Chapter - VI

Summary and conclusion

Abstract

This chapter summarizes the results derived from the present investigations. The comparative study of various properties of the composites with respect to filler concentration, different ions and ion fluence is presented. It also derives the conclusions of the present study and future perspectives.

Summary and conclusions

The thesis is concerned with the high energy ion beam irradiation effects in polymer composites which fascinated considerable attention for purposes of polymers in radiation environment and also in the improvement of new electronic devices. To achieve this goal, polymers have traditionally been considered as an excellent host matrix for composite materials and mixing with metal nanoparticles. SHI irradiation of polymers/polymer composites alters the chemico-physical properties considerably. The nature of changes depends upon properties of polymer composites, such as the composition and molecular weight and on the mass and energy of the incident ions and other conditions also.

The composite films of different concentrations of metal nanoparticles of silver (Ag), copper (Cu), and Nickel (Ni) powder in PMMA and PS were prepared by casting method in which THF and toluene was used as a solvent respectively. The films prepared at Department of Physics, The M. S. University of Baroda, Vadodara. These films were irradiated with 85 MeV C- ions and 120 MeV Si-ions at fluences of 1 x 10^{11} ions/cm^2, 1 x10^{12} ions/cm^2 using high energy ion beam facility of Inter University Accelerator Centre (IUAC), New Delhi, India. 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. Due to the interaction of radiation/energetic particle with polymer composite material absorbs its energy and active species such as radicals are produced initiating various chemical reactions. The different responses to radiation for different polymers are intrinsically related to the chemical structures of the polymer /polymer composite materials. The synthesized polymer nanocomposites were subjected to different characterizations, mainly structural, thermal, optical, magnetic and electrical properties and surface morphology before and after irradiation. The comparative results are summarized as follow;

(I) Structural modification:

The crystallite size of pristine and irradiated composites was studied by means of X-ray diffraction. The crystallite size was calculated using Scherrer's formula as discussed in chapter 2. It is appearant that crystallite size increases with filler concentartions which is responsible to the crytalline nature of fillers in both composites. In the case of PMMA/Ag(/Cu/Ni) nanocomposites, crystallite size of fillers decreases slightly upon irradiation with both the ions. It is also observed that the intensity of the peak decreases and to some extent broadening of the peak after irradiation offers confirmation of decrease in crystallinity. Since no significant change in the peak position is observed, this reveals that lattice parameters do not change significantly with both ion beams irradiations. Results show that the ion beam irradiation causes large amount of energy deposition in the material which leads to decrease in crystallite size. It may be attributed to splitting of crystalline grains due to absorption of large amount of energy and it also reflects the formation of disorder system. The irradiation may induce chain scissioning, which is also corroborated by DSC analysis, assumed to be responsible for the reduction in crystallinity of the composite. Rather in the case of PS/Ag(/Cu/Ni) nanocomposites, the diffraction patterns of the irradiated samples by 85 MeV C-ions and 120 MeV Si ions exhibited an increase in the peak intensity and a decrease in the full width at half maximum (FWHM) corresponding to all observed peaks of Ag/Cu/Ni nano particles. This behaviour may be attributed to cross-linking effect and resulted in the alignment of the polymeric chains, which is also corroborated by the results of DSC analysis. The results for highest concentration and fluence are summarized in Table 6.1.

Table 6.1(a): Crystallite size of composites for PMMA+ Ag/Cu/Ni systems

Sample	Pristine		C Beam	Si Beam
	2θ	Crystallite size (nm)	Crystallite size (nm) $(1x10^{12})$ ions/cm^2	Crystallite size (nm) $(1x10^{12})$ ions/cm^2
PMMA+ 15%Ag	38.07	32.64	30.14	29.98
	44.24	33.17	30.67	29.34
	Average	32.91	30.41	29.66
PMMA + 15%Cu	46.39	12.36	11.68	10.54
	58.01	12.24	11.22	10.39
	Average	12.30	11.45	10.47
PMMA + 15%Ni	44.60	10.40	11.05	10.67
	51.27	11.10	10.21	9.58
	Average	11.52	10.63	10.13

Table 6.1(b): Crystallite size of composites for PS+ Ag/Cu/Ni systems

Sample	Pristine		C Beam	Si Beam
	2θ	Crystallite size (nm)	Crystallite size (nm) $(1x10^{12})$ ions/cm^2	Crystallite size (nm) $(1x10^{12})$ ions/cm^2
PS+ 15%Ag	37.87	37.98	38.51	38.88
	44.11	37.87	38.19	38.90
	Average	37.93	38.35	38.89
PS + 15%Cu	46.18	11.89	12.98	13.52
	57.23	12.06	13.11	13.78
	Average	11.97	13.05	13.65
PS + 15%Ni	44.60	10.40	11.50	11.88
	51.27	11.10	11.75	12.24
	Average	10.75	11.62	12.06

(II) Thermal response:

The glass transition temperature (Tg) of pristine and irradiated samples was studied by DSC thermograms. At the glass transition temperature, the weak secondary bonds that stick the polymer chains together are broken, and the macromolecule starts to move. The influence of metal nanoparticles and irradiation on the glass transition behaviour of polymer matrix (PMMA/PS) was investigated with dynamic DSC technique. When the inter-particles distance is small enough, then the polymer between two particles can be considered as a thin film. Assuming that there is small or no interfacial interaction between the filler and matrix exists and then Tg decreases as explained by Ash et al according to thin film model. It reveals that the ion irradiation leads to polymer chain scissioning and a subsequent reduction in the molecular weight. As a result, the system moved toward the more disordered state in the case of PMMA+Ag (/Cu/Ni) nanocomposites. The Tg of pristine composites increases with filler concentration and also further increases upon irradiations in PS/Ag(/Cu/Ni) nanocomposites. This behaviour probably arises due to branching (cross-linking effect) when islands of nanoparticles are bonded with polymeric chains. This lowers the mobility of the chains, and as a result, the glass transition temperature increases in the nanocomposites. These results are also corroborated with XRD results. The results for highest concentration and fluence are summarized in Table 6.2.

Table 6.2(a): Glass transition temperature of composites for PMMA+ Ag/Cu/Ni systems

Sample name	Tg (Pristine)	Tg (C beam)	Tg (Si beam)
PMMA + 15 %Ag	71.4	65.8	64.2
PMMA + 15 %Cu	71.9	61.8	61.5
PMMA + 15 %Ni	77.8	76.8	72.8

Table 6.2(b): Glass transition temperature of composites for PS+ Ag/Cu/Ni systems

Sample name	Tg (Pristine)	Tg (C beam)	Tg (Si beam)
PS + 15 %Ag	71.9	72.7	73.2
PS + 15 %Cu	72.9	73.3	74.8
PS + 15 %Ni	71.5	73.7	75.7

(III) Optical response:

UV–vis spectroscopy is an important tool to investigate the value of optical band gap energy (Eg). It is observed that optical absorption increases with increasing energy loss and this absorption shifts from UV to visible region for all irradiated nanocomposite samples. With increase of electronic energy loss, the nanocomposites become gradually opaque to the visible light and the absorption edge shifted from UV towards the visible. This is consistent with the observation that the material changes from transparent to opaque with increase of energy deposition. The increase in absorption with irradiation may be attributed to the formation of a conjugated system of bonds due to bond cleavage and reconstruction. The shifting of absorption edge towards visible is generally considered to result from carbonization of the material under irradiation which is also corroborated to the dielectric results. It is noticed that band gap values shifted to lower energy in composites for irradiated samples. The obtained results for highest concentration and fluence are summarized in Table 6.3.

Table 6.3(a): Band gap energy of composites for PMMA+ Ag/Cu/Ni systems

Sample	Pristine		C Beam		Si Beam	
	Band gap in eV	No. of carbon atoms(N)	Band gap in eV	No. of carbon atoms(N)	Band gap in eV	No. of carbon atoms(N)
Pure PMMA	4.58	56	4.38	61	4.26	65
PMMA + 15%Ag	3.82	80	3.65	88	3.21	114
PMMA + 15%Cu	3.78	82	3.55	90	3.22	113
PMMA + 15%Ni	3.84	80	3.55	90	3.43	100

Table 6.3(b): Band gap energy of composites for PS+ Ag/Cu/Ni systems

Sample	Pristine		C Beam		Si Beam	
	Band gap in eV	No. of carbon hexagon rings	Band gap in eV	No. of carbon hexagon rings	Band gap in eV	No. of carbon hexagon rings
Pure PS	4.38	~1	4.21	~1	3.89	~1
PS + 15%Ag	3.90	~1	3.60	~1	3.30	~2
PS + 15%Cu	3.98	~1	3.65	~1	3.40	~2
PS + 15%Ni	4.02	~1	3.75	~1	3.43	~2

(IV) Surface morphology:

Surface morphology was studied by means of scanning electron microscope (SEM) which gives 2-D surface topography of sample surface. The analysis shows that the filled partilces are distributed randomly in the matrix which display continuous contact between themselves and formed conducting paths. After irradiation, significant changes in surface morphology were observed. Considerable damage in the polymeric structure was observed after irradiation, which is also responsible for decrease in crystallinity of the material as indicated by XRD analysis in PMMA nanocomposites. This may be attributed to large sputtering effect due to irradiation in PMMA nano composites. Wherea in PS nanocomposites, the surface becomes smoothen upon irradiation.The decrease in roughness may be attributed to the decrease in density of metal particles on the surfaces of the films, which is also responsible for increase in crystallinity of the material as indicated by XRD analysis. This is attributed to the defect enhanced surface diffusion in the case of PS nano composites.

(V) Magnetic properties:

The temperature (T) and magnetic field (H) variations of the magnetization (M) were measured with a SQUID (superconducting quantum interference device) magnetometer. The temperature variations of M for the zero field- cooled (ZFC) and the field-cooled (FC) cases were measured from 5-300 K at applied field ,H = 500 Oe. Hysteresis measurements were carried out at 300 K with magnetic field swept from 50 kOe to -50 kOe. The magnetic parameters extracted from the measurements are listed in Table 6.4.

The increase in the values of M_S and H_C after irradiation may be attributed to the change in exchange and dipolar interactions mediated by the matrix.

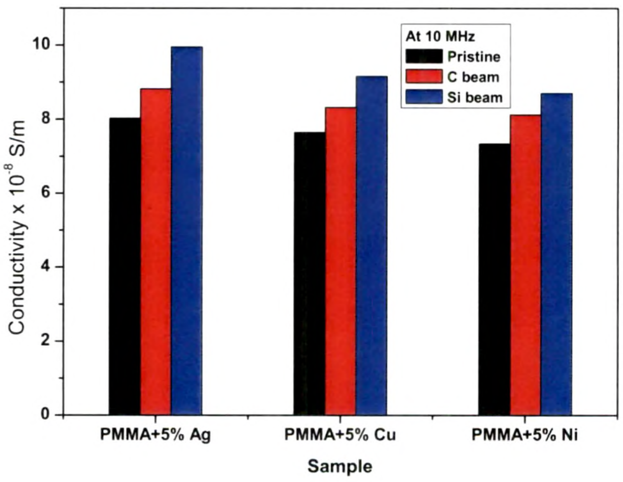
FC magnetization decreases continuously with the increase of temperature. Such characteristic behavior of FC magnetization data is attributed to ferromagnetism in material in both nanocomposites.

Table 6.4: Magnetic properties of composites for PMMA+Ni and PS+Ni systems.

Sample		Pristine	C Beam	Si Beam
PMMA+15%Ni	Saturation Magnetization (M_S) (emu/gm)	0.085	0.107	0.120
	Coercive Field (H_C) (Oe)	138	147	150
	Remnant Magnetization (M_R) (emu/gm)	0.015	0.020	0.022
PS + 15%Ni	Saturation Magnetization (M_S) (emu/gm)	0.077	0.097	0.109
	Coercive Field (H_C) (Oe)	136	145	155
	Remnant Magnetization (M_R)(emu/gm)	0.014	0.019	0.022

(VI) AC electrical properties:

Conductivity: The AC electrical properties of all composites were studied in the frequency range of 100 Hz to 10 MHz at an ambient temperature.



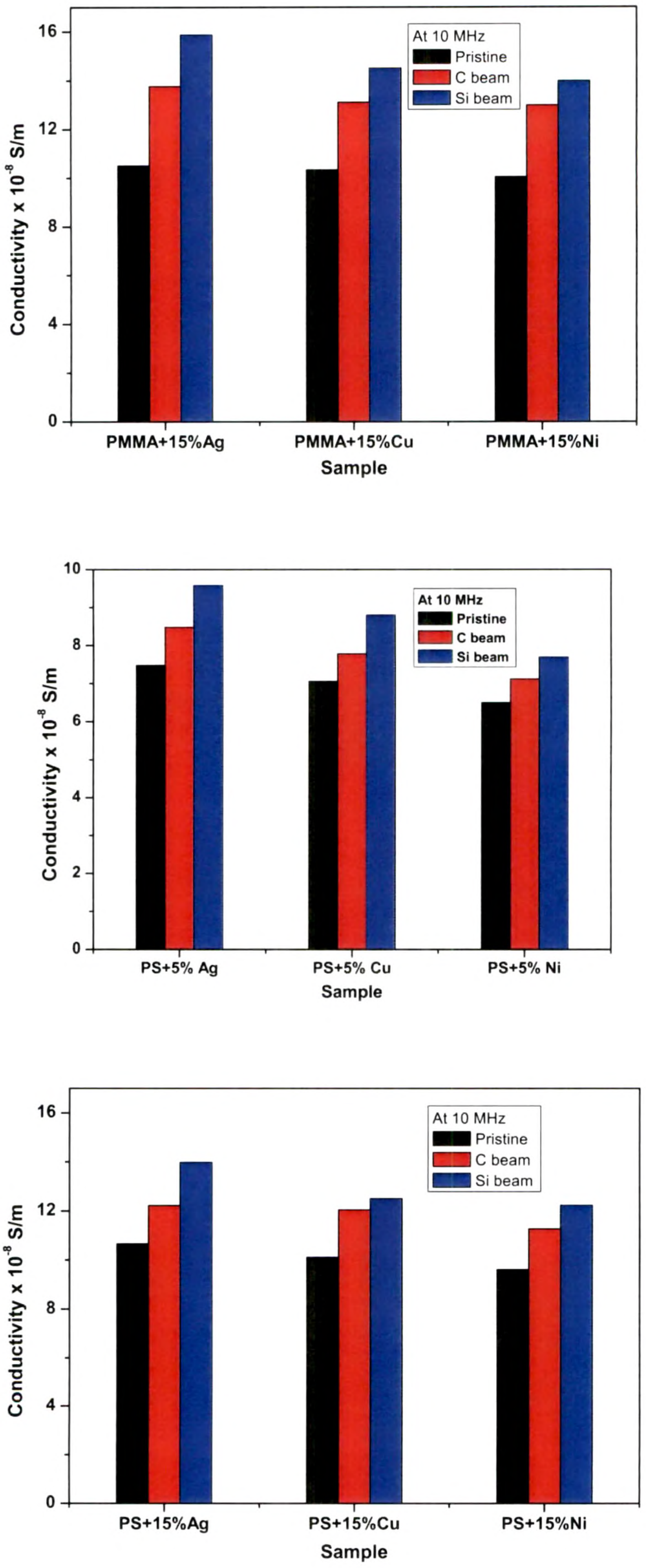
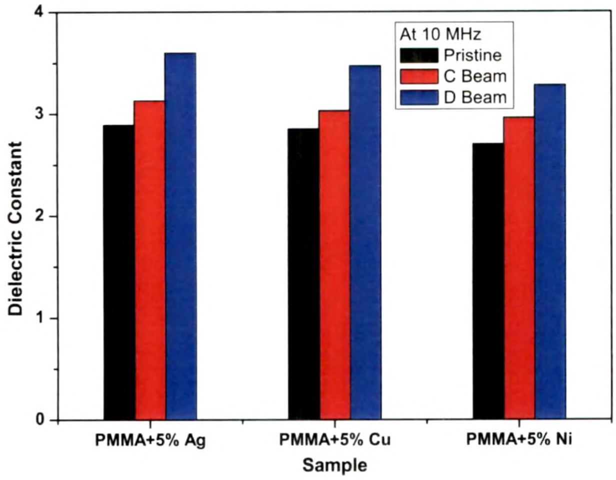


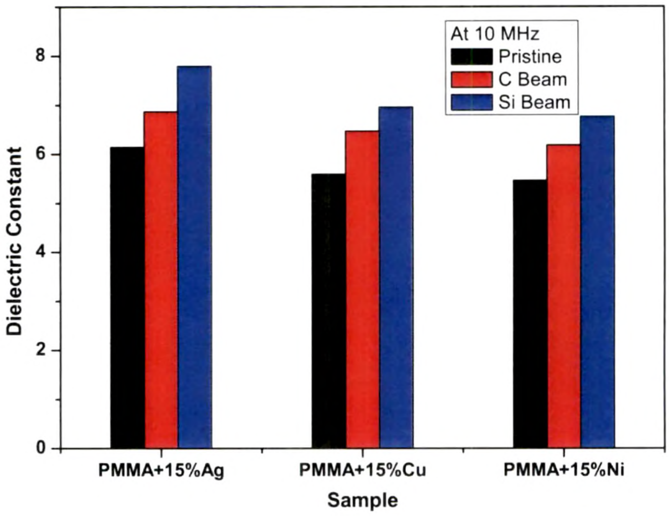
Fig.6.1 Comparison of conductivity of pristine and irradiated samples at a frequency of 10 MHz

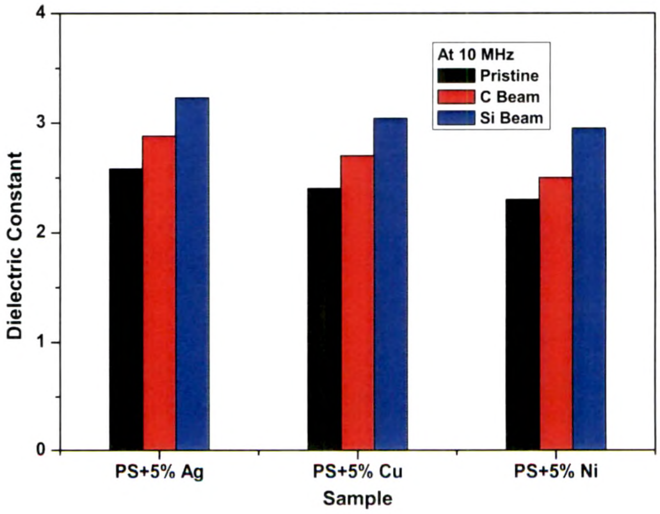
AC electrical conductivity of all pristine and irradiated samples for different ion species and at the concentrations of 5% and 15% and a constant frequency (10MHz) is shown in Fig.6.1. The increase in conductivity with metal nanoparticles concentration for pristine samples may be attributed to the conductive phase formed by dispersed metal nanoparticles in polymer matrix. The increase in conductivity is related to a possible increase in the number of conduction paths created between the filler particles aggregates in the composite and as a consequence electrical path is built up in the composites due to the decrease in the width of the potential barrier. Therefore more charge carriers may be able to 'hop' by tunnelling; resulting in the increase in the bulk conductivity and it also increases with increasing filler concentration. Conductivity is further observed to increase upon irradiation. Irradiation is expected to promote the metal to polymer bonding and convert polymeric structure into hydrogen depleted carbon network due to the emission of hydrogen and /or other volatile gases. It is this carbon network that is believed to make the polymer more conductive.

Dielectric constant: The dielectric constant of all composites was calculated in the frequency range of 100 Hz to 10 MHz.

The values of the dielectric permittivity for nanocomposites depend both on the measuring frequency and also nano filler concentration. Especially, the dielectric behaviors of nanocomposites with different metal nanoparticles concentrations in the low frequency range (< 1kHz) are found to be increased which is due to the interfacial space charge polarization. The higher the nanofiller loading level, the larger the total effective area of the interfaces between the polymer matrix and the filler, and the thinner the insulating spacers separating nanoparticles, resulting in the considerable increment of the interfacial space-charge polarization at these frequencies. As observed from figure, the dielectric constant remains almost constant up to 100 kHz. At these frequencies, the motion of free charge carriers assumed to be constant through the polymer matrix. It is also observed that dielectric constant increases upon irradiation. The increase in dielectric constant may be attributed to the chain scission, cross linking and as a result an increase in the number of free radicals, unsaturation etc. At higher frequency regions, (i.e., beyond 100 kHz), the charge carriers migrate through the dielectric and get trapped against a defect sites and induced an opposite charge in its vicinity. So, the polarization of trapped and bound charges cannot take place and that reduced the dielectric constant. According to the Dissado and Hill theory, in intra-cluster motions, the relaxation of a dipole will produce a 'chain' response in its neighbouring dipoles and the reaction of the neighbouring dipoles will, in turn, affect the first dipole, so the overall effect will be seen as a single-cluster dipole moment relaxation. This reduces the dielectric constant at these frequencies. For the sake of comparison, the dielectric constant of all pristine and irradiated samples for different ion species and at the concentration of 5% and 15% and a constant frequency (10MHz) is shown in Fig.6.2.


4
3
2
1
0
Dielectric Constant
At 10 MHz
Pristine
C Beam
D Beam
PMMA+5% Ag
PMMA+5% Cu
PMMA+5% Ni
Sample


8
6
4
2
0
Dielectric Constant
At 10 MHz
Pristine
C Beam
Si Beam
PMMA+15%Ag
PMMA+15%Cu
PMMA+15%Ni
Sample


4
3
2
1
0
Dielectric Constant
At 10 MHz
Pristine
C Beam
Si Beam
PS+5% Ag
PS+5% Cu
PS+5% Ni
Sample

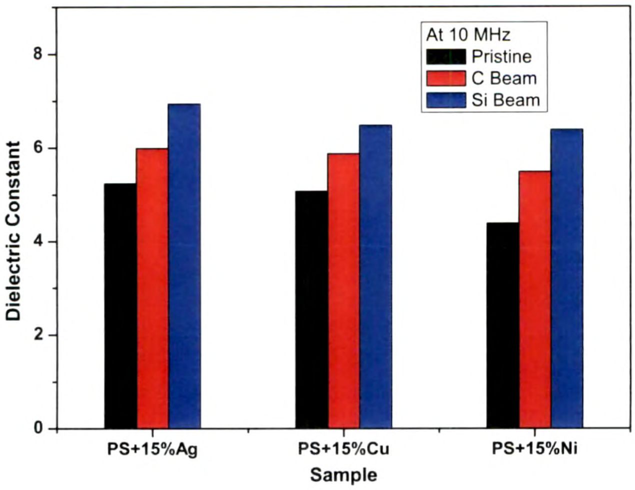


Fig. 6.2 Comparison of dielectric constant of pristine and irradiated samples at a frequency of 10 MHz

Dielectric loss: The dielectric loss of all composites was studied in the frequency range of 100 Hz to 10 MHz. In general, the dielectric loss of the dielectric material causes from distortional, dipolar, interfacial, and conduction loss. The dielectric loss decreases exponentially with the increase of log frequency. It is observed that dielectric loss increases moderately with the concentration of filler and also with the ion fluence which may be featured to the interfacial polarization mechanism of the heterogeneous system. Positive value of dielectric loss in all the cases represents the inductive behavior of the material.

Conclusion:

Present work deals with the synthesis of polymer nanocomposites and effect of ion beam irradiation on these nanocomposites. Based on this study, we have concluded that ion beam irradiations alter all the properties of polymer nanocomposites. An XRD analysis reveals that the crystallite size of the composites decreased after ion beam irradiation which is also corroborated by the DSC analysis due to the chain scissioning upon irradiation in PMMA nanocomposites. In PS nano composites, we observed cross linking effect upon irradiation. It was observed from the UV- visible spectroscopy analysis that the band gap value moved to the lower energy on doping with metal nanoparticles, as well as upon irradiation. SEM images showed damages upon ion beam irradiation. The magnetic properties enhanced after ion beam irradiation which may be attributed to the exchange dipolar interaction of particles in the matrix and generation of free radicals. The dielectric properties of the composites increased with the increase of metal content. These phenomena could be interpreted from interfacial polarization of heterogeneous systems. It is evsigaed that the new composite materials synthesized in the present work have potential applications such as microelectronics, satellite, telecommunication, packaging, biomaterials etc where material with low dielectric constant is required. Rather material with high dielectric constant can be used for EMI shielding application.

Future Plan

Physical properties of bimetallic nanoparticles embedded polymer matrix by ion beam irradiation

During the past decade, the design and synthesis of bimetallic nanomaterials have attracted considerable attention, because they show multiple functionalities and prominent catalytic activity, electrical, chemical and optical properties over monometallic nanomaterials. Polymer nanocomposites have 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. Synthesis of nanocomposite polymers is easy due to their ease of processing, solubility and less toxicity. The modification of polymeric material by irradiation with swift heavy ions has gained considerable interest in the last two decades because of significant change in the chemico-physical properties of the materials. 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. The samples will be prepared by chemical route method in which different bimetallic nanoparticles dispersed in polymer matrix and will be irradiated by different ion beams. These samples will be characterized by X-ray diffraction, TEM/SEM, DSC, UV-Visible spectroscopy, SQUID measurements and dielectric spectroscopy.