Chapter 1

Introduction

Abstract

This chapter deals with the general introduction, importance of radiation in the field of material science, polymers and polymer metal composites, their impact on present day technologies. A brief description about heavy ion and important fundamental process involved in ion beam interaction with polymer are discussed in order to understand the basic physical and chemical processes induced by energetic heavy ion beam. This chapter also deals with the mechanism of polarization in dielectrics and motivation for the present work.

1.0 Introduction

In the development of mankind polymers have played a very important role. They are widely used in science and technology particularly in space and nuclear technologies, in addition to various applications in day to day life , infact anything from clothing the naked to powering a space vehicle to even replacing a human organ. This explains why this age is called as the "polymer" age. The extensive utilization of polymeric materials and the rapid development of polymer science have created an increased interest in various problems of physics of polymers.

Ion bombardment may modify 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 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 electron 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 anneal 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.

1.1 Importance of Radiation in the Field of Material Science

Ion beam techniques, today, have made deep inroads into many branches of the materials science, and have been unequivocally proved to be indispensable either because of their unchallenged power in some respects or because of the unique superiority over the other contemporary techniques in use. The vast range of the present applications of the ion beams extends from the surface cleaning, etching and thinning, thin film preparation and ion-pumping to the modification of numerous physical and chemical properties of solids like semiconduction, superconduction, optical friction, wear, oxidation, corrosion and catalysis etc. Further as analysis techniques, ion beams are used to identify and locate impurities and to determine materials composition utilizing one or many effects caused by the target stimulation; these include backscattering, channeling, nuclear reaction products, X-rays, sputtering and optical photons. Moreover, the advent of more recent applications in nuclear energy related research fields like simulation of radiation damage in materials of use in fission and fusion reactors by neutral beam injection have given remarkable boost to the activities in ion beam production, handling and interaction with materials

Hence, the field of ion- material interaction is still evolving very rapidly and it is extremely difficult even to enlist all possible disciplines. Academic aspect of this field is also as exciting as its applied front In fact, the study of slowing down of ions in matter and the development of high resolution semiconductor particle detectors like silicon surface barrier, lithium drifted germanium, have made possible the understanding of nuclear physics to a level where it is today. The molecular ion beams have also been made used to study the structures of molecular ion projectiles.

Interaction of ion beams with insulating target is quite different from those of observed in conductors. In general it gives destruction of the surface by stress, deformation, fracture electrical break-down and blistering etc [1]. The chemical changes arise due to ion beam hitting in insulator in general and polymer in particular, are important parameters during their study.

Many fields such as microelectronics, biology and medicine, surface and membrane technology, magneto-optics and low temperature physics require a high degree of geometric control on a microscopic scale. Ion irradiation offers a possibility to modify the properties of the materials in a controlled way on microscopic scale. Ionizing radiations have definite range of penetration; a high local confinement of deposited energy can be generated conveniently in large quantity. The created damage zones can be stored indefinitely in many insulators and can be used to initiate a phase transformation process that modifies the material along the latent track. One ion suffices to induce-physically and chemically a submicroscopic change in the target material and there by can render it susceptible to the development process [2].

A lot of work in the field of ion beam irradiation has been carried out to investigate the interaction of charged particles with matter [3]. The application of ion beams now a days range from the use of low energy ions in the filed of surface technology to the application of relativistic heavy ion in radiation therapy [4].

1.2 Polymers and Polymer Metal Composites

A polymer is a substance composed of molecules which consist out of a long sequence of one or more species of atoms or groups of atoms linked to each other by primary, usually covalent bonds. Polymers that consist of one type of monomers are called homopolymers. If a polymer is derived from more than one monomer, it is called a copolymer. The covalent bonds involved are characterized by high binding energies (146 to 628 kJ/mole), short bond lengths (0.11 to 0.16 nm), and relatively constant angles between successive bonds [5].

In general, polymer chains are very flexible, and therefore are coiled up with some free volume in between. The simplest chains are of linear skeletal structure which may be presented by a chain with two ends. Branched polymers have side chains, or branches, of significant length which are bonded to the main chain at branch points (junctions), and are characterized in terms of the number and size of the branches. Network polymers have three dimensional structures in which each chain is connected to all others by a sequence of junction points and other chains. Such polymers are said to be cross-linked.

Polymers are usually classified into three groups: thermoplastics, elastomers and thermosets. Thermoplastics are linear or weakly branched polymers with negligible entanglement. They can be crystalline or amorphous. Those which crystallize do not form perfect crystalline materials but instead are semi-crystalline with both amorphous and crystalline regions. The crystalline phases of such polymers are characterized by their melting temperature (T_m). Many thermoplastics are completely amorphous polymers which exist as glassy solids. These polymers are characterized by their glass transition temperature (T_g), the temperature at which they transform from glassy state (hard) to the rubbery state (soft).

Elastomers are cross-linked rubbery polymers that can be stretched easily to high extensions and which rapidly recover their original dimensions when the applied stress is released. Thermosets are rigid network polymers in which chain motion is greatly restricted by a high degree of cross-linking.

Over the last decades, polymers have been used successfully in many industrial applications, including adhesion, packaging, thin films, biomaterials, and coatings. Polymers have excellent bulk physical and chemical properties, are inexpensive and easy to process. Due to their low cost, easy processibility, low weight, high corrosion resistance, high electric resistance, durability, etc polymers are fast replacing metals and alloys in many applications and are extensively used now days in the field of industries, science and technologies, particularly in space and nuclear technology [6].

Polymer composites filled with metal are of interest for many fields of engineering. This interest arises from the fact that the electrical characteristics of such composites are close to the properties of metals where as the mechanical properties and processing methods are typical for plastics [7, 8]. Polymers and metals come into contact in many areas of modern technology. Automobiles are increasing assembled using adhesives rather welds [9], metals catalysts are embedded in polymer electrolytes for fuel cells [10] and prosthetic device frequently feature acrylic bone cement in contact with metallic implant materials. Polymers are also used as substrates in the deposition of metallization lines for integrated circuit.

The application of ionizing radiations in polymeric materials and metal polymer composites has grown due to the fact that the physical and chemical properties of the polymers can be modified by ion beams in a controlled way [11, 12]. Interest has also evolved in the peculiar nature of the ion-polymer interaction, and it is also important to understand effect of ion beam on a more fundamental level how the polymers interact with metal fillers. Thus the field of polymers and polymer composites modification by ion beam, and its characterization has become a very challenging field owing to its vast technological applications.

1.3 Heavy Ions

Atom consists of nuclei and electrons. If some of the negatively charged electrons orbiting the tiny positively charged nucleus are removed from the atom, an ion is left. If heavy atoms undergo this process, they are called heavy ions. In the last two decades heavy ions have emerged as a major tool in atomic and nuclear physics. Light and heavy atoms ionized to a high degree resemble those found in hot stars. Hence, the actual situation in stars could be simulated and clarified through laboratory experiments on earth. The information about the nuclear structure can be obtained by the production of deformed heavy system by ions of different energies. Various areas of research in nuclear physics are fusion reactions, high spin states, dissipative collisions, deep inelastic collisions and exotic nuclei etc. In addition the relativistic heavy ion collisions provide the challenging and wide-open frontier of modern nuclear science. The discovery of new elements and the search for super heavy elements is another field where heavy ion research is aimed at. The development of the techniques for accelerating particles led to the construction of new accelerators, and modification in the existing linear accelerators, cyclotrons, phasotrons and synchrophasotrons with a view to accelerate ions of heavy atoms to energies ranging from a few MeV to several GeV per nucleon.

1.4 Effect of Ion Irradiation on Polymers/ Polymer Composites

The irradiation of energetic ions affects the physico-chemical properties of polymers and polymer composite materials. The primary phenomena associated with the interaction of radiation with the polymers are chain scission, chain aggregation, molecular emission and formation of double bonds [13-16]. Various gaseous species are released during irradiation. The most prominent emission is of hydrogen, followed by less abundant heavier molecular species which are scission products from the pendant side groups and chain-end segments. Cross-linking occurs when two free dangling ions or radicals pairs on neighbouring chains unite. Double and triple bonds are formed when two neighbouring radicals in the same chain unite. Cross-linking enhances the modulus and hardness of the polymer. In partially crystalline polymers, it imparts a non-melting behaviour and above the crystalline melting point the cross-linked polymer exhibits rubber elasticity. Radiation degradation is random chain scission process, which reduces the molecular weight of the polymer, thus, plasticising the material. All these effects depend on the composition, density, molecular weight of the polymer, temperature and time of irradiation, mass, energy, charge and fluence of the ion beam.

The modifications of polymer properties under ionizing radiation is a subject of widespread importance due to the increasing use of polymers in hard radiation environments encountered in nuclear power plants, space-crafts, sterilization irradiators, high energy particle accelerators, etc. The role of the molecular structure of polymers exposed to radiation has been recognized since the early development of radiation chemistry in the 50s allowing the establishment of rough guides to predict the evolution of polymer properties. Some polymers, in particular, undergo mainly chain scissions, whereas others are cross-linked under irradiation. However this classification no longer applies under real conditions due to the high sensitivity of polymers to their environment, in particular in the presence of oxygen. For this reason, the role of oxygen in aging studies is crucial for materials exposed to low dose rates for long periods, as it is the case in nuclear power plants or for the storage of nuclear wastes. Finally, the formulation of commercially available polymers induces another level of complexity. The introduction of various kinds of additives (anti-oxidants, plasticizers, organic of inorganic fillers, processing agents, etc.) is performed to adjust polymer properties for specific applications. In particular elastomers often include a large fraction of fillers, such as carbon or silica particles, which contribute to the final material properties. The knowledge of the filler influence under irradiation remains however limited. We will see the large effects induced by organometallics fillers in PMMA and PVC polymers.

Recently, there has been growing interest in the swift heavy ion (SHI) irradiation of the polymeric material. The modification of polymers using ion beam bombardment is now a well established area of material science research. In the early years, ion beam modification was brought about by using low energy ionizing beams comprising mainly of fast electrons, low energy ions, gamma-rays, etc. The availability of heavy ion accelerators has brought new impetus to the field of ion beam modification. As a result of the large energy deposited in the material of interest by the incoming swift heavy ion beam, dramatic modifications in material properties have been observed [17-21].

1.5 Swift Heavy Ion Interaction with Polymeric Materials: Fundamental Principles and Applications

The study of the effects induced by energetic heavy ions on polymers has attracted growing attention [22-32] in recent years, both for the fundamental interest in non conventional ion beam effects mainly to understand the radiolysis and polymerization mechanisms (with respect to the conventional photon, electron or neutron effects) and for potential technological applications. Swift heavy ions (SHI) provide a unique way of material modification, which other wise is not possible by conventional radiations. The reason is very high value of the electron stopping power of the ions $(dE/dX)_e$ or Se, which induces an unusual high density of electron-hole pairs close to the ion path. As to the technological applications, physical and chemical changes induced by SHI irradiation may lead to large modifications in the macroscopic properties of the polymer.

The modification induced by the high-energy heavy ions in polymeric materials may be understood only if the particularities of the energy transfer from the ion to the target are considered. When an energetic particle passes through a polymeric material, it losses its energy mainly through four processes

1) Electronic stopping "Se" (inelastic collisions with target atomic electrons resulting in excitation and ionization)

2) Nuclear stopping "Sn" (elastic collision with screened target nuclei, resulting in displacement of the target atoms)

3) Phonon decay and

4) Plasmon decay.

Among the four processes, the first two produce most significant effect in changing the materials properties and the latter two consist mainly of thermal energy losses by atoms and electrons as their energy decay through thermal vibrations and it is assumed that they do not have any significant impact on material properties. The energy loss by phonons is mostly from recoil atoms and thus its magnitude of loss increases with increasing ion mass because larger ions produce more recoil atoms. Energy losses by plasmons are essentially negligible.

In the case of SHI the first process of energy loss i. e. electronic excitation and ionization as a result of inelastic collision with target electrons, predominates over the other energy loss processes. The electronic processes involve the ejection of electrons and the formation of excited states. The primary products produced during the process are electrons, ions, atoms in excited states, free radicals, and molecules. The energy of an excited molecule may be distributed among its neighbors as phonons or excitons, or it may cause a chemical bond to break, when the excited energy localizes in a particular chemical bond. Thus polymers can break down even by pure ionizing radiation sources such as UV or γ-rays, as in the degradation of polymers in a natural environment.

However, such radiolysis scission frequently causes the loss of side groups, such as hydrogen. This reaction produces unsaturated bonds (-C=C- and -C≡C-) in the polymeric chain, or cross-linking when the cleavage of the C-H bonds occur on adjacent molecules. The chains can be cross-linked by double bonds also. The important term Linear Energy Transfer (LET), which is generally used to describe the energy deposition per unite path length by one ion (eV/nm/ion), is essentially electronic LET, in case of SHI induced modifications.

Here we describe the fundamental process involved with energy transfer in polymers by energetic ion beams, distinguished the effects induced by heavy ion beams from other source of irradiation, specially the contributions of electronic and nuclear stopping on material modifications, the mechanisms involved in cross-linking and scission processes, besides the ion track formation mechanism and applications of track membranes.

1.5.1 Energy Loss Mechanism

The fast ions are continually decelerated during passage through matter. During this process, they transfer considerable amount of energy to the electron and nuclei of the material along their path in a very short period of time. This high local energy density leads to the irreversible chemical and structural changes. The incident energetic ion, depending upon the energy, interacts with the target through two main processes: (i) interaction with target nuclei called nuclear stopping and (ii) interaction with target electrons called electronic stopping. In the low energy regime, the nuclear energy loss arises from collisions between the energetic particle and target nuclei which cause atomic displacements and phonons. Displacement occurs when the colliding particle imparts energy greater than certain displacement threshold energy, E_d, to a target atom. Otherwise knock-on atoms cannot escape their sites and excited lattice atoms and electrons lose their energy through vibrational decay as phonons and plasmons, respectively. The energy that recoil requires to overcome the binding forces and to move more than one atomic spacing away from its original site is E_d. As the nuclear collision occurs between two atoms with electrons around nucleus, 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 momentum transfer from the ion to target atom and the interatomic potential between two atoms Thus the nuclear stopping varies with ion velocity as well as with the charges of two colliding atoms. Nuclear stopping becomes important when an ion slows down to approximately to Bohr velocity i.e the velocity of orbital electron. Therefore, the maximum energy loss due to nuclear stopping occurs near the end of an ion track. For nuclear stopping, the distribution of the energy transferred to the material by the energetic particle per unit distance, called the energy loss, has a maximum around 1 KeV per amu and extends to around 100 KeV per amu The energy loss of an ion in the material as a function of the ion energy is shown qualitatively in Figure 1.1.

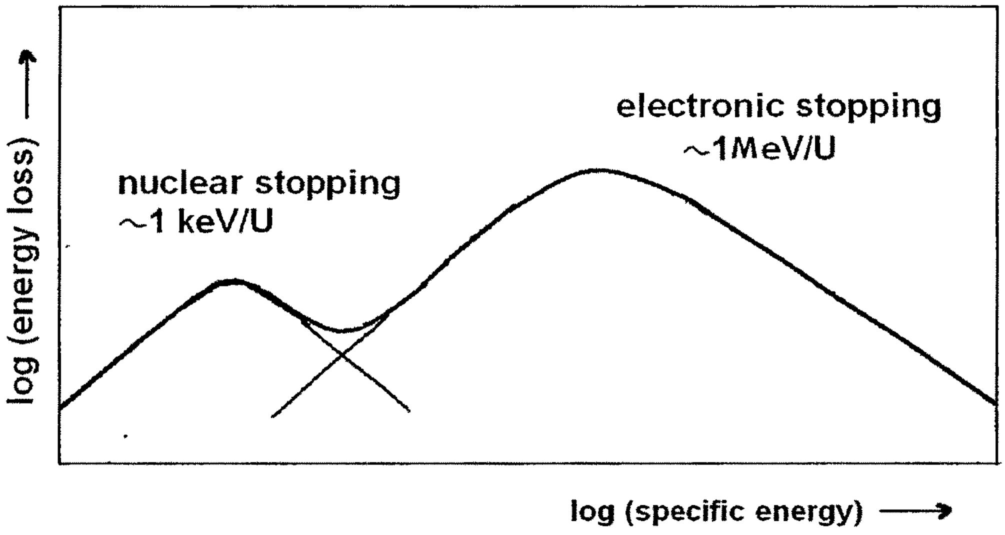

Figure 1.1 Qualitative curve of the energy loss of an ion in the material as a function of the ion energy, shown on a log-log scale [2].

As the energetic ion passes through a medium, its orbital electrons are stripped off to varying degree, depending upon the ion velocity. The effective charge on positive ion depends upon ion velocity and Bohr velocity. Electronic energy loss arises from electromagnetic interaction between the positively charged ion and target electrons. One mechanism is called glancing collision (inelastic scattering, distant resonant collision with small momentum transfer) while the other is called knock-on collision (elastic scattering, close collisions with large momentum transfer). Both glancing and knock-on collisions transfer energy through electronic excitation and ionization.

Electronic excitation is the processes in which an orbital electron is raised to a higher energy level, whereas, in ionization, an orbital electron is ejected from the atom. All excited electrons (plasmons) eventually loss energy as they thermalize. Glancing collision are quite frequent but each collision involves a small energy loss (<100eV). On the other hand, knock-on collisions are very infrequent but each collision imparts a large energy to a target electron. These knock-on electrons are often called δ-rays or secondary electrons. The theoretical and experimental evidence suggested that approximately one half of the electronic energy loss is due to glancing collisions and other half to the knock-on collisions [34, 35]. Nuclear collisions create recoil atoms and these recoil atoms also lose their energy through nuclear electronic processes until all excited electrons and atoms are thermalized by dissipating energy through phonons and plasmons. The phonons and plasmons decay mostly through thermal and radiative processes. For small atoms such as H or He, nuclear stopping is negligible because their nuclear collision cross-sections are very small at most energies of number of nucleons. The unit is taken eV/A^0 used for the energy loss per unit path length or Linear Energy Transfer (LET). The energy partitioning between the different loss processes can be simulated by Monte Carlo simulation program “Stopping and Range of Ions in Matter (SRIM)” [35].

1.5.2 Ion-Beam Induced Property Changes

During irradiation, various chemical and structural changes occur in the polymeric materials [36-38]. Various gaseous molecular species are released during irradiation. The most prominent emission is hydrogen, followed by less abundant heavier molecular species which are scission products from the pendent side groups and chain-end segments, and their reaction products. Cross-linking occurs when two free dangling ions or radical pairs on neighboring chains unite, whereas double or triple bonds are formed if two neighboring radicals in the same chain unite. Figure 1.2 illustrates various functions and chemical entities created by irradiation. It has been well established that mechanical, physical and chemical property changes in polymers are determined by the magnitude of cross linking and scission, and that cross-linking enhances mechanical stability while scission degrades mechanical strength [39].

The main features of change in property induced by ion-beam irradiation and potential application areas were described below.

Cross-linking generally increases hardness and slows diffusion, improves wear and scratch resistance, and decreases solubility in chemical solvents. Electrical conductivity and optical density increase due to the formation of cross-links and conjugated double and triple bonds by irradiation. The delocalized π-electrons in the conjugated bonds are loosely bound and thus more mobile than the covalent σ-bond electrons.

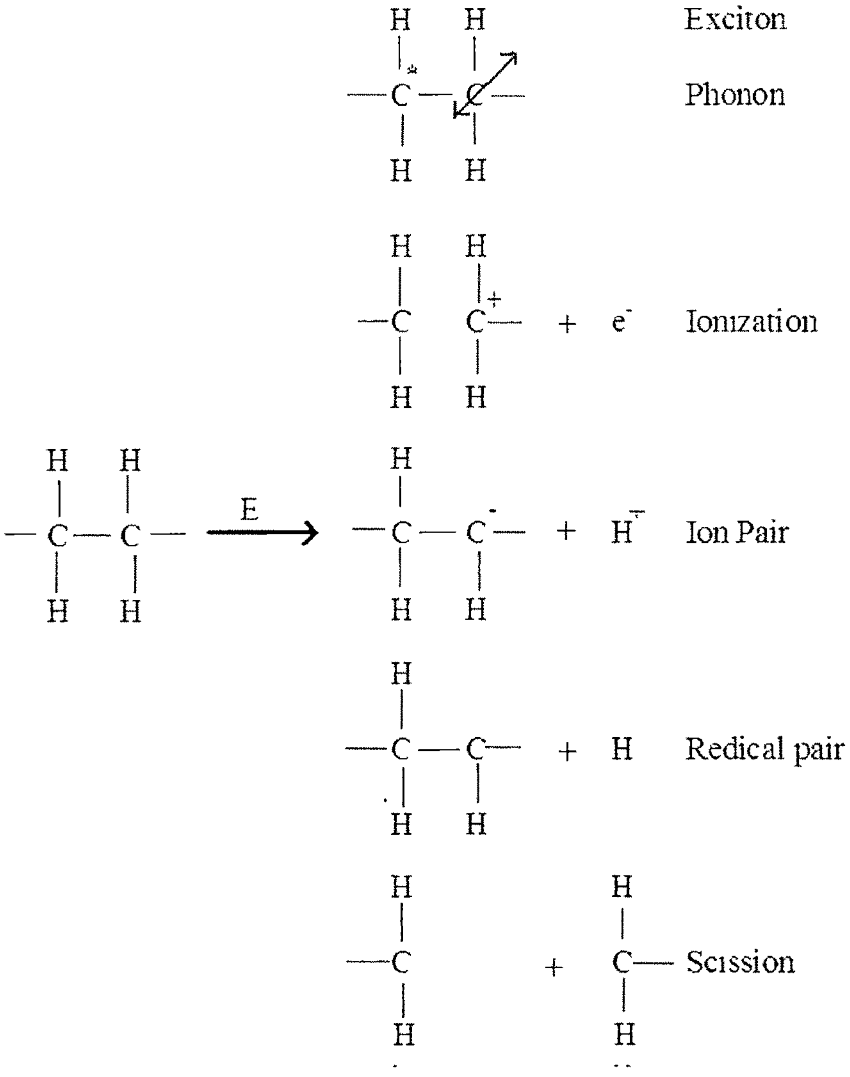

Figure 1.2 Typical effects of ion irradiation which include electronic excitation, phonons, ionizations, ion pair formation, radical formation and chain scission [22].

Furthermore, charge carriers mobility increases by cross links which facilitate the transport of charge carriers across the chains. Otherwise, charge carriers must hop across the chains for conduction. The loosely bound π-electrons can be excited by the energies of visible light, and thus colour changes occur because light is absorbed when these electrons are excited. Radiation induced defects such as anions and radicals (donars) and cations (acceptors) form a broadened band in the band gap and result in the absorption of light as well. Energetic blue light is absorbed first and the colour changes from pale yellow to reddish brown and eventually to a dark colour with increasing irradiation dose. At very high dose a metallic cluster appears because light is scattered by the abundant π-electrons similar to the effect of free electrons in metals. On the other hand, scission causes bond breakage and increases dissolution of polymers in solvents. This feature has been used for lithography and positive-resists in electronic industry [40].

1.5.3 Swift Heavy Ion Irradiation Studies on Polymers

Swift heavy ion irradiation of polymers produces significant changes, in the polymer properties such as, solubility, molecular weight, optical, mechanical and thermal properties. These modifications are due to very high value of electronic stopping power, Se, $(dE/dx)_e$, as already described in the previous sections. Passage of swift heavy ion through the polymer leaves a trail of highly damaged region concentrated along the ion path, known as latent ion track. Heavy ions are unique tool for manufacturing statistically distributed pores of predictable cross sections and particle density. The track diameter depends on the amount of electronic energy deposited, type of ion and polymer materials properties. The core radius observed is typically in the range of 2-6 nm for ion energy 1 MeV/amu to few tens of MeV/amu. The latent tracks are discreteness entities, which are distributed at random with a negligible overlap. The discreteness condition is restricted to ariel track density below 10^{12} ions/cm^2. Above this limit the distinction between the damaged zones and the unaffected bulk material gradually vanishes.

There are several reports on the study of SHI induced tracks in polymers and the studies mainly confined to use these latent tracks for nuclear particle detectors and micro filter's membranes etc [41-43]. The effect of ion track can be enhanced by using suitable development processes (track etching). Therefore, it requires a low dose 10^{10} to 10^{12} ions/cm^2. The heavy ions loose their energy in the polymer at a rate of a few 100 eV to 2 keV/A^0, which is above the threshold for homogeneous track etching. These etched latent tracks can be utilized in the making of field emitters, micro filters with special shape and size. Ion track membranes can be modified by further processing (grafting).

However, there are very few studies done relating to nature of interaction of SHI with polymer and the processes involved in the formation of latent track [44]. SHI induced radiolysis of polymer i.e. underlying radiation chemistry is not yet understood completely. The interaction of SHI with polymers produces a complexity of phenomenon like chain scissioning, gas evolution, cluster formation, free radicals, formation of new and double bonds etc. The new entities may react each other and with the molecules of the solids. Direct evidence of such processes is the change in the molecular weight distribution and solubility of the polymer [45-47].

(A) Nature of Track

The mechanism of ion track formation and its detailed structures also poorly understood, and much more efforts are required in this area. What is known is that on the passage through matter energetic ions lose energy mainly via inelastic collision process and induce a continuous trail of highly excited and ionized target atoms along their path and the associated secondary process leads to permanent radiation damage. The cylindrical zone of damaged material, along the ion path is known as latent ion tracks and has a diameter of a few nanometers. The track core is surrounded by a much larger halo whose size is determined by the range of the δ-electrons which cause further damage such as chain scission, cross-links, formation of free radicals etc. These chemically activated species undergo reaction in a time scale of milliseconds to hours. Although, we can characterize the size, nature of defects and relative radiation sensitivity of the material but the detailed chemistry of the production of reactive site is still not known.

(B) Radiation Grafting

Grafting or reactive groups such as enzymes, gels, or catalysts in the latent tracks in the polymer could be used to modify the physical and chemical properties of the polymers. Irradiation and grafting can be simultaneous or consecutive processes [49, 50].

(C) Cluster Formation Induced by SHI in Polymers

There are three different concepts on emergence of clusters during ion irradiation.

(1) For moderate energy transfer, the clusters could be produced along the ion track due to cross-linking and degradation of polymeric chains, so that their linear structures are rearranged in compact 3D-form.

(2) If the polymer has a grain structure, which gets modified by ion irradiation, the polymeric grains form clusters.

(3) For very high-energy transfer, highly excited carbon atoms are formed along the track, which tend to condense as clustered objects.

More recently it has been found that SHI irradiation can produce fullerene molecules along the ion track. This adds a new dimension to polymer nanotechnology as the remarkable electronic properties of the fullerene might be exploited. Fink et al [51] have studied in detail the cluster growth along the ion tracks of energetic ions and shown that a threshold energy density is required for cluster growth to set in. The cluster growth was found to scales with the mean transferred electronic energy density of the polymer. They also studied the influence of doping on the cluster size.

1.6 Mechanisms of Polarization in Solid Dielectrics

Engineering materials, based on their electrical properties can be divided into four distinct categories according to the purpose they serve: (1) conductors (2) semiconductors (3) magnetic materials, and (4) electrical insulating materials-dielectrics.

A dielectric is a medium or material that maintains an electric field with little supply of energy from outside source. If a dielectric material is inserted into an electric field it will become polarized, and the flux density of the electric field at the position of the dielectric material insertion will change. The flux density field, D, and applied field, E in the ideal dielectric materials (dielectric with no electric losses) are related through the following relation:

$$D=\varepsilon'.E \qquad (1.1)$$

Where ε' designates the dielectric constant of such a material.

Dielectric properties of any real dielectric material can be described by the dielectric constant, which is a complex quantity. In dielectric analysis and electrostatics the following notation is used for complex dielectric constant, ε^*,

$$\varepsilon^* = \varepsilon' - j.\, \varepsilon'' \qquad (1.2)$$

The real part ε' defines insulating properties and the imaginary part ε'' describes conductive properties of the dielectric material. Conductivity exists in all real dielectrics and it is used to measure the effectiveness of the dielectric material. To describe the complex nature of the dielectric constant, one would have to consider a dielectric material being placed between the electrodes of a parallel plate condenser attached to a sinusoidal voltage source where loss and charging currents develop. In this thesis, the real part of the complex dielectric constant (ε') and loss tangent ($\tan \delta$) which is expressed as:

$$\tan \delta = \varepsilon''/\, \varepsilon' \qquad (1.3)$$

A dielectric material can react to the applied electric field because it contains charge carriers that can be displaced. On the macroscopic scale the mechanism of polarization can be explained by investigating the surface charge distribution on the plates of a condenser connected to a voltage source [Fig 1.3]. Dielectric medium inside the condenser will become polarized by the electric field E, by means of the alignment of electric dipoles contained in the dielectric material. In electrostatics, an electric dipole is defined as an entity in which equal positive and negative charges are separated by a small distance, forming an electric dipole moment [Figure 1.4a]. Exposed to the applied electric field, electric dipoles will tend to align themselves in the direction of the field [Figure 1.4b]. In the parallel condenser, with voltage source applied, all the dipole ends of the opposite charge inside the dielectric material will be neutralized. However an uncompensated surface charge will remain, negative at the top, positive at the bottom plate (or vice versa depending on the applied source direction). Respecting the laws of electrostatics, the electric field between the plates must be proportional to the voltage applied regardless whether the dielectric is present or not. With the presence of the dielectric material in the condenser, some of the surface charges on the plates are neutralized by being bound by the dipole ends. Therefore, the required magnitude of the electric field E can be maintained only if more charges flow from the applied voltage source Thus resulting in an increase of charge density Q' at the condenser plates, of which some are bound and thus do not contribute to the electric field [Figure 1.3].

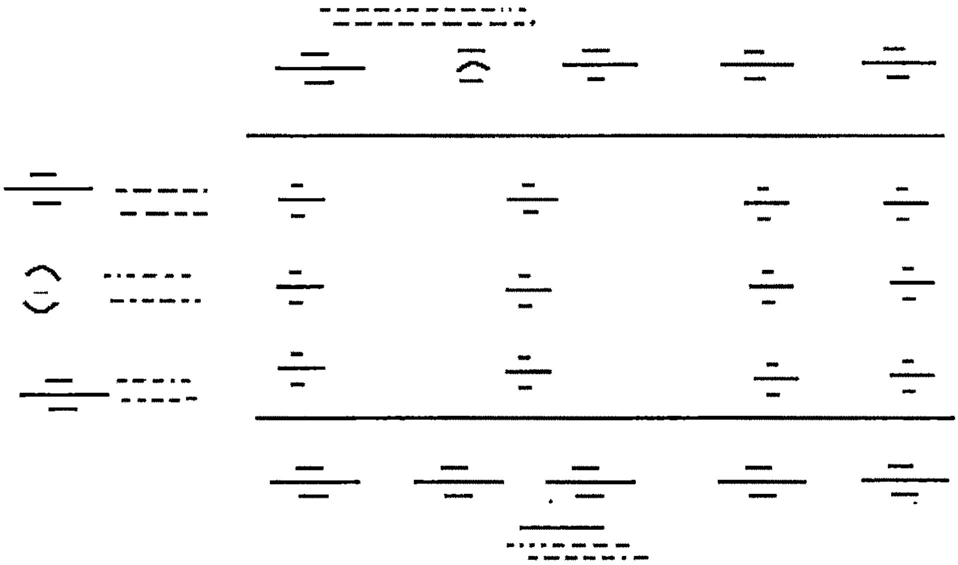

Figure 1.3 Polarization in dielectric (macroscopic view) [52]

The amount of charge at the plates Q' can be expressed as: $Q'=Q+Q_B$, where charge designated as Q_B is the bound charge density and Q is the initial charge. Taking into account the bound charges, the density of the flux lines (also known as electric displacement field D) is expressed as.

$$D= \varepsilon_0 . E + Q_B = \varepsilon_0 . E + P \qquad (1.4)$$

Where the bound charge is called polarization vector and usually in electrostatics is designated as P and ε_0 is the permittivity of the free space. For many dielectric materials, polarization is related to the applied field through the relation [51]:

$$P = D - \varepsilon_0 . E = (\varepsilon' - \varepsilon_0)\ E = \chi . \varepsilon_0 . E \qquad (1.5)$$

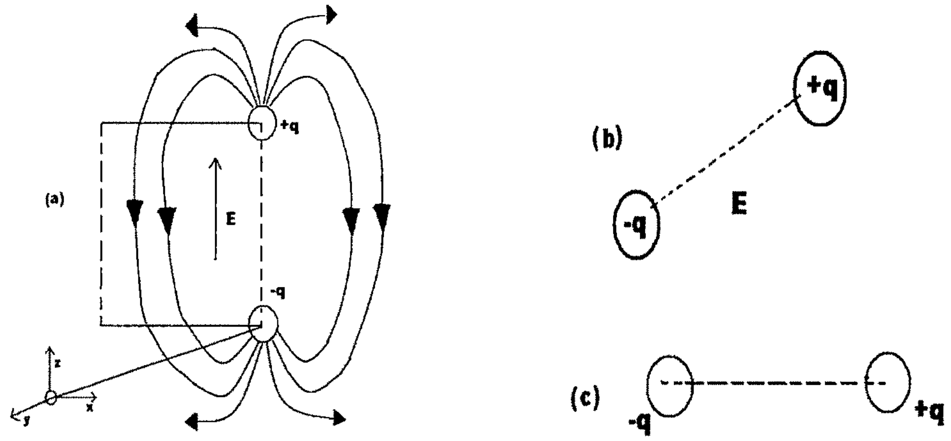

Figure 1.4 (a) Electric dipole (b) Alignment of a dipole (c) Final dipole alignment with field.

The factor $\chi = P/ \varepsilon_{0\,E} = \kappa' - 1$ is known as electric susceptibility of the dielectric material, and $\kappa' = \varepsilon'/ \varepsilon_0$ is the relative dielectric constant.

The polarization vector P, is also equivalent to the dipole moment per unit volume of the material [52]. The dipole moment per unit volume can be thought of as resulting from the additive action of elementary dipole moments p^{-}:

$$P = N.\, p^{-} \qquad (1.6)$$

Where N is the number of elementary particles per unit volume. The dipole moment of the elementary particle, furthermore, it assumed to be proportional to the local electric field strength, E', that acts on the particle [53]:

$$p^{-} = \alpha\, .E' \qquad (1.7)$$

The proportionality factor α, is called polarizability and it measures the average dipole moment per unit field strength. Based on previous equations the polarization can be expressed as:

$$P = (\kappa' - 1).\, \varepsilon_0.\, E = N.\, \alpha\, .E' \qquad (1.8)$$

Which links the macroscopic measured permittivity to the three molecular parameters: the number of contributing elementary particles per unit volume, N; their polarizability, α; and the locally acting electric field, E'.

This field (E') will normally differ from the applied field E, owing to the polarization of the surrounding dielectric medium. It is the objective of the molecular theories to evaluate all these parameters and thus to arrive at an understanding of the phenomena of polarization and its dependence on frequency, temperature and applied field strength.

In the dielectric analysis of composite materials, three mechanisms of polarization are observed: (i) electronic polarization (ii) ionic polarization (iii) dipole polarization

1.6.1 Mechanism of Electronic Polarization

Matter electrically speaking consists of positive atomic nuclei and negative electron clouds. Upon application of an external electric field the electrons are displaced slightly with respect to the nucleus [Figure 1.5]; Induced dipole moments cause the electronic polarization of the material

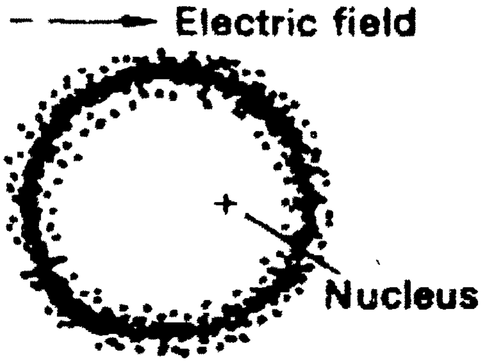

Figure1.5 Electronic polarization [52]

Electrons of the inner atomic shells have critical frequencies higher than 10^{19} [Hz] (X-ray range) for most engineering materials. Consequently, an electromagnetic field of a frequency higher than $\approx 10^{20}$ [Hz] cannot excite any vibration in the atoms; hence it has no polarizing effect on the material, which has for this frequency the same permittivity as a vacuum ($\varepsilon' / \varepsilon_0 = 1$) [Figure 1.6]. For frequencies higher than $\approx 10^{20}$ [Hz], the relative permittivity is close to unity. If the frequency of the applied electromagnetic field is lower than the resonant frequency of the electrons in the inner shell of the atom, these electrons can vibrate with the applied field, polarizing the material in that respect. Electronic polarization gives rise to the relative permittivity above the unity. When the frequency of the applied electromagnetic field is in the range of 10^{14} – 0^{15} [Hz] (optical range to U. V.) valence electrons take part in the overall dielectric polarization of the material and relative permittivity rises [Figure 1 6]. For dielectric materials exhibiting electronic polarization as the only type of polarization, the dielectric constant is independent of frequency for frequencies less than 10^{12} Hz. For this type of polarization, the displacement of electrons is purely elastic in nature and as soon as the electric field is removed, as during the discharge of a capacitor, the electrons return to their initial (no applied field) normal state positions. The entire process takes place without irreversible energy absorption in setting up the electric field which causes electric polarization i.e. the energy of a charged capacitor is fully released on discharge. Consequently, electronic polarization gives rise only to the charging current component.

Electronic polarization decreases with the rise of temperature due to thermal expansion. This dependence is determined by the magnitude of the temperature coefficient of the dielectric.

$$\alpha_e = \frac{1}{\varepsilon}\,\frac{d\varepsilon}{dT} \quad [{}^0C^{-1}] \qquad (1.9)$$

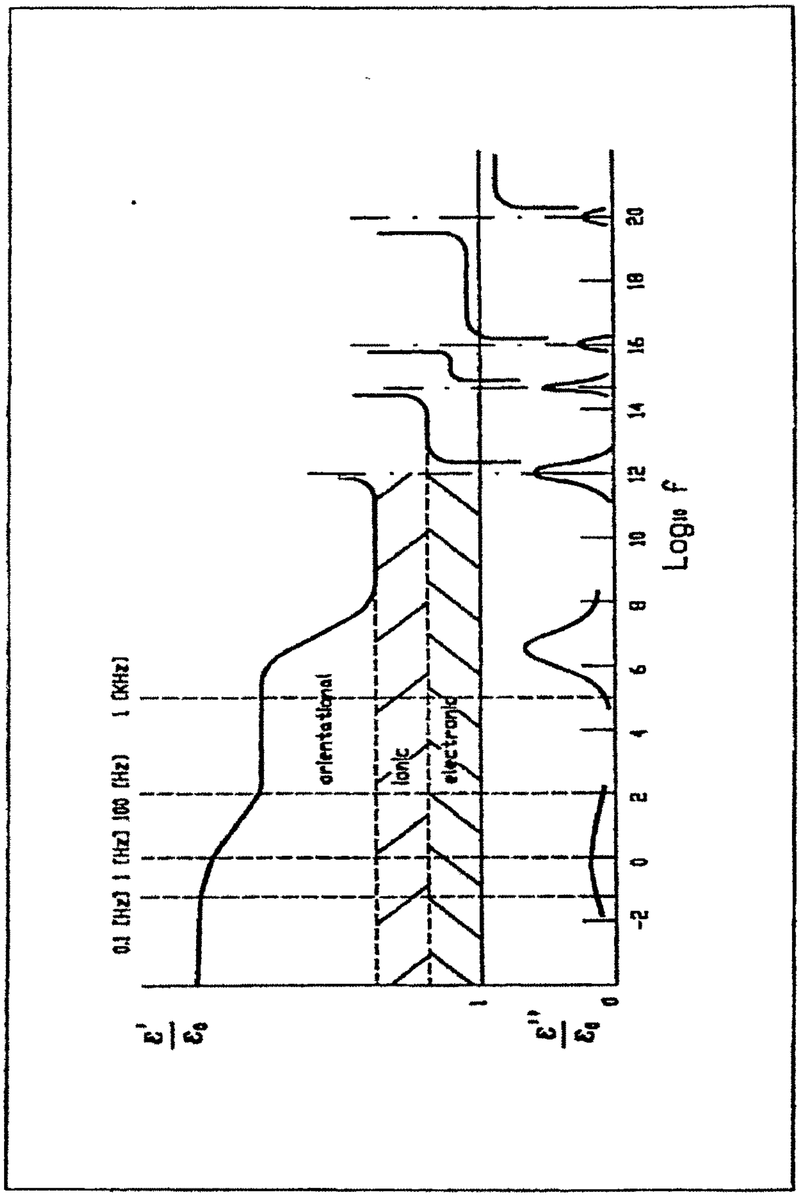

Figure 1.6 Polarization mechanisms versus frequency in dielectric material.

1.6.2 Mechanism of Ionic Polarization

Certain dielectric materials may undergo another type of polarization in addition to electronic polarization. This type of polarization is called ionic and it is also does not give rise to a loss current. Ionic polarization, which is characteristic of ionic crystals, consists of displacement of ions brought about by an applied electric field. The positive ions are shifted in the direction of the negative electrode and positive ions in the direction of the negative electrode. Displacement from the equilibrium position existing in the absence of the applied field is inherently small and like in the case of electronic polarization being elastic in nature, give rise only to charging current which supplements that contributed by electronic polarization. Since the currents resulting from the ionic polarization and electronic polarization are in phase, a dielectric in which these two components are set up will give greater capacitance resulting in higher dielectric constant. Ionic polarization time is greater than electronic, due to the much greater mass of the ions. Most dielectric materials experiences ionic polarization in the frequency range of less than 10^{13} Hz. Like in the case of electronic polarization, the dielectric constant associated with the ionic polarization is independent of frequency [Figure 1.6] for frequency less than 10^{12} Hz.

Dielectric materials subjected to intense ionic polarization have a dielectric constant associated with the positive temperature coefficient. This can attributed to a weakening of the elastic forces that act upon the ions at the crystal lattice points under the effect of temperature rise, and also to increase thermal motion, both making for greater ion displacement on application of an external electric field. Although temperature increase causes thermal expansion, and thus leads to a certain decrease in electronic polarization, in most materials this effect is less pronounced than the increase in ionic polarization due to the rise of temperature and therefore the net dielectric constant increases with temperature rise.

1.6.3 Dipole (Orientation) Polarization

The structure of the molecules has a strong influence on polarization processes. In many dielectrics the molecules contain an inherent electric dipole moment even in the absence of the electromagnetic field. Such molecules have the centers of their positive and negative charges displaced with respect to each other and therefore from the dipole. These molecules are called polar molecules. When an electric field is applied to materials containing polar molecules another type of polarization occurs in dielectric called orientation or dipole polarization. Upon applying the field to polar dielectrics, dipoles experience tension due to the existence of electromagnetic field. The distance between the centers of the positive and negative charges becomes greater and the dipole moment increases. The electric field forces a certain reorientation of the dipoles. The dipoles rotate, so that the positively charged ends face negative electrode and the negative dipole ends positive electrode. The tension to which the dipoles are subjected, as well as, their orientation in the field corresponds with the direction of the displacement electrons contributing to the electronic polarization. Oriented dipoles increase the overall dielectric constant of a material [Figure 1.6]. Orientational polarization will be more intense as the dipole moment of the molecules increase.

The dependence of dielectric constant and loss tangent on the frequency and temperature is shown for several engineering materials in Figures 1.7 and 1.8.

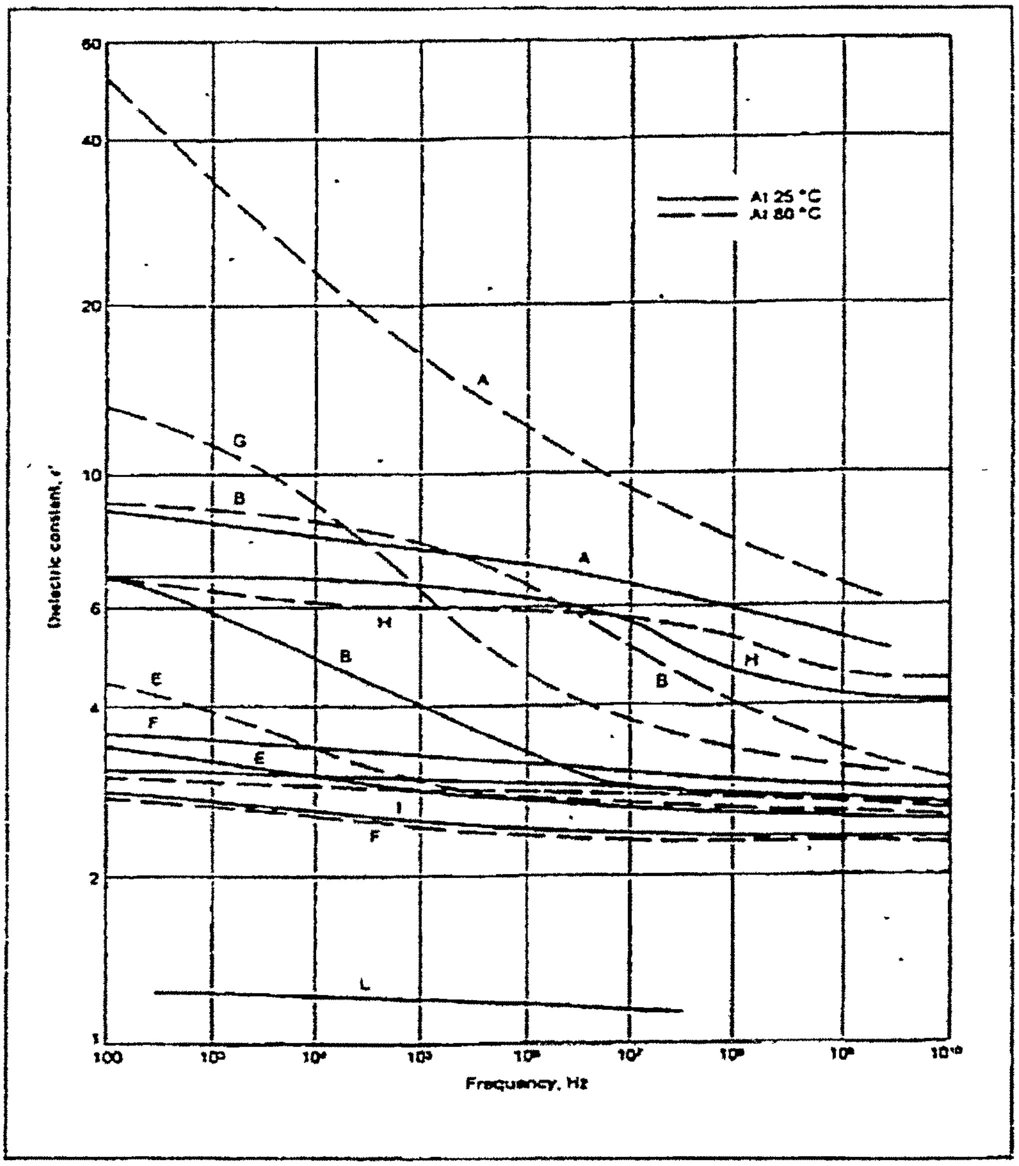

Figure 1.7 Dielectric constant vs frequency and temperature A clear cast phenolic resin, B plasticized PVC, E polymethyl methacrylate, F, polychlorotrifluoroethane, G nylon, H neoprene, I plasticized ethylcelluloze, L polyurethane foam (0.033g/cm^3) [55].

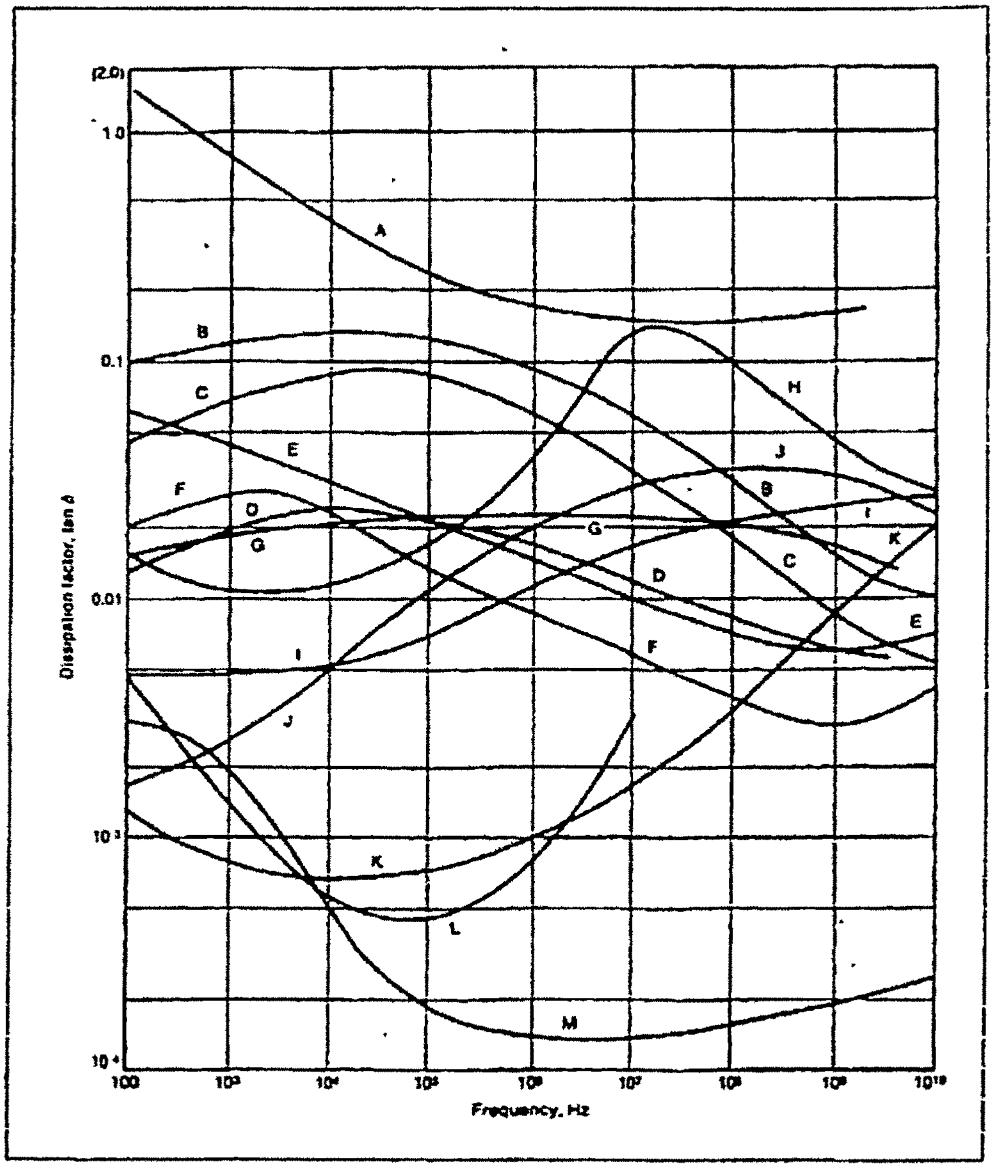

Figure 1.8 Dielectric tangent vs frequency and temperature A clear cast phenolic resin, B plasticized PVC, C polyvinyl chloride, D unplasticized PVC, E polymethyl methacrylate, F, polychlorotrifluoroethane, G nylon, H neoprene, I plasticized ethylcelluloze, J epoxy cast resin, K silicone rubber, L polyurethane foam, M polystyrene [55].

1.7 Research Objectives

Traditionally polymer matrix composites materials have been thought of primarily as insulating materials and, as such they have been used in applications like power tool handles, cable, jackets, capacitor films and electronic packaging materials. More recently, however, there is a growing market need for polymer-composites materials with increased electrical conductivity. There is an increasing interest in the polymer-matrix composites prepared by mixing two or more constituents to make up some disadvantages in single material. For instance by combining different conductivity fillers with polymer, polymer composites with special physical property applied in electronic industry areas, such as capacitor can be fabricated. On one hand, though ferroelectric ceramics with high dielectric constant have been used as dielectric materials in capacitors, the flexibility of ceramic materials is very poor. On the other hand, some polymers are very flexible, easy to fabricate at low temperature and they also possess high dielectric break down but low dielectric constant. The presence of filler in polymer matrix affects both electrical as well as mechanical properties. To prepare the composites with excellent dielectric property, therefore the effective utilization of filled polymers depends strongly on loading fillers homogeneously throughout polymer and effective microstructure in the composites. Furthermore, interfaces among the different phases in composites play also an important role on deciding the dielectric property. The composites are regarded as heterogeneous and many relations have been proposed to depict their dielectric property in terms of physical properties of their constituents. The dielectric property of the composites depends on the volume fraction, size and shape of conducting fillers, and also on other factors such as, preparation method, interface and interaction between the fillers and the polymers

Ion beam irradiation has long been recognized as an effective method for modifying the properties of diverse materials, including polymers and polymer composites. Important properties of polymer composites i. e. mechanical property, thermal stability, chemical resistance, melt flow, process ability and surface properties significantly improved by ion beam irradiation. Ion irradiation of such polymer composites can result in significant changes in the chemical structure of filled filler and polymer surface layers including (i) degradation of chemical bonds and backbone structure, (ii) crosslinking of polymer chains. A filled polymer differs substantially from the free one in wide range of properties. These materials can be crosslinked to obtain useful properties. Our interest in dispersion of organometallic compound is mainly because of ion irradiation induced enhancement of both electrical conductivity and mechanical (hardness) properties of polymers.

It is also important to study the radiation effects on polymers since polymeric materials are extensively used as part of safety systems of nuclear power plants or alternative current generators and also polymer have many uses in industrial and medical fields, where in some cases, they may be exposed to high radiation doses, which affect their properties. Electrical and thermal properties of which highly affected by radiation and its study has great interest owing to its vast applications.

The motivation behind the present work is to study ion induced modification of organometallics dispersed polymer films and pure polymer films by investigating dielectric, structural , microhardess, thermal properties and surface morphology.

1.8 Present Work

In the present work, an attempt has been made to characterize the effects of 80 MeV O^{6+} and 120 MeV Ni^{10+} ions irradiation on the physico-chemical properties of organometallics dispersed polymers and pure polymers using various experimental techniques have been made. It is hoped that the findings in this work would be of important relevance to the material science and applications of polymers/ polymer composites.

Following studies have been made:

1) Electrical properties (i.e. conductivity, dielectric constant, dielectric loss) of ferric oxalate dispersed polymethyl methacrylate (PMMA), ferric oxalate dispersed polyvinyl chloride (PVC), nickel-diemethyl glyoxime dispersed PMMA films and pure polymers such as kapton (PI), polycarbonate (PC), polyether sulphone (PES) and blended polyvinyl chloride (PVC) with poly ethylene terephthalate (PET), at different fluences, using 80 MeV O^{6+} and nickel-diemethyl glyoxime dispersed PMMA films at different fluences and concentrations using 120 MeV Ni^{10+} ions have been studied in the frequency range 50 Hz -10 MHz using LCR meter.
2) Microhardness of ferric oxalate dispersed polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), nickel-diemethyl glyoxime dispersed PMMA films and PI, PC, PES and PVC-PET blends were also studied using Vickers microhardness indenter.
3) Surface morphology of ferric oxalate dispersed polymethyl methacrylate (PMMA), polyvinyl chloride (PVC), nickel-dimethyl glyoxime dispersed PMMA

films were studied using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

4) Crystallite size of Ni-DMG dispersed PMMA films was investigated using XRD analysis.

5) Mossbauer study was also carried for a case of ferric oxalate dispersed PMMA film.

6) Thermal and structural properties of PI, PC, PES and PVC-PET blends were also studied using TGA/DSC analysis and FTIR spectroscopy.

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