CHAPTER VII

SUMMARY OF THE RESULTS
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Polymethyl methacrylate (PMMA) has attracted wide attention of many research workers, because of its manyfold uses in Industry. Major uses are for sheets, glazing, skylight and decorative purpose. From the survey of the literature, it is evident that very little work has been done on PMMA composites. In the present work, attention has been paid to understand the processes responsible for the changed behaviour of the composite as far as its electrical properties are concerned. It is found that the properties of the electrets are governed by many factors such as polarizing temperature, field, concentration of the impurities etc. TSDC, electrical conductivity, dielectric behaviour spontaneous current emission, are proved to be important tools to understand the nature of the traps, accumulation of charge carriers and the mobility of the charge carriers.

Thermally stimulated discharge current (TSDC) study helps to understand the mechanism involved in the electret formation. In this study pure polymethyl methacrylate (PMMA) as well as PMMA composite are studied. Attention has been paid to study the effect of forming fields $E_p$, polarizing temperature $T_p$, on TSDC spectra and the following results are obtained.
(i) TSD spectra of pure PMMA consists of two peaks at about 368°K and 438°K (fig. 3.1). The position of these peaks are found to be independent of the field, but current value increases with increasing field. Peak position shifts towards the higher temperature side as polarizing temperature increases (fig. 3.2).

(ii) The addition of Ferrocene in to PMMA (PMMA composite) by different weight ratio is found to cause no regular variation in TSD thermograms (fig. 3.3 and 3.4), therefore composite of PMMA : Malachite Green were prepared by adding 20 mg, 50 mg, 70 mg, 100 mg of Malachite Green to PMMA by weight ratios.

(iii) Two peaks are observed, one at lower temp. (368°K) and other at higher temperature (433°K) in thermograms. First peak shifts to higher temperature side and second peak shifts to lower temperature side. The current shows an increasing trend in negative direction and peak appears, on increasing the concentration of Malachite Green (fig. 3.5). At higher concentration (100 mg), only one peak appears in the positive direction in place of two peaks at 383°K ± 3°C along with a peak in negative direction at 453°K ± 2°C.
To see the effect of electrode variation on TSDC spectra, the lower electrode was always Aluminium, and the upper electrodes were Aluminium/silver/copper.

In Aluminium-composite-silver/copper system, TSD thermogram consists of single peak, observed at higher temperature in positive direction (fig. 3.7, 3.9).

TSD thermograms, with polarity change system, is quite different from that, observed in simple system, i.e. lower grounded and upper being positive. Two peaks, one in positive direction, lower temperature and the other in negative direction at higher temperature side, were observed (fig. 3.8, 3.10).

Calculations of activation energy, characteristic relaxation time, for different polarizing conditions, have been done by initial rise method from the slopes of their respective initial rise plots. These values have been listed in table 3.1.

The charge released during the discharge was evaluated by integrating the current Vs. temperature/time curves, for different $E_p$'s and listed in table 3.1 (fig. 3.11).
The electrical conduction properties of the polymers are also found to be governed by the choice of electrode, therefore it was felt to undertake this study for PMMA composite. Field and temperature were the two variable parameters in this study. Field is varied from $2.5 \times 10^3 - 2 \times 10^4 \text{ V cm}^{-1}$ in eight steps while temperature was varied from $363^\circ\text{K} - 383^\circ\text{K}$ in five steps. Measurements are taken in following ways - 

(i) The isothermal I-V characteristics plotted in the form of log I vs log V curves, exhibit almost similar nature for all temperatures from $363^\circ\text{K} - 383^\circ\text{K}$. The curves show two distinct regions. In both these regions, the curves exhibit approximate linear relationship, separately. These two straight lines with different slopes form a knee at a point. The knee appearing between the two regions is sharp and can be seen clearly which appears to lie nearly $1 \times 10^4 \text{ V cm}^{-1}$, (fig. 4.3).

(ii) The effect of electrode variation is also studied in PMMA: Malachite Green complexes. Fig. 4.5, gives log J vs $E^{1/2}$ plots with three metal electrodes, Aluminium, silver, copper. All the curves exhibit linearity in lower and higher field regions.
(iii) Variation in conductivity with temperature at different fields \((\log \sigma \text{ Vs } 10^3/T)\) is shown in fig. 4.6. Their slopes give the corresponding values of activation energy. All curves are of similar nature with nearly similar slopes.

(iv) The Schottky plots show variation of current density with field in the form of \(\log J \text{ Vs } E^{1/2} \) (fig. 4.7). These plots show perfect linearity in higher field region, while Poole–Frenkel plots in the form of \(\log \sigma \text{ Vs } E^{1/2} \) (fig. 4.8) show deviations of some points.

(v) Fowler–Nordheim plots, \((\log J/V^2 \text{ Vs. } 1/V)\) are shown in fig. 4.9. All the curves display similar nature showing a decreasing trend. They do not yield linearity in higher field region. Richardson plots \((\log J/T^2 \text{ Vs. } 1/kT)\) at different field values are shown in fig. 4.10. These curves are of similar nature and slopes.

To understand further, the mechanisms/processes responsible for the conduction behaviour, spontaneous current emission study is proved to be a potential tool. It also helps in understanding the migration of charge carriers.
(i) Polymer composite sandwiched between two metallic electrodes generate appreciable current with heating.

(ii) The magnitude and direction of current depend on the choice and combination of electrode materials. If the two electrodes are of the same kind of metals (Al-composite-Al) the magnitude of current is small, and direction is uncertain. If the two electrodes are of different kinds of metals, the current is higher and the direction of current is determined by the combination (with respect to external circuit) of two electrodes (fig. 5.1).

(iii) Thinnest film (10 μm) gives maximum short circuit current while with thickest film, (20 μm) lowest current is observed (fig. 5.2).

(iv) With increasing heating rates the magnitude of current increases (fig. 5.3).

(v) Increase in concentration of Malachite Green in PMMA: Malachite Green matrices increases the order of spontaneous current (fig. 5.4).

The study of variation of dielectric constant with frequency and temperature helps in understanding the different relaxation processes responsible for the
orientation or deorientation of the charge carriers.
Any change in the segmental chain or the main chain of the polymer is also reflected in the dielectric study of the polymer composite. Moreover, any phase transition can also be very well studied by dielectric measurements. Keeping this in view dielectric study of PMMA and PMMA composite was undertaken -

(i) For pure polymethylmethacrylate sample the variation of capacity (permittivity) and loss factor (\( \epsilon'' \)) as a function of temperature at a fixed frequency (200 Hz) is shown in fig. 6.1.

(ii) Permittivity and loss factor show slight increase in values, as concentration of Malachite Green is increased. Peak position is shifted towards the higher temperature side with increase in concentration (fig. 6.2).

(iii) Variation of capacity and loss factor as a function of temperature at a constant frequency (200 Hz) for different electrode system have been observed (fig. 6.3).

(iv) Variation of loss tangents with temperature at different frequencies is shown in fig. 6.4. The magnitude of both the loss peaks was found to decrease as frequency increases.
CORRELATION OF VARIOUS INFERENCES
The knowledge of electrical conduction of a material is of great importance to understand fully the mechanisms responsible for thermoelectric and photoelectric polarization of the material. Since polarization and electrical conduction are caused by the motion of the electrically charged particles, a correlation between these two phenomena could be established. It will be useful to find some typical difference between these phenomena.

The electrical conduction in matter is associated with generation of charge carriers and their mobility. In the absence of an external field, carriers present in the bulk of the polymer are in a state of random motion, so that their net contribution towards current is zero. During polarization (at least during electronic and dipole polarization) the charges linked with definite molecules of matter are brought in to motion. These charges cannot leave the confines of a given molecule where electrical conduction is caused by the motion of free charges which can move in matter over comparatively large distances, and in the limiting case, through the entire thickness of a dielectric from one electrode to the other. In the case of polar polymer like PMMA the possibility of the presence of ionic carriers cannot be ruled out. Hence the picture
of electrical conduction in such polymers is of a complex nature.

Polarization takes place in all molecules of a dielectric, it is its bulk property. At the same time, conduction in a dielectric is often and practically fully determined by the presence of a slight amount of impurities and can not be attributed to its basic substance. Conduction in a dielectric can appreciably be weakened with purification of its substance. Therefore, when two or several dielectrics which do not interect chemically are mixed, the dielectric constant 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 conductivity of a dielectric since even a slight addition of another substance may some times enhance by several orders the conductivity of the dielectric. The effect of the negligible amounts of impurities on the conductivity of semi-conductors may sometimes be much more pronounced.

The process of transport of carriers in macromole-
cular compounds involves a kind of intermediate states generally called "traps". If a carriers falls in to such a trap it is captured and is no longer free for a certain time and its probability of recombination with a carrier
of opposite sign is increased greatly. However, it may also escape from the trap after receiving a certain amount of energy. The relative probability of the two processes depends on the height of the traps and mean energy of carrier. If the carrier is captured in a deep trap, there is little chance of escape. Than for carriers trapped in shallow traps. There is also a probability that the carriers once released from shallow traps may be retrapped at deep levels. The net effect is that charge is effectively transported from one locality to another. Hence a knowledge of traps parameters like density, distribution etc., is needed to understand the mechanism of charge and energy transfer in polymeric systems. Charges may also be injected in to dielectric by other means, e.g. electrode polymer interface, irradiation and detrapping from localized level etc. The extrinsic nature of carriers was observed during dark electrical conduction studies of composite PMMA.

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 a motion of a relatively small number of charged particles for relatively large distances.
While the conduction current exists so long as a direct field 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 field. In the presence of a sinusoidal alternating field, the conduction current coincides in phase with the field, while the displacement current (in a linear dielectric) being also sinusoidal, as a quarter of a period ahead of the field.

Temperature dependence of conductivity of composite (PMMA: Malachite Green) shows an inflection near the glass transition temperature of the polymer. The capacitance of pure PMMA as well as composite films, increases with temperature. The TSD current spectra of PMMA films, and also in composite films give a peak near the glass transition temperature of the polymer. The results shows that the effective conductivity of composite films determined at linearly increasing temperature, can be interpreted by the superposition of conduction and polarization processes. However, it may be mentioned that the inflection on the $\sigma(T)$ curve does not necessarily correspond to the glass transition temperature.
even though the inherent conductivity becomes a predominating component in the vicinity of Tg. This concept can be applied to the polar polymers like poly methyl methacrylate.\(^1\)

Poly methyl methacrylate (PMMA) have different stages of well known transitions. In our (present) investigation transitional changes were observed in all studies. Polymer structure changes near Tg, i.e. glass transition - temperature, (lies in between 363\(^\circ\)K to 383\(^\circ\)K). Every polymer has a certain region of temperature, where its chain becomes highly mobile. During investigation, transitional changes were observed in all studies. The linear growth of \(\alpha\)-peak with poiling fields suggest field effects.\(^2\) The I-V characteristics in composite films yielded perfect linearity at 363\(^\circ\) and 383\(^\circ\)K temperature respectively for the entire range of field. This suggests the field and temperature assisted mechanism of Schottky - Richardson for the conduction of charge carriers. From all these studies it has been found that in the neighbourhood of transition temperature, the mobility of the polymeric chain increases and the space charges may be destroyed and as a result, the ohmic conduction is observed for the entire range of field.
The storage of the charge in a polymer electret is greatly affected by the structure of the forming polymeric matrix. The effect in polymers can be produced not only by the conventional procedure but can also be obtained by some structural changes by mixing of the matrix with suitable impurities. The impregnation of Malachite Green in PMMA seems to change the concentration of carriers. Because of the impurities, structural defects, imperfections in amorphous polymers, there are large number of traps which may be supposed to be randomly distributed throughout the bulk of the specimen.

Our measurements of electrical conductivity, computation of dielectric constant and loss behaviour and depolarization of the polarized specimen under thermal stimulation provide these data for composite. They also elucidate the various molecular processes which take place in PMMA. In TSDC studies a "current reversal" was found. The occurrence of current reversal may be because of the excitation of trapped internal potentials by heat. The space charge peak of "reverse polarity" obtained with PMMA: Malachite Green matrices during TSDC at elevated temperatures and field may be because of the release of the excess charges and trapped internal potentials on thermal treatment of composite. The increase in
conductivity in composite were also observed. The rise in the conductivity in low and high field region may be due to number of free carriers and increased mobility of charge carriers. The guest molecules are undoubtedly responsible for the presence of deeper traps while defects of the chain structure give rise to shallow traps. The trapping activity of guest molecules depends on their electron affinities and ionization potentials.

The pronounced effect of electrode material on conductivity of composite, TSD currents suggests the injection of carriers in to dielectric from electrode - polymer interface. The injection of charges in PMMA composite from outside agencies (viz. electrode - polymer interface, Malachite Green impregnation, field etc.) may develop extrinsic conduction in the dielectric. These injected charge carriers may be responsible for the observed electrical conduction. The linearity in high field region supported by electrode effects suggested the RS mechanism for electrical conduction. At higher fields and higher temperatures, thermal detrapping of trapped states seems to work in conjunction with the RS mechanism.
REFERENCES


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