Chapter 6

Summary and Conclusion

Abstract

This chapter gives summary and conclusions derived from the present investigations and also future perspectives, as well as possible extension of the present work.

Summary and Conclusion

In today's era of modern technology polymeric composites/ blends are replacing many conventional materials in a rapid sequence, which has generated a demand for developing new polymeric composites/blends with improved mechanical performance. Electrical and mechanical properties are the major parameters to evaluate the performance of developed material.

Polymer composites filled with metal are of interest for many fields of engineering. This interest arises from the fact that electrical characteristics of such composites are close to the properties of metals, where as mechanical properties and processing methods are typical for plastics. The achievement of metallic properties in such composites depends on many factors, and it is just the possibility of controlling the electrical and physical characteristics which determines the variety of ranges of their applications. The transfer conditions of the electric charge and heat flow determine the electrical and thermal conductivity level in the heterogeneous polymer-filler system, in which the conduction phase is formed by dispersed metallic or carbon filler. Although in some publications it was observed that the percolation behavior of the conductive composite depends on filler particle size, shape and spatial distribution within polymer matrix.

Ion irradiation is an effective tool for introducing impurities into the surface layer to a depth of several micrometers. The modification of the material depends on its properties, as well as ion irradiation parameters (ion type and energy, ion current density, target temperature etc.).

During irradiation, various physical and chemical processes take place in the polymer Coulombic interactions between ions and electrons of host atoms, excessive bond stretching due to localized energy deposition, and atomic displacement by nuclear collision can release pendant atoms such as hydrogen, and cause bond breakage or chain scission Thus, various gaseous molecular species are released during irradiation. The most prominent species are hydrogen, molecular scission products from the end group as well as pendant groups of the polymer, and their reaction products Radicals or dangling bonds are created by the release of pendant atoms such as hydrogen. Crosslinking occurs when two free dangling bonds on neighboring chains unite, whereas double or triple bonds are formed if two neighboring radicals in the same chain unite.

It has been well established that mechanical, physical, chemical property changes in polymers are determined by the magnitude of cross-linking and scission, and that cross-linking enhances mechanical stability while scission degrades mechanical strength. Although both electronic and nuclear energy transfer can induce cross-linking as well as scission as would be intuitively expected, experimental evidence suggested that electronic stopping causes more cross-linking while nuclear stopping causes more scissions. This provides much of the basis for understanding the material response to irradiation.

The present work is carried out on organometallic compounds (ferric oxalate and nickel-dimethylglyoxime) dispersed in polymethyl methacrylate (PMMA) and polyvinyl chloride (PVC) at different concentrations and also few polymer like polyimide (PI), polycarbonate (PC), polyether sulfone (PES) and blended polyvinyl chloride (PVC) with poly ethylene teraphthalate (PET). These polymers comprise a class of engineering thermoplastic with high thermal and hydrolytic stability. These polymers are applicable in many areas e.g. in electronic, medical, aerospace applications etc. These polymeric materials were irradiated with 80 MeV O^{6+} ions/ 120 MeV Ni^{10+} ions at different fluences. Most of the work on various polymeric materials reported in literature is focused on the modification of chemical properties by ion beam irradiation. But little information is available on their mechanical and electrical properties e g. microhardness, dielectric constant, dielectric loss.

The radiation induced changes in electrical, microhardness, structural, thermal properties and surface morphology are investigated using different characteristic techniques. The findings of the present work are presented below.

6.1 Electrical Properties

The AC electrical frequency response of ferric oxalate and Ni-DMG dispersed in PMMA and PVC films and pure polymers such as PI, PC, PES, and blended PVC + PET was studied in the frequency range 50Hz – 10MHz at ambient temperature.

The following conclusions were drawn:

1 AC electrical conductivity was studied with respect to frequency for the pristine and irradiated samples at different concentration of ferric oxalate, Ni-DMG dispersed PVC and PMMA composites. A sharp increase in conductivity was observed around 100 kHz in pristine as well as irradiated samples. It was also observed that conductivity increases on increasing concentration of dispersed compounds as well as those irradiated at the fluence of 1x 10^{11} ions/cm^2 and 1x 10^{12} ions/cm^2. The increase in conductivity

with different concentration of organometallic compounds for pristine samples may be attributed to the conductive phase formed by dispersed organometallic compound in polymer matrix. It is known that electrical conductivity of such composites depends on the type and concentration of the dispersed compound. As a result the conductivity of dispersed films increases on increasing the concentration of organometallic compound in the polymer matrix. It is also observed that after the irradiation the conductivity increases on increasing concentration of the dispersed compound and also with fluence. Irradiation is expected to promote the metal to polymer bonding and convert the polymeric structure into hydrogen depleted carbon network. It is this carbon network that is believed to make the polymers more conductive.

The dependence of ac conductivity on frequency at ambient temperature for pristine and irradiated samples of pure polymer films indicates a sharp increase in conductivity. It is also observed that conductivity increases as fluence increases. The increased conductivity due to irradiation may be attributed to scissioning of polymer chains and as a result an increase of free radicals, unsaturation etc.

An AC field of sufficiently high frequency applied to a metal-polymer metal structure may cause a net polarization, which is out of phase with the field. This results in AC conductivity, it appears at frequency greater than that at which traps are filled or emptied.

2 The dielectric constant was investigated with respect to frequency for pristine and irradiated samples. When the fillers are dispersed in the insulating

polymer, the dielectric constant of composites increases with the concentration of filler. Such results have been observed experimentally. The partial agglomerations also increase with increasing the filler concentration as observed from AFM/SEM. The dielectric constant remains almost constant up to 100 kHz. At these frequencies, the motion of the free charge carriers is constant and so the dielectric constant presumably remains unchanged. It is also observed that dielectric constant increases as fluence increases. The increase in dielectric constant may be attributed to the chain scission and as a result an increase in the number of free radicals, etc. As frequency increases further (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. At these frequencies, the polarization of trapped and bound charges can not take place and hence the dielectric constant decreases. The dielectric constant decreases at higher frequencies (i.e. beyond 100kHz) obeys the Universal law of dielectric response given by $\varepsilon \alpha f^{n-1}$, where n is power law exponent and varies form zero to one ($0<n<1$). All organometallic dispersed pristine and irradiated films show that the frequency dependence of dielectric constant, ε, obeys Universal law. The observed nature of the fluence dependence of dielectric constant in studied frequency range can be explained by the prevailing influence of the enhanced free carriers due to the irradiation. The plot of dielectric constant with frequency for the pristine and irradiated samples of pure polymer films indicates that dielectric constant remains almost constant over a wide frequency range. At these frequencies, the mobility of the free charge carriers is constant and so dielectric constant remains unchanged. It is also observed that dielectric constant increases as fluence increases. The increases in dielectric properties due to irradiation may be attributed to scissioning of polymer bonds and as a result increase in free radicals and unsaturation etc. The dielectric constant decreases at higher frequencies (i.e. beyond 100kHz) and obeys the Universal law of dielectric response given by $\varepsilon \alpha f^{n-1}$, where n is constant, the value of n lies between zero to one ($0<n<1$).

3 Plot of tan δ v/s frequency indicates that tan δ decreases exponentially as frequency increases. It is also observed that loss factor increases as concentration of organometallic compounds increases. Further moderate increase in the tanδ occurs due to the irradiation. The growth in tanδ as increase in the conductivity is brought about by an increase in conduction of residual current and the conduction of absorbance of current. Dielectric loss vs frequency response indicates that tanδ is changing very moderately beyond a frequency of 1 kHz, suggesting that these polymeric films can be used as dielectric in capacitors being used above 1 kHz frequency.

6.2 Microhardness

The microhardness studies enable us to understand the issues related to the mechanical behavior (elastic-plastic deformation characteristics) of polymer films.

Vickers' microhardness indentations were carried out on the surface of the pristine and irradiated films of ferric oxalate and Ni-DMG dispersed PVC and PMMA films and also on pure polymers such as PI, PC, PES, and blended PVC + PET at ambient temperature in the load range from 50-1000mN and a constant loading time of 30s

The Vickers' hardness value (H_V) and applied load (P) shows the nature of microhardness in the above samples. Initially, the microhardness increases with load and there after, beyond certain load, H_v trends to attain a saturation value which can be explained on the basis of strain hardening phenomenon 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, therefore represents the true hardness of the bulk material, since at high loads the indenter penetration depth is also high and surface effects become insignificant. It is also observed that hardness increases as fluence increases. This may be attributed to cross-linking effect due to emission of hydrogen and/or other volatiles gases. The hydrogen depleted carbon network make the polymer harder.

6.3 Surface Morphology

AFM/SEM analysis help in understanding the issues related to morphology, compatibility and formation of nanosize domain.The surface morphology of pristine and irradiated films of ferric oxalate and Ni-DMG dispersed PVC and PMMA films were invesigated using AFM and SEM. Each AFM image was analyzed in terms of surface average roughness (Ra). It was found that roughness increases as organometallics concentration increases. The increase in roughness may be due to the increase of density and size of metal particles on the surface of the polymer films. It is also observed that after irradiation the roughness of the surface decreases and the surface becomes significantly smoother. This relative smoothness is probably due to defect enhanced surface diffusion.

After irradiation partial agglomeration of filler and flake-like structures could be seen in the micrographs of SEM.

6.4 Mossbauer Studies

Mossbauer spectra were recorded for the 10% ferric oxalate dispersed PMMA samples before and after irradiation. It was observed that there is a formation of Fe-O (could be Fe_2O_3 phase) complex in to the polymer matrix, by consequently breakage of Fe-C bonds which were observed in unirradiated sample. From Mossbauer spectra, the value of the quadropole splitting (QS) and isomer shift (IS) for the irradiated samples showed that Fe is in the state 3+ or more. The spectra indicate the formation of magnetic sextet (Fe-O) with a doublet (Fe-C). The % of absorption was low due to less quantity of irradiated material.

6.5 Structural Modification

6.5.1 X-ray Diffraction Analysis

The changes in the crystallinity of pure PMMA and Ni-DMG compound dispersed at different concentrations of 5%, 20% and 40% in PMMA films due to high energy ion beam irradiation were investigated by X-ray diffraction analysis.

It was observed that the crystallite size increases with increasing the concentration of filler, which may be attributed to increase in the density of particles with the increase of dispersed of Ni-DMG compound in polymer matrix. It was observed from the XRD analysis that the crystallize size decreases as ion fluence increases. It reveals that irradiation leads to a narrow size distribution of particles by allowing minimum-sized nanoparticles to melt and fast quenching results in average sized particles in the sample.

With the increase ion of fluence, the average diameter increases until complete amorphization of the polymer. The particles become free standing, and under heavy dose, some of them coalesce into bigger-sized grains and some split into smaller grains, the nature of coalescence or splitting solely depends upon the relative positions of the grains with respect to the point of ion impact. In our case ion irradiation indicates that size distribution of Ni-DMG particles is narrow due to deposition of huge amount of energy and resulted in spliting/melting of nanometric grain and amorphicity increases with the fluence due to breakage of bonds chain or scission. The results are listed in the following Table.

Table-: Average particle size of pristine and irradiated samples.

Sample	**Pristine** Average crystallite size (A^0)	**At $1x10^{11}$ ions/cm^2** Average crystallite size (A^0)	**At $1x10^{12}$ ions/cm^2** Average crystallite size (A^0)
PMMA+5% Ni-DMG dispersed film	223.167	205 987	205.987
PMMA+20% Ni-DMG dispersed film	346.342	335.624	322.107
PMMA+40% Ni-DMG dispersed film	374.479	347.207	347.588

6.5.2 FTIR Analysis

The peak analysis was done to study the disappearance of some existing bonds, emergence of new ones and structural changes which includes the deterioration in intensity and position of the characteristic bonds. The FTIR spectra of pristine and irradiated PI, PC, PES, and blended PVC + PET polymers were studied.

The conclusions derived are as follows.

1. The FTIR spectra of pristine and irradiated PI samples show that there was only a slight change in the signal intensity from the irradiated sample as compared to the pristine sample. This is consistent with resistance of the polyimide sample to change by ion irradiation. The presence of ladder structure of bonds may be responsible for such a high resistance. The minor changes in the peaks of irradiated samples may be due to the breakage of one or two bonds in the ladder structure, but this will not change the overall structure of the polymer. These observations confirm that PI is resistant to bond degradation under ion irradiation.
2. The FTIR spectra of pristine and irradiated PC indicate that there is only a slight change in the intensity of the irradiated sample as compared to the pristine sample. The minor changes in the peak- intensities of irradiated samples may be due to the breakage of few bonds in the polymer structure.
3. The FTIR spectra of pristine and irradiated PES samples indicate that there is a chemical degradation of the irradiated polymer by swift heavy ion irradiation and intensity of most of the functional group declines as fluence increases. The change in the intensities of the functional groups of irradiated samples may be due to breakage of bonds in the structure and creation of double/triple bonds. It is also revealed that the position of functional groups

shifted to lower wave number region on increasing the fluence due to loss in molecular weight of the sample.

4 The FTIR spectra of pristine and irradiated blended PVC + PET show that the absorption bands characteristic of all the functional groups decline, confirming their destruction (i.e. chain scission) by irradiation. These functional groups vanish gradually as irradiation proceeds. This may be attributed to scissioning of polymeric chains / chemical bonds and formation / emission of low molecule gases and radicals due to irradiation. There is a significant change in the structure of polymeric blends due to irradiation at higher fluences of 1.8×10^{13} ions/cm^2 and onwards.

6.6 Thermal Analysis (TGA and DSC)

The weight loss in a sample due to constant supply of heat energy at a predetermined heating rate can be attributed to the chemical reactions, decomposition, solvent and water evolution, oxidation etc. Thermogravimetry recorded the weight of a substance in air, heated at a controlled rate, as a function of temperature. The conclusions drawn from this study are given below.

1 The TGA study of PI indicates that in all the cases (pristine and irradiated) a stable zone (no weight loss), slow decomposition zone, fast decomposition zone and residual decomposition zone were observed. The irradiation presumably enabled the polymers to undergo a slow decomposition from the moment of application of heat. This slow decomposition showed a weight loss of about 0.5%, 3.7%, and 5.2% for pristine and irradiated samples at a temperature of 400°C. Around 50% of the sample material remained undecomposed in all cases. Thermograms indicate that thermal stability of the

PI degrades progressively during irradiation due to the emission of hydrogen gas and /or other volatile gases, which implies that chain scission proceeds preferentially compared with cross linking.

DSC thermograms of PI show that heat distortion temperature (HDT) was observed around 350^0C, and no significant change was observed due to irradiation. As DSC study was done in the temperature range 40^0C-350^0C, no T_g and T_m were obtained.

2 The thermal decomposition behaviour of pristine and irradiated (at the fluence of $2.4x10^{13}$ions/cm^2) PC show that there is no significant change in the stability of irradiated sample.

DSC thermograms indicate that there is no change in glass transition temperature. It reveals that PC is thermally stable upto the fluence of $2.4x10^{13}$ ions/cm^2. The minor change in stability has been observed due to breakage of few bonds in polymer structure.

3 TGA thermograms of pristine and irradiated PES indicate that the stable zone for irradiated samples reduced to 284^0C at the fluence of 3.6x 10^{13}, which was up to 444^0C for pristine sample. The weight loss of about 33% has been observed for pristine sample where as irradiated samples show a weight loss of about 42-45% at the temperature of 800°C. It is observed that activation energy decreases from 108.03 KJ/mole to 44.24 KJ/mole for pristine and irradiated ($3.6x10^{13}$ ions/cm^2) samples. This indicates that irradiated sample decomposed earlier than pristine.

The DSC curves for pristine and irradiated PES films show that the glass transition temperature (T_g) was observed at 223°C in pristine and slight changes were observed in irradiated samples (ie. 220 °C at a fluence of $3.6x10^{13}$ ions/cm^2), no melting temperature (T_m) was observed due to limited heating temperature.

4 Thermograms of blended PVC + PET show two steps decomposition. As depicted from TGA thermogramms that stable zone decreases as fluence increases. The stable zone was observed up to 190^{0}C for pristine and reduced up to 100^{0}C at a fluence of 3.6x10^{13}ions/cm^2. It indicates that degradation of the polymer matrix under irradiation, making it to decompose earlier than the pristine sample. No significant change has been observed at the second stage of decomposition for the pristine and irradiated samples. It was observed that activation energy decreases from 26.19 KJ/mole to 15.71 KJ/mole due to irradiation.

DSC thermogramms of pristine and irradiated blended samples show that there is no significant change in T_g upto the fluence of 3.6x10^{13} ions/cm^2, due to limited heating temperature, no melting temperature (T_m) was observed.

6.7 Future plan

Effect of SHI Irradiation on Magnetic and Dielectric Properties of Transition Metal Embedded Polymer Matrix

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. Polymer nanocomposites have been developed as candidates for different types of sensing applications. The conductive and absorptive properties of insulating polymers doped with conducting materials, and the absorptive properties of insulating polymers with non-conducting fillers are sensitive to exposure to gas vapours. Therefore, they can be used to monitor the existence and concentration of gases in the environment.

Electromagnetic interference (EMI) suppression is another area in which polymer nanocomposites can make great advances. All electronic devices generate and emit radiofrequency waves that can interfere with the operation of electronic components within the same device as well as other electronic devices. Miniaturization of electronic equipment requires components to be packed very close to each other, which increases the problem of electromagnetic interference. When an electromagnetic wave is incident upon a conductive surface, energy is reflected and absorbed. The ability of a material to shield electromagnetic energy, whether it is unwanted energy entering a system or escaping a system, is called its shielding effectiveness (SE). It is comprised of losses due to absorption, reflection, and re-reflection. EMI suppression over a wide band frequency range requires tunability of the impedance (Z), which depends on the tunability of the complex permeability (μ) and complex dielectric constant (ε). (Note that the electrical conductivity (σ) is contained in the imaginary part of ε.) The conductivity plays an important role in a material's ability to shield electromagnetic energy. Conducting materials such as typical metals, along with capacitors and ferrites are commonly used in EMI suppression The materials most commonly used in EMI suppression have disadvantages in terms of their weight, corrosion and physical rigidity that could be overcome with the development of new materials. Composite materials such as conducting and insulating polymers doped with magnetic nanoparticles may be light weight, flexible alternatives to the bulk metal components for the above mentioned applications.

The proposal deals with the ion induced modifications of magnetic metal nanoparticles embedded in polymer matrices with different thermal conductivities. The effect of SHI irradiation on changes in their size, shape and spatial distribution will be studied as a function of the initial size and volume fraction of the particles. The materials will be prepapred by chemical routes (sloution polymerization, sloution casting method). Metal oxide nanoparticles will be syntheiszed by chemical methods in which polymer will be used as a protecting agent. The samples will be prepapred by taking different volume fraction of magentic nanoparticles in polymers and ion beam induced changes will be characterized by X-ray diffraction, TEM/ SEM and AFM/MFM. Changes in magnetic anisotropy of the prticles as a function of their shape will be studied by magnetometry. Change in dieletric properties will be studied by dielectric spectroscopy.

Work plan:

(1) Synthesis of metal oxide nanoparticles: metal oxide NiO and Fe_2O_3 will be synthesized using chemical methods in which water soluble polymer will be used as a protecting agent.

(2) These nanoparticles will be characterized by different techniques such as TEM, AFM, FTIR, SEM and XRD.

(3) Preparation of polymer and metal oxide nanocomposites: NiO and Fe_2O_3 nanoparticles will be dispersed in polymethylmethacrylate (PMMA) polystyrene (PS), and polyimide (PI) with varying concentrations of these nanoparticles. These nanocomposites will be processed using melt blending, sol-gel and sonication techniques. The concentration of nanoparticles will be varied in a controlled way.

(4) These polymeric nanocomposites will be irradiated using different swift heavy ions ie. Li, C and Si ions.

(5) Magnetic properties, dielectric properties and structural and surface morphology/ topography will be studied using different characterization techniques.