Chapter 3: Experimental Details

ABSTRACT

Some important properties of polymers used in the present work are discussed in this chapter. The specific detail about target preparation, thickness measurement, estimation of range and energy loss using SRIM code, irradiation and characterizations of theses polymers are reported here.

3.1 INTRODUCTION

During irradiation, various physical and chemical processes take place in the polymer. Coulombic interaction between ions and electrons of host atoms, excessive bond stretching due to localized energy deposition, and atomic displacement by nuclear collision can release pendant atoms such as hydrogen, and cause bond breakage or chain scission. Thus, various gaseous molecular species are released during irradiation. The most prominent species are hydrogen, molecular scission products from the end groups as well as pendent groups of the polymer, and their reaction products. Radicals or dangling bonds are created by the release of pendent atoms such as hydrogen. Cross linking occurs where two free dangling bonds on neighbouring chain unite, where as double or triple bonds are formed if two neighbouring radicals in the same chain unite. It has been well established that mechanical, physical and chemical property changes in polymers are determined by the magnitude of cross linking and scission and that cross linking enhances mechanical stability while scission degrades mechanical strength. Although both electronic and nuclear energy transfer can induce cross linking as well as scission as would be intuitively expected, experimental evidence suggests that electronic stopping causes more cross linking while nuclear stopping causes more scission [1].

Some important features of the polymers under taken for study have been presented in this chapter. Name of these polymers are introduce here [2-12]. We have also discussed the preparation of samples, irradiation etc and measurement by different characterizations techniques as discussed in the Chapter 2 (article 2.3).

3.2 IMPORTANT PROPERTIES OF POLYMERS UNDERTAKEN FOR STUDY

3.2.1 Polypropylene

Polypropylene is one of the versatile polymer, it can be used as a plastic as well as fiber. As a plastic it is used to make things like dishwasher-safe food containers. As a fiber, polypropylene is used to make indoor-outdoor carpeting. It works well for outdoor carpet because it is easy to make colored polypropylene because polypropylene does not absorb water. Applications include (for homopolymers) appliance housings, house wares, packaging, cassette holders and fibers, monofilaments and slit-film tapes; for copolymers pipes, containers, seat shells and automotive parts e.g. battery cases and bumpers though the latter are often made from more heavily elastomers-modified polypropylene.

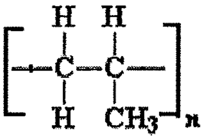
Structurally it is a vinyl polymer, and is similar to polyethylene, only that on every other carbon atom in the backbone chain has a methyl group attached to it. A semi-crystalline, white, semi-opaque commodity thermoplastic made in a very wide variety of grades and modifications. It is a linear polyolefin which can be compared in many ways to high density polyethylene (HDPE) and that is manufactured in a very similar way. The catalysts used control the polymer's stereo regularity quite well so that commercial polypropylenes are usually predominantly isotactic. Polypropylene has good chemical but poor UV resistance (unless stabilized or protected).

Physical Properties

Composition

$-\!\!\left[C_3H_6\right]_n\!\!-$

Structure of Polypropylene



polypropylene

Density 0.9 g/cm^3

Glass Transition Temperature T_g -18 °C

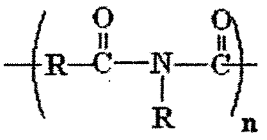
Melting Temperature 175 °C

Heat deflection Temperature 60-65 °C

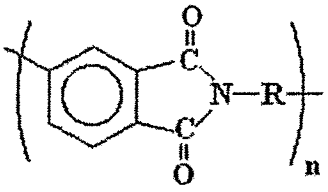
3.2.2 Polyimide/Kapton (PI)

Polyimide is a very interesting group of incredibly strong and astoundingly heat and chemical resistant polymer. Their strength and heat and chemical resistance are so great that these materials often replace glass and metals, such as steel, in many demanding industrial applications.

It is used for the struts and chasis in some cars as well as some parts under-the-hood because they can withstand the intense heat and corrosive lubricants, fuels and coolants. Also used in the construction of many appliances as well as microwave cookware and food packaging because of their thermal stability, resistance to oils, greases and fats and its transparency microwave radiation. It can also be used in circuit boards, insulation, fibers for protective clothing, composites, and adhesives. Polyimides usually are in two forms. The first of these is linear structure where the atoms of the imide group are part of linear chain. The second of these structures is a heterocyclic structure where the imide group is part of cyclic unit in the polymer chain.


$\left(R-\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}} \right)_n$

linear polyimide



aromatic heterocyclic polyimide

Aromatic heterocyclic polyimides are typical of most commercial polyimide. This polymer has such incredible mechanical and thermal properties so that they are used in place of metals and glass in many high performance applications in the electronics, automotive, and even the aerospace industries. It comes from strong intermolecular forces between polymer chains.

Normally infusible, colored (often amber) high performance polymers with predominantly aromatic molecules of high thermal stability. Semi-fabricated shapes are usually supplied by the polymer manufacturer and made by powder sintering or working with more tractable pre-cursors and completing polymerization in final form, though some melt-processable grades of resin are available. They have excellent high temperature properties and radiation resistance, inherently low flammability and smoke emission, low creep and high wear resistance and are very expensive. They have moderately high water absorption and are prone to hydrolysis and attack by alkalis and concentrated acids.

Kapton's basic properties are combined with an extra attribute increased electrical or thermal conductivity, improved corona resistance, opacity and thermo plasticity.

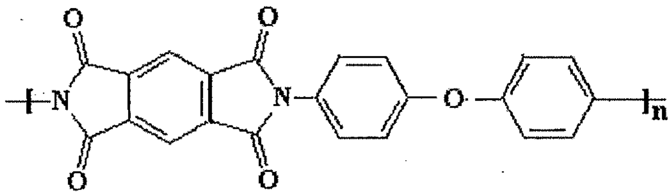
Films are used for capacitators, insulation, printed circuit boards and in aerospace; other applications include engine components, bearings, and mechanical parts exposed to radiation.

Physical Properties

Composition

$-[C_{22}H_{10}N_2O_5]_n-$

Structure of Polyimide



Density 1.42 g/cm^3

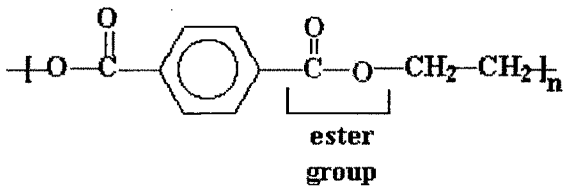
Glass Transition Temperature T_g 385 °C

Melting Temperature > 400 °C

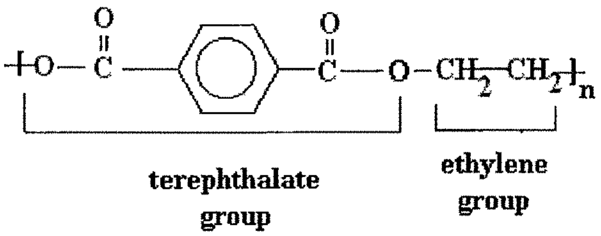
Heat Deflection Temperature 360 °C

3.2.3 Polyethylene terephthalate (PET)

The most common thermoplastic polyester, this polymer is often called just "polyester". These polymers are in the form of fibers and plastics too. Polyesters have hydrocarbon backbones which contain ester linkages.



Polyethylene terephthalate /PET are made up of ethylene groups and terephthalate groups.



The ester groups in the polyesters chain are polar, with the carbonyl oxygen atom having a negative charge. The positive and negative charges of different ester groups are attracted to each other. This allows the ester groups of nearly chains to line up with each other in crystal form, so they can form strong fibers.

PET is a hard, stiff, strong dimensionally stable material that absorbs very little water. It has good gas barrier properties and good chemical resistance except to alkalis (which hydrolyze it). Its crystallinity varies from amorphous to fairly high crystalline; it can be highly transparent and colorless but thicker sections are usually opaque and off-white.

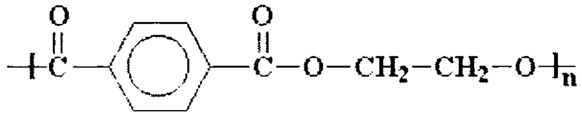
Applications include bottles and electrical components but it is probably most widely known as the biaxially oriented and thermally stabilized films used for capacitors, graphics, and film base and recording tapes etc.

Physical Properties

Composition

$-[C_{10}H_8O_4]_n-$

Structure of Polyethylene terephthalate



Density 1.3-1.4 g/cm^3

Glass Transition Temperature 69 °C

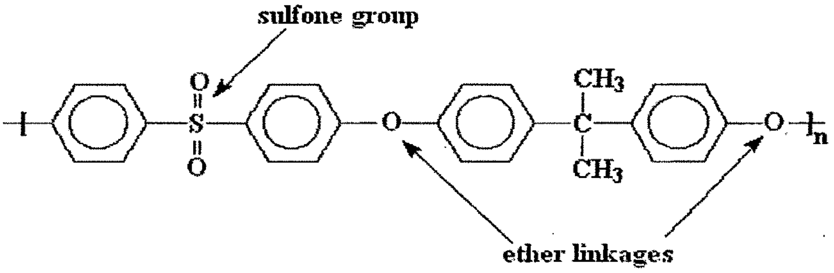
Melting Temperature 265 °C

Heat Deflection Temperature 80 °C

3.2.4 Polyether sulfone (PES)

An amorphous, transparent and pale amber high performance thermoplastic with the common characteristics of Polyether ether ketone (PEEK). Polyether sulfone/PES is high performance polymers. It acts more like polycarbonate, but PES is much more heat resistant. It also can stand up well to water and steam, so they are used to make things like cookware and medical products that need to be sterilized between uses.

PES gets their name because they have ether groups and sulfone groups in their backbone chains.



It has relatively high water absorption and, in common with many other plastics, drying is essential before e.g. thermoforming. It has poor fatigue characteristics and is prone to environmental stress cracking but has good long term thermal ageing resistance and reasonable radiation resistance. Its chemical resistance is not as wide as PEEK's; hence stable solutions can be made if solvents are correctly chosen.

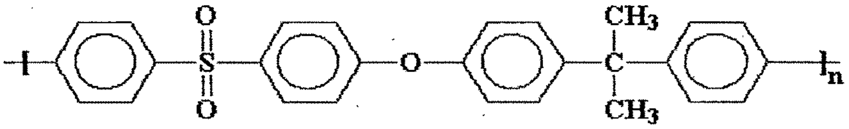
Applications include electrical and electronic components, medical etc. equipment that needs repeated sterilization and photographic accessories.

Physical Properties

Composition

$-[C_{27}H_{22}O_4S]_n-$

Structure of Polyether sulfone



Density 1.37 g/cm^3

Glass Transition Temperature 225 ℃

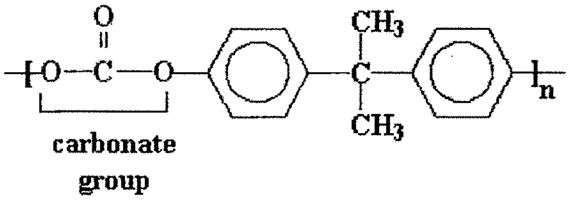
Melting Temperature >400 ℃

Heat Deflection Temperature 203 ℃

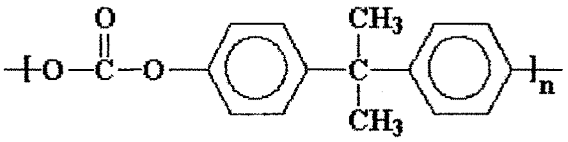
3.2.5 Polycarbonate/Makrofol-DE

A crystal clear and colorless, amorphous engineering thermoplastic notable for its high impact resistance. It has reasonably good temperature resistance, good dimensional stability and low creep but somewhat limited chemical resistance and is prone to environmental stress cracking.

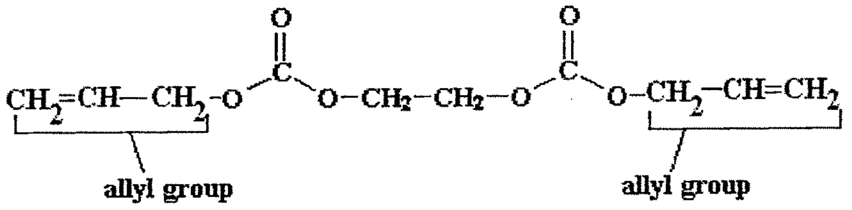
Polycarbonate is a clear plastic, used to make shatterproof windows, lightweight eye glass lenses. Polycarbonate gets its name from the carbonate groups, in its backbone chain.



There is a fundamental difference in the two types of PC. One is polycarbonate of bisphenol A, is made from bisphenol A and phosgene. Polycarbonate bisphenol A is thermoplastic.



The other polycarbonate can make up by allyl groups. These allyl groups have carbon-carbon double bonds in them. It can polymerize by free radical vinyl polymerization. The two allyl groups will become parts of different polymer chains. The carbonate containing groups for the cross links between the polymer chains. This cross linking is making the material very strong. This polycarbonate is thermoset.



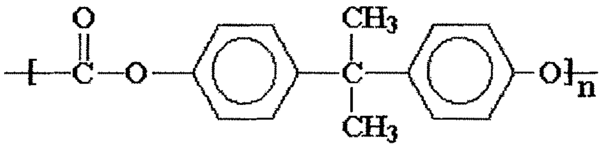
Applications include glazing, safety shields, lenses, eyeglasses, casings and housings, light fittings, kitchenware (microwaveable), medical apparatus (sterilisable) and CD's (the discs).

Physical Properties

Composition

$-\!\!\left[C_{16}H_{14}O_{3} \right]_n\!\!-$

Structure of Polycarbonate



Density 1.2 g/cm^3

Glass Transition Temperature 150 °C

Melting Temperature 265 °C

Heat Deflection Temperature 128-138 °C

3.2.6 Blend Polymer (Polyvinyl chloride + Polyethyleneterephthalate)

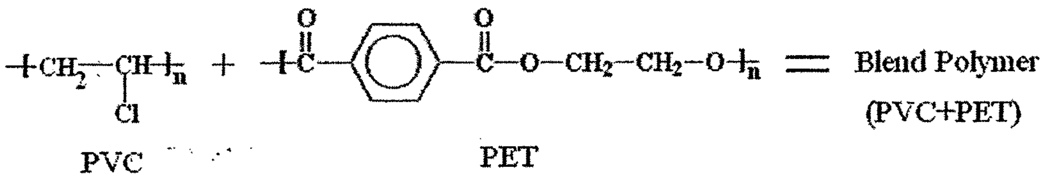
This polymer was prepared in the laboratory in equal proportion of PVC (IPCL make) with commercial grade PET (Garware make) in two roll mill. The PVC and PET were taken in granules form and in pure form too (wt/wt). The mixture was transformed into sheet at around 125 °C for half an hour.

Physical properties

Composition

$$-[C_2H_3Cl]_n- + -[C_{16}H_{14}O_3]_n-$$

Structure of polymer blend



Density 1.68 g/cm^3

	PVC	PET
Glass Transition Temperature	87 °C	69 °C
Melting Temperature	–	265 °C

Table 3.1 shows some of the physical and chemical properties of all the polymers used in the present work.

Table 3.1: Some of the physical and chemical properties of the polymers used.

	Poly Propylene (PP)	Polyimide (PI)	Polyethylene Terephthalate (PET)	Polyether Sulfone(PES)	Polycarbonate (PC)	Polyvinyl chloride (PVC)
Physical Properties						
Density (g cm^{-3})	0.9	1.42	1.3-1.4	1.37	1.2	1.4
Colour	transparent	amber	white	pale amber	transparent	Off white
Flammability @ 0.4mm	HB	V0	HB	V-0	V0-V2	V0
Limiting oxygen index (%)	18	53	21	34-41	25-27	42
Refractive index	1.49	1.66	1.58-1.4	1.65	1.584-6	1.54
Resistance to Ultra-violet	Poor	Poor	Fair	Fair	Fair	Good
Water Absorption-over-24 hours (%)	-	0.2-2.9	0.1	0.4-1	0.1	0.03-0.4
Water absorption - equilibrium (%)	0.03	0.2-2.9	<0.7	2.2	0.35	0.03-0.4
Electrical Properties						
Dielectric constant @ 1MHz	2.2-2.6	3.4	3.0	3.7	2.9	2.7-3.1
Dielectric strength (kV mm^{-1})	30-40	22	17	16	15-67	14
Dissipation factor at 1MHz	0.0003 - 0.0005	0.0018	0.002	0.003	0.01	0.025

Surface resistivity (Ohm/sq)	10^{13}	10^{16}	10^{13}	-	10^{15}	-
Volume resistivity (Ohm cm)	10^{16}-10^{18}	10^{18}	$>10^{14}$	10^{17}	10^{14}-10^{16}	10^{16}
Thermal Properties						
Heat-deflection temperature °C - 0.45MPa	100-105	-	115	>260	140	70
Heat-deflection temperature °C	60-65	360	80	203	128-138	67
Lower working temperature °C	-10 to -60	-270	-40 to -60	-110	-135	-30
Specific heat kJ kg^{-1} K^{-1}	1700 - 1900	1090	1200 - 1350	-	approx. 1200	1.0-1.5
Thermal conductivity @ 23°C	0.1-0.22	0.10-0.35	0.15-0.4	0.13-0.18	0.19-0.22	0.12-0.25
Upper working temperature °C	90-120	250-320	115-170	180-220	115-130	50-75
Glass transition Temp. °C (T_g)	-18	385	69	225	150	83
Melting Temp. °C (T_m)	175	>400	265	>400	265	-
Mechanical Properties						
Abrasive resistance – ASTM D1044	13-16	-	-	6	10-15	-
Coefficient of friction	0.1-0.3	0.42	0.2-0.4	40-80	0.31	-
Compressive Strength	-	-	-	-	>80	-
Elongation at break (%)	150-300, for biax film >50	8-70	M94-101	M88	100-150	60

Hardness - Rockwell	R80-100	E52-99	13-35	85	M70	R106-120
Izod impact strength (J m^{-1})	20-100	80	0.37-0.44(oriented)	0.4	600-850	20-1000
Tear Strength	-	20	18-54	7.5-16.9	12-29	-
Tensile modulus (GPa)	0.9-1.5, for biax film 2.2-4.2,	2.0-3.0	2-4	2.4-2.6	0.37	2.5-4.0
Tensile strength(MPa)	25-40, for biax film 130-300,	70-150	80, for biax film 190-260	70-95	2.3-2.4	25-70
Chemical Resistance						
Acids - concentrated	Good-Fair	Poor	Good-Poor	Good-Poor	Good	Good-Poor
Acids – dilute	Good-Fair	Fair	Good	Good	Good	Good
Alcohols	Good	Poor	Good	Good	Good	Good
Alkalis	Good	Poor	Poor	Good	Good-Poor	Good
Aromatic hydrocarbons	Fair	Good	Good-Fair	Good	Poor	Poor
Greases and Oils	Good-Fair	Good	Good	Good-Fair	Good-Fair	Good
Halogenated Hydrocarbons	Good-Poor	Good	Good-Poor	Good	Good-Poor	Fair-Poor
Halogens	Poor	Fair	Fair-Poor	Fair-Poor	Poor	Fair
Ketones	Good	Good	Good-Fair	Good	Poor	Poor

3.3 IRRADIATION AND CHARACTERIZATION

In the present investigation six different polymers, viz. polypropylene, polyimide/kapton, polyethylene terephthalate, polyether sulfone, polycarbonate/makrofol-DE and polymer blend of PVC and PET have been irradiated with 3 MeV proton beams. The detailed descriptions of these polymers including their structure, composition, density, utilization etc are given in the beginning of this Chapter (article 3.2).

3.3.1 Target Preparation

PVC and PET were blended in equal proportion in the laboratory by two roll mill (**Figure 3.1**). The PVC (IPCL make, India) and PET (Garware make, India) were taken in granules form and in pure form too (wt/wt). The mixture was transformed into sheet at around 125 °C for half an hour.

Two roll mill consist of a main rotor and a main gear which is connected with the other two gears moving in opposite directions. This gear is attached to the two rotors having a smooth surface and both heated by electrical filament. After half an hour, the sheet was cooled on the rotor. The sheet was removed from the rotor as soon as temperature comes down to ambient temperature. This was further cooled for seven/eight hours and then taken for study.

Other polymers, such as PP, PI, PET, PES and PC are available commercially.

Four pieces of above polymers of size 15mm X 15mm (each) were cut from commercially available sheets. These were washed thoroughly by soap solution and deionized water. The cleaned samples were then dried inside a vacuum desicator. Three/Four identical samples of each polymer were mounted on a vertical vacuum shielded sliding ladder. The target holder was made by Aluminum.

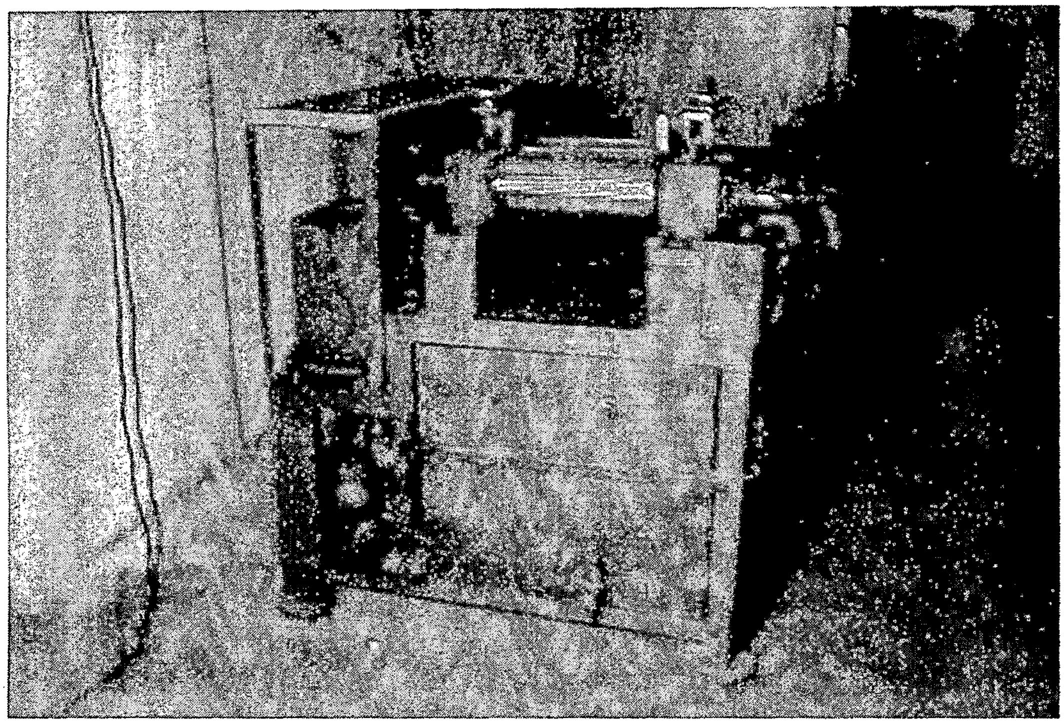


Figure 3.1: Two roll mill.

3.3.2 Thickness Measurement

The thickness of these polymers were measured by a sensitive digital instrument. Sensitivity of the instrument was 0.001mm. The thickness of the samples was measured at 8 -10 different places chosen at randomly and average value was calculated. The measured thickness of the polymers is listed in **Table 3.2**.

Table 3.2: Thickness of the polymers used.

Name of polymer	Thickness (μm)
polypropylene (PP)	10 μm
polyimide/ Kapton (PI)	70 μm
polyethylene terephthalate (PET)	230 μm
polyether sulfone (PES)	275 μm
polycarbonate (PC)	413 μm
blend polymer (PVC+PET)	460 μm

3.3.3 Calculation of Range and Energy Loss by SRIM-Code

The interaction mechanism of ion beam with polymeric materials has been discussed in the article 1.8 of Chapter 1.

SRIM is a group of programs which calculate the stopping and range of ions (10 eV - 2 GeV/amu) into matter using a full quantum mechanical treatment of ion-atom collisions (this refers to the moving atom as an "ion", and all target atoms as "atoms"). This calculation is made very efficient by the use of statistical algorithms which allow the ion to make jumps between calculated collisions and then averaging the collision results over the intervening gap. During the collisions, the ion and atom have a screened Coulomb collision, including exchange and correlation interactions between the overlapping electron shells. The ion has long range interactions creating electron excitations and plasmons within the target. These are described by including a description of the target's collective electronic structure and interatomic bond structure when the calculation is setup (tables of nominal values are supplied). The charge state of the ion within the target is described using the concept of effective charge, which includes a velocity dependent charge state and long range screening due to the collective electron sea of the target [13].

TRIM (the Transport of Ions in Matter) is the most comprehensive program included. TRIM will accept complex targets made of compound materials with up to eight layers, each of different materials. It will calculate both the final 3D distribution of the ions and also all kinetic phenomena associated with the ion's energy loss: target damage, sputtering, ionization, and phonon production. All target atom cascades in the target are followed in detail.

- **Types of calculation**

SRIM-code is being used to calculate the ion distribution and quick calculation of damage, detailed calculation with full damage cascades, calculation of surface sputtering, Neutron / Electron / Photon cascades, various ion energy / angle / positions, special multi-layer biological targets, stopping powers for ions in gases and the stopping of ions in compounds.

In the present work we have calculated the projected range of ions in compounds/polymers along with the electronic and nuclear stopping power.

- **The stopping of ions in polymers**

A large dictionary of compounds has been integrated into the programs. The stopping of ions in compounds is executed using the formalism described in "The Stopping of Ions in Compounds", by J. F. Ziegler. The dictionary of compounds can be accessed from the programs whenever they ask you to describe your target. By typing "T" the programs enter the dictionary.

About 100 compounds are described in the dictionary. You may add other compounds by editing the file COMPOUND.DAT. At the top of this file are instructions about how the dictionary is constructed, and then the dictionary shows its 100 examples. You will need to know not only the composition of the compound, but also the chemical bonding state of the light elements such as H, C, N, and O. It is easiest to find a compound in the dictionary which closely resembles your new compound, and just alter the parts of this definition.

- **Results obtained from SRIM**

Projected range of 3 MeV proton beam in all polymeric samples was calculated using the code SRIM-2000 [14].

In polypropylene the projected range was calculated to be 147.44 µm, which is 14.7 times the thickness of sample. The calculations indicate that 99.94% of energy lost due to electronic interaction. The electronic stopping power $(dE/dx)_e$ is 1.33 X 10^{-1} eV/Å whereas nuclear stopping power $(dE/dx)_n$ is 8.77 X 10^{-5} eV/Å.

The projected range in kapton/polyimide was calculated to be 110.2 µm, which is 1.57 times the thickness of the sample. It is observed that 99.94% of energy lost in 70 µm thick Kapton is electronic in nature; the electronic stopping power $(dE/dx)_e$ is 1.3 X 10^{-1} eV/Å and nuclear stopping power $(dE/dx)_n$ is 7.66
X 10^{-5} eV/Å.

The projected range in polyethylene terephthalate (PET) was calculated to be 112 µm. The thickness of the sample is two times more than the projected range. The electronic stopping power $(dE/dx)_e$ and nuclear stopping power $(dE/dx)_n$ were found to be 1.3 X 10^{-1} eV/Å and 6.58 X 10^{-5} eV/Å respectively.

The projected range in polyether sulfone (PES) was calculated to be 114 μm, which is 2.4 times less than the thickness of PES film. The electronic stopping power $(dE/dx)_e$ and nuclear stopping power $(dE/dx)_n$ were found to be 1.07 X 10^{-1} eV/Å and 6.37 X 10^{-5} eV/Å respectively.

In polycarbonate, the projected range was calculated to be 125.8 μm which is 3.2 times less than the thickness of PC film. The electronic stopping power $(dE/dx)_e$ and nuclear stopping power $(dE/dx)_n$ were found to be 1.13 X 10^{-1} eV/Å and 6.9 X 10^{-5} eV/Å respectively.

The projected range in polymeric blend of PVC and PET was calculated to be 128 μm which is 3.6 times less than the thickness of the blended film. The electronic stopping power $(dE/dx)_e$ and nuclear stopping power $(dE/dx)_n$ were found to be 1.08 X 10^{-1} eV/Å and 6.48 X 10^{-5} eV/Å respectively.

The results are summarized in the **Table 3.3**.

3.3.4 Proton Irradiation

These samples were irradiated by 3 MeV proton beam at the Physics Department, Punjab University, Chandigarh. The irradiation was performed in vacuum (10^{-6} Torr) at room temperature. The beam current density was of the order of 35 nA/cm^2 and the samples were irradiated at three/four different fluences of 10^{13}, 10^{14}, 0.5 X 10^{15} and 10^{15} ions/cm^2. The proton beam of diameter 6 mm was incident perpendicularly on the target. The details are listed in **Table 3.4**.

Table 3.3: Range and energy loss of 3 MeV proton in polymer used.

Polymer	Projected Range (μm)	$(dE/dX)_e$ eV/Å	$(dE/dX)_n$ eV/Å
polypropylene(PP)	147.44	1.33×10^{-1}	8.77×10^{-5}
polyimide/kapton(PI)	110.2	1.3×10^{-1}	7.66×10^{-5}
polyethylene terephthalate (PET)	112	1.3×10^{-1}	6.58×10^{-5}
polyether sulfone(PES)	114	1.07×10^{-1}	6.37×10^{-5}
polycarbonate(PC)/ makrofol-DE	125.8	1.13×10^{-1}	6.9×10^{-5}
blend polymer (PVC+PET)	128	1.08×10^{-1}	6.48×10^{-5}

3.4 CHARACTERIZATION OF POLYMERS

The radiation induced changes in the structural (FTIR –spectroscopy), electrical (an LCR meter), microhardness (Vickers' microhardenss tester), thermal behaviour (TGA and DSC) are investigated by using different techniques as discussed in the Chapter 2 (article 2.3).

Table 3.4: Irradiation details of polymers.

(i) Ions – Proton

(ii) Energy - 3MeV

POLYMER	FLUENCE (IONS/CM^2)	BEAM CURRENT	CURRENT DENSITY
polypropylene(PP)	10^{13},10^{14},10^{15*}	20 nA	35 nA/cm^2
polyimide/kapton(PI)	10^{13},10^{14},10^{15}	20 nA	35 nA/cm^2
polyethylene terephthalate (PET)	10^{13},10^{14}, 10^{15}	20 nA	35 nA/cm^2
polyether sulfone(PES)	10^{13},10^{14}, 0.5X10^{15} ,10^{15}	20 nA	35 nA/cm^2
polycarbonate(PC)/ makrofol-DE	10^{13},10^{14},10^{15}	20 nA	35 nA/cm^2
blend polymer (PVC+PET)	10^{13}, 0.5X10^{14}, 10^{14}, 10^{15}	20 nA	35 nA/cm^2

* Sample was burnt

3.4.1 FTIR Spectroscopy

The absorption measurements of the samples were made on the Michelson Series FT-IR spectrometer (Bomem Canada, MB 104).

Spectra of all pristine and irradiated polymers were taken in the wave number range 4000 cm^{-1} to 510 cm^{-1} in transmittance mode and it was recorded after 10 times of scan. The spectrum of air is also taken as reference spectrum for all spectra of polymer samples. The variation of transmittance (%) for the pristine and irradiated polymers were compared and the peak analysis was done to study the disappearance of some existing bands, emergence of new ones and structural changes which includes the alteration in position and intensity of characteristic bands with a resolution of 4 wave numbers. The general description of the spectrometer is given below [15].

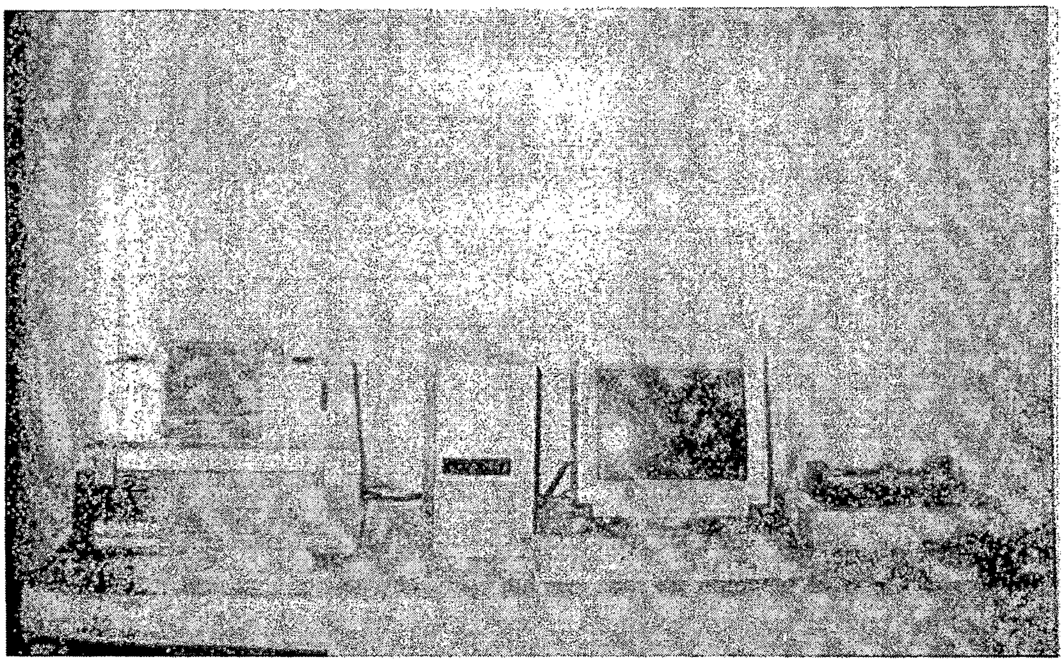


Figure 3.2: FTIR Spectrometer.

The spectrometer is a self contained unit consisting of one sample compartment and a sealed interferometer compartment. The sample compartment is enclosed in a purge cover provided with channel infrared radiation to the sample position and to the detector. The instrument compartment contains a stabilized infrared light source, the Michelson interferometer and infrared–transmitting "beam splitter", a Helium-Neon laser for measurement of scan position, power supplies and electronic assemblies. The cast aluminum compartment is sealed air, which can erode the beam splitter. The photograph of the FT-IR spectrometer is shown in **Figure 3.2**.

3.4.2 Optical Microscope

The surface morphology of pristine and irradiated samples were done by using optical microscope (Carl Zeiss, Model: Axiotech) [16]. The Axiotech microscope permit applications in reflected and transmitted light. Brightfield, darkfield, polarization, interference contrast, fluorescence, 3D microscopy etc. can be performed in reflected possible in transmitted light using microscope. Surface study of polymer is possible up to 1000X magnification with the help of microscope. The image can be seen directly on computer attached with the microscope. In this study, we used 200X magnification for surface morphology of all polymer samples (pristine as well as irradiated at different fluences).

3.4.3 Vickers' Microhardness

In order to study the Microhardness of the samples the point indentation technique is employed. For the purpose, Anton Paar's MHT-10 Microhardness Tester with video measurement system is used which shown in **Figure 3.3**.

The necessary equipment (MHT-10Vickers sensor) [16] for the purpose is always to be optical microscope and is shown in schematically in **Figure 3.4**.

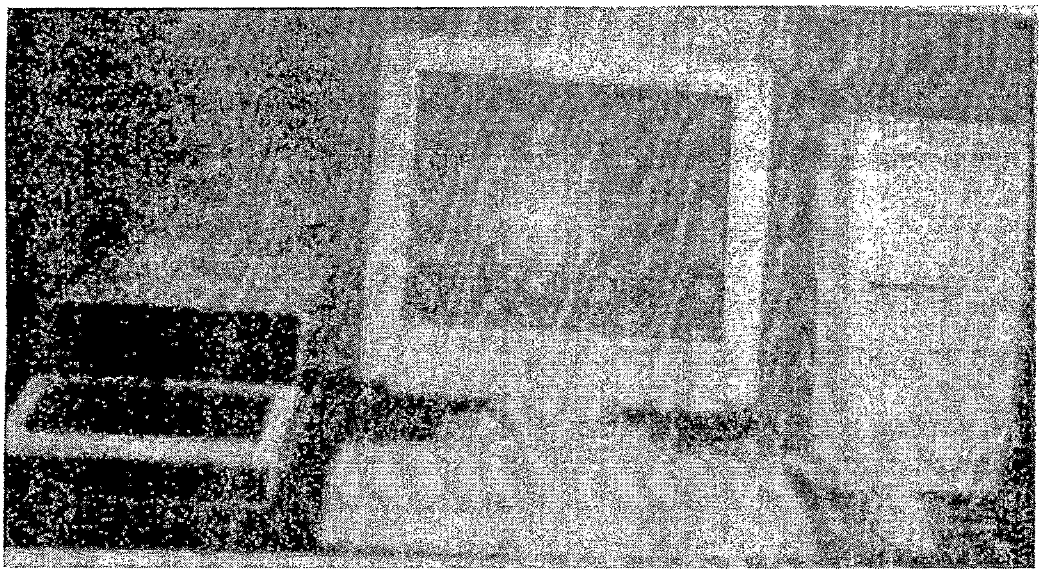


Figure 3.3: Vickers' Microhardness Tester with computer setup.

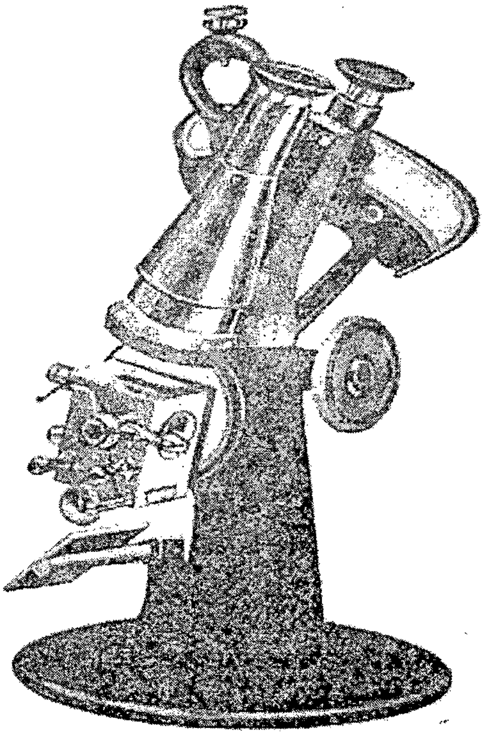


Figure 3.4: Microscope used in Vickers' Microhardness Tester.

All pristine and irradiated samples subjected to indentation test were studied at ambient temperature. The specimen to be indented is mounted on a horizontal platform inserted in the collect. Loads ranging from 100 mN - 1000 mN were used for making indentations, keeping the time of indentation constant as 30 seconds in all cases, since micro hardness was observed to be independent of indentation time. To avoid surface effect, the distance between two consecutive indentations was more than three times the diagonal length of the indentation mark.

The area for the indentation is selected by using bright field objections. After selection of area and objective is replaced by Vickers Microhardness system. The diamond tip approaches the specimen surface at a defined speed (3.5-250μm/s) which is specified by the control unit depending on the preselected forces. The maximum approach speed can be limited to 70 μm/s. The diamond tip indents into the specimen at a preselected force gradient. The actual force is permanently measured and approaches the preselected value without overshooting. The force is held constant for the duration of 10 seconds of the preselected dwell time; the diamond tip is automatically retracted to the resting position. The status LED flashes when measurement is running. The end of the measurement is signified acoustically; after that the control unit selects the calculate mode. The diamond indenter marks the print on the sample surface. By reversing the motion, the indenter is removed and the indented region examined with the reading objective through the filler eye-piece or CCD camera infrared to the HCL computer. The diagonal of the indentation mark measured for different loads, is fed to the tester, and thus it shows directly the calculated value of the hardness on the screen.

3.4.4 LCR Meter

Multifrequency 4284A precision LCR meter "Hewlett Packard" make shown in **Figure 3.5** and **3.6** is a high performance fully automatic test instrument designed to make measurements simple and much easier of various component parameter values of an impedance element in a relatively low frequency, region, covering 20Hz to 1MHz with a basic accuracy of 0.1%. It can measure inductance (L), resistance (R), dissipation factor (D), quality factor (Q), conductance (G), susceptance (B), reactance (X), in addition, the absolute value of the vector impedance (Z) and phase angle (?) over a wide range of frequencies with high accuracy and speed [17]. One can measure parameters for ten different frequencies at one instant of time. The measuring range of capacitance is from 0.01 pF to 100 mF, inductance from 10nH to 100kH, resistance and impedance from 10 mO to 100 MO, all measured with basic accuracy of 0.1% to 10% depending on the test level signal and frequency at a typical measurement speed of 10 ns to 100 ns in respect of both parallel and series equivalent circuits. The meter can be of particular help in the experimental assessment of devices in testing of solids. The versatile capabilities of the meter are maximized by the availability of the special test fixtures and the installation of options providing internal D.C bias supply and memory back up.

The capacitance and dissipation factor (dielectric loss) was measured at a time at ambient temperature using Hewlett Packard 4284A LCR meter for all pristine and irradiated samples. For measurement, polymer sample was kept in between two thin copper plate of diameter 6 mm and measured in the frequency range 0.1-100 kHz/1 MHz. In LCR meter, parallel circuit mode Cp-D was used for all measurement.

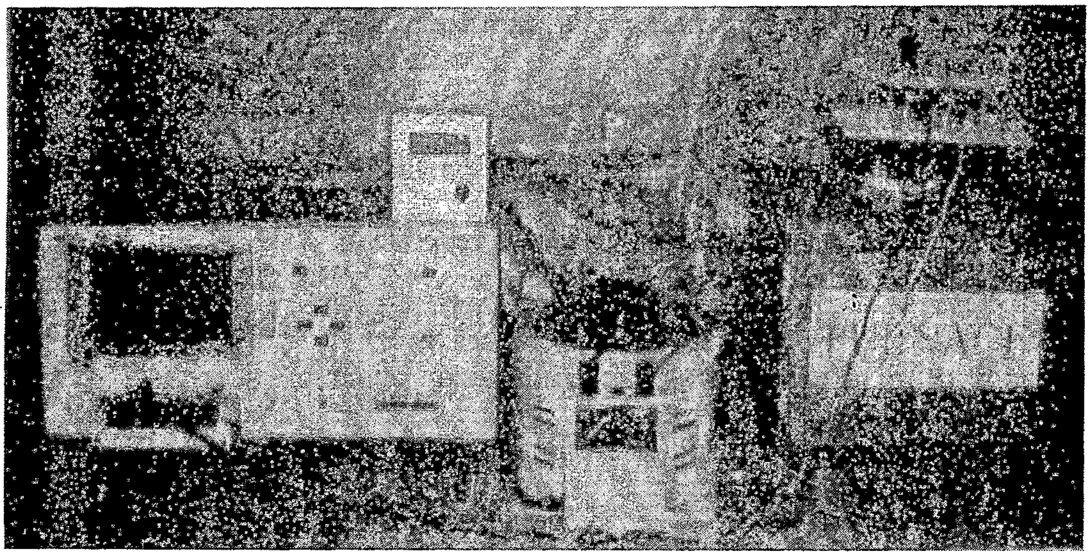


Figure 3.5: **Set up for capacitance measurement using 'Hewlett Packard' LCR meter.**

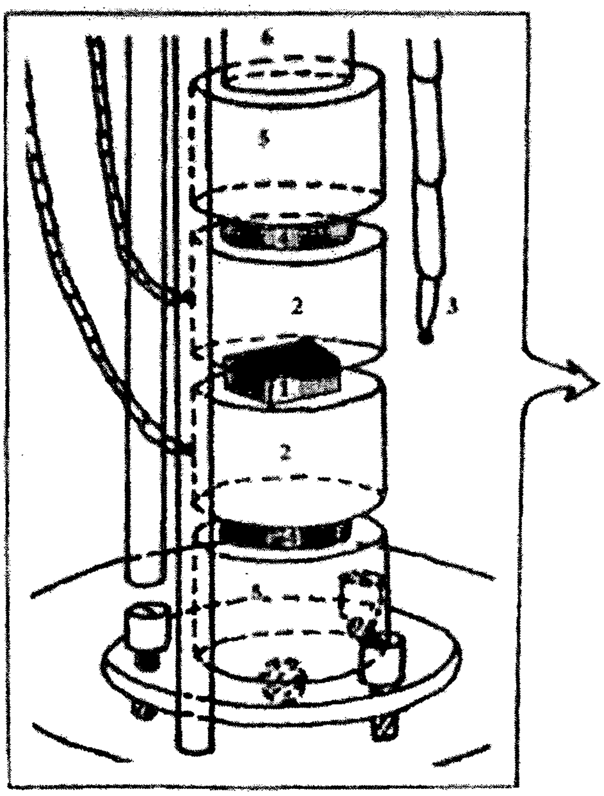


Figure 3.6: **Sample holder used for electrical conductivity measurement.**

3.4.5 Thermogravimetric Analysis

Thermogravimetric analysis was done for the pristine and irradiated polymers using a simple automatic SIEKO thermal analyser TGA-220 [18]. The samples were cut into very small pieces, crimped in small aluminium pan and weighed in a micro balance. The samples were then heated up to 500°C. The heating rate for this instrument was 10°C/min. The temperature range scanned was 40-500°C. The resulting weight loss is recorded as a function of temperature in TGA thermogram. The weight loss results from chemical reaction, decomposition, solvent and water evolution, oxidation etc. The error in TGA recording in the TGA thermogram ±2°C.

The TG/DTA 220 use a horizontal differential system balance mechanism. Sample weight changes are measured as described below. This instrument contains three basic units: 1) the measuring unit, 2) temperature control unit, 3) the recording unit. **Figure 3.7** shows the sketch diagram of TGA measurement.

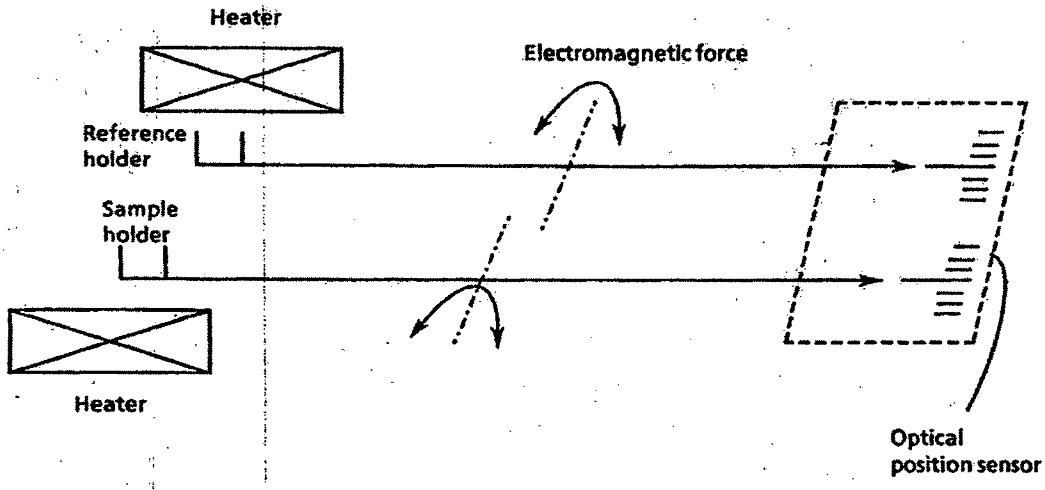


Figure 3.7: Sketch diagram of TGA measurement.

The sample balance beam and reference balance beam are independently supported by a driving coil/pivot. When a weight change occurs at the beam end, the movement is conveyed to the opposite (rear) end of the beam via the driving coil/pivot, and optical position sensors detect changes in the position of a slit. The signal from the optical position sensor is sent the balance circuit. The balance circuit supplies sufficient feed back current to the driving coil so that the slit returns to the balanced position. The current running to the driving coil on the sample side and the current running to the driving coli on the reference side is detected and converted into weight signals. **Figure 3.9** shows the set up of TGA analysis.

3.4.6 Differential Scanning Calorimetry

DSC measures the gains and losses of heat accompanying the phase transitions. The measurements were done using SIEKO thermal analysis system [18]. Air was used as flushing gas for the measurements. In the same way, the samples were cut into small pieces and crimped in aluminium pans. The samples were weighed in microbalance. Aluminium was taken as the reference material. Heat power was adjusted to 10°C/min. The temperature range scanned was 40-325°C. The thermogram was obtained for heat flow in the sample as a function of temperature. The type of thermal reactions (endothermic/exothermic) shown by the polymer on application of heat was studied. The error in DSC recording in the DSC thermogram ±2°C.

The DSC 220 measurement chamber is designed for heat flux DSC measurement. The temperature of the high conductance heat sink is accurately controlled by the heater in accordance with the temperature program. The heat sinks temperature is conducted from the heat conducting surface through the thermal resistance material into the sample and reference holders and containers. **Figure 3.8** shows the sketch diagram of DSC measurement.

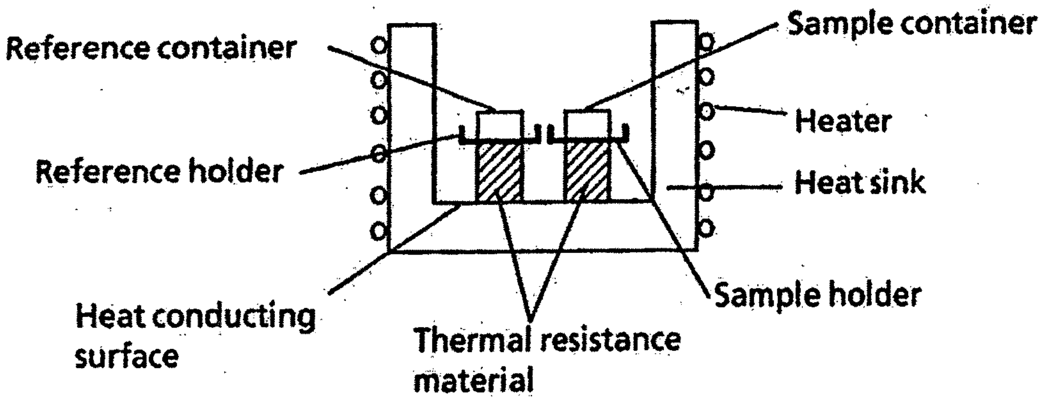


Figure 3.8: Sketch diagram of DSC measurement.

This increases or decreases the temperature of the sample and reference. The heat flow passing through the thermal resistance material is proportional to the temperature difference between the heat conducting surface on one end and the sample holder on the other end. The specially designed heat sink is accurately controlled to maintain a uniform temperature at the heat conducting surface. Therefore, the measured difference in heat flow through the sample holder and reference holder is proportional to the sample and reference temperature differences. In this way, a heat flux type DSC detects the temperature difference signal and outputs it as a DSC signal. The experimental setup for DSC is shown in **Figure 3.9**.

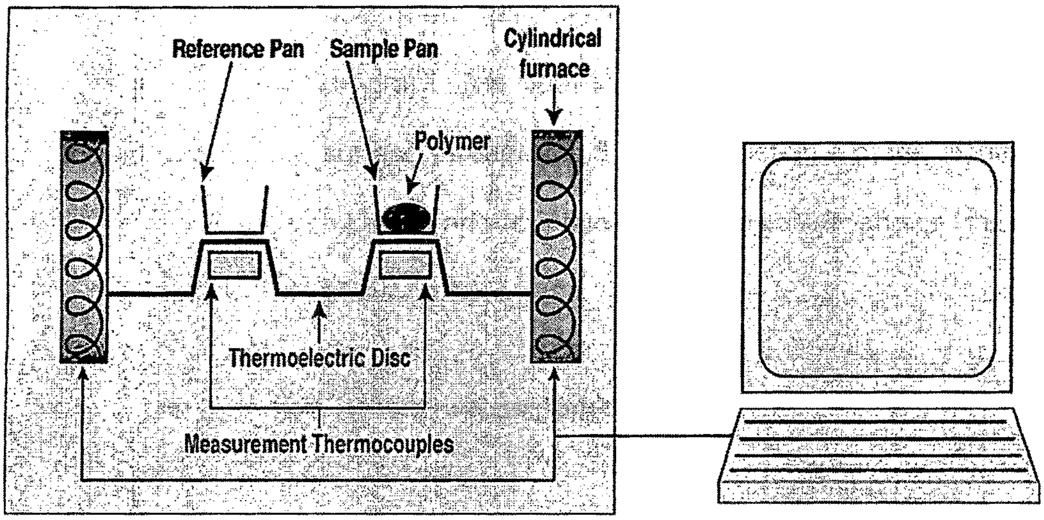


Figure 3.9: TGA/DSC measurement with computer setup.

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