Chapter – I

Introduction

Abstract

This chapter concerns with the fundamentals of polymers composites and nano composites. The importance of ion beam irradiation in the field of nano science and technologies is explained on the basis of energy loss of ion beam in the polymeric samples. The effects of ion beam irradiation on physical properties of nano composites are explained. The purpose of this chapter is to describe the context of the work, the overall objectives of the study and the structure of the thesis.

1.0 Introduction to rapid pace of polymers and polymer composites:

Polymers are a large class of materials consisting of many small molecules (called monomers) that can be linked together to form long chains, thus they are known as macromolecules. On the basis of different chemical structures, physical properties, mechanical behaviour, thermal characteristics, stereochemistry, polymers can be classified into following ways like natural and synthetic polymers; organic and inorganic polymers; thermoplastic and thermosetting polymers; plastics, elastomers, fibers and liquid resins; atactic, isotactic and syndiotactic polymers.

Polymeric materials are generally insulating or nonconductive materials in nature and normally used in electric and electronic applications as insulators, but polymers are too flexible and too weak to be used in various specific applications. [1-2]. Since the increasing demand for lighter, economic, chemically resistive, conductive materials created a need for new materials often called composite materials.

A composite material composed by material in which two or more distinct structurally complementary substances are combined to produce structural or functional properties not present in either of the individual components. In the world of high tech engineering and materials science, composites are more easily explained by mixtures of chemically different materials that are insoluble in each other and are thus represented by distinct phases: usually a continuous phase (matrix) and a discontinuous phase (may be filler).

1.1 Classification of composites:

Composites may be classified into different types by the way of reinforcement and matrix used in materials.

1.1.1 Classification based on reinforcements:

Composites can be classified as particle-reinforced composites in which particles used as reinforced phase and fiber-reinforced composites where reinforcing phase is in the form of fiber [3]. The particle-reinforced composites can be further classified into large-particle composites and dispersion-strengthened composites based on particle size. Based on fiber alignment and length, the fiber reinforced composites can be classified further into three categories [4],

1. Continuous and aligned
2. Discontinuous and aligned
3. Discontinuous and randomly oriented

1.1.2. Classification Based on Matrix

Based on the matrix used in materials can be mainly classified as [5]

1. Polymer Matrix Composites (PMC)

In polymer matrix composites, the matrix phase is polymer and the reinforcing phase may be metals, fibers or ceramic particles. They are being used in various medical applications and sensing applications.

2. Metal Matrix Composites (MMC)

For metal matrix composites, the matrix is a ductile metal or alloy and the reinforcing medium is continuous like fibers of carbon, silicon carbide, boron and alumina or any others. Also disadvantages of metals used as matrix include corrosion, high density, high stiffness, release of metal ions may cause allergic reactions and not cost effective. Therefore, metal matrix composites are more expensive than polymer matrix composites [6, 7].

3. Ceramic Matrix Composites (CMC)

In ceramic matrix composites, particulates, fibers or whiskers of one ceramic material are embedded into the matrix of another ceramic material. Ceramic composite materials are meant for high temperature applications like heat shield of re-entry spacecrafts.

1.2 Classification of polymer composites:

The polymer composites can be classified into three categories:

1. Macro composites: Polymer macro-composites are heterogeneous composites of polymers and macro sized fillers. The macroscopic characteristics of the composite often reflect its own microstructure.

2. Micro composites: Composites employing micron size fibers with high aspect ratio or fine hollow spheres or fibers as reinforcement are called micro composites. The matrix may be any polymer. The reinforcing phase will be a continuous fiber or short fiber or micron sized fillers such as metal particles. The main advantage of using fibers is to improve strength, stiffness, and thermal stability of composites.

3. Nano composites: Polymer nanocomposites are usually comprised of the composites of polymers with dispersed inorganic nanofillers. The nanofiller can be an insulator, a semiconductor or a metal, and can have spherical, cylindrical, or flake shapes. The polymer (matrix) can be conductive or non-conductive in nature.

Polymer nanocomposites have recently received significant attention because of the new and superior properties (*e.g.* electrical, thermal and mechanical) to conventional composites of these materials and may be synthesized using surprisingly simple and inexpensive techniques [8, 9]. Various aspects can control the physicochemical properties of nanocomposites such as the particle separation, the interphase interactions, the character of the polymer molecular structure, the method of the nanocomposite preparation and so on [10-13]. However we have used nanocomposites in the present work.

1.2.1 Promising Applications of polymer composites/nanocomposites:

Polymers play important role in human life. Other naturally occurring polymers like wood, rubber, leather and silk are serving the humankind for many centuries now. Modern scientific tools revolutionized the processing of polymers thus available synthetic polymers like useful plastics, rubbers and fiber materials.

Commercial and industrial applications of polymer composites/nanocompsoties are so varied that it is impossible to list them all. Only the major structural applications areas is highlighted here which include packaging industry, gas sensing application, oil industry, aircraft, space, automotive, furniture, sporting goods, marine, infrastructure, in electronics, building construction, power industry, medical industry (e.g., bone plates, implants), and in many other industrial products [14].

The progress in doing things much smaller, lighter and faster than before them already been existed has already been going on for many years. This enhanced exactness could facilitate existing products and processes to be more effective/cost effective, hence require less raw materials and energy. This is especially true in the most of fields like IT, electronic and energy industry, space, medical, military and security fields [15].

1.2.1.1 Focussed or Novel application:

(1) Gas sensing:

Polymer nanocomposites have been developed as candidates for different types of sensing applications. The conductive and absorptive properties of insulating polymers doped with conducting materials, and the absorptive properties of insulating polymers with non-conducting fillers are sensitive to exposure to gas vapours. Therefore, they can be used to monitor the existence and concentration of gases in the environment [15, 16].

(2) EMI shielding:

EMI is the kind of environment pollution. Electromagnetic interference (EMI) suppression is another area in which polymer nanocomposites can make great advances. All electronic devices like TV, radios, computers, motors generate and emit radiofrequency waves that can interfere with the operation of electronic components within the same device as well as other electronic devices. Miniaturization of electronic equipment requires components to be packed very close to each other, which increases the problem of electromagnetic interference. When an electromagnetic wave is incident upon a conductive surface, energy is reflected and absorbed. The ability of a material to shield electromagnetic energy, whether it is unwanted energy entering a system or escaping a system, is called its shielding effectiveness (SE) [17, 18]. EMI shielding can be achieved by coating of conductive layer of metal or by making materials from a plastic embedded with metal particles/nanoparticles which is having good conductivity. Metals are more common for shielding because of good conductivity. Also disadvantages with metals used include corrosion, high density, high stiffness, release of metal ions may cause uncertain reactions and not cost effective [6, 7]. Inclusion of metal particles in polymer matrix can solve all the difficulty which is generated with pure metals.

Requirements for shielding:

A material is shielded if the surface of the material is electrically conductive enough to shield against influence from outer fields. Minimum requirements in electric fields as mentioned below

a) Shielding against electrostatic fields

b) Protection against direct charge

c) Static discharge through contact with grounded conductors: a minimum build-up of electrostatic discharging through friction.

The electromagnetic waves can attenuate by shielding materials by three ways of mechanism [19]

a) By reflection at the surface: Reflection requires mobile charge carriers like electrons or holes which interact with electromagnetic radiation. This requirement can be achieved by doping of metal particles in a polymer.

b) By absorption due to thickness of the shield: For absorption, electric and magnetic dipoles require which interact with the field. The electric dipoles may be provided by materials having high dielectric constant or magnetic dipoles by magnetic nanoparticles. Polymers having dielectric constant (> 8) can fulfil the requirement.

c) By multiple reflections: This refers to the multiple reflections at the various surfaces or interfaces in the shield. This can be done by adding nanoparticles or nanoscales so that large surface area or interface area exists in the shield [20].

So the composite materials composed of insulating or conducting polymers doped with metallic particles/nanoparticles serve good for EMI shielding application.

1.3 Science with Ion Beam Irradiation:

Energetic ion beams play a vital role in the field of research and it has been exploited by researchers in different ways in materials science [21]. Ion beam effect on the materials depends on many factors like ion energy, mass of ions, fluence and ion species. The materials modification can be done by two ways, low energy ion (a few tens of keV to a few MeV) implantation and swift heavy ion irradiation (typically a few tens of MeV and higher). The ions lose energy when they traverse through the material which is either used in displacing atoms (of the sample) by elastic collisions or in exciting or ionizing the atoms by inelastic collision. The former is the dominant process at low energies where the displacement of atoms due to elastic collisions is insignificant [22]. In the inelastic collision (cross-section~10^{-16}cm^2) the energy is transferred from the projectile to the atoms through excitation and ionization of the surrounding electrons. The amount of electronic energy loss in each collision varies from tens of eV to a few keV per Angstrom (Å).

The interaction of charged particles with a target can be analysed by considering independently inelastic interactions with target electrons and elastic interactions with screened target nuclei. The former interaction is responsible of the "electronic stopping", (dE/dx)e, that dominates at high velocities, the latter of the "nuclear or atomic stopping", (dE/dx)n that dominates at low velocities.

1.3.1 Ion solid interaction in materials:

Fundamentals of ion solid interaction:

(i) Ion sources:

The basic requirement in this field is the availability of source of energetic ions. There are many small accelerators available and being used exclusively for ion implantation research (energies up to 2–3 MeV). Swift heavy accelerated ions (up to GeV) depending on the material irradiated, being the capacity to access a large range of lower energies using 'absorbing' foils of different thickness and different material.

(ii) Stopping Power:

Once an energetic particle beam strikes matter it immediately begins to transfer energy to the target system. The energy deposition process is commonly described by the 'stopping power' (−dE/dx), the energy transfers per unit path length of an ion on its trajectory. It is also convenient to split up the particle stopping into two basic and dominant energy transfer mechanisms. One arises from 'ballistic' billiard ball type atomic collisions with the target atoms ('nuclear' energy transfer) and the other from excitation and ionization of the target electrons ('electronic' energy transfer). Light ions of any energy, and energetic heavy ions with stopping powers in keV/Å range, deliver much more energy via electronic excitation than by nuclear collisions. For low energy heavy ions with stopping powers in eV/Å range, the nuclear energy transfer dominates.

The total stopping power is then the sum of both components whose reciprocal integral defines the total projectile range. Both stopping powers increase with increasing energy, reach a maximum and thereafter fall away as shown in Fig 1.1

If the energy transferred to the primary atom ‘knocked on’ is sufficiently high, there can then be secondary, tertiary and higher order atomic knock-ons all of which, if sufficiently localized, comprise an energetic atomic cascade in the target as shown in Fig. 1.2.

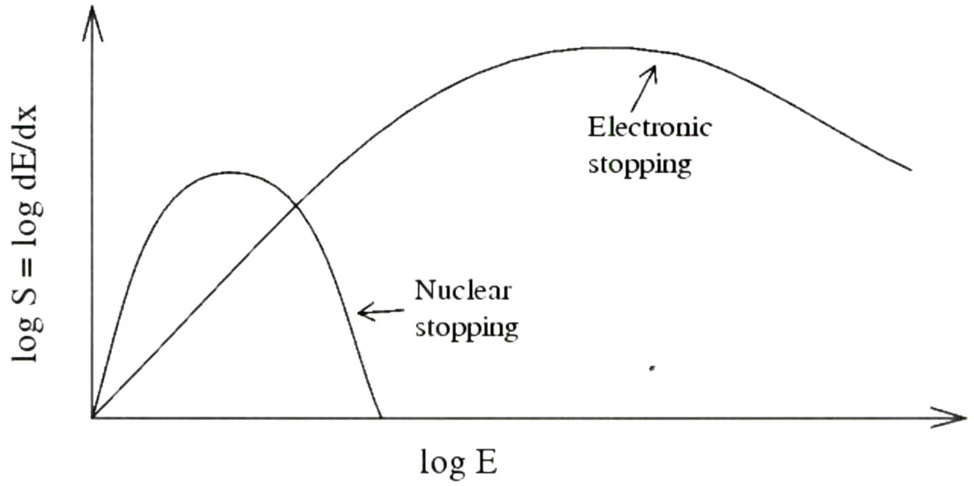

Fig. 1.1 Graph for projectile ion energy versus energy loss

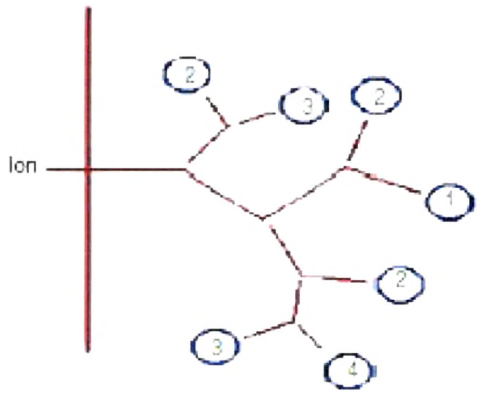

Fig. 1.2 Schematic of ion–solid interaction induced cascade collision

1.3.2 Energy losses:

When an energetic ion passes through a solid, it loses energy through elastic and inelastic scattering processes. The ions lose energy during their passage through the material, which is spent in either displacing atoms by elastic collisions (nuclear stopping) or exciting the atoms by inelastic collisions (electronic stopping). The energy lost due to nuclear stopping is called nuclear energy loss and one due to electronic loss is known as electronic energy loss. Apart from these two events, another mechanism which takes place during slowing down of incident ions is charge exchange process between the ion and the atoms of the solid. This can be expressed as

$$\left(\frac{dE}{dX}\right)_{Total} = \left(\frac{dE}{dX}\right)_{Elect} + \left(\frac{dE}{dX}\right)_{Nucl} + \left(\frac{dE}{dX}\right)_{ChargeExchange}$$

Since charge exchange loss represents a small fraction of total energy loss, which can be neglected.

$$\left(\frac{dE}{dX}\right)_{Total} \cong \left(\frac{dE}{dX}\right)_{Elect} + \left(\frac{dE}{dX}\right)_{Nucl}$$

$$\cong S_e + S_n$$

Nuclear and electronic energy losses are schematically shown in Fig. 1.1.

1.3.2.1 Nuclear energy loss:

Nuclear energy loss is due to elastic binary collision between a projectile ion and target atoms. This is based on the screened Coulomb potential and impulse approximation. If one knows the form of potential between two atoms, one can calculate value of nuclear stopping power.

1.3.2.2 Electronic energy loss:

The energy loss per unit path length of the ion is known as Specific Energy Loss. This is also termed as stopping power or linear energy transfer (LET). In 1913, Bohr first proposed the theory of electronic energy loss S_e of energetic ions in solids [23]. With electronic stopping one means slowing down due to the inelastic collisions between electrons in the medium and the ion moving through it. The term inelastic is used to signify that the collisions may result in excitations in the electron cloud of the ion; therefore the collision cannot be treated as a classical scattering process between two charged particles. Since the number of collisions an ion experiences with electrons is large, and since the charge state of the ion while traversing in the medium may change frequently, it is very difficult to describe all possible interactions for all possible ion charge states. Instead, the electronic stopping power is given as a simple function of energy Se (E) which is an average taken over all energy loss processes for different charge states. It can be theoretically determined to an accuracy of a few % in the energy range above several hundred keV from theoretical treatments, the best known being the Bethe-Bloch formula [24].

1.3.2.3 Overview of the slowing down process:

Energetic ions entering into material medium, it immediately interacts with many electrons simultaneously. In such encounter, the electron experiences an impulse from the attractive Coulomb force as the projectile ion passes its area. Sometimes this impulse may be sufficient either for excitation or for ionization. The energy, which is transferred to the electron, comes from the energetic ion. So, the velocity of the ion will decrease as a result of the encounter. By the time ion interacts with many electrons, so the net effect is to decrease its velocity continuously until it is stopped.

The swift heavy ions can move a few microns to tens of microns in the target because a single encounter of ions with an electron does not deflect from its path. So, these particles pass a definite range in a given material. In the beginning of the slowing-down process at high energies, the ion slows down mainly by electronic stopping, and moves almost in a straight path. The process is schematically illustrated in Fig. 1.3.

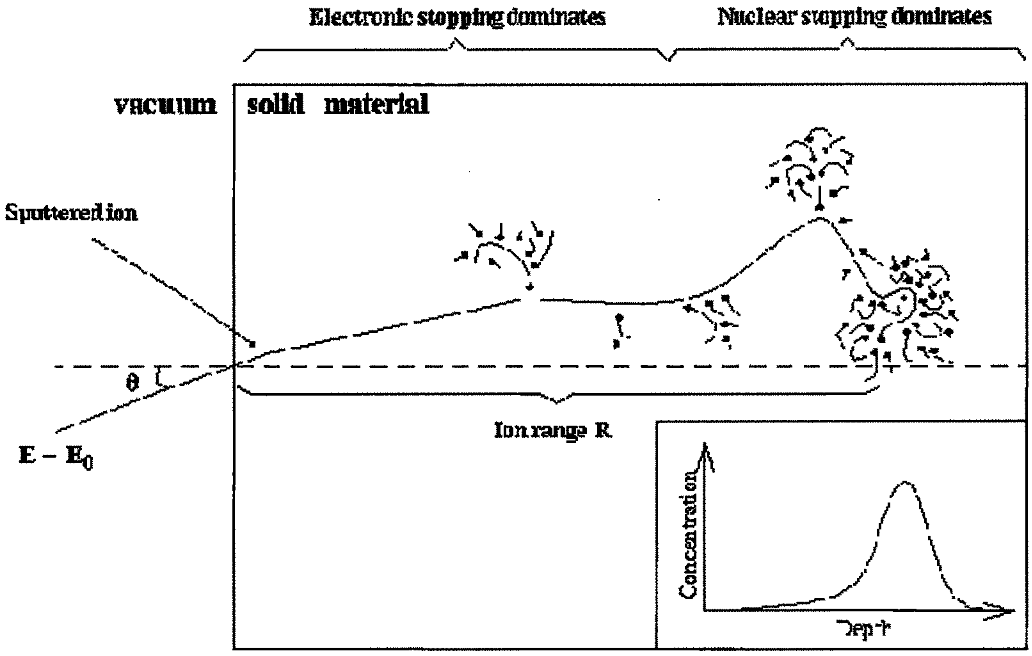

Fig. 1.3 Interaction of ion beam with target material

1.4 Overview on Ion beam induced modification:

1.4.1 Low energy ions:

A study involving ion-solid interactions in the range of eV to few keV is usually called in low energy range. There are two possibilities either materials are made up by ion implantation or low energy ion irradiation.

Low energy ion beam irradiation may have various applications and invariably expose completely new eras in various fields, particularly in materials science and device technology. Low energy accelerators are now standard tools and their exploitation in engineering materials of all kinds of interest: electronic, biological, and metallurgical etc. provide very fruitful activity. Energetic ion beams, when penetrate through the interface of different materials, produce massive atomic transport across the interface which results in many stable, unstable or even thermodynamically non-equilibrium phase formation around the interface. Due to the improved electrical, chemical or optical properties of the ion irradiated materials, ion beam induced mixing of metal/metal or metal/semiconductor systems occupy a major share of the accelerator based materials research.

1.4.2 Swift heavy ions:

In the inelastic collision (cross-section 10^{-16} cm^2) energy is transferred from the projectile to atoms of the matter through excitation and ionization of their surrounding electrons. The amount of electronic energy loss in each collision varies from a few eV/Å to a few keV/Å. For a swift heavy ion (SHI) moving at a velocity comparable to the Bohr velocity of electron, this is the dominant mechanism for transfer of energy to the material causing the modification of its properties. The main difference of materials modification by ion implantation and swift heavy ion irradiation is that in ion implantation the incident low energy ions get embedded in the material cause changes whereas in swift heavy ion irradiation the impinging ions do not get embedded in the materials due to their larger range.

1.5 Ion beam induced modifications in polymeric films:

Polymer/polymer composites materials are scientifically important for research because of their diverse applications like filtration, protective coating, medical science, nanoscale designing, nuclear power plant, space-crafts etc [25, 26]. Studies concerning to the study of the effect of gamma and electron irradiation and swift heavy ions on polymeric materials have been reported in literatures. The modification of polymeric material by irradiation with swift heavy ions has gained considerable interest in the last two decades due to easy access to heavy ion accelerators [27-31]. SHI irradiation of polymers/polymer composites alters the chemico-physical properties considerably. The macroscopic changes are examined in terms of chemical, optical, thermal, magnetic and electrical modifications by means of bond breaking, main-chain scissoning, crosslinking, carbon cluster formation, volatile species liberation, and formation of new chemical bonds [32-34]. Improvement in mechanical, structural and dielectric properties, density, chain length, crystallinity, solubility, and also in the optical transmission properties of the polymers have been reported [34-39]. The nature of changes depends upon properties of polymers, such as the composition and molecular weight, and on the mass and energy of the incident ions and other conditions also.

Polymer nanocomposites with functional metal nanoparticles have much interest due to their cost effectiveness, processibility and high flexibility, rendering possible many applications such as non linear optical switches, magnetic data storage, micro wave absorbers, photovoltaic cells and smart structure [40]. In such kind of applications good adhesion should present between polymer and metal nanoparticles. The interaction between polymer and metal is usually weak but it can be improved or enhanced by means of irradiation. When polymer nanocomposites are irradiated with energetic particles, new adsorption sites might be created which improved polymer-metal adhesion. Irradiation makes possible more prominent polymer-metal bonding and enhances the properties of the nanocomposites [41, 42].

In the present concern, we have used Si^{+11}, C^{+6} ions to study the effect of ion species, energy, fluence on the composites. The effect of ion beam on different properties like dielectric, magnetic, structural and optical properties have been explained in respective sections.

1.5.1. Dielectric properties and improvements due to ion beam irradiation:

The dielectric properties of materials play a fundamental key role in the explanation of physical phenomena in many branches of modern science and engineering. Dielectric spectroscopy a powerful technique provides a linkage between the dynamics of molecular motion of the individual constituents of a complex material and the characterization of its bulk properties. It is important for investigating a variety of dielectric for both electrical and non electrical applications. The dielectric properties are used to describe electrical energy storage, dissipation and energy transfer [43, 44].

There are a number of different dielectric mechanisms, connected to the way a particular medium reacts to the applied field. The electronic polarization occurs in a neutral atom when the electric field displaces the electron density relative to the nucleus it surrounds. Atomic polarization is observed when the electronic cloud is deformed under the force of the applied field, so that the negative and positive charges are formed. Dipole relaxation originates from permanent and induced dipoles aligning to an electric field and heavily dependent on temperature and chemical surrounding. Ionic relaxation comprises ionic conductivity, interfacial and space charge relaxation which predominates at low frequency. Interfacial relaxation occurs when charge carriers are trapped at interfaces of heterogeneous systems. Dielectric relaxation as a whole is the result of the movement of dipoles (dipole relaxation) and electric charges (ionic relaxation) due to an applied alternating field, and is usually observed in the frequency range 10^2-10^{10} Hz [45].

The situation when a constant voltage is applied to a set of juxtaposing capacitor plates. The relation between the amount of free charge, Q, and the voltage drop, V, is $Q = CV$, where C is the capacitance of the capacitor,

$C = \varepsilon_o A/d$, A and d are the cross-sectional area of the plates and thickness between them respectively. ε_o: dielectric permittivity of air = 8.85×10^{-12} F/m.

The relative dielectric constant is then defined as the ratio between the flux density in vacuum and in the dielectric,

$k' = \varepsilon' / \varepsilon_0$

Loss tangent is expressed by,

$\tan \delta = \varepsilon'' / \varepsilon'$

where real part ε' defines insulating properties and imaginary part ε'' describes conductive properties of the dielectric material.

There are reports on the effect of ion beam on the dielectric properties of the polymers. There exists few reports on gamma, neutron and electron irradiation of non polymeric materials. These studies provide frame work to some general idea about the effects expected here.

Dielectric loss/constant increases upon irradaition as it is associated with more pronounced electron transitions, the more electron participate in electron hopping phenonmenon created between amorphous zones of destructed polymers [46].

Conductivity by ion beam irradiations of polymers/polymer composites

The results reported that the increase in conductivity value of irradiated samples is increased with increase in radiation dose. The increase in the conductivity due to swift heavy ion irradiation may be attributed to formation of defects and carbonaceous clusters arising due to scission of the polymer chain [47]. The ion beam irradiation leads to charge accumulation at these sites. The increase in crystallinity of the material also contributes to the increase in conductivity after irradiation due to decreased scattering of charge carriers [48]. Frequency dependent conductivity could be attributed to the release of trapped charges in the disordered system. It is observed that with the increase of fluence the AC conductivity of the nanocomposite increases. This may be attributed to release of more trapped charges in the composites, due to huge electronic energy deposition upon SHI irradiation.

Previously, many literatures have been reported on the permanent modifications in electrical properties of both ordinary and conducting polymers by ion beam irradiation [49]. However, we can conclude few reasons for increasing conductivity in brief,

(i) Creation of conjugated double bonds in the back bone chain of the polymer

(ii) Introduction to donor-acceptor complex in the polymer matrix

(iii) Adding conductive fillers such as metallic nanoparticles

(iv) Hopping mechanism

(v) Conversion of the polymeric structure to hydrogen depleted carbon network [50-52].

1.5.2 Structural changes in composite materials:

Ion beams can modify molecular structure in polymers in a controlled way leading to change in behavior. Ionization trail produced by SHI causes bond cleavages and free radicals produced at one site react in a molecular site of different types from their original site. These are responsible for most of the chemical transformations observed in polymer films: chain scission, crosslinking and double and triple bond formation. Irreversible cleavages of bonds within macromolecule produce volatile species [53-55]. It is known now that ion irradiation of polymers not only leads to the destruction of short range order but also the destruction of long range order. To understand the process of structural modification, in the present study, we have carried out XRD analysis. From the XRD, we can determine changes in crystallite size and percentage (%) crystallinity of the material upon irradiation.

1.5.3 Optical properties of materials upon irradiation:

The promotion of electrons in the σ, π and n orbitals from ground state to the higher energy states which are described by molecular orbitals due to the absorption of light energy by polymeric samples in the UV and visible regions. Many of the optical transitions which occur due to the presence of impurities have energies in the visible region of the spectrum, consequently the defects are referred to as colour centres. The effect of ion beam interaction with polymers produces damage and leads to the generation of new defects and charge states [56, 57]. A shift in the absorption edge towards longer wavelength is also observed upon irradiation. The excitation of π electron requires smaller energy and hence, transition of this type occurs at longer wavelengths. The optical band gap E_g is found from tauc's equation [58]. From the change in band gap energy upon irradiation makes it clear to understand the change in polymeric materials.

1.5.4 Thermal properties of materials with irradiation:

The important property of the polymer is the glass transition temperature (*T*g), which is defined as the temperature at which the plastic becomes hard and brittle when cooled rapidly after heating. At the glass transition temperature, the weak secondary bonds that stick the polymer chains together are broken, and the macromolecule starts to move. With respect to ion irradiation the change (increase/decrease) in glass transition and melting temperature are observed. So we can confirm the processes of chain scissioning or crosslinking [59].

1.5.5 Changes in Surface morphology:

Ion irradiation of polymers leads in general different mechanisms depending upon ion beam, energy of ion beam, mass and charges. Sometimes it leads to an increase in the surface roughness due to the large sputtering effects [60]. Sometimes it is seen that the surface becomes smoothening upon irradiation because of surface diffusion [61].

1.5.6 Changes in magnetic property:

Zero-Field-Cooled (ZFC)/Field-Cooled (FC) magnetization and magnetic hysteresis measurements were performed using a superconducting quantum interference device (SQUID) magnetometer from 5 K to 300 K to investigate the magnetic properties of the polymer nanocomposites. Magnetization was increased upon irradiation which may be attributed to the creation of free radicals and interaction of particles mediated by the matrix which is also corroborated with the M-H measurements.

1.6 literature survey on selection of filler nanoparticles (Ag, Cu, Ni):

Nobel metal nanoparticles have shown much interest in high-performance catalysts, nanoscale electronic and optoelectronic devices, optical data storage systems, photochemistry, and biological sensors [62]. Nanoparticles particularly of silver reserve important role in the electronic industries.

Over the last decades silver nanoparticles have found applications in catalysis, optics, medical and other areas due to their unique size-dependent optical, electrical and magnetic properties. Currently most of the applications of silver nanoparticles are in biotechnology and bioengineering, textile engineering, water treatment, and silver-based consumer products. There are numerous literatures on the synthesis and characterization on silver polymer nanocomposites [63-66]. X. Huang et al [67] reported that the PVDF/Ag nanocomposites have high dielectric constant and high thermal conductivity and observed no percolation till the loading of 20% of Ag. Igoris Prosyčevas et al [68] observed that nanocomposites (PMMA-PET/ Ag) produced by variation of silver layer thickness shown shifting the plasmon resonance wavelength in the UV-VIS region and looked promising in producing of ultra thin colour filters. Z. H. Mbhele et al [69] investigated an increment in the Young's modulus and strength of the nanocomposite with an increase in Ag content in the PVA-Ag composites. In-situ formed Ag nanoparticles in the Ag/CB/epoxy composites increased the dielectric constant (K) value due to the pilling of charges at interfaces and decreased the dissipation factor (Df) due to the Coulomb blockade effect as studied by J. Lu et al [70]. P. Gonon [71] et al found that very low percolation threshold obtained (1%) which is believed to be related to a segregated distribution of the fillers (Ag) in the epoxy matrix. Y. Oh [72] observed that the resistivity of the silver/conducting polymer composite was decreased by 83% by the addition of silver-plated single-walled carbon nanotubes. M. K. Abyaneh [73] et al examined that PMMA/Ag composites exhibited a semiconductor-like conductivity at higher temperatures, a rapid metallic conductivity at middle range and nearly temperature independent conductivity at lower temperatures. A. Tang et al [74] fabricated an electrically bistable device using nanocomposite films consisting of silver nanoparticles and a semiconducting polymer by a simple spin-coating method.

Copper nanoparticles are the most abundantly used metal nanoparticles in electronics applications due to its high conductivity and low cost. The development of miniaturized nano devices that integrate electronic, photonic, chemical, and/or biological features is important for electronic and sensing devices [75]. Genaro A. Gelves et al [76] has demonstrated that the electrical percolation of metal nanowires in PS nanocomposites occur at percentage of 0.25–0.75 vol% for Cu nanowires [76]. They also exhibited EMI SE of more than 20 dB for copper nanowire concentrations of only 1.3 vol% and sheet thickness of 0.21 mm [77]. Oleg A. Yeshchenko et al [78] have grown copper nanoparticles on the silica matrix and observed that the efficiency of the luminescence increases appreciably due to decrease of particle size. I.H. Tavman [79] studied the tensile strength, elongation at break and toughness and observed decrease of these properties with increasing copper content which was attributed to the introduction of discontinuities in the structure of PE/Cu composites. G.G. Fedoruk et al [80] investigated conduction mechanism and sensing response of copper phthalocyanine (CuPc)–polymer composites. A.S. Luyt [81] reported the thermal and electrical conductivities of the composites (LDPE/Cu or LLDPE/Cu) were higher than that of the pure polyethylene matrix for both the LDPE and LLDPE and observed percolation concentration at 18.7 vol.% of copper for both polymers. V. Divya et al [82] explained the XRD studies in conjunction with the BJH method and reveals that the composite has crystalline nature with a mesoporous structure with a diameter of 3.5 nm in copper-polyaniline composites. Qing-Bo Wei et al [83] reported the response mechanism of the PAM-g-PVA/Cu films to solvent vapors on the basis of swelling theory, interaction between solvent vapor molecules and nanocomposites as well as the type and strength of interaction that each solvent vapor exhibits on the material. The effect of copper weight percent and surfactants on the conductivity and stability of the composite (PVP/Cu) has been investigated by Long Quoc Pham et al [84].

As an important transition metal, Ni nanoparticles have wide range applications in the fields of permanent magnets, magnetic fluids, magnetic recording media, solar energy absorption, fuel cell electrodes, catalysts etc. So the Ni nanoparticles have fascinated considerable attention [85]. Plenty of reports have been published on the synthesis of nickel nanoparticles by different experimental techniques [86-88]. Carbon–nickel nanocomposite thin films were prepared by ion beam cosputtering a graphite target having a nickel chip attached to its surface and magnetization measurement revealed superparamagnetic nature of composites by F. C. Fonseca et al [89]. The elastic properties showed an improvement with increase in filler (Ni) content but breaking stress and breaking strain were found to decrease in the rubber-nickel nanocomposites as observed by E. Muhammad Abdul Jamal et al [90]. Min Zhi Rong et al studied the interaction between the nanoparticles (Fe, Ni, co) and the grafted polymer (PMMA, PS) by thermal analysis and X-ray photoelectron spectrometry. It was found that there is a strong interfacial interaction in the form of electrostatic bonding in the polymer-grafted nanoparticles [91]. When the inspection frequency of the conductive composite film prepared by carbon fiber/Ni nanoparticles is 1000 MHz, its shielding effectiveness can reach to 28 dB as reported by Ho Chang et al [92]. The size and distribution of the Ni nanoparticles were strongly depend on the heat treatment temperature, indicating that this method allows microstructural tuning of polyimide/Ni nanocomposites as examined by K. Akamatsu et al [93]. D. E. El-

Nashar et al [94] determined the mechanical, electrical, and magnetic properties of natural rubber (NR) composites containing iron or nickel nanoparticles at different percentage varying from 0 to 120 phr (part of magnetic particle per hundred rubber) at room temperature. Jai Prakash et al [95] investigated the synthesis of magnetic nanocomposites by ion beam mixing technique using swift heavy ion irradiation of Ni-Teflon bilayer system and showed that the coercivity of the nanocomposite is found to be 112 Oe at room temperature which is two orders of magnitude larger than that of the bulk Ni (0.87 Oe).

1.7 Reviews on selected polymers (PMMA/PS):

Polymethyl methacrylate (PMMA) belongs to a family of synthetic polymers. It is better known as acrylic. PMMA is a tough, highly transparent material with excellent resistance to ultraviolet radiation and weathering. It can be coloured, moulded, cut, drilled, and formed. These properties make it ideal for many applications including airplane windshields, skylights, automobile taillights, and outdoor signs. PMMA can be further modified by incorporating different additives. These modifications are typically performed to improve specific properties of the polymer. Examples of properties that can be adjusted in this way are impact resistance, chemical resistance, flame retardancy, light diffusion, UV light filtering, or optical effects. S. Agrawal et al [96] studied the UV-Vis measurement and showed red shift in optical absorption and bandgap changed from 4.38–3.60 eV as the irradiation (100 MeV,Si^{+7} ions beam) fluence increased with respect to pristine CdCuS/PMMA nanocomposite polymer film. The study showed that, after the plasma (exposure time 0 to 60 s) treatment, the surface of PMMA film was etched, and oxygen-containing polar groups were introduced into the surface. These two processes can induce a remarkable decrease in water contact and a significant increase in surface energy and the surface properties of PMMA films were improved accordingly as examined by Z. Fang [97]. R. Kumar et al [98] examined the slight shift of peak position and significant changes in peak intensity in the XRD analyses. XRD results showed a decrease of 4.12% in crystallite size of 145 MeV Ne^{6+} ions irradiated sample at the higher fluence of 10^{12} ions/cm^2. Sumit Kumar et al [99] had prepared the multi-walled carbon nanotube (MWCNT) dispersed PMMA composite membranes for hydrogen gas permeation application. Photo-responsive properties of Ag/PMMA nanocomposite films indicate that the conduction paths could be destroyed by illumination and rebuilt in dark condition as observed by C. Chen [100]. It was found that the luminosity of ZnO/PMMA nanocomposite enhanced after irradiation with Ni^{+8} (100 MeV) ions as reported by S. Sharma et al [101]. The mechanical characterization revealed that radiation (50MeV Li^{+3}) significantly modifies the mechanical properties of the PMMA/PC blends [102]. P. Meneghetti et al [103] synthesized a novel polymer gel electrolyte with improved ionic conductivity and stable lithium interfacial resistance, which could be used for battery applications using PMMA/clay nanocomposites. The electrical resistivity and oscillatory shear rheological properties of the composites as a function of MWCNT geometry, functionality, and concentration were measured by C. McClory in PMMA/ MWCNT nanocomposites [104]. Large amounts of material with good antistatic and conductive properties prepared in an inexpensive way using chemically oxidative modification of poly(methyl methacrylate) particles by pyrrole method as investigated by M. Omastova et al [105]. Notwithstanding the remarkable importance of poly(methyl methacrylate) as a prototype polymer for positive resist (scission rate higher than cross linking rate) the literature studies on the chemical effects induced by energetic beam irradiation on this polymer are relatively scarce [106-110]. The interest for

PMMA is considerable also because it has been reported in literature that beyond a threshold fluence (that in turn depends on the ion) the resist turns negative: i.e. the cross linking rate becomes higher than the scission rate [111]. D. Singh etal [112] studied the temperature dependent dielectric properties and observed that it enhanced with increasing temperature in PMMA/Al composites. Also Singh etal [113] investigated the effect of 120 MeV Ni ions on PMMA/Ni and result showed that surface roughness increased upon irradiation.

Polystyrene (PS) is one of the most important polymers of nowadays. Its popularity stems from the fact that it possesses many good properties, such as good processability, rigidity, transparency, low water absorbability, and that it can be produced at low costs. However, polystyrene has some disadvantages, such as sensitivity to chemicals and food materials with high oil content, poor UV-resistance and brittleness, which limit its applications. Polystyrene is mainly used in the packaging industry [114]. Hong et al. [115] carried out surface modification of ZnO nanoparticles by grafting polystyrene to improve their dispersibility, to reduce photocatalytic properties, and to obtain good UV shielding capability to promote their use in cosmetics. V. Komolprasert et al suggested that irradiation did not generate any new chemicals in the PS polymer containing either yellow or blue colorant at a concentration of up to 1% (w/w) from analytical results [116]. M. Pattabi et al reported the effect of 8 MeV electron beam irradiation of polystyrene substrates on the morphology of silver particulate films deposited at 455 K in a vacuum of 8 x 10^{-6} Torr [117]. L.C. Costa et al studied the dc conductivity and the true dielectric response, at low frequencies, of the composites made by dispersing the high conductivity PPy particles in the insulating matrix of PS [118]. S.A. Saqan et al [119] studied the mechanical, thermal, optical and electrical properties of polystyrene/alum composites as a function of alum content and applied field frequency. D. Olmos et al observed neither the cryomilling process nor the presence of BaTiO3 particles (up to 40% wt) seem to alter the structure of the PS polymer [120]. J. Kuljanin-Jakovljevic et al investigated that the higher concentration of CdS (20%) in the (PS/CdS) composite induced acceleration of the thermal degradation, approaching the rate of degradation of the pure polystyrene matrix [121]. Different types of photochromophores and initiators were applied to prepare PS nanocapsules and their effects on the morphology of the capsules were investigated by M. Han [122]. The selectivity permeation results revealed that the MWCNT/PS composite membranes can be used as nanofilter for selective permeation of H_2 gas as observed by S. Kumar [123]. Improvement of the thermal stability of the PS matrix with the usage of the CdS-filler particles in the micrometer size range was demonstrated by J. Kuljanin et al [124]. The dependence of Maxwell–Wagner–Sillars or interfacial polarization of polystyrene–AlN composites on AlN volume fraction has also been studied by S. Yu [125]. E. Balanzat et al [126] proposed that the breaking of the phenyl group, due to multi-ionisation of the ring, could play a major role in the damage process at high electronic stopping power. The relaxation time and the activation energy determined for different composites decrease with increasing temperature as studied by S A Sbeih et al [127].

1.8 Objective of work:

The central intention of the present work is to synthesize the nanocomposites which can defeat some of the tribulations which are not overcome by pure polymer up to now. The injection of material into a target specimen in the form of an accelerated ion beam offers a most valuable tool for altering its physical, chemical, structural, surface and interface properties in a controlled manner and tailoring new materials for basic and applied research for science and technology. On the basis of review carried out on the similar work till this date, ion beam irradiation has proved unique technology for polymer modification. So the physico-chemical properties after ion beam are explained in details. As stated in the previous sections, after taking low and high dielectric material applications in consideration, the fillers are appropriately selected. Synthesis, characterization and processing of low dielectric constant polymer materials are a leading premise for microelectronics, satellite, telecommunication, packaging, biomaterials etc. Rather material with high dielectric constant can be used for EMI shielding application. Therefore taking in mind the drawbacks of pure polymers and metal nanoparticles, nanocomposites have been synthesized to fulfil the requirements. As mentioned above, the dielectric and other physical properties enhanced after doping of the metal nanoparticles. So the different types of conductive nanoparticles were used as filler viz. silver (Ag), nickel (Ni), copper (Cu) are dispersed in poly methyl methacrylate (PMMA) and polystyrene (PS) for making polymer nanocomposites. The irradiation effect on these nanocomposite films was studied with respect to ion specie, energy and fluence. For this purpose 120 MeV Si^{10+}, 85 MeV C^{6+}beams were used. AC electrical, structural, chemical, thermal, magnetic properties and surface morphology of pristine and irradiated nanocomposites are investigated by means of various techniques in the present work.

References:

[1] R. L. Orefice, J. A. C. Discacciati, A. D. Neves, H. S. Mansur, W. C. Jansen, Polymer Testing 22 (2003) 77-81.

[2] R. S. Sethi, M. T. Goosey, Special Polymers for Electronics & Optoelectronics; J. A. Chilton, M. T. Goosey, Eds.; Chapman & Hall: London, (1995) pp 14-46.

[3] T. Richardson, "Composites A Design Guide", Industrial Press Inc, New York (1987).

[4] J. C. Anderson, K. D. Leaver, R. D. Rawlings, J. M. Alexander, Material Science and Engineering, Chapman and Hall India, Madras, India (1990).

[5] D. L. C. Deborah, Composite Materials: Science and Applications Functional Materials for Modern Technologies, Springer, London (2002).

[6] S. Ramakrishna, J. Mayer, E. Wintermantel, K. W. Leing, Biomedical applications of polymer composite materials: a review. Composites Sci. and Tech 61 (2001) 1189.

[7] K. S. Suslick, Sonochemistry Science 247 (4949) (1990) 1439-1445.

[8] B. Lin, G. A. Gelves, J. A. Haber, U. Sundararaj, Ind. Eng. Chem. Res. 46 (2007) 2481–2487.

[9] G. A. Gelves, U. Sundararaj, J. A. Haber, Macromol. Rapid Commun., 26 (2005) 1677–1681.

[10] G. Schmidt, M. M. Malwitz, Curr. Opin. Coll. Interface Sci. 8 (2003) 103–108.

[11] M. B. Muradov, A. Sh. Abdinov, R. H. Hajimamedov, G. M. Eyivazova, Surf. Eng. Appl. Electrochem., 45 (2) (2009)167–170.

[12] S. Stankovich, D. A. Dikin, G. H. B.Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen, R. S. Ruoff, Nature, 442 (2006) 282–286.

[13] O. Breuer, U.Sundararaj, Polym. Compos., 25 (2004) 630–645.

[14] S. Wood, R. Jones, A. Geldart, The Social and Economic Challenges of Nanotechnology (No. 0-86226-294-1). Swindon, UK: The Economic and Social Research Council (2003).

[15] J. R. Li, J. R. Xu, M. Q. Zhung, M. Z. Rong, Carbon 41 (2003) 2353-2360.

[16] H. Supriyatno, K. Nakagawa, Y. Sadaoka, Sensors and Actuators B76 (2001) 36-41.

[17] R. Morrison, Solving Interference Problems in Electronics. John Wiley & Sons, Inc., New York (1995).

[18] D.White, A Handbook on Electromagnetic Shielding Materials and Performance. Don White Consultants, Inc.: Germantown, MD (1975).

[19] F. Rodrigues, C. Cohen, C. K. Ober, L. A. Archer, " Principles of Polymer Systems" Eds. D. T. Schanck, D. P. Teston, Taylor and Francis, New York, London (2003).

[20] D. D. L. Chung, Carbon, 139 (2001) 279-285.

[21] D. K. Awasthi, Current Science, 78 (11) (2000) 1297-1306.

[22] D. Kanjilal, Current Science, 80 (12) (2001) 1560-1566.

[23] W. Bolse, Mater. Sci. Eng. R 12 (1994) 53.

[24] W. E. Burcham, Elements of nuclear physics, Longman, London and New York, (1979).

[25] Kamlendra Awasthi, Vaibhav Kulshreshtha, B Tripathi, N K Acharya, M Singh and Y K Vijay, Bull. Mater. Sci., 29(3) (2006) 261–264.

[26] T. Barbari, W. Kores and D.Paul , J. Polym. Phys. 26 (1988) 709.

[27] A. Srivastava, T.V. Singh, S. Mule, C.R. Rajan, S. Ponrathnam, Nucl. Instr. Meth. B,192 (2002) 402.

[28] T. Hioki, S. Noda, M. Sugiura, M. Kakaeno, K. Yamada, Kawamoto, J. ,Appl. Phys. Lett., 43 (1983) 30.

[29] U.A. Sevil, O. Güven, A. Kovács, I. Slezsák, Radiation Physics and Chemistry, 67 (2003) 575.

[30] P. Sonar, A.L. Sharma, A. Chandra, K. Muellen, A. Srivastava, Current Applied Physics, 3 (2003) 247.

[31] Alok Srivastava, Virendra Singh, Chetna Dhand, Manindar Kaur , Tejvir Singh, Karin Witte and Ulrich W. Scherer, Sensors, 6 (2006) 262-269.

[32] A. Qureshi, N. L. Singh, Sejal. Shah, P. Kulriya, F. Singh, and D. K. Avasthi, Nucl. Instrum. Methods Phys. Res. B 266 (2009) 1775.

[33] R. Singhal, A. Kumar, Y. K. Mishra, S. Mahopatra, J. C. Pivin, and D. K. Avasthi, Nucl. Instrum. Methods Phys. Res. B 266 (2008) 3257.

[34] D. Fink, M. Mueller, and L. T. Chadderton, Nucl. Instrum. Methods Phys. Res. B 32 (1988) 125.

[35] S. Balanzat, S. Bouffard, A. Le Moe¨l, and N. Betz, Nucl. Instrum. Methods Phys. Res. B 91 (1994) 14.

[36] J. P. Biersack, A. Schmoldt, and D. Fink, Radiat. Eff. Defects Solids 140 (1996) 63.

[37] A. M. P. Hussain and A. Kumar, Eur. Phys. J. Appl. Phys. 36 (2006) 105.

[38] K. R. Nagabhushana, B. N. Lakshminarasappa, G. T. Chandrappa, D. Haranath, and F. Singh, Radiat. Eff. Defects Solids 162 (2007) 325.

[39] S. Sarmah and A. Kumar, Phys. Status Solidi A 207(10) (2010) 2279–2287.

[40] Chaitali Gavade, N. L. Singh, Dolly Singh, Sejal Shah, A. Tripathi, D. K. Avasthi, Integrated Ferroelectrics, 117 (2010) 76–84.

[41] J. Delmonte: Metal/Polymer composites, Van Nostrand Reinhold New York (1990).

[42] A. Heilmann " Polymer films with embedded metal nanoparticles" Eds R. Hull, R. M. Osgood, J. Parisi , Springer, Berlin, Heidelberg, New York, (2003).

[43] F. Kremer, A. Schönhals, Broadband dielectric spectroscopy, Springer, (2003).

[44] A.J. Jonscher, "Dielectric relaxation in solids", Journal of Physics D: Applied Physics, 32(14) (1999) 57-70.

[45] "Dielectrics (physics)". Britannica. (2009) pp. 1(Online).

[46] L. H. Sperling, Introduction To Physical Poly. Sci., John wiley & sons, New York, (1992).

[47] Prerna Aggarwal, Virendra Singh, Arjun Singh, U. W. Scherer, Tejvir Singh, Madan L. Singla, Alok Srivastava, Radiation Physics and Chemistry 81 (2012) 284–289.

[48] S. Sarmah and A. Kumar, Phys. Status Solidi A 207(10) (2010) 2279–2287.

[49] D. Fink (Ed.), Transport Processes in Ion Irradiated Polymers and Applications, Springer Series in Materials Science, Vol. 65, Springer-Verlag, (2004).

[50] A. Harper Charles, Modern Plastics Handbook, McGraw Hill, New York, (1999).

[51] R. O. Ebewele, " Polymer Science and Technology", CRC Press, London, (2000).

[52] Anjum Qureshi, N. L. Singh, Sejal Shah, F. Singh, And D. K. Avasthi, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry 45 (2008) 265–270.

[53] H.W. Choi, H. J. Woo, W. Hong, J.K. Kim, S. K. Lee, C.H. Eum, Applied Surface Science 169-170 (2001) 433-437.

[54] Lakhwant Singh, Ravinder Singh, Nuclear Instruments and Methods in Physics Research B 225 (2004) 478–482.

[55] R. Kumaravel, K.Ramamurthi, Indra Sulania, K. Asokan, D. Kanjilal, D. K. Avasti, P. K. Kulria, Radiation Physics and Chemistry 80 (2011) 435–439.

[56] A. Semwal, A. Negi, R. G. Sonkawade, J. M. S. Rana, R. C. Ramola, Indian J of pure and App Phy 48 (2010) 496-499.

[57] H S Virk, P S Chandi And A K Srivastava, Bull. Mater. Sci. 24(5) (2001) 529–534.

[58] A. Das, S. Dhara and A. Patnaik, Physical Rev B 59 (1999) 11069.

[59] Virendra Singh, Tejvir Singh, Amita Chandra, S.K. Bandyopadhyay, Pintu Sen, K. Witte, U.W. Scherer, Alok Srivastava, Nuclear Instruments and Methods in Physics Research B 244 (2006) 243–247.

[60] N L Singh, Sejal Shah, Anjum Qureshi, A Tripathi, F Singh, D.K.Avasthi, P M Raole, Bull. Mater. Sci., 34(1) (2011) 81–88.

[61] Sejal Shah, Dolly Singh, Anjum Qureshi, N L Singh, K. P. Singh, V. Shrinet, Indian journal of pure and applied physics, 46 (2008) 439-442.

[62] D. Zhang, L. Qi, J. Yang, J. Ma, H. Cheng, and L. Huang, Chem. Mater., 16 (2004) 872.

[63] Jian Xu, Xia Han, Honglai Liu, Ying Hu, Colloids and Surfaces A: Physicochem. Eng. Aspects 273 (2006) 179–183.

[64] B. Raneesh, A. Pragatheeswaran, P. Dhanasekaran, P. Chandrasekaran, Nandakumar Kalarikkal, Journal of Ovonic Research, 6(4) (2010) 187 -191.

[65] A. Sreekumaran Nair, Nadappuram P. Binoy, Seeram Ramakrishna, T. R. R. Kurup, Lai Wah Chan, Cheong Hian Goh, Md. Rafiqul Islam, Thomas Utschig, T. Pradeep, Applied materials and interfaces, 1(11) (2009) 2413–2419.

[66] Osman Eksik, A. Tuncer Erciyes, Yusuf Yagci, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry 45 (2008) 698–704.

[67] Xingyi Huang, Pingkai Jiang, Liyuan Xie, Applied Physics Letters 95 (2009) 242901.

[68] Igoris Prosyčevas, Judita Puišo, Asta Guobienė, Sigitas Tamulevičius, Ramūnas Naujokaitis, Materials Science 13 (2007) 188-192.

[69] Z. H. Mbhele, M. G. Salemane, C. G. C. E. van Sittert, J. M. Nedeljkovic, V. Djokovic, A. S. Luyt, Chem. Mater. 15 (2003) 5019-5024.

[70] Jiongxin Lu, Kyoung-Sik Moon, Jianwen Xu and C. P. Wong, J. Mater. Chem., 16 (2006) 1543–1548.

[71] P. Gonon, A. Boudefel, Journal of Applied Physics 99 (2006) 024308.

[72] Youngseok Oh, Daewoo Suh, Youngjin Kim, Eungsuek Lee, Jee Soo Mok, Jaeboong Choi and Seunghyun Baik, Nanotechnology 19 (2008) 495602 (7pp).

[73] M. Kazemian Abyanehabd, S. Jafarkhani and S.K. Kulkarni, Journal of Experimental Nanoscience 6(2) (2011) 159–173.

[74] Aiwei Tang, Shengchun Qu, Yanbing Hou, Feng Teng, Hairen Tan, Jie Liu, Xingwang Zhang, Yongsheng Wang, and Zhanguo Wang, Journal of Applied Physics 108 (2010) 094320.

[75] George H. Chan, Jing Zhao, Erin M. Hicks, George C. Schatz, and Richard P. Van Duyne, Nano letters, 7(7) (2007) 1947-1952.

[76] Genaro A. Gelves, Bin Lin, Uttandaraman Sundararaj, Joel A. Haber, Adv. Funct. Mater. 16 (2006) 2423–2430.

[77] Genaro A. Gelves, Mohammed H. Al-Saleh and Uttandaraman Sundararaj, J. Mater. Chem. 21 (2011) 829–836.

[78] Oleg A. Yeshchenko, Igor M. Dmitruk, Andriy M. Dmytruk, Alexandr A. Alexeenko, Materials Science and Engineering B 137 (2007) 247–254.

[79] I.H. Tavman, Powder Technology 91 (1997) 63-67.

[80] G.G. Fedoruk, D.I. Sagaidak, A.V. Misevich, A.E. Pochtenny, Sensors and Actuators B 48 (1998) 351–355.

[81] A.S. Luyt, J.A. Molefi, H. Krump, Polymer Degradation and Stability 91 (2006) 1629-1636.

[82] V. Divya, M.V. Sangaranarayanan, European Polymer Journal 48 (2012) 560–568.

[83] Qing-BoWei, Yan-Ling Luo, Chang-Hu Zhang, Li-Hua Fan, Ya-Shao Chen, Sensors and Actuators B 134 (2008) 49–56.

[84] Long Quoc Pham, Jong Hwa Sohn, Chang Woo Kim, Ji Hyun Park, Hyun Suk Kang, Byung Cheol Lee,Young Soo Kang, Journal of Colloid and Interface Science 365 (2012) 103–109.

[85] Huazhi Wang, Xinli Kou, Jie Zhang, Jiangong Li, Bull. Mater. Sci., 31(1) (2008) 97–100.

[86] R S Ningthoujam, N S Gajbhiye, Sachil Sharma, Pramana- J. Phys.72(3) (2009) 577-586.

[87] Xiao-Min Ni, Xiao-Bo Su, Zhi-Ping Yang, Hua-Gui Zheng, Journal of Crystal Growth 252 (2003) 612–617.

[88] Huazhi Wang, Xinli Kou, Jie Zhang, Jiangong Li, Bull. Mater. Sci. 31(1) (2008) 97–100.

[89] F. C. Fonseca, A. S. Ferlauto, F. Alvarez, G. F. Goya and R. F. Jardim, Journal Of Applied Physics 97 (2005) 044313.

[90] E. Muhammad Abdul Jamal, P.A. Joy, Philip Kurian, M.R. Anantharamana, Materials Science and Engineering B 156 (2009) 24–31.

[91] Min Zhi Rong, Ming Qiu Zhang, Hong Bing Wanga, Han Min Zeng, Applied Surface Science 200 (2002) 76–93.

[92] Ho Chang, Yun-Min Yeh, Kouhsiu-David Huang, Materials Transactions, 51(6) (2010) 1145- 1149.

[93] K. Akamatsu, K. Nakahashi, S. Ikeda, H. Nawafune, Eur. Phys. J. D 24(2003) 377–380.

[94] D. E. El-Nashar, S. H. Mansour, E. Girgis, J Mater Sci 41 (2006) 5359–5364.

[95] Jai Prakash, A. Tripathi, J.C. Pivin, Jalaj Tripathi, A.K. Chawla, Ramesh Chandra, S.S. Kim, K. Asokan, D.K. Avasthi, Adv. Mat. Lett. 2(1) (2011) 71-75.

[96] Shweta Agrawal, Subodh Srivastava, Sumit Kumar, S S Sharma, B Tripathi, M Singh, Y K Vijay, Bull. Mater. Sci. 32(6) (2009) 569–573.

[97] Zhi Fang, Yuan Liu, Kun Liu, Tao Shao, Cheng Zhang, Vacuum 86 (2012) 1305-1312.

[98] Rajesh Kumar, S.A. Ali, Paramjit Singh, U. De, H.S. Virk, Rajendra Prasad, Nuclear Instruments and Methods in Physics Research B 269 (2011) 1755–1759.

[99] Sumit Kumara, Anshu Sharma, Balram Tripathi, Subodh Srivastava, Shweta Agrawal, M. Singh, Kamlendra Awasthi, Y.K. Vijay, Micron 41 (2010) 909–914.

[100] Cheng Chen, Junguo Li, Guoqiang Luo, Yuanlu Xiong, Qiang Shen Lianmeng Zhang, Applied Surface Science 258 (2012) 10180– 10184.

[101] Sarla Sharma, Rishi Vyas, Subodh Shrivastava, Y.K. Vijay, Physica B 406 (2011) 3230–3233.

[102] Manasvi Dixit, Deepika, Mahesh Baboo, Kananbala Sharma, N. S. Saxena, D. K. Avasthi, Pawan K. Kulriya, International Journal of Polymeric Materials 59 (2010) 873–890.

[103] Paulo Meneghetti, Syed Qutubuddin, Thermochimica Acta 442 (2006) 74–77.

[104] Caroline McClory, Tony McNally, Mark Baxendale, Petra Pötschke, Werner Blau, Manuel Ruether, European Polymer Journal 46 (2010) 854–868.

[105] Maria Omastova, Juraj Pavlinec, Jurgen Pionteck, Frank Simon, Stanislav Kosina, Polymer 39(25) (1998) 6559–6566.

[106] D. Fink, L.T. Chadderton, F. Hosoi. H. Omichi, T. Sagusa, A. Schmoldt, L. Wang, R. Klett and J. Hillenbrand, Nucl. Instr. and Meth. B 91 (1994) 146.

[107] J. Davenas, P. Thevenard, G. Boiteux, M. Fallavier and X.L. Lu, Nucl. Instr. and Meth. B 46 (1990) 317.

[108] R. Kallweit, U. Roll, P. Eichinger, H. Strack and A. Piker, Mater. Res. Symp. Proc. 268 (1992) 363.

[109] J.C. Corelli, A.J. Steckl, D. Pulver and J.N. Randall, Nucl. Instr. and Meth. B 19/20 (1987) 1009.

[110] I. Adesida, C. Anderson and E.D. Wolf, J. Vat. Sci. Technol. B 1 (1983) 1182.

[111] T. M. Hall, A. Wagner, L P. Thompson, J. Appl. Phys. 53(1982) 3997.

[112] Dolly Singh, N.L. Singh, P. Kulriya, A. Tripathi and D.M. Phase, Journal of Composite Materials, 44 (2010) 3165.

[113] N. L. Singh, Sejal Shah, Anjum Qureshi, A. Tripathi, F. Singh, D.K. Avasthi, P. M. Raole, Bull. Mater. Sci., 34 (2011) 81–88.

[114] P.L. Ku, Advances in Polymer Technology, 8(3) (1988) 201-223.

[115] Hong RY, Li JH, Chen LL, Liu DQ, Li HZ, Zheng Y, Powder Technology 189 (2009) 426–432.

[116] V. Komolprasert, Todd Diel, G. Sadler, Radiation Physics and Chemistry 75 (2006) 149–160.

[117] Manjunatha Pattabi, S.C. Gurumurthy, Ganesh Sanjeev, A.B. Gaikwad, Nuclear Instruments and Methods in Physics Research B 269 (2011) 1534–1539.

[118] L.C. Costa, F. Henry, M.A. Valente, S.K. Mendiratta, A.S. Sombra, European Polymer Journal 38 (2002) 1495–1499.

[119] S.A. Saqan, A.S. Ayesh, A.M. Zihlif, E. Martuscelli, G. Ragosta, Polymer Testing 23 (2004) 739–745.

[120] D. Olmos, J.M. Martínez-Tarifa, G. González-Gaitano, J. González-Benito, Polymer Testing 31 (2012) 1121–1130.

[121] J. Kuljanin-Jakovljevic, M. Marinovic Cincovic, Z. Stojanovic, A. Krkljes, N.D. Abazovic, M.I. Comor, Polymer Degradation and Stability 94 (2009) 891–897.

[122] Mijeong Han, Eunha Lee, Eunkyoung Kim, Optical Materials 21 (2002) 579-583.

[123] Sumit Kumar, Subodh Srivastava, Y.K. Vijay, International journal of hydrogen energy 37 (2012) 3914-3921.

[124] J. Kuljanin, M. Vuckovic, M. I. CComor, N. Bibic, V. Djokovic, J.M. Nedeljkovic, European Polymer Journal 38 (2002) 1659–1662.

[125] Suzhu Yu, Peter Hing, Xiao Hu, J. Appl. Phys. 88(1) (2000) 398-404.

[126] E. Balanzat, S. Bouffard, A. Bouquerel, J. Devy, Chr. Gate, Nuclear Instruments and Methods in Physics Research B I 16 (1996) 159- 163.

[127] S. A. Sbeih and A. M. Zihlif, J. Phys. D: Appl. Phys. 42 (2009) 145405 (7pp).