Chapter-3

Experimental Details

This chapter deals with the properties of polymers, preparation of polymeric target, estimation of range and energy loss using SRIM code, irradiation and measurements of structural, electrical, surface morphology, microhardness, tensile testing and thermal stability.

Chapter 3

Experimental Details.

Chapter 3

Experimental

3.1 Introduction.

Insulators are by definition, materials with a very low electrical conductivity. For crystalline materials this means that there is a relatively large band gap between the highest occupied electron band, which is completely full, and the next higher band, which is empty. This often means that the material is transparent or partially transparent in the visible spectrum. Impurities and defects, introduced by ion bombardment, often have electronic energy levels which lie within the gap. Thus optical spectroscopies, which probe the electronic energy levels of atoms and defects are obvious candidates for use with insulators; these methods are of limited use with semiconductors and essentially of no use with metals. Spectroscopies which measure the vibrational properties of the atom which make up the sample material can often be useful as well. This would include both infrared spectroscopy and laser Raman spectroscopy. Both of these methods can be used on semiconductors, and again both are of little use for the characterization of metals.

Although the various types of radiation interact with matter in different ways, the primary process is the production of ions and electrically excited states of molecules which, in turn, may lead to the formation of free radicals. Radiation – generated mobile electrons which become trapped at sites of low potential energy, are also produced. The first phenomenon leads to permanent chemical, mechanical and electrical changes of the material; the second results in temporary electrical changes in performance.

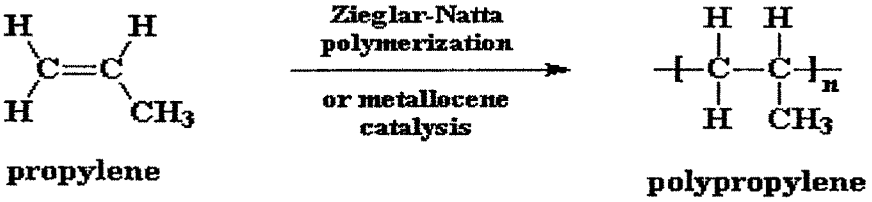
The modifications of polymer properties under ionizing radiation is a subject of widespread importance due to the increasing use of polymers in hard radiation environments encountered in nuclear power plants, space-crafts, sterilization irradiators, high energy particle accelerators, etc. The role of the molecular structure of polymers exposed to irradiation has been recognized since the early development of radiation chemistry in the 50s allowing the establishment of rough guides to predict the evolution of polymer properties.

3.2 Properties of Polymers used for study.

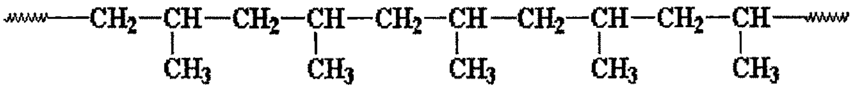
In the present investigation five different polymeric materials were used viz. PP, PET, PET + PVC, KAPTON, PVC + EVA . Table 3.1 gives a brief description about the properties of the polymers used. The structure and utilities of the polymers are given below [1-9].

3.2.1 Polypropylene (PP)

Polypropylene (PP) is the lightest known industrial polymer. Structurally it is a vinyl polymer. Every Carbon atom in the backbone chain has a methyl group attached to it. Polypropylene can be made from the monomer propylene by Ziegler-Natta polymerization as shown below.



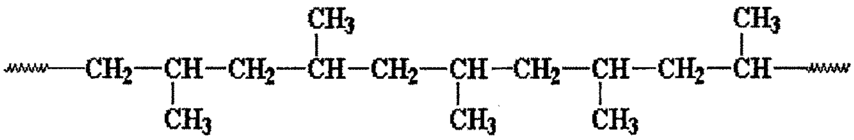
Polypropylene can be made by different tacticities i.e. isotactic, syndiotactic or atactic. Most polypropylene used is isotactic. This means that all the methyl groups are on the same side of the chain as shown below.



$$\sim\!\sim CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-\sim\!\sim$$

isotactic polypropylene

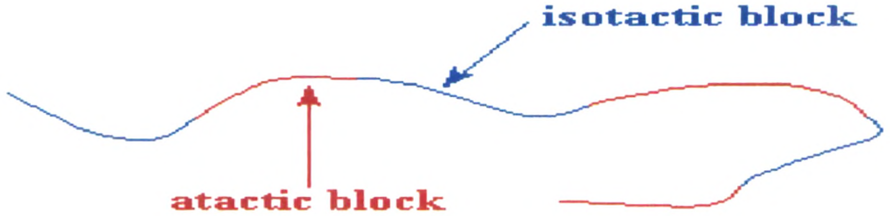
At times atactic polypropylene is also used. Atactic means that the methyl groups are placed randomly on both sides of the chain as shown below.



$$\sim\!\sim CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\sim\!\sim$$

atactic polypropylene

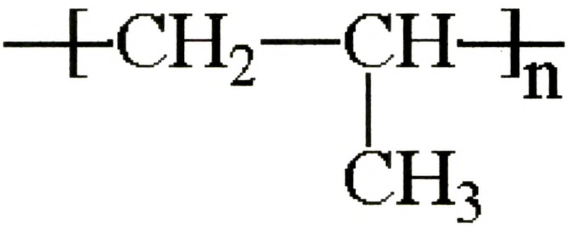
Using special metallocene catalysts polypropylene polymer can be made containing isotactic polypropylene and atactic polypropylene blocks in the same polymer chain as shown below.



This kind of polymer is rubbery, and makes a good elastomer, because the isotactic blocks form crystals by themselves, but because the isotactic blocks are joined to the atactic blocks, each little hard clump of crystalline isotactic polypropylene will be tied together by soft rubbery tethers of atactic polypropylene.

Atactic polypropylene would be rubbery without help from the isotactic blocks, but it wouldn't be very strong. The hard isotactic blocks hold the rubbery isotactic material together, to give the material more strength.

The isotactic polymer is highly crystalline and melts at 208°C. The polymer molecules are essentially linear and have configuration of 3_1 helical structure. Its structure is given below.



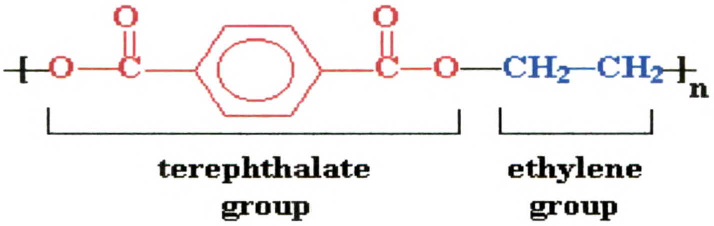
$$-\!\!\left[CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} \right]_n\!\!-$$

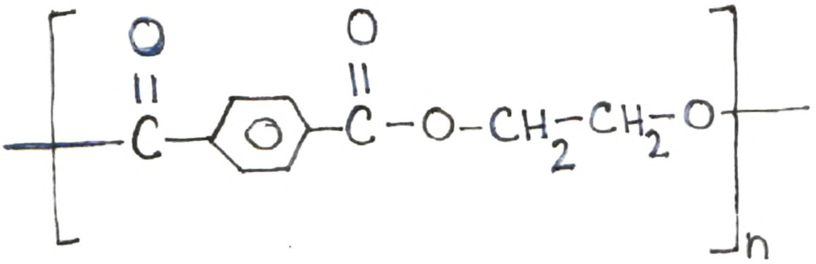
It is a transparent, soft and thermoplastic polymer. Being highly crystalline, it exhibits high stiffness, hardness and tensile strength. It has a very high strength-to-weight ratio.

It is insoluble at room temperature in many of the known solvents, but can be dissolved in aromatic and chlorinated hydrocarbons above its melting temperature. It is resistant to many chemicals such as acids, alkalis and oils. It has excellent mechanical and dielectric properties. It is used in refrigerators, radios, televisions, package films, pipes, storage tanks, seat covers, monofilaments, ropes, sterilized moulded articles, etc.

3.2.2 Polyethylene Terephthalate (PET)

PET is one of the most popular and commercially available polymers marketed under the trade name of Terylene or Terene. Polyethylene Terephthalate (PET) is a semi-crystalline polymer, with a melting point of about 265°C. Semicrystalline polymers have a characteristics microstructure rather different from that of metals [3]. According to the available literature [4-5], the semicrystalline polymers are made of stacks of thin (100-150 A) crystalline 10-100μm^2 sheets of lamellas. The polymeric molecular chain (mol. Wt. 104 -106) having a length of ~1 µm, is assumed to be folded several times within a single lamella which itself is surrounded by amorphous regions. Sometimes a chain may extend beyond a lamella. The lamellas and amorphous regions, are thus well entangled making the whole structure mechanically intact. The volume ratio of these two regions gives the percentage crystallinity of the bulk polymer which depends on different treatments given to it during or after its processing. Polyethylene is the simplest polymer, composed of chains of repeating $-CH_2-$ units. It is produced by the addition polymerization of ethylene, $CH_2=CH_2$ (ethene).The chemical structural formula of PET is $(C_{10}H_8O_4)n$. It has the following structural formula.





PET is 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 hydrolyse it). Its crystallinity varies from amorphous to fairly high crystalline. It can be highly transparent and colourless but thicker sections are usually opaque and off white. The degree of branching of a polymer determines its state of ordering. The more linear a polymer is, i.e. the less side branches it has, the higher in the potential crystallinity. It is resistant to heat and moisture. It is virtually un-attacked by many chemicals. It has a very good mechanical strength up to 175°C. It is a soft, transparent and a thermoplastic polymer.

PET is hard, tough, and resilient. PET has too low a glass transition temperature that is the temperature at which PET becomes soft. Polyethylene terephthalate (PET) is a highly crystalline polymer. Its glass transition temperature is 74°C.

It is used in the manufacture of containers, such as milk bottles and laundry detergent jugs. It is used in the production of plastic films, such as those used in sandwich bags.

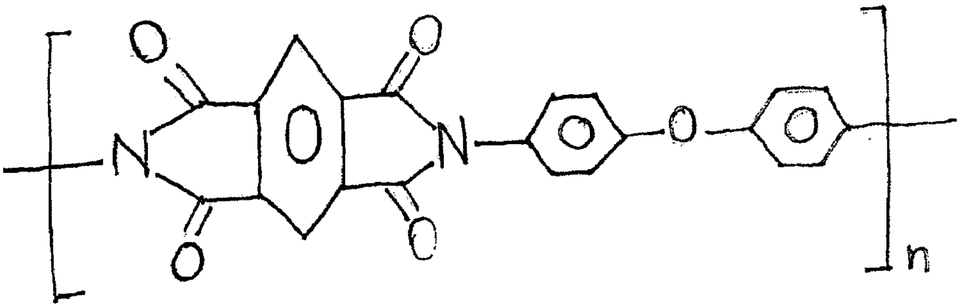
Polyesters can be both plastics and fibers. Balloons found in hospitals are made of a polyester film made by DuPont called Mylar. The balloons are made of a sandwich, composed of Mylar and aluminum foil. Materials like this, made of two kinds of material, are called composites.

Polyethylene Terephthalate (PET) is highly used as a thermoplastic fiber. Transparent sheets and castings can be formed from this polymer. Other applications include bottles and electrical compounds. 'PET' films are used for capacitors, graphics, film base and recording tapes etc. besides in wide applications in nuclear and space technologies. It is used in garment manufacture, magnetic recording tapes, aluminized sheets, etc.

3.2.3 Polyimide (PI) / Kapton

Polyimides represent an important class of high-temperature, solvent-resistant polymers. Often, polyimides are formed by a two stage process. The first step involves the polycondensation of an aromatic dianhydride and aromatic diamine to form an intermediate poly(amic acid). Dehydration of the poly(amic acid) at elevated temperatures yields the polyimide (PI) structure. Unlike the intermediate poly(amic acid), the cured (i.e. fully imidized) PI is insoluble and infusible and has high temperature and oxidative stability and good electrical insulation properties and radiation resistance. Commercially important PI is a polypyromellitimide that is available as film is Kapton.

Kapton is one of the heat resistive and most technologically important polymer which has attracted the attention of scientists and material engineers since the last few decades. It has wide applications in different technologies especially in nuclear and satellite fabrication technology [A]. It has sufficient U.T.S. and its working temperature ranges from liquid Helium temperature to 400°C for continuous use. Its structure is as shown below:



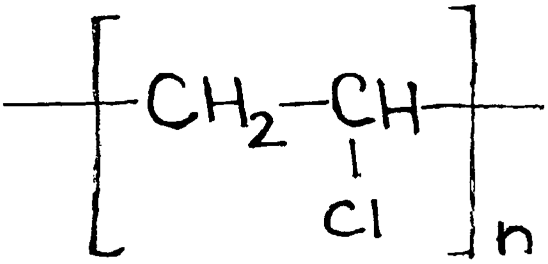
Polyimide is yellow in colour, transparent, soft and is a thermoplastic polymer. It has excellent thermal stability, good dielectric properties and excellent mechanical strength. It can withstand a temperature of 425°C without undergoing any degradation. Kapton has high radiation resistance. Hence it is a suitable polymer for radiation application.

It is used in the insulation coating of electromagnetic wirings, surface coatings in supersonic aircraft, backings and windows in many nuclear physics experiments, microfilters, IC fabrication, passivations and multiplayer interconnections in microelectronics, etc. Kapton has wide applications in different technologies especially in nuclear and satellite fabrication technology. Typical uses for polyimides include electronics, sleeve bearings, valve seatings and as the matrix component of graphite composites for compressor vanes in jet engines and other aerospace applications [6].

3.2.4 Polyvinyl Chloride (PVC)

Polyvinyl chloride (PVC) is an important polymer used extensively. Its molecular formula is[-(-CH_2 -CHCl-)n-]. Polyvinylchloride (PVC) is one of the most important polymers currently used worldwide. This is because PVC is one of the cheapest polymers to make and has a large range of properties so can be used to make hundreds of products.

Its structural formula is



$$\left[\mathrm{-CH_2-\underset{\displaystyle Cl}{\underset{|}{C}H}-}\right]_n$$

PVC is formed by the polymerisation of vinyl chloride (chloroethane) monomer units. Polymerization of vinyl chloride, CH_2=CHCl (chloroethene), produces a polymer similar to polyethylene, but having chlorine atoms at alternate carbon atoms on the chain.

The vinyl chloride polymers are mainly amorphous thermoplastics with very good chemical resistance. PVC is the most widely used member of the vinyl family. On every other carbon in the backbone chain, one of the hydrogen atoms is replaced with a chlorine atom. It is produced by the free radical polymerization of vinyl chloride. Resins of polyvinyl chloride are hard, but with the addition of plasticizers a flexible, elastic plastic can be made.

Polyvinyl chloride (PVC) is rigid and somewhat brittle. PVC has a good chemical resistance, especially against oils. It has a high strength-to-weight ratio and is a good electrical and thermal insulator. PVC is also self-extinguishing per UL flammability tests. PVC may be used to temperatures of 140°F (60°C) and is readily available in sheets, rods, and tubing. PVC may be cemented, welded, machined, bent and shaped readily. It is water resistant. It has flame resistance, too, because it contains chlorine. When you try to burn PVC, chlorine atoms are released, and chlorine atoms inhibit combustion.

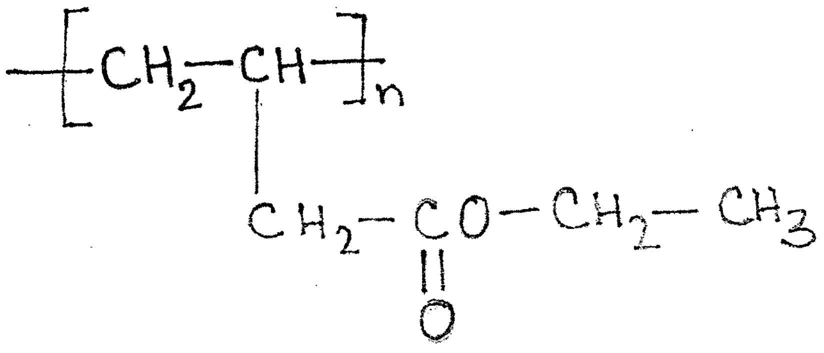
PVC consists of polar molecules attracted to each other by dipole-dipole interactions due to electrostatic attractions of a chlorine atom in one molecule to a hydrogen atom in another atom. These considerable intermolecular attractions between polymer chains make PVC a fairly strong material. Uncompounded PVC is colourless and rigid and possesses poor stability towards heat and light.

About two-thirds of the PVC produced annually is used in the manufacture of pipes and fittings. It is also used in the production of "vinyl" sidings for houses and clear plastic bottles. When it is blended with a plasticizer such as a phthalate ester, PVC becomes pliable and is used to form flexible articles such as raincoats and shower curtains. Their combination with plasticizer opens up many useful applications, ranging from artificial leather to injection molding components. This plastic has found extensive use in the manufacture of wires and cables. Cloth and paper can be coated with it to produce fabrics that may be used for upholstery materials and raincoats [7,8].

3.2.5 Ethyl Vinyl Acetate (EVA)

EVA is a polymer which has excellent quality of heat resistance and heat stability. It has long life and good mechanical properties. It shows excellent thermal stability and limited viscosity change and discoloration when formulated with a suitable antioxidant. Due to its structure EVA has high versatility in hot melt formulations thus EVA's are leading polymers for hot melt manufacturing. Due to its high compatibility they can be formulated in combination with natural or synthetic tactifiers.

EVA is highly flexible polymer compatible with many other polymers and additives and are easy to process. It is highly flexible, thus it is highly resistant to rupture. They have high cohesive strength and are highly compatible.EVA is obtained by high pressure radical polymerization.



A large range of PE waxes, modified waxes or plasticizers and their intrinsic stability can be enhanced by the right choice of antioxidant or uv / light stabilizers.

Since EVA is highly heat resistant EVA based hot melts are able to fulfill various requirements in applications such as packaging, book binding or label sticking. EVA is used for packaging, wood working, medical, transportation or assembly. Wood, textile, powder and automotive coating by EVA are very popular. Construction/Infrastructure coatings are also very popular [9].

Table 3.1 Typical Properties of polymers used in the present work.

Property		Polymer				
		PP	PET	PI	PVC	EVA
Mechanical	Density (gcm^{-3})	0.90	1.37	1.43	1.38/1.55	0.92/0.96
	Tensile strength (Ncm^{-2})	21/37	47	75/100	50/75	10/20
	Elongation at break (%)	20/800	50 / 300	4/9	10/50	600/900
	Modulus of elasticity intension (N/mm^2)	1100 / 1300	3100	23000 / 28000	1000/3500	7/120
Electrical	Volume resistivity(Ωcm)	$>10^{17}$	10^{16}	$>10^{16}$	$>10^{15}$	$>10^{15}$
	Surface resistivity (Ω)	10^{13}	10^{16}	10^{14}	10^{13}	10^{13}
	Dielectric constant at 50Hz	2.27	4.0	3.5	3.5	2.5/3.2
	Dielectric constant at 10^6Hz	2.25	4.0	3.4	3.0	2.6/3.2
	Dissipation factor (tan δ) at 50Hz	$< 4 \times 10^{-4}$	2×10^{-3}	2×10^{-3}	0.011	0.003/0.02
	Dissipation factor (tan δ) at 10^6Hz	$< 5 \times 10^{-4}$	2×10^{-2}	5×10^{-3}	0.015	0.03/0.05
	Dielectric strength - 124 - KV/25μm (ASTM D 14a)	800	500	--------	200/400	------

Thermal	Maximum service temp. (^{o}C)-short term	140	200	400	75/100	65
	Maximum service temp. (^{o}C)-continuous	100	100	260	65/85	55
	Minimum service temp. (^{o}C)-continuous	0/-30	-20	-200	-5	-60
	Heat distortion temperature (^{o}C) VSP (Vical 5 kg) DIN 53 460	85/100	188	------	75/110	-----
	Heat distortion temperature (^{o}C) ASTM D 648 1.86/945 N/mm^{2}	45/120	-----	240/-	60/82	34/62
	Coefficient of linear thermal expansion (k^{-1} x 10^{4})	150	70	50/63	70/80	160/200
	Thermal conductivity (w/mk)	0.17 / 0.22	0.24	0.6/0.65	0.14/0.17	0.35
	Specific heat (k5/kgK)	2.0	1.05	188	0.85/0.9	2.3
Optical	Refractive index	1.49	-------	-------	1.52/1.55	-----
	Clarity	Transparent/ opaque	Transparent/ opaque	Opaque	Transparent/ opaque	Transparent/ Opaque
Water	mg (4d) DIN 53492	< 0.01	18/20	---------	3/18	-------

absorption	% (24h) ASTM D 570	0.01 / 0.03	0.30	0.32	0.04/0.4	0.05/0.13
Chemical	Acids Concentrated	Excellent	Good	Good	Good	Fair
	Acids Dilute	Excellent	Good	Good	Moderate	Good
	Oxidation	Excellent	-------	-------	-------	------
	Alkalis	Excellent	Poor	Fair	Moderate	Good
	Aromatic Hydrocarbons	Fair	Fair	Poor	Not resistant	Moderate
	Greases and Oils	Poor	Good	Fair	Moderate	Moderate
	Halogens	------	Good	Fair	Moderate	Not resistant
	Ketones	Good	Good	Excellent	Not resistant	Not resistant
	Solvents (room temp.)	None				

3.3 Irradiation and Measurements

3.3.1 Target Preparation

PVC and PET blends:

The polymeric blend of PVC (IPCL make,) with commercial grade PET (Garware make) was prepared in the laboratory in equal proportion in a two roll mill, and then pressed in a hydraulic press to convert it into a sheet. PVC and PET were taken in granules form and in pure form too (wt/wt). The mixture was transformed into a sheet at around 125°C for half an hour.

Figure 3.1 Picture of Two roll mill.

Two roll mill (**Figure 3.1**) consists 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 the temperature comes down to ambient temperature. Each sheet was cooled further for 7/8 hours and then taken for various measurements.

Similarly, the polymeric films of pure PVC and EVA and their blends in different proportion (i.e. 30:70; 50:50 and 70:30) were prepared in the laboratory. The PVC and EVA were taken in granule form and in pure form too (wt/wt). The pure and mixture in the above proportion were transformed into sheets, in two roll mill at around 125°C for half an hour.

Other polymers (i.e. PP, PET and PI) were available commercially.

Four/five pieces of PP, PET, PI, blended PVC and PET; PVC and EVA of size 1.5 x 1.5 cm^2 were cut from the sheets. These were washed thoroughly by soap solution and deionised water. The cleaned samples were then dried inside a vacuum desicator.

3.3.2 Thickness Measurement of Samples

The thickness of these polymers was measured by a sensitive digital instrument. Sensitivity of the instrument was 0.001mm. The thickness of the polymers was measured at 7-8 places chosen randomly. The thickness of samples is listed in **Table 3.2**

Table 3.2: Thickness of the polymers.

Polymer	**Thickness**
PP	320μm
PET	230μm
PI	70μm
PVC + PET	460μm
EVA	0.45mm
PVC + EVA (50:50)	0.25mm
PVC + EVA (70 : 30)	0.28mm
PVC + EVA (30 : 70)	0.35mm
PVC	0.15mm

3.3.3 Li^{3+} Ion Irradiation

Three / Four pieces of each polymer of size 1.5x1.5 cm^2 were cut from the sheet. These samples were mounted on a vertical vacuum shielded sliding ladder and irradiated in a general purpose scattering chamber (GPSC) by using a 50MeV Li^{3+} ion beam available from a 15UD pelletron at the Nuclear Science Center, New Delhi. The irradiation was made at different fluences ranging from 10^{12} to 10^{14} ions/cm^2. The beam current was maintained around 20nA in order to avoid excessive heating. The residual pressure in the target chamber was 10^{-6} Torr. The irradiated samples were stored at room temperature in air. The details are listed in **Table 3.3**.

Table 3.3 Details of the irradiation of the polymers.

Sr.No.	**Sample (polymer)**	**Fluence (ions/cm^2)**	**Current (nA)**	**Time of irradiation (min.)**
1.	PP	2.4×10^{12}	20	1.
	PP	3.4×10^{13}	28	10.
	PP	1.5×10^{15}	20	60 .
2.	PET	3.0×10^{12}	25	1.
	PET	3.0×10^{13}	25	10.
	PET	1.3×10^{14}	18	60.
	PET	2.5×10^{14}	17	120.

3.	Kapton (PI)	5.2×10^{13}	14	30.
	Kapton (PI)	10.4×10^{13}	14	60.
4.	PVC + PET	2.3×10^{12}	19	1.
	PVC + PET	2.3×10^{13}	19	10.
	PVC + PET	1.3×10^{14}	19	60.
	PVC + PET	2.5×10^{14}	15	120.
5.	PVC + EVA(50:50)	$\sim 10^{12}$	5	2.
	PVC + EVA(50:50)	$\sim 10^{13}$	5	20.
	PVC + EVA(50:50)	$\sim 10^{14}$	5	200.
6.	PVC + EVA(70:30)	$\sim 10^{12}$	5	2.
	PVC + EVA(70:30)	$\sim 10^{13}$	5	20.
	PVC + EVA(70:30)	$\sim 10^{14}$	5	200.
7.	PVC	$\sim 10^{12}$	5	2.
	PVC	$\sim 10^{13}$	5	20.
	PVC	$\sim 10^{14}$	5	200.
8.	EVA	$\sim 10^{12}$	5	2.
	EVA	$\sim 10^{13}$	5	20.
	EVA	$\sim 10^{14}$	5	200.

3.3.4 Calculation of Range and Energy loss using SRIM Code

The interaction mechanisms of ion beam with polymeric materials is discussed in article 1.7 of chapter 1

SRIM consists of a number of computer programs. This program is used to calculate the stopping and range of ions (10eV – 2 GeV / amu) into matter giving a quantum mechanical treatment to the ion-atom collisions. The calculation is made very efficient by the use of statistical algorithms which allows the ion to jump between calculated collisions and then averaging the collision result 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 given). The charge state of the ion within the target is described using the concept of effective charge, which included a velocity dependent charge state and long range screening due to the collective electron sea of the target.

The particle's energy is reduced after each free-flight path by the amount of electronic energy loss and then (after the collision) by the so-called nuclear energy loss which is the result of transferring momentum to the target atom in the collision. Each ion's history is terminated either when the energy drops below a pre-specified value or when the particle has moved out of the front or rear surface of the target.

TRIM (the Transport of Ions in Matter) is the most comprehensive program, included in SRIM. This computer program is available for targets of several layers of different composition. The program provides output for one and two dimensional distributions of ion range, energy deposition, reflection and transmission characteristics of planar targets, ion's energy loss, target damage, sputtering, ionization, and phonon production. In practical applications of the TRIM program, for e.g. in studying the sputtering yield (recoil atoms of a few eV being knocked out of the surface), the TRIM results yield quite satisfactory agreement with the experimental data.

At high energies it is quite efficient as it takes into account the natural increase in free-flight paths; a particle's free-flight path between noticeable collisions is long at high energies and is steadily reduced in the course of slowing down. The TRIM program contains provisions for dealing with very high energies and includes relativistic electronic energy loss and straggling for high energies. For e.g. energies below 1 MeV / amu the electronic straggling, however was found to be of little importance for the projected range profiles and is usually neglected. Some kind of electronic straggling at low energies can be introduced however by using the built-in option of treating the electronic energy loss as dependent on the distance of closest approach in the individual collisions.

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

In the present work we have calculated the projected range of 50 MeV Li^{3+} ions in each polymer along with the electron and nuclear stopping power using latest SRIM code [10].

Results Obtained from SRIM.

In Polypropylene (PP) the projected range was calculated to be 526μm, which is 1.64 times the thickness of the sample. The calculations indicate that 99.95 % of energy is lost due to electronic interaction.. The electronic stopping power $(dE/dX)_e$ is 5.358 eV/A° where nuclear stopping power $(dE/dX)_n$ is 3.227×10^{-3} eV/A°. The energy deposited in the medium comes out to be 38 MeV.

In Polyethylene terephthalate (PET) the projected range was calculated to be 398μm, which is 1.73 times the thickness of the sample. The calculations indicate that 99.95 % of energy is lost due to electronic interaction.. The electronic stopping power $(dE/dX)_e$ is 7.185 eV/A° where nuclear stopping power $(dE/dX)_n$ is 3.894×10^{-3} eV/A°. The energy deposited in the medium comes out to be ~37.0 MeV.

In Polyimide (PI / Kapton) the projected range was calculated to be 396 μm, which is 5.65 times the thickness of the sample. The calculations indicate that 99.94 % of energy is lost due to electronic interaction.. The electronic stopping power $(dE/dX)_e$ is 7.224 eV/A^0 where nuclear stopping power $(dE/dX)_n$ is 0.0038 eV / A^0.

In blend of Polyvinylchloride (PVC) and Polyethylene terephthalate (PET) the projected range was calculated to be 382μm.The thickness of the sample is 1.2 times larger than the range. The electronic stopping power $(dE/dX)_e$ is 7.538 eV/A^0 where nuclear stopping power $(dE/dX)_n$ is 4.153×10^{-3} eV/A^0.

In blend of Poly vinyl chloride (PVC) and Ethyl Vinyl Chloride (EVA), the projected range was calculated to be 476 μm. The electronic stopping power $(dE/dX)_e$ is 5.96 eV/A^0 where as the nuclear stopping power $(dE/dX)_n$ is 3.40×10^{-3} eV/A^0.

3.4 Characterization of Irradiated and Pristine Polymers.

The characterization of the pristine and irradiated samples were done by different techniques as discussed in chapter 2 (Fourie transform IR spectroscopy, optical microscope / scanning electron microscope, Vickers' microhardness Tester, AC electrical frequency response and mechanical). The instrumental set up and the experimental conditions are described below.

3.4.1 FTIR Spectroscopy.

The FTIR spectra of the pristine as well as irradiated samples of each polymer were recorded in transmission mode using Fourier transforming instrument (model 104-Bomem, Canada) keeping air as reference. The measurements were done in the wave number range 4000-510cm^{-1} and the transmittance (or absorbance) spectra of the polymers were obtained (transmittance % or absorbance as a function of wavenumber). 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 the characteristic bands with a resolution of 4 wave number. The errors, while recording the spectra might be due to stray radiation, zero setting of the instrument, non continuous samples, atmospheric absorption, slit width, scan speed etc.

Figure 3.2 FTIR Spectroscopy set up.

The FTIR spectra can be used to observe the change occurring due to the ion beam interaction with the polymer. Functional group analysis for the irradiated and pristine films were carried out by means of Fourier transform infrared spectroscopy (Bomen, Canada, model MB 104), with a resolution of 4 wave number. The FTIR spectra of these films were taken in the transmission mode.

3.4.2 Resistance, Capacitance and Dielectric loss (tan δ) Measurement

Variable Frequency digital LCR meter (General Radio, USA, model 1689), was used for measuring resistance in 0.00001 Ωto 99999 k Ωand capacitance in 0.00001pF to 99999 μF range. The range can be extended by a factor of 10,000 times more or less as per the requirement. Two measurement modes are available for operating this meter: Continuous and Triggered. (any one of the two measurement modes can be used). For the work of this thesis Triggered mode was used. In this mode the measurement is initiated by the start button. The result is displayed until the next measurement is started [11].

Figure 3.3 Experimental set up to measure electrical properties.

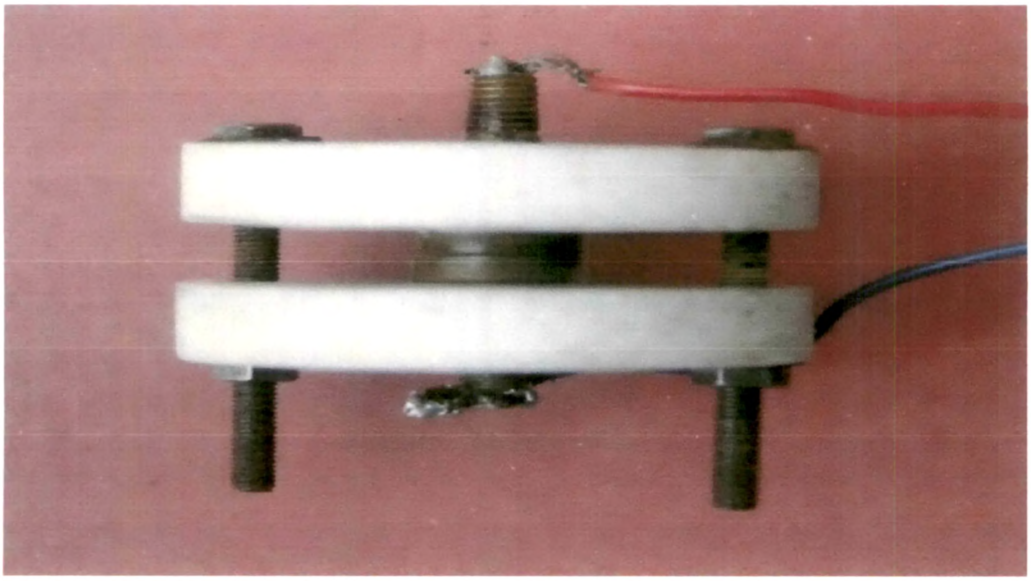


Figure 3.4 Sample Holder to measure electrical properties.

Four-probe method was used to measure resistance, capacitance and tanδ. The resistance, capacitance and tanδ of the samples was measured by a constant voltage method. This technique results in a much more stable and reliable impedance measurement than the conventional constant current method. Electrical contact on the sample were made by applying an air drying type of silver paste, and then the sample was mounted between the two electrodes of the specially designed sample holder (as shown in **Figure 3.2**).

The a.c. electrical response of different samples was measured at ambient temperature. Resistance, Capacitance and tanδ was measured as a function of frequency. The frequency was varied in a range from 0.05 to 100 KHz for all the samples. Similarly, the measurement were also made at different temperatures. This was done by placing the specially designed sample holder (a shown in figure 3.2) in a furnace, where the temperature was maintained with copper-constant thermocouple. The temperature was varied from ambient temperature to 150°C.

The resistivity and conductivity were calculated using equation 2.4 and 2.5 of article 2.3.1 of chapter 2.

The dielectric constant was calculated using equation 2.9 of article 2.3.1 of chapter 2.

3.4.2 Optical and Scanning Electron Microscopy.

Optical micrographs of pristine and irradiated Kapton films were recorded at 120X magnification. For accurate investigation of irradiated film, pictures with enhanced magnification of 281 X, 2.34 KX and 4.51KX, were recorded using scanning electron microscope (SEM). The SEM used in our study at FCIPT, Gandhinagar was Leo, Electron Microscopy, U.K., (model no. 440I).

3.4.3 Hardness Measurements

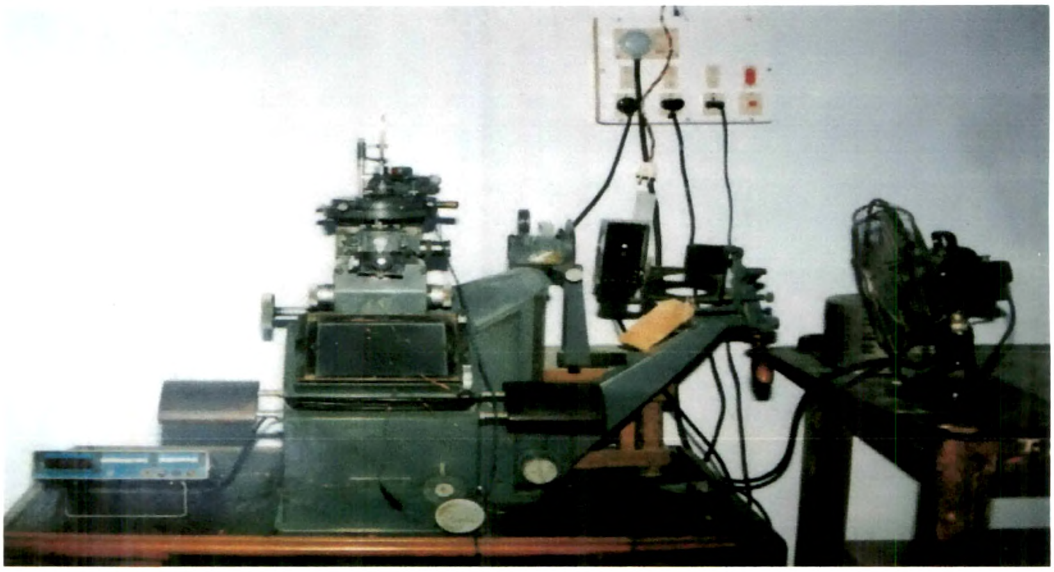


Figure 3.5 Vickers' Projection Microscope.

The method of indentation in hardness measurement is the most widely used method, primarily because it does not require large specimens and on a small specimen a number of measurements can be made. Indenters have been known to be either sharp or increases, the indenter tends to be blunt and the influence of friction and prior strain hardening decreases. Also the value of constraint factor C in the relation between hardness and yield stress i.e. H=CY tends to 3 as the effective cone angle increases [12]. The stress field produced by such as indenter closely approximates to the prediction of elastic theory.

The Vickers' diamond pyramidal indenter used in the present study has included angle of 136° which is a good compromise to minimize frictional effects and at the same time to give a well defined geometrical square to the indentation mark. Also for metal to diamond contact, the coefficient of friction ranges from about 0.1 to 0.15 making the frictional effects less pronounced [13].

The samples were mounted on a horizontal platform inserted in the collect of Vickers microhardness tester which was attached to a metallurgical microscope. The area for the indentation is selected by using bright field objectives. After selection of the area, an objective is replaced by Vickers' micro hardness indenter sensor from rotating nosepiece. Loads ranging from 100mN to 1000 mN were used for making indentations, keeping the time of indentation constant as 30 seconds in all cases, (the diamond tip indents into the specimen at a pre-selected force gradient) since microhardness is observed to be independent of indentation time. The force is held constant for the duration of 10 seconds and then the diamond tip is automatically retracted to the resting position. To avoid surface effects, the distance between two consecutive indentations was kept more than three times the diagonal length of the indentation mark. The indented impressions were square shaped. The diagonal lengths of indentation marks were measured using a filar micrometer eyepiece at proper magnification and averages of these diagonal lengths were recorded.

The Vickers' microhardness was calculated using the formula 2.15 as discussed in article 2.3.6 of chapter 2.

3.3.5 Tensile Testing.

Mechanical properties of the sample were tested on Instron Tensile tester, an American tester which uses the bonded wire type of the strain gauge. Several inter changeable load cells containing the strain gauges are used. The rate of traverse can be adjusted between 2mm/min to 1000mm/min. Load was varied and the load-extension curve was obtained. Load/volume (gm/mm^3) was varied in the range from 0 to 225 gm/cm^3 and the elongation curve was obtained. The cross head speed (mm/min.), traverse speed (chart speed) (mm/min.) and Gauge length (mm) for all the samples was kept 10.0. The width of all the samples was kept 1.0 mm. The thickness of various samples was as mentioned in article 3.2.2 of chapter 3. The sample volume (mm^3) for PVC / EVA (70:30) was 2.8, for PVC / EVA (50:50) was 2.5, PVC / EVA (30:70) was 3.75, EVA 4.55 and PVC 1.5 respectively. The chart was connected to the load cell.

From the graph obtained, the value of stress and strain was calculated and a plot of strain v/s stress was plotted. From this graph the values corresponding to breaking load (g), breaking load per volume (g/mm^3), breaking elongation (mm), yield load (g), yield load per volume g/mm^3, yield elongation (mm) was calculated [14].

3.3.6 Thermogravimetric Analysis.

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. The instrument used for the work of this thesis is Shimadzu Thermogravimetry System TGA-30, ans SEIKO Thermal analyzer TGA 220 as discussed in article 2.3.3 of chapter 2. The range knob has two series of positions, ± mg and %. With this knob set at one of the ± mg positions, ± 0.5 ~ ± 100 mg, the pen deflects full scale when the sample weight changes ± 0.5 ~ ± 100 mg, regardless of the original weight of the sample.

The recorder indicates the proportion of the weight change to the original weight,(i.e. when the entire sample evaporates) the recorder pen deflects to 100%. This is convenient because the ratio of weight loss can be directly read without knowing the original weight [15].

The weight of the sample was measured in the following procedure. A clean empty cell is placed on the sample pan. The instrument is adjusted for zero, (the zero knob of the recorder is adjusted so that the pen is at the zero line of the chart).

Air was taken as the atmosphere medium and the sample was heated from ambient temperature to 600°C for all the samples at a constant heating rate of 10°C/min. To heat the sample Kanthal wire heater was used. The temperature was maintained using a Chromel-alumel thermocouple. The instrument recorded the thermograms on the chart as a function of weight to temperature.

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