CHAPTER 1

Introduction

This Chapter starts with an introduction of polymer and polymer composites. The importance of ion beam irradiation in the field of materials science and present day technologies is explained. It also includes brief description about energy loss mechanism of ion beam. A detailed literature survey of polymer/ composites and objective for the present work is emphasized in this chapter.

1.0 Introduction of Polymer

Polymer science was developed in the industrial laboratories due to the need to make and understand new kinds of materials i.e. plastics, rubber, adhesives, fibers, and paints. Only much later, the polymer science came to academia. Perhaps because of its origins, polymer science tends to be more interdisciplinary than most science combining chemistry, chemical engineering, materials, and other fields as well. Polymers are basically long-chain molecules of very high molecular weight, often measured in the hundreds of thousands (g/mole). For this reason, the term "macromolecules" is frequently used when referring to polymeric materials.

Some aspects of polymers include their molecular weight and molecular weight distribution and how their atoms are organized within the chain. Many polymers crystallize and the configuration of the crystalline material can depend on the conditions the polymer was crystallized with. Some polymers do not crystallize and are called amorphous polymers. Thermal behavior of the polymer depends on its molecular weight and molecular structure. One of the important thermal properties is the glass transition temperature, the temperature where the polymer goes from a glassy state to a rubbery state. Other molecular structure dependent properties includes; modulus, stress relaxation and elongation to break [1].

1.0.1 Classification of polymer

Polymers can be separated into two different groups depending on their behavior when heated. Polymers with linear molecules are likely to be thermoplastic. These are substances that soften upon heating and can be remolded and recycled. They can be semi-crystalline or amorphous. The other group of polymers is known as thermosets. These are substances that do not soften under heat and pressure and cannot be remolded or recycled. They must be remachined, used as fillers, or incinerated to remove them from the environment.

(i) Thermoplastics

Thermoplastics are generally carbon containing polymers synthesized by addition or condensation polymerization. This process forms strong covalent bonds within the chains and weaker secondary Van der Waals bonds between the chains. Usually, these secondary forces can be easily overcome by thermal energy, making thermoplastics moldable at high temperatures. Thermoplastics will also retain their newly reformed shape after cooling. A few common applications of thermoplastics include: parts for common household appliances, bottles, cable insulators, tape, blender and mixer bowls, medical syringes, mugs, textiles, packaging, and insulation.

(ii) Thermosets

Thermosets have the same Van der Waals bonds that thermoplastics do. They also have a stronger linkage to other chains. Strong covalent bonds chemically hold different chains together in a thermoset material. The chains may be directly bonded to each other or be bonded through other molecules. This "cross-linking" between the chains allows the material to resist softening upon heating. Thus, thermosets must be machined into a new shape if they are to be reused or they can serve as powdered fillers. Although thermosets are difficult to reform, they have many distinct advantages in engineering design applications including:

1. High thermal stability and insulating properties.
2. High rigidity and dimensional stability.
3. Resistance to creep and deformation under load.
4. Light-weight.

A few common applications for thermosets include epoxies (glues), automobile body parts, adhesives for plywood and particle board, and as a matrix for composites in boat hulls and tanks.

Polymers are increasingly being used in a wide variety of applications in electronics and photonics, most of which used polymers in their traditional role as engineering materials (e.g., circuit boards, molded products, wire and cable insulation, encapsulants, and adhesives). In addition, many other unique applications require material properties that only polymers can provide.

1.1 Composites

Composites materials consist of two or more constituents materials bonded together so that the gross properties of the composites are superior to these constituents; e.g., the desirable's properties (high strength, high stiffness and low weight) are maintained, while the undesirable properties (low ductility) are suppressed.

Composite materials are usually designed for use as structural materials. With the rapid growth of the electronics industry, they are finding more and more electronic applications. Due to the vast difference in property requirements between structural and electronic composites, the design criteria are different. While structural composites emphasize high strength and high modulus, electronic composites emphasize high thermal conductivity, low thermal expansion, low dielectric constant, high/low electrical conductivity, and/or electromagnetic interference (EMI) shielding effectiveness, depending on the particular electronic application. Low density is desirable for both aerospace structures and aerospace electronics. Structural composites stress processability into large parts, such as panels, whereas electronic composites emphasize processability into small parts, such as stand-alone films and coatings. Because of the small size of the parts, material costs tend to be less of a concern for electronic composites than for structural composites. For example, electronic composites can use expensive fillers such as silver, aluminum and copper particles, which provide high electrical conductivity [2].

A major driving force behind the development of composites has been to produce materials with improved specific mechanical or electrical properties over existing materials. In addition, polymer composites are useful in applications where the environment would be detrimental to other materials. Cost is ever present in the engineering equation and it is the balance of cost and performance that determine whether or not a polymer composite will be preferred over an alternative structural material option.

1.1.1 Classification of composites

Composites, in general are classified either based on the matrix or the structural components.

(i) Matrix based composites

(i.a) Metal matrix composites (MMC)

Metal matrices of iron, nickel, tungsten, titanium, aluminium, and magnesium are generally used for high temperature usage in oxidizing environment.

(i.b) Polymer matrix composites (PMC)

The reinforcing filler particles are dispersed in a thermoset or a thermoplastic resin in these composites. Polymer Matrix Composites are very popular due to their low cost and simple fabrication methods.

(i.c) Ceramic matrix composites (CMC)

Ceramic matrices are often used with carbon, ceramic, metal and glass fibres. These are used in rocket engine parts and protective shields. Glass matrices are mostly reinforced with carbon and metal oxide fibres. Heat resistant parts for engine, exhausts and electrical components are their primary applications. Carbon matrices with carbon whiskers or carbon fibres as reinforcement are used for desired properties. Carbon in the form of diamond and graphite has high heat capacity per unit weight and therefore selected as ablative materials.

(ii) Structural components based composites

(ii.a) Fibre reinforced composites

These contain reinforcements having much greater length than their cross-sectional dimensions. They may be continuous (with lengths running the full length of the composite) or discontinuous (of short lengths). These fibres may be unidirectional, cross woven or random. Typical examples are glass fibre reinforced plastics, carbon fibres in epoxy resins, wood (a composite of cellulose in a matrix of lignin), vehicle tyres in which rubber is reinforced with nylon cords.

(ii.b) Particulate filled composites

These include materials reinforced by spheres, rods, beads, flakes, and many other shapes of roughly equal axes. The example of these are polymeric materials incorporated with different fillers such as glass spheres or finely divided powders, polymers with fine rubber particles, etc.

(ii.c) Laminar composites

These are composed of two or more layers held together by the matrix binder. These have two of their dimensions much larger than the third. Wooden laminates, plywood and some combinations of metal foils, glasses, plastics, film and papers are laminar composites. Some ceramic and metallic composites also fall in this category.

(ii.d) Skeletal composites

These are composed of continuous skeletal matrix filled by a second matrix. For example, honey comb structure of the polymer filled with additives.

1.2 Advantages of composites

- Very high specific strength. Which means very high strength and low weight
- Great freedom of shape. Double curved and complex parts can be produced simply.
- High degree of integration possible, which means simple integration of stiffeners, inserts, cores, and production of self supporting structures in one or two production cycles.
- Material can be tailored. Which means fit for the loads / performance the end product has to perform during its lifetime
- Excellent chemical resistance against acids, chemicals etc.
- Excellent weather/water resistance. Material has almost no corrosion, takes on little water which leads to low maintenance cost especially on the long run.
- Composites have excellent RAM features (Radar absorbing materials). It's also possible to make special laminates which are radar and sonar transparent.
- Excellent impact habits
- Excellent electrical habits, concerning isolation but also conduction, dielectric habits, EMI shielding etc. Structures can be tailored on RF transparency but can also be made RF reflecting. Great for telecom especially UMTS frequencies.
- Great thermal isolation habits, fire retardancy habits, and high temperature performance.

1.3 Fillers for polymer composites

The idea of adding fillers to thermoplastics and thermosets to improve properties, and in some cases decrease the cost, has been very successful for many years. However, as one desirable system property is changed, nearly all of the other physical and mechanical properties are affected. Hence, it is essential to optimize the filler type, composition and the processing parameters to obtain the best performance from the composite materials. The properties of composites comprising electrically conductive particles dispersed in an insulating polymer matrix have been studied in present work [4–9]. Carbon and metal powders, e.g. Ni, Cu, Ag, Al and Fe, have all been used as fillers. Carbons utilized include carbon nanotubes, carbon fibre, graphite, pyrolytic carbons and carbon blacks, the latter having large variations in purity and morphology. The metal powders offer well-defined morphology and a higher intrinsic conductivity than carbon black. In general, at low filler content the conductive particles are well separated and the composite is insulating, with an electrical conductivity only slightly higher than that of the pure polymer. Initially the conductivity increases slowly with filler concentration, but then rises rapidly over a narrow concentration range to give a high conductivity with only a weak dependence on further increase in filler concentration.

1.4 Impact of polymer composites on present day technology

Polymer films containing metal particles are being investigated for a broad variety of applications in microelectronics, optical filters, magnetic or optical data storage devices. Irrespective of the technological background, the combination of such extremely dissimilar materials as metals and polymers is very attractive from a fundamental point of view. There is a special interest in the study of combinations of polymers with metals that are rather chemically reactive, and so the literature is dominated by studies of these composites. Conductive metal polymer composites, which are lightweight material and combine the inherent processability of polymers with the electrical conductive of metals, have been used in the number of applications such as electromagnetic interface (EMI) shields, antistatic devices, thermistors and conducting coatings. Because of technological importance of these composites, their electrical properties have been widely studied [10-17].

1.5 Application of Polymer and Polymer composites

Polymeric materials are currently used extensively because of their excellent materials properties, like high optical clarity, low attenuation and weathering ability, etc., and are more and more sought for their electronic properties. The attractive materials properties, combined with relatively low cost of production, have led to their widespread use in the manufacture of microwave, electronic and photonic systems. This use is largely attributed to the ease of processing and tailoring their properties to suit a wide range of applications.

The main spheres of existing and potential applications of conductive-polymer composites are listed below:

(i) Electromagnetic interference (EMI) shielding

Electromagnetic interference (EMI) is the electromagnetic (EM) radiation emitted by electrical and electronic equipments. EMI among electronic devices such as computers, mobile phones, radios, and airplane navigators can degrade device performance [18–22]. It also causes potential health hazards such as insomnia and cancer. With the rapid proliferation of electronic and telecommunication devices, control over EMI becomes imperative but remains a challenge. To control the increasing EMI, it is vital to develop new materials with enhanced EMI shielding capacity. According to the EM theory, high frequency EM radiation only occurs in the surface layer of an electrical conductor.

To reduce the impact of EM radiation, better and more versatile EMI shielding materials have always been the topic of investigation and research.

An electromagnetic wave passing through a shielding material layer can be attenuatedin three ways [23],

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.

Metals have been used for EMI shielding due to their high conductivity. Metals suffer, however, from the inherent disadvantages of corrosion, heavy weight, and poor processibility. Moreover, with the miniaturization of equipment and integration of circuits in limited areas, the possibility of leakage increases as the gaps between circuit units become narrower. Also, the conducting material setting on a circuit for EMI shielding can act as an antenna causing malfunctions in the electronic equipments. Electromagnetic interference can be propagated by both conduction and radiation. Shielding enclosures, including those made of conductive composites, are primarily designed to protect against the latter.

(ii) Heating Elements

An attractive use of metal- or metalloid-filled polymers is conductive piping. These self-heating pipes are particularly important in the petrochemical and mining industries where heated hoses, tubes and ducts can facilitate the transport of viscous products or prevent the freezing of liquid feedstocks, water or wastes. Immediate advantages of such composites over alternative approaches are low current densities, absence of a high-temperature sources, reduction of thermal hot-spots, inherent corrosion resistance, and long-term thermal stability.

(iii)Conductive Adhesives

The use of electrically conductive adhesive has expanded rapidly in the microelectronics industry. The major applications for electrically conductive adhesive are die attachment, liquid crystal display (LCD), and surface-mounted assembly of packaged components on printed wiring board (PWB's). Electrical conductive adhesive can be used as solder replacement, interconnection, sealing, electrical shielding, various electronic components bonding, fastening and brazing [24, 25].

Unlike other types of adhesives, electrically conductive adhesives perform two primary functions. First, conductive adhesives form joints with sufficient strength so that they can bond two surfaces, and second, an electrical interconnection is formed between the two bonded surfaces. This dual functionality is usually achieved in composite form by dispersion of particles in an insulating adhesive matrix [26,27]. Conductive adhesives are also useful in joining heat-sensitive materials that would be adversely affected by the heat of the welding or brazing. Conductive caulks are used to join larger gaps when electrical or thermal continuity is needed, or when shielding is required.

1.6 Ion irradiation

Ion beam irradiation has nowadays become useful tool for sterilization of medical items, preparation of biomedical materials, insulation jacketing of power cables, membranes technology, recycling, polymerization, grafting and modification of polymers improvement of thermal and mechanical properties of polymer through vulcanization [28]

1.6.1 Mechanism of ion polymer interaction

Sift heavy ions (SHI) beams play a vital role in the modification of the properties of the materials. It penetrates deep into the materials and create damage resulting from bond breakage, which becomes more important in organic films, since recovery of the damage by annealing becomes too difficult. Bond breakage in organic materials generally resulted in the formation of smaller molecules, many of which may be volatile and easily desorbed changing the chemistry of polymer composites easily and irreversibility.

These changes in the target depend on its temperature and material used; the gaseous environment and type of ions, their kinetic energy and density of the ion flux. As the ion penetrates the solid target it collides with the atoms on the target materials [29-37]. These collisions cause the atoms and electrons to shift slightly from their equilibrium position and which generates excited phonons which can dissipate energy as they propagate. Atoms and electrons can leave their positions in the target, if the transferred energy from the penetration ion is higher than the ionization energy of the target atoms (for the electron) or energy of bonding in molecule (for the atom). If a recoiled atom or electron has enough kinetic energy, it can transfer energy upon hitting other atoms and electrons. This produces a cascade of collision. All defects to the structure caused by the displacement and recoiling of atoms and electrons from a target knows as "spur" of the penetrating ion.

The collision events of flying ions in the target can be considered based on the theory of scattering particles. The energy loss by the penetrating ion at collision with the atoms in the target depends on the angle of ion attack, interaction of ion with atom and electrons and density of the target. If we assume that the excitation process of the electron and atom are not correlated, the energy transfer is the sum of electron and nuclear stopping effects.

$$\frac{dE}{dx} = N[\, S_n(E) + S_e(E)]$$

Where $S_n(E)$ and $S_e(E)$ are nuclear and electron cross section of stopping effects and N is the atomic density of the target [31,37].

1.6.2 Energy loss process of ion in solids

Charge particle penetrating solids losses energy through two processes: (1) energy transfer to electrons, termed as electronic energy loss (S_e); and (2) energy transfer to the atoms of the solids termed as nuclear energy loss (S_n). In both cases the interaction is basically of a Coulomb type. For the electronic case it is purely Coulombic while in the nuclear case it is in the form of screened Coulomb potential. The two mechanisms have different energy dependence. In the electronic case, there is a peak in the energy loss cross section at projectile energies of the order of several MeV, while in the nuclear case, the peak is at much lower energies of the order of 0.1-10KeV. Typical energy loss (stopping power) curves for both cases are shown in Fig.1. In ion interaction theory, the electronic and nuclear energy losses are treated as uncorrelated: if one or other contribution is negligible. It is simply ignored.

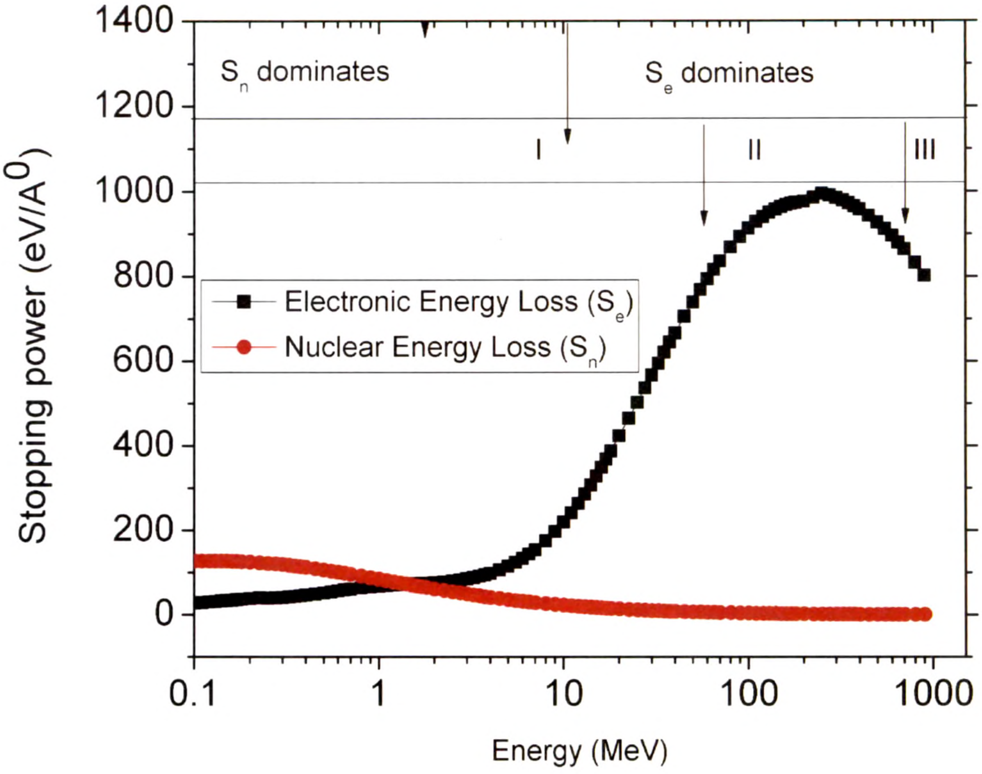

Fig.1 Shows the variation of energy with stopping power (eV/A^0) for 140 MeV silver ions in PMMA.

1.6.2.1 Electronic energy loss (S_e)

The electronic energy loss or stopping can be analyzed by considering three velocity domains (Fig. 1) namely, $\upsilon < \upsilon_0 Z_1^{2/3}$ (region I), $\upsilon \sim \upsilon_0 Z_1^{2/3}$ (region II) and $\upsilon > \upsilon_0 Z_1^{2/3}$ (region III). Here Z_1 is the atomic number of projectile, $\upsilon_0 Z_1^{2/3}$ corresponding to the orbital velocity of K- shell electron associated with the projectile atom. In region I, which is pertinent to the present study, the projectile charge becomes neutral and electronic stopping increases with υ. A simple equation (Eq.) for the electronic stopping of ions in this energy range, derived by Lindhard and Scharff [38].

$$-\left(\frac{dE}{dx}\right) = \xi_e 8\pi a_0 e^2 N \frac{Z_1 Z_2}{Z_1^{2/3} - Z_2^{2/3}} \frac{\upsilon}{\upsilon_0}$$

Where $\xi_e \sim Z_1^{1/6}$, a_0 is the Bohr radius and e is the electronic charge, Z_2 is the atomic number of the target atom and N is the target atomic density. In region II the projectile is partially ionized and the degree of ionization increases with υ. A maximum of the electronic stopping occurs at a velocity slightly about $\upsilon_0 Z_1^{2/3}$. In region III, the electronic stopping decreases with increasing υ. The projectile is considered fully ionized and stripped of its electron in region III while moving at high velocities.

1.6.2.2 Nuclear energy Loss (S_n)

With nuclear stopping one means elastic collisions between the ion and atoms in the sample.

The total stopping power S_t, is the sum of the electronic stopping power, S_e, due to interactions

with target electrons, and the nuclear stopping power, S_n, due to interactions with target nuclei.

$$S_t = S_e + S_n \qquad (1)$$

The derivation of nuclear energy loss uses two main assumptions (1) a simple screened Coulomb potential and (2) the impulse approximation. A universal potential of BBL (Zeigler-Biersack Littmark) has been proposed by Ziegler et. al. [39] for the calculation. Using this universal potential they obtained an analytical expression for universal nuclear stopping for pratical calculations as:

For sufficiently high projectile energies, $S_t >> S_e$.

S_n, in units of eV/(10^{15} atoms/cm^2), for any projectile with energy E (keV), is given by

$$S_n = \frac{8.4622\, Z_1 Z_2 M_1\, S_n(\varepsilon)}{(M_1 + M_2)\,(Z_1^{0.23} + Z_2^{0.23})}$$

where the reduced ion energy, ε, is defined as

$$\varepsilon = \frac{32.53\, M_2\, E_0}{Z_1 Z_2 (M_1 + M_2)\,(Z_1^{0.23} + Z_2^{0.23})}$$

M_1 and M_2 are the projectile and target masses (amu), and Z_1 and Z_2 are the projectile and target atomic numbers. For $\varepsilon \leq 30$ keV,

$$S_n = \frac{\ln(1 - 1.1383\,\varepsilon)}{2[\varepsilon + 0.01321\,\varepsilon^{0.21226} + 0.19593\,\varepsilon^{0.5}]}$$

For e>30 keV, unscreened nuclear stopping is used, and $S_n(\varepsilon)$ simplifies to

$$S_n = \frac{\ln\,\varepsilon}{2\varepsilon}$$

S can be converted to units of MeV/(mg/cm^2) with multiplying by $0.6022/M_2$.

1.6.2.3 Ion range

The ion range is a distance over which an ion dissipates its energy completely via elastic and inelastic collisions. The nuclear energy loss occurs in discreet amounts ranging from eV to serval KeV during each collisions. On the contrary, the electronic loss occurs continuously and acts as a drag force on the moving ion. The mean range (R) of the ion in an amorphous target can be obtained by following equation [40]:

$$R(E) = -\frac{1}{N}\int_0^E \frac{dE}{(S_n(E) + S_e(E))}$$

Where E is the energy of the ion and E is a dummy variable for integration. Due to probabilistic nature of the energy transfer process, the amount of energy loss varies from one collision to other and is reflected as a statistical variation in the range of individual ions. This leads to a strangling in the ion range which is roughly within 30% of the mean range.

1.6.2.4 Straggling

The energy resolution normally composed of two contributions: detector resolution δE_d and energy straggling δE_s. Assuming the two contributions are independent and satisfy poissions statistics, the total resolution δE_l is given by

$$(\delta E_l)^2 = (\delta E_d)^2 + (\delta E_s)^2$$

As energetic particle moves through medium loses energy via many individual encounters. Such a discrete process is subjected to statistical fluctuations. As a result, identical energetic particle which have the same initial velocity, do not have exactly the same energy after passing through thickness t of homogeneous medium. The energy loss E is subjected to fluctuations. The phenomena is called energy straggling. Energy straggling places a finite limit on the precision with which energy losses, and hence depth can be resolved.

1.7 Polymer metal based composites and literature survey

The purpose of this literature review is to provide background information on the issues to be considered in this thesis and to emphasize the relevance of the present study. This thesis embraces some related aspects of polymer composites with special reference to their different properties. The topics include brief review:

(1) Review on carbon black composites

(2) Review on Aluminium composites

(3) Review on copper composites

Traditionally, composites have been fabricated with emphasis on properties such as mechanical strength. However, the concept of composite materials has been extended to electronic applications also. One such class of composite materials is particulate-filled conductive polymer matrix composites. These composites consist of a polymer matrix in which a second phase, which is either a metal or a carbon-based filler, has been dispersed, usually by conventional methods of polymer processing, e.g., injection molding, extrusion. The driving force behind the development of conductive composites has been the need of having light materials, which combine the inherent processability of polymers with the electrical conductivity of metals. Such metal-polymer composites are the strong candidates for a broad range of applications, such as high charge-storage capacitors, electrostriction, etc. [41-68]. However, most of these studies are related to the dc electrical conductivity of these composites. Not much attention seems to have been paid to the dielectric properties and ac conductivity of these composites. This is especially the case with metal-polymer composites. Conductor-polymer systems containing carbon-based fillers, on the other hand, are more thoroughly investigated.

The metal powders offer well-defined morphology and a higher intrinsic conductivity than carbon black. In general, at low filler content the conductive particles are well separated and the composite is insulating, with an electrical conductivity only slightly higher than that of the polymer. Initially the conductivity increases slowly with filler concentration, but then rises rapidly over a narrow concentration range to give a high conductivity with only a weak dependence on further increase in filler concentration. The percolation theory is commonly used to describe the behavior in the region of rapidly varying conductivity [69, 70]. The conductivity rises at the percolation threshold as the conductive particles begin to aggregate to produce chains of particles in intimate contact, providing conductive paths spanning the sample. The conductivity increases rapidly as more percolation paths form until saturation is approached, when the conductivity rises slowly to its maximum value.

This model fails below the percolation threshold, where it predicts that the composite is an insulator. Effective medium theories have been developed that provide a good description of the evolution of the conductivity across the full range of filler concentrations [71-72].

1.7.1 Review on carbon black composites

Many kinds of conductive fillers have been used with insulating polymers such as carbon black (CB), carbon fibres and metallic powders. CB is a material that has found widespread use in a number of applications; the purpose of adding CB filler is to improve the physical properties of polymers, where CB with high structure has a high ability to form a continuous network in the polymer matrix and hence leads to higher conductivity. CB was also used as shielding materials of high voltage cables [73]. Traditionally, CB has been used as a pigment in black ink as well as for toners in copy machines and printers. CB has also been added to rubber to improve its wear characteristics [74]. There are many studies in the literature which concern the dielectric and electric behavior of the polymer/CB composites above room temperature; the general result of these studies is that polymer/CB composites exhibit a positive temperature coefficient (PTC) of resistivity and negative temperature coefficient of resistivity.

In the work carried out by D.S. McLachlan et al [75], they reported the complex ac conductivity of a carbon black composite as a function of frequency, composition, and temperature. It is observed that conductivity increases with filler content and also with increasing temperature. At low content, samples behaves like insulating material but again loaded with higher values of content, sample behaves like semiconducting materials. An anomalous peak in the real dielectric constant as a function of composition is also observed close to the percolation threshold.

Alexander et al [76] reported the anomalous temperature dependence of the electrical conductivity of carbon/PMMA. Temperature dependent conductivities are described well by thermally activated tunneling model that includes a change in the tunneling barrier height, area, and/or width above 100K. This effect is because of chain reorientation due to methyl group rotation on the polymer back bone.

R. Tapilus et al [69] studied experimental characterization and modeling of the electrical conductivity of carbon fibre reinforced polypropylene/polyaniline complex blends. They reported the studies on blend of PP and PANI- complex and their short and long carbon fibre reinforced composites with respect to their electrical properties. It became obvious that in case of carbon fibre reinforced composites, the conductivity was related to various micro structural details, such as fibre concentration, orientation, average length and length distribution. Samples with higher average fibre length became, for instance, conductive at lower fibre loadings, as a result of an earlier formation of electrical conductive pathways. A correlation between the electrical conductivity and a network formation of the PANI- complex was found in injection-molded PP/PANI-complex- blends. The percolation threshold of these blends could be observed at PANI-complex concentration of 6.3 %. The microscopic studied shows that the PANI-complex network formation on surface layer of the samples started at the same concentration. The network structure became denser with increasing PANI-complex content, which resulted in slightly improved conductivity.

T. A. Ezquerra et al [77] reported the electrical conductivity of graphite, carbon black and carbon fibre polymeric composites over a broad frequencies range covering from dc to 10^9 Hz. The dc electrical conductivity in particulate composites, carbon black and graphite exhibit a dependence on the conductivity additive concentration which can be explained on the basis of percolation theory. Lower percolation threshold and higher conductivity values are observed upon comparing carbon black with graphite composites due to difference in particle size. In both systems, it was shown that tunneling conduction among particle could be the predominant conduction mechanism. In both systems conductivity exhibits a frequency dependence which becomes stronger as concentration decreases.

Z. M. Elimat et al [78] reported the AC electrical conductivity of poly(methyl methacrylate)/carbon black composite. It was observed that the temperature dependence of ac conductivity for the given composites is strongly influenced by the conductivity behavior of the CB concentration. The impedance was found to decrease with increasing temperature and frequency. The relaxation time of the conduction process showed temperature, frequency and filler concentration dependence. The percolation threshold was observed at specific CB concentrations. The overall dependence of the electrical conductivity of the composites on temperature was found to be similar to the semiconducting behavior. The overall conduction mechanism is related to electrons transfer through the CB aggregations distributed in the polymeric matrix.

A. Madhuri et al [79] reported the spectral behavior of complex permittivity of carbon black/epoxy composites at low frequency as a function of temperature and filler concentration. The experimental data exhibits a typical dielectric relaxations process below the percolation threshold appeared to be in quantitative agreement with the predication of Jonscher universal response.

Hongfeng Xie et al [80] investigated the electrical resistivity of low density polyethylene/carbon black composites irradiated with $^{60}C_0$ γ rays as a function of temperature. It was reported that the radiation crosslinking is an effective way to eliminate the negative temperature coefficient (NTC) effect of CB-filled polymer composites. In CB/LDPE composites, with increasing radiation dose, the carbon black particles are restricted by crosslinking network. Although with the increasing dose the positive temperature coefficient (PTC) effect is improved, the NTC effect cannot be eliminated completely except for a dose of 400 KGy. These results show that the PTC and NTC behavior originated from the difference in thermal expansion of sol gel in the irradiated composites.

Xiao-Su Yi et al.[81] studied the irradiation influence on the resistivity behavior of carbon-black loaded polyethylene composites. They reported the resistivity behavior of CB loaded PE composites irradiated at different energies, doses and temperatures. The electron beam radiation affects the temperature-dependent electrical behavior in such a manner that the PTC intensity becomes lower and the hysteresis loop becomes larger for both the room temperature (RT) and melting temperature (MT) samples. Particularly for the MT sample, the reduction in PTC intensity is very significant. However, the NTC intensity decreases for both samples, as well as the resistivity decreasing rate.

An extensive works have been carried out on various aspects of polymer carbon black composites, but not many researchers have reported the ion beam induced modification of carbon black filled polymer composites. In view of this, the present work is undertaken to estimate and measure the electrical, structural, thermal and surface properties of polymer carbon black composites in systematic way before and after ion beam irradiation.

1.7.2 Review on aluminum metal composites

Singh et al [10] studied the dielectric properties of aluminum – epoxy composites and reported the increase of dielectric constant with concentration of aluminum flakes.

Moon Kyong Na et al [82] reported the electronic characterization of Al/PMMA[poly(methyl methacrylate)]/p-Si and Al/CEP(Cyano Ethyl Pullulan)/p-Si structures. They studied the capacitance–voltage (C–V) and current–voltage (I–V) behaviors of the aluminum/PMMA/p-Si and Al/CEP (Cyano Ethyl Pullulan)/p-Si MIS (metal–insulator–semiconductor) structures at various frequencies ranging from 20 kHz to 1 MHz and for a bias voltage ranging from 50 V to +20 V. No hysteresis was observed in the C–V curve for both films as deposited and annealed (70–200 ^{0}C).

Kaleem Ahmed et al [83] reported the electrical conductivity and dielectric properties of alumina/multiwalled carbon nanotube composites as a function of MWNT content. They reported that the electrical conductivity increased sharply as the content of MWNT was close to percolation threshold of 0.79 vol%.

Huang et al [84] studied the electrical properties of polyethylene/ aluminum nano composites. It was observed that the dielectric properties (dielectric permitivity and loss tangent) of PE/Al nano-composites depend not only on the Al- nano filler concentration but also depend on the frequency as well as on temperature.

Ellimat et al [85] again studied the ac electrical properties of aluminum- epoxy composites. They have reported that ac electrical conductivity increases with the content of aluminum, temperature and frequency.

Bishay et.al.,[86] reported the electrical, mechanical and thermal properties of polyvinyl chloride composites filled with aluminum powder. It was observed that the percolation threshold, which is the filler concentration after which the conductivity increases many orders of magnitude with very little increase in the filler content of PVC/Al composites, depend upon the measuring temperature, i.e. whether it is below or above the glass transition of the polymer matrix. The electrical conductivity of PVC/Al composites was found to be in the order of 10^{-8} S cm^{-1}, and recommended this composites for its applications in electrostatic dissipation. It was also observed that the gradual decrease of the mechanical strength may be because of higher filler content i.e the interaction between fillers and polymer matrix is impeded and resulting in lower strength of the respective composites.

Hence, metal polymer composites systems have studied extensively on different aspect but radiation induced effect on Al/PMMA and Al/PVC or metal polymer composites has not been reported yet. So this thesis is concerned primarily with the electrical behavior (viz., electrical conductivity, dielectric properties, percolation etc), structural, thermal and surface morphology of the composites before and after ion beam irradiation.

1.7.3 Review on copper metal composites

V.H. Poblete et al. [87] performed the effect of the filler content on the electrical conductivity, percolation threshold and structural distribution of the copper powder particles of different size embedded into PMMA, prepared by compression molding. It was observed that the 10 vol% copper composite presented conductivity between 11 and 13 orders of magnitude higher than that of pure PMMA. The experimental results are in agreement with the theoretical model considering the percolation path theory for a segregated structure.

M. P. Alvarez et. al. [88] reported the submicron copper-low-density polyethylene conducting composites. The conductivity of these composites was measured as a function of copper content, and the composite fabricated with a 10 vol % copper presented a conductivity 15 orders of magnitude higher than that of pure LDPE. The enhancement in conductivity can be explained by means of segregated percolation path theory and the experimental results are in agreement with the theoretical law.

By understanding literature above, it is found that copper metal composites have great potentials for electrical application. So the present study was undertaken with the objective in mind to prepare copper metal polymer composites by unconventional method and evaluate their electrical, structural, thermal and surface morphology of the composites before and after ion beam irradiation.

1.8 Ion beam modification of polymer and polymer composites

In recent years there has been a growing interest towards the modification of surfaces and thin layers of polymers. Ion beam technique is widely used as a flexible and powerful tool for different materials surface engineering, including polymers. The increased attention in the ion implantation of polymeric materials is due to the possibility of precise control of the technological parameters for fundamental research purposes, and also considering some possible applications to device fabrication. The ion irradiation of polymers causes various processes, such as macro-molecular destruction, cross-linking, free radicals formation, carbonization and oxidation [89-91]. The understanding of certain structural re-arrangements influence on the suitable properties of polymers open a way to design devices with required parameters, involving such applications as optical filters, absorbers, reflectors, etc.[92-94]. The optical properties of ion implanted polymers, being of particular interest for modern optoelectronics and photonics, have been extensively explored [95, 96]. Extending the understanding of the ion beam induced structural re-arrangements effect on the relevant optical properties of polymer materials reveals new approaches to the design of devices with desired parameters, and leads to the development of high-performance polymers applications in different optical elements and luminescent devices [97].

It is well known that ion irradiation is an effective way to increase electrical conductivity and induce irreversible changes in the macroscopic properties of polymers, due to chain scission, cross-linking, electronic excitation and mass losses [97, 98-101].

In focus of this study is ion beam (MeV) interaction with some polymers, i.e. poly(methyl methacrylate) (PMMA) and poly vinylchloride (PVC). The Poly (methyl methacrylate) (PMMA) is a prototype polymer of considerable interest for both technological and scientific reasons. PMMA, known as a positive photo-resist for its degradation upon irradiation has been the subject of more investigations in radiolysis than many other polymers. The degradation pathway of this polymer depends upon the way the energy is released in the macromolecular film. Under deep UV, X-ray or particle beams this polymer degrades via a random scission mechanism giving rise to many main chain scissions (and subsequently decrease of the molecular weight), increase of the number of double bonds and release of simple gaseous molecular species such as hydrogen (H_2) and other volatile gases i.e. CH_4, CO, CO_2, CH_3OH and $HCOOCH_3$ (methyl format). The formation of such a volatile species is clearly connected to the degradation of the ester pendent group of PMMA ($-COOCH_3$) [102-107].

PVC is one of the electrical insulators, which is used for manufacturing low tension-range cables and of electronic devices. The modification induced by energy transfer to PVC involves dehydrochlorination, the formation of radicals that generate polarizable units by oxidation as chemical processes and the increase in the polarizability of degraded samples [108-110].

1.8.1 Review on ion beam modification of Polymethylmethacrylate (PMMA), polyvinylchloride (PVC) and polymer composites

A significant number of reports are available in literature about ion- polymer interactions.

H.W. Choi et al [111] studied the structural modification of poly methyl methacrylate PMMA by proton implantation (350 keV) at the ion fluence range from 2x 10^{14} to

$1x10^{15}$ ions/cm^2. The Infrared, Raman, RBS measurements give evidence for the ion induced structural changes of PMMA. The infrared and Raman measurement show the decrease of C=O and C-O bonding and the RBS measurement shows the decrease of oxygen content. This means that pendant group (COOCH3) is readily decomposed and eliminated by outgasing with proton irradiation.

A.Varada Rajulu et al [112, 113] have used light transmission and solubility techniques to study the effect of 28Si ion irradiation on polymer blend (PS/PMMA). They studied the infrared spectroscopic investigation of polymethylmethacylate/ polyvinylchloride blend films irradiated with 28Si ion beam. The infrared spectra show some structural changes due to irradiation at the fluences of $5x10^{11}$, $5x10^{12}$ and $1x10^{13}$ ions/cm^2. Abstraction of hydrogen chlorine, C=O, CH_2 and CH_3 are indicated. The abstraction of HCl increased with fluence in all the blends under study.

A. L. Stepanov et al. [114] synthesized the silver nanoparticle in polymethylmethacrylate by 30KeV Ag+ ion implantation at doses from $3.1x10^{15}$ to $7.5x10^{16}$ ions/cm^2. The optical extinction spectra of the metal nanoparticles in the polymer or/and amorphous carbon were modeled using Mie theory and qualitative agreement was observed with experimental data by taking into account the carbonization phenomena in polymer due to the radiation induced effect.

E. K.Her et al [115] studied the angled nano-scale tunnels with high aspect ratio using a focused ion beam (FIB) on polymethylmethacrylate (PMMA). The fabrication parameters such as ion fluence, incidence angle, and acceleration voltage of the Ga+ ion beam were first studied on the PMMA surface to explore the formation of the nano-scale configurations such as nano-holes and cones with diameter in the range of 50–150 nm at an ion beam acceleration voltage of 5–20 kV. It was also found that the PMMA surface exposed to FIB was changed into an amorphous graphitic structure.

Abdel- Hamid et. al.,[116] reported the electrical resistivity of the unplasticized poly(vinyl chloride) copolymer (UPVC) films irradiated with high-energy proton beam, as a function of both ion energy and ion dose. Upon irradiation with beam energy ranging from 25 up to 37MeV and at a beam fluence of 0.225×10^{10} ion/cm^2, the room-temperature resistivity of the insulating films decreased by four orders of magnitude from its original value. Furthermore, using 25MeV proton beams over a wide range of fluence (10^{11}–10^{15} cm^{-2}), the room-temperature resistivity of the films decreased by only three orders. Then, the dependence of the resistivity on the ion energy and fluence was also observed as the temperature T was progressively increased up to 373 K. The observed behaviour of resistivity agrees with the charge transport model, consistent with a hopping mechanism in the polymer.

Ciurina et al [117] studied that the dielectric properties and thermal stability of gamma irradiated inorganic nanofiller modified PVC. It is observed that the sharp modification in the permittivity and dielectric loss of neat and irradiated PVC samples over the low frequency range may be explained by the interaction between external electrical field and the dipoles formed during high energy exposure. The material characterization is completed by the thermal stability assay based on the accumulation of carbonyl units in the sample matrices, which provides the differences in the molecular level contact between host polymer and fillers.

The different properties (such as electrical, structural mechanical and surface properties) on organometallic/metal polymer composites have been investigated by Qureshi et.al.[118] and Shah et.al.[119] using different ion beam irradiations. It is observed that electrical conductivity and dielectric properties increase with increasing the organometallic content in polymer matrix and also with ion beam fluence [118-119]. However, not much work has been reported in the literature on the polymer metal composite materials irradiated with high energetic ion beam. Inspired by previous work [118-119], we have extended our work to study the effect of high energy ion beam irradiation on conductive metal polymer composites system. In the work reported here, three different types of conductive particles were used as filler viz. carbon black (CB), aluminum (Al), copper (Cu). Poly methylmethacrylate (PMMA) and polyvinylchloride (PVC) were used as polymer matrices for making composites. These composites were irradiated with 140 MeV Ag^{+11} ions at different ion-fluences at Inter University Accelerator centre (IUAC) New Delhi.

1.9 Objective and scope of the research work

The above reviews of the historical developments in the field of composites indicate that there is good scope for improvement in the properties of polymers in particular thermoplastic polymers by incorporating them with conductive fillers. Metals, fibers and carbon can be incorporated in plastics to enhance their performance. So, the present study was undertaken to synthesize the conductive polymer composite systems by chemical route method. The purpose of metal polymer composite system is to use for EMI shielding due to their high conductivity. The review of literatures survey revealed that ionizing radiation induced changes in polymers/polymer composites and undergo drastic modification. Ion beam irradiation of such polymer composites can result in significant changes in the chemical structure of filled filler and polymer surface layers including degradation of chemical bonds and backbone structure and also crosslinking of polymer chains. The properties of composites such as thermal stability, mechanical properties, chemical resistance, process ability and surface properties significantly improved by ion beam irradiation. Therefore, a detailed study on ion induced effects on composite materials is carried out. A significant alteration of the electrical, structural, thermal and surface properties of the composites was obtained due to ion beam irradiation.

In the work reported here, three different types of conductive fillers were used like carbon black (CB), aluminum (Al) and copper (Cu). Polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC) were used as polymer matrices for making composites. These composites were irradiated with 140 MeV Ag^{+11} ions at different fluences.

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