Chapter 1: Introduction

ABSTRACT

This chapter deals with brief introduction about ion beam in material science, historical development of polymers, structure, morphology and its applications as well as effects of radiation on polymers, fundamental principles of the ion beam interaction with the polymers and the present work.

1.1 INTRODUCTION

The main developments in polymer science during the past thirty years have been improving our knowledge of the relationship between the structure of polymers and their properties. More recently, the ability to manufacture polymers with specific structures has been invented, although there is still much to learn about the development of "tailor made" polymers. Polymers, in performance, characteristics, offer unique properties, application prospects and diversity which are not found in any other class of materials. The quest of new materials has been with mankind from ancient times. Polymers, although introduced in the material field in a meaningful manner only very recently occupy a major place and position in our life today.

Ion bombardment may modify/improve certain properties of materials that have been the driving force behind much of this research. Ionizing radiation is applied in the plastics industry due to its ability to effect cross-linking, a process whereby polymer chains link together in a three-dimensional network. The intentional degradation of polymer materials is another application of ionizing radiation. It results in a decrease of the molecular weight. Low-pressure plasmas are also useful for altering surface properties of polymer materials to satisfy the demand of certain applications without altering the bulk properties. For instance, plasmas can be used for the surface activation of plastics in order to improve the adhesion of various materials. Practical applications for radiation processing of materials have been evolving since the introduction of this technology nearly fifty years ago. Materials response to high energy ion-beam was considerably different from those induced by e-beam and gamma rays.

From metals to semiconductors to organic films, the damage effects become increasingly more important, since the ability of the solid to annealed to recover the original order to realize the chemical effect of the impurity. While metals recover even at room temperature, most semiconductors need a high temperature. Further, bond breakage of organic molecules in general results in the formation of an ensemble of smaller molecules, many of which may be volatile. As a result during the implantation process, material is expelled from the original solid thereby producing an irreversible change.

1.2 ION BEAM IN MATERIAL SCIENCE

Over the last five decades, there has been a prolific growth in the field of ion accelerators have been extensively used for ion beam modification of materials with energetic ions. On the other hand, the uses of swift heavy ions (a few MeV/amu) from the high energy accelerators offer the advantage of engineering of materials in a unique way. It has been further strengthened due to the availability of a variety of ion beam analysis techniques to characterize the materials synthesized/modified by ion. Thus, materials research using a wide range of energetic ions has led to a reasonable understanding of ion-solid interaction and its consequences over a depth scale ranging from atomic monolayer on the surface to the ion penetration depth of typically micrometers (for MeV ions).

1.2.1 Material Analysis

In principle all of these processes happen during ion beam irradiation, if properly detected, may be utilized to extract some important information about the material exposed. In fact many of them have now been proved as very powerful and convenient analysis techniques. For example, ion back-scattering is used as mass sensitive depth microscopy. Since the energy of the back scattered particles at a given angle depends upon the mass of the scattering centre, i.e. the target atom, therefore, energy spectrum of these particles directly relate to the masses of various atoms constituting the target. By knowing the energy loss of the ions going in and coming out and cross-section of scattering, direct information about concentration versus depth is obtained. When back-scattering is used in conjugation with channeling very precise information about lattice location of impurities is obtained. Back-scattering and channeling experiments are done with light ions (proton and helium) at high energy MeV range. However, low energy scattering also has been used to do mass and structure analysis of surface [1, 2].

Sputtering is also used as analysis technique as secondary ion mass spectrometry (SIMS). Essentially the sputtering target particles are accelerated and mass analyzed. Secondary electrons emitted due to ion bombardment can also be detected and used to do chemical analysis of the samples similar to the well developed Auger electron spectroscopy [3]. X-rays emitted due to light ion bombardment (He^+) provide excellent tool for elemental analysis and have much superiority over the conventional electron induced emission studies. Optical radiation also has been shown to be useful as technique of surface analysis and is known as SCANIR (Surface compositional analysis by neutral and ion impact radiation) [4].

1.2.2 Material Modification

The success of ion implantation techniques in modifying the electrical properties of semiconductors is well known [5-8]. It provides an alternative approach to the well developed diffusion techniques for fabrication of semiconductor devices.

However, this technique is now being proved as a very promising tool to tailor wide range of other physical and chemical properties of material surface also, including metals and insulators. Mechanical surface properties like friction and wear can be greatly reduces by implanting suitable ions into the substrates. For example, Hartley et al [9] observed significant decrease in coefficient of friction of the steel surface implanted with molybdenum and sulpher and reduction in wear, by an order of magnitude, of copper and steel implanted with boron, nitrogen and molybdenum. Preparation of superconducting alloys has been attempted, and at least it is demonstrated that ion implantation offers an excellent method to improve superconducting properties [10].

This technique can be used to dope suitable impurities in wide band gap materials used as phosphorous. The selection of impurities may be made either to provide excitation or deexcitation between impurity levels, or through states in the host energy bands [6]. Miniaturization of optical systems consisting of lasers, mirrors, prisms, lenses and gratings using ion beam techniques is another important field being worked out [11].

Chemical and electrochemical surface properties can be suitably modified to produce desired results. For instance, implantation can be used to produce a new surface alloy or compound which is resistant to corrosion and oxidation, an example being nitrogen implanted silicon [12]. A review on oxidation behavior of ion implanted metals can be found in Dearnaley [13]. Besides the above mentioned technological fields expecting large impact from ion beam techniques, many others, are well under consideration. These include various branches in electrochemistry, infrared sensors and magnetic bubbles.

1.2.3 Radiation Damage Simulation

Fission reactors have traveled a long way in the journey of power production, and still today huge effort is being put to modify the existing designs, heat transfer systems and quality of constructional materials to optimize the energy excitation and enhance their life time safe operation. Through the operation of these commercial reactors and many reactors specifically built as problem finders, several problems have come into light which, if not overcome, may result in catastrophic failure or premature shut down of the reactor. These problems are mainly related to the long term irradiation of reactor components with nuclear particles resulting due to fission process (neutron, fission fragments and transmutation products like alphas, protons, and gammas). The agglomeration of point defects, due to irradiation, resulting in swelling may range from 7 to 60% during the reactor life time depending upon its operating conditions. However, a tightly built reactor design without leaking any room to accommodate such swelling may fail even at very low swelling levels (<1%). The problem is further complicated due to the fact that voidage results in loss of ductility, therefore, enabling the material to fail in brittle fashion when the stress developed due to swelling, or the thermal stress, due to some accidental temperature excursions exceeds the yield strength of the material. Besides these the rate of growth of voids is dependent on many factors like displacement rate, impurity content (including fission gasses), micro structural defects, external and internal stresses and change in chemical composition of the material obviously influence their behavior in course of time.

The fusion reactors are yet to come into operation, however, recent successes in achieving the plasma temperature and densities near ignition condition in magnetic confinement geometries, tokamak and mirror design [14-16] and promising results from inertial confinement experiments using laser, electron or ion beams [17-19] have seeded high hopes in eventual utilization of fusion energy source on commercial basis. Even after successful achievement of fusion conditions, the further impedance is anticipated to come from the material side. However, the material requirements of fusion reactors are unique and in many respect still not well defined, specially of the first wall, which faces the fusion plasma directly. The reason for this is the complex irradiation environment resulting from D-T fusion and the criticality for sustaining fuel burn [20,21]. In order to control the unwanted implications of radiation damage and to avoid the dangerous accidents it is of utmost importance to estimate the long term irradiation effects and properly take them into account in the design prior to under taking the construction. However, studies on a reactor throughout its life time to get such information is not practical in view of rapidly growing demands for power, therefore, simulation studies [22] using ion beams are enforced. The idea behind simulation is to increase the damage rate to achieve total displacement per atom equivalent to that expected for the life period of the reactor. Ion beams serve this purpose as they possess large collision probabilities and their current densities are available from μA-mA.cm^{-2} range to control the incident flux. Thus neutron damage of a typical reactor expected to occur in few decades can be simulated in few hours using ion beams [23-25]. However, monoenergetic ion beams of light gases obtained from accelerators are understood to support and promote the void nucleation and influence their onward growth. To study the effect of energy spectrum on surface erosion due to blistering in a fusion device, a sequential implantation procedure was adopted by Guseva et al [26]. Kaminsky et al [27] more particular about metals and alloys. Moreover, some more systematic approaches under consideration consists of producing multicomponent ion beams of varying energies and fluxes to strike the target simultaneously, and possibly coupling the beam chamber with transmission and scanning electron microscope to have on-line study of the dynamics of the various processes.

Briefly, the radiation emanating from the fusion plasma due to D -T burn consists of neutrons having energy distribution around 14 MeV, charged and neutral deuterium, tritium and helium atoms over the energy range of few eV—3.5 MeV, and X-rays due to bremsstrahlung in the energy range eV-keV. The first wall and other internal components like limiters (used to keep the plasma away from striking the wall), divertors (used to guide the outer most layer of plasma out of the main vacuum chamber), wall armors (used to receive shine through of the particles form the neutral beam injection), electrical insulation (super conducting magnets, cables etc.) and mechanical components (o-rings, seals etc) receive this wide spectrum of particles. Resulting effects on the surfaces exposed, are the material erosion due to physical and chemical sputtering, blistering and exfoliation/flaking, and evaporation due to thermal load [28-36].

The various wall erosion processes may affect the functioning of a reactor in two ways; by disturbing vacuum and mechanical integrity and by contaminating the fusion plasma. In magnetically confined fusion devices small leak developed due to either erosion or the crack formation (due to the accidental thermal loadings) may shut down the reactor. In addition to this, stresses developed due to volume swelling or temperature gradients combined with loss of ductility due to bubbles and voids, may result is catastrophic mechanical failure of the components [37].

1.3 POLYMER

What is a polymer and what's in it? Normally the word polymer is used when talking about molecules whose molecular weight (or size) is in the range of several thousands or more. Most of the time when we talk of polymer we were talking about molecules with molecular weights of hundreds of thousands, or even millions.

Polymers are substances containing a large number of structural units joined by the same type of linkage. These substances often form into a chain-like structure. In other cases, the chains are branched or interconnected to form 3-dimensional networks. The repeated unit of the polymers is usually equivalent to the monomers or starting material from which the polymer is formed. The large size of polar macromolecules consist of molecules of its low molecular analogues, joined to one another, 'n' times by chemical bonds, where 'n' is the degree of polymerization and can take on very large values (up to 100s to 1000s) [38,39]. The number of monomers present in a macromolecule determines the molecular weight of a polymer (M_w). It may be tens or hundreds or even sometimes millions of carbon units and equals the molecular weight of the initial monomer M multiplied by the degree of polymerization 'n' i.e. M_w=nM.

1.3.1 Historical Background of Polymer

Polymers in the natural world have been around since the beginning of time. Starch, cellulose, and rubber all possess polymeric properties. Man-made polymers have been studied since 1832. Today, the polymer industry has grown to be larger than the aluminum, copper and steel industries combined.

Early growth of polymer science came in the middle of the last century, yet the early developments of polymers are not recorded. However, natural polymeric products have been used through out the ages but most of the developments of polymer science have taken place in the 20th century. The first hypothesis of the existences of macromolecules was advanced by Kekule in 1887 when he proposed that natural organic substances consist of very long chain of molecules from which they derive their special properties. In 1868 John Wesley Hyatt of New York had already manufactured the first synthetic plastic producing celluloid by treating cotton with nitric acid and camphor. John Trode Scant (1608-1662), the English traveler and gardener, is given the credit of introducing guttapercha, to western civilization of another natural resin from the east. Another English man Thomas Hancock, discovered that if the rubber was highly sheared or masticated, it becomes plastic and hence capable to flow due to several times reduction in molecular weight. In 1839 Charles Goodyear found that rubber when heated with sulfur can retain its elasticity over a wide range of temperature that the raw material can have, and that it has greater resistance to solvents. He patented it out in 1844. Later, W. Brockendon termed this process as Vulcanization.

In 1893 Emil Fisher suggested a structure for natural cellulose having a chain of glucose units. He also postulated that polypeptides are long chain of polyamino acids. In 1909, American scientist, Leo Backeland from two very common chemicals (Phenol and Formaldehyde) developed a resin (which was later named after him as Bakelite) that could be molded into hard infusible articles. In 1912, Jacques Brandenburger introduced a famous transparent materials, cellophane.

Hermann Staudinger who received the Noble Prize in Chemistry in 1924, for his pioneering work in macromolecular Chemistry and proposed the linear structure for polystyrene and natural rubber. As soon as the idea of macromolecules having linear structure was recognized, many materials e.g. Cellulose acetate (1927) Polyvinyl Chloride (1929). Formaldehyde resins etc. were discovered.

Again it needed a scientist (Wallanec H. Carothers) with broad vision to provide a new concept for the development of synthetic polymers and produced linear condensation polymers such as polyester and polyamides. His group including, Paul J. Flory [40-42] who received Noble prize in Chemistry in 1974, made basic research efforts to study long chain molecules made from di-functional monomers resulting in the development of Neoprene, Polyester and Polyimide.

Subsequently rapid development of many important polymers e.g. Acrylics and Polyvinyl acetate in 1936, Polystyrene in 1938, Malamine formaldehyde in 1936, Polyester and Polyethylene in 1941 took place.

A brilliant scientist Kerl Zeigler of Max Planck Institute, Germany, was involved in synthetic organometallic chemistry. He observed that exposure of ethylene to some aluminum alkyle compounds led very rapidly to polymerization of the ethylene. He and Giullio Matta extended the work to other olifines. They received the Noble Prize in 1963 for their discovery of stereo specific polymerization.

Within a decade or so, several polymers started appearing in newer and newer forms with increasingly better properties from the laboratories of scientists all over the world. In broad sense one can conclude that polymer industry came into existence only after 1900 and rapid development of polymer science has taken place during last three decade. The period saw the development of several Copolymers and Organometallic polymers. Now a days various types of conducting polymers are also growing with newer and newer form. A large number of processing techniques accompanying them are also under development.

1.3.2 Various Types of Polymer

The monomers in a polymer can be arranged in a number of different ways. Both addition and condensation polymers can be linear, branched, or cross-linked.

- **Linear polymer**

A linear polymer [**Figure 1.1**] is a polymer molecule in which the atoms are more or less arranged in a long chain. This chain is called the backbone. Normally, some of these atoms in the chain will have small chains of atoms attached to them. These small chains are called pendant groups. The chains of pendant groups are much smaller than the backbone chain. Pendant chains normally have just a few atoms, but the backbone chain [**Figure 1.2**] usually has hundreds of thousands of atoms.

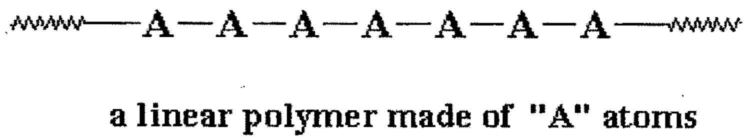


Figure 1.1: Linear polymer.

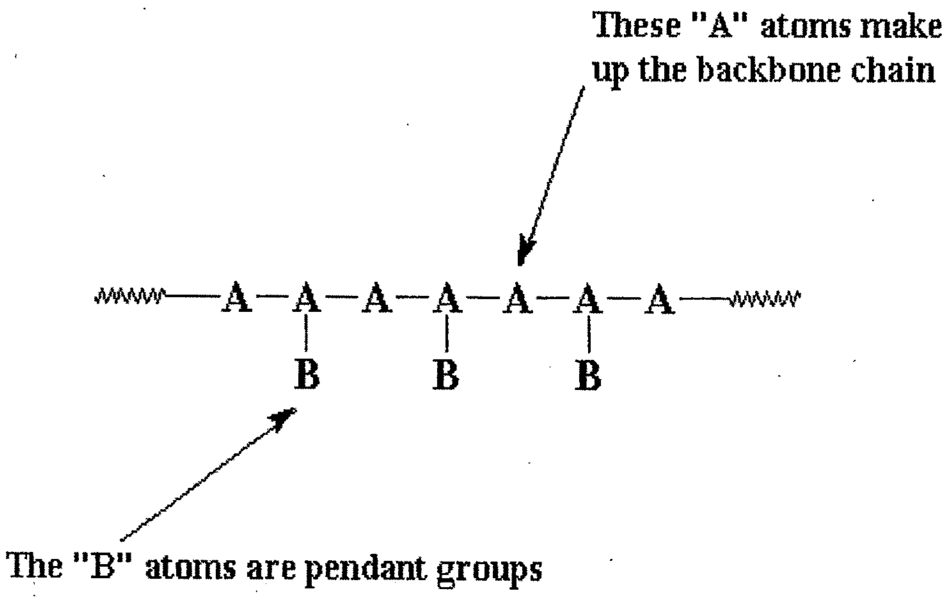


Figure 1.2: Polymer with back bone chain and pendant.

The atoms that make up the backbone of a polymer chain come in a regular order, and this order repeats itself all along the length of the polymer chain [**Figure 1.3**].

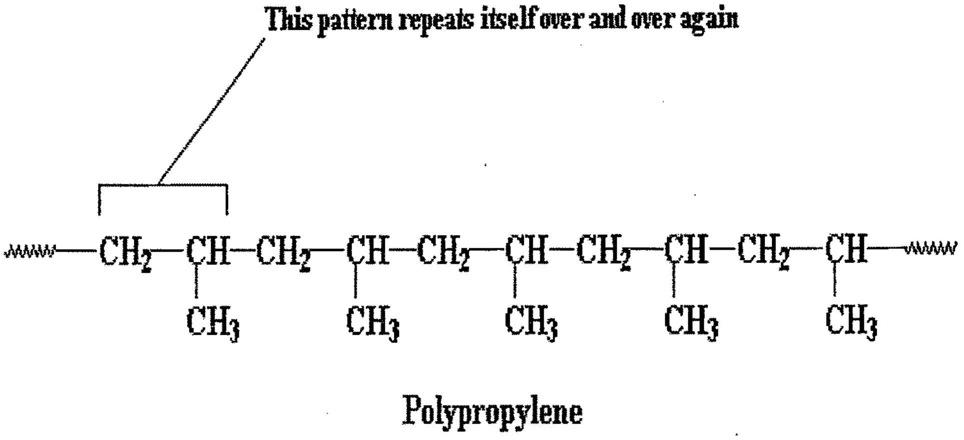


Figure 1.3: Repeating structure.

For example, in polypropylene, the backbone chain is made up of just two carbon atoms repeated over and over again. One carbon atom has two hydrogen atoms attached to it, and the other has one hydrogen atom and one pendant methyl group.

This unit of a carbon with two hydrogen atoms followed by a carbon atom with a hydrogen atom and a methyl group repeat itself over and over again along the backbone chain. This little recovering structure is called the repeat structure or the repeat unit.

- **Branched and crosslink polymer**

Polymer can come in other structures, though; polymer can be made in a lot of other arrangements, too [**Figure 1.4**]. Not all polymers are linear in this way. Sometimes there are chains attached to the backbone chain. This is called branched polymer. Some polymer, like polyethylene, can be made in linear or branched versions.

The branch chains have some strange habits. Sometimes, both ends of the branch chains are attached to the backbone chains of separate polymer molecules. If enough branch chains are attached to two polymer backbone chains in a sample, it will become a giant network. Polymers like this are called cross linked polymers. These cross linked are tie all the polymer molecules together. Cross linked polymers are usually molded and shaped before they are cross linked.

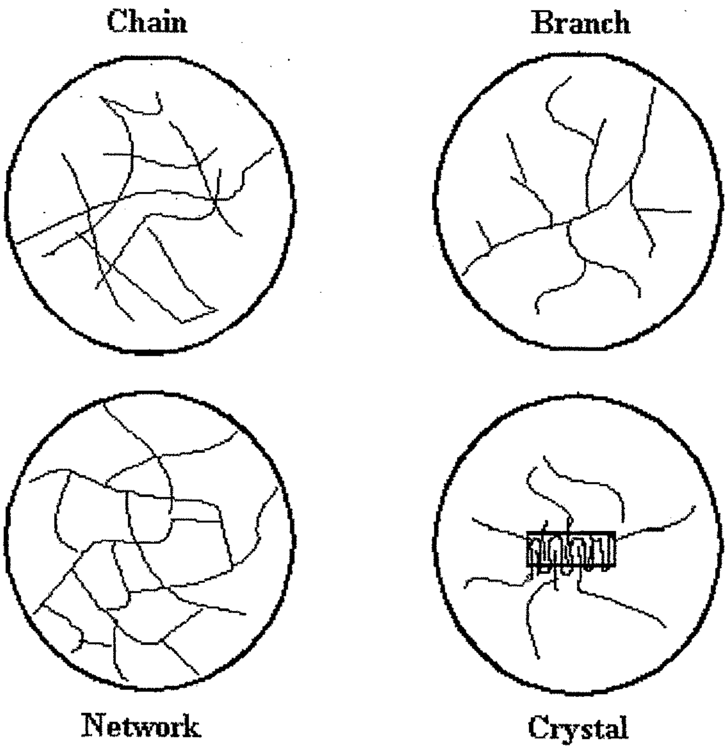


Figure 1.4: Various types of polymers.

- **Thermoplastic and elastomers**

Once cross linking has taken place, usually at high temperature, the object can no longer be shaped. Because heat usually causes the cross linking which makes the shape permanent, we call these materials, thermoset.

As plastics become easier to mold and shape when they are hot, and melt they get hot enough, we call them thermoplastic. Thermoplastic which are not cross linked and can be reshaped once molded. Lightly cross linked, it's a flexible rubber. Heavily cross linked, it's a hard thermo sets.

Some polymers which are elastomers include polyisoprene or natural rubber, polybutadiene, polyisobutylene and polyurethanes. Elastomers can be stretched to many times their original length and can bounce back into their original shape without permanent deformation.

Not all amorphous polymers are elastomers, some are thermoplastics. Whether an amorphous polymer is a thermoplastic or an elastomers depends on its glass transition (T_g) temperature. This is the temperature above which a polymer has a T_g below room temperature, that polymer will be an elastomers, has a T_g above room temperature, it will be a thermoplastic, because it is hard and glassy at room temperature [43-53].

1.4 STRUCTURE AND MORPHOLOGY OF POLYMERS

Segments of polymer molecules can exist in two distinct physical structures. They can be found in either crystalline or amorphous forms. A detailed study of polymer structure has been carried out by many scientists [54-62]. The structural details of polymers are closely related with their chemical and physical properties. The micro structural studies have revealed that the basic structural elements of high polymer are the linear chain molecules. The Russian Scientist Lebedev [63] deserves credit for having conceived the idea of a long chain structure. He polymerized butadiene and assigned to the product a cyclo-octadine structure. Soon afterwards Lebedev [64] proposed a chain structure for polybutadine and rubber. Staudinger [65] differentiated linear and non-linear or network polymer. A lot of X-ray diffraction analysis of polymers by Sponsor, Dore, Mayer, Mark and Freudenberg etc. provided additional evidences for the higher molecular weight theory and long-chain structure. The description of the morphology and the interpretation of properties of semi-crystalline polymers remained a subject of a very deep and divisive debate for more than two decades. The basic structural elements of high polymer solids are the chain molecules. The variety of their structure and flexibility permit different modes of organization.

X-ray structure analysis is one of the most potential and direct techniques to study the structure of the material. When this method was applied to polymers, some interesting phenomena were observed revealing their internal structure. It was observed that a good majority of polymers diffract X-rays like any crystalline substances and many behave like amorphous materials giving very broad and diffuse X-ray diffraction pattern. On the basis of these results one can classify polymers into two broad groups – one which can be produced in crystalline state and the other in amorphous state.

1.4.1 Crystalline Polymer

Crystalline polymers are only possible if there is a regular chemical structure (e.g., homopolymers or alternating copolymers), and the chains possess a highly ordered arrangement of their segments. Crystallinity in polymers is favored in symmetrical polymer chains; however, it is never 100%. These semi-crystalline polymers possess a rather typical liquifaction pathway, retaining their solid state until they reach their melting point at T_m.

The basis for crystallinity in polymer is quite complex. The simplest element of the structure of crystalline polymer is its crystalline unit cell formed by several atoms (parts of Chains). In a unit cell each atom in the long chain molecules, is covalently bonded to its neighbor and the atom cannot move independently from one location to another, its neighbor must move in a highly prescribed manner since nearest neighbor along the chain direction must always be the same atom.

This restricted mobility of bulky long chain of polymer molecules prevented 100% crystallinity, even if it shows similar results as that observed as that in observed in metals i.e. increase of crystalline phase with annealing. The basic requirement for crystallinity is chemical regularity along the polymer chain (tactic) than is why higher crystallinity is not possible in atactic.

The X-ray crystallographic analysis of the unit cell of polyethylene by Bunn [66] marked an important point in the understanding of polymer science. Up to 1975 it was believed that the crystalline structure is of the fringe miscelle type [62] and the chains are frozen into non-equilibrium position due to lack of mobility. A typical miscelle [**Figure 1.5**] was supposed to be bundle of several tens of hundreds of different molecules which after leaving the miscelle and passing through amorphous regions would randomly form other miscelle. It provided a basis for understanding most of the experimental data such as IR spectroscopy and X-ray diffraction patterns. This two phase, fringed miscelle model enjoyed widespread recognition and popularity. Simple experiments independently performed by Fischer, Keller and Till [67-69] change the entire cource of study of the structure of polymers. The experiments led subsequently to the conclusion that mechanical properties are much more intimately related to morphology as compared to crystallinity in single crystal of polyethylene.

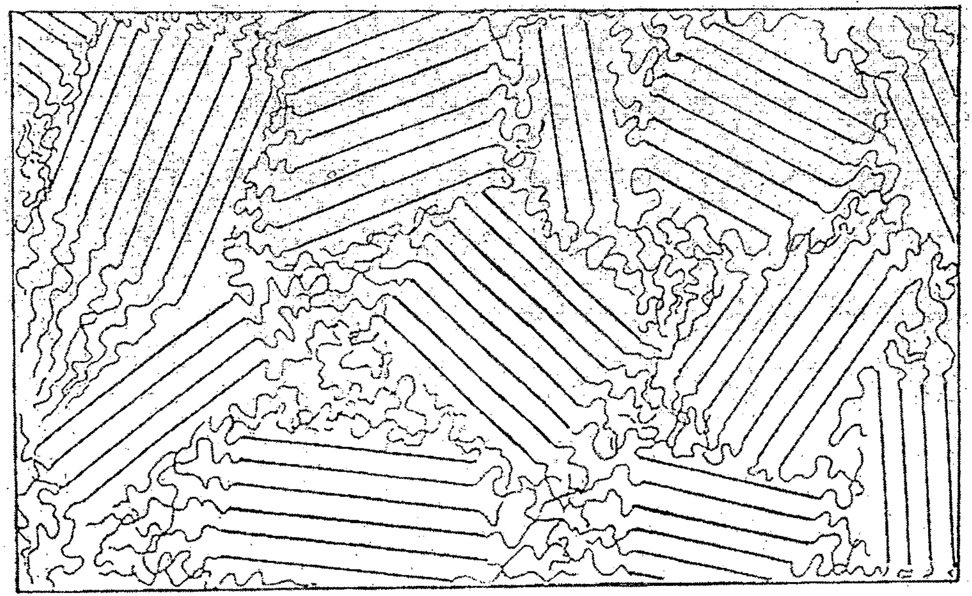


Figure 1.5: Fringed micelle concept for polymer morphology.

Polymer single crystals in their simplest form are monolayer flat plane lamella which are often rhomboid. Their thickness is typically 100-200 Å and width extending up to the micron range. It was found from Electron diffraction patterns, that the long axes of the chain molecules are perpendicular to the broad surface of the lamella, or very nearly so. Some sort of the chain folding is necessary to create the regularity in the lateral packing of the chains required by a unit cell because of the thickness of the lamella which is only about one-twentieth of the length of the chain.

A lot of work on electron microscopy of polymers and small angle X-ray scattering regarding chain folding in polymers has been done. Still the chain folding is debatable and does not have much relevance with experimental and theoretical aspects. The controversies regarding chain folding are divided into following categories.

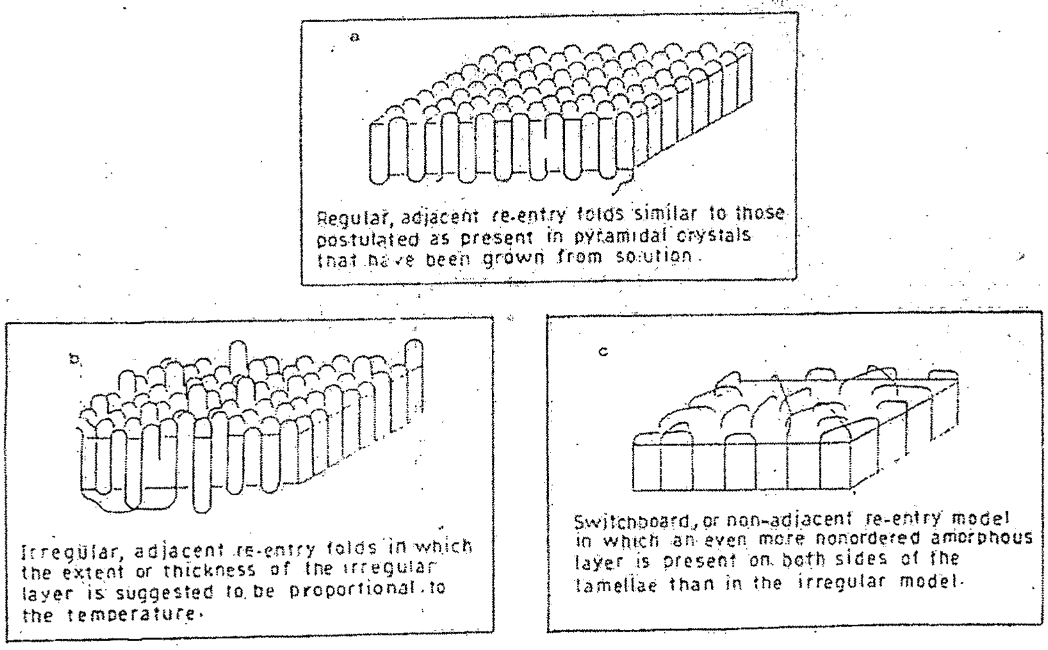
(a) Regular, adjacent re-entry folds,

(b) Irregular, adjacent re-entry folds,

(c) Switch board or non-adjacent re-entry model.

The regular, adjacent re-entry model **[Figure 1.6a]** appears to be a limiting case which can be realized in practice only under most carefully controlled conditions for crystallization environment and for molecular weight uniformity. In the melt crystallized system, where one crystal lamella is developing in very close proximity to another growing lamella, it is simple to envisage a fraction of chain transversing more that one lamella, providing "tie molecules" that contribute strength to the assembly. Such a composite structure of lamella shaped crystals inter spread with the amorphous region of loose loops and tie molecules, lead itself to a more realistic interpretation of the dynamic loss phenomenon and other mechanical properties. The various transitions of mechanical loss behavior can also be interpreted by "irregular adjacent re-entry model" **[Figure1.6b]** which provides both crystalline and amorphous regions in a single complex "phase". Third model **[Figure 1.6c]** is now effectively disregarded.

We know that molecules and their trajectories are not observed by electron microscopy. In order to resolve the nature of this interfacial structure, one needs different means and various other logical arguments. The efforts in this direction have been going on for more than 20 years. On tracing the history of this problem it can be seen that many of its aspects are now clearly at the point of resolution [70,71].



Regular, adjacent re-entry folds similar to those postulated as present in pyramidal crystals that have been grown from solution.

Irregular, adjacent re-entry folds in which the extent or thickness of the irregular layer is suggested to be proportional to the temperature.

Switchboard, or non-adjacent re-entry model in which an even more nonordered amorphous layer is present on both sides of the lamellae than in the irregular model.

Figure 1.6: Models proposed for chain folding in single crystals of polymers.

The spiral growth of the polymer crystal of polyoxymethylene is one of the most interesting complexities [72]. Multilayer structure with a small fraction of molecules interconnection overlapping lamellas was observed when polymer was crystallized from more concentrated solutions. In bulk crystallization, lamella thickness up to an order of 100 Å or even greater could be observed [73]. The lamella thickness depends on the molecular weight and crystallization conditions under atmospheric pressure.

In spite of the observation of larger crystalline dimensions, it was very strongly and vociferrlously argued through the 1960's and much of the 1970's that the chains were regularly folded in bulk-crystallized polymers [54,74,75]. The major principles that were widely enunciated to support regularly folded chain in bulk crystallized polymers were that-

- The chain units in crystalline homopolymers should be assigned to either the interior of the crystallites or to the smooth interface.
- Chain units connecting crystallites were rare events and, if they existed at all, adopted ordered confrontations and
- Deviations in properties from those expected from macroscopic crystals were widely known and accepted.

1.4.2 Amorphous Polymer

Amorphous polymers do not show order. The molecular segments in amorphous polymers or the amorphous domains of semi-crystalline polymers are randomly arranged and entangled. Amorphous polymers do not have a definable T_m due to their randomness. At low temperatures, below their glass transition temperature (T_g), the segments are immobile and the sample is often brittle. As temperatures increase close to T_g, the molecular segments can begin to move. Above T_g, the mobility is sufficient (if no crystals are present) that the polymer can flow as a highly viscous liquid. The viscosity decreases with increasing temperature and decreasing molecular weight. There can also be an elastic response if the entanglements cannot align at the rate a force is applied. This material is then described as visco-elastic. In a semi-crystalline polymer, molecular flow is prevented by the portions of the molecules in the crystals until the temperature is above T_m. At this point a visco-elastic material forms. These effects can most easily be seen on a specific volume versus temperature graph. In the area between T_g and T_m, the semi-crystalline polymer is a tough solid. The amorphous material changes to a viscous liquid after T_g. This is when the material can be easily deformed. At this point a visco-elastic material forms. These effects can most easily be seen on a specific volume versus temperature graph [**Figure 1.7**].

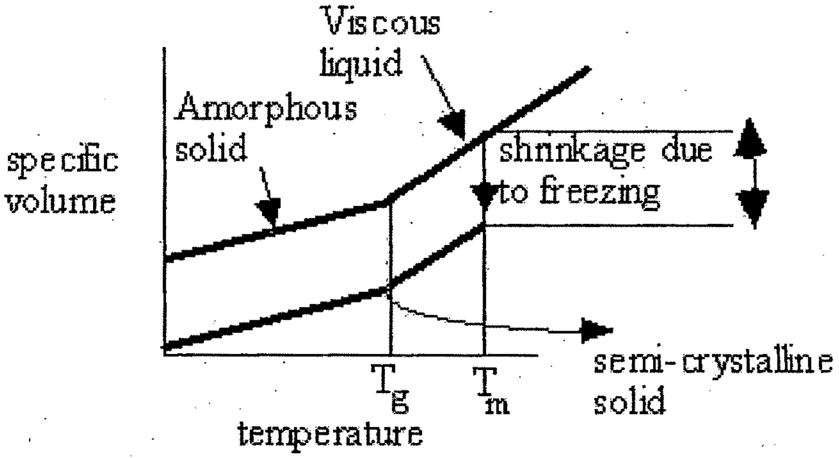


Figure 1.7: Specific volume versus temperature graph.

The most prominent change in the physical properties of polymer takes place at its glass-transition temperature (T_g), that characteristic property of the individual polymer. In fact, all relaxation mechanisms depend on the structure of the transforming group and on the environment provided by the molecular segments. Also, the packing density of the molecules will determine such properties as strength, stiffness and permeability.

Most of the physical parameters mentioned above will also play an important role with regard to the charge storage and charge transport phenomena in polymers.

Until about 1960 the general view prevailed that the polymers were considered to be isotropic, non crystalline like that in many rubber, glossy polymers, PVC, PMMA, PC or quenched semi crystalline polymers such as Teflon, Mylar which have a random confrontation and that the random coil. During years following 1960 the concept of a close range-order of the chain molecules within X-ray amorphous polymers gained growing support.

The evidence for a close range order was thought to be derived from a comparison of segments volume and amorphous density from electron microscopic observation of structural elements from calorimetric investigations, crystallization kinetics and from a study of network orientation. After 1970 Kriste, Fischer, Cotton and their associates [76-78], applied neutron-scattering techniques to amorphous polymers in addition to employing light and small angle X-ray scattering and spectroscopic methods. Flory [79] summarized his extended observations on polymers in solutions rubbery networks in favor of random coil structure of chain in bulk.

It was proposed that amorphous states and defect rich, originally ordered states are commensurable [80-82]. They have retained elements of close range order. Their amorphous states are not principally but only gradually different from well ordered states. The model for amorphous state which is still controversial, is now divided in the following four groups shown schematically in **Figure 1.8** respectively.

a. Interpenetrating random coil [77,54]

b. Honeycomb and Meander model [81]

c. Folded chain fringed misceller grains [82]

d. Fringed misceller domain structure [82]

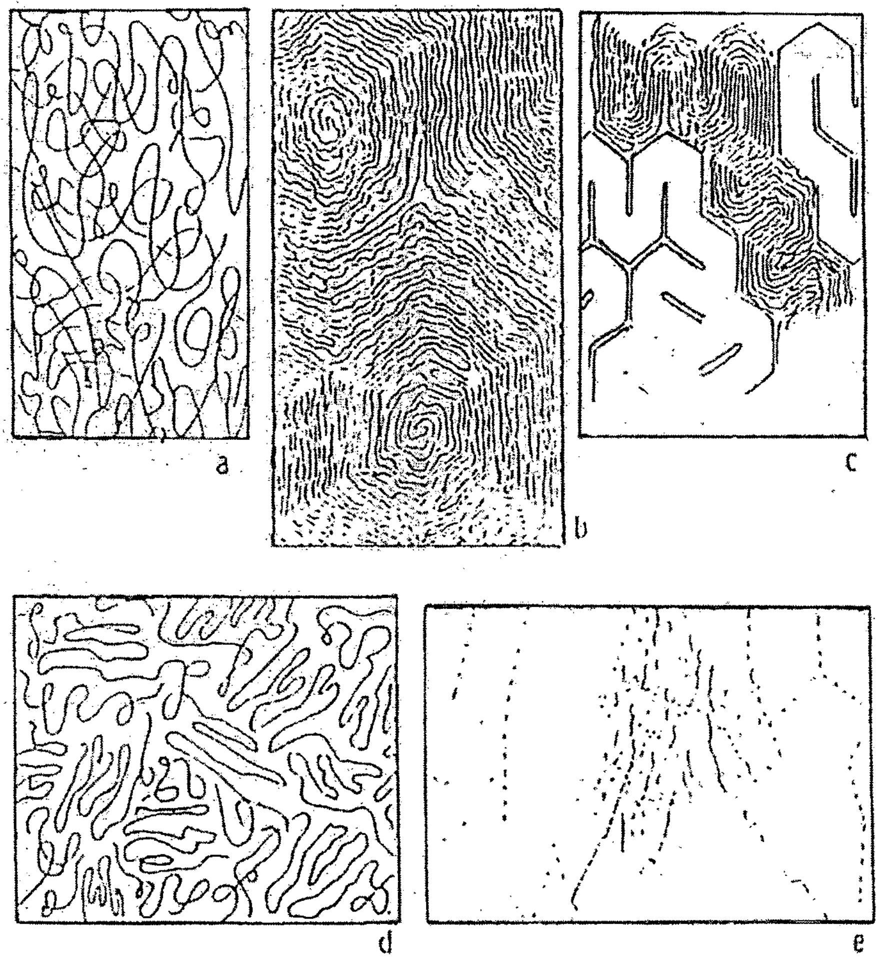


Figure 1.8: Model representations of the amorphous state: (a) interpenetrating coils, (b) and (c) honeycomb and meander model, (d) folded chain fringed micellar grains and (e) fringed micellar domain structure.

Further there is a great variation of crystallinity from more that 90% to less than 5% for a given polymer, although unit cell parameters remain invariant of microscopic densities over a large range. The variation of crystallinity, spectroscopic, results and melting temperature measurements, can be explained only when there are high interfacial energies. In other words it suggests the presence of diffuse interfacial zones which is also supported by thermodynamic calculations.

From these results it is concluded that there is a lamella like crystalline regions, which represents the three dimensional ordered structure and a diffused interfacial region (not having sharp boundary). These interfacial regions contain several internal defects of the same order of magnitude as that observed in the pure crystalline low molecular weight materials. Details of the structure still need to be worked out, but there must be some type of anisotropic orientation of the chain in the region close to the Basel plane of the lamella. On the basis of the existing experimental and theoretical knowledge, the most suitable schematic model can be worked out as shown in **Figure 1.9a** and **Figure 1.9b**, where, crystalline zones are inter linked with amorphous zones irregularly.

Another important characteristic of polymer is the crystalline morphology or super-molecular structure, which concerns with relative arrangement of the crystallites to one another. Observations of spherulites in different types of crystalline polymers, lead us to believe that the factor governing the super molecular structure does not represent an universal mode of polymer crystallization. The most important heterogeneities are derived from the tendency of many polymer to crystallize partially. More or less well defined crystalline lamellas are found in the form of single crystals i.e. stacked or grown upon each other in the form of shearing layer structure, as twisted aggregates in spheulities and in the form of sandwich like structure in highly oriented fibrils [54-56].

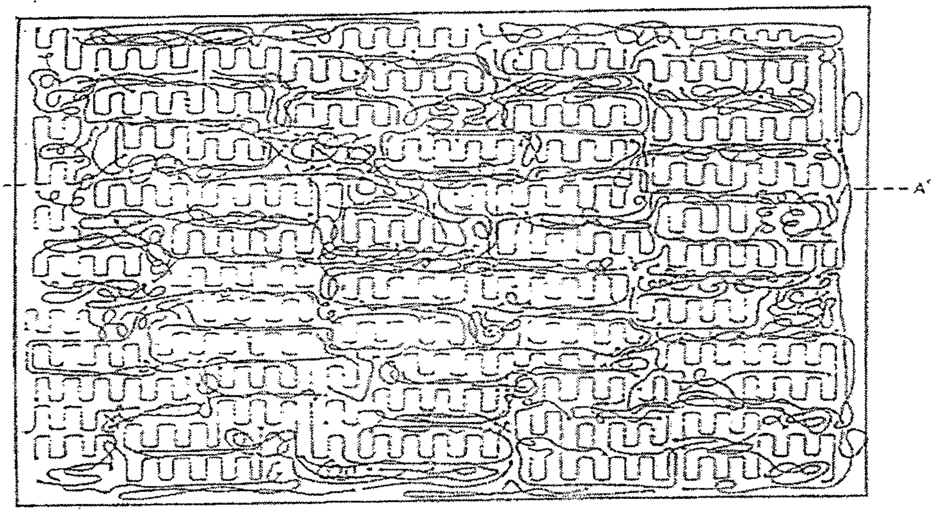


Figure 1.9a: Cross-sectional view of the structure of semi-crystalline polymers.

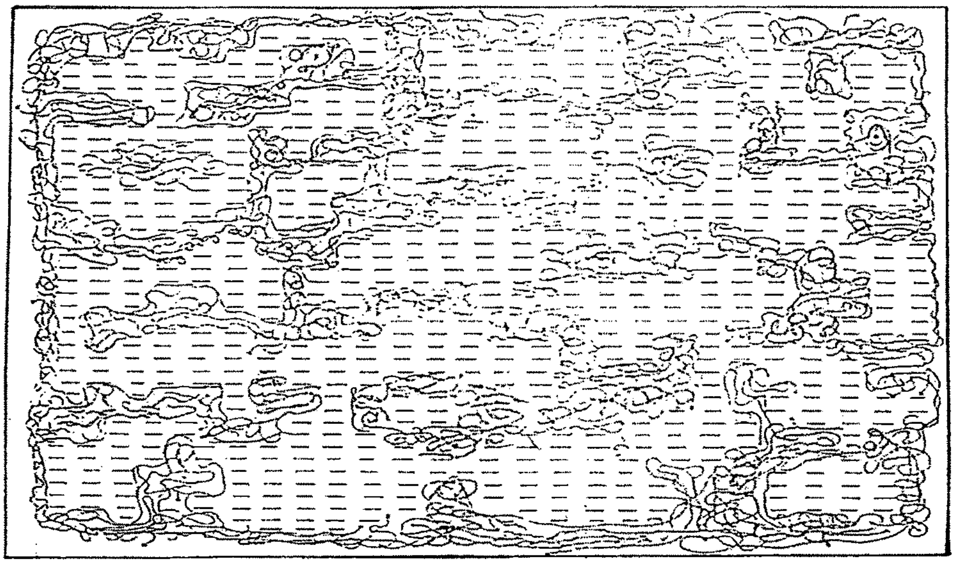


Figure 1.9b: View from parallel to the machine-drawing plane of the structure of semi-crystalline polymers.

Yoon and Flory's [71,79] comparison of the intensity distribution for several morphological models with the experimental scattering data, Schelten's [83] small angle neutron scattering observations, can not be explained by regularly folded and adjacent re-entry model. The boundary between two spherulites resembles grain boundaries; these grain boundary zones are enriched in low molecular weight material, impurities, chain ends, and defects. Since the cohesion between chains within a crystal's lamella is much stronger that the intercrystalline interactions. This renders certain stability to the lamella elements in the samples deformation. Although much remains to be done by neutron scattering, a definite structure can be deduced only when the results for the radius of gyration and the complete scattering functions are taken into account.

1.5 APPLICATIONS OF POLYMERS

To name a few desirable properties–high strength, light weight, good flexibility, special electric properties, semi conducting, and high temperature stability, resistance to chemicals, amenability for quick and mass production and for fabrication into complex shapes in a wide variety of color–some polymers will almost always meet your requirement. Polymer can be converted into strong solid articles, flexible rubber-like sheets, swollen jelly-like food materials etc. They can be used to band objects, seal joints, fill cavities, bear load-impact, anything from clothing the naked to powering a space vehicle to even replacing a human organ. Polymers already have a range of applications that far exceeds that of any other class of material available to man. Polymers, in performance characteristics, offer unique properties, application prospects and diversity, they also offer novelty and versatility which is not found in any other class of materials. Polymers, although introduced in the materials field in a meaningful manner only very recently, occupy a major place and position in our life today.

Today, the polymer industry has grown to be larger than the aluminum, copper and steel industries combined.

Polymers already have a range of applications that far exceeds that of any other class of material available to man. Current applications extend from adhesives, coatings, foams, and packaging materials to textile and industrial fibers, elastomers, and structural plastics. Polymers are also used for most composites, electronic devices, biomedical devices, optical devices, and precursors for many newly developed high-tech ceramics.

1.5.1 Nuclear Field

The influence of radiation on the properties and performance of a polymer differs according to polymer back bone. All materials have been found to break at very high radiation doses. Indeed, below the destructive level of exposure, radiation, treatment can impart many benefits and enhance properties of commercial value. The Mylar and Mylar like materials are quite in use in severe radiation environments such as those encountered in space, fusion and fission reactors. During the normal operation of the nuclear reactor plant, gamma-rays and neutrons that escape through the walls of the reactor core are the major radiations. The energy spectrum of gamma-rays ranges from a few keV to about 8 MeV and for the neutrons (>10 MeV). The dose rate will vary with location, but is typically found to range from about 10 to 100 radian per hour (rad h^{-1}) with an average rate of 50 rad h^{-1}. This would give an integrated dose of about 2 X 10^2 radian over 40 years of operation. Such a dose is sufficient to cause catastrophic failure of the plant.

1.5.2 Space

Radiation can be used to polymerize a monomer in the solid state and to modify surface for adhesive bonding. The use of polymer in space vehicle, polymers and composites selected for this application must have good resistance to radiation. It is extensively used in aerospace applications as radiation resist materials, ablation materials, structural material (in the form of gaskets, O-rings, instruments panel, seating etc.) and electrical (insulation, cables, transformer bindings etc.) components. Fortunately, polymer is the only material in which the effect of radiation improves some of their physical properties to certain extent. In fact moving space crafts, polymers have an edge over metals and wood due to favorable strength to weight ratio of fiber reinforced polymers. In supersonic aircraft's where heating caused by the air friction, is a serious problem. Polymers can be safely used due to their low thermal conductivity, high specific heat and endothermic decomposition, because heating and thermal damages will be limited to their upper surface layer only. The thermal application of polymer is to maintain the satellites or space vehicles at room temperature. Suitable coating of the polymeric substrate meets this requirement by arranging the ratio of solar energy absorbed (α) and thermal radiating energy (ε) emitted by the surface at the desired temperature for the payload with small internal power dissipation ~1.2. Specially some pigments, paints and polymers show almost negligible change in outer space, in addition to wide ranges of α, ε and α/ε values by varying the thickness of polymer films and the type of metal used as reflecting under coating. Their stability has been tested extensively both in laboratory and in space because of their outstanding α/ε values.

1.5.3 Medicine

Many biomaterials, especially heart valve replacements and blood vessels, are made of polymers like Dacron, Teflon and polyurethane. Various polymeric drugs have been developed for the treatment of diseases. A polymeric drug is a polymer that contains a drug unit either as part of the polymer backbone as a terminal group or as a pendant unit of the polymer backbone. Sterilizable of medical disposables (e.g., syringes, surgical gowns and lab ware) by γ- irradiation has become increasingly important due to the limitations of alternative techniques such as the in efficiency of steam sterilization and the possible carcinogenesis of ethylene oxide used in "cold" sterilization. Some polymers such as others polystyrene and polysulfone are very radiation resistant, but others such as polypropylene will readily degrade upon irradiation.

1.5.4 Sensor

Polymeric material used to make biometric sensors (polymer thick-film sensors) to capture fingerprints, iris geometries, hand geometry and other physiological quantities. Piezoelectric and piezoresistive sensors have been printed on flexible polyesters, then bonded to smartcard blanks. Polymers able to withstand high temperatures and reactive environments make thick film well suited for making gas sensors. In the case of a lambda sensor to measure the oxygen content in exhaust gases in order to control the air-fuel ratio.

Application of Bio-sensor technology used as contaminant detection as well as transdermal drug delivery systems

In differential pressure designs of fuel level sensors, thick film is again used for its ability to function in aggressive environments.

1.5.5 Agriculture and Agribusiness

Polymeric materials are used in and on soil to improve aeration, provide mulch, and promote plant growth and health.

1.5.6 Consumer Science

Plastic containers of all shapes and sizes are light weight and economically less expensive than the more traditional containers. Clothing, floor coverings, garbage disposal bags, and packaging are other polymer applications.

1.5.7 Industry

Automobile parts, windshields for fighter planes, pipes, tanks, packing materials, insulation, wood substitutes, adhesives, matrix for composites, and elastomers are all polymer applications used in the industrial market.

1.5.8 Sports

Playground equipment, various balls, golf clubs, swimming pools, and protective helmets are often produced from polymers.

Despite the great deal of attention given at the present time to the building of regular molecular construction in chains of monomers, efforts to produce new polymers have not lessened.

1.6 IMPACT OF POLYMERS ON PRESENT DAY TECHNOLOGY

The importance of macromolecular substances or polymers is matched by their ubiquity. Polymeric structures are distinguished at the molecular level form other materials by the concentration of groups to form chains, often of great length. Those chemical structures of this multivalency manifested by certain atoms, notably carbon, silicon, oxygen, nitrogen, sulfur and phosphorus and in the capacity of these atoms to enter into sequential combinations. Polymers have played a growing role in our civilization in this century as they have joined and complemented conventional structural materials such as metals, ceramics, wood, leather, textiles, and paper etc. Their rapid growth has been due to various advantages over conventional materials in terms of processibility, wide range of rigidity/flexibility, toughness, wide range of lubricity/adhesion, thermal and electrical insulation, wide range of clarity/opacity and color, resistance to corrosive chemicals as well as overall advantage of economical superiority.

In precise engineering designs for high performance polymers have often suffered from certain limitation: low elastic modulus, strength and creep prone, lesser than perfect lubricity, higher coefficient of thermal expansion, poor heat resistance etc. Reinforced polymers have been developed over the past 70 years to overcome many mechanical problems. But the difficulty in the processing of the reinforced polymers, results in limited design possibilities. Low lubricity, changed electrical properties, loss of clarity and color, and increase in the cost.

On the basis of ease in processibility, versatility in product design, broad range of modulus, toughening by polyblendings, electrical and chemical resistance, sufficient clarity and color range and overall low cost, a commodity of thermoplasts namely, polyolifines, styrene polymer and polyvinyl chloride have been developed during past four decades. Due to this combination of different properties, they have grown 75% of the total plastic market. However, as engineering materials they still suffer from major limitations in modulus, creep resistance, lubricity, thermal expansion, heat sensitivity and heat aging, which make engineers reluctant to use them in demanding applications.

With the commercialization of polytetraflouroethylene (Teflon) and its family, by DuPont in 1948 [84], the plastic industry gained an important material which is outstanding for self-lubricating bearings and seals, heat and chemically-resistant gasketing, cookwares and high temperature-high performances electrical insulation (melting point 327°C). Polyhexamethylene adipamide (Nylon 66) was commercialized by DuPont in 1939 for fibers and in 1950 for molded plastics which led to continuing steady growth in application such as gears, bearings, canes, wire and cables, textiles with other members like Nylon 6, Nylon 612, Nylon 61, 11,12 etc. In 1954, originally ICI developed polyethylene terephthalate (PET) as fiber which was found to be moisture and crease resistant and superior to cotton. They further prepared it as biaxially oriented films, having superior mechanical, thermal, electrical, chemical and impermeable qualities as compared to cellulose. Despite its higher cost, it is suitable for photographic films, as capacitor's dielectric, taps for recording and food packaging etc. The other members of this group are polybutylene terephthalates, polyoxybenzoate and poly bisulphenol terephthalates which are growing steadily.

From the beginning of World War II, the combination of glass fabric with thermoset polyesters resulted in tremendous improvement in its rigidity, strength, toughness, creep resistance and dimensional stability-making plastics to compete and even to surpass steel for the first time. One of the interesting observations of the formation of gaseous products during the processing of some of the resins, was characterized as "unfit for commercial use" at that time, which however was found to have wide applications later under the name 'Foam'. In 1930's Dunlop and Talalay were responsible for industrialization of foam. With the development of many other synthetic elastomers during the last five decades, many flexible and semiflexible foams were produced namely polyvinyl chloride, polyolefin, polyurethane, silicones, phenolics foam, urea formaldehyde foam etc.

Another useful application of polymer is in the form of fiber. Although the history of fully synthetic fibers is of only fifty years, yet production of synthetic fibers today is in billions of kilograms per year. The fiber like Nylon 66 (invented in 1938), polyacylonitrile fibers (1950) polyethylene terephthalate (1953, as Terylene and Dacron), polypropylene (1950) and polyfluoro carbon (flame resistant fibers), polybenzimidazole, aramides (high modulus fibers and strong like graphite and ceramics) have been developed and used in textile industry.

They have smaller volume compared to cotton and have growing importance in textiles.

Polymers are also very promising for protective coatings. Dating from prehistory and Cro-Magnon man, coating process was developed slowly from artistry to technology. Due to their hardness, inertness, adhesion, thermal resistance and optical property, the synthetic (polyurethanes, epoxis, amino resins) and natural polymers are widely used as coating materials. Adhesives are the diplomats of the polymer world. Initially starch, protein glues and natural rubber were used as adhesives. They are, however, replaced by three new families of adhesives having outstanding performance. They are (i) epoxies, the iso-cynates and polyurathanes for plywood and portable-board, (ii) synthetic rubber for construction, textile bonding and pressure sensitives and (iii) polyvinyl acetate for bonding of metal etc.

1.7 RADIATION EFFECTS ON POLYMERS

Ionizing radiation is a unique and powerful means of modifying polymers, particularly since the changes occur when materials are in a solid state, as opposed to chemical or thermal reactions carried out in hot or melted polymers.

Many polymers are susceptible to degradation and cross-linking upon exposure to high-energy ionizing radiation (radiolysis) such as γ-radiation, electron beams, and X-rays. Sometimes, these effects can be used to advantage.

Interaction between high energy ions and polymer chains involves several differences with respect to other ionizing radiations because the high value of energy loss and the spatial distribution of deposited energy. These energy-rich species undergo dissociation, abstraction, and addition reactions in a sequence leading to chemical stability. The stabilization-process-which occurs during, immediately after, or even days, weeks, or months after irradiation-often results in physical and chemical cross-linking or chain-scission.

Polymer is an important group of materials which are often used in reactor and other radiation environments, it is necessary to know what changes they undergo in composition, structure, physical, mechanical and electrical properties, when subjected to nuclear radiations. These materials are distinctly different from metals or other inorganic solids as they have low melting points and decompose on heating. They are macromolecules built of simple units of covalent bonds of energy 3.5-4.0 eV and can be split by heat or high energy irradiations. These properties depend upon their chemical structure, molecular weight, crystallinity and other materials present like plasticizers, stabilizers and filters. These composites are too complicated for understanding the phenomenon of radiation damage and therefore investigations have to be made on well defined pure polymers and later can be extended to filled system.

Fortunately or unfortunately polymers are more radiation prone than any other engineering materials, even few M Rad is sufficient to cause severe modification in chemical and physical properties of high molecular weight substance, which are used on industrial scale and at an economic cost. Whether a radiation effect on polymers is beneficial or harmful depends upon its applications.

Most of the chemical changes in polymers are nearly similar to those in organic substance, both the permanent and transient type. In discussing this type of work we may distinguish between:

(a) Production of polymer by irradiation of monomer (radiation polymerization).

(b) Modification of polymer where no chain reaction is involved.

(c) Modification of polymer by a chain reaction (for low molecular weight substances).

The present study is limited with second part i.e. modification of polymers by irradiation or effect of irradiation on polymers. Although the primary chemical effect of radiation on long chain polymers are not inherently very different from those occurring in low molecular weight compounds, this subject has received a considerable amount of attention for several following reasons.

(a) Small chemical changes can produce a large physical changes readily assessable by a number of techniques developed for polymer research.

(b) The range of condition under which the material is irradiated can be varied and the effect of conditions on the radiation process thereby deduced.

(c) Many of these reactions take place in the solid state so that the effect of irradiation of organic materials, crystalline, amorphous and oriented can be determined.

(d) Long chain polymers can serve as a simple model for biological materials and indeed many of the radiation effects observed in radiobiology are closely parallel to those found in simple long chain polymers.

(e) Several of the processes involved have found large scale industrial use.

(f) Radiation sterilization of pharmaceuticals.

All the above mentioned requirements or changes occur in high polymers through two major processes- cross linking and degradation (scissioning), due to irradiation.

In the cross linking process the two neighboring chains of polymer form bonds with each other become rigid in three-dimensional network; in other process i.e. chain scissioning, chain may be cleaved into smaller molecules to produce a weaker material. Both may occur at the same time, and over a long range of absorbed dose, the more predominant reaction will control the useful properties of the structure. Cross linking occurs in the amorphous portion through a number of intermediate processes of energy exchange and free-radical formation [85].

- **Chain-scissioning**

A permanent break in a linear molecular chain can also occur as a result of the radiation interaction, resulting in a more rapid degradation of physical properties. The process, known as scission, occurs simultaneously with cross linking, and the predominance of the scission reaction is much dependent on temperature and other conditions during the irradiation [86-87]. Polymers which undergo main-chain scission as the primary radiation induced mechanisms degrade in engineering properties very rapidly in radiation exposures, are not normally recommended for service in radiation environment.

A more descriptive term for this and the associated processes in which cleavage of an inter or intra-molecular bond occurs is degradation. When the fracturing reaction takes place at random along the polymer chain the average molecular weight decreases rapidly while the total mass changes very little. The result is a very rapid decrease in hardness, increases in elongation and decrease in tensile strength. The formation of volatile by-products produces out-gassing, mass-reduction and often corrosive reactions with adjacent materials in the component. The number of scissions is proportional to dose and they occur at random. In view of these facts radiation furnishes an excellent method of providing polymer of accurately controlled weight and weight distribution, and has in fact been used for this purpose on an industrial scale.

- **Cross linking**

The basic phenomenon of radiation induced cross linking of linear polymers is a simple reaction.

Broadly speaking the main observation can be presented follows:

(a) The degree of cross linking is proportional to radiation dose.

(b) It depends little on the type of high energy radiation.

(c) It depends little on dose rate.

(d) It does not require unsaturated or other more reactive groupings.

(e) With some exceptions (aromatic group) it does not vary very greatly with chemical structure.

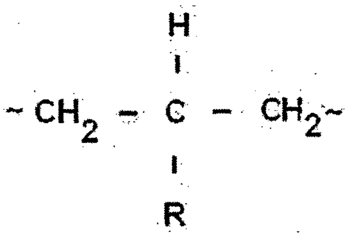
(f) The efficiency of cross linking, represented by G-value (number of cross links formed per 100 eV of energy absorbed) is little influenced by molecular weight. However the G-value changes by the presence of certain additives relatively in small concentration.

(g) It generally occurs in the amorphous portion through a number of intermediate processes of energy exchange and free radical formation.

The types of radiation and their interaction with organic materials lead to a dosimetry discussion, relative stability of polymer structure and the types of additives that contribute stabilization to the basic polymer matrix. Dosimetry is an applied and fast growing subject now a days. To approach the objectives and it is necessary to determine the degree of these influences on exact test condition, and to be familiar with the interaction of various types of radiation with molecules, the mechanisms of reactions induced by the radiation and the effects they have on the functional properties of the materials, and specially the specific properties most critical to the service application. An excellent and vast effort in this regard has been made by ASTM [88].

Tabulations of many studies of polymer materials according to chemical structure versus radiation degradation have been utilized to theories why scission predominates in some polymers and cross linking in others. Thus some of these observations have led to the following conclusions [85].

(a) Scission predominates in polymers which have the following structure



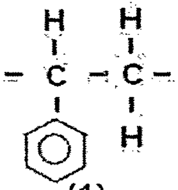
$$\sim CH_2 - \underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}} - CH_2\sim$$

(b) Polymers have low heat of polymerization. If a polymer has a tendency to form monomer, on pyrolysis it normally undergoes scission during irradiation.

(c) In branched chain hydrocarbons, scission appears to be predominant over cross-linking.

(d) In polymers having a C–O repeating group, the scission occurs very rapidly.

Polymers containing aromatic group show greater stability in general as compared to the polymers containing aliphatic groups, due to energy dissipation by resonance within the ring structure. Bopp and Sissman (1953) [89] have determined a ranking of relative stability of various polymers structure according to chemical structure from higher radiation tolerance value to radiation prone –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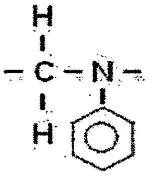
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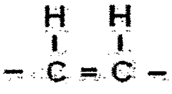
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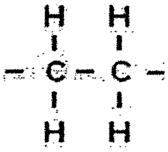
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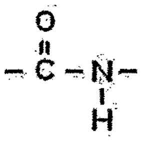
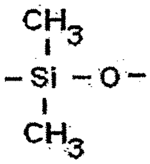
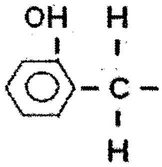
(4)


$-\overset{O}{\overset{\|}{C}}-\underset{H}{N}-$

(5)


$-\overset{CH_3}{\underset{CH_3}{Si}}-O-$

(6)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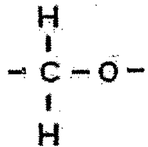
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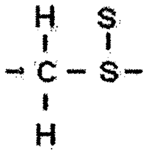
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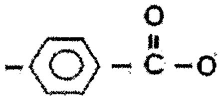
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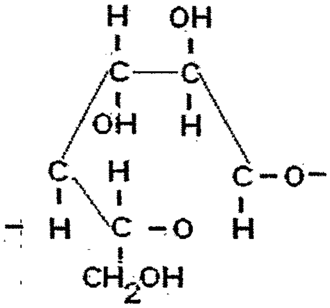
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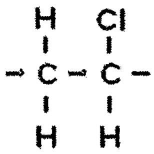
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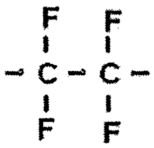
(12)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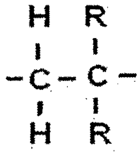
(13)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(14)

1.8 ION BEAM MODIFICATION OF POLYMERIC MATERIALS: FUNDAMENTAL PRINCIPLES.

When a charged particle passes through a medium, it sets nearly electrons in motion by its electronic field and also creates a large number of secondary electrons by knock-on collisions. The particle thus loses its energy by transferring its energy to the medium until it slows down and stops. These energy losses are collectively known as electronic stopping. The particle also loses its energy by displacing atoms in the medium by nuclear collisions. These energy loss processes are known as nuclear stopping. While most electronic energy loss stems from primary ions, most nuclear energy loss comes from recoil atoms created by primary ions. This is because several recoil atoms can be created by a primary ion with lower energies and consequently larger nuclear stopping cross-section [90].

Although recoil atoms also lose their energies by electronic processes, their contributions are small compared to those of primary ions because low energy recoil atoms have small cross-section for electronic stopping. For small atoms such as H or He, nuclear stopping is negligible because their nuclear collisional cross-sections are very small at most energies of interest. Nuclear stopping however becomes important for ion species with a larger nuclear of nucleons. The unit eV/nm/ion or simply eV/nm is used for the energy loss per unit path length or linear energy transfer. Displacement damage is usually considered to be the most important cause of material modification in solids.

1.8.1 Nuclear and Electronic Stopping

When an energetic particle penetrates into a polymer medium, it loses energy by two main processes, namely, by interacting with target nuclei and by interacting with target electrons. The former process is called nuclear stopping and the latter electronic stopping.

Nuclear energy loss arises from collisions between the energetic particle and target nuclei, which cause atomic displacements and phonons. Nuclear energy loss by inelastic collision (nuclear reactions) is not considered here. Displacement occurs when the colliding particle imparts an energy greater than a certain displacement threshold energy E_d, to a target atom. Otherwise, knock-on atoms can not escape their sites and their energy dissipates as atomic vibrations (i.e. phonons). E_b is the energy that a recoil requires to over come the binding forces and to move more than one atomic spacing away from its original site. Since the nuclear collision occurs between two atoms with electrons around protons and neutrons, the interaction of an ion with a target nucleus is treated as the scattering of two screened particles. Nuclear stopping is derived with consideration of the momentum transfer from ion to target atom and the interatomic potential between two atoms. Thus nuclear stopping varies with ion velocity as well as the charges of two colliding atoms. Nuclear stopping becomes important when an ion slows down to approximately the Bohr velocity (orbital electron velocity). For this reason, the maximum nuclear energy loss near the end of the ion track, for high energy ions. The Bohr velocity can be derived from the uncertainty principle as $V_B \approx (1/4\pi\varepsilon_0)(e^2/\hbar) \approx 2.2\times10^6 m/s$, where $1/4\pi\varepsilon_0$ = 9.0 X 10^9 Nm^2/C^2, e_0 is the permittivity constant, e is a unit charge and

? is Planck's constant divided by 2π. The velocity of a 1 MeV He ion is about 6.9 X 10^6 m/s.

Electronic stopping is determined mainly by the charge state of the ions and its velocity. When an ion passes through a medium, its orbital electrons are stripped off in varying degree developing upon the ion velocity (v_{ion}). The effective charge on a positive ion is given, in terms of ion velocity (v_{ion}) and Bohr (orbital electron) velocity (v_B) by Northcliffe [87] as

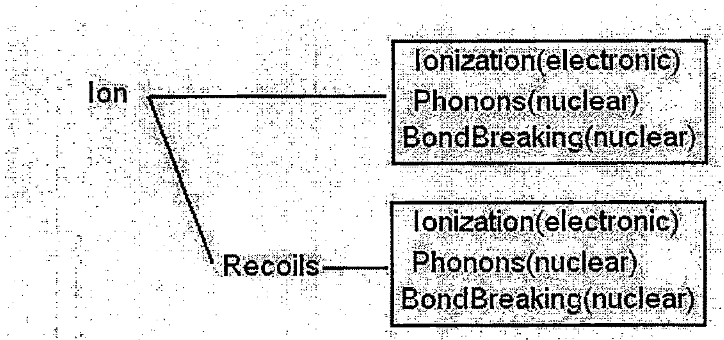
$$Z^*_{eff} = Z\left[1 - a\exp\left(-b\frac{V_{ion}}{V_B}Z^{-2/3}\right)\right] \qquad (1.1)$$

Where Z is the atomic number and a and b are fitting constants. There have been scores of proposed empirical formulae such as; $Z^*_{eff} = Z \times \left[1 - \exp\left(-\kappa\beta / Z^{2/3}\right)\right]$; where $\beta = V_{ion}/c$ and c is the speed of light. Somewhat different values have been assigned for coefficient "k" by various authors; 25 by Pierce and Blann [92] and 130 by Barkas [93], for example. All expressions give a similar trend. He-ions are almost completely stripped to an average charge of +2 at around 1 MeV or ≥ 0.3 MeV per amu. The higher the Z, the higher the energy required to fully strip an atom.

Electronic energy loss arises from electromagnetic interaction between the positively charged ion and the target electrons. One mechanism is called glancing collision (inelastic scattering, distant resonant collisions with small momentum transfer) and the other is called knock-on collision (elastic scattering close collisions with large momentum transfer). Both glancing and knock-on collision transfer energy in two ways: electronic excitation and ionization. All excited electrons (plasmons) eventually lose energy as they thermalize. Electronic excitation is the process in which an orbital electron is raised to higher energy levels, whereas, in ionization, an orbital electron is ejected from the atom. Glancing collisions are quite frequent but each collision involves a small energy loss (<100 eV). On the other hand, knock-on collisions are very infrequent but each collision imparts a large energy to a target electron (>100 eV). These knock-on electrons are often called d-rays or secondary electrons. Theoretical and experimental evidence suggested that approximately one half of the knock-on collisions [94,95]. This phenomena is often referred to as the equipartition principle and has been confirmed by experiment [96], where two well defined peaks at low and high energy were observed for protons channeled through mono-crystalline copper. The energy loss ratio for channeled and unchanneled protons was approximately 0.5. The "best-channeled" particles had a stopping power of the order of one half the stopping powers in the corresponding solid. The half of the energy loss in the channeled direction was attributed to glancing collisions.

Nuclear collisions create recoil atoms and these recoil atoms also lose their energy through nuclear and electronic processes until all excited electrons and atoms are thermalized by dissipating energy through phonons and plasmons. For most ion energy range of interest, nuclear stopping by small atoms such as H or He is negligible because the Rutherford cross-section and momentum transfer by the low mass atoms is small. Nuclear stopping, however, becomes important for ion species with a large number of nucleons.

Figure 1.10 summarizes the energy partitioning in the Monte Carlo Simulation Programme Stopping and Range of Ions in Matter (SRIM) [97]. The electronic energy loss constitutes the ionization and excitation energy loss by the primary ion as well as by recoil atoms. Every recoiling target atom loses E_b (binding energy) when it leaves its site. E_b is the difference in energy for the atom in its site and removed to an infinite distance. Binding energy for most organic polymers is not known well. Typical lattice binding energies, E_b, of 1-3 eV, are suggested for organic compounds in the SRIM instruction manual. Nevertheless, actual binding energies could be higher considering strong covalent bonds in organic polymers. A usage of a different value of E_b affects the energy partition between bond breaking energy and phonon energy, but the total nuclear LET remains the same in SRIM calculation. The bond breaking energy E_b, (called the vacancy LET, because the number of vacancies which are produced by bond breaking are counted) is treated separately and is derived by multiplying the number of displacements (vacancies plus replacements) by E_b. In the Kinchin-Pease approximation described below, replacements are not calculated and so the displacement number is equal to vacancy number. The minimum or thresold energy required to break the bonds and displace the atom over a lattice potential is called the displacements energy (E_d). Although the values of E_d are not well known for polymers, they are believed to be in the range of 10-30 eV, considering the energy required in breaking strong covalent bonds and placing the released atom over a certain distance. Note that at least two bonds should be broken to release a carbon atom. When a recoil atom does not have sufficient energy to displace another atom, the remaining energy is dissipated in lattice vibration (phonons). The nuclear energy loss is equal to the sum of the phonon LET and vacancy LET (number of vacancies times E_b). The integral area under the six curves sums to 100 keV, the energy received by the system. The phonon contribution from the ions is small compared with that of the recoils because one ion produces many recoils.



$$\text{Electronic LET} = (\text{LET})^{\text{ionization}}_{\text{by ion}} + (\text{LET})^{\text{ionization}}_{\text{by recoils}}$$

$$\text{Nuclear LET} = (\text{LET})^{\text{bonds}}_{\text{by ion}} + (\text{LET})^{\text{bonds}}_{\text{by recoil}} + (\text{LET})^{\text{phonons}}_{\text{by ion}} + (\text{LET})^{\text{phonons}}_{\text{by recoil}}$$

Figure 1.10: Energy partitioning in SRIM.

In the Kinchin-Pease approximation, the recoils are not individually followed in the Monte-Carlo calculation. However the flight paths of the primary ions are tracked and the energy losses are calculated using ZBL stopping powers [97]. S_n and S_e formulas given below. The defect producing energy or damage energy (E_v) is obtained from the energy transferred (T) from the primary ion to a target atom by taking into consideration electronic losses which arises due to the interaction between overlapping electron shells during nuclear collisions. The electronic losses of the recoils are calculated using an approximation to the LSS theory developed by Norgett et al [98]. The transferred energy and the damage energy are given below. The electronic energy loss (ionization and excitation) energy loss by recoils (E_r) is obtained by subtracting E_v from T,

$$T = \frac{4M_1M_2}{(M_1 - M_2)^2} E \sin^2\left(\frac{\theta}{2}\right) \tag{1.2}$$

$$E_v = \frac{T}{1 - \kappa_d g(\varepsilon_d)} \tag{1.3}$$

$$E_r^1 = T - E_v \tag{1.4}$$

Where E is the kinetic energy of the incident atom, θ is the scattering angle in the center of mass system, M_1 and M_2 are the mass numbers of the colliding and target atom, respectively. The latter three parameter which account for the electronic loss, are given by

$$\kappa_d = 0.1337 Z_2^{2/3} M_2^{-1/2} \tag{1.5}$$

$$g(\varepsilon_d) = \varepsilon_d + 0.40244\varepsilon_d^{3/4} + 3.4008\varepsilon_d^{1/6} \tag{1.6}$$

$$\varepsilon_d = 0.01014 Z_2^{-7/3} T \tag{1.7}$$

Where Z_2 is the atomic number of the target atom. From the energy E_v, the number of displacements is calculated by employing a modified Kinchin-Pease model (NRT model [98]).

$$V_{NRT} = 0 \qquad \text{if } E_v < E_d \tag{1.8}$$

$$V_{NRT} = 1 \qquad \text{if } E_d < E_v < 2.5\,E_d \tag{1.9}$$

$$V_{NRT} = \frac{0.8E_v}{2E_d} \qquad \text{if } E_v > 2.5\,E_d \tag{1.10}$$

In the NRT model, the displacement efficiency factor 0.8 is introduced to account for realistic atomic scattering instead of the hard core approximation where efficiency factor is unity (billiard ball type collision), and the number 2 in the denominator is included on the grounds that an atom must have a kinetic energy at least twice the displacement thresold energy in order to cause a net additional displacements which includes vacancies and replacement collisions.

As described already, both nuclear and electronic stopping depend upon the kinetic energy or velocity of the colliding atom because the velocity determines the interaction time. In the SRIM full cascade calculation, the ZBL stopping powers are used for both the primary ion and recoils. A mathematical expression for the nuclear stopping cross-section is given by

$$S_n = \int_0^x \mathrm{T}(\mathrm{E}_0, p) 2\pi p dp \qquad (1.11)$$

Where E_o is the initial kinetic energy of the atom, T the transferred energy defined above, and P is an impact parameter, P is the distance by which the collision misses being head-on, and is a measure of the directness of the collision or straightness of the flight path, which is determined by particle velocity and the interatomic potential between the two colliding particles.

A mathematical expression for the electronic stopping cross-section is given by

$$S_e = \int \mathrm{I}(v, \rho)(\mathrm{Z}_1^* v)^2 \rho dV \qquad (1.12)$$

Where I (v, p) is the stopping interaction function, v is the ion velocity, ρ is the target electron density, Z_1^* is the effective particle charge and dV is a volume element. I (v, p) varies with the particle velocity and plasma oscillation frequencies of the electrons in the stopping medium. Fast particles (v > > Bohr velocity) have little interaction time and so electronic stopping decreases with increasing velocity beyond this velocity. Slow particles (v < Bohr velocity) pick up electrons, so have a lower effective charge. Therefore, a maximum in the electronic stopping occurs near the Bohr velocity. LET is simply given by

$$\frac{dE}{dx} = NS(E) \tag{1.13}$$

Where N is the atomic density of target. In evaluating the damage produced by irradiation, the unit of displacements per atom (dpa) is often used. The expression of displacement dose in dpa is given by

$$dpa = \frac{0.8}{2E_d}\left(\frac{dE}{dx}\right)_{nuclear} \times \frac{ionfluence}{target \quad atomic \quad density} \tag{1.14}$$

One dpa is the dose at which, on average, each atom has been, displaced from its lattice position once. The term “dose” is expressed often in terms of the energy deposited per unit mass of material, generally in units of eV/kg or Gy (=100 Rad) whereas the “fluence” indicates the number of ions injected per unit area of target material (ions/m^2). In the conversion from fluence to dose, the SI unit of Gray(Gy) is obtained by multiplying the fluence (ions/m^2) by the LET (eV/nm) and dividing by the specific gravity of the target material (kg/m^3) and finally using a conversion factor of 1 Gy = 6.24 X 10^{18} eV/kg.

1.8.2 Electronic vs Nuclear LET

An important question is what controls the magnitude of cross-linking and scission. During irradiation, various physical and chemical processes take place in the polymer. Nuclear collisions cause atomic displacements, which can then lead to chain scission or release of pendant atoms. Superposition of phonon waves can also lead to bond breakage, but the probability of such events is small because phonons have insufficient energy density to start with. Polymers have a fairly large free volume, often larger than 20% and atomic density in such a loose system is relatively small compared to that in a medium with a compact lattice structure, such as a metal. Therefore, in polymers, most nuclear displacements occur fairly independently. The probability to cause simultaneous displacement of two atoms from neighboring chains and create two radical pairs for cross-linking is small in nuclear processes. Heavy and low energy ions with less than a few keV have large nuclear LET and are thus generally not desirable for cross-linking. An excellent example for the nuclear displacement damage effect was demonstrated by Hunn and Christensen [99]. They were able to lift free-standing, single crystal diamond layers by causing a maximum damage ~2 μm depth below the crystalline diamond surface with 4-5 MeV C-ions and selectively oxidizing the damaged layer. An amorphized layer underlying a crystalline diamond surface was also confirmed by Rutherford backscattering spectroscopy in a channeled geometry for 1 MeV Ar irradiated diamond, in that disordering was the least near the surface where the electronic LET was the highest [100]. An important implication of these results is that the displacement damage followed the nuclear LET profile and that the least damage was observed at the surface where the electronic LET was maximum.

On the other hand, when the electronic LET is high, a considerable volume around the ion projectile is influenced because of the Coulombic field produced by glancing collisions and ionization (δ-rays) by knock-on collisions. This results in production of active chemical species, cations, anions, radicals and electrons along the polymer chains. Coulombic attraction and repulsion among these active species cause violent bond stretching and segmental motion in the polymer chains, which can then lead to cross-linking as well as bond breakage. Thus, both electronic and nuclear energy transfer can induce cross-linking as well as chain scission. However, as pointed out above, nuclear stopping causes more scission due to the nature of independent displacement damage and the simultaneous production of two radicals in neighboring chains is low. On the other hand, electronic stopping cause more cross-linking due to collective excitation (plasmons), which produce a large excited volume thereby resulting in coercive interaction among the ions and radical pairs produced within the volume. These trends have been confirmed by G-value and hardness measurements as well as other experiments [101,102]. With increasing ion energy, electronic LET increases and nuclear LET decreases. **Figure 1.11**, electronic LET becomes an even more important factor for ions of 1 MeV compared to 100 keV.

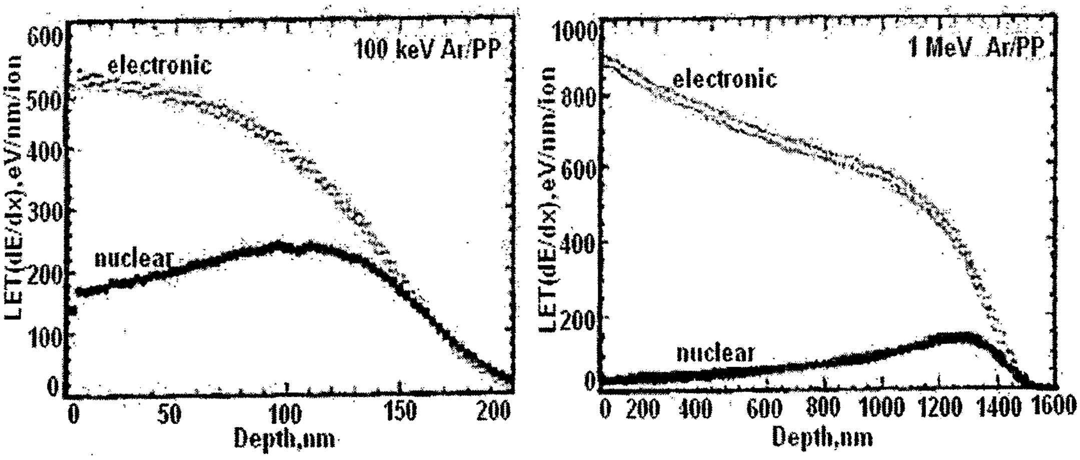


Figure 1.11: SRIM calculated electronic (ionization) and nuclear (Phonons+vacancies) LET for 100 keV and 1MeV Ar ion irradiation of polypropylene.

The magnitude of ionization varies with ion velocity and charge state. Thus it is desirable to use atomic species with large atomic number and employ high energy ions, so long as the velocity of the ion is not too high and so the energy density (LET) does not become too small due to small stopping power and large r_c and r_p. Note that too fast ion has a short interaction time and yields large r_c and r_p.

1.8.3 High vs Low LET

As discussed already, the magnitude of ionization depends upon the deposited energy along the ion track or LET. The electronic LET for 1 MeV Ar is about 960 eV/nm for polystyrene, whereas those e-bema and γ-rays are in the range of 0.2-0.36 eV/nm. Increasing the energy of e-beam or γ-rays does not increase the LET due to the limited effective charge or ionizing capacity, only the depth of penetration increases with increasing energy beyond certain energy. For 1 MeV Ar ions, about 24 (960/40) ion pairs or spurs are created per nm, whereas, for e-beam or γ-rays, only 0.009 (0.36/40) spurs are created per nm. In other words, the average distance between the spurs is 0.042 nm (40 eV/960 eV/nm) for 1 MeV Ar and 111nm (40ev/0.36 eV/nm) for e-beam or γ-rays. In the case of high LET, spurs overlap, the probability for two radical pairs to be in neighboring chains is increased, and cross-linking is facilitated. For low LET, spurs develop far apart and independently, the deposited energy tends to be confined in one chain (not in the neighboring chain) leading to scission. For this reason, low LET e-beams are used in photolithography to make PMMA soluble. However, it should be pointed out that cross-linking is also polymer structure dependent, and even low LET ionizing radiation sources such as e-beam and UV can cause a limited degree of cross-linking for certain polymers.

1.9 PRESENT WORK

In the present work, we have studied the effects of 3 MeV proton in few polymers like polypropylene, polyimide, polyethylene terephthalate, polyether sulfone, polycarbonate, blend polymer (polyvinylchloride + polyethylene terephthalate).

- **Literature survey**

There have been only few reports on radiation induced modification in polypropylene (PP). Wang et al [103] studied the effects of 100keV proton irradiation on polypropylene, which leads to cross-linking between the macromolecules of the polymer and enhancing its mechanical properties. Mishra et al [104] studied the optical and electrical properties of 2 MeV electron and 62 MeV proton irradiated PP. Mishra et al [105] also studied the effect of 2 MeV electron irradiation on PP and observed decrease in optical band gap which leads to increase in the conductivity.

Several investigations have been made on radiation induced modification in polyimide (PI)/Kapton. Shrinkage effects of polyimide films under ion beam irradiation have been reported by Xu et al [106]. Terai and Kobayashi [107] studied the changes of composition and structure of PI due to 4 MeV Ni^{3+} ions induced carbonization by surface characterization techniques and electric resistance measurement. Garg and Quamara [108] investigated the effects of 100 MeV Si^{+} beam on conduction behaviour of PI. Virk et al [109] studied the physical and chemical response of 70 MeV carbon ion irradiation on PI by using UV-visible, FTIR and XRD technique. Mishra et al [104] studied the optical and electrical properties of 62 MeV proton irradiated PI film. Spectroscopic and thermal behaviours of PI induced by 2 MeV electrons were also studied by Mishra et al [110].

Extensive work has been reported on radiation induced modification in polyethylene terephthalate (PET) from past few decade. The IR transmission spectra have been measured for keV to MeV light and heavy ion irradiated PET foils by Fink et al [111]. Ciesla and Starosta [112] reported the DSC, FTIR and XRD studies on PET film irradiated with high energy heavy ions at high fluences. Steckenreiter et al [113], Biswas et al [114], Mishra et al [104] also studied optical and electrical properties of PET after 2 MeV electron and 62 MeV proton irradiation. Tripathy et al [115] studied the effects of irradiation by various energetic ions on the physical properties of PET.

Only a few reports have been mentioned the effects of low and high energy ions on polyether sulfone (PES). Wang et al [116] studied the dose rate effects on the electrical properties of PES implanted by 50 keV atomic and molecular nitrogen ions. Bridwell et al [117] reported a more comprehensive study of ion implanted PES in an attempt to relate electrical conductivity to specific radiation damage mechanisms using He, B, C, N, Ar and As ions. Evelyn et al [118] studied the chemical structure of PES by 5 MeV α-irradiation.

Radiation induced modification in polycarbonate (PC) have been studied earlier by various researcher. The chemical modifications induced by SHI on a model compound of PC reported by Ferain and Legras [119]. Fink et al [111] studied the IR transmission of keV to MeV light and heavy ion irradiated PC. The degradation process in PC was studied by SHI irradiation by Steckenreiter et al [120]. Chemical changes in PC induced by very high energetic ions (>GeV) were studied using ex-situ FTIR spectroscopy by Wang et al [121] and Zhu et al [122].

Chipara and Reyes-Romero [123] studied the nature of free radicals and exchange interaction among them on the basis of track structure of SHI irradiated PC, by electron spin resonance (ESR). Dehaye et al [124] studied the chemical modifications in bisphenol A polycarbonate induced by swift heavy ion irradiation and analysed in situ by means of FTIR spectroscopy. Studies of thermal and structural properties of 62 MeV proton irradiated PC were carried out at different doses by Mishra et al [110].

No work has been reported on radiation induced modification on blended polymer (PVC+PET).

However the effect of MeV ion beam irradiation on microhardness has not been reported so far. We have made a systematic study of AC electrical frequency response along with the thermal stability and types of thermal reactions on application of heat to the polymer. The structural changes as well as the surface morphology were studied by using FTIR spectroscopy and optical microscope.

Following properties have been studied for the pristine and irradiated polymers.

- **Structural property**

The simplest application of IR spectroscopy is for polymer identification. Comparison of the positions of absorptions in the IR spectrum of a polymer sample with a characteristic absorption region, leads to identification of the bonds and functional groups present in the polymer. The spectra of irradiated and pristine polymer samples were recorded in the transmission mode using Bomem spectrometer. The absorbance spectra were recorded as a function of wave number. The absorbance before and after irradiation has been compared and peak analysis has been used to interpret the chemical structural changes. The most common absorptions occur in the wave number range 4000-500 cm^{-1} and for this reason IR spectra are usually recorded over this range.

- **Surface morphology**

Microscopy is used to visualize morphology of polymers and/or polymer systems including polymer blends, composites and systems with inorganic fillers and/or reinforcing components. Preparation procedures are adjusted to any kinds of heterogeneities (e.g. crystalline/amorphous, differing mechanical properties of the constituents), and preparation techniques specific of the individual kinds of microscopy are used to obtain specimens.

Studies on ion beam effects on polymers have gained significance in recent years, in view of the potential applications such as in surface science. The chemical constitutions, stereo regularity, configuration and conformational aspects of polymers govern the specific surface features, while the external condition such as temperature, pressure or ion implantation influence the physical states and different physical properties [125,126].

Surface morphology of all pristine and irradiated polymers samples were studied by using Carl-Zeiss Microscope (Axiotech-CCD).

- **Mechanical property (microhardness)**

The mechanical properties of a polymer are the facets of behavior that are evident when the polymer is subject in some form to a mechanical stress. One of the most important mechanical characterizations of a polymer is its tensile stress-strain properties. An underlying molecular conception of the principles of mechanical behavior is fairly well in hand for amorphous polymers; the theories encounter considerably more difficulty in developing a coherent picture for partially crystalline materials. Nevertheless, certain generalizations can be made on mechanical properties as a function of the crystalline-amorphous character. Hardness is another important solid state property to characterize a material. Hardness of a solid may be broadly defined as its ability to resist penetration by another harder solid. The ability of a material to resist permanent deformation is usually considered as an interpretation of hardness [127].

Microhardness of pristine and irradiated polymers were studied using Vickers' Microhardness indentations at different loads in the range of 100-1000mN at room temperature.

- **Electrical properties**

Many polymeric materials have been very successful in electrical applications because of one or more outstanding properties, such as dielectric constant, arc resistance and loss factor etc. Crystallinity can affect the dielectric constant, however, through the difference in density between crystalline and amorphous regions. Electrical properties are influenced more by dipole asymmetry than by the presence of polar groups as such. When the dipoles are able to respond readily to change in the electric field (low frequency or high temperature) the dielectric constant is high. At high and low frequencies, the dipoles can either respond completely or not at all to the change in field, and the loss factor, the product of dielectric constant and power factor, is low. The power factor is the sine of the angle of phase difference due to the delay in movement of the dipole with the change in field [128].

In the present work, the AC electrical properties, viz., conductivity, dielectric constant and dielectric loss were studied as a function of frequency ranging from 0.1-1MHz at room temperature for pristine and irradiated samples.

- **Thermal properties**

Thermal methods of analysis of polymers are important in that these techniques can provide information about the thermal stability of polymers, their lifetimes or self-life under particular conditions, phases and phase changes occurring in polymers and information on the effect of incorporating additives in polymers. The use of the thermal analysis curve to study both physical and chemical change occurring in the sample on heating. The "interpretation" of a thermal analysis curve therefore consisting in relating the features of the property-temperature curve (peaks, discontinuities, changes, of slop, etc.) to possible thermal events in the sample, i.e. chemical reactions or physical transition resulting from the change in the sample temperature [129].

Thermal properties; Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) were studied using SIEKO thermal analysis (TGA-220) and SIEKO calorimeter (DSC-220).

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