CHAPTER VI

CORRELATION
The present work was undertaken to understand the mechanisms taking place in electrical conduction and polarization of pure EC, PMMA and their blend films. Since polarization and electrical conduction are caused by the motion in space of the electrically charged particles of a dielectric, there is a certain affinity between these two phenomena. It will be useful to find some typical differences between these phenomena.

During polarization, the charges linked with the definite molecules of matter are brought into motion. These charges cannot leave the confines of a given molecule whereas, electrical conduction is caused by the motion (drift) of free charges (carriers) which can move in matter over comparatively large distances and, in limited cases, through the entire thickness of a dielectric from one electrode to the other.

Polarization takes place in all the molecules of a dielectric; it is its bulk property. At the same time, conduction of a dielectric is often and practically fully determined by the presence of a slight amount of impurities (contaminants), and is not attributed to its basic substance. Conduction of a dielectric can appreciably be weakened with purification of its substance. Therefore, when two or several dielectrics which do not interact chemically are mixed, the permittivity of the resultant mixture may be evaluated to a first approximation from the arithmetic rule of mixing. This rule may prove totally unsuitable for calculating the resistivity of a dielectric, since even a slight addition of another substance
may sometimes reduce by several orders the resistivity of the dielectric. The effect of negligible amounts of impurities on the resistivity of semi-conductors may sometimes be much more pronounced.

Thus, the physical picture of polarization of a dielectric may be represented as a negligibly small displacement in space of a very large number of charged particles of matter, and the physical picture of electrical conduction of a dielectric as the motion of a relatively small number of charged particles over relatively large distances.

The displacement of charged particles during polarization may be regarded as an elastic shift of charges. When the effect of the voltage applied to a dielectric is discontinued, the displaced charges may tend to return to their initial positions, which never happens in the phenomenon of electrical conduction.

While the conduction current exists so long as a direct voltage is applied to a dielectric, the displacement current (capacitative current) appears only when the direct voltage is applied or taken off or, generally, when the magnitude of the applied voltage is changed. A capacitative current can exist in a dielectric for a long time only under the action of an alternating voltage. In the presence of a sinusoidal alternating voltage, the conduction current coincides in phase with the voltage, while the displacement current (in a linear dielectric) being also sinusoidal, is a quarter of a period ahead of the voltage.

Thermally stimulated discharge current spectra \(6,7\) are very useful for an understanding of the processes of polarization and
for throwing light on conduction mechanisms. Electrical conduction in polymers is governed by trapping levels. Much can be learnt about traps with the help of TSDC spectra.

The electrical properties of pure EC, PMMA and EC:PMMA blends have been investigated in detail with a view to have a clear picture of the effect of blending on charge storage and transport properties of polymers. The details of the various studies undertaken have been described in different chapters of the present thesis. The results so obtained have been discussed at length in the light of the available literature at relevant places in the thesis. Nevertheless, with a view to present a unified picture of various results, it is suggestive to review the several important findings of the present investigation.

To make polarization processes more clear, thermally stimulated discharge of electrets was studied on pure and blended samples. The experimental conditions varied were forming field, temperature and electrode materials. Our measurements show two peaks. The low temperature peak was located in the range 60-90°C, while the high temperature peak was located around 115\(+\)15°C. The peak current, and total charge released corresponding to this peak was found to increase linearly with the forming field. The activation energy values associated with this peak were 0.16-0.20 eV. The above characteristics of low temperature peak were considered to indicate that the peak was the manifestation of dipolar reorientation. Similar behaviour was observed in the blend samples also. The position of the second peak was found to be independent of the forming field, temperature, and
blending. The activation energy values associated with this peak were 0.20-0.49 eV. The total charge released for this peak was found to vary nonlinearily with the forming field for pure as well as blended samples. However, for blended samples, the value of total charge released was higher than that in pure samples.

The magnitude of the depolarization current was found to depend on the blend composition. This was explained in the light of plasticization effect which results in increased net dipole orientational polarization owing to more available free volume together with the increased molecular mobility for moderate wt\% of PMMA in EC and reduced net orientational polarization due to increased intermolecular interactions at higher wt\% of PMMA.

Analysis of short circuit TSC's from thermally charged samples indicated that the polarization is produced combindly due to dipolar orientation and space charge localization in various traps existing in the samples. Occurrence of two peaks under certain conditions for short circuited electrets indicated the presence of two processes of dipolar polarization with different relaxation times.

Activation energy calculated for second peak has been found always to be more than that or first peak. This shows that the energetically shallower traps are located on or near the free surface of the sample while the energetically deeper traps are located in the bulk of the sample.

Space charge effects were also considered to be responsible for obsorbed TSDC thermograms. Space charge built-up by migration of ions over microscopic distances gives a non-uniform hetrocharge, whereas, trapped injected space charge results in a
non-uniform homo or hetero-charge, depending upon the work function of the metal electrodes. Any significant effect of electrode materials on TSDC characteristics has not been observed.

The isothermal transient currents were analysed by considering the effect of variation of forming field, temperature and electrode materials for pure and blend samples. Our measurements indicate that the transient currents vary linearly with the applied field. Further, the transient currents have been found to be thermally activated over the temperature range of the present investigation. Log I - Log t plots have been found to follow the Curie-Von-Schweidler law.

The modification in transient behaviour on blending PMMA with EC has been explained on the basis of plasticization effect which increases free volume and molecular mobility and lowers Tg.

Pronounced departure at higher temperature and fields has been considered as an indication of the possibility of space charge effect in the blends.

The systematic analysis of the various results from such study has indicated that the time dependent discharging current may combindly be due to dipole reorientation and space charge dissipation.

Conduction studies in dark were undertaken in the temperature range of 30°C to 80°C and with field ranging from 10 to 100 kV/cm. The conductivity was also found to be thermally activated. Activation energy values were found to lie in the range 0.41 to 0.62 eV.
The conductivity of polyblend has been found to increase due to the incorporation of organic substances. Amplitude of conduction current increases with the concentration of blend substance. Structural defects such as carbonyl group or double bonds yield shallow or intermediate traps. From the shallow traps, carriers are released thermally, while deep trapping levels occur where charge carriers stay longer. TSD current study shows that charged carriers are trapped at the polymer phase boundary or at the new trapping sites created by the incorporation of sensitisers\textsuperscript{11}.

Activation energy was calculated by temperature variation of conductivity curve and initial rise method of TSDC. The value of activation energy obtained by initial rise method was found to be a bit higher than that obtained from conductivity curve. The most probable cause of this difference may be the formation of surface stages\textsuperscript{12,13}. Though the mechanism responsible for the formation of surface states has not been understood yet, the surface states\textsuperscript{13} are among the factors which affect the injection phenomenon.

The dark conduction current measurements on pure and blend samples revealed that the modified Poole-Frenkel effect is the dominant process governing the electrical behaviour. The theoretical values of coefficients of PF mechanism are in fair agreement with the experimental values of the coefficients obtained from the slopes. This indicates that the conduction phenomenon is due to intrinsic charge carriers generated by field assisted thermal excitation of impurities or trapping sites in
the formation of the polymer blend. The density of such trapping sites is probably increased on blending due to increased crystalline amorphous interfacial area. Blending also produces plasticization effect modifying the charge transport behaviour of the polymer. The high activation energy values observed in the present case have been considered to give an indication of the possibility of ionic conduction in the polymer.

Metal-polymer /polyblend-metal systems generate a short circuit current which is weak at room temperature and becomes quite appreciable at elevated temperatures. The phenomenon of spontaneous current emission owes its origin to one or more of the following processes-
(a) electronic process between metal electrode and dielectric (b) electrochemical process at the metal-dielectric interface and within the bulk of the dielectric (c) rotation of dipoles and of molecular complexes and (d) water activated processes.

The SCE at room temperature from a moisture soaked sample has a high magnitude because water in contact with metal can give rise to an extra electric potential by orientation of its dipolar molecules and flow of electrons from/into electrodes. Further the presence of dissolved oxygen molecules and hydrogen ions (H\textsuperscript{+}) makes the interface similar to that between an electronic conductor and an ionic conductor. This decreases the resistivity of the polymer and eventually a strong current is observed. High heating rate accelerates the process of dissociation of loosely and strongly bound water. Reorientation of dipoles and rotation of molecular complexes are also accelerated at high heating
Increase in film thickness decreases the spontaneous current. However, with the thinnest film the burst of current indicates as if the insulating film acquired extra charges. It is expected that the thinnest film may be compared with an insulating charged sheet. On thermal induction the existing electric field induces SCE. The defect levels/charges/ions present within the bulk of the thick films may come to the surface due to gradual thinning of the film producing a net field across the two surfaces of the film. Injection of charges between interface did the rest.

Blending generally increases the short circuit current and probably by polarizing action due to dipole mechanism or due to trapping of free charge carriers which are supplied in large numbers by the additives.

It is well known that moisture absorption in cellulose and its derivatives occur in the amorphous region only\textsuperscript{14}. EC used in the present investigation has Tg some where between 60 - 75 C. Hence above 80 C perhaps the crystallinity of EC increases and therefore above 80 C very short variations in SCE is observed due to inaccessibility to water vapours\textsuperscript{15}. So at elevated temperatures the current from different heatings may attain similar magnitudes because then only internal field of the dry system would be giving SCE.

The moisture absorption percentage of EC is reported\textsuperscript{16} to be 2.0% in 24 hours at 80.0% relative humidity and 3.0% in 100% humidity. Hence increase in the magnitude of current is a
moisture activated phenomenon.

Drying of the fresh sample in the thermostat at a constant temperature, activation centres present in the amorphous region are destroyed resulting in the shortage of particular type of charge carriers which would have been otherwise released on thermal induction. Hence it seems that due to moisture content, particular type of charges are enhanced. This action of moisture is somewhat in the line of plasticizer effect of water molecules present in or absorbed by cellulosic materials\textsuperscript{17}.

Transitions obtained near room temperature are affected by heating rates markedly. With increasing heating rates, the magnitude of the peaks increases correspondingly. This may be either due to the combined effect of plasticization due to moisture content and rotation of polar hydroxyl side groups on account of different heating rates on thermal induction or due to experimental error.

Currents of reverse polarity are thought to be due to currents of trapped internal potentials\textsuperscript{18}. It is also not improbable that up to this higher temperatures trapping sites would be destroyed and charges of only one sign gives unidirectional current. Thus in the present work the studies on spontaneous current seem to support the same mechanisms which are employed for the explanation of short circuit TSDC transient charging current and steady state conduction current. The spontaneous current phenomena also seems to be moisture activated phenomena alongwith two types of charge trapping centres.

176
In the present work various techniques have been employed to investigate the polarization processes along with the estimation of various parameters involved. Anticipating the difficulty to analyse the experimental data, in such complex situations when in one and the same temperature range, the various decay mechanism may compete, the different techniques are used to interpret the experimental results. These measurements verify the processes responsible for dipolar and space charge polarization.

The various results described above have indicated that the electret state in pure and blended samples is due to dipole polarization space charge polarization. The space charge polarization has been considered to be due to the injection of electronic carriers from the contacting electrodes followed by their localization in various traps distributed spatially and energetically in the sample. The former being more contributive at low temperature while the latter process comes into play at high temperatures.

Various features of transient currents in discharging mode spontaneous current and also of dark conduction and short circuit TSCs together with the different material parameters derived from such measurements have been found to be in agreement with the dipolar polarization as well as space charge polarization.
REFERENCES


177