Polarization in poly (vinyl chloride) (PVC) and poly (methyl methacrylate) (PMMA) blends films investigated by thermally stimulated depolarization current technique

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Abstract   Thermally stimulated depolarization current (TSDC) characteristics in short circuit configuration have been studied in the laboratory grown PVC and PVC PMMA blends of different wt % composition ratio as a function of polarizing field and polarizing temperature Films of thickness 100μm were thermally polarized with fields of 25,50,60 and 75 kV/cm at temperatures 50, 70, 90 and 110°C The TSDC thermograms obtained, exhibit a broad hump between 50 - 90°C and well-defined peak between 128 - 148°C The high temperature peak is considered to be associated with interfacial polarization due to space charge accumulated at the crystalline amorphous boundaries The hump which is observed between 50 90°C is attributed to the relaxation of dipoles connected to the main chain of PVC having a continuous spectrum of activation energy and relaxations times The results also indicate that PVC dipoles in the polyblend are so entangled that their contribution to the total polarization of the polyblend samples become insignificant

In the quest of developing strong and stable electrets and finding suitable substitutes for electrophotographic, semiconductor and even superconducting materials [1], the charge storage and transport behaviour of a number of polymeric materials have been studied by various techniques. As a result, a wealth of experimental data is now available on electrical behaviour of many pure and doped polymers. Thermally stimulated depolarization measurements have shown that the charge stored in an electret is very much sensitive to the structure of electret forming material and even the electret state in a polymer can be produced not only by conventional methods, but also by merely bringing about some structural changes in the electret forming material [2]. Appropriate model systems are, however, required to understand in clear terms this dependence of molecular relaxations/motions on the molecular and supermolecular structure of the polymeric material. These findings have prompted studies on multicomponent polymers i.e. polymer composites, copolymers, polymer alloys and blends [3]. Polymer

blends have however, attracted more attention due to possibility of tailoring end-product to suit the specific requirements by simple means. Poly (mer) blend is a mixture containing at least 2 wt % of two or more polymers and/or copolymers.

The present paper reports the results of thermally stimulated depolarization current measurements undertaken on PVC:PMMA polyblends with the view to have a better understanding of the charge storage and transport behaviour and also its dependence on the polymer structure. PVC is a linear, polar, semicrystalline polymer well known for its excellent insulating properties. On the other hand, PMMA is a branched amorphous polar polymer with excellent mechanical properties.

PVC and PMMA used in the present investigation were obtained from M/s Chemical Agency, Bombay (India). Blend films of 100μm thickness were prepared by solution evaporation technique on plane glass substrates using chemically pure dimethyl formamide (DMF) as a common solvent. Blend films of different compositions were prepared by taking PVC and PMMA in 100:00, 95:05, 90:10 and 80:20 weight % composition ratio.

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The films were bilaterally aluminized over a central circular area of 36 mm diameter. The samples were thermally polarized with fields of 25,50,60 and 75 kV/cm at temperatures 50,70,90 and 110°C. After polarizing for 1 hr at the desired temperature, the samples were cooled down to room temperature under the application of field. Total time of polarization was adjusted to 2 hour in each case. The TSDC's of the electrets thus formed were obtained by reheating the samples at a linear rate of 2 k/min and the current was monitored by a Keithley 610 C electrometer.

Typical TSDC thermograms for pure PVC and PVC:PMMA:90:10 blends polarized with a field of 50 kV/cm at different temperatures 50,70,90 and 110°C are shown in Figures
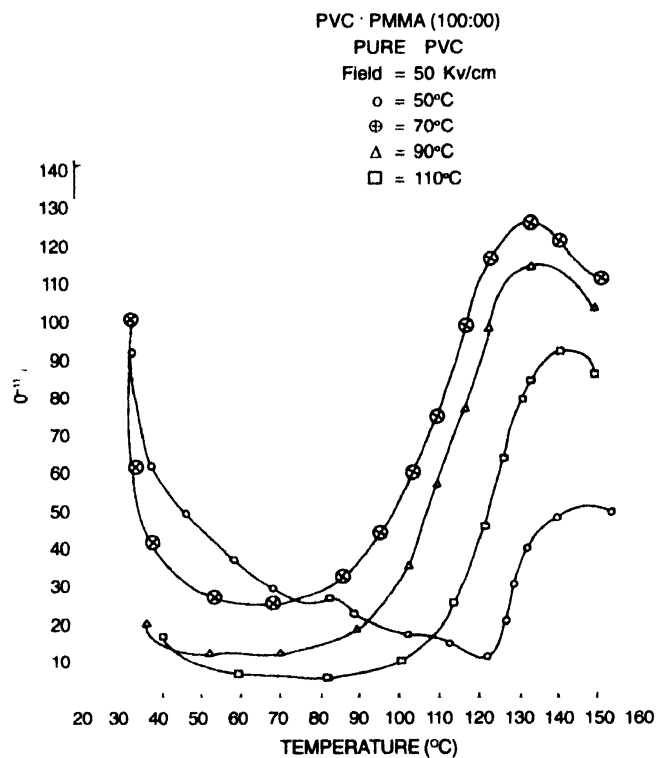

Figure 1. TSDC thermograms for pure PVC specimen polarized with the field of 50 kv/cm at different temperatures.
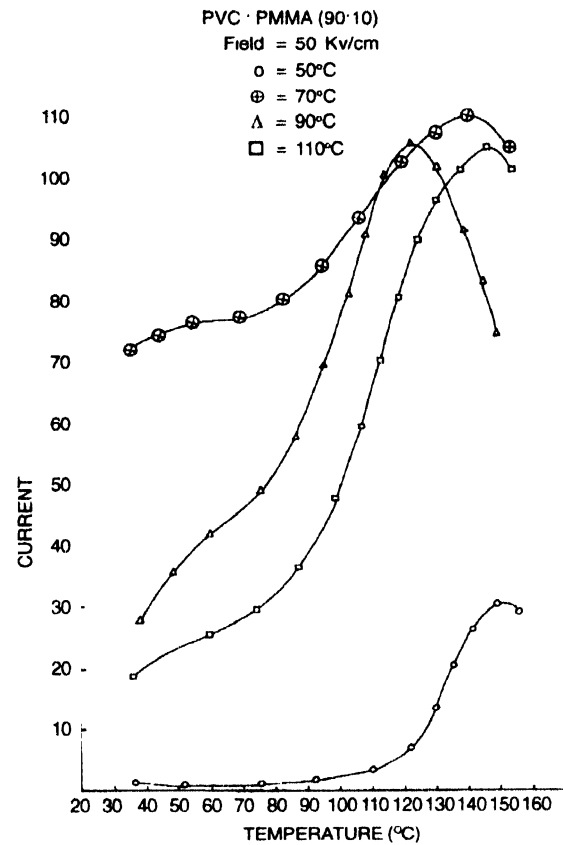
1 and 2. Figures 3 and 4 depict for pure PVC and PVC:PMMA:80:20 samples polarized with various fields at temperature 90°C. It is clear from these thermograms that a well-defined peak is observed between 128 to 148°C both in the case of pure PVC as well as PVC:PMMA blends. Sometimes, a hump is also observed between 70 to 90°C. Further, the initial value of current is high in the case of pure PVC indicating the existence of a peak at temperature 30°C. The activation energy associated with the peak observed at high temperature has been calculated by initial rise method of Garlick and Gibson [4] and was found to be less than 1.0 eV always. The total charge delimited under the high temperature peak was determined by calculating the time integral I(t) dt over the depolarization current using Trapezoidal rule. The released charge for pure PVC has been plotted as a function of polarizing field and shown in Figure 5. A nonlinear

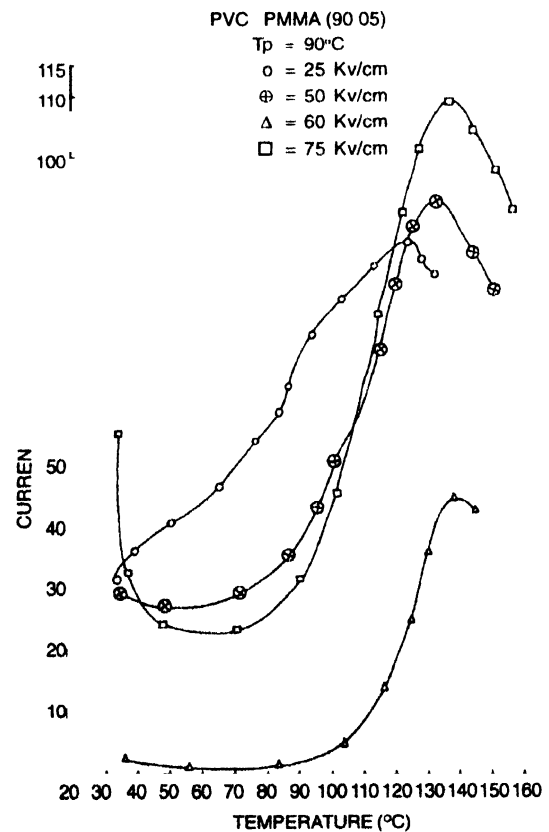**Figure 2.** TSDC thermograms for PVC · PMMA   90 10 specimen polarized with the field of 50 kv/cm at different temperatures

Figure 3. Short circuit TSD thermograms for PVC:PMMA::95:05 specimen charged at 90°C with fields 25, 50, 60 and 75 kv/cm.

field dependence is clearly evident. Similar behaviour was found in various PVC : PMMA blends.

PVC : PMMA (80:20)
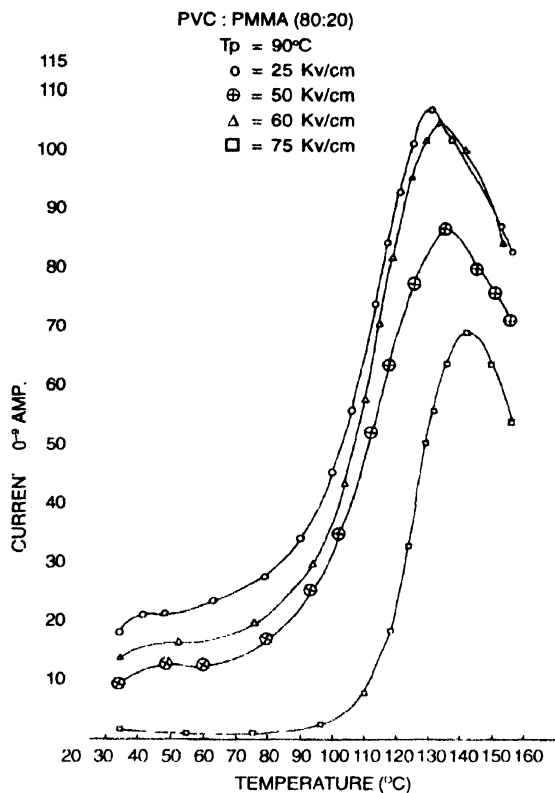
Tp = 90°C
o = 25 Kv/cm
⊕ = 50 Kv/cm
△ = 60 Kv/cm
☐ = 75 Kv/cm

Figure 4. Short circuit TSD thermograms for PVC PMMA 80 20 specimen charged at 90°C with fields 25, 50, 60 and 75 kv/cm.

In polymeric materials, various types of molecular relaxations are possible. The only motions possible at low temperatures are local motions of molecular groups, *e.g.*, rotation of side groups
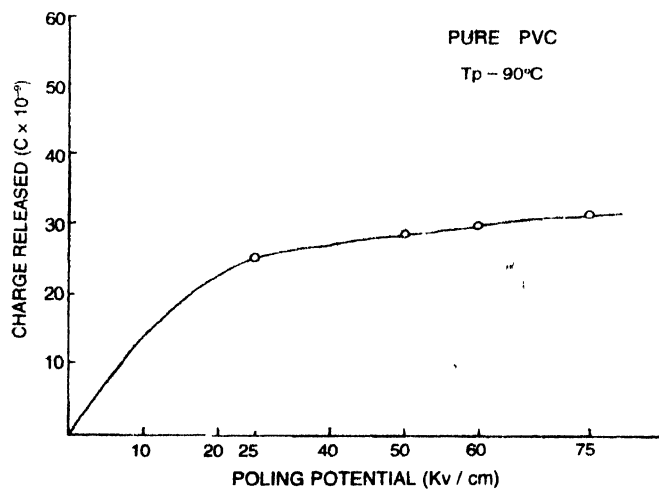

Figure 5. Charge released as a function of polarizing field

or internal motion within side groups. At high temperatures, segments of main chain become mobile. The main chain then becomes flexible so that the polymer softens and becomes

rubbery. The temperature at which these conformational rearrangement of the main chain segments set in, is called glass-rubber transition temperature. In semicrystalline polymers, relaxations involving the crystalline parts or the internal phase are also possible.

Poly vinyl chloride is largely an amorphous polymer It is characterised by three relaxations designated as β-relaxation occurring at low temperature, α-relaxation around the glass-rubber transition temperature, T_g and α_1-relaxation occurring at temperatures well above T_g [5, 6]. PMMA is a branched amorphous 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. So that the polymer exists in three different forms-isotactic, syndiotactic and atactic. The properties of PMMA are strongly polar due to the presence of ester group ($COOCH_3$). The hindered local motion of these groups below the glass-rubber transition temperature gives rise to β-relaxation peak [7]. The cooperative motion of these ester group with the main chain, manifest itself at and near the glass rubber transition temperature in the form of α-peak [8]. The two dipole peaks are broad and arise from a distribution in relaxation times. Above the α-peak, a third peak has also been reported due to the motion of space charges.

The hump observed between 60 to 90°C in the present case, may be identified with the α-relaxation observed near T_g in case of PVC [9-15]. From the present investigation, it is not possible to draw any clear conclusion about the variation of the position of the hump with the polarizing temperature and polarizing field. None the less, since its location is around T_g, the origin of the hump can be associated with the cooperative motion of the polar side group along with the main chain of PVC. The broadness of the hump can be understood in terms of distributed relaxation, very common in amorphous polymers like PVC and PMMA. The hump is also observed to broaden towards the low temperature with the increasing content of PMMA in the case of PVC : PMMA blends. This can be understood in terms of the plasticization effect brought about by blending. Plasticization is known to increase the molecular mobility, free volume, the intermolecular interaction and lower the T_g. The relaxation motion of even the low temperature polarizations or dipoles and their activation is therefore, expected to be possible with more available free volume or smaller packing density even at low temperatures [16]. It can therefore, be concluded that the mechanism responsible for the hump is characterized not only by discrete level of activation energy having a single relaxation time, but it can be a complex process having a continuous spectrum of activation energy and relaxation time. Considering the existence of a broad single hump, it can also be concluded that PVC:PMMA form a compatible blend in the studied range of composition

From the above thermograms, it is also evident that the current is initially high in the case of pure PVC and PVC:PMMA

95:05 blends. However, in the case of PVC:PMMA 90:10 and 80:20 blends, the initial value of current is low. Further, the hump observed between 60 to 90°C is also absent (except in few cases). It can be safely concluded that there exists a peak at temperature lower than 30°C in the case of pure PVC and PVC:PMMA 95:05 blend and this peak is absent in other blends. As said earlier, PVC is known to exhibit a β-relaxation associated with the rotation of chlorine side group at temperatures below the glass rubber transition temperature [5,6]. The measurement in the present investigation, has been carried out at temperature above 30°C (*i.e.*, above room temperature). The peak located below 30°C, therefore, could not be observed in the present investigation. Comment can however be made about the lower value of initial current in the case of PVC:PMMA 90:10 and 80:20 blends. It appears that because of increased intermolecular interaction on blendings, dipoles are entangled in such a way that the contribution of orientation of dipoles towards the polarization of the sample in the presence of an applied field becomes negligible. This may also be the cause for the elimination in the blend samples of the hump observed near Tg in pure PVC and PVC:PMMA 95:05 blends.

A well-defined peak is observed between 128 to 148°C in the present investigation in the case of pure PVC as well as various PVC:PMMA blends. The peak temperature as well as total charge delimited under this peak, have been found to exhibit a nonlinear field dependence. In view of the above characteristics, the peak can be identified as space charge peak. It can be observed from the various thermograms that the peak current increases with the polarizing temperature but decreases for higher temperatures of polarizations. It seems that during poling, charge carriers are getting trapped at the crystalline amorphous phase boundaries present in pure PVC and PVC:PMMA blends and peak in thermograms is due to release of such trapped charge carriers. It has been reported that at temperatures from 130 to 148°C, melting of PVC crystallites takes place. The lower value of the peak current for samples polarized at high temperatures may be attributed to this melting of PVC crystallites due to syndiotactic form which would be generally present in PVC [17,18]. Melting of crystallites entails the loss of trapping sites for space charge accumulation as a consequence of which the depolarization current is decreased.

The nature of the field dependence of the charge release may be explained in the following manner.

The internal field created by the trapped space charge decreases the external applied field. The effect of the internal field would be to decrease the apparent charge carrier mobility.

The stored charge is expected to exhibit a saturation characteristic as shown in Figure 5 by pure PVC. However, the internal field due to trapped space charge becomes nearly constant at higher polarizing field. The effect of internal field may then decrease relative to the applied external field so that the apparent mobility of charge carriers again increases. The stored charge therefore, tends to increase at higher polarizing field. It is also evident that the magnitude of peak current increases with the content of PMMA in the PVC:PMMA blends. Both PVC and PMMA are amorphous polymers but have markedly different electrical conductivities and dielectric properties. The increase of PMMA content in the PVC:PMMA blends can be expected to increase the net crystalline amorphous interfacial area where the charges are trapped during polarization process. The release of such a large number of charge carriers during the depolarization will therefore, result in a higher value of current in the case of PVC:PMMA blends.

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