

Thermally stimulated depolarization current behaviour of poly (vinylidene fluoride) : poly (methyl methacrylate) blend system

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Abstract : The blend system of semicrystalline poly (vinylidene fluoride) (PVDF) with amorphous poly (methyl methacrylate) (PMMA) has been investigated in detail, for thermally stimulated depolarization current behaviour. Bilaterally, aluminized solvent cast blend samples of various wt% composition, PVDF · PMMA = 100 : 00, 90 : 10, 80 : 20 and 70 : 30 were thermally charged with field ranging from 50 to 125 kV/cm at temperatures from 50 to 110°C. The poling field, temperature and composition dependence of the short circuit thermally stimulated depolarization current (SC-TSDC) thermograms of such samples (electrets) suggest that the relaxation originates from the orientation of dipoles and the motion of charge carriers in the blend system. The results also show that the electrets of such blends, however, in comparison to the two component homopolymers store more charge.

Keywords : Short-circuit thermally stimulated depolarization (SC-TSDC), electrets, antiplasticization, anomalous current.

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1. Introduction

In recent years, considerable interest has been shown to the study of polymer blends. Many techniques including thermal analysis and scattering methods have been applied to look at microscopic and macroscopic phenomena with regard to crystallization, morphology and interfacial properties [1–5]. TSDC is a powerful technique with sensitivity comparable to dynamic mechanical and dielectric measurement. For the standard TSDC experiment, which is comparable to dielectric loss measurement, the low equivalent frequency

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($\cong 10^{-3}$ Hz) [6] and high sensitivity makes TSDC quite useful for the study of amorphous relaxation in crystallizable 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.

PVDF and PMMA is one of the few known miscible polymer blend. Several TSDC and dielectric studies of PVDF : PMMA blends have been reported [1-5,7,8]; however, there are certain discrepancies between the results reported [9,10]. The interpretation of results in case of blend is extremely difficult due to complexity of polymer relaxations which is further magnified in blends by the complex morphology. Furthermore, blends obtained by different methods, *i.e.* melt mixed, solvent cast, *etc.*, differ considerably in morphology [10]. Most of the experimental studies have been concerned with the melt mixed blends while only a few studies have been undertaken on solvent cast samples.

In this paper, we report results of short circuited TSDC measurements on solvent cast PVDF : PMMA blends (upto PVDF content of 70 wt%). The results have been discussed with respect to the correlation between structural as well as dynamical properties and electrical properties of heterogeneous polymer.

2. Experimental

PVDF material (product of Aldrich Chemical Company, Inc. 19, 270-D η_D^{20} 1.4200, d 1.740) and PMMA (low molecular weight) (obtained from Wilson Laboratories, Bombay) were used in the present investigation. Polyblends were solvent cast on plane glass plates kept in an air oven by dissolving the two polymers in required wt% in their common solvent dimethyl formamide (DMF) (LR Grade) at 60°C. Films of various wt% composition, PVDF : PMMA :: 100 : 00, 90 : 10, 80 : 20 and 70 : 30 so obtained and dried at 60°C for one week, were subjected to room temperature outgassing for 24 hours at a pressure of 10^{-6} torr. Aluminium electrodes were deposited on both sides of these samples over a central circular area of 3.6 cm diameter. For SC-TSDC measurements, the samples were thermally polarized at temperatures 50, 70, 90 and 110°C with fields of 50, 75, 100 and 125 kV/cm using a stabilized DC power supply (model HV 4800 E from Electronic Corporation of India Ltd., Hyderabad). The required voltage was applied for 45 min at the desired temperature and then the sample was cooled to room temperature in 45 min with the field still on. The total time of polarization was thus adjusted to 1.30 hr in each case. The TSDC run was performed by reheating the polarized sample (electret) at a linear rate of 3°C min⁻¹ and the discharge current was recorded by a Keithley 610°C electrometer.

IR absorption spectra of the samples were also recorded using a Perkin-Elmer spectrophotometer (model 1720 X) to yield information about morphology of the samples.

3. Results

(i) Effect of poling temperature :

Figure 1 shows thermograms for pure PVDF samples polarized with a field of 50 kV/cm at different temperatures, 50, 70, 90 and 110°C. It is clear that the thermograms are characterized with two peaks at 70 and 122°C and a third peak is observed at 160°C.

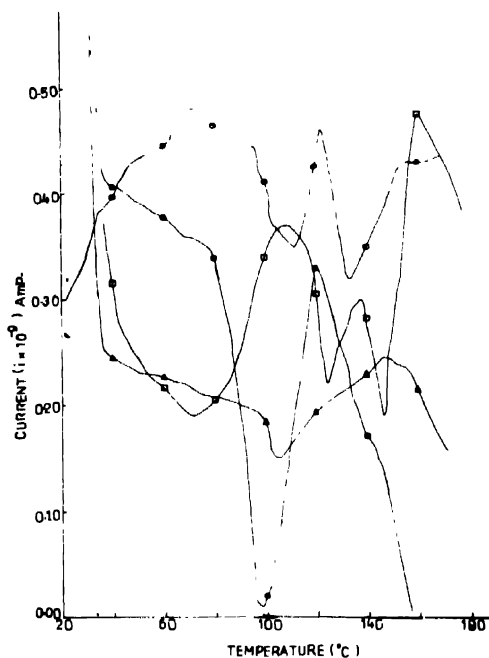


Figure 1. TSDC thermograms obtained for pure PVDF polarized with a field of 50 kV/cm at different temperatures : \circ —50, \bullet —70, \square —90 and \triangle —110°C.

The thermograms for 70°C show only a hump at 78°C and a sharp peak at 120°C; in case of the sample polarized at 90°C, two very well-developed peaks are observed at 110 and 140°C; and the samples polarized at 110°C exhibit a broad hump around 110 and a peak at 140°C. The thermograms for electrets prepared with the higher fields (not shown), do not show any peaks except for the sample polarized with the field of 75 kV/cm which exhibits peaks at 95 and 140°C for polarizing temperature of 70°C. It is also evident from the figure that the initial value of the current is high showing existence of a peak below 30°C.

Figure 2 shows TSDC's for 90 : 10 blend samples polarized with a field of 50 kV/cm. The thermograms exhibit probably two overlapping peaks in the temperature intervals 85–98, 78–102 and 122–140°C in the case of 50, 70 and 110°C polarizing temperatures. In the case of 90°C, the two peaks are well separated. The profile of the

peaks increases in magnitude and shifts towards higher temperatures with increase in the polarizing temperature. The thermograms for the samples polarized with the higher fields (not shown) are characterized with an initial hump followed by a peak, probably two overlapping peaks, in the temperature interval 95–140°C that show increase in magnitude

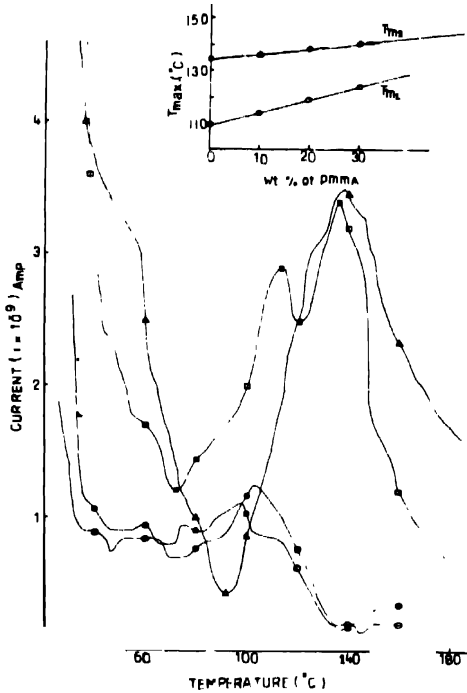


Figure 2. TSDC thermograms obtained for 90 : 10 blend with the field of 50 kV/cm at different temperatures : —○— 50, —●— 70, —□— 90 and —△— 110°C

Inset shows dependence of peak temperatures (T_{max}) on wt% composition of blends.

and shift towards higher temperature with increase in the polarizing field. However, for the electrets obtained with the fields 100 and 125 kV/cm the peak current magnitude is reduced for the higher polarizing temperatures.

TSDC's for the 80 : 20 blend samples polarized with the field of 50 kV/cm at different temperatures are shown in Figure 3. In this case, also, the thermograms exhibit a peak in the temperature range 95–140°C which shows a shift towards higher temperatures with increase in the forming temperature. The peak magnitude decreases with increase in temperature for low fields; however for the higher forming fields, the peak magnitude increases again with increase in the forming temperature. Again, for the electrets obtained at polarizing temperature of 90°C, two separate peaks are seen. Surprisingly, in the case of the highest forming temperature 110°C, the current is found to exhibit anomalous behaviour and flows in the direction which is same as the charging current.

TSDC's for 70 : 30 blend samples polarized with a field of 50 kV/cm at different temperatures are shown in Figure 4. All the thermograms are characterized with a single

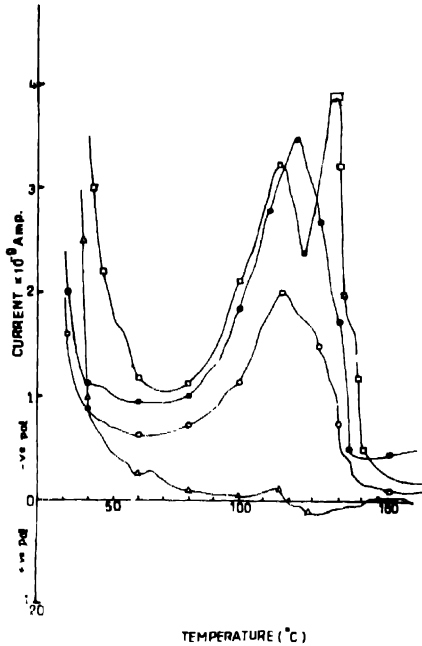


Figure 3. TSDC thermograms obtained for 80 : 20 blend with the field of 50 kV/cm at different temperatures : —○— 50, —●— 70, —□— 90 and —△— 110°C

peak. However, the magnitude of the peak current is reduced with increase in the forming temperature. Again, in some cases at the low forming fields, the thermograms show anomalous behaviour. A clear anomalous peak at 110°C is observed in case of the electrets obtained with a field of 50 kV/cm at the temperature of 70°C.

(ii) *Effect of poling field :*

Typical field dependence of the TSDC thermograms of various blends is exhibited in Figure 5. It is evident that the magnitude of the peak current increases for moderate fields; however, it decreases for higher fields.

(iii) *Effect of wt% composition of the blend :*

The dependence of TSDC thermograms on the wt% composition of the various blends polarized with the forming field of 50 kV/cm at the forming temperature of 50°C is shown as inset in Figure 5. It is evident that the magnitude of peak current I_m is minimum for pure PVDF samples at all the fields. As the wt% of PMMA is increased in the blend, upto 20 wt%, the peak current is increased. However, for maximum wt% of PMMA (*i.e.* 30 wt% in the present investigation), the peak current magnitude is decreased for all the field

values. Similar results are observed for the blends polarized at temperatures of 70, 90 and 110°C.

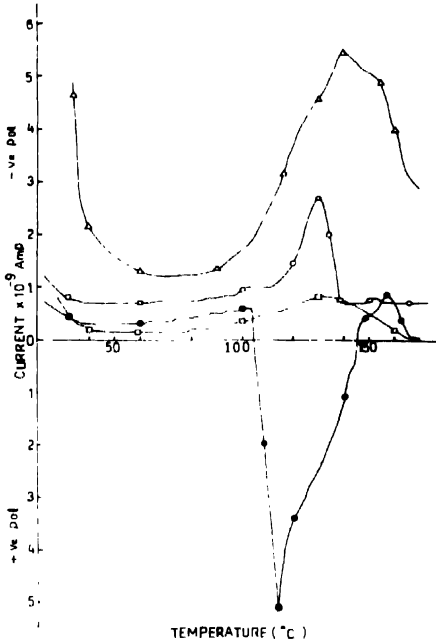


Figure 4. TSDC thermograms obtained for 70 : 30 blend with the field of 50 kV/cm at different temperatures : ---○--- 50, —●— 70, ---□--- 90 and ---△--- 110°C

4. Discussion

Persistent polarization in thermally charged specimens may arise due to various mechanisms, the important among which are dipolar polarization, space charge polarization or translation and trapping of charge carriers at microscopic distances or accumulation near the electrodes and interfacial or Maxwell-Wagner effects, *i.e.* the trapping of charge carriers at phase boundaries. The charge originated in TSDC due to dipole orientation or trapping of charges in defect or dislocation sites is known to give rise to a 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 electrodes.

In the present investigation, the thermally stimulated discharge current, in general, is found to flow in the normal direction, *i.e.* opposite to the charging current; however in some cases, for certain part of the discharge cycle, it exhibits an anomalous behaviour and flows in the same direction as the charging current. Thus, processes involving heterocharge formation are mainly responsible for polarization in the blends.

Relaxation processes in the crystalline polymers are related to molecular motions of amorphous and/or crystalline chains. Three distinct relaxations have been observed in PVDF : (i) α_c : Crystal relaxation from 20 to 160°C at 1 to 10⁶ Hz, (ii) α_a : Amorphous relaxation from -66 to 0°C at 10 to 10⁶ Hz which is due to micro-brownian motion of the main chain in the amorphous phase and (iii) β : Amorphous relaxation from -66 to -47°C at 10 to 10⁵ Hz. The TSDC cycle in the present investigation has been carried out at temperatures above the room temperature, *i.e.* 30°C which is much above the temperature of amorphous relaxations. Nevertheless, the high value of initial current observed in all the thermograms does point towards the existence of at least one relaxation peak at some temperature below 30°C.

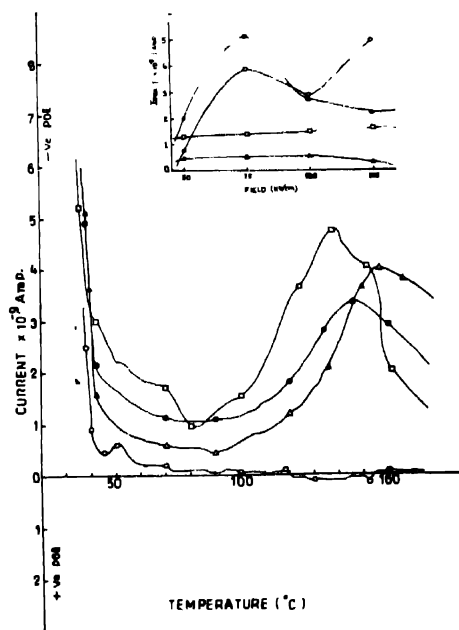


Figure 5. TSDC thermograms obtained for 80 : 20 blend polarized at temperature 90°C with different fields : —○— 50, —●— 75, —□— 100 and —△— 125 kV/cm.

Inset shows the dependence of peak current (I_{max}) on the wt% composition of the various blends : —○— 70 : 30, —●— 80 : 20, —□— 90 : 10 and —△— 100 : 00.

The thermograms for the pure PVDF electrets obtained with the low polarizing fields of 50 and 75 kV, are characterized with peaks at 95–112 and 140–160°C for the moderate polarizing temperature of 70°C while the thermograms for higher fields of 100 and 125 kV do not show any peak.

The low temperature peak observed in the present investigation may be the α_c -dipole relaxation peak occurring in the crystalline phase of PVDF. This relaxation has been observed by several workers for phase II (or non-polar α -phase) PVDF [11,12]. From the

IR absorption spectra shown in Figure 6, we can infer that the PVDF crystals in our solvent cast samples are also mainly of phase II. The absorption band at 488, 532, 616, 766, 796, 856 and 976 cm^{-1} are the characteristic bands associated with phase II structure.

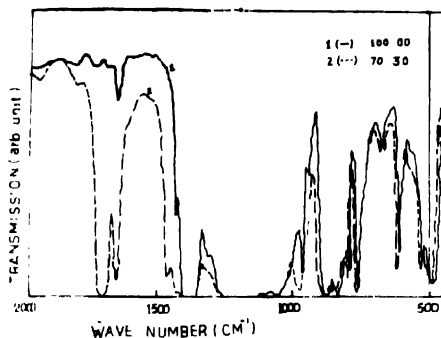


Figure 6. Infrared absorption spectra for pure PVDF and 70/30 blend.

The high temperature peak observed in the present investigation, is probably an additional relaxation process. PVDF is a semicrystalline polymer consisting of lamellae crystals and amorphous regions. The amorphous regions reside mostly between the crystalline lamellae. Sasabe *et al* [13] have reported the possibility of such an additional peak in the frequency interval below the α_c relaxation and at high temperature. They have assigned it to an interfacial polarization at crystalline-amorphous boundaries or to the rubbery flow of the polymer chains. Similar relaxations at low frequencies and high temperatures have also been observed in other polymers and biological material, viz. PET [14], PMMA [15], Nylon [16], all of which have been attributed to a charge, build-up at the interfaces in the bulk or close to the electrode-dielectric interface.

Since PVDF is a semicrystalline polymer, the charge storage and transport in it is expected to be dominated by various localized levels in the amorphous regions and also at the crystalline amorphous boundaries. Further, since it is a polar polymer, the probability of the presence of intrinsic charge carriers in it is also sufficiently high, particularly at high temperatures. Incidentally, in heterogeneous heteroelectrets of PVDF, 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 carriers are also likely to be trapped in different trapping sites leading to space charge effects which fundamentally influences all the charging and transport processes. Their high concentration, often enables them to contribute discernibly to the SC-TSDC.

The magnitude of the peak current is found to decrease with the polarizing temperature except in the case of the electret obtained with the highest polarizing field of 125 kV/cm at the highest temperature 110°C of the present investigation. This shows that in addition to dipolar orientation, space charge and trapping effects are also operative in the present case. Yano *et al* [17] also have attributed the observed high value of static permittivity ϵ_s in PVDF to ionic space charges.

In general, the decay of space charges in heterogeneous system is ascribed to ohmic dissipation alone; any motion of charges is neglected. They are considered to be neutralized by opposed carriers replenished at the phase boundaries by the unequal ohmic conduction current (M-W discharging). The occurrence of interfacial space charge polarization, requires that there be enough carriers of a sufficiently 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 the PVDF crystals as well as the crystalline-amorphous boundaries in addition to those of the amorphous regions. The thermograms for the blends show probably two overlapping peaks in the temperature range 88-140°C which increase in magnitude and shift towards higher temperatures with increase in temperature. The increase in magnitude and shift towards higher temperature of the peaks is due to an increase in the total polarization at higher temperatures. Astonishingly, for 100 : 00, 90 : 10 and 80 : 20 electrets, the two peaks are well-separated for the electrets obtained with the polarizing field of 50 kV/cm at the polarizing temperature of 90°C. PMMA exhibits an α -relaxation at the glass transition temperature 95–105°C. It is difficult to distinguish the contribution of the PVDF molecular orientations, since both PVDF and PMMA exhibit maxima in the same temperature range. However, it can be concluded that the lower temperature part/peak is associated with the α -relaxation of PVDF and PVDF/PMMA molecular motions at their common glass transition temperature. The polarizing temperature of 90°C being close to the T_g of PVDF : PMMA blend, the molecular motions associated with it manifest their contribution clearly as a separate peak. Further, the polarizing field being sufficiently low, this peak is not masked remarkably by any other relaxation process occurring in the blends and hence is clearly seen. Increased random molecular motions in case of 70 : 30 blend probably overcome the dipolar orientation processes resulting in appearance of a single peak in this case.

We have plotted the T_{max} of the two TSDC maxima against the blend composition as shown in inset of Figure 2. It is evident that the T_{max} of the two peak is shifted linearly towards the higher temperature with the increase in PMMA content upto 30 wt% studied in the present case. This indicates that upto 30 wt% of PMMA, the two homopolymers PVDF and PMMA form compatible blend. Even if some phase separation takes place as reported by others, the system is atleast not multiphase. The onset of mobility of the dipoles both of PVDF and PMMA at their glass transition temperature corresponding to a linear shift of the relaxation peaks towards the high temperature, implies that the addition of PMMA produces hardening in PVDF, raises its T_g and thus acts as an antiplasticizer for PVDF [18].

The magnitude of the current is minimum for pure PVDF and as the wt% of PMMA is increased, the magnitude of current increases. Thus, the variation of structure and the poling condition influences the magnitude of the TSDC current as expected for the appearance of interface charges. In addition to the formation of interface charges, owing to the different conductivities, the polarity of the 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 interfaces as suggested by a number of authors [19,20].

Since no electrode dependence has been reported in PVDF [21] and because the space charge effects have been observed [22], then the high temperature relaxation-process may be due to motion of space charges trapped at the crystalline-amorphous boundaries. A change in the relative contribution of the dipolar and interfacial processes with the PMMA wt% concentration and shift of T_g towards higher temperature may be responsible for the observed shift of the peak to higher temperature side.

The anomalous TSDC's flowing in the same direction as the charging current observed under certain charging field and temperature conditions for the blend samples can be understood to be due to space charge formation and partial blocking of the metal-polymer contact as suggested in literature [6].

Considering one type of carriers, electrons for example, we may have a distribution of charges just after charging. The concentration of trapped charge carriers is highest near the charging electrode and decreases with distance towards the other electrode. Usually, the carriers move towards the nearest charging electrode (outflow) and recombine with their image charges on the electrode. This results in the observed normal TSDC in various cases. However, if the charge carriers return rate towards the nearest electrode exceeds the charge carrier exchange rate at the electrode, the carrier will diffuse and inflow towards the farther electrode. Such suppression is considered to be due to partial blocking of the other polymer-metal contact. Under such conditions, the observed current becomes anomalous. Obviously, diffusion only becomes significant for large gradients which may be found particularly in hetero-electrets of amorphous and semicrystalline blends of PMMA : PVDF.

In the present case, the number of shallow traps with small detrapping time is considered to increase with increasing wt% of PMMA; hence the total amount of space charge will be relatively greater at low temperature charged samples with higher wt% of PMMA, than the samples with small wt% of PMMA charged at the same temperature. The easier release of carriers from such traps is supposed to cause a high return rate of carriers from such traps to the nearest probing electrode resulting into the partial blocking of the electrode which leads to anomalous current for such samples. The transfer of charges from shallow to deeper traps for high temperature charged samples results in reduced return rate of the carriers released from the shallow traps causing the current to remain normal as opposed to the anomalous peak observed for the low temperature charged samples.

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