

A black and white illustration of a computer monitor. The monitor has a thick black border and a smaller, slightly inset inner border. The screen area is white and contains the text 'CHAPTER 6' in a large, black, serif font. The monitor is supported by a dark, rectangular base with a curved top edge.

CHAPTER 6

CHAPTER 6

SUMMARY OF THE WORK AND FUTURE PERSPECTIVES

6.1. SUMMARY OF THE WORK

The widespread applications and technological importance of the polymers evoked us to induce some desirable modifications in their properties so as to enhance their applicability. The main challenge was to modify the polymers with low LET particles like electrons. In the preceding chapters, electron induced modifications in physical, chemical, structural and topological properties of some selected polymers have been studied by different characterisation techniques. The salient features of the present work are summarised polymer wise as follows:

6.1.1. Dose dependent modification induced in Polyallyl diglycol carbonate (PADC) by 2 MeV electrons

Modification in different properties of PADC has been studied as a function of 2 MeV electron-dose.

- ◆ A 14% decrease in optical band-gap from that of the pristine has been observed in the PADC irradiated by 235 kGy of electron.
- ◆ The optical band-gap was found to be an inverse function of electron dose. A relation has been derived to calculate the energy-gap for PADC irradiated to different electron doses:

$$E_g = - 0.0021 D + 3.6,$$

where, D is the electron dose in kGy

E_g is the energy band-gap in eV.

So, there is a possibility of decreasing the energy band-gap by bombarding higher doses of electron.

- ◆ The inter-chain separation was not affected by electron irradiation and no cross-linking was observed after the bond cleavage due to irradiation.
- ◆ Variation in transmittance was found to be less for higher doses of 2 MeV electron, which implies that it can be used as a reliable dosimeter for large doses of electron.

- ◆ The thermal stability of PADC could not be improved by electron irradiation because of chain-scission in the polymeric structure. Thermal stability was observed to be decreasing with increase in electron dose. No residual decomposition was observed in the electron irradiated PADC samples.
- ◆ The heat involved in the exothermic phase transition was found to be decreasing with increase in electron dose.
- ◆ Increase in dose of electron irradiation enhanced the amorphous nature of PADC.
- ◆ The electron irradiation promoted chain-scissioning in PADC, which in turn affected the etch-rates of PADC detectors.
- ◆ Bulk etch-rate and track etch-rate was found to be increasing with increase in electron dose. The bulk etch-rate of PADC irradiated to 235 kGy dose of electron was found to be 4 times higher than that of the pristine PADC.
- ◆ The track registration sensitivity and the etching response of PADC was improved by increasing the dose of electron irradiation.
- ◆ The heavy-ion track registration capacity of the PADC can be improved by pre-irradiating it with electrons. In other words, electron irradiation can be used to sensitise the PADC detector.

6.1.2. *Electron induced modification in Polypropylene*

The effect of 23 kGy of 2 MeV electron on PP has been studied and the following conclusions were drawn.

- ◆ The isotactic nature of PP was not destroyed due to electron irradiation.
- ◆ The increase in absorbance of CH₂ wagging vibration after electron irradiation indicated the increase in chain length of hydrocarbon due to addition of more CH₂ groups, which might be due to some cross-linking induced by electron irradiation in the polymer.
- ◆ An increase in thermal stability of PP was observed after electron irradiation, which can be attributed to pre-dominant cross-linking by electron bombardment.
- ◆ The increase in melting temperature due to electron bombardment has been attributed to secondary ion induced crystalline regions distributed inhomogeneously on the surfaces of strongly stressed interlamella and interspherulite spaces, characterised by considerably high values of mechanical surface energy.
- ◆ A broad region of crystallisation exotherms was observed in the case of irradiated PP.

- ◆ The increase in main peak intensity and emergence of new peaks after electron irradiation indicated an increase in crystallinity of the irradiated PP.
- ◆ The decrease in optical band-gap in the irradiated PP implies an increase in conductivity of the polymer, which has been also verified by A. C. conductance measurement.
- ◆ The surface roughness of PP was found to decrease after electron irradiation.

6.1.3. *Electron induced modifications in Polyethylene terephthalate*

The modifications induced 23 kGy dose of 2 MeV electron in PET are summarised as follows:

- ◆ Increase in absorbance of the characteristic bands in PET in the FT-IR region indicate the amorphisation of the polymer. The process of amorphisation was enhanced because of the irradiation of the samples in air.
- ◆ The presence of aromatic groups in the polymer structure accounted for the stability of the polymer.
- ◆ Amorphisation of the polymer indicated that PET underwent some chain-scission by electron bombardment.

- ◆ A decrease in thermal stability of the polymer was observed due to electron irradiation, which is due to chain-scission in the polymer.
- ◆ The melting temperature of PET was also decreased by electron irradiation.
- ◆ The shift in main peak of X-ray diffraction spectra and decrease in its intensity indicated the destruction of crystalline structure of the pristine polymer due to electron irradiation followed by the amorphisation.
- ◆ There was no change in the optical band-gap of PET after electron irradiation.
- ◆ The bulk etch-rate for the fission fragments in PET increased due to electron irradiation thereby, decreasing the activation energy of etching.
- ◆ The electron irradiation has converted the PET into an easily etchable material.
- ◆ The surface roughness of the polymer decreased after electron irradiation.

6.1.4. *Electron induced modifications in Polyimide*

The modifications induced 23 kGy dose of 2 MeV electron in PI are summarised as follows:

- ◆ The degradation of PI by electron irradiation is characterised by the decay of the imide group.
- ◆ Oxidative degradation of hydrogen bonds of amides was further enhanced due to electron irradiation in the presence of air.
- ◆ There was no change in the optical band-gap observed due to the electron irradiation.
- ◆ The thermal stability of PI decreased by electron irradiation. Though the stable zone remained the same in the pristine and the irradiated PI, yet the irradiated PI decomposed completely at a relatively lower temperature.
- ◆ The irradiated PI showed a decrease in the melting temperature also.
- ◆ There was an increase in bulk etch-rate and hence a decrease in activation energy of etching due to chain-scissioning in the irradiated PI.
- ◆ Electron irradiation converted the PI into an easily etchable material.
- ◆ The surface roughness of the pristine PI was reduced by electron irradiation.

6.1.5. *Electron induced modifications in Polytetrafluoro ethylene*

The modifications induced 23 kGy dose of 2 MeV electron in PTFE are summarised as follows:

- ◆ An increase in absorbance and emergence of some additional absorbance bands in the electron irradiated PTFE is evident from FT-IR studies.
- ◆ A 50% decrease in the optical band-gap of PTFE by electron bombardment show the impact of electron irradiation in enhancing polymer's conductivity.
- ◆ The stable free radical detected from ESR spectra of the irradiated PTFE was responsible for decrease in energy band-gap.
- ◆ A decrease in thermal stability of the PTFE was observed due to chain-scission, leading to a decrease in the strength of the polymer after electron irradiation.
- ◆ The melting temperature of PTFE was reduced by electron irradiation.
- ◆ The decrease in intensity of the main peak in the electron irradiated PTFE, in the diffraction spectra, further supports the decrease in crystallinity by electron irradiation.

- ◆ The chain-scissioning and formation of smaller fragments might be the reason for increase in roughness of the irradiated PTFE.

6.1.6. Modification of PADC through electron-target collision

The mode of energy-loss by 2 MeV electrons when they pass through different metallic layers, the impact of energy-loss phenomena on the track registration property and thermal characteristics of PADC were studied.

- ◆ The total energy-loss by the electron beam is the sum of the energy-loss due to ionisation and that due to radiation. The energy-loss by electrons was found to be a direct function of the charge, mass, thickness and density of the target material.
- ◆ The energy-loss by electrons was calculated to be maximum in Lead foil because of its large atomic number and thickness followed by that in Molybdenum and then in Gold foil.
- ◆ The effect of chain-scission was observed to be maximum in the 1st PADC sample of each stack due to high energy deposition, resulting in a higher bulk etch-rate than the successive PADC samples of the same stack.

- ◆ The 1st PADC of Gold stack was found to be having the highest bulk etch-rate owing to minimum energy-loss of electron beam while passing through the Gold foil.
- ◆ The bulk etch-rate of the PADC of Lead stack was found to be minimum because of the maximum energy-loss by electron while traversing through the Lead foil.
- ◆ The thermal analysis of the PADC sample showed that the PADC of the Lead stack was comparatively more stable due to maximum energy-loss of electron through the Lead foil. A minimum energy deposited on the 1st PADC sample of the Lead stack caused the least damage to it.

Thus, the energy-loss by electrons can be controlled by placing suitable metal foils accordingly. In addition to this, desirable modifications in the detectors can be achieved by controlling the energy-loss of ion beams by placing appropriate metal foils.

6.2. FUTURE PERSPECTIVES

6.2.1. *Future applications of the modified polymers*

The present work has resulted in providing some important data base regarding the modifications produced in the selected polymers by electron irradiation, which will further enhance the technological applicability of the polymers.

- ◆ PADC can be satisfactorily used as a reliable dosimeter for high-energy electrons.
- ◆ The modification in etching response and efficiency of PADC by electron irradiation will further enhance its utility as a track detector.
- ◆ The 235 kGy dose of 2 MeV electron increased the bulk etch-rate of PADC by four times. This indicates that the use of still higher doses can improve the track registration sensitivity of PADC. In other words, electron irradiation can be used to sensitise the PADC detector.
- ◆ As the ability of Polypropylene to withstand thermal strain increases after electron irradiation, this modified polymer can be used in high temperature works.

- ◆ The conductivity of Polypropylene has also been improved by electron irradiation. This lightest polymer may possibly find its application in micro-electronics.
- ◆ The formation of stable free radical and a 50% decrease in the optical band-gap by electron irradiation in Polytetrafluoro ethylene further enhances the applicability of this widely used polymer.
- ◆ Electron induced degradation of PTFE extends its applicability as lubricants and in production of perfluoro intermediates useful in textile industries.
- ◆ Electron irradiation has enhanced the bulk etch-rate, thereby decreasing the activation energy of etching in Polyimide and Polyethylene terephthalate. This enhances the applicability of these polymers as track detectors and in development of nuclear track micro/nano- filters (NTMF).

6.2.2. Future extension of the present work

Following subsequent investigations may augment present studies for a deeper understanding of the induced modifications in the polymers:

- ◆ Online measurements and study of energy-loss phenomena of electrons by Electron Energy Loss Spectrophotometer (EELS) can provide a deeper insight to the entire energy-loss process.
- ◆ Positron annihilation spectroscopy (PAS) can be employed to study the free volume in the irradiated polymers.
- ◆ Depth profiling techniques can be used to probe implanted or penetrating matter along the ion tracks in the irradiated polymers.
- ◆ Simulations of tracer mobility along the ion tracks in polymer i.e., Diffusion simulations can be performed to understand non-trivial shapes of the measured depth profiles of implanted ions or penetrants.
- ◆ The electrons with energy above the critical value, which results in a considerable radiative loss by bremsstrahlung emission, can be used to study the effect of bremsstrahlung on the detectors.
- ◆ Some other investigations on the irradiated polymers like thermoluminescence, annealing characteristics, hydrogen loss

studies, etc. can provide more information on the induced modifications.

- ◆ Studies at higher doses of electron will be significant for alkyne group formation in Polyethylene terephthalate, in decreasing the band-gap in Polyimide and in improving the etching response of these two polymers to electron irradiation.
- ◆ The impact of heavy ion irradiation on the same polymers can be done in order to have a comparative study on the effect of the low and high LET radiation on polymers.
- ◆ The study of the impact of electron irradiation on polymers can be extended to some other polymers like Polycarbonates, Polyvinyl chloride, Cellulose nitrate, Silicon rubber, SR-86 etc.