

CHAPTER 6

Summary and conclusions

This chapter summarizes the research work and outlined its significant conclusion and future plan of work.

This thesis is concerned with radiation induced modification of conductive composites of conductor-polymer systems. Conductive polymer composites, which are lightweight materials and combine the inherent processability of polymers with the electrical conductivity of metals, have been used in a number of applications such as electromagnetic interference (EMI) shields and anti-static devices etc. Because of the technical importance of these composites, their electrical properties have been widely studied.

The present study was undertaken to synthesize the conductive polymer composite systems by chemical route method. A details study of its electrical properties as a function of composition (i.e filler concentration) frequency and fluence of silver ion beam was carried out. Due to the interaction of radiation /energetic particle with polymer composite materials, the polymer/polymer composite material absorbs its energy and active species such as radicals are produced, thereby, initiating various chemical reactions. There are three fundamental processes that are the results of these reactions. The different responses to radiation for different polymers are intrinsically related to the chemical structures of the polymers/polymer composite materials. A significant alteration of the electrical, structural, thermal properties and surface morphology of the composites was obtained due to ion beam irradiation.

Six composite systems, viz. CB/PMMA, Al/PMMA, Cu/PMMA, CB/PVC, Al/PVC and Cu/PVC were chosen to meet the objectives of the study. Also other commercially available composites systems were chosen to study the electrical and optical properties using ion beam irradiation. The prepared polymer composites samples were subjected to different characterizations, manily electrical, structural, thermal and surface morphology before and after ion irradiation.

(I) Electrical properties

- (1) AC conductivity was studied with respect to frequency, filler concentration and ion fluence and also studied the temperature dependence ac conductivity of all pristine composites. The result reveals that the 0% and 10 wt% composites showing insulating behavior. After doping with higher concentrations (20, 30 and 40 wt%) in polymer matrix, samples show conducting behavior. It is assumed that an electrical conducting path and network of connections could be formed in the composites with increasing the content of the filler. It is known that the electrical conductivity of such composites depends on the type and concentration of the filler. It is also observed that the conductivity increases on increasing irradiation fluence. Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure in to a hydrogen depleted carbon network due to the emission of hydrogen and/or other volatile gases, which is believed to make polymer more conductive. Variation in conductivity of composites as a function of different conductive additives (fillers) dispersed for 40 wt % in two different polymer matrices and also with two different ion fluences (1×10^{11} ions/cm² and 1×10^{12} ions/cm²) at fixed frequency (i.e. 10MHz) are shown in Fig.6.1. comparing all six set of composites, the highest conductivity has been observed in case of Cu/PMMA composites. It is also observed that PMMA matrix composites have higher conductivity than that of the PVC matrix composites because in the case of PMMA, the distribution of filler is more packed than PVC.
- (2) One of the interesting features of conductivity is its temperature dependence, which allows one to understand conduction mechanisms in materials. The ac

conductivity also increases as temperature increases for all pristine composites. The phenomenon, that is, an increase in conductivity (or a decrease in resistivity) with an increase of temperature is termed as negative temperature coefficient (NTC) of resistivity.

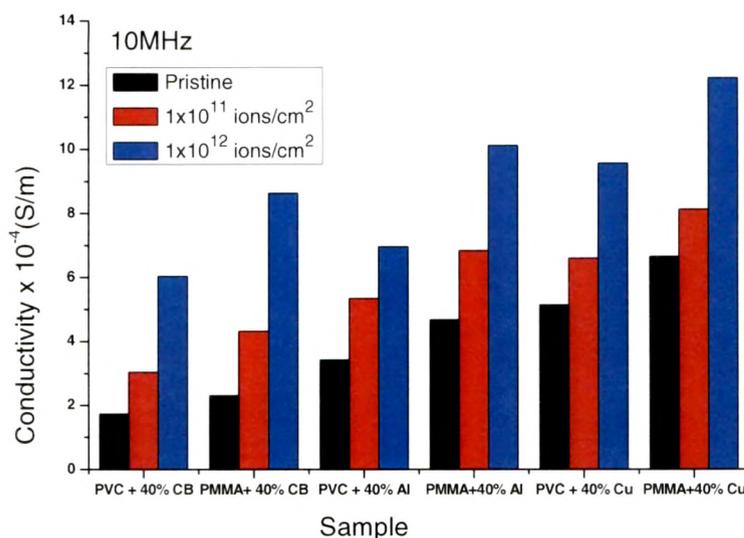


Fig.6.1. Variation in conductivity with respect to different conductive composites and also with different ion fluences at a fixed frequency (10MHz) for 40wt% of fillers.

The enhancement in dielectric constant with an increase in filler content of dispersed phase is attributed to interfacial (or Maxwell-Wagner-Sillars) polarization - a phenomenon that appears in heterogeneous media consisting of phases of different dielectric permittivities and conductivities and is due to the accumulation of charges at the interfaces. For all composite systems, the dielectric constant is moderately decreased with an increase in frequency. But in case of PMMA/CB and PVC/CB dielectric constant is constant with increase in frequency. It was also observed that the magnitude of the

dielectric constant increased due to irradiation at different ion fluences. 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 different conductive additives dispersed for 40 wt% in two different polymer matrices and also with two different ion fluences (1×10^{11} ions/cm² and 1×10^{12} ions/cm²) at fixed frequency (i.e. 10MHz) are shown in Fig.6.2.

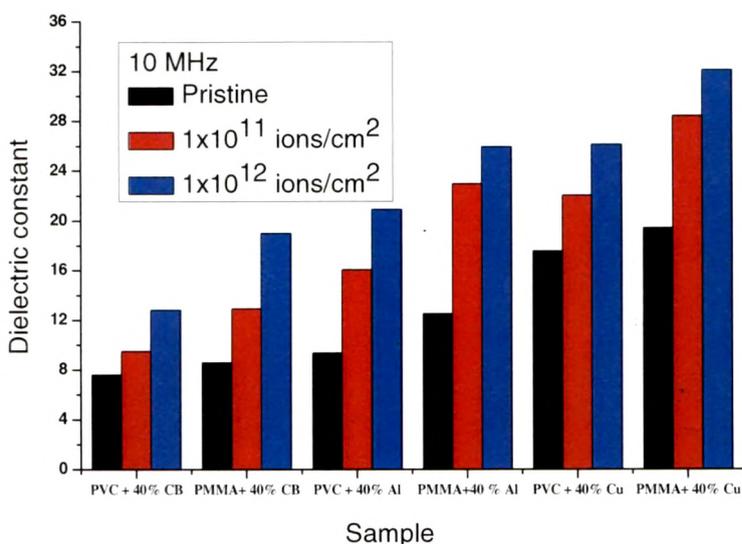


Fig.6.2. Variation in dielectric constant with respect to different conductive composites at different ion fluences and at a fixed frequency (10MHz) for 40wt% of fillers.

- (3) The temperature dependence dielectric constant of all pristine composite systems under study could be explained on the basis of two competing mechanisms that take place when the temperature of a filled-polymer is increased: (i) increased segmental mobility of polymer molecules at elevated temperature, below T_g which increases dielectric constant.(ii) Differential

thermal expansion of the polymer and metal. The thermal expansion coefficient of the polymer is greater than that of metals, which disrupts the clusters of metal particles-result in decrease of dielectric constant. But in the present case, we observed an increase of dielectric constant with temperature so, it can be said that the segmental mobility is dominant process in these composites.

- (4) The dielectric loss is observed to be high at low frequency and decreases as frequency increases. The dielectric loss is observed to increase upon ion beam irradiation. Positive value of dielectric loss in all the cases represents the inductive behaviour of the material. Variation in dielectric loss of composites as a function of different conductive additives dispersed for 40 wt% in two different polymer matrices and at two different ion fluences (1×10^{11} ions/cm² and 1×10^{12} ions/cm²) keeping frequency constant (i.e. 10MHz) is shown in Fig.6.3.
- (5) The significant change in dielectric loss was observed with increasing temperature in all cases but no loss peak was observed.
- (6) We have also studied the effect of 140 MeV Ag⁺¹¹ ion irradiation on the some commercially available pallet samples (PP/TiO₂, PP/GF and HDPE/ CB). In these composites the conductivity is also observed to increase upon ion irradiation. The dielectric property of composites is greatly altered by ion irradiation for all three pallet samples. Thus irradiation makes the polymer more conductive. This might be attributed to breakage of chemical bonds, resulted in an increase of free radicals, unsaturation etc.. It is also observed that dielectric constant obeys universal law of dielectric response at high frequency. The Cole- Cole curve shows that the diameter of the semi circle

decreases upon ion irradiation, which reveals that the conductivity of the composites increases after ion beam irradiation.

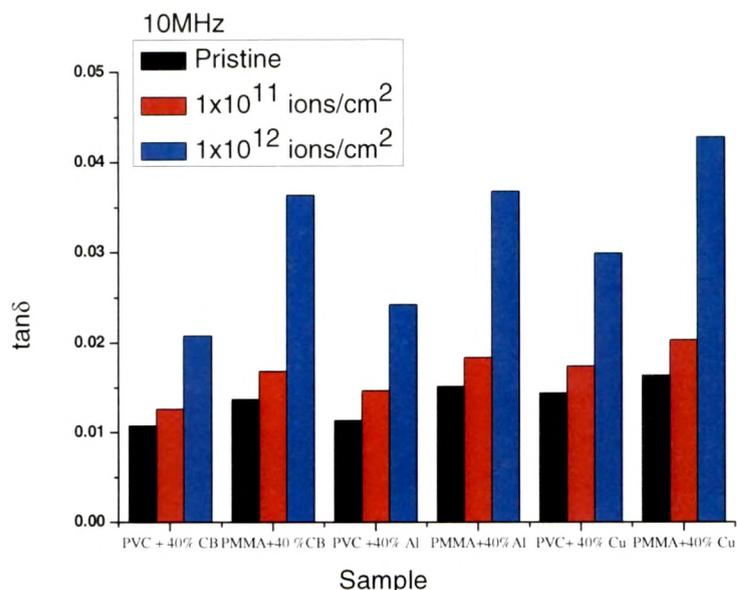


Fig.6.3. Variation in dielectric loss with respect to different conductive composites at different ion fluences and at a fixed frequency (10MHz) for 40 wt% of fillers.

(II) Structural properties of the system

The X-ray diffraction studies show that pure polymer is amorphous in nature. But doping some conductive additives (fillers) in polymer matrix, the composites show semi crystalline nature. The crystallite size and percentage crystallinity have been calculated before and after the irradiation. In case of carbon black composites, the composite system changes into more disorder state upon ion beam irradiation. The other composites systems (i.e. Al/PMMA, Cu/PMMA) show increase in intensity at low fluence, which reveals that the sample became crystalline at low fluence. Interaction of ion beam with composites resulted in the formation of gaseous products accompanied by cross linking i.e. formation of intermolecular bonds at the lower fluence (i.e. 1

$\times 10^{11}$ ions/ cm^2). On further increase of the fluence, ion irradiation induced large amount of energy deposited in the composites and leads to decrease in intensity and broadened the diffraction peaks. This tends towards the amorphisation at higher fluences due to increase of unsaturation, free radicals etc. and resulted in decrease in crystallite size, which may be attributed to splitting of crystalline grains. This type of result was also observed in case of Al/PVC composites, but two other composite systems (i.e. CB/PVC and Cu/PVC) show amorphous nature.

(III) Thermal properties

Thermal property of the composites was studied by DSC analysis and it reveals that the glass transitions temperature (T_g) shifted to higher temperature on increasing the filler concentration and decreases upon ion beam irradiation PMMA/CB and PVC/CB composites. It means that the composite system was shifted towards disordered state i.e. amorphisation of the system. It was also confirmed by XRD result. And other composites viz PMMA/Al, PMMA/Cu, PVC/Al and PVC/Cu show that the T_g shifted towards higher temperature at a fluence of 1×10^{11} ions/ cm^2 , which reveals that the composites became more crystalline. On further increase of the fluence (i.e. 1×10^{12} ions/ cm^2), T_g shifted to lower temperature which reveals that the irradiation leads to chain scission and subsequently reduction in molecular weight. As a result the system changed towards more disordered state.

(IV) Surface analysis

Surface morphology was studied by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM gives surface average roughness and 3-D as well as 2-D images of the samples while SEM gives 2-

D surface topology for larger dimension of sample surface. Both characterizations were done to study the effect of ion irradiation on sample surface. From AFM studies, it is observed that the surface average roughness of the composites increases with filler concentrations, which may be due to the increase in density and size of conductive particles on the surface of polymeric films. Also, the surface roughness increases upon ion irradiation for all composites except for PVC/CB. The increase in surface roughness is due to large sputtering effect but in case of PVC/CB the surface roughness decreases upon ion irradiation due to defect enhanced surface diffusion. The SEM images are used to examine texture of fractured surface of the composites. It can be seen that the metal particles are isolated at lower concentration (10 wt%) i.e. there is no interaction between them. As the filler content is increased (40 wt%), clusters of metal particles are formed. A cluster may be considered as a region in the polymer matrix, where particles are in physical contact or very close to each other. It is also corroborated with electrical conductivity result. Aggregates of micro clusters are clearly visible on the surface and metal/polymer phases increase due to ion beam irradiation.

(V) Optical properties

UV- visible is important tools to determine the information about band structure of solids. Insulators/semiconductors are generally classified into two types: (a) direct band gap, and (b) indirect band gap. In the case of direct band gap semiconductors, the top of the valance band and the bottom of the conduction band both lie at same zero crystal momentum (wave vector). If the bottom of the conduction band does not correspond to zero crystal momentum, then it is called indirect band gap semiconductor. Optical band gap was

determined for PP/TiO₂, PP/GF and HDPE/CB composites samples before and after ion beam irradiation. We have observed that direct and indirect band gaps for PP/TiO₂ and PP/GF composites but could not found in HDPE/CB composites. The UV-Vis spectroscopy studied shows that a shift in the absorption peak towards higher wavelength was found, indicating a decrease in energy band gap of the composites after SHI irradiation, which gives rise to the increase in conductivity of polymer in all cases.

Future Plan

Synthesis of metal nanoparticles in polymer matrix by ion implantation

At the modern technological time, there is a strong demand to develop new techniques to fabricate and measure the properties of nanomaterials and relevant devices. Significant advancement was made over the last decades in both fronts. It was demonstrated that materials at the nanoscale have unique physical and chemical properties compared to their bulk counterparts and these properties are highly promising for a variety of technological applications.

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on such physical properties of nanomaterials include optical detectors, laser, sensor, imaging, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine.

In recent years, there have been an efforts to develop polymer-based nanomaterials because of their importance in microelectronics and fabrication of nano-electronics devices. Metal-polymer systems are one such polymer-based material. These metal-polymer systems have been widely studied for (i) metallization of polymer which is of much interest in microelectronics for multilayer devices, coatings, the packaging industry and (ii) synthesizing metal-polymer nanocomposites which are of considerable interest in thin-film device applications and nano-electronics devices etc. In particular, the nanocomposites of noble metals are of rich interest because of their optical applications. Surface/interface modification in metal-polymer systems can be achieved using low-energy and high-energy ions as well. Low-energy ions up to a few hundred keV available from ion implanters undergo nuclear stopping and the energy loss in this process is called the nuclear energy loss (S_n). The energy transfer is sufficient to displace an atom from its lattice site, which later can cause other atoms to

recoil resulting in a collision cascade. Low ion-beam irradiation is most interesting for near surface modifications. High-energy ions undergo electronic stopping, dominant at high energies (MeV range) and cause the excitation or ionization of the atoms by inelastic collisions.

Thermoplastic polymers PMMA and PS will be used for polymer matrix and metal nanoparticle (Ni, Ag, Au) will be used for the preparation of metalized polymer by electron beam evaporation technique and also sputtering technique. The sample will be characterized by Rutherford back scattering (RBS), Atomic force microscopy (AFM), Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and UV-Visible Spectroscopy.