Chapter 2: Instrumentation and Technique

ABSTRACT

This chapter deals with irradiation facility and techniques used to study the polymer modification, i.e. Variable Energy Cyclotron, FTIR, LCR meter, TGA, DSC, optical microscopy and Vickers' microhardness techniques.

2.1 INTRODUCTION

The bombardment of materials with energetic ions or atoms can give to many changes within the target materials. These changes may be due to damage of the target caused by the transfer of energy from the incident particles to the atoms of the target or they may be due to the chemical effects of the incident particles once they have come to rest in the target or to a combination of both. In order to understand the interaction of the incident particles with the target materials, it is necessary to measure the changes that have been induced in the target due to exposure to the incident beam of ions or atoms.

However, these changes in macroscopic properties are due to alterations in microstructural properties such as chemical bonding and phase distribution. In order to develop an understanding of why the macroscopic changes occur and how to optimize the changes for a particular application, it is necessary to characterize the microstructure of ion bombardment materials and relate the alterations in microstructure caused by the bombardment to the macroscopic changes.

This chapter will described brief description about the Variable Energy Cyclotron and characterization technique that are commonly used for ion bombarded insulators.

2.2 IRRADIATION FACILITY

The Variable Energy Cyclotron at Chandigarh is a classical Machine which was transferred from the Department of Physics, Rochester University, Rochester (N.Y.), U.S.A. [1]. It has been functioning with resolved beams of protons, deuterons, alphas and He^{3++}. The beams of protons of energy from 1 to 5 MeV, deuterons of 4 MeV, alphas from 7 to 8 MeV and He^{3++} up to 11 MeV have been obtained at the target. It is single Dee classical cyclotron with arrangements for variable frequencies from 10 to 20 MHz, and a main magnetic field up to a maximum of 14 K Gauss. This permits the variability of the energy of the various accelerated ions. The layout plan of the whole setup is shown in **Figure 2.1**.

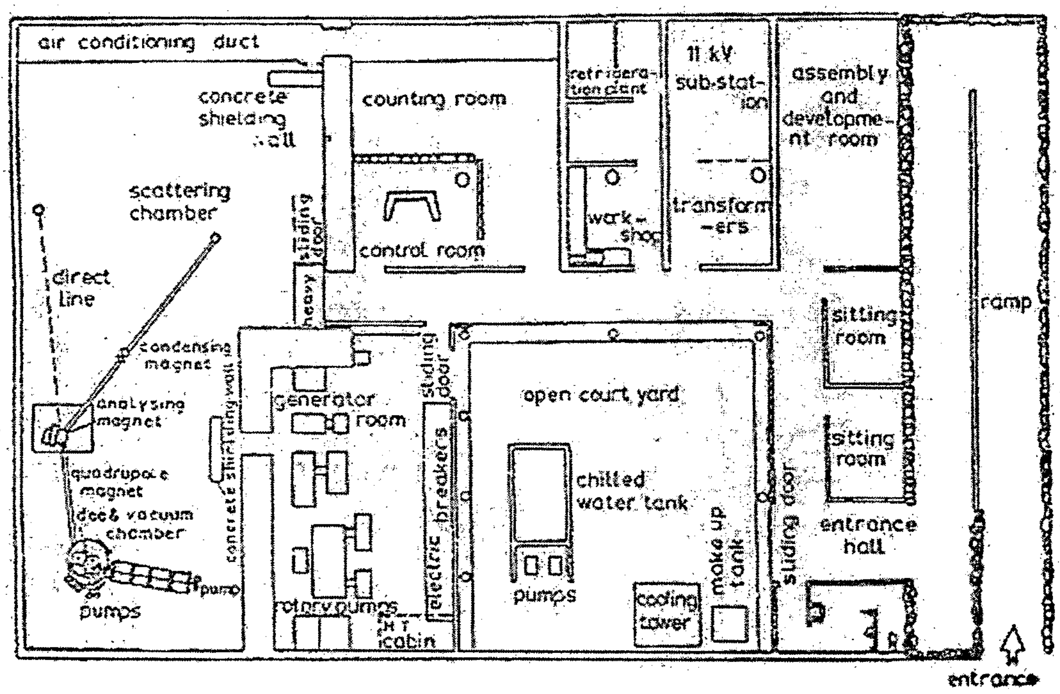

Figure 2.1: General layout plan of the cyclotron laboratory.

All the operations of the machine are controlled from a control desk. It is possible to maintain a pressure of 5 X 10^{-6} mm Hg in the whole vacuum system. A total power of 110 kW is required when the machine is fully operative with all the accessories.

2.2.1 The Main Magnet

The lids of the main chamber form the tips of the pole pieces of the main magnet (67.5 cm in diameter) and serve as the main magnetic field as well as the seal to the vacuum as shown in **Figure 2.2a** and **2.2b**. The magnet has four current-carrying coils-two on each side, each carrying a maximum current of 100 A, at 100 V. The current is supplied by a DC generator whose output is stabilized by a feedback system, as shown in **Figure 2.3**, by using the shunt in series of the coils and a DC amplifier. The stability of the magnetic fields is better than 1 in 10^5 which was indicated by the stability of the resonance signal of the NMR probe on the oscilloscope. The mapping of the profile of the magnetic fields is accomplished by using a search coil and a flux meter with a sensitivity of relative measurement up to 1 Gauss. However, it must be mentioned that the mapping is not very accurate, as the profile of the magnetic field was measured by a flux-meter, with respect to the field at the centre. The absolute value of the field at centre, however, was measured by an NMR probe with much better accuracy. The radial fall-off of the field is shown in **Figure 2.4a**.

The field index $\eta = \left(\frac{-dB}{B} \Big/ \frac{dr}{\gamma} \right)$ varies from zero at the centre to 0.1 at the extraction radius of 27.5 cm. It is thus a weak focusing machine. The azimuthal variation of the magnetic field at different radii is shown in **Figure 2.4b**. The pole fields are so aligned that the contribution of the first harmonic is less than 10 Gauss up to the extraction radius as shown in **Figure 2.4c**. Therefore no appreciable shift in the beam centre was noticed.

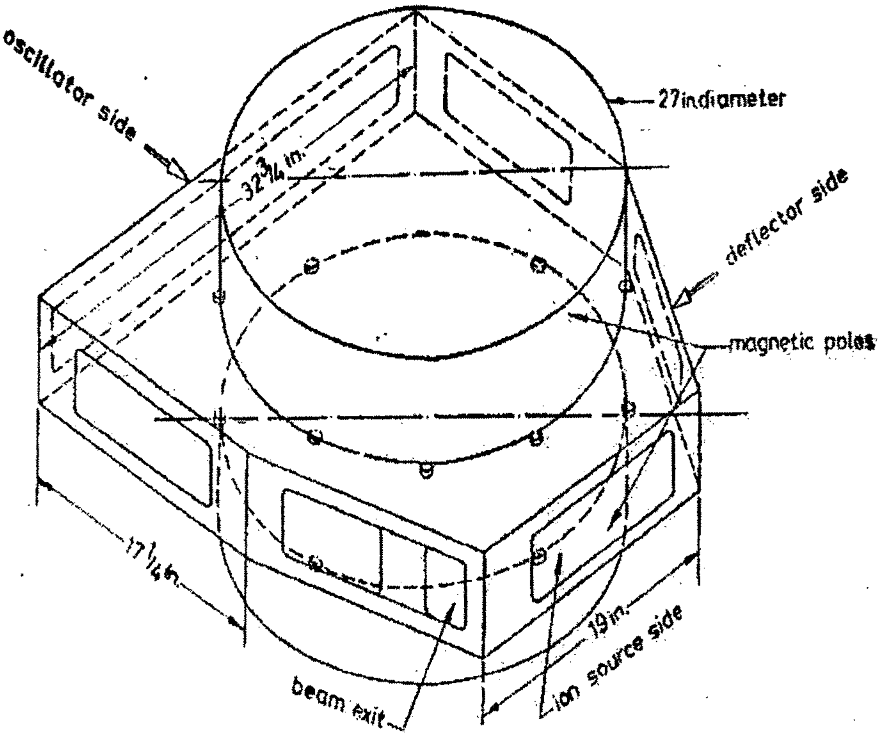

Figure 2.2a: Configuration of Dee chamber with the pole pieces. The spaces are also shown.

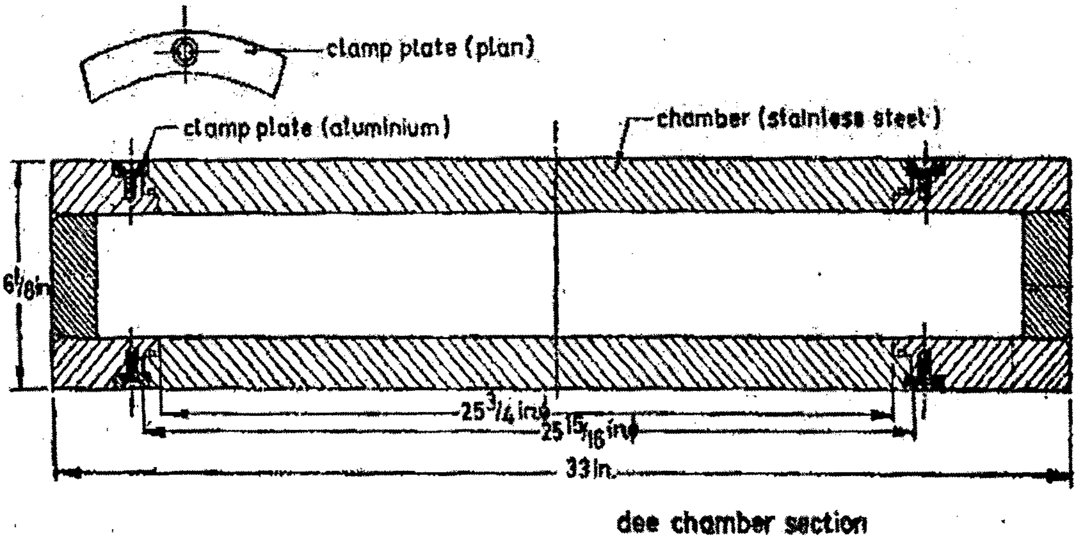

Figure 2.2b: Profile of the clamp plate attached to the chamber.

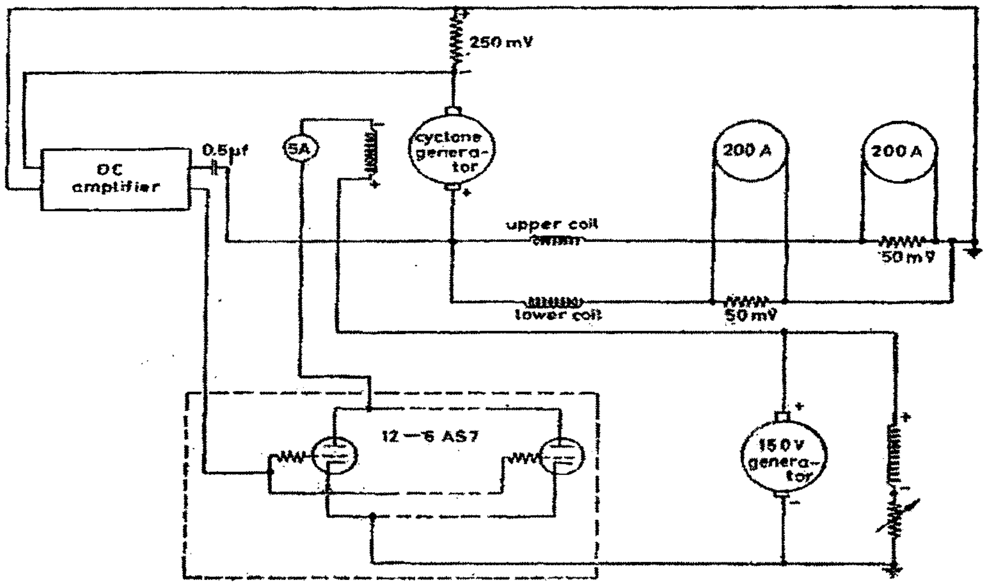

Figure 2.3: Circuitry used for stabilizing the voltage of the DC generator for the main magnet and the analyzer.

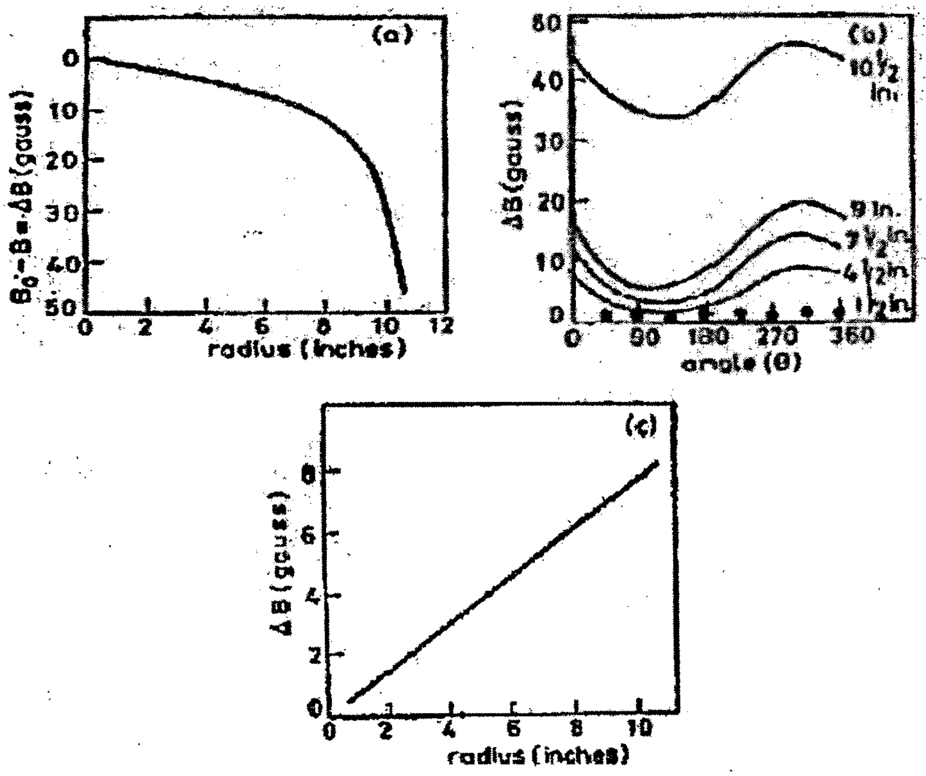

Figure 2.4: Variation of the magnetic field of the main magnet in the chamber.

2.2.2 The Oscillator

The oscillator is driven by RCA 5771 tube which is a 25 KVA triode with water cooled anode. A 10 ft long and 26 inch outer diameter cavity with the dee stem of 3 inches diameter, forms the tank circuits of the oscillator tube which is coupled to the tube by filament leads through coupling cylinder of 10 inches diameter. The shorting bar controls the frequency of the oscillator by providing terminated line-the termination being provided by a plate, which connects the stem of the cavity with the outer cylinder. The position of the plate can be controlled from the control desk. For maximum frequencies say at 20 mega-cycles, the required oscillator power is of the order of 20 KVA. The plate voltage is 10 KV. There is no special provision either for stabilization for the oscillator power supply or the amplitude of the Dee voltage. The high Q of the oscillator circuit and the resonance conditions of the circuit, take care of both the stability of the frequency and the Dee voltage.

2.2.3 The Ion Source

The machine was provided with the hooded arc-Ion-Source which was some what modified for better flexibility. The Ion-Source is now provided with the remote control arrangement for the filament movements in the two perpendicular directions. The chimney of the Ion Source may also be moved in X-Y-Z direction to place the plasma-exit hole to any desired position so as to maximize the output current. The output current was found to be quite sensitive to the inclination and position of the ion-source with respect to Dee. The filament of the Ion Source can be replaced with disturbing the Vacuum. The gas flow is being controlled by two Edward's needle valves. The power (6.3 V, 300 A) to the filament of the ion source, which was originally provided by a DC motor generator set, has now been replaced by a DC power supply of 6.5 V and 300 A.

2.2.4 The Deflector

The Deflector, which deflects the Ion beam out of the orbit, is of electro state type, with a provision of maximum D.C. voltage of about 70 K.V. The blade of the deflector is made of copper with the oil cooling arrangement and the septum is made of very thin tungsten plate. The position of the blade and the septum of the deflector may be controlled remotely from the control desk; this is needed for optimizing the extraction of the beam from the deflector. The septum is kept at ground potential while high voltage is applied on the blade which is made of hollow copper conductor. The blade of the deflector is cooled by circulating the mixture of transformer oil+CCl_4 (ratio 1:2) using a centrifugal pump. The heat of the oil is removed by circulating chilled water.

2.2.5 Vacuum System

The vacuum inside the machine is obtained with the help of four 6" and one 9" diffusion pump. The fore vacuum to the diffusion pumps is provided by a kinney Rotary pump. The addition of the diffusion pump to the oscillator cavity helped to improve the vacuum in the cavity by a factor of tow when compared to the Rochester set-up. This increased the stability of the oscillator many times. The position of some of these pumps which also includes the oscillator cavity.

2.2.6 Control System

The various power points in the cyclotron are interlocked with each other; and with various cooling and shielding devices to ensure the safety of the various components, as well as of the personnel. As for example, the heavy door, at the entrance to the cyclotron, cannot be opened; if the beam is on. Similarly, the current in the magnet coil or in the filament of the oscillator tube cannot be applied, if the cooling system is not turned on and so on so forth.

The detailed characteristics of the machine are summarised in the **Table 2.1**.

Table 2.1: The detailed characteristics of the machine are summarized as below.

1.	Maximum magnetic field (Main Magnet)	14 K Gauss.
2.	Maximum Power Consumption in Magnet	40 K V A (400 amperes at 100V)
3.	Weight of the magnet:	20 tons.
4.	Size of the pole pieces:	26 inches.
5.	Gap distance between the pole pieces	65/16 inches.
6.	Frequency range of the oscillator	10 MHz to 20 MHz.
7.	Maximum power of the oscillator	25 K V A
8.	Dee Voltage:	30-40 K V.
9.	Dee size	25 inches dia.
10.	Ion Source	Hooded Arc type.
11.	Vacuum	5 X 10^{-6} mm of Hg.
12.	Distance of the analyzing magnet from the chamber	12 ft.
13.	Distance of the target from the analyzing magnet.	18 ft.
14.	Internal beam	15 micro amperes.
15.	External beam	1.5-2 micro amperes.
16.	Analyzed beam	0.5- micro amperes.
17.	Attainable energies and particles:	
	(a) Protons:	2-8 MeV
	(b) Deuterons:	1-4 MeV
	(c) Alphas	2-8 MeV
	(d) He^3	2-11 MeV
18.	Total power consumption:	100 K V A.

2.3 CHARACTERIZATION TECHNIQUE

Characterization of a material is essentially the determination of structural, thermal, mechanical, electrical properties etc. The necessary input for the characterization and the analysis of polymers is the adequate understanding of the instrumentation involved. Off-line measurement to study the physico-chemical properties of pristine and irradiated polymer samples by different characterization techniques viz. IR spectroscopy, optical microscope, microhardness, electrical frequency response and thermal analysis are described here.

2.3.1 IR Spectroscopy

Infrared spectroscopy is the study of the interaction of infrared light with matter. It is one of the most powerful analytical techniques which offer the possibility of chemical identification. One of the most important advantages of infrared spectroscopy over the other usual methods of structural analysis is that it provides useful information about the structure of molecules quickly, without lengthy evaluation methods.

The technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules of chemical substances vibrate at many rates of vibration, giving rise to close-packed absorption bands, called an IR absorption spectrum which may extend over a wide wavelength range. Various bands will be present in IR spectrum which corresponds to the characteristic functional groups and bonds present in chemical substance. Thus, an IR spectrum of a substance is a fingerprint for its identification.

The infrared region of the electromagnetic spectrum covers a wide range of wavelengths from about 800 nm (end of visible region) to about 0.2 nm (beginning of the microwave region). The positions of bands in IR spectra are represented either in wave numbers (ν) or wave lengths (λ). The reciprocal centimeter has been referred to as 'Rydberg' and 'Kyser'. Band intensities in IR spectrum may be expressed either as transmittance (T) or absorbance (A). Transmittance is defined as the ratio of radiant power transmitted by a sample to the radiant power incident on the sample. On the other hand, absorbance is defined as the logarithm, to the base of 10, of the reciprocal of the transmittance, i.e.

$$A = \log_{10}\left(\frac{1}{T}\right) \qquad (2.1)$$

When a molecule absorbs radiation, its energy increases in proportion to the energy of the incident photon, and is expressed by the relation.

$$\Delta \mathrm{E} = h\nu = \frac{hc}{\lambda} \qquad (2.2)$$

where h is the Plank's constant, λ wavelength of radiation and c the velocity of light.

Spectrometers may be either dispersive or non dispersive. In the former class are those instruments using gratings of prisms as the dispersing elements. Non dispersive type includes Fourier Transform Spectrometer. In the case of Fourier transform infrared (FTIR) spectrometers; although the final spectrum is the same as that produced on a dispersive spectrometer, the interferometer spectrometer operates on an entirely different principle. The basic optics are extremely simple. Such a device produces an interferogram which must be decoded to yield a spectrum. This process would seem to be an unnecessarily complicated way to obtain a spectrum, but the interferometer has important advantage in energy transmission over the dispersive spectrometer. FTIR spectrometer does not use slits. So the instrument is through putting the entire radiation beam at all times during scanning. The resolution depends only on the length of travel 'l' of the movable mirror and is equal to $(2l)^{-1}$. Thus for a 1 cm traverse the resolution is 0.5 cm^{-1}. For a 50 cm traverse (experimentally very difficult) the resolution would be 0.01 cm^{-1}. Moreover, the radiation is not dispersed in the interferometer; all of the source radiation (except that absorbed by the sample) is contributing to the signal at all times. Another advantage of the interferometer-computer combination is that the interferogram and resulting spectrum can be stored and manipulated within the computer [2]. The FTIR spectrometer used in our measurement was Bomem Canada (Model MB-104), at Physics Department, M.S.U., Baroda.

The specifications of the instruments are listed below.

Source	Glowbar, high intensity and power stabilized
Wavenumber precession	0.0 cm^{-1} controlled with an internal He-Ne laser
Detector	high speed Deuterated Triglycine Sulfate (DTGS)
Resolution	4 cm^{-1} fixed
Beam Spliter	Proprietary ZnSe design
Wavenumber Range	6000 cm^{-1} to 510 cm^{-1}

There is no routine adjustment to be made on the spectrometer.

2.3.2 Optical Microscopy

Modern compound microscopes are designed to provide a magnified two-dimensional image that can be focused axially in successive focal planes, thus enabling a thorough examination of specimen fine structural detail in both two and three dimensions. The optical components are mounted on a stable, ergonomically designed base that allows rapid exchange, precision centering, and careful alignment between those assemblies that are optically interdependent. Together, the optical and mechanical components of the microscope, including the mounted specimen on a glass micro slide and cover slip, form an optical train with a central axis that traverses the microscope base and stand.

Modern compound microscopes feature a two-stage magnifying design built around separate lens systems, the objective and the eyepiece (commonly termed an ocular), mounted at opposite ends of a tube, known as the body tube. The objective is composed of several lens elements that together form a magnified real image (the intermediate image) of the specimen being examined. The intermediate image is further magnified by the eyepiece. The microscopist is able to observe a greatly enlarged virtual image of the specimen by peering through the eyepieces. The total magnification of a microscope is determined by adding the individual magnifications of the objective and eyepiece. The basic concepts associated with optical microscopy, including objectives, eyepieces, condensers, stages, magnification, numerical aperture, optical aberrations, and a variety of related topics.

Microscopes are instruments designed to produce magnified visual or photographic images of objects too small to be seen with the naked eye. The microscope must accomplish three tasks: produce a magnified image of the specimen, separate the details in the image, and render the details visible to the human eye or camera. This group of instruments includes not only multiple-lens (compound microscopes) designs with objectives and condensers, but also very simple single lens instruments that are often hand-held, such as a loupe or magnifying glass. The image of an object can be magnified when viewed through a simple lens. By combining a number of lenses in the correct manner, a microscope can be produced that will yield very high magnification values. In the optical microscope, when the light from the microscope lamp passes through the condenser and then through the specimen, some of the light passes both around and through the specimen undisturbed in its path. Such light is called direct light or undeviated light. The background light passing around the specimen is also undeviated light.

Some of the light passing through the specimen is deviated when it encounters parts of the specimen. Such deviated light (diffracted light) is rendered one-half wavelength or 180° out of step with the direct light has passed through undeviated. The half wavelength out of phase, caused by the specimen itself, enables this light to cause destructive interference with the direct light when both arrive at the intermediate image plane located at the fixed diaphragm of the eyepiece. The eye lens of the eyepiece further magnifies this image which finally is projected onto the retina, the film plane of a camera, or the surface of a light-sensitive computer chip.

What has happened is that the direct or undeviated light is projected by the objective and spread evenly across the entire image plane at the diaphragm of the eyepiece. The light diffracted causes destructive interference and reduce intensity resulting in more or less dark areas. These patterns of light and dark are what we recognize as an image of the specimen. Because our eyes are sensitive to variations in brightness, the image becomes a more or less faithful reconstitution of the original specimen [3, 4].

2.3.3 Vickers' Microhardness

Microhardness test method is one of the most common and reliable methods for microhardness measurement of solid surfaces. In this test a very small diamond pyramid is placed on the sample and a small applied load of 10 to 1,000 mN is used. This low amount of load creates a small indent that must be measured under a microscope. The indentation hardness has been used as a research tool for solids for identifying the various constituents of an alloy or to estimate the amount of deformation produces by a particular metal-working process, including creep properties [5]. The general definition of indentation hardness of the indenters is the ratio of load applied to the surface area of the indentation. Meyer [6] proposed that hardness should be defined as the ratio of load to the projected area of indentation. Hence hardness has the dimensions of stress. Thus, the hardness of a solid is defined in general as resistance to deformation. The deformation in turn is a function of interatomic forces. The indentation hardness value depends on the material, nature of bonding and elastic modulus of the material and it can be used to determine plastic resistivity against the dislocation motion.

On the basis of this definition and Meyer's law; $P = ad^n$ for spherical indenters, he derived a formula for calculation of hardness. The basic qualitative meaning of hardness turns out to be a measure of resistance to plastic deformation. For practical purpose, hardness of the material may be broadly defined as its ability to resist penetration by another particular material. It is a relative property of which depends on the elastic and plastic properties of both the penetrated body and the penetrater. In addition to this, hardness of a material depends strongly on the method of measurement which usually combines in it various material properties like elastic modulus, yield stress, physical imperfection, impurities and work hardening capacity. The most popular and simplest method of hardness measurement is the static indentation hardness method. If the specimen is anisotropic, the ridging and sinking of material around the mark may produce complicated offsets specially with pyramidal indenters. To accommodate various shapes, sizes and hardness of the specimens a combination of indenter, load, loading procedure and means of indenters are used. For conical mad pyramidal indenters, the hardness number will be independent of load for all loads above a certain minimum value depending on specimen material.

Two common microhardness tests are Knoop microhardness and Vickers microhardness. The difference between them is simply the shape of the diamond pyramid indenter. The Vickers indenter is a square pyramid, while the Knoop diamond is an elongated pyramid shape. Indentation-induced surface defects can be studied by comparing the same area before and after indentation. The Vickers hardness test uses a square-based pyramid diamond indenter with an angle of 136° (α) between the opposite faces at the vertex, which is pressed into the surface of the test piece using a prescribed force, F. The time for the initial application of the force is 2 s to 8 s, and the test force is maintained for 10 s to 15 s. After the force has been removed, the diagonal lengths of the indentation are measured and the arithmetic mean, d, is calculated. Hardness being the ratio of load applied to the surface area of indentation, which for a Vickers' diamond pyramid indenter, is represented by the equation

$$H_V = \frac{2P \sin \alpha/2}{d^2} \tag{2.3}$$

where Hv is the Vickers' hardness number, P is the applied load in kg, d, in millimeter is the average diagonal length of the indentation mark and α is the angle between two opposite faces. With the particular geometry in our indenter, we use the formula,

$$H_V = 189096 \cdot P/d^2 \tag{2.4}$$

where P is in Newton and d in μm. The experimental error in Hv is computed by the relation [7],

$$H_V = 189096 \cdot \left[\left(\frac{\Delta P}{Y} \right) + \left(\frac{P \Delta Y}{Y^2} \right) \right]^{1/2} \tag{2.5}$$

where $Y=d^2$ and $\Delta Y=2\Delta d$; ΔP, ΔY and Δd being errors on P,Y and d respectively.

The Carl Zeiss Axiotech-Microscope along with its accessories used in the present work at Physics Department, S. P. University, Vallabha Vidyanagar.

2.3.4 AC Electrical Properties

If a polymer containing polar groups is placed in an electric field, orientation of its units and smaller kinetic units will be observed at definite field frequency ratios, and this gives rise to definite values of dielectric constant and tan δ / dissipation factor.

The main process that takes place in any dielectric under the influence of the electric field is polarization, i.e. the limited displacement of bound charges or orientation of dipole molecules. The phenomena underlying dielectric polarization may be judged of from the dielectric constant and the dissipation factor (loss angle or tan δ). If the polarization of a dielectric is attended by the thermal dissipation of electrical energy, which heats the dielectric. Heating of a commercial dielectric may result from free charges present in small leakage current (conduction current) under the effect of the applied voltage. The presence of this current in the dielectric body and over its surface attests to electrical conduction in the dielectric, which can quantitatively be expressed in terms of the volume and surface conductivities, respectively, being inversely proportional to the volume and surface resistivities.

In general polymers are insulators - that is they don't conduct electricity or heat. In fact one of the most common uses of plastic is as insulation for electric wires. However scientists have discovered that certain classes of polymers called conjugated polymers, which contain many double bonds in their structure, are actually semi-conductors with unusual electrical properties [8,9].

2.3.4.1 AC conductivity

The study of electrical conduction is one of the important electrical characteristics of dielectric material required not only for practical applications but also for the interpretation of the various physical phenomena. Electrical conductivity is an elegant experimental tool to probe the structural defects and internal purity of material. The profound changes which occur in physical and chemical nature of a material essentially give information through its conductivity data. Useful information regarding the mobility and generation as well as the movement of lattice defects in hydrogen bonded molecules can also be obtained by studying the electrical conductivity of the material.

The polymers can conduct electricity and they emit light when a current is passed through them. The electrical conductivity of a polymer depends on the presence of free ions not connected chemically with the macromolecules. The molecular chain proper does not participate in the transfer of electric charges. Therefore the conductivity of polymers depends largely on the presence of low-molecular-mass impurities that can serve as sources of ions. The effect of chemical constitution has only an indirect effect on the mobility of the ions. In the glassy state, the conductivity of polymers is approximately 10^{-13} to 10^{-19} $\text{ohm}^{-1}\cdot\text{cm}^{-1}$.

A capacitor when charged under an a.c. voltage will have some loss current due to ohmic resistance or impedance by heat absorption. If Q be the charge in coulomb due to a potential difference of V volts between two plates of a condenser of area A, and interpolate distance d, then a.c. conductivity ($\sigma_{a.c.}$) due to a.c. voltage $v\left(v_o e^{i\omega t}\right)$ is given by the relation

$$\sigma_{a.c.} = \frac{J}{E} \qquad (2.6)$$

Where J is the current density and E the electrical field strength vector which is $E = D/\varepsilon$; D being the displacement vector of the dipole charges and ε is the complex permittivity of the material. For a parallel plate capacitor the electric field intensity (E) is the ratio of the potential difference between the plates of the capacitor to the interplate distance i.e.

$$E = \frac{V}{d} \qquad (2.7)$$

Since $\frac{Q}{A} = \frac{V\varepsilon}{d}$, the current density $J = dq/dt$ is given by

$$J = \frac{dq}{dt} = \frac{d}{dt}\left(\frac{V\varepsilon}{d}\right) = \frac{\varepsilon}{d}\frac{dV}{dt},$$

$$\therefore J = \frac{\varepsilon}{d} Vj\omega \qquad (2.8)$$

Substituting for E and J in (2.6)

$$\sigma_{a.c.} = \frac{J}{E} = \varepsilon j\omega$$

$$= \left(\varepsilon - j\varepsilon''\right)j\omega = \varepsilon' j\omega + \omega\varepsilon'', \qquad (2.9)$$

in order that a.c. conductivity may be a real quantity, the term containing j has to be neglected, hence

$$\sigma_{a.c.} = \omega\varepsilon'' \qquad (2.10)$$

In any dielectric material, there will be some power loss because of the work done to overcome the frictional damping forces encountered by the dipoles during their rotation. If an a.c. field is considered, then in an ideal case the charging current I_c will be 90° out of phase with the voltage. But in most of the capacitors due to the absorption of electrical energy some loss current, IL will also be produced, which will be in phase with the voltage. Charging current I_c, and loss current IL, will make angles δ and θ, respectively with the total current, I, passing through the capacitor. The loss current is represented by sin δ of the total current, I. Generally sin δ is called the loss factor but when d is small, the sin δ = δ = tan δ. The two compounds ε and ε' of the complex dielectric constant, ε, will be frequency dependent,

$$\varepsilon'(\omega) = D_0 \cos(\delta/E_0) \tag{2.11}$$

$$\varepsilon''(\omega) = D_0 \sin(\delta/E_0) \tag{2.12}$$

Since the displacement vector in a time varying field will not be in phase with E and hence there will be a phase with E, producing a phase difference d between them. From (2.11) and (2.12), we have

$$\tan\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} \tag{2.13}$$

Substituting the value of ε" (w) from (2.13) into (2.10), we have

$$\sigma_{a.c.} = \omega\varepsilon'(\omega)\tan\delta \tag{2.14}$$

Where $\omega = 2\pi f$ and $\varepsilon' = \varepsilon_0\varepsilon_r$, where ε_r is the relative permittivity of the material and ε_0 the permittivity of free space. So

$$\sigma_{a.c.} = 2\pi f \tan\delta\varepsilon_0\varepsilon_r \tag{2.15}$$

Dielectric constant or relative permittivity can be calculated by using the formula

$$\varepsilon_r = \frac{C \times t}{\varepsilon_0 A} \tag{2.16}$$

From equations (2.15) and (2.16) one can get the relation,

$$\sigma_{a.c.} = \frac{2\pi f \tan\delta C t}{A} = \frac{2\pi f C D t}{A} \tag{2.17}$$

where, D (Dissipation Factor) = tan δ.

This equation (2.17) has been used to calculate the a.c. conductivity of the polymers at a given frequency.

2.3.4.2 *Dielectric constant*

Dielectric Constant is used to determine the ability of an insulator to store electrical energy. Various polarization mechanisms in solids such as atomic polarization of the lattice, orientational polarization of dipoles, space charge polarization etc. can be understand easily by studying the dielectric properties as a function of frequency and temperature. The dielectric constant is the ratio of the capacitance induced by two metallic plates with an insulator between them to the capacitance of the same plates with air or a vacuum between them. It measures the inefficiency of an insulating material. If the material to be used for strictly insulating purpose, it would be better to have a lower dielectric constant. The dielectric constant of solids can greatly vary in magnitude with variations in their structural properties. Any mechanisms of polarization can proceed in solid bodies. Solid nonpolar dielectrics obey the same regularities as nonpolar liquids and gases.

A vacuum capacitor with an electric field E between its metallic plates has an interfacial charge $Q_0 = \varepsilon_0 E$, where $\varepsilon_0 = 10^7 / 4\pi c^2 = 8.854 \times 10^{-12}\ F/m$ is the dielectric permittivity of free space. If the field E varies with temperature, the charge Q_0 follows exactly, there is no “inertia” in the vacuum response. If the capacitor is filled with a material medium-gaseous, liquid or solid-the charge induced is increased by the polarization P of the medium, so

$$Q = Q_0 + P = \varepsilon_0 (1 + \chi) E = \varepsilon E, \qquad (2.18)$$

where ε is the permittivity and χ the susceptibility of the dielectric medium.

The dielectric constant, ε, of the sample was computed using the formula

$$\varepsilon = C/C_0 \qquad (2.19)$$

where C is the measured capacitance and $C_0 = \varepsilon_0 A/t$, where ε_0 is the permittivity of free space (8.854 X 10^{-12} F/m), A is area of the electrode and t is thickness of the sample. The loss tangent is the dissipation factor itself.

Carrier polarization covers a very wide range of mechanisms and materials, the one common feature being that the charge carriers involved move by discontinuous hopping jumps between localized sites-they may be electrons, polarons or ions. Electrons or polarons normally hop between sites randomly distributed in space and in energy but it is almost impossible to distinguish between them experimentally. The d.c. conductivity is determined by the most difficult hops in percolation paths between the two electrodes, whereas the a.c. conductivity is thought to arise from more limited displacements, with two – center hopping said to constitute the high-frequency limit. By contrast, ions move typically over much smaller, nearest-neighbor distances and it is particularly interesting to note, therefore, that neither the magnitude of the a.c. conductivity, its activation energy nor, in particular, its frequency dependence can be taken as reliable guides to the nature of the dominant carrier responsible for polarization.

2.3.4.3 Dissipation factor / tan δ

Dissipation factor is defined as the reciprocal of the ratio between the insulating materials capacitive reactance to its resistance at a specified frequency. The dielectric loss in an insulating material can be described by the power dissipated per unit volume, called the specific loss, often, in evaluating the degree to which a dielectric can dissipate the energy of the field; use is made of the angle dielectric loss and also the tangent of this angle.

The dielectric loss angle δ is the complement of the dielectric phase angle ϕ to 90°. The angle ϕ is the angular difference in phase between the voltage and current in the capacitive circuit. In the ideal case, the current phasor in such a circuit will lead the voltage phasor by 90°, and the loss angle δ will be zero. As the thermal dissipation of the electrical energy rises, the phase angle ϕ decreases, but the dielectric loss angle grows and so its function tan δ.

Two types of dielectric loss have been established for all polymers. The first type of dielectric loss, called dipole-segmental, is associated with orientational rotation if the polar units of the macromolecule under conditions where segmental movement is possible, i.e., in the high-elastic state (above the T_g of the polymer). The second type, called dipole-group, is due to orientation of the polar groups themselves. Losses of this kind may also occur below the T_g (glass transition temperature), i.e., in the high elastic state.

Multifrequency 4284A precision LCR meter "Hewlett-Packard" make are used in the present work at Physics Department, S. P. University, Vallabha Vidyanagar.

2.3.5 Thermal Analysis

Thermal analysis is defined as a group of methods based on the determination of changes in chemical or physical properties of material as a function of temperature in a controlled atmosphere. Polymers typically display broad melting endotherms and glass transitions as major analytic features associated with their properties. Both the glass and melting transitions are strongly dependent on processing conditions and dispersion in structural and chemical properties of plastics. Weight loss with heating is a common phenomenon for polymers due to degradation and loss of residual solvents and monomers.

2.3.5.1 Thermogravimetric analysis (TGA)

Thermogravimetry is a technique which records the weight of a substance in an environment, heated or cooled at a controlled rate, as a function of time or temperature. This technique provides the analyst with quantitative measurement of any weight changes associated with a transition at varying temperature. The measurements carried out in the presence of environment, whether it is inert or oxidative, reflects the useful information regarding characterization of the sample.

It has very good atmosphere control including computer controlled gas switching. The programs allow component separations, decompositions studies, proximate analysis of coal, and auto stepwise analysis of filled polythene, polymers, curing point measurements, high temperature studies, thermal studies, thermal stability and compositional analysis.

Thermogravimetric analysis (TGA) is based on the measurement of the weight loss of the material as a function of temperature. TGA operates on a null-balance principle, using an electromechanical transducer coupled to a taut-band suspension system. The sensitivity of the balance is 0.1 µg. TGA curve provides information concerning the thermal stability of the initial sample, intermediate compounds that may be formed and of the residue if any. In addition to thermal stability, the weight losses observed in TGA can be quantified to predict the pathway of degradation or to obtain compositional information. The ability to vary atmosphere during the TGA evaluation, particularly from an inert to a reactive gas, provides additional information about a material composition and its stability. The experimental data offer more sophisticated understanding of reactions occurring at materials heating. Ability to obtain measurements at higher temperatures is most useful for inorganic materials such as cements, clays, ceramics, superconductors and metals.

This is one of the fastest-growing analytical techniques for the evaluation of the thermal decomposition kinetics of polymeric materials. It involves continuous weighing of the polymer as it is subject to a temperature programme. This technique can provide quantitative information about the thermal decomposition of polymeric materials from which the thermal stability of the polymer can be evaluated. The lifetime of a polymer can be estimated from these kinetic data. As the heating rate increased, the thermogravimetric change occurred at higher temperature. A linear correlation was obtained by plotting the logarithum of the heating rate or scan speed against the reciprocal of the absolute temperature at the conversion or weight loss percentage. The slope was directly proportional to the activation energy and known constants.

The activation energy for the polymer decomposition process was calculated from the TGA patterns using the equation [10].

$$\ln\left[\ln\left(\frac{m_0}{m}\right)\right] = -\frac{E}{R}\left(\frac{1}{T}\right) + const \qquad (2.20)$$

where E is the activation energy of decomposition, m_0 is the initial mass, m is the mass at temperature T and R is the universal gas constant.

Specifications:

Weight measurement	Horizontal differential balance method
Sample weight	maximum 200 mg
Measurable Temperature	Room temperature (35°C) to 1100°C
Heating rate	0.01°C/min~200°C/min
TG measurement Range	± 0.1 mg ~ ± 200 mg
Gas Flow	Max 1000 ml/min

2.3.5.2 Differential scanning calorimetry (DSC)

Calorimetry involves the measurement of relative changes in temperature and heat or energy either under isothermal or adiabatic conditions. Chemical calorimetry where the heat of reactions are measured, usually involve isothermal conditions. The Differential Scanning Calorimetry (DSC) is the fundamental technique of thermal analysis used to study and analyze the sample properties such as melting, glass transition, thermal history, crystallization, curing point, reaction kinetics and oxidative stability. It is also used to find specific heat, purity, polymorphism and chemical reaction measurements. In materials characterization calorimetry usually involves an adiabatic measurement. In Differential Scanning Calorimeters (DSC), heat a sample (a small piece of material contained by a pan) and a reference (an identical empty pan, thus negating the thermal effect of the pan) at a fixed rate (~10 °C per minute) and measures thermal differences in the two. When an exothermic or endothermic change occurs in the sample material, power (energy) is applied or removed from the calorimeter. This amount of power involved is directly proportional to the energy change which is measured and recorded. DSC uses a sample and reference heated by different resistive heaters and also monitored separately. This device has the advantage that changes in heat capacity can be directly measured. It is a unique method in the sense that it makes use of constantan disc as the primary means of heat transfer to the sample and reference positions as well as one element of the temperature measuring thermoelectric junctions. The cell temperature is controlled by using a silver heating block, a resistance wound heater and a closely coupled Platinel II control thermocouple. The block temperature is monitored by the control thermocouple and the appropriate amount of power is supplied to the heater as determined by the difference signal between control thermocouple and the output of programmer. Heat from the block then flows radially through the constantan disc towards the sample and reference platforms. Temperatures at the raised sample and reference platform are monitored by chromel-constantan thermocouple formed by a junction of the constantan disc with a chromel wire at each platform position. The difference signal between these two thermocouple junctions is fed to the amplifier and which is monitored on the Y-axis of the X-Y recorder. Variance in the sample property, energy absorption or release, weight or dimensional change etc. is read on the Y axis as a function of sample temperature on the X-axis of the recorder. This difference is reported as "Heat Flow", which is the output data of the DSC [11].

Specification:

Temperature range	-150°C~725°C	
DSC detection range	±100μW/f.s ~ ±100mW/f.s	
Programme rate	0.01°C/min ~ 100°C/min	
Sample amount	open sample pan	max.100 μl
	Hermetic sealed sample container	max 15 μl
Cooling	Available when fully automatic gas cooling unit is converted	
Controlled cooling	Controlled cooling possible down to -100°C at a rate of 10°C/min when fully automatic gas cooling unit is converted.	

The thermal analysis of polymeric samples was done using the SIEKO thermal analyzer TGA-220 and DSC-220 at Bayer ABS, Moxi, India.

REFERENCES

[1] I M Govil and H S Hans, Proc.Indian Acad.Sci. (Eng Sci.) 3 (1980) 237.

[2] A Lee Smith, Applied Infrared Spectroscopy, Chemical Analysis, Vol.54John Wiley and Sons, New York, (1974).

[3] S Inoue and R Oldenbourg, Handbook of Optics, Vol.2, McGraw-Hill, New York, (1955).

[4] M Abramowitz, Microscope Basics and Beyond, Vol.1,(Olympus America Inc., New York (2003).

[5] B W Mott, Micro-indentation and Hardness Testing, Butterworth Scientific Publications, London (1956).

[6] E Z Meyer, Verdeutsch Ing., 52 (1908) 645.

[7] P N Kotru, A K Razdan, B M Wanklyn, J. Mater. Sci. 24 (1989) 793.

[8] N P Bogoroditsky, V V Pasynkov, B M Tareev, Electrical Engineering Materials, Mir Publishers, Moscow (1979).

[9] A K Jonscher, Review Article, The Universal dielectric response, Nature, 267 (1977) 673.

[10] A Broido, J. Polym Sci., 7(1969)1761

[11] H J Flammersheim, Differential scanning calorimetry: (an introduction for practioners), Springer (2003).