Chapter VI
Summary and Conclusion

Abstract

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

Summary and Conclusions

The main objective of this work was to prepare composite materials which can withstand against radiative environment and to enhance its properties by irradiation. To achieve this goal, polymer composites were synthesized. Change in the electrical and mechanical properties of polymer based materials could be successfully achieved by mixing the polymer matrix with organometallic compound/metal particles. Ion beam irradiation proved to be a suitable technique to alter the chemical and physical properties of the polymer/polymer composites. In this work, influence of ion beam irradiation on different polymer composites is studied, with respect to ion beam parameters (e.g. ion energy, specie and fluence), filler factors (e.g. specie, concentration) and polymer chemistry. A significant alteration of the electrical, mechanical, structural, chemical and surface properties of the composites was obtained due to ion beam irradiation.

PMMA was synthesized by solution polymerization technique. Polymer composites were prepared by doping different concentrations of fillers (e.g. Ferric oxalate, Palledium acetylacetonate, Nickel dimethylglyoxime and Ni powder) in polymethyl methacrylate (PMMA). Composite films were prepared by solution casting method at Department of Physics, M. S. University of Baroda, Vadodara. Ion beam irradiation effect on these polymer composites have been studied for three different ion beams. The samples were irradiated with 3 MeV proton beam using Cyclotron of Punjab University, Chandigarh and swift heavy ions of Ni^{10+} (120 MeV) and Ag^{11+} (140 MeV), produced by 15 UD Pelletron accelerator at IUAC, New Delhi. Irradiations were performed in fluence range from $1x10^{11}$ to $1x10^{13}$ ions/cm^2.

The dielectric, mechanical, structural, chemical, thermal and surface properties of pristine and irradiated films were studied by means of various characterization techniques. The effect of filler factors and ion beam parameters on polymer is carried out. The comparative results are discussed in this chapter.

(I) 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. It was observed that a sharp increase in conductivity was observed after 100 kHz for pristine and irradiated samples.

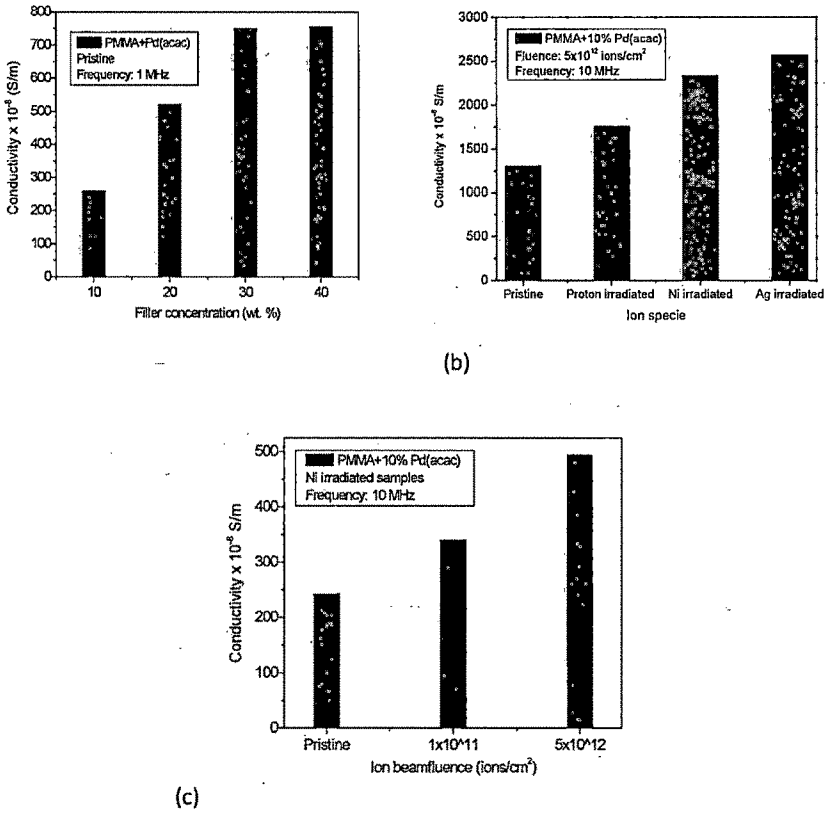

Fig. 6.1 Variation in conductivity with respect to (a) filler concentration (b) ion specie and (c) ion fluence at 10 MHz for PMMA+Pd composites

The conductivity increased after dispersion of filler and also upon ion beam irradiation. The increased conductivity with filler concentration is attributed to the conductive phase formed by dispersed conductive filler in polymer matrix. The effect of filler concentration on conductivity is shown in Fig. 6.1(a). The conductivity further observed to increase after ion beam irradiation. Ion beam irradiation expected to promote the metal to polymer bonding and convert the polymeric structure into hydrogen depleted carbon network by emission of hydrogen and/or other volatile gases. It also depends on ion specie (Fig. 6.1(b)). This figure shows that SHI induced considerable enhancement in conductivity of the composites. The conductivity increases with ion fluence which attributes to scissioning of polymeric chains and as a result creates free radicals, unsaturation etc. in the polymeric material. The fluence dependence of ac conductivity is shown in Fig. 6.1(c).

Dielectric constant: The dielectric constant was calculated in the frequency range of 100 Hz to 10 MHz for pristine and irradiated samples.

Dielectric constant remains almost constant up to 100 kHz. At low frequencies, the motion of free charge carriers is almost constant and therefore dielectric constant apparently remains unaffected. At higher frequency (beyond 100 kHz), the charge carriers migrate through the dielectric and get trapped against the defect sites. At these frequencies, the polarization of trapped and bound charges can not take place and hence the dielectric constant decreases. The decrement obeys the Universal law of dielectric response.

The scissioning of polymeric bond due to ion beam irradiation produces free radicals, unsaturation etc which are responsible for the enhancement of dielectric constant after irradiation. Variation in Dielectric constant of composites as a function of filler concentration, ion specie and ion fluence are shown in Fig. 6.2 (a, b, c) respectively.

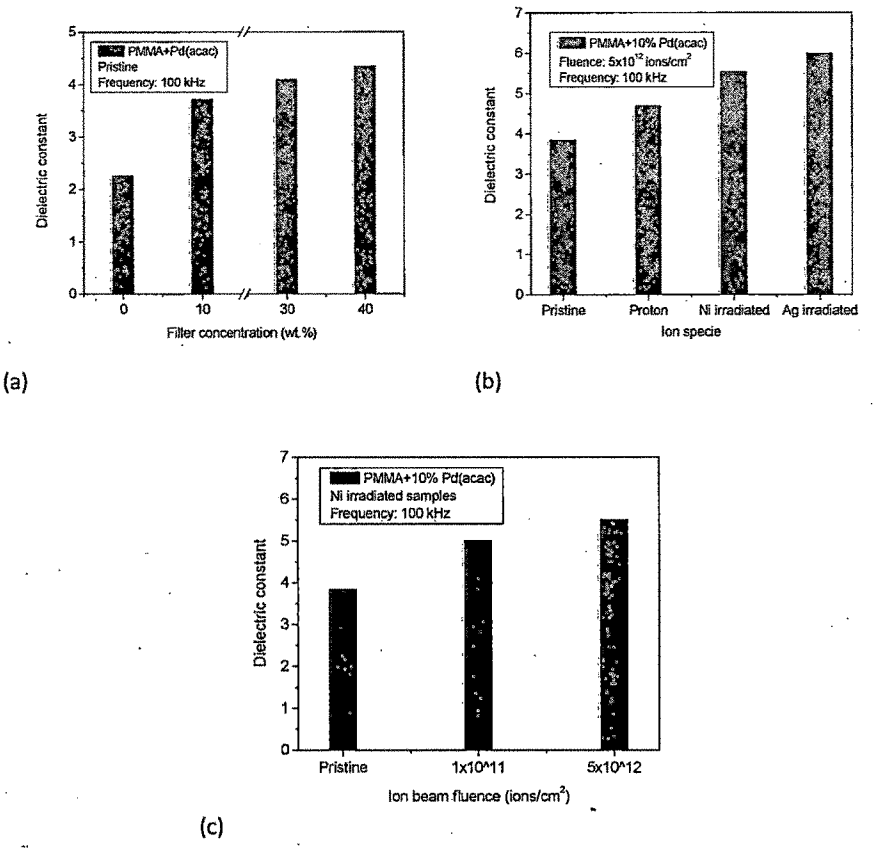

Fig. 6.2 Variation in dielectric constant with respect to (a) filler concentration (b) ion specie and (c) ion fluence at 10 MHz for PMMA+Pd composites.

Dielectric loss: Dielectric loss factor (tanδ) was also studied for the same frequency range viz. 100 Hz to 10 MHz. Fig. 6.3(a,b,c) represents the dependence in dielectric loss on filler concentration, ion specie and ion fluence respectively. It is observed that tanδ decreases exponentially as frequency increases. It is also observed that loss factor increases with filler concentration and after ion beam irradiation. Positive value of dielectric loss in all the cases represents the inductive behaviour of the material.

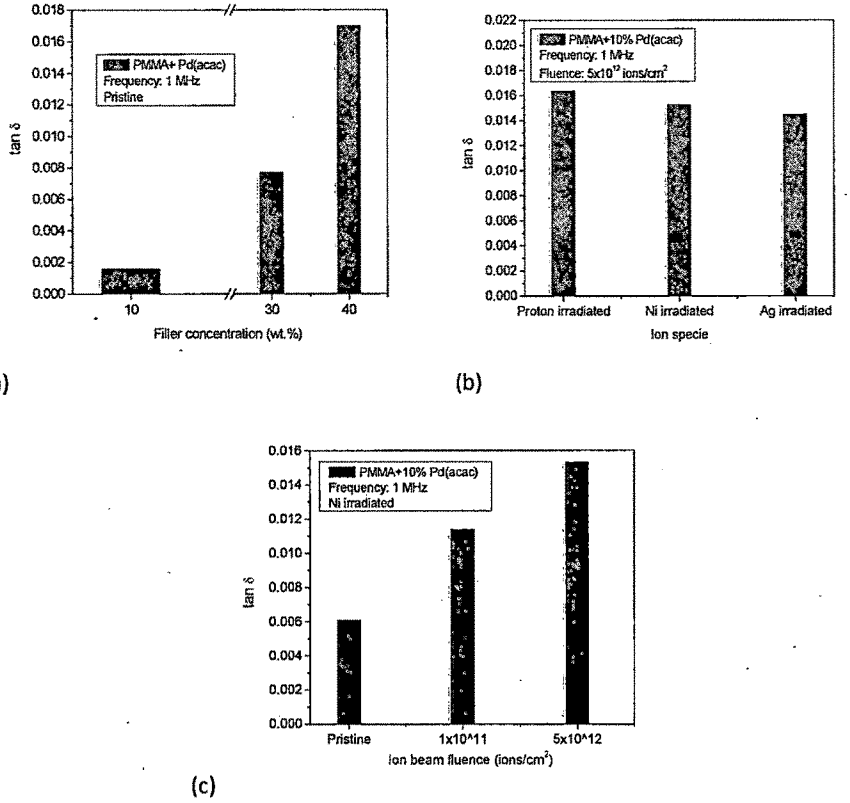

Fig. 6.3 Variation in dielectric loss with respect to (a) filler concentration (b) ion specie and (c) ion fluence for PMMA+Pd composites.

(II) Microhardness

The microhardness studies enable us to understand the issues related to the mechanical behaviour (elastic-plastic deformation characteristics) of polymeric films.Vicker's Microhardness indentations were carried out on the surfaces of the pristine and irradiated films of PMMA+Fo at ambient temperature in the applied load ranging from 10 to 1000 mN and a constant loading time of 30s.

Initially microhardness increases with load and beyond a certain load, it attains saturation which represents the strain hardening. On applying load, the polymer is subjected to some strain hardening and beyond certain load the polymer exhausts its

strain hardening capacity and hardness tends to become constant. The value obtained from the saturation region represents the true hardness of the bulk material. It is observed that hardness improves with filler concentration (Fig. 6.4(a)). The bond between polymeric chain and organometallic compound and also the hydrogen depleted carbon network might be responsible for making polymer harder. Hardness further increases with irradiation fluence (Fig. 6.4(c)) as well as with heavier ion beam as shown in Fig. 6.4(b).

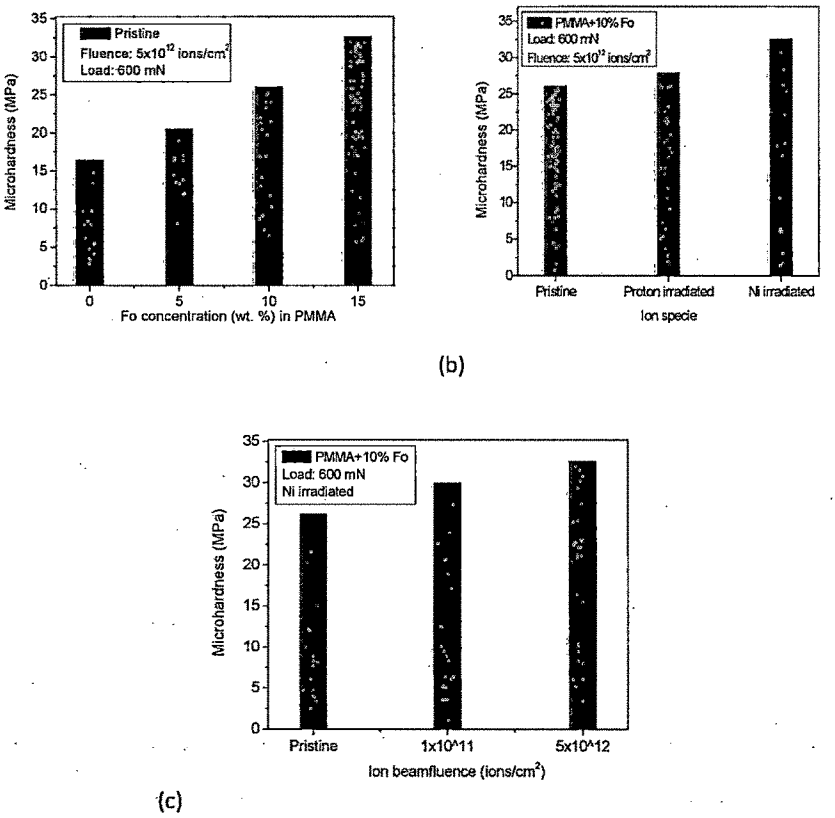

Fig. 6.4 Vicker's microhardness as a function of (a) filler concentration and (b) ion specie and (c) ion fluence at a load of 600 mN

(III) Structural modification

(a) X-ray diffraction analysis

Crystalline size and % Crystallinity of pristine and irradiated composites were studied by means of X-ray diffraction. Crystalline size was calculated using scherrer's equation as discussed in Chapter-2. It is apparent that the crystalline size and % crystallinity increases with filler concentration (Fig. 6.5(a)) which is responsible to the crystalline nature of filler. But it reduces after ion beam irradiation which is attributed to splitting of crystalline grains due to large energy deposition by SHI. It is responsible for changing the composite system towards disordered state.

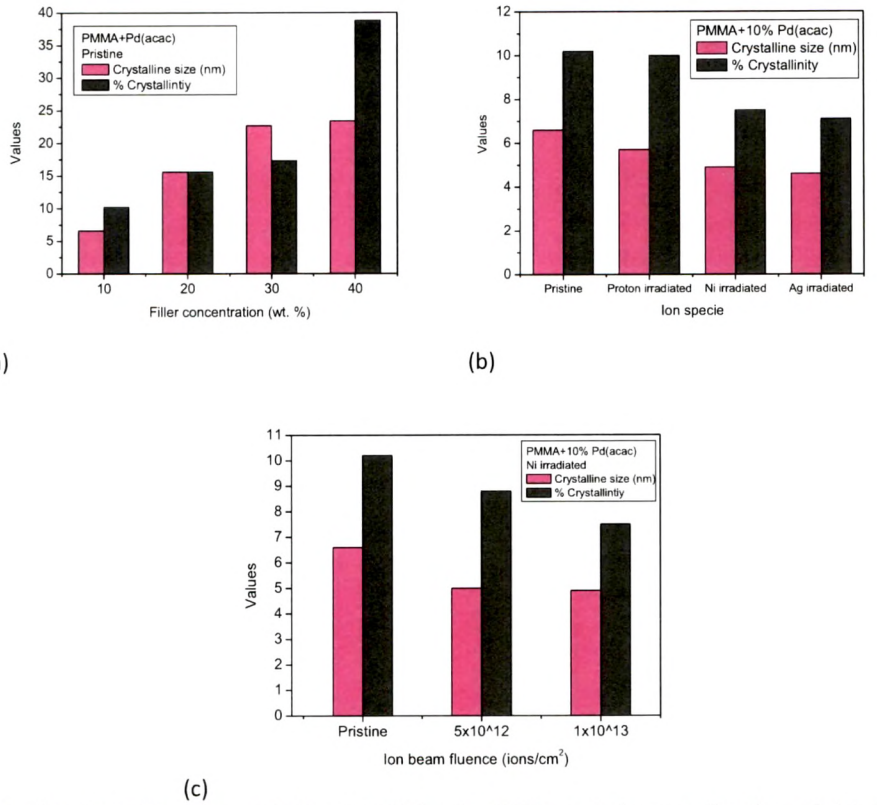

Fig. 6.5 Crystalline size and % crystallinity by XRD analysis as a function of (a) filler concentration (b) ion specie and (c) ion fluence for PMMA+Pd(acac) composites.

The amorphization causes decrement in Tg of the irradiated samples as observed from DSC analysis. The effect of ion specie and ion fluence on crystalline size and % crystallinity is shown in Fig 6.5 (b, c) respectively.

(b) FTIR analysis

As the metal and polymer are extremely different materials, the interaction between metal and polymer is generally very weak. The cohesive energy of polymer is typically two orders of magnitude lower than the cohesive energy of metals. FTIR spectra show the interaction between macromolecule and filler particles. Small shift and alteration in the peak position are observed due to changes in the nearest surrounding of functional groups because of the presence of filler particles.

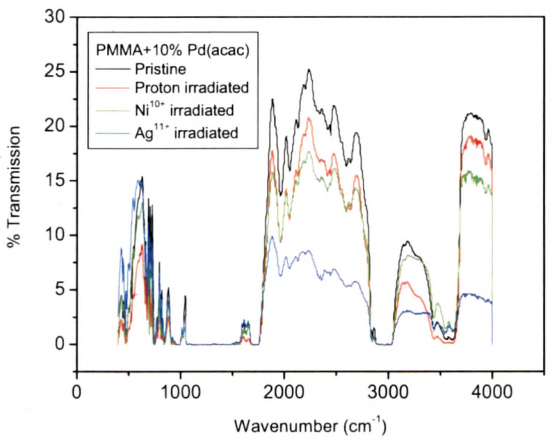

Fig. 6.6 FTIR spectra for pristine and irradiated films of PMMA+10%Pd(acac)

The peak corresponding to -OH stretching vibration for pristine PMMA was observed at 3610 cm^{-1} and it shifted to 3620 cm^{-1} for 30% Ni doped polymer. The reduction in peak intensities after irradiation in almost all cases is attributed to the breakage of few chemical bonds and formation of free radicals, unsaturation, etc. due to emission of hydrogen and/or other volatile gases. It is observed that intensity of functional groups

decreases as filler concentration increases. Case study is being carried out to assess the effect of ion beam specie on function group present in the composites and presented in Fig. 6.6. Spectra show that the C–O, C=O bonds and CH_2, CH_3 groups diminish with irradiation. It reveals the formation of carbon network due to the emission of hydrogen and/or other volatile gases. It is responsible for the amorphization of the composites after irradiation, which is also corroborated with XRD results.

(IV) Surface Morphology

Surface morphology was studied by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM gives surface average roughness and 3-D images of the samples while SEM gives 2-D surface topography for larger dimension of sample surface. Both characterizations were done to study the effect of ion beam on the surface of the sample. From AFM it was observed that the average surface roughness (R_a) decreases after light beam (i.e. proton) irradiation. This might be attributed to defect enhanced surface diffusion. Whereas, R_a increases after SHI irradiation, which is responsible to large sputtering effect due to SHI. Thus light and heavy ion induces different process on the surface. However in all cases, the average surface roughness increases with increasing the filler concentration. The increase in roughness may be due to the increase of density and size of metal particles on the surface of the polymer films. SEM doesn't give exact roughness value but the blister, agglomeration like phenomenon was observed in the micrographs of SEM.

(V) Thermal Analysis-Differential scanning calorimetry

Glass transition temperature (Tg) of pristine and irradiated samples was studied using DSC thermograms. The results show that the Tg decreases after ion beam irradiation. Glass transition temperatue of unirradiated PMMA film was obtained around 98°C.

For pristine film of PMMA+40%Pd, the Tg obtained around 102 °C, and decreases to 89.3 °C after proton irradiation. It further decreases to 78.3 °C upon Ni^{10+} irradiation. It is attributed to the formation of disorder structure by SHI irradiation. No appreciable change in Tg was found for PMMA+40% Ni after proton irradiation. In case of PMMA+15% Fo, Tg changes from 103 °C (for pristine) to 98 °C after Ni^{10+} ion irradiation at a fluence of $5x10^{12}$ ions/cm^2. The decrease in Tg after irradiation is responsible for amorphization of the material as confirmed by XRD analysis also.

(VI) Optical and magnetic properties.

Because of the growing interest in polymer nanocomposites, thin films of Fe doped PI was prepared by Co-sputtering of polymer and metal at RF frequency. The SHI irradiation effects on such composites were carried out. These samples were irradiated with 120 MeV Ni^{10+} ions at a fluence of $5x10^{12}$ ions/cm^2. Magnetic properties of the samples were studied by means of MFM/SQUID. It was observed from MFM images that, on increasing the Fe concentration, magnetic intensity of the films increases but it decreases after irradiation. Similar results are also observed from SQUID analysis. Optical property was studied by means of UV-Vis spectroscopy. Optical band gap was determined for composite films. It decreases slightly with increasing Fe concentration. However no significant change in optical band gap was found after irradiation.

Conclusion

Present work represents the synthesis of polymer composites/nanocomposites and effect of ion beam irradiation on these composites. Based on this study, we have concluded that there is significant enhancement in dielectric as well as mechanical properties of the composites after ion beam irradiation. However thermal and structural properties are observed to degrade upon irradiation. This alteration is

prominent for SHI irradiation. Because SHI impart large amount of energy in the material due to higher charge compared to proton, it is responsible for the alteration of the properties. SHI increases the surface roughness and improves the surface adhesion properties. Based on above finding it is valid to say that the material with desire properties can be achieved by changing filler properties and also ion parameters. It is envisaged that the new composite materials synthesized in the present work have potential applications such a light weight capacitors, data storing or packaging devices and in telecommunication where material with low dielectric constant is required. Ni doped PMMA composites are particularly appropriate for EMI shielding because of their high dielectric constant and conductivity. Advance research areas like, nuclear power plants and aerospace industry also require such type of material because certain desire properties of these materials can be tailored according to requirement in radiative environment. The dielectric properties of a material are of great concern for telecommunication applications. Since the signal propagation delay time is proportional to the square root of the dielectric constant of the transmitting medium, a low dielectric constant is often desirable.

Future Plan

Dielectric and magnetic properties of nanoparticles embedded polymer matrix by ion beam irradiation

Polymer nanocomposites are potentially important due to the fact that they offer a number of significant advantages over traditional polymer composites. Conventional composites usually require a high content of the filler phase to achieve the desired properties of the composite material. Nanocomposites can achieve the same properties with a much smaller amount of the filler, producing materials of lower density and higher processibility. The properties of nanomaterials can be tailored via the size, shape of constituents particles, their interaction with other particles and the polymer matrix. The effect of SHI irradiation on their properties and spatial distribution will be studied as a function of the initial size and volume fraction of the particles. The materials will be prepared by chemical routes. Metal oxide nanoparticles will be synthesized by chemical methods in which polymer will be used as a protecting agent. The samples will be prepared by taking different volume fraction of metal oxide nanoparticles in the polymers and ion beam induced changes will be characterized by X-ray diffraction, TEM/ SEM and AFM/MFM. Changes in magnetic anisotropy of the particles as a function of their shape will be studied by magnetometer. Change in dielectric properties will be studied by dielectric spectroscopy.