Nature of Thermally Stimulated Discharge Current in Pure and Blend Samples of PVC and PMMA

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Abstract—Thermally stimulated depolarization currents (TSDC) in pure polyvinyl chloride (PVC), polymethyl methacrylate (PMMA) and their blend samples have been investigated at 100 °C using different fields 45, 65, 85 and 105 kV/cm. Single current maxima observed in pure PVC samples at around 150 ± 10 °C. Two well resolved peaks designated as α and β positioned at around 90 ± 5 °C and 160 ± 10 °C observed in case of pure PMMA. TSDC thermograms for blends of PVC and PMMA represent single peak around 140-180 °C. The order of current in polyblend samples was higher compared to individual polymer. Peak current and the total charge released was, however, found to increase non-linearly with the forming field. Depolarization kinetic data i.e. activation energy, charge released and relaxation times for pure and polyblend samples were calculated using existing theories.

Keywords— Polyvinyl Chloride (PVC), Polymethyl methacrylate (PMMA), Induced dipoles; Polarization; Space charges; TSDC; Activation energy, Charge released, Relaxation time.

I. Introduction

The researchers are working extensively on all possibilities to discover new and modified polymers. Presently everyone is aiming at modification of existing polymers [1-7]. The existing polymers can be modified by the modification of monomers in the initial stage or blending different types of polymers together to get tailor made properties so that the properties of two polymers can be clubbed together and suppress their drawbacks [8-11].

The polymers have become very important in our lives because of their many applications and valuable properties like light weight, less cost, ease of processing, tailoring possibilities, toughness, flexibility, large strength to weight ratio and ease of fabrication. There are now many more types of polymers having special properties which make them increasingly interesting for electronics, optoelectronics and associated applications. These polymers include those having unique combination of electrical, optical, thermal, chemical and physical properties. Examples of such polymers include intrinsically conducting polymers, as well as those which emit light or exhibit dielectric properties such as piezoelectricity and Pyroelectricity. Many of these newer polymeric material offer significant potential advantages over the traditional materials they replace. In some cases applications which cannot be produced by other means have been manufactured using polymeric materials. These include photoresists (radiation-sensitive polymers used in semiconductor processing), as well as polymers exhibiting non-linear optical properties [12].

Many nonconducting polymers are able to store a considerable amount of electrical charge for a long period of time. The stored charges may be real charges, polarization charges or both. Permanently charged materials, which are called electrets, have been utilized in many technical applications such as electroacoustic transducers, radiation devices, electret filters or electrophotography [13]. Beside this, polymers also find valuable applications in bio-engineering: for understanding of membranes natural signals, biological memory in regeneration, electrical mediation in tissue growth and various other phenomena.

In order to overcome disadvantages such as poor mechanical properties of polymers from renewable resources, or to offset the high price of synthetic biodegradable polymers, various blends and composites have been developed over the last decade. Blending two polymers of appropriate physical and chemical nature can produce materials with improved properties [14].

Polyvinyl chloride (PVC) has an amorphous structure with polar chlorine atoms in the molecular structure. Its density is 1.352 g cm-3 at 100 °C, melting point 212 °C, glass transition temperature (Tg) is 81 °C. PVC has been found to be miscible with a number of structurally different polymer and copolymers. Polymethyl methacrylate (PMMA) is amorphous and polar in nature, having high impact strength and extremely high weatherability. Optically clear (92% transmission, theoretical limit for normal incidence, in the visible region) through the visible wavelength range; very little ultraviolet absorption until 260 nm. It is highly sensitive to electron radiation. Its density is 1.17-1.20 g cm-3, melting point 130-140 °C, glass transition temperature (Tg) is 120 °C.

Obviously, investigation of properties that may help in studying polymer structure are very important in the field of polymer physics and these properties can be investigated using various studies. Here we made an attempt to investigate the properties using Thermally Stimulated Discharge Current (TSDC).
II. Experimental procedure

The samples used in present investigation were of pure PVC, pure PMMA and their blends [90:10 (PVA:PMMA), 80:20 (PVA:PMMA) and 70:30 (PVA:PMMA)]. The pure and polyblend samples were obtained by dissolving desired weight ratio of PVC and PMMA in common solvent i.e., Dimethyl Formamide (DMF). A homogenous solution of PVC and PMMA obtained using a Teflon coated magnetic stirrer at 40 °C. After that, it was carefully poured on a clean glass plate (avoiding any air bubble) floating on mercury pool kept inside thermostat at 60 °C. The poured solution was kept inside a thermostat oven for 24 hours during which complete solvent was evaporated and a thin film was deposited on glass plate. Film was removed carefully from the glass plate using a sharp blade [15]. The aluminium foils were used as electrodes and obtained samples were sandwiched between these electrodes of 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 inside the oven was raised to the desired value (T_p) i.e., 100 °C maintained for half an hour. After this the power supply was turned ON and the desired polarizing voltages (V_p) i.e., 45, 65, 85 and 105 kV/cm was applied. The sample was kept under the influence of polarizing fields at polarizing temperature 100 °C for 30 minutes. It was then allowed to attain room temperature with applied polarizing field. The rate of cooling was adjusted in such a way that the thermostat could reach the room temperature within 30 minutes. The total time polarization was thus adjusted to be 90 minutes in each case. The field was then removed and the thermo-electret was then short circuited at room temperature for 5 minutes to remove the frictional and stray surface charges.

For TSDC measurement, the samples were short circuited between aluminum electrodes through an electrometer then they were reheated at a linear heating rate of 3 °C/min. The depolarization current was recorded at regular temperature intervals using Electrometer Amplifier Model EA 815, ECIL. For each measurement a fresh sample was taken and the TSDC was recorded.

III. Result and discussion

The different prepared samples i.e., pure PVC and PMMA and their polyblends in different weight ratios i.e., 90:10; 80:20 and 70:30 (in PVC:PMMA combinations) were designated as P1, P2, P3, P4 and P5 respectively. Thermally stimulated depolarization current (TSDC) spectra for P1, P2, P3, P4 and P5 samples polarized with poling fields 45, 65, 85 and 105 kV at 100 °C respectively are shown in Fig. 1 & 2.

The TSDC spectra for pure PVC, polarized at constant temperature 100 °C with fields 45, 65, 85 and 105 kV/cm, exhibit single peak at around 142-150 °C are shown in Fig 1(a). Initially current was of the higher order and decays with temperature for a particular span. Fig. 1(b) shows the dependence of TSDC behavior of pure PMMA on polarizing fields 45, 65, 85 and 105 kV/cm polarized at constant temperature 100 °C. These spectra are characterized by two well resolved peaks designated as α and ρ respectively, positioned at around 90 ± 5 °C and 158-166 °C. TSDC thermograms for polyblends P3, P4 and P5 poled at 100 °C with fields 45, 65, 85 and 105 kV/cm represent single peak around 154-178 °C (Fig. 3). The order of current in polyblend samples was higher compared to individual polymer. The depolarization kinetic data i.e. activation energy, charge released and relaxation times for pure and polyblend samples poled at 100 °C with different polarizing fields are listed in Table 1. The activation energy associated with the peak observed at high temperature (T_m) was calculated by initial rise method [16]. The total charge delimited under the different temperature peaks was determined by calculating the time integral I(t)dt over the depolarization current using the Trapezoidal rule. Relaxation time corresponding to maximum current has been evaluated using the value of activation energy and summarized in tables.

The processes taking place during discharge are similar to those occurring during charging. Generally speaking, they only behave in an opposite way. The net charge of an electret usually arises from aligned dipoles and space charges. However, before the electret formation, the neutral polymer already contained free charges; they manifest themselves in conduction current when a field is applied. These do not contribute to its net charge, but are responsible for its ohmic conductivity. The decay of the charge of electrets during TSDC results from dipole reorientation, excess charges motion and ohmic conduction. The thermal agitation will reorient the
aligned dipoles at random. The motion of excess charges originates from space charge called drift and diffusion. The first motion is due to the local electric fields forcing the mobilized excess charges to drift towards opposite charges, whereby electric neutrality is restored. The thermally stimulated discharge conductivity is induced by thermal release of dipoles, ions and trapped electrons [17].

Polyvinyl Chloride (PVC) is known to exhibit three relaxation processes, β, α and ρ [18]. The β peak occurs in the glassy state of the polymer usually below room temperature and is due to the local reorientation of the polar side groups while the α peak is found at the glass rubber transition temperature $T_g$, where either the segment motion of the main chain, or the disorientation of the polar side group carrying a net dipole moment sets in. The third process, ρ, which is observed at temperatures higher than those for α process, is probable due to the charge accumulation (space charge) near the electrodes. In the TSDC thermograms of PVC the observed peak around 142-150 °C, corresponds to ρ-peak and the activation energy associated with this discharge process is 0.35 eV.

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 peak height increases almost linearly with an increase in forming field. The total charge released associated with this peak was also found to increase linearly with the forming field, these characteristics further supports that the low temperature peak observed in the present investigation may be considered to arise due to dipolar motions in PMMA with distribution in relaxation frequencies [19-22]. 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. The second peak observed at 158-166 °C was found to correspond to an activation energy value of 0.389-0.421 eV. The peak current and the total charge released associated with this peak was, however, found to increase non linearly with the forming field indicates that a build up of space charge near the electrodes occurs and hence this peak may be designated as the space charge ρ peak. The TSDC cycle in the present investigation has been carried out around the room temperature i.e., ≈ 30 °C, which is much above the temperature of β-relaxation. Nevertheless the high value to initial current observed in all the thermograms of PVC and polyblends does point towards the existence of at least one relaxation peak at some temperature lower than the room temperature.
The decrease in the intensity of current, in the case of pure PMMA, with poling field can be explained on the basis of hetero-space charge formation (electrode polarization). The polarization may be caused due to dipole orientation and charge trapping. As long as the release of hetero-charges from such a large number of trapping sites does not lead to the blocking of the electrode, it will enhance the TSDC current. However, if the return rate of the released charge exceeds the charge exchange capacity of the electrode, blocking of the electrode results. This blocking of the electrode will suppress the carrier flow to the nearest electrode and may result in their movement to the farthest electrode. This will decrease the TSDC current and hence the intensity of polarization. Detrapping of this large amount of charge results in electrode blocking and decrease in TSDC current.

But at the same time, the peak shift towards higher temperature (non-linear dependence/variation) with increase in polarizing temperature which is a characteristic of space charge peak. This apparent contradiction may be explained on the basis of induced dipoles. It seems that during polarization both positive and negative charge carrier get trapped in the deeper traps and thus from induced dipoles. Later, these induced dipoles get aligned in the polarizing field [23-25]. It is therefore likely that the dipolar peak either gets masked by the space charge peak, or its contribution to the total polarization is very small.

A decrease in activation energy is observed in present case with the increase in polarizing fields and weight% composition. This suggests that the 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 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 [26]. Table 1, show that the relaxation time decreases with poling field.

It was found that magnitude of current increases with different weight% of PMMA in PVC. It is expected that the number of shallow traps with small detrapping time is considered to increase with increasing weight% of PMMA, hence the total amount of space charge will be relatively greater at low temperature charged samples with weight% of PMMA than the samples with small weight% of PMMA charged at the same temperature. This may also be attributed to an increased orientational effect on dipole owing to more available free volume due to plasticization effect. Because of the heterogeneous structure and charge carriers injected in the bulk may pile up at the phase boundaries. Plasticization causes loosening of the structure and provides greater mobility to charge carriers resulting in the increase of peak current [27].

In PVC: PMMA matrices, containing different percentage of PMMA at least two phase coexist and discontinuity of structure at such boundary increases. Because of the difference of carrier conductivity in different phases, the carriers get trapped at the interphases of phase boundary. Further the dipoles may also originate due to trapping of both positive and negative charge carriers in the deep traps in such a way as to form induced dipoles. Such trapped charge carriers may be generated in the bulk because of ionization of impurities or may get injected in the bulk from impurities. Thus, they lead to induced dipole polarization in the polyblends. It is just possible that contribution of a permanent dipole of the host material is masked by the peak due to induced dipoles. In the blends, dipoles of the polar component are so constrained that under the field of the polarization, either that do not orient or their contribution to the total polarization is almost negligible as compared to the contribution of the induced dipoles, which are formed by the deep trapping of charge carriers originating in the bulk during polarization. In fact the higher value of activation energy is taken as an indication of induced dipole formation because in this case the energy required disorienting the charge carriers and for their subsequent release from the trapping sites is expected to be higher. Increase in the magnitude of TSD current on blending can also be understood in terms of the trapped spaces charges. Blending increases net crystalline-amorphous interfacial volume producing more sites for trapping of carriers. Increase in trapping sites with weight% of PMMA content leads to trapping of larger number of charge carriers in them.

The observed dependence of charge (Q) on forming field (Ep) 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 Q 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 [28]. 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 the 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 [29].

The peak current and the total charge released associated with this peak was, however, found to increase non linearly with the forming field indicates that a build-up of space charge
near the electrodes occurs and hence this peak may be designated as the space charge \( p \) peak.

Distribution of relaxation time in polymers arises due to the different size and shape of the polar groups/dipoles originated during a polarization and this depend on the poling temperature. The relaxation time decreases with increase of polarizing field and can easily be explained from the fact that relaxation phenomenon is due to the internal friction of the polymer which depends exponentially on temperature [30].

References


