Chapter 5: Summary and Conclusion

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The irradiation of polymeric materials by energetic ions affects their physico-chemical properties. The primary phenomenon associated with the interaction 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 of 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 chain unite. Double and 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, plasticizing the material. All these effects depend on the composition, density, molecular weight of the polymer, and time of irradiation, mass, energy, charge and fluence of the ion beam.

Polymers, although introduced in the materials field in a meaningful manner only very recently, occupy a major place and position in our life today. To name a few desirable properties-high strength, light weight, good flexibility, special electric properties, high temperature stability, and resistance to chemicals, amenability for quick and mass production and for fabrication into complex shapes in a wide variety of colour-some polymers will almost always meet our requirements.

The present work is carried out on few polymers like polypropylene, polyimide, polyethylene terephthalate, polyether sulfone, polycarbonate and blend of polyvinyl chloride and polyethylene terephthalate. This polymer comprises a class of engineering thermoplastic with high thermal and hydrolytic stability. These engineering polymers are applicable in many areas e.g., in electronics, medical applications and aerospace applications etc. These selected polymers were irradiated with 3 MeV proton beam at different fluences i.e. 10^{13}-10^{15} ions/cm^2. Most of the work on various polymeric materials reported in literature is focused on the modification of the chemical properties by ion beam irradiation. But little information is available on their mechanical and electrical properties e.g., microhardness, dielectric constant and dielectric loss.

The radiation induced changes in structural, electrical, microhardness, thermal properties and surface morphology are investigated using different characterization techniques. The following general conclusions are drawn from the present study.

Structural Analysis

The variation of transmittance (%) for the pristine and irradiated polymers were compared and the peak analysis was done to study the disappearance of some existing bands, emergence of new ones and the structural changes which includes the alteration in position and intensity of the characteristic bands.

The FTIR spectra of pristine and irradiated PP are almost same except minor change in intensity. The irradiation gives rise the modification of C=C bond at 2049 cm^{-1} and CH_3 symmetric stretching at 2838 cm^{-1}. The helix structure of PP has not been affected by proton irradiation.

It is observed from the comparison of FTIR spectra of pristine and irradiated (up to 10^{15} ions/cm^2) polyimide that no significant change has been observed in the overall structure of the polymer. The minor changes observed in the intensity of the irradiated samples as compare to the pristine one, it may be due to the breakage of few bonds in the structure. It may be concluded that PI is highly resistant to radiation degradation.

The FTIR spectra of polyethylene terephthalate, polyether sulfone and polycarbonate/MFD indicate that these polymers get chemically degraded at the highest proton fluence used, viz. 10^{15} ions/cm^2. On the other hand, no significant change in vibrational frequency occurs up to the fluence of 10^{14} ions/cm^2 which implies that inter-chain separation is not affected much by proton irradiation. Most of the peak positions were found to be unshifted. Only the absorbance or transmittance value of particular functional groups changed. This might be due to the breakage of few bands in the structure.

In the case of blend polymer (PVC+ PET); no significant change in intensities was observed up to the fluence of 10^{13} ions/cm^2. It is observed that the absorption bands characteristic of all functional groups declines, they vanish gradually as irradiation proceeds. This might be attributed to the scissioning of polymer chains and the formation/emission of low molecule gases and radicals due to irradiation.

However, in the case of PET, PES and blended polymers, there is drastic fall in transmittance value at the highest fluence, it may be speculated that scattering from the surface could also be a contributing factor in reducing the intensities of the transmittance bands.

Electrical Properties

Proton irradiation of polypropylene, polyimide, polyethylene terephthalate, polyether sulfone, polycarbonate/MFD and blend polymer leads to chain scission and cross linking and as a result, there are changes in the electrical properties (conductivity, dielectric loss and dielectric constant). The conductivity, dielectric loss and dielectric constant were observed to increase with the increase of fluence. The increase in electrical properties with the fluence, 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 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. The dielectric constant remains almost unchanged over a wide frequency range i.e. up to 100 kHz and then decreases at higher frequencies. At lower frequencies, the mobility of free charge carriers is constant and thus the dielectric constant is constant. As the frequency increases the charge carriers migrate through dielectric and get trapped against a defect sites and induce an opposite charge in its vicinity, as a result the mobility of charge carriers is slowed down and the value of dielectric constant decreases.

Thermal Analysis (TGA and DSC)

The weight loss in a sample due to constant supply of heat energy at a predetermined rate can be attributed to the chemical reactions, decomposition, solvent and water evolution, oxidation etc. Thermogravimetric analysis was carried out for all pristine and irradiated ($10^{14}/10^{15}$ ions/cm^2) samples up to the temperature of 500 °C. It is observed that the thermal stability of all polymers are found to decrease at the fluence of 10^{15} ions/cm^2. The decrease in thermal stability may be attributed to the scissioning of polymeric chains. This denotes a degradation of the polymer matrix under proton irradiation, which is also corroborated by FTIR spectra.

In case of PP, PC and PET the TGA were also recorded for the lower fluence i.e. 10^{14} ions/cm^2. As depicted from thermograms of PP, the weight loss is observed about 10% and 16% for pristine and irradiated samples respectively. The degradation of polymer matrix under proton irradiation and making it to start decomposition earlier than pristine PP. However in the case of PET, no appreciable change has been observed up to the fluence of 10^{14} ions/cm^2. This indicates that the system remains reasonably organised up to the fluence of 10^{14} ions/cm^2, which is also corroborated with FTIR spectrum at this fluence.

The TGA thermograms of PI indicate that there is a weight loss of about 12% and 18% for pristine and irradiated samples respectively at the temperature of 500 °C.

The TGA thermograms of PES indicate that there is a weight loss of about 5% and 10% for pristine and irradiated samples respectively at the temperature of 500 °C.

Thermograms of blended polymer show two step decomposition. As depicted from the TGA thermograms that the stable zone disappeared for the irradiated (10^{15} ions/cm^2) polymer, which was observed up to 169 °C for pristine polymer. TGA thermograms indicate a degradation of the polymer matrix under proton irradiation making it to decompose earlier than the pristine sample. No appreciable change has been observed in the second stage.

Differential scanning calorimetry (DSC) measurements were carried out for all pristine and irradiated (10^{14} ions/cm^2) samples up to the temperature of 325 °C. No appreciable change has been observed in polyimide and polyether sulfone. Due to limited heating temperature, no melting temperature (T_m) was obtained.

The DSC thermograms of PET indicate that there is no significant change in melting temperature at the fluence of 10^{13} ions/cm^2. By increasing the fluence up to 10^{14} ions/cm^2, the radiation damage effects became more evident and the melting endotherm (T_m) decrease from 262 °C (pristine) to 248°C.The decrease in melting temperature with fluence further support the fact that scissioning of chemical bonds by proton irradiation, which resulted in decrease of molecular weight.

The DSC thermograms of PC indicate that, glass transition temperature (T_g) appeared around 146 °C and no melting endotherm (T_m) peak was observed. By increasing the fluence up to 10^{14} ions/cm^2, T_g was shifted to lower temperature (144 °C). The minor change observed due to the cross linking and scissioning, which is also corroborated by TGA thermogram and FTIR spectrum at the fluence of 10^{14} ions/cm^2.

For blended polymer, DSC thermograms recorded for pristine and irradiated samples at the fluence of 10^{13} ions/cm^2 and 10^{14} ions/cm^2. It is observed that the melting endotherm (T_m) shifted to slightly higher temperature and then decreases to the lower temperature on increase of the fluence from 10^{13} ions/cm^2 to 10^{14} ions/cm^2. This change clearly indicates that up to the fluences of 10^{13} ions/cm^2, the system remains reasonably organized but gets quite disorganized with some residual energy when fluence of 10^{14} ions/cm^2 is used.

Mechanical Property (microhardness)

The microhardness indentations were carried out on the surface of the pristine and irradiated films at ambient temperature at different applied loads from 100-1000 mN and a constant loading time of 30 seconds. It is observed that microhardness increases with the load up to 300 mN and then saturate beyond the load of 400 mN. The increase in hardness with loads can be explained on the basis of the strain-hardening phenomenon. On applying the load, the polymer is subjected to some strain hardening and beyond certain loads 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 the hardness increases as fluence increases. This may be attributed to the cross linking effects. However on further increase of the fluence, the polymer degrades its mechanical strength and as a result the hardness decreases at the fluence of 10^{15} ions/cm^2 for PET, PES and blended polymer.

Surface Morphology

It is observed from the naked eyes that the colour of the polymer changes from its original colour to light yellow – yellow - dark brown as fluence increases. The optical micrographs of pristine and irradiated samples do not appear to be flat (smooth), but seems to be rough. The roughness of the polymeric surface increases as fluence increases.

Future Plan of Work

Over the past decade, improvements in technology have made it possible to expand surface modification of polymer substrates. At the same time, more sophisticated manufacturing and fabrication methods have broadened the demand for modified polymers. A variety of new products required properties that can best be delivered by polymeric materials, specifically those polymers whose surface characteristics have been modified. In particular the subject of activity would involve irradiation-induced modification of polymers. We are mostly interested in low-energy ion beams (down to 2-5 keV), and in adapting plasma modification techniques. The scope of this study encompasses polymer materials and technologies in terms of applications, processes, and properties. The field of biomedical applications needs polymers that, besides satisfying the physical requirements of their application, show the so called "biocompatibility", reacting properly with the biological environment in which they are employed. Since biocompatibility involves the interface between the device and the biological environment, surface modification techniques can be of a great help to solve this problem avoiding costly changes of materials.