CHAPTER II
EXPERIMENTAL DETAILS
2.1 INTRODUCTION

Virtually, all the polymers are either amorphous or partially crystalline macromolecular compounds. However, the crystalline regions are macroscopic (≥ 1000 Å) in size. Since it is not possible to obtain crystals of polymers large enough to allow proper handling, these have to be studied either in the form of compressed pellets or slabs cast from the melt, or thin films. The increasing demand for microminiaturisation of components for electronic applications has further stressed the need for growth and development of thin insulating polymer films. Consequently, thin films of pure polymers, polymer composites and polymer blends are being extensively studied instead of pellets or slabs [1-2]. Also, the results on pellets are viewed with suspicion because of interfacial effects, role of surface conduction and large anisotrophy.

This chapter describes the experimental details of the investigations presented in the thesis. We briefly discuss methods of preparation of thin film and measurement of their thickness, types of electrodes and vacuum coating unit.

2.2 METHODS OF POLYMER FILM FORMATION

Thin films of polymers are obtained by a large variety of methods. Some excellent reviews [3-6] have appeared in the literature on the methods of preparation which are discussed briefly in the following sections.
2.2-1 THERMAL EVAPORATION

Thin films are produced from polymers by thermal evaporation of bulk material. Here the material to be deposited is heated to a high temperature at a very low pressure and in extremely clean conditions where it vapourises. The vapour is then allowed to condense on a substrate placed above the source to form a film. Thermal evaporation was reported to lead to a wax like deposit on a substrate, together with gaseous fractions and solid residue. Evaporated polymer films are contaminated due to the vigorous boiling action of the molten polymer, and due to the rapid evolution of breakdown products. However, uncontaminated films can be obtained by choosing a low evaporation temperature and thus a slow rate of deposition and by specially designed thermal evaporation methods [7], combination of internal baffles and flash evaporation [8] and laser evaporation.

2.2-2 COMBINATION OF INTERNAL BAFFLES AND FLASH EVAPORATION

In this technique, the polymer to be evaporated is taken in the powder form and is made to drop in the form of fine particles from a mechanically agitated hopper on to a hot crucible fitted inside, with baffles so that numerous discrete evaporations may occur.

2.2-3 LASER EVAPORATION

Here the material is heated by the enormous power of a laser source. The evaporation in this process generally takes
place from the surface of the material only. Very thin films
can be obtained as the amount of energy released in each burst
is very large.

2.2-4 PYROLYSIS

The thermal decomposition of a compound to yield a
deposit of the stable residue is called pyrolysis. Szwarc
[9] discovered that the vacuum pyrolysis of xylene, on
condensation could lead to poly-p-xylene which were
contaminated by low molecular weight by-products. Gorham [10]
used di-p-polymer which is pyrolysed in vacuum at 600 C. This
process forms two molecules of p-polymer which instantaneously
polymerize when incident on a substrate maintained at less
than 30 C. The above formed polymer is a high molecular weight
leniaca poly-p-polymer. The advantage in this process is that
the films seemed to have better electrical, mechanical,
optical properties compared to the other types of preparation.

2.2-5 SPUTTERING

The ejection of atoms from the surface of a material by
bombardment with energetic particles is called sputtering. The
ejected or sputtered atoms can be condensed on a substrate to
form a thin film. The chief advantage of this method is that
the deposition rate remains constant. Various sputtering
systems such as glow discharge and rf-sputtering are based on
the effect that the free electrons ejected from the evaporant
can be accelerated in an electric field to cause further
ionization of the residual gas and such ionization will result in further bombardment of the surface of the target and a self sustaining reaction. Some other systems are based on increasing the electron path lengths so that the self sustained system can work at relatively low pressures.

2.2-6 GASEOUS DISCHARGE

Thin films of polymers can be obtained when a gas discharge is maintained in the vapour of monomer. Since the pressure maintained is of the order of 1 mm Hg. The discharge is a cold one and no hot cathode emission is necessary. The problems associated with high gas pressures and substrate heating have been minimised by utilizing a longitudinal magnetic field to compress the glow discharge in a tube and rf electrodeless excitation.

2.2-7 HOT PRESSING METHOD

The first method of film fabrication was hot pressing. In this method the polymer powder is placed in between two ferrotype photographic plates and hot pressed at a temperature 10-15 C above the crystalline melting point under pressure. The film is then removed from the press and immediately quenched in ice-water in order to prevent any crystallization, if necessary. Then the film is stretched in order to obtain necessary thickness.
2.2-8 CASTING METHOD

Preparation of thin films of polymers from solvent casting is a very satisfactory method of film formation. In this method, the polymer dissolved in the appropriate solvent is poured on a clean surface of glass plate and is spread to an even thickness with a doctor blade. A dust shield is placed above the solution and the film is allowed to form in air. When the film is dry, the plate is immersed in water and the film floats. In most cases the film is then dried in a vacuum chamber for about 8 hrs followed by exposure to room temperature.

2.2-9 FILM BLOWING

Biaxial stretching by applying a pressure difference across the film or by elevated temperatures gives rise to thin film. This method consists of placing the polymer film under a hold down ring that secures the film over a circular opening in a heavy teflon disk. Pressure is then applied to one side of the polymer film and a "balloon" blows through the opening in the teflon disk. The entire assembly is placed in a vacuum oven which allows heating under an inert atmosphere or vacuum. Some polymer films are successfully blown to thickness of 10 to 30 μm. The blowing process is very difficult to control and have to be done at a high temperature, near the crystalline melting point.

2.2-10 PHOTOLYTIC PROCESS

Photolytic process is used for the formation of thin
dielectric layers for use in thin film circuit insulation. In this process the films are obtained when the surface is irradiated with ultraviolet light in the presence of monomer vapour. Polymer films formed in this method are quite stable and the reliability is excellent down to 50 Å. Dielectric properties of photopolymer films have been studied in many cases and found to possess the properties of the bulk polymer.

2.2-11 VACUUM EVAPORATION

Hogarth and Iqbal [11] have prepared thin films of polypropylene by vacuum evaporation technique. Polypropylene was evaporated at a pressure of $6 \times 10^{-5}$ torr from a stainless steel blade which was maintained at a temperature of 335°C. The film was deposited on to a previously deposited copper or aluminium base electrode. However, the polymer films prepared by this method are generally not free from pin holes.

2.2-12 FILM FROM POLYMER SOLUTION

All the methods for film preparation discussed above involve immediate polymerization. As such, they are not expected to give useful films for research purposes. Further, the polymer formed by these techniques may have different degree of polymerization and may contain undesired impurities. Polymer films prepared by vacuum deposition technique are also not useful as they are not expected to be free from pin holes. Moreover, polymer blend films cannot be obtained by the above methods as it is difficult to control the quantities of
constituent polymers during evaporation and polymerization. Films with uniform degree of polymerization and high purity can be prepared from polymer solution using highly pure polymer as solute and inert solvents of AR grade. The blending percentage can also be controlled easily by dissolving known amounts of the constituent polymers in solution.

There are two main methods available for preparing thin films from polymer solution:

(a) Isothermal immersion technique, and

(b) Casting from solution.

(a) Isothermal Immersion Technique

Solution of suitable concentration is kept at a desirable temperature and substrate is immersed into it vertically for a given period of time depending upon the required film thickness. When the film is deposited, the substrate is slowly taken out and dried by hot air. The deposited film is then gently detached using a sharp knife edge [12-13]. Polyblend films can also be prepared by dissolving desired quantities of constituent polymers in a solution. Rastogi and Chopra [14] have studied this method in detail and found that the thickness of the film depends upon the concentration of the solution, its temperature, nature of the substrate and the time for which substrate is kept immersed in the solution.

This method requires a great care in selecting the temperature and concentration of the solution. Also,
sophisticated mechanical instrumentation is required for taking out the substrates from the solution, keeping them exactly vertical to the solution surface. Lack of proper instrumentation and care may result in the films containing air bubbles and of nonuniform thickness.

(b) Casting from Solution

The polymer solution of known concentration and quantity is spread over an optically plane clean glass plate of known area which is placed horizontally over a mercury pool. Solvent is allowed to evaporate at a suitable constant temperature and the resulting film is gently detached from the substrate. Films of different thicknesses may be obtained using solutions of different concentrations. The films obtained by this method are of uniform thickness and perfectly plane surface, if prepared carefully. Also, an elaborate cleaning procedure must be adopted for substrates.

(i) Choice of substrate and its cleaning

An ideal substrate should not react with the polymer or its solvent or the surrounding atmosphere; it should be resistant to chemical corrosion, especially to those which are commonly used for cleaning purposes. Its surfaces must be smooth and easily washable for repeated use. Its softening and melting points should lie much higher than the temperature of investigation. It should be made of hydrophobic material. Out of various substrates, like metal foils, crystals, glass etc., glass is the best of all.
(ii) Choice of Solvent

To grow the best quality, smooth films, free from pinholes the rate of vaporization of the solvent should be kept sufficiently slow. This can be achieved by using a solvent of high boiling point.

(iii) Solution Concentrations

It is preferable to use the solution of low concentration for the film deposition. Experiments indicate that the films grown from thick solutions have considerably different thicknesses at different spatial points. They may also trap air bubbles in their structure. The best procedure is to keep the slides immersed in thin solution over a small period of time about (20 minutes).

(iv) Solution Temperature

Temperature of a solution markedly affects the growth of films. Hot solution give rise to thinner depositions due to a lower value of viscosity. It is better to use the solution whose temperature lies in the neighbourhood of room temperature. It is necessary since the substrate acquires the temperature of the solution when dipped into it and if it is much higher than room temperature, the rate of vaporization of solvent would greatly enhance during the process of drying which is undesirable. The temperature of solution is kept a bit higher (about 5 C) than room temperature so as to make the compensation for temperature fluctuations arising due to
change in the weather. A magnetic stirrer is used to eliminate the temperature gradients.

2.3 PRESENT EXPERIMENTAL TECHNIQUE

Thin polymer films were deposited by the solution grown technique which involves the isothermal immersion of a substrate into the polymer solution of suitable concentration held at a constant temperature for a certain time. The rate of growth of the polymer film and thickness of the film depends on the nature of the substrate and the solvent and also on the concentration and solvent temperature, and on the subsequent time for which the substrate is left immersed in the solution.

Polyvinyl formal (PVF) films were deposited from the solutions of fixed concentration (1.5 grams of PVF dissolved in 50 cm$^3$ of the solvent 30:20 benzene and ethanol). The solution of the particular concentration was prepared in a glass beaker by dissolving the required amount of PVF in the solvent at 40°C. The solution was continuously stirred by means of magnetic stirrer for about 45 mins. The solution was stirred and heated simultaneously until it ensures a homogeneous mixing.

Freshly and neatly cleaned blue star micro-glass slides with vacuum deposited lower electrode (Al) were used for the deposition. The substrates were held inside the constant temperature bath vertically above the solution. When the
solution and substrates acquired the required temperature the substrates were isothermally immersed in the solution for fixed time. After withdrawal of the film substrates from the solution, they were washed in the solvent and then dried in hot air oven for more than 24 hours maintained at a temperature of 40°C.

2.4 MEASUREMENT OF FILM THICKNESS

The thickness of polymeric films can be measured by a variety of methods. They may be described under the following three categories:

(i) Mechanical methods,
(ii) Optical methods, and
(iii) Electrical methods.

2.4.1 MECHANICAL METHODS

This includes two important methods, namely Stylus method and Weighing method.

(A) Stylus Method

In this method, a fine pointed stylus is moved over a stepped surface formed by the edge of the film on the substrate. The transverse displacement suffered at the step is fed to an electronic circuit for amplification and recording, and the thickness of the film is computed. The method is very simple but its accuracy is very low [15-17].
(B) Weighing Method

This method is applicable only to films of uniform thickness. Since mass is defined as density multiplied by volume, and the area and the mass of the film can be measured precisely using vernier callipers and physical balance, the thickness of the film can be computed by the formula:

\[ d = \frac{M}{\rho \times a} \]

where \( M, \rho, a \) and \( t \) are the mass, density, area and thickness of the film, respectively. Obviously, the sensitivity of the method depends upon the measuring accuracy of \( M \) and \( a \). Though it is not always possible to cut the substrate in a well defined area. Further, the area selected for thickness measurement may not be representative of the area under investigation [17,18].

2.4-2 OPTICAL METHODS

Ellipsometry, interferometry and light sectioning methods are the important methods belonging to this category.

(A) Ellipsometry

This method is used for the measurement of thickness of transparent films. It is based on evaluating the change in the state of polarization of light reflected from the film and the substrate. However, as it is time consuming and involves complicated mathematical calculations [19].

(B) Interferometric Methods

Interferometric methods include those devices which
make use of interference of light, e.g., Newton's ring set up, Michelson interferometer, Fabri-Perrot etalon, etc. Film thickness is determined by observing the shift in the interference fringes (due to change in path difference of reflected or transmitted light rays) on moving from film surface to the substrate. The technique is mainly used for measuring thickness of optically smooth films yielding consistent results [20].

(C) Light Sectioning Methods

In case of thin films of more than 1 mm thickness, measurement can be made using travelling microscope movable in vertical direction. Light sectioning microscope can also be used for precise thickness measurements, however, the method becomes quite inaccurate for films of uniform thickness. A brief description of this method is as follows:

Light from a slit is projected on to the sample surface at an angle of 45°. An observing microscope making an angle of 45° to the sample surface and 90° with the illuminating light beam is used for observing the separation of slit images. In case of opaque films, slit is projected across a step in the film; however, in the case of transparent films step is not necessary as the two images are obtained because of reflection from the upper and lower surfaces of the film [21-22].

According to Brown [23], the separation of slit images due to reflection across the step can be measured with an
eyepiece micrometer to an accuracy of 0.1 mm in 1 to 400 m range. In case of transparent films, the actual film thickness \( d \) can be calculated from the apparent film thickness \( d' \) and the index of reflection \( n \) of the medium using the relation:

\[
d = d' (2n^2 - 1)^{1/2}
\]

2.4-3 ELECTRICAL METHODS

Thickness of thin films can also be determined conveniently by measuring the capacitance of a condenser having film as a dielectric. This method gives accurate result for uniform films. Vacuum evaporated electrodes are deposited on both the surfaces of the film to form a parallel plate condenser. Plane metallic electrodes can also be used for very good uniform surfaces. Capacitance of thin condenser thus formed is measured and the thickness is calculated using the observed value of the capacitance, area of the metallic electrodes and dielectric constant of the film. Absence of pin holes and uniformity of film surfaces are the two main advantages of this method. It is, therefore, most suitable for solution grown thin films.

2.5 TYPES OF ELECTRODES

The following four types of electrodes are used for making electrical contacts with polymer films for studying the electrical storage and transport properties:

(i) Pressed metal-foil electrodes,
(ii) Painted electrodes,
(iii) Liquid contact electrodes, and
(iv) Vacuum deposited electrodes.

2.5-(i) PRESSED METAL-FOIL ELECTRODES

Film is sandwiched between two plane metallic foil electrodes of desired shape, area and good surface finish. Springs are used to ensure uniform pressure throughout the film surface. However, in the case of polymers, when measurements are carried out at high temperatures, such electrodes are disadvantageous. At high temperatures, the polymer is softened. Due to pressure of the electrodes on the film, its thickness is reduced and this sometimes results in breakdown of the polymer film. Further, under ambient humid atmospheric conditions, practically all metallic electrodes except gold and platinum form oxide and other chemical coating over their surfaces. This affects the experimental results by contaminating the film surface as improper transfer of charges takes place through contaminated surfaces.

2.5-(ii) PAINTED ELECTRODES

Electrodes of desired shape and area can be painted on film surface using conducting graphite or silver paints. However, the use of painted electrodes is not possible on most of the polymers, since the thinner present in the conducting paint may attack the film surface. Hence, the use of painted electrodes is restricted to those polymers only, which are inert to the thinner used with conducting paints.
2.5-(iii) LIQUID CONTACT ELECTRODE

In this method, non-metallized surface of an unilaterally metallized film specimen is kept in contact with a liquid such as water or ethyl alcohol so that a thin uniform layer of liquid rests over the non-metallized surface of the film. A potential is applied between the metallic electrode and rear unmetallized surface of the film. A double charge layer is formed at the solid-liquid interface and as a result of interaction between electrostatic and molecular forces, charge transfer to polymer film takes place. Electroces should be withdrawn and liquid evaporated before removal of voltage to ensure charge retention on the specimen surfaces. Recently, non-wetting liquid-insulator contact electrodes have also been employed. Monocharge electrets have also been prepared using liquid contact electrode obtained by filling one side metal polymer gap with liquid and leaving the other filled by air.

2.5-(iv) VACUUM DEPOSITED ELECTRODES

Vacuum deposition method is probably the best and most convenient for depositing metallic electrodes of desired size and shape. The metal can be vacuum evaporated on any metallic or non-metallic substrate or film specimen. No air gap exists between the evaporated electrode and the substrate. The electrodes can be very conveniently used for measurements at low as well as high temperatures, provided the melting point of electrode metal is higher than the temperature of measurements.
In the present investigation, vacuum deposited metal electrodes are used.

2.5-(v) VACUUM COATING UNIT SYSTEM

The metal electrodes were deposited by vacuum evaporation technique using a Vacuum Coating Unit. The Vacuum Coating system was assembled using necessary accessories. The vacuum coating unit has been employed to achieve a vacumm of $2 \times 10^{-6}$ torr, in the evaporation chamber. A pirani-penning gauge system measures the vacuum in the belljar. A low tension transformer capable of providing 100 amperes at 10 Volts was used for resistive heating of tungsten spiral/boat to which the material to be evaporated was fed. Metals like aluminium, copper and silver of high purity of 99.99% are used for the deposition of electrodes.

Vacuum evaporated metal electrodes were deposited on polyblend thin films using Hind High Vacuum Coating Unit, Model 12-A4.

(a) MAIN PARTS OF THE COATING UNIT

The unit consists of the following parts:

1. Vacuum chamber: This consists of
   A. Hemispherical glass belljar with a L-shaped rubber gasket for air sealing,
   B. Support for substrate or specimen to be coated,
   C. Molybdenum boat or a tungsten filament for heating the material to be evaporated,
D. Hinged metallic shield for controlling the deposition rate of the material,
E. High tension discharge unit (electrodes) for ionic bombardment, and
F. Substrate rotator.

2. Rotary pump

3. Diffusion pump

4. Pirani gauge (for measuring coarse vacuum)

5. Penning gauge (for measuring high vacuum)

6. Electric supplies to the chamber:
   A. A low tension supply - for filament and boat,
   B. A high tension supply - for glow discharge cleaning of the substrate, and
   C. Variac for LT and HT supply.

7. Valves:
   A. Backing valve ($V_1$) - this connects the rotary pump with the diffusion pump,
   B. Roughing valve ($V_2$) - this connects the rotary pump with the vacuum chamber,
   C. Baffle valve ($V_3$) - this connects the diffusion pump with the vacuum chamber,
   D. Air admittance valve ($V_4$) - this allows air to enter into the vacuum chamber, and
   E. Gas inlet valve ($V_5$) - this allows gas to enter into the chamber at the desired rate.
(b) OPERATION OF THE COATING UNIT

At the start all valves were closed and the rotary pump was turned on. It initially evacuates the tubes connecting the rotary pump and the junction of the backing and roughing valves. When the pressure shown by the pirani gauge attained a value less than 0.5 torr, the backing valve $V_1$ was opened for connecting the rotary pump with the oil diffusion pump. Circulation of water in the tubes surrounding the diffusion pump was started and the heater of the diffusion pump was turned on.

Approximately half an hour later with the diffusion pump ready, the backing valve $V_1$ was closed and the roughing valve $V_2$ was operated for connecting the vacuum chamber directly with the rotary pump. The pressure inside the vacuum chamber was allowed to fall to $10^{-2}$ to $10^{-3}$ torr. After which the high tension supply was switched on. This caused ionization of the rarefied air inside the vacuum chamber with the net result that the substrate was cleaned by ionic bombardment. The HT was switched off after 5 minutes.

The pressure inside the vacuum chamber was allowed to fall up to 0.002 torr so as to establish a rough vacuum. After this valve $V_2$ was closed and valve $V_1$ was opened again so that the rotary pump was connected to the diffusion pump for maintaining the backing vacuum. With valve $V_1$ open, the baffle valve $V_3$ was opened to connect the diffusion pump with the
vacuum chamber. The vacuum was maintained by reading the pressure on the Penning gauge. When the vacuum had reached a pressure value of $10^{-5}$ torr, the low tension supply was switched on. When the Al pellet kept in the spiral tungsten filament started to evaporate, the hinged metallic shield was swung out to allow the deposition of the metal vapour on the surface of the specimen. In this way aluminium electrodes of 5.5 cm diameter were prepared.

With the deposition over, the filament and heater currents were switched off. Valve $V_3$ was closed and the fine vacuum Penning gauge was switched off. After 10 min the air admittance valve $V_4$ was opened to leak air into the vacuum chamber making the bell jar free to be removed and the electrodes deposited film to be taken out. The coating unit was closed down by first turning off the diffusion pump heater with the rotary pump still running and the backing valve open. After 15 minutes when the boiler of the diffusion pump was cooled, the backing valve was closed and the rotary pump was switched off. Finally the water circulation in the diffusion pump was stopped.

### 2.6 CIRCUIT CONFIGURATION AND PRINCIPAL EQUIPMENT

The instruments used were practically common to all the studies undertaken in this thesis. The experimental circuitry was not complicated in all the cases. The current measuring cell with its constructional details and the specifications of
Fig. 2.1 - Arrangement Of Current Measurement
the other measuring instruments are described in the following
subsections.

2.6-1 ARRANGEMENT OF CURRENT MEASUREMENT

A schematic diagram showing the sample mounting is shown
in Figure 2.1. The sample polarization and current measurement
have been carried out in this cell using an assembly which is
dry, rigid and well-established. This assembly have the
following proprieties (i) high insulating resistance, (ii)
freedom from picking up of spurious potentials and induced
charges due to physical motion of the system, (iii) negligible
leakage current and less microphonic. To achieve the required
degree of precision every consideration of perturbing
parameters was taken into account, while designing the
electrode assembly.

2.6-2 OTHER INSTRUMENTS USED AND THEIR SPECIFICATIONS

(i) Electrometer Amplifier - Model 600B KEITHLEY

Current : $10^{-5}$ to $10^{-14}$ amps (full scale for both
polarities)

Accuracy : 3%

Voltage range : 10 mV to 10 V (full scale for both
polarities)

Accuracy : ± 0.1 mV

Input impedance : Greater than $10^{14}$ ohms in open position
of input impedance switch
(voltage measurements)

(ii) High voltage unit - Type 4800 B

Manf. : Electronic Corporation of India Ltd.,
Hyderabad

Output voltage : ± 50 to +3,000 volts

(iii) Stabilizer - Nelco stabilizer

Regulation : ± 1% from no load to full load
REFERENCES


