Modification of Metal Oxide Doped Polymer Nanocomposites Using Ion Beam Irradiation

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1. Introduction

Polymer composites have found widespread applications in automobile, electronics, and consumer products etc. They have properties such as higher strength and stiffness compared to pure polymer [1,2]. However, properties achieved by traditional composites involve compromises, for example, stiffness is obtained at the cost of toughness. Polymer composites provided a new way to overcome the limitations of traditional counterparts [2,3].

Organic/inorganic nanocomposites are generally organic polymer matrix with inorganic nanoscale building blocks. They usually contain unique properties of nanofillers leading to materials with improved properties. A defining feature of polymer nanocomposites is that the small size of the fillers leads to a dramatic increase in the interfacial area as compared with traditional composites. This interfacial area forms a significant volume fraction of interfacial polymer with properties different from the bulk polymer even at low loadings. Polymer nanocomposites, which are a lightweight material and combine the inherent processability of polymers with nanoparticles, have been used in the number of applications such as electromagnetic interface (EMI) shields, communication device, capacitor, dosimeter and LED etc. [4–6].

Among the wide variety of thermoplastics polymers, polystyrene (PS) is one of the most popular and widely-used aromatic polymers because of its excellent transparency, processability, good chemical stability. An essential property of an aromatic polymer is radiation stability [7], whereas, PVA is an aliphatic polymer that has properties like high chemical stability, high thermal stability, good storage capacity and non-toxic. PVA has filler dependent properties [8]. The physicochemical properties of polymers viz polystyrene and PVA are being tailored extensively in various fields by incorporating inorganic materials as per requirements.

Radiation-induced modification in polymeric materials is an active area of research from the scientific and technological perspective. Radiation viz electromagnetic or charged particle passes through a polymer, the incident energy is transferred to the medium and as a result ionization and excitation of the target molecules take place. The electromagnetic radiation deposits energy uniformly to the entire volume of material and ionized polymeric materials via energetic secondary electrons [9]. The deposited localized energy to the polymer by electromagnetic radiation is quite small. The interaction of ion beam with a solid is a non-equilibrium process, while the deposition of localized energy due to swift heavy ion beam is tremendously high. It occurs in a very small volume ($\sim 10^{-17}$ to 10^{-16} cm^3) [10]. The change in the desired properties of the polymeric matrix can be engineered by selecting energy, mass and fluence of the swift heavy ions. Irradiation is a technique to improve physicochemical properties of polymer for applications in interdisciplinary fields. But there is still a lack of information about gamma and SHI irradiation-induced effects on physicochemical properties of polymeric materials. Therefore, the objective of the present thesis is to study the effects of gamma and SHIs irradiation on physicochemical properties of polymeric materials as a function of filler level and irradiation dose.

2. Literature Survey :

The considerable works have been done to investigate the structural, optical, luminescence and electrical properties of metal oxide-polymer nanocomposites. These properties of polymers can be improved dramatically by incorporation of metal oxide nanoparticles like Al_2O_3, SiO_2 etc. or other conducting polymers. Al_2O_3 nanoparticles have outstanding properties involving high thermal conductivity and mechanical strength, electrical insulation, high adsorption capacity, inexpensive and non-toxic. Over past decades, Al_2O_3 nanoparticles offer the potential for wide application in packaging, biomedical application, automobile industry and so on. Many reports are available on the preparation and characterization of Al_2O_3 nanoparticles and its polymer nanocomposites. Investigation of luminescence properties of Al_2O_3 was reported by Kostyukov et al. [11]. Nagabhushana et al. [12] have studied the change in structural and luminescence properties of Al_2O_3 nanocrystals due to 120 MeV Au^{9+} ions. Sengwa et al. [13] 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. [14] reported the thermal behaviour of Chitosan/Al_2O_3 polymer nanocomposites. Canimkurbey et al. [15] studied the effect of Al_2O_3 on 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. [16] reported the influence of Al_2O_3 on thermal, spectroscopic, structural and electric properties of PEO/$LiClO_4$ polymer electrolytes. This sample was prepared by solution casting method. Pradeepa et al. [17] 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.

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 red-emitting phosphor among all rare earth sesquioxide [18,19]. A few reports are available on synthesized and characterization of Eu^{3+} ions doped composites. Umamaheswari et al. [20] synthesized europium (III) oxide decorated reduced graphene oxide. They concluded that it is used as an amperometric sensor for chloramphenicol. This material sense even low 1.32nM concentration. Kibombo et al. [21] developed europium oxide doped TiO_2 aerogel photocatalyst. The photocatalytic properties of this material showed higher than pure TiO_2. Dehelean et al. [22] 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 spectroscopic and photoluminescence. Europium (III) oxide and gold deposited europium (III) oxide synthesized by Aazam et al. [23]. Deposition of gold was carried out by photo-assisted deposition method. They have studied photocatalytic activity for degradation atrazine under visible light and also investigated their luminescence properties. They reported that the gold deposited europium (III) oxide has high photocatalytic activity than europium (III) oxide. Dandekar et al. [24] 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 their structural, spectroscopic, luminescence properties and surface morphology using X-ray diffraction, FTIR, photoluminescence and SEM. Chitosan$_n$[C$_2$mim][Eu(SCN)$_4$] membranes were synthesized by Leones et al. [25]. They have investigated structural, electrical, luminescence properties and surface morphology. They suggested that this material is a good contender for electroluminescent devices. Alves et al. [26] prepared chitosan/europium triflate polymer electrolytes. They studied their structural, photoluminescence properties and surface morphology. Garcia-Torres et al. [27] studied the photophysical properties of Eu(tta)$_3$ (phen)/polymer hybrids. They have used polyvinyl butyral, polysulfone and polyurethane as polymer matrix. They have concluded that this material has potential application in optical devices fabrication.

Singh et al. [28] investigated the electrical transport properties of PVA-PVP-NaI-SiO_2 nanocomposite polymer electrolytes. Tański et al. [29] synthesized PVP/SiO_2 nanofibrous composite and investigated the optical properties of these composites. Singh et al. [30]reported that the tensile and flexural properties of SiO_2/epoxy improved as a function of nanoparticles. Hema et al. [31] prepared PVA:PVdF:LiCF$_3$SO$_3$:SiO_2/TiO_2 nanocomposite polymer electrolytes and studied the effect of nanofiller on electrochemical, mechanical and thermal properties of polymer electrolytes. Ketabi et al. [32] 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 this nanocomposite polymer electrolytes exhibited a high capacitive response at 1 V/s. Zhang et al. [33] 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 studied the ionic conductivity and optical properties as a function of nanofiller were reported by Pehlivan et al. [34].

Gao et al. [35] 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 and formyl group, respectively. The luminescence properties of Eu^{3+} was drastically enhanced due to the presence of such acids. Demkiv et al. [36] studied the luminescence and kinetic properties of PS/BaF_2 polymer nanocomposites. Tripathi et al. [37] studied non-linear optical properties of Cds/PS nanocomposites. They reported that the absorption region was shifted from the UV region to visible region due to doping of Cds nanoparticles. PL emission spectra of PS/Cds nanocomposites in the yellow and green region were reported. Mingwang et al. [38] 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. [39] reported the change 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.

Karaman et al. [40] 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 supercapacitor application. Ahmad et al. [41] reported the potential use of

$(PVA)_{0.7}$ $(NaBr)_{0.3}$ $(H_3PO_4)_{xM}$ solid membrane as 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. [42] fabricated a solid-state supercapacitor cell, which contained 3D nanostructured MnO_2/CNT as 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 · s^{-1}. This solid-state device exhibited excellent cycling stability with a capacitance loss of only 11% after 3000 cycles with a discharge current of 20 mA and suggested its potential applications such as photovoltaic cells, renewable energy storage device and wearable electronics. Prajapati et al. [43] reported the effect of gamma irradiation on the electrical properties of PVA – H_3PO_4 complexed electrolytes. They studied the variation in ac conductivity and dielectric constant with the frequency, temperature and irradiation dose. They concluded that CBH model is useful for studying the electrical conduction mechanism of this complexed system. Prajapati et al. [44] also studied the effect of 50 Mev Li^{3+} ion on PVA: H_3PO_4 : Al_2O_3 thin film (70:30:10) with different fluences. It 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 explained that beyond critical fluence, conductivity decreased.

The effect of radiations such as electromagnetic (e.g. UV, Xray or Gamma photons) or particle (electron, neutron or charged species) on polymers have been widely studied, while the effect of SHI irradiation has received considerable attention over the past few decades for purposes of polymers in radiation environment and also in the development of new electronic devices [45]. The deposited energy may be transformed into atomic motion which leads to modify the physicochemical properties of polymer such as solubility, molecular weight, mechanical, electrical and optical properties [46]. It can result in processes such as chain scissioning, crosslinking, alteration of unsaturation, radical formation and loss of volatile fragments etc. [47,48]. The magnitude of these processes depends upon properties of polymer, energy of ions and irradiation condition. 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 pendant side group. In crosslinking, 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 the properties of polymer brings a new approach to design devices. The radiation effect on physicochemical properties of polymer needs to be investigated, especially, when, a device is made from such polymer employed in the radiation environment. Irradiation is a method to modify physicochemical properties of polymer nanocomposites for various applications.

3. Objective

In the present studies, three systems based on polystyrene and polyvinyl alcohol were prepared via solution casting technique. The self-sanding pristine polymeric films of (i) PS/Al_2O_3 polymer nanocomposites (ii) PS/Eu_2O_3 polymer nanocomposites (iii) PVA/H_3PO_4/SiO_2 nanocomposite polymer electrolytes were prepared in the laboratory. C^{6+} (90 MeV) ion and gamma rays were selected for irradiation of the polymeric films. The effect of ion beam and gamma irradiation on optical, luminescence, structural and dielectric properties of the polymer nanocomposite have been investigated and discussed.

4. Experimental Method :

PS/Al_2O_3, PS/Eu_2O_3, PVA/H_3PO_4/SiO_2 polymeric films were synthesized using the solution casting method. All samples were irradiated with gamma rays and 90 MeV carbon ion. The effects of gamma rays and SHI ions on optical, luminescence, structural and dielectric properties of the pristine polymer nanocomposites and nanocomposite polymer electrolyte have been investigated and discussed in the following chapters;

Chapter 1. Introduction

This chapter presented a general background describing the effect of swift heavy ion and gamma irradiation on polymeric films. In-depth literature review of pristine and irradiated polymer nanocomposites and their development described along with the object of the present study.

Chapter 2. Synthesis method and Characterization techniques

In this chapter, the synthesis method for polymer films has been discussed with the external condition. The working principle of Pelletron accelerator used for swift heavy ion beam irradiation at Inter University Accelerator Centre (IUAC), New Delhi, India, has been explained. Also, the projectile range, electronic energy loss and nuclear energy loss of swift heavy ions for proposed polymer nanocomposites have been obtained through SRIM code. The different techniques such as X-ray diffraction techniques, Atomic force microscopy, Fourier Transformation Infrared spectroscopy, Photoluminescence, thermoluminescence, Differential scanning calorimeter, dielectric spectroscopy have been discussed in details.

Chapter 3. Effect of Gamma and 90 MeV C^{6+} ion beam irradiation on physicochemical properties of Polystyrene/Al_2O_3 polymer nanocomposites

This chapter described the results of various characterization of metal oxide nanoparticles dispersed Polystyrene nanocomposites. These composites were irradiated with gamma rays and 90 MeV C^{+6} ions. The effect of gamma and swift heavy ion irradiation on structural, optical, luminescence, electrical properties and surface roughness of aluminum oxide nanoparticles doped polystyrene have been discussed in details. Structural properties were studied using X-ray diffraction. The optical bandgap of materials decreased with filler concentrations and also upon irradiation. Luminescence properties of nanocomposites increased with increasing irradiation dose. The irradiation-induced defects on the polymer surface, which serve as radiative centers resulting in increased photoluminescence (PL) intensity. Thermoluminescence glow curve intensity increased with irradiation dose. Thermal property of nanocomposite was studied by DSC analysis. It reveals about the glass transitions temperature (Tg). The glass transition temperature increased on the incorporation of nanofiller concentration and decreased upon irradiation. The average surface roughness of the composites also changed as revealed from AFM studied. The results of all characterization techniques have been correlated to give a better and clear view of dielectric, structural, luminescence, optical, electrical, thermal properties and surface morphology.

Chapter 4. Effect of Gamma and 90 MeV C^{6+} ion beam irradiation on physicochemical properties of PS/Eu_2O_3 polymer nanocomposites

This chapter illustrated the result of the characterization of Eu_2O_3 dispersed PS polymer nanocomposites. These nanocomposites were irradiated with gamma rays and 90 MeV C^{+6} ions at various irradiation doses. The various results of experimentations before and after irradiation have been described. The results obtained from various characterization techniques showed the dependence of different properties of polystyrene after incorporation of filler and irradiation. The structural, thermal, optical, luminescence and dielectric analysis were carried out to study the effect of nanoparticles and irradiation dose. Photoluminescence emission spectra have been recorded with an excitation wavelength of 247 nm. PL emission exhibited peaks around 595, 612 and 617 nm wavelength. Thermoluminescence glow curve of irradiated samples recorded at a heating rate 3 K S^{-1}. The activation energy and kinetic parameters of the samples were evaluated using thermoluminescence GCD fitting method. The surface morphology of nanocomposites was studied by AFM. It was observed that the electrical properties of polymer nanocomposites enhanced after irradiation.

Chapter 5. Effect of Gamma and 90 MeV C^{6+} ion beam irradiation on physicochemical properties of PVA/H_3PO_4/SiO_2 nanocomposite polymer electrolytes

This chapter focused on the characterization of PVA/H_3PO_4/SiO_2 polymeric films for electrolyte applications. The obtained polymeric film was studied as a function of nanoparticles level and irradiation dose. These films were irradiated with gamma rays and C^{+6} (90 MeV) ions at different irradiation dose. Optical alteration upon irradiation has been studied by employing Tauc and Fink approaches. Complexation and structural rearrangement upon radiation treatment have been studied by using XRD and FTIR spectroscopy. Modification in the relaxation process and conductivity of nanocomposite polymer electrolyte due to irradiation have been investigated by dielectric spectroscopy. The average surface roughness of the nanocomposite polymer electrolyte also changed as revealed from AFM studied.

Chapter 6. Conclusion

In this chapter, the brief summary of the result obtained by gamma and C^{+6} (90 MeV) ion beam irradiation are explained on the basis of the application of the prepared polymer nanocomposites.

List of Research Paper Published in Internation Journals

1. Proton Beam Induced Modification of Luminescence Properties of Polystyrene/Al_2O_3 Polymer Nanocomposites
   Shilpa Bhavsar, N. L. Singh, S. V. Suryanarayana, K. V. R. Murthy
   Journal of Fluorescence volume 29, pages 1007–1012 (2019).
   doi: https://doi.org/10.1007/s10895-019-02414-z; **Impact Factor= 1.913**

2. Effect of γ-irradiation on thermal and thermoluminescence properties of polystyrene/europium (III) oxide composite film
   Shilpa Bhavsar, N.L. Singh, Birendra Singh
   Luminescence. 35 (2019) 412-417.
   doi:10.1002/bio.3742 **Impact Factor= 1.855**

3. Effect of γ-irradiation on optical properties of Eu_2O_3-doped polystyrene polymer films
   S. Bhavsar, Gnansagar B. Patel, N.L. Singh
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   doi:10.1002/bio.3541.

4. Investigation of optical properties of aluminium oxide doped polystyrene polymer nanocomposite films
   S. Bhavsar, Gnansagar B. Patel, N.L. Singh
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   doi:10.1016/j.physb.2017.12.055.

5. SHI induced modification in structural, optical, dielectric and thermal properties of poly ethylene oxide films
   Gnansagar B. Patel, **Shilpa Bhavsar**, N.L. Singh, F. Singh, P.K. Kulriya,
   Nucl. Instruments Methods Phys. Res. Sect. B 379 (2016) 156–161.
   doi:10.1016/j.nimb.2016.04.018. **Impact Factor= 1.270**

Presentation in Conference:

1. Influence of gamma radiation on optical properties of Al_2O_3-doped polystyrene polymer films
   Shilpa Bhavsar, N.L. Singh
   AIP Conference Proceedings 2220 (2020) 080056.
   doi: http://doi.org?10.1065/5.0001829 **Impact Factor= 0.400**

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