Chapter –I

Introduction

Abstract

This chapter deals with the fundamentals of polymers and polymer composites. The importance of ion beam irradiation in the field of material science and present day technologies is explained. A brief description about energy loss mechanism of ion beam and its effects on the properties of polymer and polymer composites is explained. A detailed literature survey and motivation for the present work is emphasized at the end of the chapter.

1.0 Introduction of new era: Polymeric age

Polymer means a particular class of macromolecules, consisting a set of regularly repeated chemical units of the similar type, or possibly of a very limited number of different types, joined end to end or sometimes in more complicated ways, to form a chain molecule.

In recent years, there is a remarkable growth in the use of synthetic organic polymers in technology, both for high-tech and for consumer-product applications. Polymers are able to replace the traditional engineering materials such as metals, due to their many desirable physical and chemical characteristics like high strength to weight ratio, resistance to corrosion, low cost etc. Because of the their versatile properties such as low density, ease of availability, ability to form intricate shapes, durability, processibility, transparency, electrical and thermal resistance, polymers has become ideal materials for many industrial applications. As scientific progress continued, polymers are introduced into every aspect of life, from medicine to food packaging to computers. Since they have become a part of our day to day life, scientists and technologists have termed this era as the `polymeric age'.

1.1 Fundamentals of Polymers

1.1.1 Classifications of polymers

The polymers are mainly classified based on:

1. Molecular Structure: The classification based on the polymer structure, linear or branched and made up of identical monomer (i.e. homopolymer) or mixture of two or more monomers (i.e. copolymers).

2. Physical State: The distinction depends on temperature, molecular weight and chemical structure of the polymer.

3. Chemical Structure: It depends on the structure of their main chain and functional group present in the structure and the synthesis process.

4. Morphological behaviour: They can be classified as amorphous or crystalline polymer according to their structural properties.

5. Polymers can also be classified as fibers, plastics, resins and rubbers based on the nature and extent of secondary valence forces and mobility among the constitutional repeated units.

6. Classification based on properties: thermoplastic, thermosets and elastomers.

The term *thermoplastic* is applied for most of the linear polymers which can be soften and flow in response to the application of pressure and heat. Thus, most thermoplastic materials can be remoulded many times, although chemical degradation may eventually limit the number of moulding cycles. In the present work, thermoplastic polymer, Polymethyl methacrylate (PMMA) has been used. The term *thermoset* is applied to most of branched or cross-linked polymers, once heated, react irreversibly so that subsequent applications of heat and pressure do not cause them to soften and flow. *Elastomers* are cross-linked rubbery polymers that can be stretched easily to larger extent and can rapidly recover their original dimensions when the applied stress is released.

1.1.2 Properties of polymers

The polymer properties are broadly divided into several categories based on the length-scale. At nano-micro scale, the properties that directly relate to the chain itself and represent polymer structure. At an intermediate mesoscopic level, the properties describe the morphology of the polymer matrix. And at the macroscopic level, properties describe the bulk behaviour of the polymer.

For instance, few properties are given below to indicate how the polymer actually behaves on the macroscopic scale.

Electrical properties: Generally two types of polymers are available (i) insulating polymer and (ii) conducting polymer. According to polymer's conductivity, it shows electrical behaviour. Present work is based on insulating thermoplastic polymer. Generally they are good dielectric material. Their electrical properties can significantly be enhanced by doping conducting filler and also by irradiating with ion beam.

Crystallinity: A synthetic polymer can be termed as a crystalline if it contains the regions of the three-dimensional ordering on atomic (rather than macromolecular) length scales usually due to the intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions; the degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material [1]. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely noncrystalline polymer to one for a completely crystalline (theoretical) polymer. Increasing the degree of crystallinity tends to make a polymer more rigid but it can also lead to higher brittleness. Polymers with a degree of crystallinity approaching to zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to scattering of light by crystalline/glassy regions.

Chemical properties: The attractive forces between polymer chains play a major role in determining the polymer's properties. Different side groups in polymer structure can lead ionic bonding or hydrogen bonding between its own chains. These stronger forces typically result in higher tensile strength and melting points.

Mechanical properties: The tensile strength of a material quantifies how much stress the material will endure before failing [2, 3]. This is very important in applications, rely on the polymer's physical strength or durability. Microhardness can determine the toughness of the material and its ability of crosslinking. Most thermoplastic polymers are having low hardness value which can be enhanced by doping different fillers. Some polymers also show improved crosslinking behaviour after irradiation.

Thermal properties: The term "melting point" when applied to polymers suggests not a solid-liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase. Though abbreviated as simply "T_m", the property is more properly called "crystalline melting temperature". Among synthetic polymers, crystalline melting pertains only to thermoplastics, as thermosetting polymers will decompose at high temperatures rather than melt. A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g), which describes the temperature at which amorphous polymers undergo a second order phase transition from a rubbery, viscous amorphous solid to a brittle, glassy amorphous solid. The glass transition temperature can be engineered by altering the degree of branching or cross-linking in the polymer or by adding plasticizer [4].

1.2 Composites

1.2.1 Polymer composites

Various metals, ceramics and polymers are considered suitable for the use in biomedical and industrial applications. However, some drawbacks of these materials make alternatives desirable. Disadvantages of metals include corrosion, high density, much higher stiffness, release of metal ions which may cause allergic reactions and low biocompatibility [5, 6]. Problems with ceramics include brittleness, low fracture strength, lack of resilience and low mechanical reliability [5]. Polymers are too flexible and too weak to be used in certain applications and their properties can adversely be affected by sterilization processes. They may also absorb liquids and swell, or leach undesirable products [7].

One of the goals of materials research is to create new materials with physical properties tailored to a particular application and to understand the mechanisms controlling these properties.

Composite materials can be developed by mixing two or more basic constituents with improved physical properties are new field of material science with dramatically increasing interest [8-11]. In composite polymers, the second component with very different properties is added to the polymer so that both components contribute to the properties of the product. The second component often increases the strength or stiffness of the product and said to reinforce it. Although composites are very important class of polymeric materials and they form a separate subject of study, it is necessary to consider the properties of both-polymer matrix and reinforcing material [12].

In composite materials, insulating materials with embedded metal particles are under focus because of their special structural properties and the extraordinary optical and electrical properties [13-15].

Depending on the filling factor f, three structure ranges can be distinguished in insulator films with embedded nanoparticles:

(i) $f \leq f_c$ – insulating structure range,

(ii) $f = f_c$ – percolation range

(iii) $f \geq f_c$ – metallic structure range.

If the filling factor (f) is below the percolation threshold (f_c), the metal particles exist separated from each other. The metal-containing film has electrically insulating properties but the conductivity is significantly higher with embedded metal particles than the conductivity of the pure insulating material. The percolation threshold f_c is defined as the filling factor where the film switches from an insulating to a metallic conductive film. In the metallic structure range, particles are no longer completely separated by the insulator matrix so the composite film has a higher electrical conductivity, nevertheless far below bulk conductivity in a solid state metal [16].

In order to achieve conduction in filled polymer systems, conductive pathways of filler particles are required throughout the polymer matrix so as to allow electrons to move freely through the material. Percolation theory quantitatively relates the electrical conductivity of the composite to the volume fraction of the filler. The composite conductivity increases slowly with increasing filler concentration till the critical volume fraction is reached. Below the threshold loading, volume resistivity is very high and decreases suddenly and significantly above the threshold, as the particles form long touching chains.

The conductivity of the filler depends on the size, shape and dispersion of the filler particles. As the size of the filler particle decreases, the surface area available for conductive contacts increases relative to particle volume, thus causing the formation of conductive pathways at lower volume fractions. Therefore the choice of filler is increasing from micro-scale to nano-scale.

Organometals are coordinate covalent compounds with a metal atom bonded to an organic liquid via bridging of O, S, P or N atoms. Very few organometallics are commercially available which are quite stable, with self-lives of a year or more. There exist also quite a number of unstable ones, those react with oxygen and therefore need special care. Most of the organometals are soluble in some solvents e.g. xylene, toluene, and tetrahydrofuran.

Organometallic compound such as ferric oxalate, palladium acetylacetonate and Ni-dimethylglyoxime are used as fillers in present work. Their properties are discussed in Chapter-2 (Section- 2.2.1). Organometallic compounds provide large number of functional groups after ion beam irradiation and consequently provide better adhesion between metal and polymer. This adhesion improves the electrical properties of the composites after irradiation.

1.2.2 Applications of polymers/polymer composites

Generally plastics, fibres, rubber, adhesives, paints and coatings are familiar as consumer products. All of these products are based on polymers and usually the same polymer can also be used for more than one application. New or expanded applications are the main reasons for the consistent growth of plastics in the last two decades. The use of PVC for pipe, conduit and sliding in construction become common. The water and soft drink bottles made of PET which now dominate grocery shelves have almost completely displaced glass bottles. Similarly, polypropylene used in the casing for almost all automobile batteries has the same basic formula as the polymer used for indoor-outdoor carpeting, transparent overwrap films, lawn furniture, and polyolefin intimate apparel.

Polymer composite materials overcome many of the shortcomings of these homogeneous materials. They are currently being used in various medical procedures and many additional applications have been proposed. Polymer composites have also been developed as candidates for different types of sensing applications. The conductive and absorptive properties of the insulating polymers doped with conducting materials and the absorptive properties of insulating polymers with nonconducting fillers are sensitive to exposure to gas vapors. Therefore, they can be used to monitor the existence and concentration of gases in the environment [17]. Composites and plastics are used in a wide variety of products from advanced spacecraft to sporting goods to joint implants. Metal doped polymer provides suitable properties for EMI shielding.

1.2.2.1 Novel applications

(i) Space application

Many spacecraft components are made up of polymeric materials and polymer based composites. These materials may suffer accelerated erosion in low earth orbit (LEO) environment due to the presence of atomic oxygen and the vacuum ultraviolet radiation from the sun and consequently experience a loss of performance. By conventional ion beam treatment, polymer samples become resistant to chemical attacks and attain greater surface hardness and wear, if a metal oxide layer is formed on the surface [18]. This can also be achieved by doping organometallic compound in a polymeric material, having large number of functional groups so that they can form a bond with polymeric material after irradiation and thereby improves the sustainability of the polymer.

(ii) EMI shielding

Almost all electrical devices generate some electromagnetic radiation. This includes motors, TV sets, radios, DVD players, computers and light switches. EMI interrupts, obstructs, degrades or limits the effective performance of electronics/electrical equipments. It can be induced intentionally, as in some forms of electronic warfare, or unintentionally, as a result of inter modulation products for instance. This unwanted electromagnetic emission is caused by rapid changes in voltages and currents within wires or circuits. EMI shielding materials can be used to overcome this problem. EMI shielding can be achieved by coating appliance housing with a conductive layer of metal or by making an entire housing from a plastic reinforced with metallic filler having good conductivity [19]. In general, metals are the most common materials for shielding, but they are heavy, expensive and tend to suffer from their poor wear or scratch resistance and corrosion [20]. On the other hand, use of polymers in the electronic devices is popular because of its properties like light weight, flexible and less expensive. In order to shield against electromagnetic interference, the technical approach, which has been considered extensively, is to incorporate electrically conductive fillers in polymer matrices.

An electromagnetic wave passing through a shielding material layer can be attenuated in three ways [20],

1. By reflection at the surface
2. By absorption due to the thickness of the shield
3. By multiple internal reflection

The primary mechanism, reflection requires the existence of mobile charge carriers (electrons and holes) which interact with the electromagnetic radiation. Thus, shield becomes electrically conducting, although a high conductivity is not required for shielding. This requirement can be fulfilled by doping the metal particles in a polymer.

The second mechanism absorption requires the electric and /or magnetic dipoles which interact with the electromagnetic field. The electric dipoles may be provided by materials having high dielectric constant or magnetic permeability. Polymers having high value of dielectric constant (>8) can satisfy this requirement.

The third mechanism of attenuation is multiple reflections. This refers to the reflections at various surfaces or interfaces in the shield. This mechanism requires the presence of a large surface area or interface area in the shield. To fulfil this requirement, the filler size should be restricted to nano-scale.

To conclude, a composite material such as conducting or insulating polymers, doped with the metallic nanoparticles is a good option for EMI shielding.

1.2.3 Polymer nanocomposites

(i) Polymer with embedded nanoparticles

Polymer matrices embedded with metal and semiconductor nanoparticles form materials that possess the unique properties arising from the nanoscopic size and shapes of the metal clusters. These materials also possess the processing and handling advantages similar to bulk materials. Different techniques are used to prepare composite thin films. RF sputtering is one of the significant methods amongst them for polymeric films.

In the competitive growth mode, where simultaneous deposition of the polymer and metal takes place, growth of embedded metal particles is substantially influenced by the coincidental growth of the polymer. For example, in co-sputtering, the size and shape distribution of the embedded metal nanoparticles can be adjusted by altering sputter parameters. Many researchers have studied the polymer films with embedded metal particles made by co-sputtering are Au-PTFE [21-23], Ag-PTFE [23], Cu-PTFE [22, 24] or Pt-PTFE [22]. In addition, carbon films with embedded nanoparticles such as Ag [25] have been prepared by co-sputtering [26].

(ii) Sputtering

Sputtering is defined as removal of material from the surface of a solid due to the impact of energetic particles. When charged particles bombard the target surface, apart from the ejection of neutral atoms of the surface material, charged atoms and electrons are also emitted from the surface. The ejected neutral target atoms condense into thin films on the substrate. This process can be realized by an experimental configuration in which the heavy positive ion such as argon strike the target surface which acts as a cathode where as the substrate holder which faces the target, acts as an anode. The mean energy of sputtered particle is of the order of 10 eV.

Some of the main advantages of sputtering as a thin film preparation technique are (a) high uniformity of the thickness of the deposited films, (b) good adhesion with the substrate, (c) better reproducibility of the films, (d) ability of the deposit to maintain the stoichiometry of the original target composition and (e) controlling the thickness of the thin film becomes relatively simple.

There are various types of sputtering processes e.g. Getter sputtering, DC sputtering, RF sputtering, Magnetron Sputtering.

Out of which, RF sputtering is used for thin film preparation in the present work. The details of sputtering unit are discussed in Chapter-2. The pristine and irradiated films, made by this process were analysed using various characterization techniques and the results are explained in Chapter-4.

1.3 Ion beam Irradiation

1.3.1 Importance of study

The amount of radiation that polymeric material encounters during their life cycle strongly depends on the radiation environment and their operating conditions. For space missions and military applications it is obvious that there is a radiation-harsh environment. However, also during their fabrication processes and also for standard terrestrial operations, the devices get effected by ionising radiation [27].

The possible experiments or realistic scenarios under which a material experiences a radiative environment are listed below.

1. Space environment

2. High energy physics experiments
3. Nuclear reactors
4. Natural environments
5. Processing-induced radiation

When polymeric material is used for such applications, a detail study of radiative environmental effect on the material is ought to be done. Such study can be carried out using energetic ion beam.

Energetic ion beam plays a vital role in the field of research in materials science [28–30]. Ion beam effect on the materials depends on the ion energy, fluence and ion specie.

There are two different irradiation mechanisms namely low energy ion (a few tens of keV to a few MeV) implantation and swift heavy ion irradiation (SHI). In case of former, the low energy ions get embedded in the material and cause modification by their presence and due to the collision cascade produced by the impinging ions. Whereas in SHI irradiation, the modification of thin films or the near-surface region of the bulk samples is due to the electronic excitation. In this case, the impinging ions do not get embedded in the film due to their large range. It is, for this reason, advisable to use thin films for SHI irradiation for a better understanding of interaction of swift heavy ion with matter. In such a situation, the elastic collision effects causing collision cascade can be safely neglected and the effect of the embedded ion does not come into the picture [31].

The fundamental interaction between MeV ions and matter can be broadly classified as "electronic", where the ion scatters electrons, or "nuclear", where the ion scatters from the nucleus of an atom. Both processes lead to a transfer of energy from the ion, which is small when an electron is scattered, but can be large when a nuclear scattering occurs. Nuclear scattering occurs with a very small cross-section, compared with electron scattering but has a much more dramatic effect when it does occur. These two energy transfer processes slow the ion and eventually bring it to the rest in solid matter. The detail of ion interaction is discussed in following section.

1.3.2 Interaction of ion beam with matter

(i) Energy loss mechanism

The first experiment on the interaction of charged particle scattered by solids were done and formulated by Rutherford. In principle, when ions traverse through solid matter they ionize the atoms or molecules which they encounter during their flight. Both electrons and positive ions lose their energy while passing through matter. The energy loss of these charged particles per unit length is defined as 'stopping power' and is usually written as:

$$S(E) = -\frac{dE}{dx}$$

where E is the energy and x is the path length. The numerical value of the stopping power is positive and minus sign in the above expression is to represent the loss of energy of the ions/electrons as the length increases. The stopping power varies with the type of the material. The energy loss can be expressed in terms of LET (Linear Energy Transfer). LET is a measure of energy deposited per unit ion path length, often represented in SI unit of eV/nm. The magnitude of ionization depends upon the deposited energy along the ion track or LET [32].

(ii) Nuclear and Electronic stopping

The stopping power depends on the type and energy of the particle and on the properties of the material through which it passes. Since the production of an ion pair (usually a positive ion and a negative electron) requires a fixed amount of energy, the density of ionisation along the path is proportional to the stopping power of the material.

Electronic stopping power: In electronic stopping, the ion slows down due to the inelastic collisions between bound electrons in the medium. The term inelastic is used to signify that the collisions may result both in excitations of bound electrons of the medium and in excitations of the electron cloud of the impinging ion.

Since the number of collisions that an ion experiences with electrons is large and the charge state of the ion while traversing the medium may change frequently, it is very difficult to describe every possible interactions for all possible ion charge states. Instead, the electronic stopping power is often given as a simple function of energy $S_e(E)$ which is an average taken over all energy loss processes for different charge states. At energies lower than about 100 keV per nucleon, it becomes more difficult to determine the electronic stopping power theoretically.

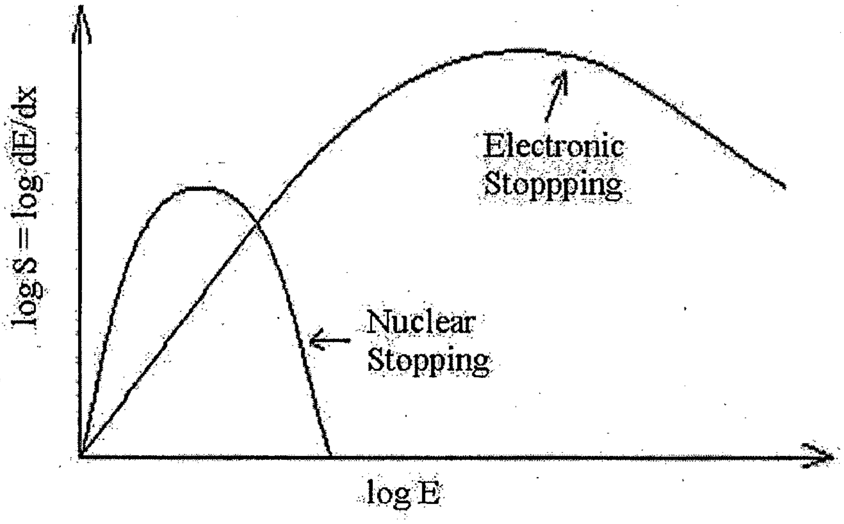

Figure 1.1 Comparison of electronic and nuclear stopping at different energy range

Nuclear stopping power: In nuclear stopping, ions lose their energy by elastic collisions between the ion and atoms in the sample. If one knows the form of the repulsive potential $V(r)$ between two atoms, it is possible to calculate the nuclear stopping power $S_n(E)$. Nuclear stopping increases with the mass of the ion. As shown in Fig. 1.1, nuclear stopping is larger than electronic stopping at lower energy range. For very light ions slowing down in heavy materials, the nuclear stopping is weaker than the electronic stopping at all energies.

At intermediate energies, the stopping power is therefore the sum of two terms:

$S(E) = S_e(E) + S_n(E)$

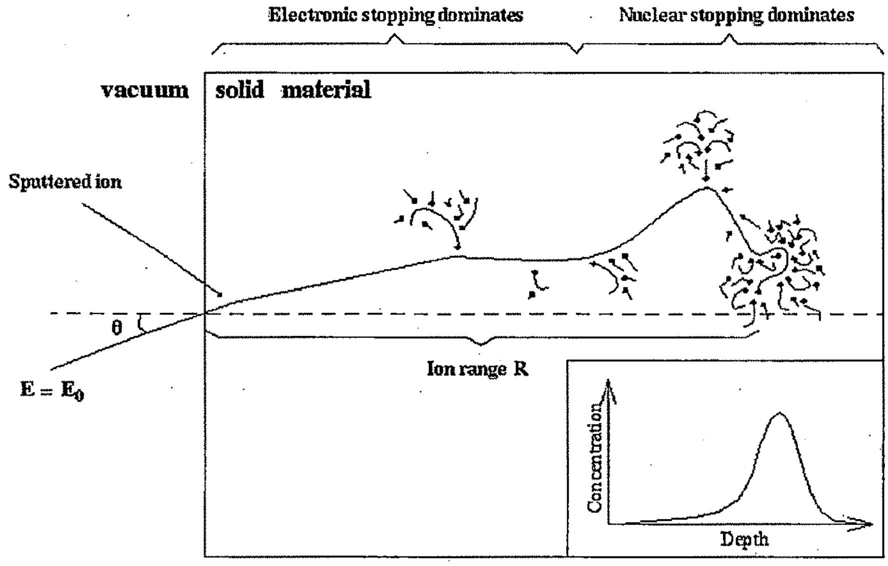

Figure 1.2 Interaction of ion beam with target material

As shown in Fig. 1.2, in the beginning of the slowing-down process at high energies, the ion is slowed down mainly by electronic stopping and it moves almost in a straight path. When the ion has slowed down sufficiently, the collisions with nuclei (the nuclear stopping) become more probable. Atoms of the solid receive significant recoil energies when struck by the ion; they will be removed from their lattice positions, and produce a cascade of further collisions in the material. These collision cascades are the main cause of damage production during ion implantation in metals and semiconductors. Fig. 1.2 shows a typical range distribution of ion energy deposited in the solid [33].

(iii)Heavy Ion Stopping Power

The commonly employed procedure for predicting heavy ion stopping power is by scaling from proton or alpha particle stopping powers. The simplest scaling law is [34]

$$\frac{S_H(v_1 Z_2)}{S_H(v_2 Z_2)} = \frac{S_{HI}(v_1 Z_2)}{S_{HI}(v_2 Z_2)}$$

In this case, velocities of protons and heavy ions must be the same. The simple approach is valid only if the effective charge of the heavy ion does not change during the slowing down process. A more appropriate procedure is to adopt the effective charge formulation. In this scheme the heavy ion stopping power is obtained from

$$S_{HI} = S_H (Z^*{}_{HI})^2 = S_H Z^2{}_{HI} \gamma^2$$

where γ is the effective charge of the ion. For the bare nuclei, i.e. protons, γ=1. An energetic heavy ion is fully stripped when the classical electron velocities are smaller than the ion's velocity. This is fulfilled when $v/v_o = 6.325\ (E[\text{MeV u}^{-1}])^{-1/2} >> 1$, satisfying the relation γ=1. Here v_o is the Bohr velocity αc = $2.19\text{x}10^6$ m s^{-1} (α is a structure constant and c is the speed of light).

(vi) Cross linking and chain scissioning phenomenon

Bond scissioning and cross-linking are the main result of high energy ion irradiation on polymer surfaces. These reactions induce structural modification and change in physical properties [35-39]. Cross-linking occurs when two radicals, produced on the neighbouring polymer units, recombine. The relative molecular mass of the macromolecule increases which resulted in an increase of melting point. Along with the cross-linking, degradation also occurs by chain scission which leads to a decrease in the molecular mass. Grafted polymers can be produced when, for example, at the polymer backbone radical sites are formed which react with monomers present as a liquid or a vapour [40].

It was well established that cross-linking or scissioning efficiency depends not only on polymer structure but also on the characteristics of the radiation sources, namely ion energy and ion specie [41]. There has been considerable discrepancy for the interpretation of chain-scissioning and cross-linking mechanisms for irradiated PMMA. In PMMA, bond scission prevails at low fluences, while polystyrene mainly undergoes cross linking. Notwithstanding the remarkable importance of PMMA as a prototype polymer for positive resist (scission rate higher than cross linking rate) the literature studies on the chemical effects induced by energetic beam irradiation on this polymer are relatively scarce [42–52]. The current interest of PMMA is also remarkable because it has been reported that beyond a given threshold fluence (that in turn depends on the ion) the resist turns negative: i.e. the cross linking rate becomes higher than the scission rate [43].

1.4 Modification of polymeric material by ion irradiation

The effect of radiations, such as γ, X-rays and electrons, on polymer have been widely reported in the literature [44, 45] since a long time, while the effects induced by keV-MeV heavy ions have attracted large interest since last few decades [46-48].

The modification of polymer properties under ionizing radiations is a subject of widespread importance due to the increasing use of polymers in hard radiation environment – encountered in nuclear power plants, space-crafts, sterilization irradiators, high-energy particle accelerators, etc. [49]. The application of radiation on polymers can be employed in various industrial sectors, i.e. biomedical, textile, electrical, membrane, cement, coatings, rubber goods, tires and wheels, foam, footwear, printing rolls, aerospace and pharmaceutical industries [50]. Ion beam irradiation provides a unique way to modify the mechanical, optical and electrical properties of polymer membranes by depositing the energy of ions in the material on the atomic scale. These modifications result from the changes of the chemical structure caused by changing the chemical bonding when the incident ion breaks the polymer chains, breaks covalent bonds, promotes crosslinking and liberates certain volatile specie [51, 52]. The nature of these changes depends on the properties of the polymer, such as the composition and molecular weight, and on the mass and energy of the incident ions, as well as on the conditions of irradiation [53].

Therefore the understanding of certain structural rearrangements influence on the properties of the polymeric materials/composites opens a way to design devices with required parameters. The radiation effect on the physical and structural properties of such materials are required to study particularly, when such devices are being used in radiation environment.

There is a practical interest in the composites consisting of dielectrics with metal nanoparticles, which has enormous potential applications such as nonlinear optical switches, magnetic data storages, microelectronic devices, etc. In such applications, a good adhesion between the polymer and the metal is required. The interaction between metal and polymer is generally very weak and the cohesive energy of polymer is typically two orders of magnitude lower than the cohesive energy of metals. The adhesion can be improved by ion beam irradiation. When organometallic compound containing polymer is irradiated with energetic ions, new adsorption sites are created resulting an improved metal – polymer adhesion. Irradiation makes the metal–polymer bonding more prominent and enhances the properties of the composites [9, 16]. Significant improvement in dielectric properties of the composites after ion beam irradiation has been reported [32]. Structural, mechanical and thermal properties are changed because of high energy ion beam interaction with polymeric materials. For the present work, we have used Proton, Ni^{10+} and Ag^{11+} ion beam to study the effect of ion specie, energy and fluence on composites. The effect of ion beam irradiation on dielectric, structural and mechanical properties and surface morphology have been explained in subsequent sections.

1.4.1 Dielectric properties and its improvement

Dielectric materials are the building blocks of functional electronic circuits, capacitors, gate dielectrics and transmission lines, are essential as electrical insulators for power distribution. Molecular solids, organic polymer resins, ceramic glasses and composites of organic resins with ceramic fillers represent typical dielectrics. The dielectric properties of materials are used to describe electrical energy storage, dissipation and energy transfer.

Electrical storage is the result of dielectric polarization. There are two important mechanisms that results the molecular polarisability. The first one is the distortional polarisability in which the applied electric field changes the electric charge distribution and induces an electric dipole moment, leading to a contribution called the distortional polarisability. The second is that the molecules of some materials have permanent electric dipoles even in the absence of any electric field. If an external electric field is applied to such a material, the molecule tends to rotate so that the dipoles become aligned with the field direction, which gives rise to an orientational polarization.

There are two types of polymers: polar and non-polar. The structure of the polymer determines whether it is polar or non-polar and this determines many of the dielectric properties of the plastic. In polar plastics, dipoles are created by an imbalance in electronic distribution and in the presence of external electric field the dipoles will attempt to align with the field. This creates a 'dipole polarization' of the material and because of movement of the dipoles is involved, there is a time element associated with the movement. Examples of polar plastics are PMMA, PVC, PA (Nylon), PC and these materials are moderately used as insulators.

The non-polar plastics are purely covalent and generally have symmetrical molecules. In these materials there are no polar dipoles present and the application of an electric field does not try to align any dipoles. But the electric field moves the electron slightly in its direction so as to create an 'electron polarization', in this case the movement is caused due to only the electron and this is effectively instantaneous. Examples of such non-polar plastics are PTFE (and many other fluoropolymers), PE, PP and PS and these materials have high resistivity and low dielectric constant.

As mentioned earlier, for polar plastics the alternating current frequency is an important factor because of the time taken to align the polar dipoles. At very low frequencies the dipoles have sufficient time to align with the field before it changes its direction and the resultant dielectric constant is usually high. At very high frequencies, the dipoles do not have time to align before the field changes its direction and so the dielectric constant is lower.

The interaction between electromagnetic waves and dielectric material is governed by Maxwell's equation over the entire frequency range. From these equations the relationship between the time varying electric field and magnetic field can be derived.

Since both the fields can cause energy storage and energy dissipation in the material, two sets of parameters are required to characterize a dielectric as a carrier of electromagnetic energy. The complex permittivity ε" can be considered a fundamental parameter for the macroscopic description of a dielectric, exposed to the alternating field.

A capacitor charged by a sinusoidal voltage source,

$$V = V_o.e^{i.\omega.t} \tag{1.4.1}$$

of the angular frequency ω=2*πf* stores, when vacuum is dielectric, a charge:

$$Q = C_o.V \tag{1.4.2}$$

and draws a charging current:

$$I_c = \frac{dQ}{dT} = j.\omega.C_o.V \tag{1.4.3}$$

where the voltage leads the current by the temporal phase angle of 90°. C_o is the capacitance of the condenser. If some other substance is used as a dielectric, the condenser increases its capacitance C to

$$C = C_o.\frac{\varepsilon'}{\varepsilon_o} = C_o.\kappa' \tag{1.4.4}$$

where ε' and ε_o are the permittivity of the dielectric medium and vacuum respectively and κ' designates the relative dielectric constant of the dielectric material.

Thus, dielectric constant of dielectric material, $\kappa' = \frac{\varepsilon'}{\varepsilon_o}$ (1.4.5)

Loss tangent is expressed by, $\tan\delta = \frac{\varepsilon''}{\varepsilon'}$ (1.4.6)

where real part ε' defines insulating properties and the imaginary part ε" describes conductive properties of the dielectric material. Measurement, prediction and analysis of ε' and ε" are required for predicting the dielectric behaviour of the composite material.

Little has been reported hitherto on the effect of ion irradiation on the dielectric properties of polymers. There exist few reports on gamma, neutron and electron irradiation of non-polymeric materials. These studies provide frame work to some general idea about the effects expected here.

Dielectric loss/constant increases with increasing fluence, as it is associated with electron transitions that are the more pronounced, the more electron that participate in the electron-hopping process between the amorphous zones were created upon polymer destruction [54].

Conductivity by ion irradiation of polymers

In general, the majority of polymeric materials are electric insulators in nature. However, they can be rendered conductive by different methods such as:

(a) Creation of conjugated double bonds in the backbone chain of polymers [55]

(b) Introduction of donor-acceptor complex in the polymer matrix [56]

(c) Adding conductive fillers such as metallic powders and carbon black [57, 58].

The effect of radiation induced crosslinking on polymeric material was studied by many workers [59, 60]. It is well known that electrical conduction in polymers can be considerably enhanced by irradiation. The increase in conductivity of irradiated polymers is attributed to the formation of conjugated structures. Also, the irregularity in the polymer chain may give rise to a hopping mechanism that will enhance the conductivity [61].

The irradiation of solid dielectric material leads to charge accumulation in its bulk. Apparently this conductivity is promoted by the charge-carrier production within the ion tracks and their separation and migration within the applied electric field. The time constant by which the conductivity changes upon switching on or off the beam are of the order of seconds to minutes, depending on the ion flux and the sample temperature [62]. Permanent modification of the electrical properties of both ordinary and conducting polymers by ion irradiation was reported long ago [63]. Since the first report, a large number of studies have been undertaken, in which the effects of ion beam irradiation on electrical properties were investigated on different polymers irradiated under various conditions [64, 65]. Generally, aromatic-ring-containing polymers show a greater improvement in conductivity upon irradiation than polymers lacking aromatic rings, for equivalent ion energy and fluence [66].

1.4.2 Structural changes in composites

In general, it is assumed that ion irradiation of polymers not only leads to the destruction of short-range order (i.e. the polymers' chemical arrangement) but also the destruction of its long-range order, especially that which concerns the polymeric crystallinity. In fact, this observation has been made frequently by many experimentalists with several polymers, after low energy ion irradiation as well as after swift heavy ion irradiation [67, 68].

Bond scission and cross-linking are the main effects of high energy ion irradiation on polymer surfaces. These reactions induce structural modification and change of physical properties [69-74]. To understand the process of structural modification, FT-IR and XRD are carried out for present work. The position, form and intensity of spectral bands obtained from FTIR spectroscopy provides useful information about the microstructure of polymers at a molecular level. The change of functional groups after irradiation was studied by the analysis of FT-IR spectra and the change of crystalline size and percentage (%) crystallinity of the compound after irradiation is investigated by XRD analysis.

1.4.3 Changes in mechanical properties

Most of the polymers show mechanical changes at very low fluence of SHI. However, polymers like PI can withstand at very high fluence before appreciable changes in their mechanical properties.

Surface hardness: Radiation-induced crosslinking results in the production of rigid, three-dimensional carbonaceous networks of strong covalent distorted bonds [75]. Also carbonization due to the splitting of the macromolecular chains and the escaped volatiles hydrogen-rich degradation products may also play an important role in polymer surface hardening.

1.4.4 Changes in Surface morphology

SHI irradiation on polymers leads, in general to an increase in the surface roughness because of the large sputtering effects [76]. Sometimes it is also observed that irradiation enhances the surface diffusion and as a result decrease in the surface roughness [77].

1.5 Selection of PMMA based composites and literature survey

Poly (methyl methacrylate) is an important commercial plastic with application in many sectors such as aircraft glazing, signs, lighting, architecture, transportation and civil construction. PMMA is chosen for our experiments because it is differentiated from other types of plastics by unique combination of economy, ease of manufacturing, high transparency and impressive optical properties. In addition, they are more inherently light stable than other polymers. PMMA is soluble in conventional organic solvents such as acetonitrile and acetone. It is often used in applications requiring good resistance to weather or moisture. Because of such versatile properties of PMMA, significant work has been carried out on this polymer. This section represents the work reported on PMMA and its composites for various applications.

Since bond scission prevails in poly(methyl methacrylate) at low fluence irradiation by protons, PMMA can be used as a positive resist in lithography [78,79]. As the Proton irradiation also affects the refractive index, so it can be used in manufacturing of passive waveguides [80, 81]. PMMA/CNT composites are used in gas sensing applications [82]. More over it was found that the mechanical properties, thermal conductivity and electrical conductance of PMMA can further be improved by doping CNT. These PMMA composites have also gained considerable biological importance in recent times. For example, composites of bioactive glass and PMMA were used as drug delivery system [83]. Now a days, PMMA is the most frequently used polymer as a bone cement for the fixation of total hip prostheses [84]. In the work carried out by Zhi et. al. [85], they reported an enhancement of mechanical and thermal properties of PMMA-BN nanotube composites. It was observed that the mechanical properties (tensile, flexural strength and modulus) of the MWCNT/PMMA composites were found to be comparable or better than the pure polymer. So the composite was suggested to be used as shielding material for improving the electromagnetic interference (EMI) shielding [86]. A substantial improvement in the electrical properties of the electrospun fibers of PANI-PMMA composites was reported by Veluru et. al.[87]. Whereas, Alex J Hsieh et al. [88] studied the high strain-rate behaviour of coextruded polycarbonate/PMMA composites. In their work, the layer of PC/PMMA was examined by using a compression split Hopkinson bar

(SHB) technique. These dynamic stress-strain measurements revealed that the apparent yield (maximum) stress of these co-extruded composites was strongly dependent on the relative thicknesses of PC and PMMA layers. Different techniques for preparing SiO_2/PMMA were described by X. Cheng et al. [89]. For containing dispersed noble metal clusters, using polymers instead of glass, significant studies on these composites have been reported [90-93]. In the case of poly(methylmethacrylate)(PMMA), a noble metal complex is dissolved in liquid monomer and polymerized at a low temperature. PMMA was used instead of glass because of its high transparency. The composites are transparent and stained in colours specific to each noble metal. The composites are expected to become useful as non-linear optical materials. A metal–composite bonded joint with a PMMA adhesive material was fabricated and tested under various loading conditions to assist a short-term and long-term design of the bonded-jointed structures [94]. PMMA can be used in electrical tunable dielectrics for microwave tunable device applications in tunable oscillators, phase shifters, embedded passive capacitors and varactors. In case of tunable dielectrics where a high dielectric tunability and low permittivity is required, it was found that the $Ba_{0.6}Sr_{0.4}TiO_3$ (BST)/poly(methyl methacrylate) tunable composites in 1-3-type structure consisting of BST rods in low-permittivity PMMA matrix are very promising. The 1-3-type BST/PMMA composites can meet the device requirement for tunable dielectric with high dielectric tenability and low permittivity [95]. Few important results for understanding the effect of filler content and change of electrical resistivity have been carried out [96]. In this study poly(methyl methacrylate) (PMMA) is filled with aluminium and showed that the resistivity is dependent on the volume concentration of filler Φ_c. In addition, for filler contents lower than Φ_c, it was seen that the PMMA/Al composite undergoes a transition from a high to a low resistance material at a critical value of the external applied electrical field. There are also few studies carried out on the variation of the permittivity spectrum with frequency. However, not much work has been reported in the literature on the composite materials irradiated with energetic ion beams. In the present work, we extended the previous studies [97, 98] by using different ion beam. The composites were prepared by doping organometallic compound/metal particles in PMMA and perceived irradiation effects on these composites. In section 2.2.1, the properties of PMMA have been discussed in detail.

1.6 Objective of the work

The main objective of the present work is to develop the composite which can conquer some of the tribulations which are not overcome by pure polymer so far. The effect of ion beam on physio-chemical properties is studied in detail. On the basis of the review carried out on the similar work so far, ion-bombardment has been proved as a unique technology for polymer modification. This is because of the fact that the energetic ion beam has been established themselves as an indispensable tool in case of the modification of nano and micro structural materials. Therefore a detailed study on ion induced effects on composite materials is carried out. As stated in previous sections, after taking low and high dielectric material applications into consideration, the filler is appropriately selected. Synthesis, characterization and process integration of low dielectric constant (~ 3-8 at 1 MHz) polymer materials are a dominant theme for microelectronics, satellite, telecommunication, packaging, biomaterials etc. Whereas material with high dielectric constant (>8 at 1 MHz) can be used for EMI shielding. Considering the drawback of pure polymer and metal materials, composites has been prepared which serves the purpose of the requirement. As mentioned earlier, organometallic compounds are useful because of their large number of functional groups which can easily make bond with the polymeric materials after irradiation and enhances the polymeric properties, at the same time presence of metal particle enhance the dielectric properties of the polymer significantly. Hence for this study, four different fillers (i.e. ferric oxalate, palladium acetylacetonate, Ni-Dimethylglyoxime and Ni powder) are dispersed in PMMA and a detailed comparative study of different fillers with their relative concentration is carried out. Three different ion beams viz. proton, Ni^{10+} and Ag^{11+} are used at different fluences to observe the effect of light ion (proton) and SHI (Ni^{10+} and Ag^{11+}) on the composites. The dependence of electrical, mechanical, structural, thermal and surface properties of polymer composites on the properties of filler material and ion beam are thoroughly examined in the present work.

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