Chapter VI

Summary and Conclusion

This chapter summarizes results obtained from various analyses and outlines their significant conclusions and future perspectives.

Summary

The thesis aims to develop materials that can withstand radiation exposure and modify their properties through irradiation. Polymer nanocomposite films, namely, PS/Al_2O_3, PS/Eu_2O_3 and PVA/H_3PO_4/SiO_2 were prepared using the solution casting method to achieve the research objective. The radiation technique proved a unique technique to modify the physicochemical properties of the polymer nanocomposites. A significant modification of structural, optical, luminescence, thermal, electrical properties and surface morphology was achieved through irradiation with Gamma rays and 90 MeV Carbon ion beam. The nature of changes depends upon polymer properties such as composition, molecular weight and nature of radiations. The polymer composites were irradiated with C-ions and gamma rays of different fluences/doses. The composite films of different concentration of metal oxide of Al, Eu and Si powder in PS and PVA were prepared by solution casting method in which THS and deionised water were used as a solvent, respectively. The films were prepared in the Department of Physics, The M. S. University of Baroda. These films were irradiated with 90 MeV carbon ions at fluences of 1×10^{11} and 1×10^{12} ions/cm^2 by using the Pelletron facility and gamma rays irradiation facility of Inter-University Accelerator Centre (IUAC), New Delhi. Radiation plays a vital role in the field of materials science. Due to the interaction of radiation/energetic ions with polymer composite material, the species such as radicals, unsaturation etc., are produced. The different responses to radiation for different polymers are intrinsically related to the chemical structure of the polymer/polymer composite materials. The comparative results are summarised as follows,

(I) Structural Properties

(i) X-ray Diffraction Analysis

The XRD patterns of PS/Al_2O_3 polymer nanocomposites show no characteristic peaks of Al_2O_3 nanoparticles, suggesting substituting of Al_2O_3 nanoparticles in voids presented in the polymer matrix. Besides this, after irradiation, the XRD patterns of nanocomposites do not alter. EDAX analysis has confirmed the presence of Al_2O_3 nanoparticles.

X-ray diffraction studies of PS/Eu_2O_3 polymer nanocomposites showed an increased crystallite size due to the inclusion of nanofiller, caused by the crystalline nature of Eu_2O_3. But after SHI irradiation, the crystallite size decreases due to the splitting of the crystalline grain. This result implies a decrease in the crystallinity of polymer nanocomposites.

The XRD plots of nanocomposite polymer electrolytes ($PVA/H_3PO_4/SiO_2$) showed an increase in the FWHM of peak ($2\Theta=19.6^\circ$) with an increase in nanofiller level and irradiation dose. The irradiations caused randomization of polymer chains, creation of free radicals and carbon-rich networks, as well as a reduction in the crystallinity of the polymers, as evidenced by the increase in FWHM. It can be seen that SHI irradiation can significantly improve the structural properties of polymeric films.

(ii) FTIR Analysis

FTIR characterization was performed to study the structural and functional features of the macromolecular system and aggregates. The interaction between polymer and nanoparticles can also be studied through FTIR. The decrease in intensity of the absorbance peaks after the inclusion of the filler in the matrix polymer is attributed to the interaction of polymer and fillers. After irradiation, the decrease observed in the intensity of vibrational bands indicates the development of a carbon-rich network by reducing hydrogen atoms. FTIR spectra of PS/Al_2O_3 and PS/Eu_2O_3 polymer nanocomposites were not altered after gamma irradiation. This may be because the benzene ring of polystyrene was not destroyed even at the highest dose of gamma radiation.

(II) Optical Properties

UV-visible spectroscopy is used to determine the optical bandgap. The absorption edge of the spectra of all composites shifted towards a higher wavelength with increasing concentration of nanofiller and irradiation dose. This shifting is generally accounted for by the carbonization of material upon irradiation. The optical bandgap of all samples was calculated using the well known Tauc’s relation. It was significantly reduced as a result of the inclusion of the filler and irradiation (as shown in table 6.1). The reason for the reduction of bandgap with irradiation dose is the escalation of free electrons and impurities due to irradiation. Another reason for this is the formation of carbon enriched cluster by the emission of hydrogen molecules. Also, due to the high value of linear energy transferred (LET) of swift heavy ions in polymeric films, the modification in the optical bandgap of all the samples is more significant than that of the gamma irradiation.

Sample	Optical Bandgap (eV)			
	Gamma irradiation (25 kGy)	Gamma irradiation (50 kGy)	SHI irradiation (1×10^{11} ions/cm^2)	SHI irradiation (1×10^{12} ions/cm^2)
PA4	4.0	3.45	3.77	3.19
PSE5	3.86	3.67	3.47	3.31
PHS10	3.73	3.54	3.35	3.23

Table 6.1 Optical bandgap of gamma rays and SHI irradiated polymer nanocomposites.

(III) Luminescence Properties

(i) Photoluminescence

PS/Al_2O_3 polymer nanocomposites exhibited broad emission peaks around 411 nm, 435 nm and 462 nm under the excitation wavelength of 380 nm. The intensity of PL emission peaks escalates with nanofiller concentration as highly populated allowed electronic transitions increases. It increases further with the irradiation dose indicating the formation of new radiation recombination centres. Comparison of PL emission spectra of pristine and irradiated PA4 samples are shown in figure 6.1.

PL emission spectra of PS/Eu_2O_3 nanocomposites were recorded at an excitation wavelength of 247 nm. The three characteristic peaks of Eu^{3+} at 595 nm, 612 nm and 617 nm are observed in PL emission spectra of PS/Eu_2O_3 nanocomposites, while a broad peak of PS is found in the range of 360-410 nm. The intensity of Eu^{3+} peaks increases after the inclusion of nanofiller and SHI irradiation but reduces after gamma irradiation, as illustrated in figure 6.2.

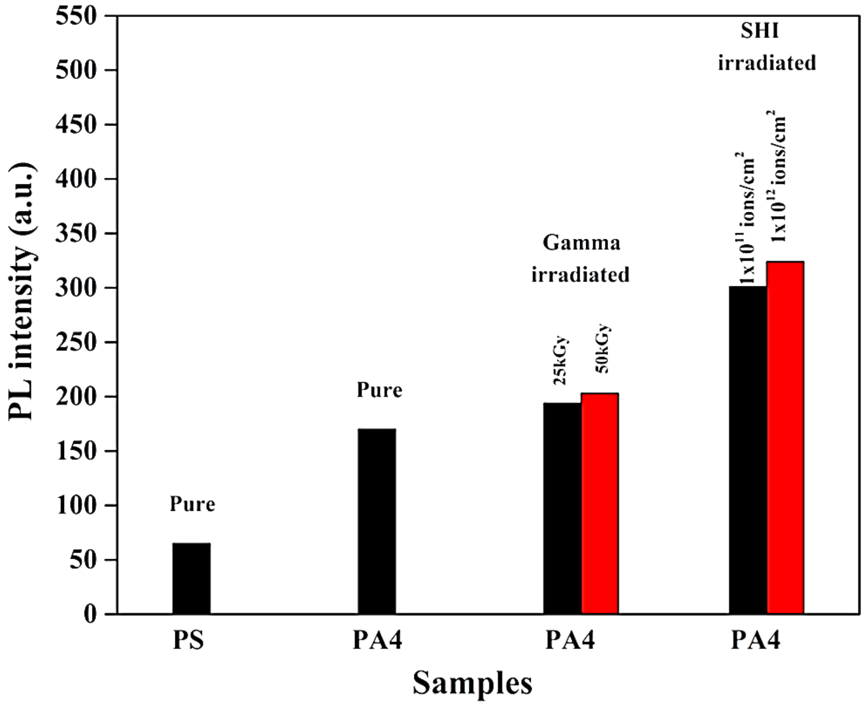

Figure 6.1 Comparison of PL emission spectra of pristine and irradiated PS/Al_2O_3 nanocomposites.

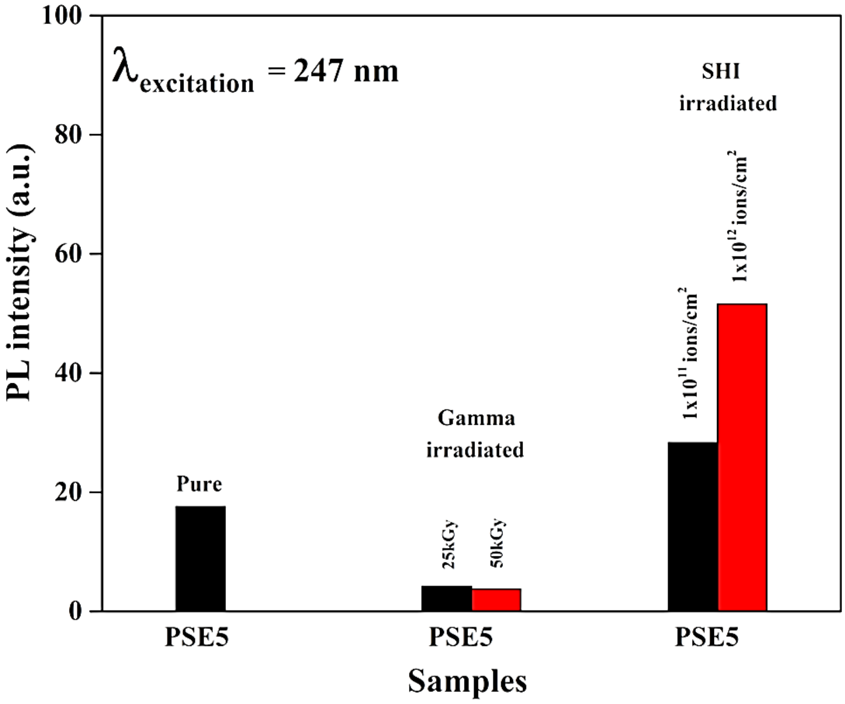

Figure 6.2 Comparison of gamma rays and SHI irradiations on intensity of PL emission peak of Eu^{3+} ion (612 nm).

Hence, the effect of SHI irradiation on PL emission spectra are high due to the accumulation of tremendously high localized energy in a small region. The result indicated that these polymeric films are a good contender for LED application.

(ii) Thermoluminescence

Thermoluminescence studies of PS/Al_2O_3 and PS/Eu_2O_3 nanocomposites were carried out after gamma and SHI irradiations. PS/Al_2O_3 polymer nanocomposites showed a maximum TL emission around 386 K whereas, for PS/Eu_2O_3 it was found to be around 415 K. The intensity of the TL glow curve increases with radiation dose. The output of the TL glow curve of PS/Al_2O_3 nanocomposites is higher for SHI irradiated samples than that of gamma-irradiated samples (figure 6.3), but PS/Eu_2O_3 sample shows high TL output on gamma exposure (figure 6.4). This indicates that PS/Eu_2O_3 shows eccentric behaviour after irradiation. Such a high TL output implies that these nanocomposites could be potentially useful in dosimetry applications.

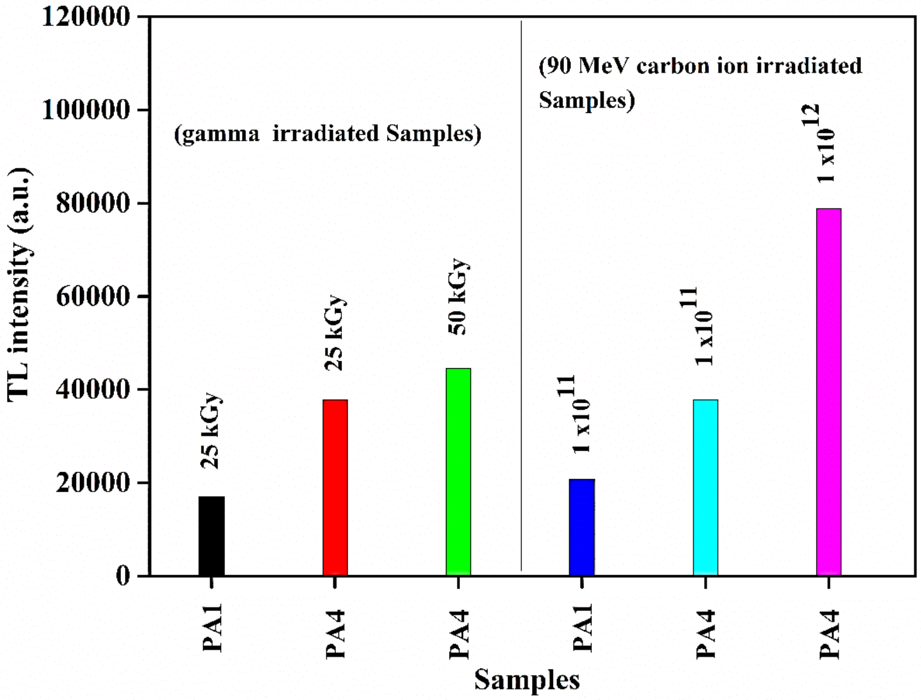

Figure 6.3 Effect of Gamma and SHI irradiations on TL glow curve intensity of PS/Al_2O_3 nanocomposites.

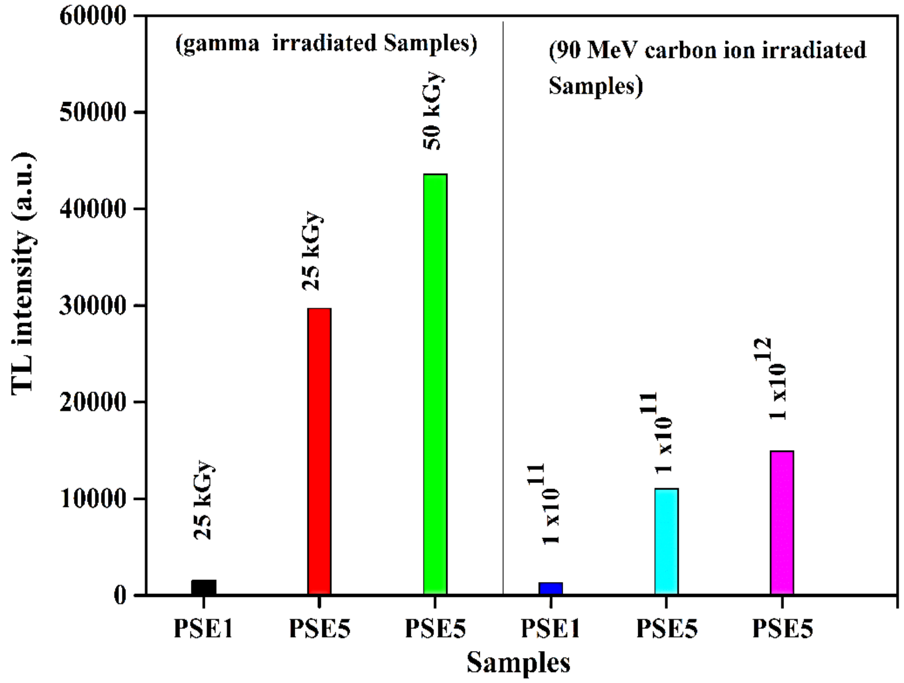

Figure 6.4 Effect of Gamma and SHI irradiation on TL glow curve intensity of PS/Eu_2O_3 nanocomposites.

(IV) AC Electrical Properties

(i) Dielectric Response

Figures 6.5 and 6.6 represent the change in the dielectric constant and dielectric loss of polystyrene-based nanocomposites after gamma and SHI irradiations, respectively. While figures 6.7 and 6.8 illustrate the change in the dielectric constant and dielectric loss of PVA based nanocomposite polymer electrolytes, respectively. The dielectric response of all polymeric films was examined as a function of filler level and irradiation dose. It is found to increase with filler level and irradiation dose. The escalation of the dielectric response of irradiated samples may be a result of the degradation of polymeric material due to the rupture of numerous bonds. The positive value of dielectric loss indicates the inductive behaviour of the material. Besides, swift heavy ions caused a momentous degradation of the polymeric material and therefore increased the value of dielectric response more effectively.

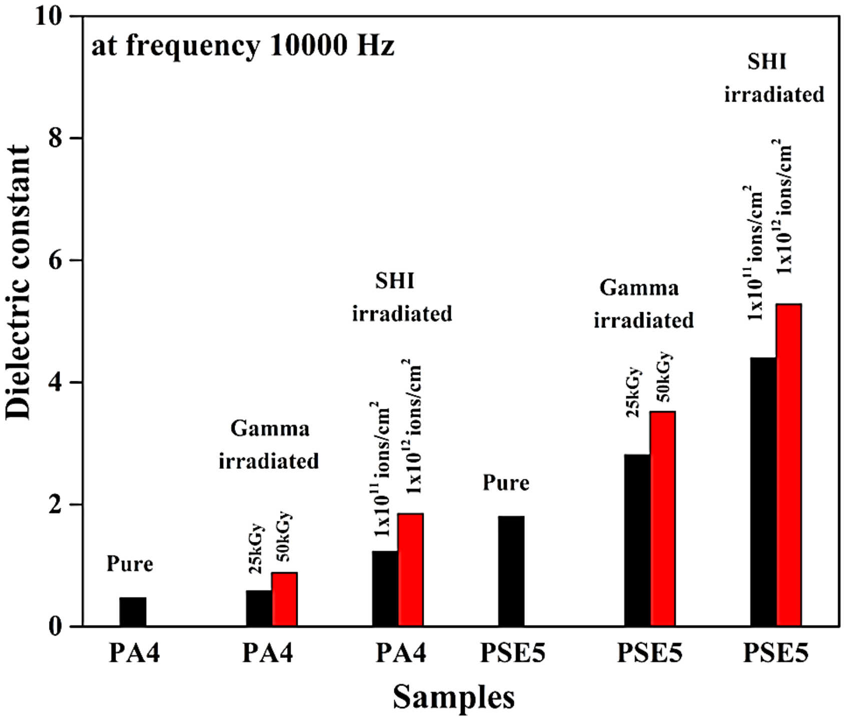

Figure 6.5 Comparison of the effect of Gamma rays and SHI irradiation on the dielectric constant of PS/Al_2O_3 and PS/Eu_2O_3 polymer nanocomposites.

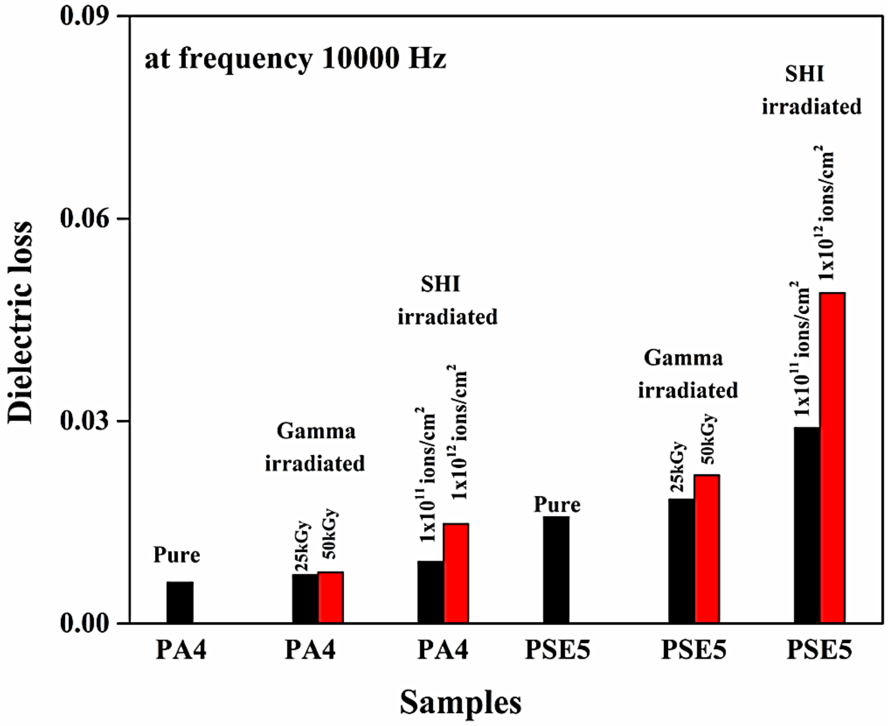

Figure 6.6 Comparison of the effect of Gamma rays and SHI irradiation on the dielectric loss of PS/Al_2O_3 and PS/Eu_2O_3 polymer nanocomposites.

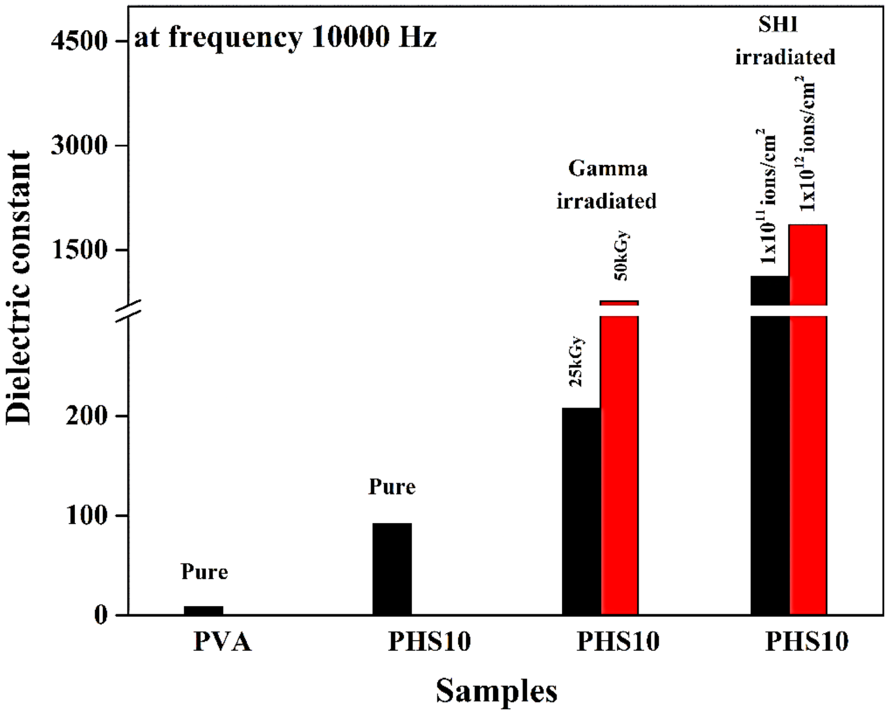

Figure 6.7 Comparison of the effect of Gamma rays and SHI irradiation on the dielectric constant of PVA/H_3PO_4/SiO_2 nanocomposite polymer electrolytes.

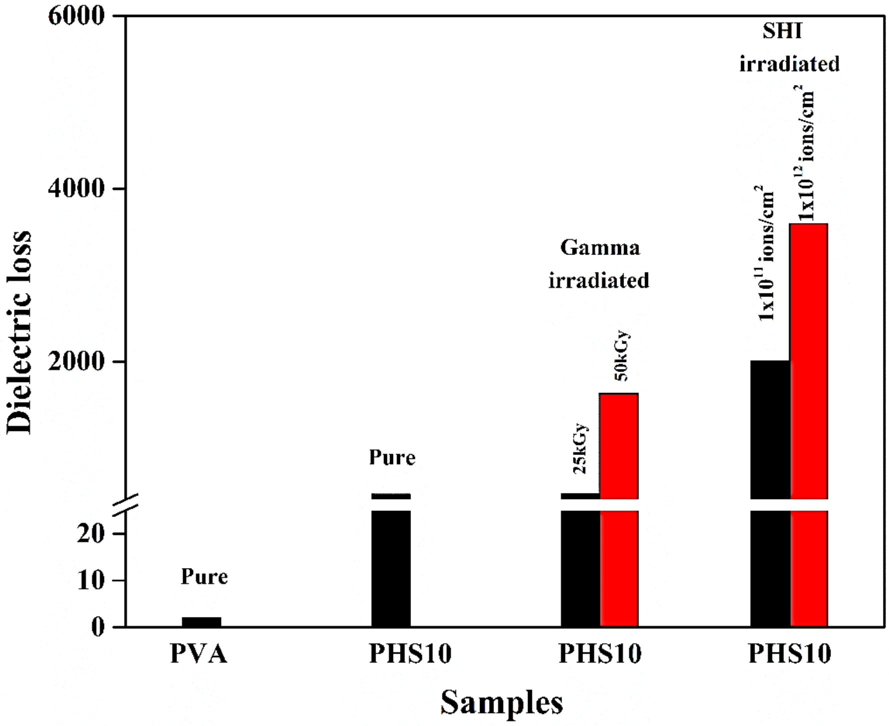

Figure 6.8 Comparison of the effect of Gamma rays and SHI irradiation on the dielectric loss of PVA/H_3PO_4/SiO_2 nanocomposite polymer electrolytes.

(ii) Conductivity

Figures 6.9 and 6.10 illustrate the effect of gamma and SHI irradiation on the AC Conductivity of polystyrene-based nanocomposites and PVA based nanocomposite polymer electrolytes, respectively. AC Conductivity of polymeric films was investigated as a function of filler level and irradiation dose. The increase in conductivity ascribes the formation of the conductive phase formed due to filler inclusion. After gamma and SHI irradiations, AC conductivity increases, implying enhancement of free volume in the polymer matrix, structural degradation, chain scission, the formation of defects and carbon-enriched network. Moreover, Swift heavy ions produced a momentous effect on the electrical properties of polymer nanocomposites because of the high value of linear energy transfer.

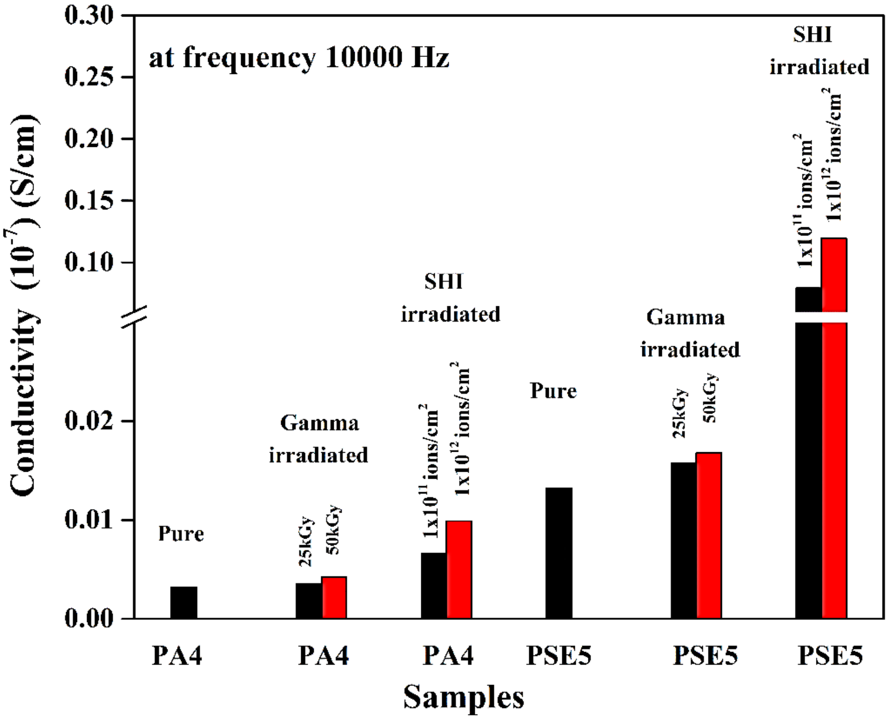

Figure 6.9 Comparison of the effect of Gamma rays and SHI irradiation on AC conductivity of PS/Al_2O_3 and PS/Eu_2O_3 polymer nanocomposites.

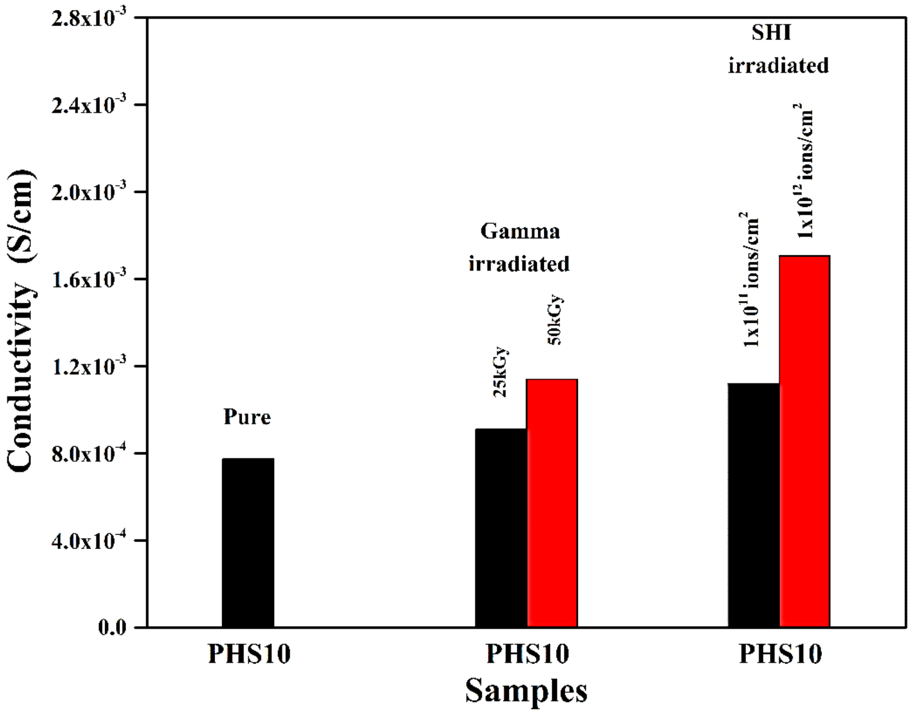

Figure 6.10 Comparison of the effect of Gamma rays and SHI irradiation on AC conductivity of PVA/H_3PO_4/SiO_2 nanocomposite polymer electrolytes.

(V) Thermal Properties

The thermal properties of all composites were investigated using differential scanning calorimetry (DSC). It was noticed that the glass transition temperature of samples (PS/Al_2O_3 and PS/Eu_2O_3 polymeric films) reduces after both kinds of irradiations, implying the system shifting to a more disorderly state.

The relative degree of crystallinity of PVA/ H_3PO_4/ SiO_2 polymeric films decreased after irradiation. This indicates that nanocomposite polymer electrolytes become more amorphous after irradiation. The results revealed decrease molecular weight due to the scissioning of the polymer chain after both kinds of irradiations. These results obtained correlated with the XRD results.

(VI) Surface Morphology

The surface morphology of all polymeric samples (PS/Al_2O_3, PS/Eu_2O_3 and PVA/H_3PO_4/SiO_2 polymeric films) was studied using atomic force microscopy, which gives average surface roughness. After both types of irradiations, the average surface roughness of all samples decreased due to high energy deposition. The decreased average roughness may be because of the escalation of density as well as size of nanofiller on the surface of polymeric films. This could be due to the defect enhanced surface diffusion. Moreover, the surface become more smoother after SHI irradiation than that of gamma irradiation. This is due to the high energy deposition by swift heavy ions than that of gamma rays.

Conclusion

The present work deals with polymer nanocomposites' preparation and investigation of the effects of gamma and swift heavy ion beam irradiations on these nanocomposites. XRD patterns of PS/Al_2O_3 remained unchanged after the incorporation of nanofillers and irradiations. XRD patterns of PS/Eu_2O_3 and PVA/H_3PO_4/SiO_2 polymeric films imply decreased crystallinity, a result consistent with DSC analysis. FTIR analysis of all samples (PS/Al_2O_3, PS/Eu_2O_3 and PVA/H_3PO_4/SiO_2 polymeric films) showed interaction of nanofillers with polymer matrices. After irradiation, the rupture of a few bonds was indicated by FTIR analysis. From UV-visible analysis, it was found that there is a decrease in optical bandgap upon both kinds of irradiations. The peak intensity of PL emission spectra of PS/Al_2O_3 nanocomposites increased with an increase in the irradiation dose. The characteristic peak intensity of Eu^{3+} ions declined after gamma irradiation, but it increased after SHI irradiation. After gamma irradiation, the PL emission peak intensity of Eu^{3+} is decreased because induced defects support the non-radiative transition by creating the additional path. TL glow intensity of PS/Al_2O_3 grew after both kinds of irradiations. The high output of Photoluminescence and Thermoluminescence suggested potential applicability in the field of luminescence. The electrical properties of all samples (PS/Al_2O_3, PS/Eu_2O_3 and PVA/H_3PO_4/SiO_2 polymeric films) grew significantly with the irradiation dose. Moreover, the change in the properties of all samples due to SHI irradiation is observed to be more than as caused by gamma irradiation, due to the high LET value of SHI radiation.

Future Plan

Effect of Gamma and SHI irradiation on Optical, Electrical and Luminescence properties of RE^{3+} (Tb^{3+}, Ce^{3+}) ions doped Bio-Polymer composites

In recent times, the development of bio-polymer based composites has drawn a lot of interest in various industrial and medical applications due to environmental concerns. The biopolymers have replaced the existing polymers in many applications and provide a unique combination of modified properties. Also, devices made from polymers become more flexible, cost-effective and easily processable. Because of these properties, polymers serve as the most popular matrices among all matrices in composites.

Rare-earth ions (RE^{3+}) have many promising applications because most of the time, they act as activators. RE^{3+} ions emit high purity colour light resulted from the 4f-4f electronic transition. It will become interesting to see the effect of different rare-earth ions on various properties of biopolymers. Rare earth oxide nanoparticles/salts can be used as dopant materials.

The composite films may be synthesized by a chemical route with different amounts of nanoparticles/salts. These composite films will be irradiated with gamma rays and swift heavy ion beam. The changes in optical, electrical and luminescence properties of samples due to both kinds of irradiation may be looked for using UV-visible spectroscopy, dielectric spectroscopy, photoluminescence and thermoluminescence.