Chapter-5

Summary and Conclusions.

In this chapter, the results obtained from the experiments performed for the work of this thesis are mentioned and also the future plan for work.

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Although the various types of radiation interact with matter in different ways, the primary process is the production of ions and electrically excited states of molecules which, in turn, may lead to the formation of free radicals. Radiation generated mobile electrons, which become trapped at sites of low potential energy, are also produced. The first phenomenon leads to permanent chemical, mechanical and electrical changes of the materials; the second results in temporary electrical changes in performance.

In polymeric materials, the formation of free radicals during irradiation leads to scission and cross-linking processes that modify the chemical structure of the insulation, generally leading to deterioration of the mechanical properties. This mechanical deterioration frequently gives rise to significant electrical property changes. However important electrical property changes sometimes occur before mechanical degradation is serious. For example, a change in dissipation factor or in permittivity might become serious for the reliable functioning of a resonant circuit. The interactions of radiation with the polymers are chain scission, chain aggregation, molecular emission and formation of double bonds. Various gaseous molecular species are released during irradiation. The most prominent emission is hydrogen, followed by less abundant heavier molecular species which are scission products from the pendant side groups and chain end segments. Cross-linking occurs when two free dangling ions or radical pairs on neighbouring chains unite. Double/triple bonds are formed when two neighbouring radicals in the same chain unite. Cross-linking enhances the modulus and hardness of the polymer. In partially crystalline polymers, it imparts a non-melting behaviour and above the crystalline melting point the cross-linked polymer exhibits rubber elasticity. Radiation degradation is a random chain scission process, which reduces the molecular weight of the polymer, thus, plasticising the material.The extent of scission and cross-linking processes depend on the composition, density, molecular weight of polymer, and time of irradiation, mass, energy, charge and fluence of the ion beam.

In an attempt to investigate the impact of Li^{3+} ion irradiation on five different polymeric materials, the present work revealed several physico-chemical modifications induced in the polymers due to the Li-ion irradiation. The major findings of the present work are presented below.

5.1 Structural Modification (FTIR Analysis)

The FTIR spectra of pristine and irradiated PP, PET, PI, blended PVC + PET and PVC + EVA polymers were studied. The conclusions derived for all the above samples are as follows.

1 In the case of PP, the main effect of irradiation is the formation of new bonds, free radicals, double bonds, etc. The transmittance value of the functional groups changed with fluence. The most important change with higher fluence (1.5×10^{14} ions/cm^2) occurs at ~ 2900cm^{-1} ;C-H stretching. Some absorbance occurs around 1680 – 1620 cm^{-1} ;C=C bonds. After a fluence of 3.4×10^{13} ions/cm^2, the absorbance is observed at 1450 cm^{-1}; C-H bond, which is also seen at the fluence of 2.4×10^{12} or 1.5×10^{14} ions/cm^2 as well as in the pristine sample. This may be due to the fact that the C-H bonding does not get affected due to irradiation. The presence of alkene and alkyne groups

in the pristine sample seems to get modified by irradiation, and can be noted by the change in the position and intensity of absorbance in the ~630 -900cm^{-1} region. The 984 cm^{-1} band (3/1 helix structure) is not affected much by irradiation though 1168 cm^{-1} band (3/1 helix structure) is affected by Li^{3+} ion irradiation.

2 The FTIR spectra of PET before and after irradiation indicate that various bands related to C-H stretching of CH_2 group at 2972 cm^{-1}, C=O stretching vibration at 1700 cm^{-1}, C-O-C stretching of ester at 1013 cm^{-1} and bending vibration of CH_2 group at 725 cm^{-1} are modified. It is also inferred from the FTIR spectra that there is no significant change in the overall structure of the polymer but a minor change in intensities have been observed up to the fluence of 3.0 x 10^{13} ions/cm^2.This might be due to the breakage of a few bonds in the structure. It may be concluded that PET is resistant to radiation atleast up to the fluence of 3.0 x 10^{13} ions/cm^2.

3 The FTIR spectra of PI indicate that there is no change in the overall structure of the polymer, but minor change in intensities have been observed, which implied that inter-chain separation is not affected much by Li^{3+} ion irradiation. Most of the peak positions were found to be unshifted. The absorption bands, as obtained from the pristine spectrum, are identified as (A) 1723 cm^{-1}; C=O stretching vibration, (B) 3074 cm^{-1}; aromatic C-H stretching, (C) 3486 cm^{-1}, N-H bending vibration, (D) 3630 cm^{-1}; OH stretching vibration. The minor decrease in the intensity (i.e. reduction in specific height) of these functional

groups (i.e. 1723, 3074, 3486 and 3630 cm^{-1}) is due to the emission of adsorbed gases just below the surface that resulted in blister formation on the surface of thermally stable kapton film. The minor changes in the intensity of the peaks of the irradiated sample may be due to the breakage of a few bonds in the ladder structure. It may be thus concluded that kapton is highly resistant to radiation degradation.

4 In PVC + PET, it is found that the absorption bands of all the functional groups decline, confirming their destruction (i.e. chain scission) by irradiation and they 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. There is a significant change in the structure of polymeric blends.

5 The FTIR spectra of PVC, EVA and blended PVC and EVA indicate that the absorbance/transmittance value of all functional groups decline, confirming the breakage of chemical bonds and formation/emission of low molecule gases and radicals.

5.2 Electrical Properties.

The AC electrical response of PP, PET and blended PVC + PET was studied in the frequency range 0.05 – 100 kHz and temperature range 40 - 150°C. It is observed that ion irradiation of polymeric film leads to chain scission and cross linking and as a result there are changes in the dielectric properties.

The following conclusions are drawn:

1 The plot of log resistivity v/s log frequency at different temperature and fluence indicates that resistivity decreases rapidly in proportion to f^1. The resistivity decreases due to increase of temperature and fluence.

2 The dependence of conductivity on log frequency at ambient temperature for pristine and irradiated samples indicates a sharp increase in conductivity at 20 kHz and conductivity increases as fluence increases. The increased conductivity due to irradiation may be attributed to scissioning of polymer chains and as a result, increase of free radicals, unsaturation, etc.

3 tan δ v/s temperature for pristine and irradiated samples at constant frequency indicates that the dielectric loss increases with the increase in temperature. The value of tan δ is also found to increase with increasing fluence. The dielectric loss is due to the perturbation of the phonon system by an electric field. The energy transferred to the phonon is dissipated in the form of heat. The growth in tan δ and thus decrease in resistivity and increase in conductivity is brought about by an increase both in the conduction of residual current and the conduction of the absorption current.

4 Plot of tan δ v/s log frequency at different temperatures and fluences indicates that with the increase in frequency, dielectric loss shows moderate increase upto 10 kHz at all temperatures and fluences, suggesting that these polymeric

films can be used as dielectric in capacitors being used below 10kHz frequency.

5 The plot of dielectric constant v/s log frequency at different fluence indicates that dielectric constant remains constant upto 100 kHz and increases as fluence increases. At these frequencies the mobility of the free charge carriers is constant and thus the dielectric constant remains constant. The increase in the dielectric constant may be attributed to chain scission and as a result the increase in the number of free radicals, etc.

6 Plot of dielectric constant v/s temperature at different fluence indicates that the dielectric constant is almost independent of temperature. The negligible change (6%) with temperature could be due to the effect of conduction corresponding to absorption current. It is also observed that dielectric constant increases as fluence increases. This increase in dielectric constant may be attributed to the chain scission which results in an increase of free radicals etc.

5.3.1 Thermal Stability

Thermogravimetry recorded the weight of a substance in air, heated at a controlled rate, as a function of temperature. The conclusions drawn for this study are given below.

1 The TGA study of PP indicates that the decomposition of the irradiated polymer started at a lower temperature compared to the pristine sample, i.e. more the fluence, less the thermal stability. This denotes a degradation of the polymer matrix under Li^{3+} ion irradiation making it to decompose earlier than the pristine sample.

2 In the thermal stability study of PET it was found that the irradiated PET sample also decomposed earlier than the pristine sample which was also due to degradation of the polymer matrix under Li^{3+} ion irradiation.

3 Thermal analysis of blended PVC + PET showed that the decomposition of the irradiated (PVC + PET) blended polymer started almost as soon as heat is supplied to it. It is also observed that the nature of the polymer decomposition depended on the fluence of the ion beam, i.e. more the fluence, less the thermal stability. This is also attributed to the degradation of the polymer matrix under Li^{3+} ion irradiation making it to decompose earlier than the pristine sample.

4 The TGA thermograms of pristine (unirradiated) pure and blended PVC and EVA indicate that there is an increase in the thermal stability of the PVC due to incorporation of EVA in equal proportion by weight. TGA analysis revealed a double step decomposition pattern for blended polymers while pure polymer exhibits single step decomposition. The blend consisting of PVC and EVA in equal proportion (50:50) exhibits better thermal property among all, indicating its possible industrial application.

5 TGA thermograms of irradiated (fluence 10^{14} ions/cm^{2}) pure and blended PVC and EVA indicate that the thermal stability of PVC due to incorporation of EVA in equal proportion by weight is still better than others. The results are similar to the pristine samples. It is also observed that blended polymer shows double steps where as pure polymer exhibits single step decomposition.

5.4 Mechanical Property

1 Microhardness.

Vickers' microhardness indentations were carried out on the surface of the pristine and irradiated films of PET and PI at ambient temperature under different applied loads ranging from 100-1000mN and a constant loading time of 30s.

It is observed that microhardness increases with the load upto 500mN for PET, 400mN for PI and then saturates beyond the load of 500mN for PET, 400mN for PI. The increase in hardness with load can be explained on the basis of the strain hardening phenomenon. On applying load, the polymer is subjected to some strain hardening and beyond a 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. It is also observed that hardness increases as fluence increases. This may be attributed to the cross-linking effect.

2 Tensile Strength

In the case of pristine pure and blended PVC and EVA the following conclusions can be drawn from the study of tensile strength.

1 The mechanical strength of EVA improved by adding PVC.

2 The yield strength of blend improved gradually by adding PVC to EVA.

3 Elongation cannot be compared as the thickness of the polymer was not the same and for better comparision the samples are required in circular filament type form.

5.5 Applications of polymer blends-Gas Sensor

Polymeric blend can be made sensitive to hydrogen gas by high energy ion irradiation. The sensitivity of gas increases to about 40 times at an optimum radiation fluence of 1.3 x 10^{14} ions/cm^{2}. Various sensor characteristics e.g. response and recovery time, change in electrical resistivity due to exposure of hydrogen suggests that an economical and reliable gas sensor can be developed with this technique.

5.6 Future plan of work.

There is growing interest in nanopores and micropores in polymers generated by swift heavy ions due to a vast variety of applications. These pores are made by controlled chemical etching of ion irradiated thin polymer foil. The micro/nano structure fabrication in the chemically etched pores depends largely on the spatial parameters of latent ion tracks. The energetic ion creates damage along its path due to its large electronic energy deposition via inelastic collisions. The diameter of the damaged area along the ion path referred to as track diameter is a quantity of interest for the understanding of basic ion insulator interaction. There have been a few attempts to measure the track diameters by scanning force micro-morphology probing equipments. A novel approach to determine the track diameters in polymers by on-line measurements of H loss using elastic recoil detection (ERD) technique is planned. The on-line measurement of H release under ion impingement will be carried out by quadrupole mass analyzer. The experimental set up is available at NSC, New Delhi.