Chapter 3

Sample Preparation and Techniques Used
3.1 Importance and Present Position of Polymer Research:

Polymers are of profound interest to society and are replacing metals in diverse fields of life, which can be further modified according to modern application. Organic-inorganic hybrid materials are hi-tech because they can present simultaneously both the properties of an inorganic molecule besides the usual properties of polymer (an organic molecule). These hybrid materials sometimes lead to unexpected new properties, which are often not exhibited by individual compounds and thus open a new avenue for chemists, physicists and materials scientists. These hybrid materials are new, versatile class of materials, exhibiting a vast application potential, due to their tailorable mechanical, optical and electrical properties (Meneghetti and Qutubuddin 2004). Hybrid materials with polymers as organic constituent are often called ‘polymer composites’.

Some polymers are chemically inert. Styrene-butadiene copolymer is widely used for electrical insulation. Because of good electrical properties and low dielectric loss at very high frequencies, polytetrafluoroethylene is used in television and radar. Polyvinylidenefluoride valves are used in chemical and nuclear industries. Some of the new materials, especially conducting polymer composites have novel properties and are finding applications in electronic devices. One of the most demanding applications of conducting polymer composites is in piezo-sensors, which are needed in robotics. Smart composites are used in defense/military applications, electronics and computers.

There has been tremendous progress made over the past few years in materials science. The interdisciplinary approach in the material research has
given rise to novel combination of materials. Polymer with metals, metals with ceramics and polymers with ceramics. The processing technology has also undergone many changes and this too has contributed to the progress in this area. Thus it may be said that a new area in material science has emerged in which there is no set limitation on the use of particular type of material or a rigid conventional processing technique. The polymer scientists are not restricted with moulding of plastics. This way a healthy combination of several materials has emerged and produced novel composites or blends, having properties, which are often beyond the imagination of earlier generation material scientists.

Fiber-reinforced polymer composite materials are fast gaining ground as preferred materials for construction of spacecraft. Recently several projects worldwide have demonstrated their acceptance as prime materials for spacecraft vehicles. There is a considerable current interest in nanoparticles and nanophase materials in view of their unique optical, electronic, mechanical and catalytic properties.

In recent years, because of the need for electrostatic charge dissipation, electromagnetic shielding etc., new polymers with high electrical conductivity have been formulated. This has led to new discoveries in the area of conducting polymers, which has now become hot topic of research.

3.2 Need of Investigation and Nature of Present Work:

Polymers being disordered material have some unique properties. Much of the work on polymers has been carried out but still there is tremendous scope.
The work and progress made in the field of polymeric research is a direct result of varying contributions from the synthetic chemists, the solid state physicists as well as the polymer scientists. A detailed understanding of the basic phenomena, combined with the capacity of synthesizing complex molecules in a form with controlled morphology, will provide us with the key for capitalizing on the potential of polymers as active electrical elements.

It has been observed from the literature that variety of work has been carried out in studying the amorphous materials. Many research workers have studied various parameters such as ac and dc conductivities, dielectric constants, mechanical, electrical, thermal, optical, elastic properties etc. of polymers. It has been shown that polymer blends have better charge storage (Khare and Srivastava 1992, Khare et al 1993) than those of the individual components. In view of these consideration, it is interesting to study the thermally stimulated discharge (TSD) current of PVC and PVAc polymer composite systems, which may give information about the molecular interaction and the extent of mixing between the two individual components and will also enable us to understand the nature of microscopic mechanism responsible for charge storage and transport in polymer composite systems.

Good quantum of work on electrical conductivity and charge storage property of individual polymers using various techniques (Taylor and Lewis 1971, Khare and Srivastava 1994, Yawale et al 2002) have appeared in the literature. Yet work on polymer composites and doped composites seems lacking.
Similar seems to be the case in so far as optical properties of composites and doped composites are concerned.

Having previewed the existing literature on polymers regarding research carried out on these and also their ever increasing usage in day to day life it was thought to be in the fitness of things to adopt polymers as materials for our present work.

The different properties viz, physical, electrical and optical etc. provide a probe to make an indepth study of polymer composites and also is capable of revealing information about the internal mechanism and structure of polymer samples. The thermally stimulated discharge current measurement technique contributes significantly to the current understanding of the charge storage and charge decay processes in polymer composites. The different techniques like X-ray diffraction, infrared spectroscopy, differential thermal analysis, differential scanning calorimeter, extended X-ray absorption fine structure, scanning electron microscopy, transmission electron microscopy and laser excited fluorescence spectroscopy etc are useful in the structural investigation of samples. In the present investigation only X-ray diffraction and IR- spectroscopy techniques are used for characterization.

The electrical characterization is also a tool for determining the polymer structure. The electrical conduction mechanism is related to the structure of polymer sample. The optical properties play prominent role for the design of the various optical components. TSDC is a basic tool for identification and evaluation of dipole reorientation processes, trapping and recombination levels in electret.
With this considerations it has been decided to study the electrical conduction mechanism, optical properties and thermally stimulated discharge current technique in PVC-PVAc polymer composites doped with PANI and BA.

In particular, the following work is carried out

1. Preparation of polymer composite samples.
2. Characterization of the samples through X-ray diffraction (X-RD) and infrared spectroscopy techniques.
4. Preparation of thermoelectrets at various poling fields.
5. Measurement of thermally stimulated discharge current with temperature for thermoelectrets.
7. Study of optical properties of polymer composites.

3.3 Choice of Solvent, Polymer and Method of Sample Preparation:

3.3.1 Choice of Solvent:

In order to reflect the characteristics of a composite sample, it is necessary that the original interaction between the molecules of a species be removed completely or at least reduced considerably. Tetrahydrofuran being non-polar and an inert solvent (Tiwari et al 1988) can meet these requirements. Hence tetrahydrofuran has been used as solvent in the present investigation. Also while selecting polymers and solvent, their solubility parameters ($\delta$) are taken into account. The significance of the solubility parameter is that, polymers are soluble
only in solvents of similar solubility parameters (δ). Typical values of solubility parameter (δ) for polymers and solvent used (Billmeyer 1984) in the present investigation are given below,

<table>
<thead>
<tr>
<th>Solvent/Polymer</th>
<th>Solubility parameter δ[J/cm³]¹/²</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>20.3</td>
</tr>
<tr>
<td>PVC</td>
<td>19.4</td>
</tr>
<tr>
<td>PVAc</td>
<td>21.7</td>
</tr>
</tbody>
</table>

The solubility can be expected if difference in solubility parameters i.e. (δ₁-δ₂) is less than 3.5-4.0, but not if it is appreciably larger. This approach to polymer solubility, pioneered by Burrel (1955) has been extensively used (Akhare 1999).

Table 3.1: Important properties of PVC-PVAc (Billmeyer 1984).

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Property</th>
<th>PVC</th>
<th>PVAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sp. gravity (gm/cm³)</td>
<td>1.16 - 1.35</td>
<td>1.19 - 1.34</td>
</tr>
<tr>
<td>2</td>
<td>Refractive index</td>
<td>1.52 - 1.55</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Effect of sun light</td>
<td>Slight</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Effect of organic solvent</td>
<td>Soluble</td>
<td>Soluble</td>
</tr>
<tr>
<td>5</td>
<td>Clarity</td>
<td>Transparent</td>
<td>Transparent</td>
</tr>
<tr>
<td>6</td>
<td>Glass transition temperature (Tₙ)</td>
<td>81°C</td>
<td>28°C</td>
</tr>
<tr>
<td>7</td>
<td>Dipole moment</td>
<td>1.73D</td>
<td>1.166D</td>
</tr>
<tr>
<td>8</td>
<td>Dipole segment loss</td>
<td>-</td>
<td>3 × 10⁻¹</td>
</tr>
<tr>
<td>9</td>
<td>Dipole group loss</td>
<td>-</td>
<td>2 × 10⁻²</td>
</tr>
<tr>
<td>10</td>
<td>Melting temperature</td>
<td>273°C</td>
<td>-</td>
</tr>
</tbody>
</table>
3.3.2 Choice of Polymer Systems:

The possibility of formation of a link between two or more molecules can be realised through transfer of charge or association between the species. This necessitates the existence of acceptor and donor sites on the component atoms. This can be realised by the choice of proton donor and proton acceptor groups (Singh and Bedi 1991 and Akhare 1999). With this consideration polyvinyl chloride (PVC) as a proton donor and polyvinyl acetate (PVAc) as a proton acceptor (Tager 1978) have been selected for the present work. The choice of these polymers thus takes account of donor-acceptor capabilities. In the present study, dc electrical conduction of donor acceptor polymeric composites doped with polyaniline (PANI) and benzoic acid (BA) was studied to identify the mechanism of electrical conduction.

3.3.3 Structure of Polymers and Dopants Selected:

![Diagram showing the structures of PVC, PVAc, Polyaniline, and Benzoic Acid]
3.3.4 Methods of Sample Preparations Used for Present Work:

The polyvinylchloride (PVC) of standard grade product supplied by Polychem Industries, Mumbai and (PVAc) of standard grade were used for the study. The two polymers PVC (1.2g) and PVAc (0.3g) were taken in the ratio of 4:1 by weight and PANI for (Series I) and BA for (Series II) of different weights 0.003g, 0.006g, 0.009g, 0.012g and 0.015g i.e. 0.2%, 0.4%, 0.6%, 0.8% and 1.0% respectively. The 1.2g PVC in 15ml of tetrahydrofuran (THF). 0.3g PVAc in 10ml of tetrahydrofuran and PANI or BA in 5ml of THF were dissolved separately. After allowing them to dissolve completely, all the three solutions were mixed together. The solution was heated at 60°C for two hours to allow polymers to dissolve completely to yield clear solution. A glass plate (15cm x 15cm) thoroughly cleaned with hot water and then with acetone was used as a substrate.

Table 3.2: Scheme of work for series I.

<table>
<thead>
<tr>
<th>Series</th>
<th>Nature of Sample</th>
<th>Dopant</th>
<th>Wt of the component (gm)</th>
<th>% of dopant</th>
<th>Sample code</th>
<th>Study carried out</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PVC-PVAc polymer composite</td>
<td>PANI (Poly aniline)</td>
<td>1.20 0.30 0.003</td>
<td>0.2%</td>
<td>PP1</td>
<td>DC Conductivity</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>1.20 0.30 0.006</td>
<td>0.4%</td>
<td>PP2</td>
<td>+</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>1.20 0.30 0.009</td>
<td>0.6%</td>
<td>PP3</td>
<td>TSDC</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>1.20 0.30 0.012</td>
<td>0.8%</td>
<td>PP4</td>
<td>+</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>1.20 0.30 0.015</td>
<td>1.0%</td>
<td>PP5</td>
<td>Optical Properties</td>
</tr>
</tbody>
</table>

Chapter III: Sample Preparation and Experimental Techniques
Table 3.3: Scheme of work for series II.

<table>
<thead>
<tr>
<th>Series</th>
<th>Nature of Sample</th>
<th>Dopant</th>
<th>Wt of the component (gm)</th>
<th>% of dopant</th>
<th>Sample code</th>
<th>Study carried out</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVC-PVAc polymer composite</td>
<td>BA (Benzoic Acid)</td>
<td>1.20 0.30 0.003 0.2%</td>
<td>PB1</td>
<td>DC Conductivity</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td></td>
<td>1.20 0.30 0.006 0.4%</td>
<td>PB2</td>
<td>+ TSDC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.20 0.30 0.009 0.6%</td>
<td>PB3</td>
<td>+ Optical Properties</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.20 0.30 0.012 0.8%</td>
<td>PB4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.20 0.30 0.015 1.0%</td>
<td>PB5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To achieve prefect leveling and uniformity in the thickness of the film, a pool of mercury was used in the plastic tray in which the glass plate was freely suspended. The solution was poured on the glass plate and allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber maintained at constant temperature (40°C). In this way the film was prepared by isothermal evaporation technique (Narayan and Singh 1983, Bahri and Sood 1983, Deshmukh et al 2005). The film was subjected to 12 hrs heating at constant temperature 50°C and kept for another 12 hrs at room temperature to remove the traces of solvent. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities.
3.4 Methods of Characterization:

3.4.1 X-ray Powder Diffraction (XRD) to Identify the Amorphous Nature and Crystallinity in the Sample:

Crystallographic techniques for the study of molecular have been extensively used in widely varying fields from mineralogy and materials science to biological and pharmacology, which gets its name from the instruments used for the material characterization. The powder diffraction equipments span a wide range of crystallinity in materials from marginally crystalline polymers and mesoporous materials to metals and highly crystallized ceramics. From the last 50 years powder diffraction has become a widely accepted analytical method for characterization of soils, ores, rocks, metals, alloys, dyes, drugs, plastics, ceramics, forensic materials and other commodities.

Recently, XRD is considered as a most versatile non-destructive analytical tool for identifying the constituents of a multiphase mixture (solid or powder sample) quantitatively and qualitatively and also to determine the amorphous content of the same sample. The XRD pattern provides the information about crystalline size, solid solution, crystallinity stress and texture and the phase composition too. Due to the internal order and periodicity of crystal they produces a well defined diffraction pattern with X-ray or neutrons. The spatial geometry and the intensities of the diffracted beams, which can be recorded on a photographic film or a detector provide sufficient details about the internal structure of crystal. Though spectroscopic and resonance techniques have played an important role, but more definite structural data has largely been acquired using X-ray diffraction method.
3.4.2 Infrared Absorption Spectroscopy (IR): To Know the Existence of Different Bands and Bond Formation:

Infrared absorption spectra are normally used to ascertain any band of local order and groups present in the sample. Identification of unknown sample of plastic, rubber or a fibre may be required for a variety of reasons. In the field of industrial research, it may be necessary to analyse the polymer sample and identify it. Infra red spectroscopy is a powerful spectroscopy technique used for the identification and characterization of polymers. Infrared spectroscopy has been used for obtaining information about the co-ordination number of ions in simple crystal structure (Duchille and Roy 1959). It has been reported by White and Roy (1964) that the IR spectral characterization of many simple structure type oxides can be related directly to the co-ordination number and inter atomic distances.

3.5 Method of Electrode Coating and Thickness Measurement:
3.5.1 Electrode Coating:

For coating the silver electrodes, the method employed by Sangawar (1995), Bahri and Sood (1983), Belsare and Deogaonkar (1998) has been used. The electrodes coating on the film of measured thickness was done by using the quick drying and highly conducting silver paste supplied by Eltecks Corporation, Bangalore. A mask of circular aperture of 2.4cm diameter was used while coating, to ensure uniformity in size of coated silver electrode. The photograph of actual studied samples is shown in the figure 3.1.
Fig. 3.1: Photograph of actual studied samples.

Fig. 3.2: Experimental assembly for I-V and TSDC measurements.
Fig. 3.3: Photograph of sample holder.
3.5.2 Method Used for Thickness Measurement:

In the present study the method by Mahendri et al (1996) has been used. For measuring the thickness micrometer screwguage with least count 0.001 cm (10 μm) was used. But for greater accuracy and resolution, a compound microscope in conjunction with an acculomter, which gives least count 13 μm and 3.3 μm at the magnification of 1:10 and 1:100 respectively, was used. A small section of the sample was taken and mounted vertically to get a clear sectional view of the thickness. The film used for the present study is of thickness 60 μm. All the films selected for the study were of thickness 60 μm. This thickness was maintained almost constant throughout the present study for the sake of a better comparison of their electrical charge storage and optical properties for the given thickness.

3.6 Experimental Techniques Used for Measurements:

3.6.1 Sample Holder:

The sample holder used for the measurement of various properties was fabricated in the laboratory. The sample holder consists of two brass electrodes of equal diameters 2.4 cm. One of the electrodes is permanently fixed with the assembly. Another electrode can be moved vertically up or down and can be locked at any desired position with the screw provided. Both the electrodes are exactly parallel to each other. The electrodes surfaces were perfectly smooth and establish perfect electrical contacts with the silver electrodes painted on the sample film. Thus loading the sample, between the electrodes forms a metal insulator metal (M-I-M) system. (Diameter = 2.4 cm, radius = 1.2 cm,
area = 3.14 x 1.2 x 1.2 = 4.5216 cm$^2$). This value of area was taken as the effective area for all calculations. The sample holder is shown in the photograph of figure 3.3.

### 3.6.2 Electric Oven:

Thermostatically controlled oven supplied by Tempo Industrial Corporation, Mumbai was used for heating purpose. It consists of a double walled chamber (electrically shielded) and the temperature control is achieved through bimetallic thermostat. The temperature accuracy is $\pm 2^\circ$C up to $80^\circ$C and $\pm 1^\circ$C ($80^\circ$C to $250^\circ$C). The power consumption is 1300W and run on 240V AC single phase. It is provided with 3-heat switch with the positions 1, 2, 3 marked on the front panel. Position 1 gives the temperature upto $150^\circ$C position 2 gives $150^\circ$C to $200^\circ$C and the position 3 gives $200^\circ$C to $250^\circ$C. The photograph of the electric oven is shown in figure 3.2.

### 3.6.3 Power Supply for Poling Sample Films:

Stabilized power supply (specifically designed for the Millikans oil drop experiment) supplied by the Nupur India Ltd. was used. It has DC voltage range 0-300V and has a facility of reversing the polarity of the voltage. The front panel reads the voltage to the accuracy of $\pm 1$V.

### 3.6.4 Pico Ammeter:

The current was recorded by using highly sensitive pico-ammeter (Model DPA 11) with an accuracy $\pm 0.2\%$ supplied by scientific Equipments, Roorkee.
This is a very versatile, multipurpose equipment for the measurement of low dc-currents. The instrument uses a well designed, precision FET input electrometer, operational amplifier AD515. The output current is read on the 3 1/2 digit panel meter. It is capable of accepting either polarities of the input current. Well regulated power supplies are incorporated to use the instrument up to 10% changes in ac voltage. It can measure the current from 1pA (1x10^-12A) to 1999 x 10^5 pA with the accuracy ± 0.2%.

3.6.5 Experimental Method for DC-Electrical Conductivity:

Thermostatically controlled oven supplied by Tempo Industrial Corporation, Mumbai was used for heating purpose. A mercury thermometer with an accuracy of ± 1°C was used for recording the temperatures. The regulated power supply supplied by Nupur, India was used as the voltage source, while the current was recorded by using highly sensitive Pico-Ammeter (Model DPA 111) with accuracy ± 0.2% supplied by Scientific Equipments Roorkee.

The sample film coated with silver electrodes was sandwiched between two brass electrodes (diameter 2.4cm) of the sample holder specially fabricated in the laboratory. This formed the metal-insulator-metal (M-I-M) system, which was placed in furnace. The electric current (I) was measured by applying the voltages 25V, 50V, 75V….300V, at different constant temperatures 323K (50°C), 333K (60°C)….403K (130°C). The details of the experimental assembly shown in figure (3.1). The parameter like electric field E, current density J, electrical conductivity (σ) have been calculated. The results have been presented in the form of tables and graphs.
3.7 Thermoelectret Preparation and Method of Measurement of Thermally Stimulated Discharge Current:

3.7.1 Thermoelectret Preparation:

The film coated with silver electrodes was sandwiched between the two brass electrodes of the sample holder specially fabricated for the study. Thus the sample holder forming metal-polymer- metal system was placed in an oven and heated up to the poling temperature \( T_p \) 353K at a nearly uniform heating rate of 1.25°C /min. The sample was allowed to remain at that temperature for about 60min. Then electric field of desired strength was applied for 1 hour at poling temperature (353K). The sample was cooled down to room temperature, keeping the field on. The total time of polarization was adjusted to be 2 hours for all the samples. On attaining room temperature, the sample was kept shorted for 20 min to eliminate the stray charges. The electrets were prepared at different d.c. polarizing fields \( E_p = 10 \text{ kV/cm}, 15 \text{ kV/cm}, 20 \text{ kV/cm}, 25 \text{ kV/cm} \) and 30 kV/cm respectively.

3.7.2 Measurement of Thermally Stimulated Discharge Current:

Thermoelectret samples, so prepared were heated at nearly uniform heating rate of 1.25°C/min. This rate of heating was achieved by suitably adjusting the position of the knob of the thermostatic control of the oven with respect to time and temperature, which would produce equal rise of temperature (5°C) in equal interval (4min) of time. The discharge (TSD) current was measured with the sensitive Pico ammeter (Model DPA 111 with accuracy \( \pm 0.2\% \) scientific equipments Roorkee), (Belsare and Deogaonkar, 1998).
3.7.3 Experimental Method for Optical Properties:

The absorbance ‘A’ and transmittance ‘T’ of samples were measured by means of CART 2390 double beam automatic scanning spectrophotometer (at Regional Sophisticated Instrumentation Centre, Chennai) in the spectral range 450-1000nm at normal incidence. The spectral dependence of both ‘A’ and ‘T’ on doping percentage of PANI and BA thin film for series I and series II are shown in figures (5.6.1) and (5.6.2) respectively.
References:


Duchillie F and Roy R *The use of infrared absorption and moler refractivity to check co-ordination* (Zeit Krist) **111** 462 (1959).


