Chapter I

Introduction

This chapter covers an outline of polymer and polymer composites, followed by their classification and applications. The significance of radiation in the field of materials science has been explained. It includes a brief description of heavy-ion and gamma rays and explains the essential process involved in the interaction of ion beam and gamma rays with the polymer. The relevant literature survey and the objectives of the present work have been stated.

1.1 Introduction

Polymers are the most exciting materials for scientific and technological applications in the present times, apart from being a class of materials essential in daily life. They are rapidly replacing traditional materials such as metals, ceramics, and many more, to fabricate optical and electronic devices. The development of polymer science requires a diversity of disciplines because of widely varying chemical structures and polymers' compositions. Hence, their equally varying properties, like cost-effectiveness, size and weight, flexibility, transparency, and ability to form a suitable shape. Such properties can be challenging to be achieved and modified in the case of ceramics and metals. Hence this class of materials, namely, polymers, stand an ideal contender for many industrial applications, too [1–3].

Polymers' properties could modify by incorporating various nanofillers such as metal oxides, carbon nanotubes, organoclays, graphite, etc. [4]. These nanofillers seem to be outstanding materials when they enter into polymer matrices due to their excellent chemical and physical properties, especially high surface to volume ratio. Moreover, polymer nanocomposites' performance is different from that of conventional polymers, depending on the interaction between the polymer and the nanofiller [5,6]. It also depends on the size, content, type, and distribution of nanoparticles in polymer matrices [6].

Most of the research in this field around the world has drawn a lot of attention for improving the properties of polymer nanocomposites and developing new materials with enhanced quality. Several methods have been recently known to enhance polymer nanocomposites' properties, such as heating, mechanical force, and radiation. The results of the radiation effect on polymer nanocomposites show that this method is quite effective in improving the quality and performance of polymer nanocomposites for applications in electronic devices and radiation environments [7]. Modification of chemical, optical, electrical, luminescence, magnetic, and mechanical properties due to irradiation may lead to breakage of bonds and intermolecular cross-linking, chain scission, and carbonaceous creation clusters [8]. After irradiation, the momentous change in properties of polymer nanocomposites heavily relies on the nature of target and irradiation parameters (that is mass, energy, fluence, LET, and many more) [9].

1.2 Radiation

Radiation means a stream of particles or waves emitted or transmitted across a medium or vacuum, e. g., electromagnetic radiation, particle radiation, and so on. Radiation is classified into non-ionizing and ionizing radiation based on the energy of particles, as follows.

1.2.1 Ionising Radiation

The ionizing radiation carries sufficiently large energy that can remove electrons from atoms or molecules in the target, resulting in atoms' ionization. The degree of ionization depends on the type and energy of incident particles/waves as well as on the target material. The ionizing radiation may originate from an X-ray tube or particle accelerator or cosmic particles from outer space or radioactive materials. This type of radiation has many practical uses in construction, medical research, and other fields. Moreover, the interaction of low linear energy transfer radiations with matter is accomplished via three different ways, i. e., Compton scattering, Photoelectric effect, and Pair production, which take place at the atomic level. Ionizing radiation can produce permanent destruction of living tissues. Sometimes it increases the probability of cancer and also can cause genetic damages.

1.2.1.1 Light Ions

Electron (e^-), nucleons (proton or neutron), deuteron (H^2), triton (H^3), and helium are the lighter ions.

1.2.1.2 Heavy Ions

An atom has negatively charged electrons and positively charged nuclei. If one or more electrons are detached from the atom, the atom becomes a positive heavy-ion. Any nucleus heavier than a helium nucleus is known as a heavy-ion, that is, ions from He^4 to U^{238}. The strength of heavy ions is measured in terms of fluence that is the number of ions incident on the target material's unit area.

1.2.1.3 Swift Heavy Ions

Swift heavy ions are heavy ions accelerated to very high energies, especially of the order of MeV to GeV. The accelerated swift heavy ions are obtained using different accelerating devices such as a linear accelerator, a cyclotron, etc. These ions could have enough mass and energy to penetrate solids

through cylindrical zones in the latter. The velocity of swift heavy ions is similar to or greater than that of Bohr electrons.

1.2.1.4 Gamma Radiation

Gamma radiation is electromagnetic radiation that arises in radioactive decay. The energy of this radiation is higher than the energies of bremsstrahlung or annihilation radiation, or x-rays. Thus, gamma radiation has high penetration power. Naturally available sources of gamma rays on earth are radioisotopes such as cobalt-60, potassium-40, while artificial sources are nuclear fusion, nuclear fission, neutral pion decay, and so on. The gamma rays traverse the material, transferring their energy to the target medium through various processes. This radiation loses its energy to the sample through absorption. The absorption of photons takes place through the three processes and results in the formation of fast-moving electrons. The interaction of these electrons with the material produces secondary electrons and so on. Since photons are attenuated, losing their energy continuously during their traverse through the target, the entire bulk material is modified by gamma radiation [10–13]. In polymers, the changes occur at the molecular level, such as cross-linking, chain scission, rearrangement of bonds, volatile species' evolution. The effect of gamma irradiation is defined in terms of absorbed dose that is the amount of energy deposited.

Radiations, namely, X-rays, cosmic rays, and UV-rays (energy higher than 10 eV) are also considered ionizing radiations.

1.2.2 Non-Ionising Radiation

Non-ionizing radiation (For example, Radio waves, Microwaves, Infrared waves, Visible light, and UV-rays) does not have sufficient energy to ionize the atom or molecule of the target material. This type of radiation has little energy to alter the target's electronic, rotational or vibrational configurations of atoms and molecules. However, this radiation is often capable of producing thermal ionization.

1.3 Polymers

Formerly, a Mexico-based rubber industry had started using polymers to make sandals, rubber bands, and bouncing balls. They had used latex of rubber trees with the juice of morning glory plants as a polymer. After that, natural polymer derivatives such as cotton, wool, and many more, started to be used.

The word 'polymer' originated from the Greek words 'poly' – meaning many and 'mer' meaning a large molecule. A polymer contains a long chain of subunits (monomers) of high molecular weights. These monomers are linked chemically in the end to end manner, forming a polymer. Therefore, a polymer is often called a macromolecule.

Due to their ease of processing, light-weights, and accessible film-forming properties, many polymers have been used for science and technology applications. But due to global warming, the preparation and use of new eco-friendly polymers have been currently in demand. Polymers are usually classified according to their sources, structures, preparation/processing, and polymerization type.

1.3.1 Classification of Polymers

1.3.1.1 Classification Based on Source

(i) Natural Polymers

These types of polymers are found naturally. Such polymers occur in humans, plants, and animals. They are categorized into three groups, i.e. Polypeptide, Polysaccharide, and Polynucleotide. These groups are associated with amino acids and proteins, starch and cellulose, DNA and RNA, respectively.

(ii) Synthetic Polymers

Synthetic polymers are prepared to fulfil a wide variety of application requirements, such as in pipes, paints, food packaging, tubing, etc. These types of polymers are artificially made according to the individual requirements - Examples: polyethylene, polyvinyl alcohol, etc.

1.3.2 Classification Based on Processing

These types of polymers classify into three groups based on their response upon heating.

(i) Thermoplastic

These types of polymers become soft when heated. They can be recycled and reassembled by applying pressure and heat. They contain linear or branched molecules, connected through strong intramolecular covalent bonds as well as weak intermolecular van der Waals bonds. Figure 1.1 describes the modification of this class of polymers' intermolecular interaction in the presence of heat.

Besides, they become a frozen liquid on cooling below the glass transition temperature - Examples: polystyrene, polyvinyl chloride, and so on [14,15].

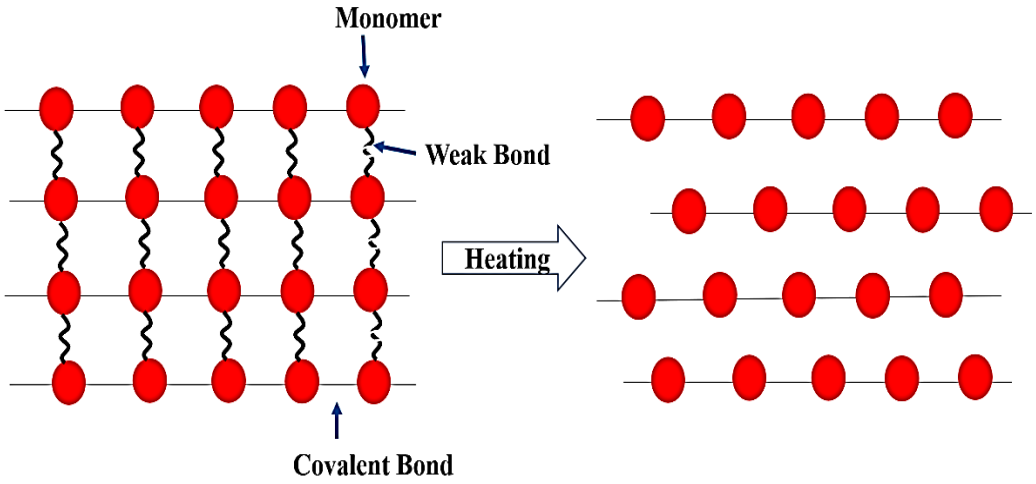

Figure 1.1 Thermoplastic polymer.

(ii) Thermoset

This type of polymers loses its physical strength under applied pressure and heat. They are not reused and recycle. Figure 1.2 represents the change in intermolecular interactions of thermosetting polymer on heating. They become highly cross-linked as well as more rigid upon heating because of strong covalent bonding- Examples: polyurea, Bakelite, etc., [14,15].

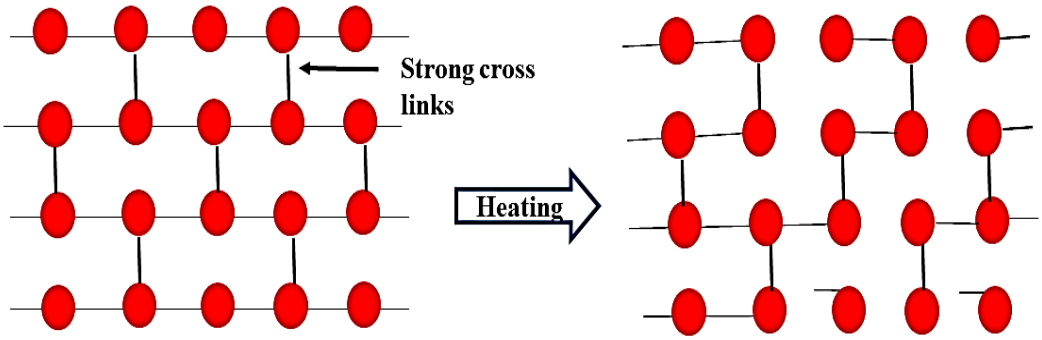

Figure 1.2 Thermosetting polymer.

(iii) Elastomers

Elastomers (Figure 1.3) are polymers that can be stretched to a large extent using a little force. They regain their original shape and size after removing the applied force, such as natural rubber and styrene-butadiene block copolymers.

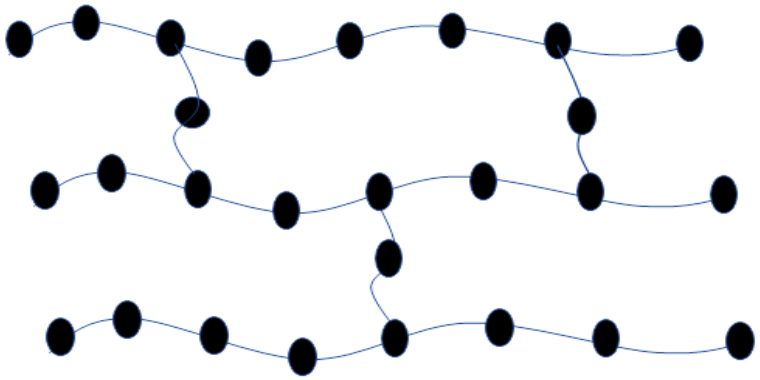

Figure 1.3 Elastomers.

1.3.3 Classification Based on the Structure

Polymers can be divided into three groups based on their structure.

(i) Linear Polymer

This type of polymer consists of many repeating units or monomers that join together, forming a straight linear structure (Figure 1.4). The main chain of a linear polymer has a few pendant groups aligned periodically with the main chain. Linear polymers have a high melting point and high density than the other three groups [14,16]. This type of polymers is more crystalline compared to others - examples: polyvinyl chloride, Teflon.

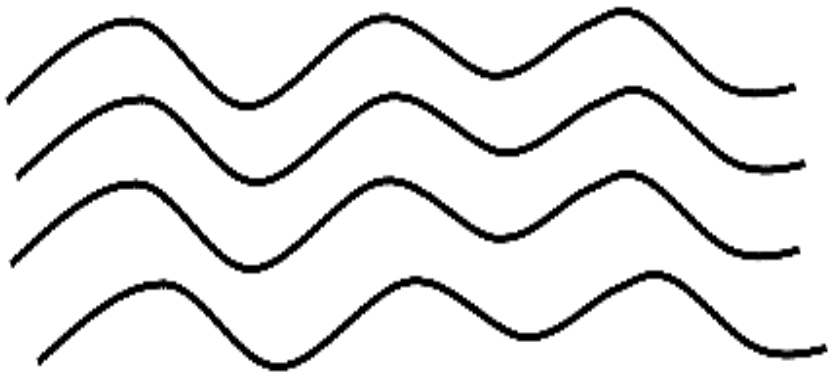

Figure 1.4 Linear polymer.

(ii) Branched Polymer

This type of polymer comprises a large number of repeating units organized in a branched structure (Figure 1.5). They are formed during the side chain reaction and have lower density and melting points [14,16]. Also, the amorphous nature of branched polymer increases with increasing branching of polymer chains - Example: Low-density polyethylene.

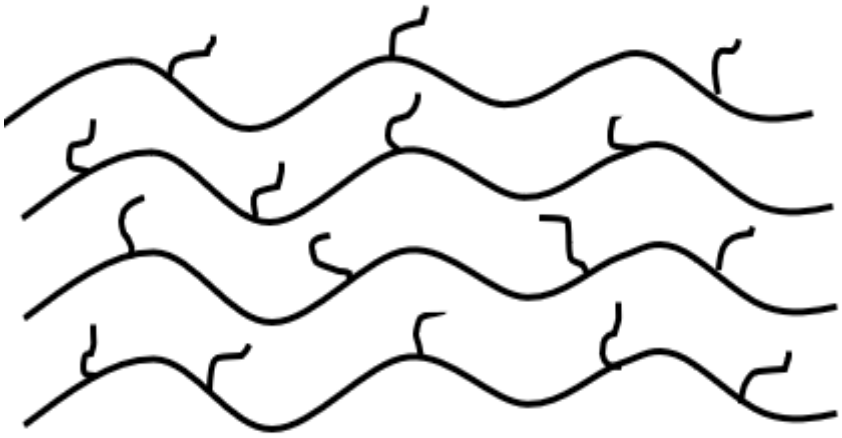

Figure 1.5 Branched polymer.

(iii) Cross-linked Polymer

This type of polymers is produced by joining adjacent linear chains with one another (Figure 1.6). They are formed during polymerization or after polymerization [14,16]. Various linear polymer chains are bonded through strong covalent bonds. Formation of such polymers occurs with the use of bi-functional and tri-functional monomers- For example Melamine.

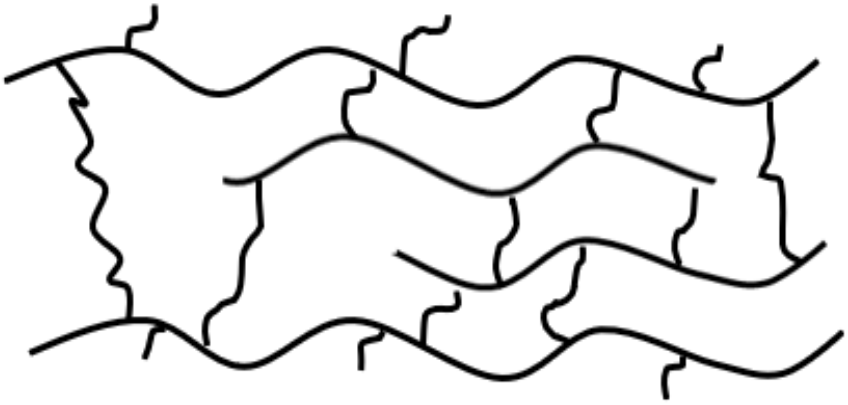

Figure 1.6 Cross-linked Polymer.

(iv) Network Polymer

This type of polymer is formed by joining monomers in a three-dimensional network during polymerization (figure 1.7) [14,16]. They are brittle and hard- Example: Epoxies.

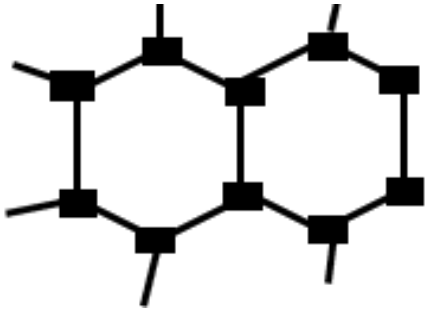

Figure 1.7 Network polymer.

1.3.4 Classification Based on the Polymerization Process

Based on the polymerization process, polymers are divided into two groups: addition or condensation and step-growth or chain growth.

(i) Addition or Condensation

During polymerization, if a monomer's successive addition forms a polymer, it is called an addition polymer. Example: polyethylene.

If the sequential addition of a monomer synthesizes a polymer by eliminating small molecules like alcohol or water, the resulting polymer is known as condensation polymer - Example: Nylon-6,6.

(ii) Step Growth or Chain Growth

In the step-growth polymerization process, the first dimer is prepared by a reaction between bifunctional or multifunctional monomers. Again a monomer is reacted with a dimer to make a trimer. Thus, a monomer is added stepwise to form the long-chain polymer - For example, Polyester, polyamide.

The polymerization process in which an unsaturated monomer or molecule is added to an active site of the polymer chain is known as chain-growth polymerization [14]. Also, in chain-growth polymerization, the cation, anion, and free radicals are added during the polymerization. It is sometimes called the addition polymerization process - Examples: polystyrene, polyvinyl chloride.

1.4 Doped Polymer

Polymers have certain limitations and new polymers that can overcome their barriers to become more expensive [17]. Therefore, one way to remove the barrier is by doping in the inorganic material. This new class of material is called a composite polymer. The mixture of two or more components of different phases with different chemical and physical properties is known as composites. The

properties of the composite are unlike the properties of its constituents. The classification of composites are as follows:

1.4.1 Classification Depending on the Size and Shape of Dispersed Phase

This type of composites is classified into two groups depending upon the dispersed phase's size and shape [18].

I. Particle Reinforced Composites

(i) Dispersion strengthened (containing particles of size about 0.01 to 0.1 micron)

(ii) Large particle composites

II. Fiber-Reinforced Composites

(i) Continuous fiber composites

(ii) Discontinuous and aligned fiber composites

(iii) Discontinuous and randomly oriented fiber composites

1.4.2 Classification Depending on the Matrix

This type of composites is classified into three groups based on the matrices.

I. Polymer Matrix Composites

In this type of composites, the polymer is used as a matrix, while metal, metal oxide, fiber, etc., are used as the dispersed phase. They find applications in medical, packaging, electronics, biomedical equipment, and gadgets, etc. They are divided into three subgroups, depending on the size of the filler [19].

(i) Macro composites

(ii) Micro composites

(iii) Nanocomposites

II. Metal Matrix Composites

In this type of composites, fibers of carbon, boron, alumina, etc., are employed as the dispersed phase. Metal matrix composite offers high strength, toughness, and increased fracture strength. Simultaneously, it has drawbacks like corrosion, high stiffness, expensiveness, and high density compared to other composites [20,21].

III. Ceramic Matrix Composites

In ceramic matrix composites, fibers of ceramic materials are used as the dispersed phase. This type of composites possesses a high melting point and has

lightweight. It finds applications in automobile parts, heat shields, and so on [22,23].

1.5 Applications of Polymer Nanocomposites

The properties of polymer nanocomposites, such as high optical clarity, ease of availability, ease of fabrication, corrosion resistance, abrasion resistance, etc., make them an important class of material. The polymer nanocomposites' properties could be influenced by interfacial bonding and dimensions and concentration of nanofiller. They have many applications, such as paint, adhesive, sensor, EMI shielding, etc. They have also drawn more attention than micrometer size composites and widely used in industrial and academic perspectives such as paint, ink, cosmetics, packaging, and many more [24]. Maji et al. suggested that polymer with inorganic dielectric nanomaterial is useful in manufacturing electronic and electrical devices [25]. The application of polymer nanocomposites can be further increased by modifying their properties in a controlled way by irradiation with gamma rays or swift heavy ions. Irradiated polymer nanocomposites have many applications, such as in wire, cables, electronic devices, medical equipment, etc. Polymer nanocomposite films may be subjected to a radiation environment with a harmful effect after a long time. These materials are often employed in a nuclear reactor, radiation source modules, particle accelerators and space vehicles, etc., [26]. Improvements in polymer nanocomposites' luminescence properties may prove fruitful in luminescence applications as in LED, dosimetry, etc. [27,28]. According to Ortiz-Morales et al., Gamma irradiated polymeric films are useful as dosimeters [28]. Polymer nanocomposites also have medical applications in sterilization of food, medical disposables, packaging, etc., [29,30].

1.6 Nanocomposite Polymer Electrolytes

Nanocomposite polymer electrolyte is used to overcome limitations of solid polymer electrolytes such as low ionic conductivity, poor electrolyte-electrode contact, and mechanical strength. It is formed by dispersing nano-sized fillers in a solid polymer electrolyte. The incorporation of ceramic nanofillers like Al_2O_3, SiO_2, TiO_2, etc., in polymer electrolytes enhances its physical, mechanical, and electrochemical properties. Incorporation of metal oxide nanoparticles has been found to improve free volume in polymer electrolytes by providing new

conducting pathways preferred by ions to traverse, increasing ionic conductivity. Moreover, the physical nature and size of fillers play a vital role in enhancing transport properties.

1.6.1 Applications of Nanocomposite Polymer Electrolytes

Due to industrialization and commercialization, nanocomposite polymer electrolytes are suitable for the direct replacement of various metallic substances. Solid-state electrolytes are generally used in different electrochemical devices such as fuel cells, electrochemical batteries, electrochemical switches, and so on.

1.7 Ion Beam Irradiation

Ion beam irradiation is a relatively recently introduced technique for use in many disciplines of science. It is considered for a wide range of current applications such as disinfection of medical items, biomedical material preparation, modification of physical and chemical properties of solids, etc. [31]. For these applications, the effect of ion beam irradiation on the material needs to be examined in detail. The effect of ion beam irradiation in solid materials depends on many parameters like target material, temperature, ion species, mass and energy of ions, and ion fluences [32–39]. The materials can be modified in two ways, i.e., low energy ion irradiation and swift heavy ion irradiation. The modification of physicochemical properties is achieved using low energy ion implantation. However, the low energy beam can induce surface modification only. Whereas swift heavy ion penetrates deep into the material, loses its energy due to interaction with matter, and produces a narrow disordered zone along its trajectory. The interaction of ion beam with matter is discussed in detail in the following section.

1.7.1 Interaction of Ion Beam with Matter

1.7.1.1 Energy Loss

When an ion beam traverses through a material, it transfers a part of its energy to the nearest target atom or molecule. If the impinging ion's energy exceeds the ionization energy of target atoms or the molecules' binding energy, electrons and atoms are displaced from their positions. If these electrons and atoms have sufficient kinetic energy, they collide with other electrons and atoms and transfer their energy. In this way, cascade collisions are produced. The energy loss of impinging ion at collision time depends on target density, ion, and ion

interaction with atoms and electrons. The energy loss is specified in terms of LET, which is described as the energy loss per unit path length, and its SI unit is eV/nm [38]. Charged particles lose their energy through two modes: (1) Electonic energy loss (2) Nuclear energy loss. Thus, the energy loss of a charged particle per unit length (i.e., stopping power) is the sum of losses due to nuclear stopping and electronic stopping.

$$\frac{dE}{dx} = N\left(S_n(E) + S_e(E)\right) \dots\dots\dots (1.1)$$

1.7.2 Nuclear and Electronic Stopping Powers

1.7.2.1 Electronic Stopping Power (S_e)

Electronic stopping power is a measure of ions' ability to slow down due to inelastic collision with the material's bound electrons. The inelastic term can be used to denote the loss of energy during the process. The number of collisions of the ion with the electrons is large, and the charge state frequently changes while the ion travels in the material. It is not easy to explain every possible interaction for all charge states of the ion. Instead, electronic stopping power is a simple energy function that provides an average of all energy loss processes for different charge states. The interaction between the energetic ion and the electrons is termed as Coulombic type. Moreover, the number of collisions in electronic stopping is large compared to that in nuclear stopping. The formula for electronic stopping power derived by Bethe and Bloch is as follows [40,41]:

$$S_e = -\frac{dE}{dx} = \frac{4\pi e^4 Z_P Z_t N_t}{m_e v^2}\left(log_e\left(\frac{2m_e v^2}{I}\right) - log_e\left(1-\frac{v^2}{c^2}\right) - \frac{v^2}{c^2}\right) \dots\dots (1.2)$$

where, v = velocity of projectile ions, Z_p and Z_t are the atomic numbers of projectile ion and that of target atom, respectively; e, m_e, and N_t are the charge and the mass of the electron and the number density of target atoms, respectively. I denote the ionization potential of the target material. Equation (1.2) is commonly employed for ions with velocities higher than the velocity of orbital electrons of the target atom.

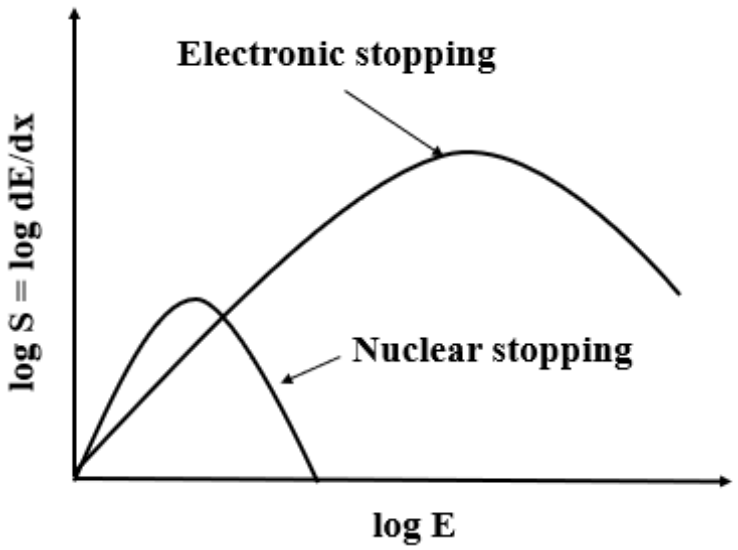

Figure 1.8 Comparison between Electronic and Nuclear stopping for Swift heavy-ion.

1.7.2.2 Nuclear Stopping Power (S_n)

Nuclear energy loss is the energy loss due to the elastic collision of ions with target nuclei and results in atoms' displacement. The colliding particle imparts more energy than the threshold energy for the displacement of atoms. This energy is needed to overcome the binding energy, and it causes atomic displacement. The energetic ion interaction with the target atom is represented by screened Coulomb potential. In the lower energy range, the electronic stopping is weaker than the nuclear stopping, as shown in figure 1.8.

1.7.2.3 Ion Range

The ion range is defined as distance travel by ion, in which ion loses its energy through elastic and inelastic collisions, and then it comes to rest. The ion range depends on the ions' mass and energy and the stopping power of the target. There is a discontinuous change in nuclear energy loss from an eV to several keV during each collision, while continuous changes are seen in the electronic energy loss. The mean ion range for ion having energy E is given as follows [42]:

$$R(E) = -\frac{1}{N}\int_{0}^{E}\int \frac{dE}{\left(S_n(E) + S_e(E)\right)} \dots\dots\dots\dots (1.3)$$

where E represents the energy of the projectile ion. The energy transfer is probabilistic, which implies a variation of the energy loss from one collision to another collision, resulting in straggling of ion range.

1.8 Gamma Irradiation

Interaction of gamma rays with matter takes place through three major processes: Photoelectric effect, Compton effect, and Pair production. During the passage of gamma rays in the medium, the probability of their absorption depends on the target parameters such as density, thickness, and cross-sectional area. Also, these processes depend on the photon energy and atomic number, as shown in figure 1.9.

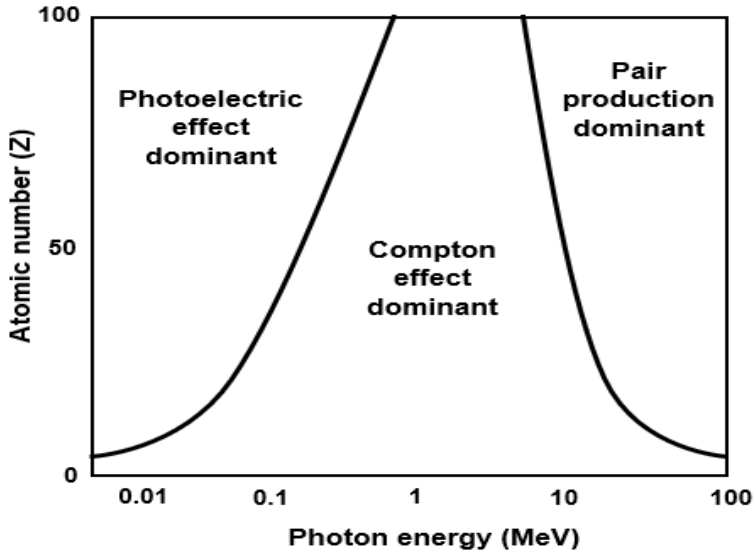

Figure 1.9 Atomic number (Z) versus Photon energy (E) diagram.

1.8.1 Photoelectric Effect

In this effect, a gamma photon interacts with a tightly bound orbital electron, and then it disappears. This results in the subsequent ejection of the orbital electron creating a vacancy. This ejected electron is known as the photoelectron. Then, the outer orbital electron tends to occupy this empty state, resulting in energy emissions. Figure 1.10 depicts the schematic diagram of the photoelectric effect. Photoelectric interaction is related to the energy of the incident photon (E) and the atomic number of attenuating medium (Z).

$$\text{Probability of photoelectric interaction} \propto \frac{Z^n}{E^3} \ldots\ldots (1.4)$$

where n varies from 3 (for low energy gamma rays) to 5 (for gamma-ray of high energy). The photoelectric effect is more significant for the target of high atomic number and photon energy less than 1 MeV. Moreover, the possibility of photoelectric absorption varies with the wavelength of incident gamma radiation.

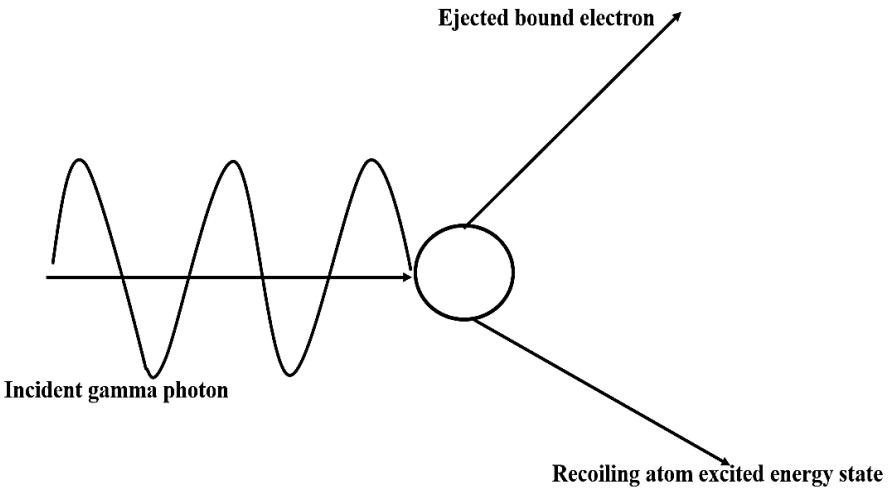

Figure 1.10 Schematic representation of the Photoelectric effect.

1.8.2 Compton Effect

In this process, a gamma-ray photon collides elastically with an electron, which is loosely bound or free in the target material. During the collision, the incident photon imparts a part of its energy to the electron and produces another photon of lower energy, travelling in a different direction. A schematic representation of the Compton effect is shown in figure 1.11.

$$\text{Probability of Compton interaction} \propto \frac{Z}{E} \ldots\ldots\ldots\ldots (1.5)$$

This effect is important for the target of high atomic numbers. The probability of Compton interaction depends on the number of electrons present in the target atom via which a photon passes.

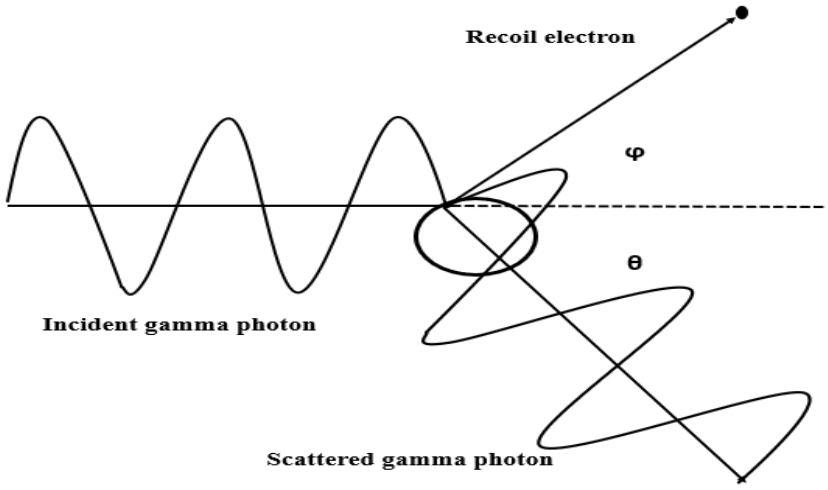

Figure 1.11 Schematic representation of Compton effect.

1.8.3 Pair Production

In this effect, a gamma-ray with energy higher than 1.022 MeV can produce the electron-positron pair in the presence of a strong electromagnetic field surrounding the nucleus (Figure 1.12). If the photon has energy higher than 1.022 MeV, the excess energy converts into kinetic energy of electron and positron.

$$\text{Probability of Pair production} \propto Z^2\,(\mathrm{E}-1.02) \ldots\ldots\ldots (1.6)$$

The probability of pair production varies with the energy of an incident photon. For high-energy gamma radiation, the pair production becomes more significant than the above two processes.

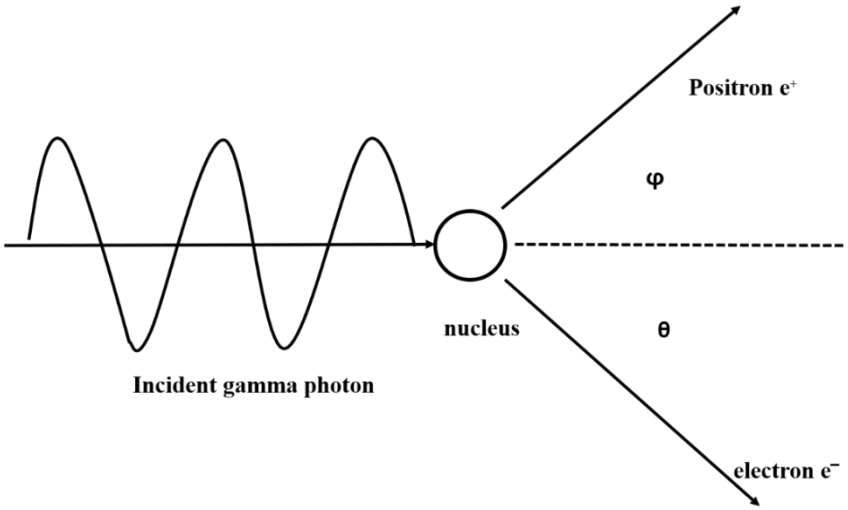

Figure 1.12 Pictorial representation of the Pair production process.

1.9 Effects of Ionising Radiation on Polymers

When polymeric materials are exposed to ionizing radiation such as gamma rays and heavy ions for some time, major processes are observed, as follows:

(i) Chain Scission and Cross-linking

Both processes, namely chain scission and cross-linking, co-occur due to irradiation. However, one of them continues to dominate over others, depending on ion beam parameters, nature of radiation condition, and target type.

Chain scission is the process that leads to a reduction in molecular weight and mechanical strength by breaking down a few bonds of the main chain. At the same time, cross-linking escalates the mechanical strength as well as molecular weight by the formation of the lateral bond between free radicals or molecules of

two or more dissimilar polymer chains of the polymer. Moreover, both processes modify the mechanical, optical, and electrical properties of materials.

(ii) Liberation of Gaseous Products

During gamma or ion beam irradiation, a few low molecular weight gases like H_2, CO_2, CH_4, and many more, liberate due to cleavage of some bonds at the polymer's main and side chains [43]. Sometimes, few gaseous products such as CO_2 may trap in the polymer, which gradually increases the local stress, leading to cracking and crazing [44].

(iii) Color Centers

Radiation-induced defects like anions, cations, free radicals, etc., generally cause a decrease in the bandgap, therefore, inciting the $\pi \rightarrow \pi^*$ transition. These delocalized π electrons are excited after absorbing visible light, which results in the alteration of the material's colour. This colour change depends on which colour of visible light is absorbed first. For example, the first colour absorbed by the material is energetic blue light, then the material's colour is changed from pale yellow to reddish-brown. Also, It may turn in black after being exposed to the high irradiation dose.

(iv) Formation of Unsaturated Group

Irradiation of polymeric materials by gamma rays or heavy ions causes the polymeric chain's scission, resulting in the formation of double or triple bonds. For instance, the yield of hydrogen gas during irradiation is proportional to the formation of main chain unsaturation [45]. Irradiation on polyvinyl chloride produced many unsaturated bonds, which modified the infrared and visible absorption spectra and created stable polyenyl radicals [46]. Also, the formation of triple bonds was noticed in polymers [47].

1.10 Literature Survey

1.10.1 Review on Aluminum Oxide

Aluminum oxide nanoparticles have outstanding properties, namely, high thermal conductivity and mechanical strength, good electrical insulation, high adsorption capacity, and, besides, they are inexpensive and non-toxic. Over the past few decades, these nanoparticles have found much potential for a wide range of applications such as packaging, biomedical applications, the automobile

industry, catalysis, etc. Several reports are available on the characterization of aluminum oxide nanoparticles and their polymer nanocomposites.

Investigation of the luminescence properties of Al_2O_3 has been reported by Kostyukov et al. [48]. Nagabhushana et al. [49] have studied the change in structural and luminescence properties of Al_2O_3 nanocrystals due to 120 MeV Au^{9+} irradiation. Sengwa et al. [50] have prepared PEO/Al_2O_3 polymer nanocomposites. They have studied the structural and electrical properties of PEO/Al_2O_3 polymer nanocomposites. Moussout et al. [51] reported the thermal behaviour of Chitosan/ Al_2O_3 polymer nanocomposites. Canimkurbey et al. [52] studied the effect of Al_2O_3 on the dielectric properties of processed PVA. They reported that the device made from 70% Al_2O_3 with PVA showed behaviour similar to the p-type organic field-effect transistor. They have suggested that this material is a good candidate for industrial applications such as large-area sensor arrays. Masoud et al. [53] reported the influence of Al_2O_3 on thermal, spectroscopic, structural, and electric properties of PEO/$LiClO_4$ polymer electrolytes. Their sample was prepared using a solution casting method. Pradeepa et al. [54] prepared PVAc/PMMA- $LiClO_4$-Al_2O_3 nanocomposite polymer electrolyte and reported the effect of Al_2O_3 on electrochemical properties of PVAc/PMMA- $LiClO_4$ polymer electrolytes.

Hence, Aluminum oxide doped polymers have been studied extensively for different purposes. Still, irradiation effect on structural, optical, luminescence, thermal and electrical properties of Al_2O_3 doped polymers has not been reported yet. Chapter 3 reports the change in structural, optical, electrical, and luminescence properties of PS/Al_2O_3 nanocomposites due to gamma and swift heavy ion irradiation.

1.10.2 Review on Europium (III) Oxide

Rare earth sesquioxides have gained more attention because of their properties and functionalities, making them a possible candidate for many applications in modern technology. Europium (III) oxide is chosen for our experiment because it is a red-emitting phosphor among rare earth sesquioxide [55,56]. Many reports are available on the synthesis and characterization of Eu^{3+} ions doped polymer composites.

Umamaheswari et al. [57] synthesized europium (III) oxide decorated reduced graphene oxide. They reported that it could be used as an amperometric sensor for chloramphenicol – it can sense as low a concentration as 1.32nM. Kibombo et al. [58] developed a europium oxide doped TiO_2 aerogel photocatalyst. The photocatalytic property of this material is better than that of pure TiO_2. Dehelean et al. [59] synthesized $_xEu_2O_3$:$_{(100-x)}[4TeO_2.PbO_2]$ (x= 0-50%) glasses. They have studied their structural, spectroscopic, and luminescence properties using Raman, electron paramagnetic resonance, and photoluminescence spectroscopies. Europium (III) oxide and gold deposited europium (III) oxide have been synthesized by Aazam et al. [60]. The deposition of gold was carried out using the photoassisted deposition method. They have studied photocatalytic activity for degradation of atrazine under visible light and also investigated their luminescence properties. They reported that the gold deposited europium (III) oxide has higher photocatalytic activity than europium (III) oxide. Dandekar et al. [61] fabricated $Eu(TTA)_3$phen/PVDF-PS, $Eu(TTA)_3$phen/PVDF-PMMA, and $Eu(TTA)_3$phen/PS-PMMA nanofibers for photoluminescent fabric designing. They have studied structural, spectroscopic, luminescence properties and surface morphology of these composites using x-ray diffraction, FTIR, photoluminescence, and SEM. Chitosan$_n$[C_2mim][$Eu(SCN)_4$] membranes were synthesized by Leones et al. [62]. They have investigated structural, electrical, luminescence properties and surface morphology. They suggest that this material is a good contender for electroluminescent devices. Alves et al. [63] prepared chitosan/europium triflate polymer electrolytes. They studied their structural, photoluminescence properties and surface morphology. Garcia-Torres et al. [64] have studied the photophysical properties of $Eu(tta)_3$ (phen)/polymer hybrids. They have used polyvinyl butyral, polysulfone and polyurethane as the polymer matrix. They have concluded that this material can find potential applications in optical devices fabrication.

Hence, Eu^{3+} based composites are investigated extensively for various attributes, but the radiation effect on multiple properties of Eu^{3+} based polymer composites has not been reported yet. So the work reported here primarily deals with the luminescence, structural, electrical, thermal properties and surface morphology of pristine and irradiated polymer composites of Eu^{3+}.

1.10.3 Review on Silicon Dioxide

Silicon dioxide nanoparticles are normally used in all metal oxide nanoparticles to increase polymer electrolytes' ionic conductivity. Singh et al. [65] investigated PVA-PVP-NaI- SiO_2 nanocomposite polymer electrolytes' electrical transport properties. Tański et al. [66] synthesized PVP/SiO_2 nanofibrous composite and investigated these composites' optical properties. Singh et al. [67] reported that the tensile and flexural properties of SiO_2/epoxy improved as a function of nanoparticles. Hema et al. [68] prepared PVA:PVdF:$LiCF_3SO_3$:SiO_2/TiO_2 nanocomposite polymer electrolytes and studied nanofiller's effect on electrochemical, mechanical and thermal properties of polymer electrolytes. Ketabi et al. [69] investigated the effect of silicon dioxide nanoparticles on the crystallinity and ionic conductivity of poly(ethylene oxide) (PEO)–1-ethyl-3-methylimidazolium hydrogen sulfate polymer electrolyte. They reported that the electrochemical performance of EDLC devices made from these nanocomposite polymer electrolytes exhibited a high capacitive response at 1 V/s. Zhang et al. [70] investigated the loading effect of SiO_2 nanowires on electrochemical and mechanical properties of P(VDF-HFP) based polymer electrolytes. Synthesis of [PEI- SiO_2]- LiTFSI nanocomposite polymer electrolyte by solution casting method and study of ionic conductivity and optical properties as a nanofiller function was reported by Pehlivan et al. [71].

1.10.4 Review on Polystyrene

Polystyrene is the most popular thermoplastics, exhibiting outstanding properties like low specific weight, low electrical conductivity, transparency, low production cost, mechanical flexibility, excellent resistance against strong acids, etc. Besides, it shows some disadvantages such as brittleness, poor UV resistance, and sensitivity to food and chemicals having high oil content. Many reports are available for the preparation and characterization of polystyrene-based polymer composites/nanocomposites.

Gao et al. [72] synthesized and characterized PS-$(MOBA)_3$-Eu(III) and PS-$(FBA)_3$-Eu(III) in which methoxy benzoic acid (MOBA) and formyl benzoic acid (FBA) bonded to the side group of polystyrene. Methoxybenzoic acid (MOBA) and Formylbenzoic acid (FBA) contain the methoxy group (electron-donating substituent group) and formyl group (electron-withdrawing substituent

group (formyl group), respectively. The luminescence properties of Eu^{3+} were drastically enhanced due to the presence of such acids. Demkiv et al. [73] studied the luminescence and kinetic properties of PS/BaF_2 polymer nanocomposites. Tripathi et al. [74] studied non-linear optical properties of Cds/PS nanocomposites. They reported that the absorption region was shifted from the UV region to the visible region due to doping of Cds nanoparticles. PL emission spectra of PS/Cds nanocomposites in the yellow and green regions were reported. Mingwang et al. [75] studied the variation of the refractive index of PS as a function of electronic energy loss values at a fixed fluence of 1×10^{12} ions/cm^2. The film was irradiated with 1.157 GeV ^{56}Fe ions at room temperature. The refractive index was observed to decrease with increasing electronic energy loss value, while the extinction coefficient was seen to increase. They have also studied the change in an extracted track radius with electronic energy loss. S Kumar et al. [76] reported the growth in optical, structural, and chemical properties of pristine and 60 MeV Ni ions irradiated Ni and Cu metal-doped PS/CdS nanocomposites. They reported the shifting of optical absorption peaks due to doping and ion beam irradiation. The effect of doping of Ni metal is more pronounced than Cu metal.

A few works have been reported on gamma and SHI irradiation on the properties of polystyrene-based composites. In the present study, aluminum oxide nanoparticles and europium (III) oxide doped polystyrene films were synthesized using the solution casting method and studied for change in their optical, thermal, luminescence, electrical and structural properties due to irradiation.

1.10.5 Review on Polyvinyl Alcohol

PVA is a biodegradable polymer with exceptional properties like high tensile strength, excellent resistance to alkalis, abrasion resistance, and non-toxicity. It is currently used in biomedical and biochemical fields due to its biocompatibility. The ionic conductivity of polyvinyl alcohol is increased upon adding inorganic materials like acids, salts, and nanoparticles. Acids such as oxalic and phosphoric acids can donate loosely bound hydrogen. The hydroxyl group of PVA picks up hydrogen from these acids when doped in a controlled way. It results in increased ionic conductivity. The nanofillers such as Al_2O_3, SiO_2, TiO_2 affect the PVA dipole orientation, and the thermal history finds the

flexibility of the polymer chains for ion migration. These nanofillers improve the transport properties and the electrode/electrolyte interface's stability and resist crystallization [77].

Karaman et al. [78] synthesized PVA-H_2SO_4-H_3BO_3 GPE and studied their electrochemical performance. They suggested that PVA-H_2SO_4-H_3BO_3 GPE is a potential candidate for a supercapacitor application. Ahmad et al. [79] reported the possible use of $(PVA)_{0.7}$ $(NaBr)_{0.3}$ $(H_3PO_4)_{xM}$ solid membrane in Phosphoric acid fuel cell application. The addition of H_3PO_4 to the PVA-NaBr polymer electrolytes has been proved to be a convenient method to increase the ionic conductivity of membranes to 4.3 x 10^{-3} S/cm at ambient temperature. Akbulut et al. [80] fabricated a solid-state supercapacitor cell, which contained 3D nanostructured MnO_2/CNT as a microelectrode array on graphite foil and H_3PO_4/PVA as the electrolyte. It showed a high capacitance value of 1.4 F at 1mV $\cdot$ s^{-1}. It exhibited retention of higher than 89% of capacitance after 3000 cycles with discharge current 20 mA and suggested its potential applications in photovoltaic cells, renewable energy storage devices, and wearable electronics.

Prajapati et al. [81] reported the effect of gamma irradiation on the electrical properties of PVA – H_3PO_4 complexed electrolytes. They studied variation in ac conductivity and dielectric constant with frequency, temperature, and radiation dose. They concluded that CBH model is useful for studying the electrical conduction mechanism in this complex system.

Prajapati et al. [82] also studied the effect of 50 Mev Li^{3+} ions on PVA-H_3PO_4-Al_2O_3 thin film (70:30:10) at different fluences. The film was prepared using a solution casting method. They observed a decreasing trend in percentage degree of crystallinity with ion fluence, which was explained using XRD and DSC analysis. They also observed that beyond critical fluence, conductivity decreases.

Earlier attempts have been made to enhance the conductivity of pure PVA by adding various acids and/or salts. But the low ionic conductivity of polymer electrolytes limits their application at ambient temperature. In the present study, (H_3PO_4) doped polyvinyl alcohol matrix along with SiO_2 nanoparticles were synthesized using the solution casting method, and change in different properties concerning gamma irradiation dose and ion fluence was studied.

1.10.6 Radiation Effect on Polymer

The effect of radiations such as electromagnetic (e.g. UV, X-ray, or Gamma photons) or particles (electron, neutron, or other charged species) on polymers have been widely studied, while the effect of SHI irradiation has received considerable attention over the past few decades. Ion beam irradiation modifies physicochemical properties of the polymer such as solubility, molecular weight, mechanical, electrical, and optical properties by deposition of the energy of ions in the material. It can result in processes such as chain scission, cross-linking, alteration of unsaturation, radical formation and loss of volatile segments, etc. [41,83]. The magnitude of these processes depends upon the properties of the polymer, energy of ions, and irradiation condition. These complex processes have been evidenced by the change in water solubility and molecular weight distribution. During irradiation, the evolution of hydrogen gas and abundant molecule species occur as a consequence of scission from the side group of the main chain as well as the pendant side group. In cross-linking, the double and triple bonds are formed by joining radical pairs or two dangling ions of neighbouring chains.

Thus, understanding the influence of structural rearrangement on polymer properties brings a new approach for designing devices. The radiation effect on polymers' physicochemical properties needs to be investigated, especially when a device is made from such a polymer employed in the radiation environment. The optical properties of SHI irradiated polymer are of particular interest for optoelectronics and investigated by Lata et al. [84]. Significant improvement in optical and structural properties of Kapton-H- polymer after ion beam irradiation has been reported by Gupta et al. [85]. Luminescence properties of PMMA/ZnO nanocomposite films are enhanced because of the change in the microstructure of PMMA after SHI irradiation [86]. Dosimetry characteristics of Polystyrene-MWCNT nanocomposites have been studied by Mosayebi A. et al., [87]. They reported that these nanocomposites showed higher sensitivity at a lower dose rate and may employ as a therapy level dosimetry system. Rathore et al. [88] investigated the effect of 55 MeV C^{5+} ion beam irradiation on thermally stimulated properties of double Polycarbonate/Polystyrene double-layered samples. They observed momentous change in thermal stimulated properties such

as thermal stability, glass transition temperature, heat capacity, activation energy, relaxation time, depolarization current upon 55 MeV C^{5+} ion beam irradiation. Singh et al. [89] studied the effect of Cu^{9+} and C^{5+} ion beams on the optical properties of CR-39 and Polystyrene polymers. They found that the change in these polymers' optical properties due to Cu^{9+} ion beam irradiation was more than that of C^{5+} ion beam irradiation. Asad Ali et al. [90] studied 50 MeV Li^{3+} induced change in free volume properties of polystyrene using Doppler broadening spectroscopy and Positron annihilation lifetime spectroscopy. They noticed a significant change in the free volume parameter after irradiation. Kumar et al. [76] investigate the effect of dopant and 60 MeV Ni ions on the chemical, optical, and structural properties of Polystyrene/CdS nanocomposites. They reported that the optical properties of these nanocomposites might improve control way using appropriate beam parameters.

Thus quite a several reports are available on the effect of irradiation on polymeric materials. We have used Gamma-ray and C^{6+} ion beam to investigate ion species' effect and their doses on polymeric composites in the present work. The effect of ionizing radiation on structural, optical, luminescence, dielectric and thermal properties has been explained in the respective sections.

1.11 Objective and Scope of Research Work

The main intention of the present research work is to synthesize polymer composites that overcome some of the disadvantages of polymers and study irradiation's effect on polymer composites' properties. Irradiation has been proved as an effective technique to alter the properties of polymer composites. It is necessary for a detailed investigation of the irradiation effect on polymer composites because polymeric materials are widely used as part of the safety systems of nuclear power plants as well as in industrial and medical fields, where they are subjected to high radiation doses.

In the present work, three different fillers were used, namely, Al_2O_3, Eu_2O_3, and SiO_2. Polystyrene and polyvinyl alcohol were used as the host matrices. All samples were irradiated with gamma rays and 90 MeV C^{6+} ions. The pristine and irradiated polymeric films were characterized using powder X-ray diffraction (XRD), Fourier Transform Infrared (FT-IR) Spectroscopy,

photoluminescence, thermoluminescence, UV-Visible spectroscopy, impedance spectroscopy, differential scanning calorimetry, and atomic force microscopy.

1.12 Organization of the thesis

The present thesis is based on planned research work in six chapters.

Chapter 1. gives a brief introduction about the polymer composites, the effect of radiation on polymer materials, etc. Literature surveys on Al_2O_3, Eu_2O_3, SiO_2, Polystyrene, and polyvinyl alcohol along with the objective of the present work are described.

Chapter 2. concerns the basic information of polymer and fillers which were employed in the present work. A detailed methodology for the preparation of samples has been discussed. A brief description of experimental techniques used for the analysis of pristine and irradiated samples is described.

Chapter 3. explains the effect of Gamma rays and 90 MeV C^{6+} ion beam irradiation on Optical, Luminescence and Electrical Properties of Polystyrene/Al_2O_3 Polymer Nanocomposites.

Chapter 4. deals with the effect of Gamma rays and 90 MeV C^{6+} ion beam irradiation on Optical, Luminescence and Electrical Properties of Polystyrene/Eu_2O_3 Polymer Nanocomposites.

Chapter 5. discusses the effect of Gamma rays and 90 MeV C^{6+} ion beam irradiation on Optical and Electrical Properties of SiO_2 doped PVA Nanocomposite Polymer Electrolytes.

Chapter 6. summarizes the results and their significance, conclusion, and future Plan.

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