by this additional relaxation process in PVDF can not be ruled out. It is difficult to comment on the relative contribution of the two processes; however, the observed activation energy values correspond well with the dipolar orientation and space charge formation in the blend. The energy required for the molecular motion or for the reorientation of the dipole in many polymers is also of the same order [30]. However, such value of activation energy may also be observed if the current into the external circuit is due to the release of charge carrier either at the T_g or through the phase change or by the migration of charge carrier at the microscopic level with subsequent trapping [31-32].

PVDF is a semicrystalline polymer while PSF is amorphous in nature. The charge storage and transport in the PSF: PVDF blends are expected to be dominated by various localized levels in the amorphous regions and also at the crystalline- amorphous phase boundaries. Further, since both PSF and PVDF are polar, the probability of the presence of intrinsic charge carriers in the blends is also sufficiently high, particularly at high temperatures. In heterogeneous heteroelectrets of the blends, these charges will mainly pile up at the phase boundaries. They are supplied there by unequal ohmic conduction currents within the two phases (Maxwell-Wagner charging). These charges are also likely to be trapped in different trapping sites leading to space charge effects which fundamentally influence all the charging and transport processes; their high concentration often results in significant-contribution to the TSDC.

The magnitude of the TSDC peak is found to increase initially with the polarizing temperature but is decreased for the highest temperature 115^0C for samples polarized with the highest field of 250kVcm^{-1}. This again shows that the short circuit TSDC exhibits a complex behavior and several processes dipolar orientation, space charge and trapping effects may be operative simultaneously in the present case. Yano *et al* [33] have also observed presence of ionic space charge in heterogeneous heteroelectrets.

In general the decay of space charges in heterogeneous systems is ascribed to ohmic dissipation alone and any motion of charges is neglected. They are considered to be neutralized by opposite carriers replenished at the phase boundaries by unequal ohmic conduction currents (Maxwell-Wagner discharging). The occurrence of interfacial space charge polarization requires that there be enough charge carriers of sufficient high mobility which is expected near T_g when ohmic conduction is sufficiently high.

The thermograms of the blends are expected to reflect the electrical properties of amorphous regions of PSF, PVDF crystals as well as the crystalline –amorphous boundaries. The hump around 100^0C is clearly observed for PB3 and PB2 samples. The magnitude of TSDC current is also modified and increased quite significantly. It appears that the thermograms for blends show probably two overlapping peaks in the temperature range 100-150^0C, which increase in magnitude and shift towards higher temperature side with increase in polarizing temperature. The low magnitude of TSD current and absence of hump in case of PB4 samples points towards insignificant contribution of $α_c$-relaxation of PVDF. This may also be due to less crystal-amorphous interfacial area available for charge storage. The decrease in TSDC in case of PB1 sample and absence of hump may be explained by assuming that the dipoles in this case are entangled in such a way that their contribution to the total polarization is decreased.

We know that TSDC's in short circuit of hetropolar electrets chiefly reflects the reorientation of dipole. Although the excess charge decay by space charge limited drift and diffusion may manifest itself to some extent; however, at any rate the dissipation of excess charges by ohmic conduction does not show up. Therefore, in order to investigate more about to hidden ohmic decay of hetro-space charges we depolarized two sided metalized electrets, in open circuit with an air gap between upper electrode and the electrets.

Thus we had a sample that was neutral owing to the metallization because the oriented dipoles will induce image charges on the adhering metal electrodes which makes the external field zero at time t= 0 . However, when the sample is heated for depolarization, the dipoles are reoriented and part of the image charges are rendered free and charge the capacitor formed by the electret . Hence, there will appear a field in the air gap and the dipole reoriented will generate a current. The free image charges forming a temporary surface charge of such a polarity that it weaken the internal field are short lived. However, for when high temperature ohmic conduction becomes high enough, they will be dissipated. This ohmic dissipation will generate a current of opposite polarity to that of the dipolar current.

In order to separate dipolar reorientation and excess charge decay by ohmic conduction we have combined the open circuit TSDC thermograms with those of short circuit thermograms.

From the open-circuit thermograms (Figure 7-8) it is evident that the depolarization current is positive/or is opposite in polarity to the short circuit current and it flows in the same direction as the charging current throughout the TSDC cycle. It is also evident from the various thermograms of open and short circuit that the decaying current is essentially independent of the initial stored charge and there is no significant effect of the applied polarizing voltage. A high initial charge/or polarization is expected to increase the field that drives the charges to the adhering back electrode; however current/decay due to ohmic dissipation of the charges does not depend on the initial stored charge. Thus, it can be concluded that space charge limited drift is not significantly responsible for the depolarization current but ohmic dissipation is the dominant mechanism for the polarization relaxation in the present case of PSF: PVDF blends.

Polar polymer show high ohmic conduction; this may arise from impurities, and adsorbed water etc. In case of PSF rotational movement of adsorbed water molecules bound to the polar groups along the polymer chain has been already been reported to effect the relaxation behavior of the polymer discernibly (9-12). Further high polarity in case of polar polymers PSF and PVDF enhance the formation of free charge carriers by facilitating the dissociation of impurities. Such carriers piled up near the electrodes form excess charges. This high concentration often enables excess charges to contribute discernibly to the shorted electrode despite the fact that most of them are dissipated unnoticed by ohmic conduction. The comparison of short- and open circuit thermograms reveals that the magnitude of open –circuit current is less than the short circuit current. However the peak observed corresponds well with peak observed between 130-160°C in case short circuit TSDC. Thus the comparison of short –circuit thermograms with air gap thermograms of two–sided metalized electrets proves unequivocally that the peak between 130-160^{0}C is caused primarily by motion of excess charges and not by dipolar relaxation.

It appears that in the studied temperature range the ohmic conduction is high enough so much so that the dissipation of freed image charges by ohmic conduction generates a positive current and of such a magnitude that it completely masks the other relaxation processes so that the resultant current is of positive polarity or corresponds to homopolar character throughout the TSDC cycle.

The magnitude of the current is minimum for PB4 sample and as the wt% of PVDF is increased, the magnitude of the TSD current increases. Thus, the variation of structure on blending and the poling conditions influences the magnitude of the TSD current as expected for the appearance of interface charges. In addition to formation of interface charges, owing to the different conductivities, the polarity of crystalline regions may also cause trapping of charge carriers at the interface. The strong dipole polarization of the crystalline regions enhances the carrier trapping at the crystalline –amorphous interface as suggested by many authors [34-35].
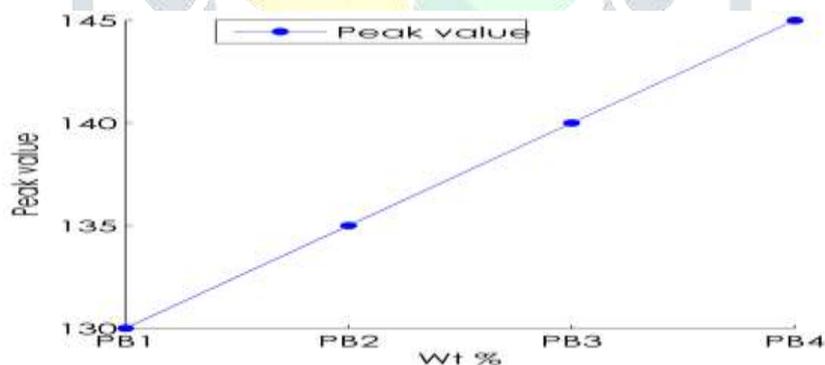

Figure 9 T_{max} versus blend composition (PB1, PB2, PB3 and PB4)

We have plotted the T_{max} of the high temperature short- circuit TSDC this peak against the blend composition as shown in Figure 9. It is evident that the T_{max} of the peak is shifted linearly towards the lower temperature with increase in the PVDF content up to the 20wt% studied in the present case. This indicates that upto 20wt% of PVDF content, the two homopolymers PSF and PVDF form compatible blend. Even if some phase separation takes place, the system is atleast not multiphase. The onset of the mobility of molecular motions of PSF and PVDF corresponding to a linear shift of relaxation peak towards the lower temperature implies that PVDF acts as plasticizer in PSF: PVDF blend. Plasticization is known to increase the free volume and mobility of molecular chains thus lowering the T_g. The observed trend in the variation of activation energy with blending may be considered to correspond well with this behaviour.

V. CONCLUSION

Thermally stimulated Depolarization current behaviour of PSF is modified significantly on blending it with PVDF. The short circuit TSDC thermograms of PSF: PVDF blends are, in general, characterized with a low temperature peak located around 75-80^{0}C and a high temperature broad peak in the temperature range 130-160^{0}C. The low temperature peak may be attributed to α_c- dipolar relaxation associated with the crystalline phase of PVDF and the high temperature peak appearing around 130-160^{0}C may be ascribed to dipolar orientations associated with the large scale molecular motions of the polymer. However, it appears that the relaxation behavior probably completely masked by ohmic dissipation of excess charges as revealed by a comparison of short- and open circuit thermograms. The observed activation

energy values of the short circuit high temperature peak correspond well with the two processes. That Polymer PVDF acts as Plasticizer in the blend. The two polymers form compatible blend in the studied composition range.

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