MODIFICATION OF POLYMERIC MATERIALS BY ENERGETIC PROTONS

BY

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Dedicated to my

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CERTIFICATE

I, Shyama Prasanna Tripathy, hereby, declare that the subject matter of this thesis entitled "Modification of Polymeric Materials by Energetic Protons" is the record of work done by me, that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any research degree in any other University/ Institute.

This is being submitted to the North-Eastern Hill University for the degree of Doctor of Philosophy in Physics.

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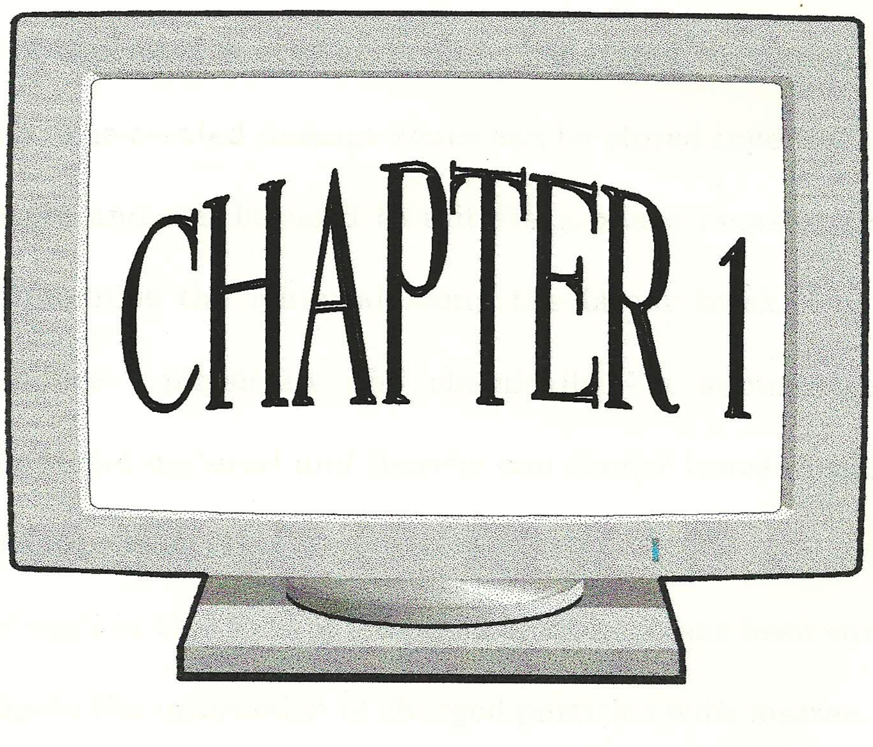
CHAPTER 1

CHAPTER 1

INTRODUCTION

1.1. IMPORTANCE OF RADIATION IN THE FIELD OF MATERIAL SCIENCE

Many fields - such as microelectronics and mechanics, biology and medicine, surface and membrane technology, magneto-optics and low temperature physics - require a high degree of geometric control on a microscopic scale. Ion irradiation offers a possibility to modify the properties of the materials in a controlled way on microscopic scale. Ionising radiations have a definite range of penetration, a high local confinement of deposited energy and can be generated conveniently in great quantity. The created damage zones can be stored indefinitely in many insulators and can be used to initiate a phase transformation process that modifies the material along the latent track. One ion suffices to induce - physically and chemically - a submicroscopic change in the target material and thereby can render it susceptible to the development process [1].

A lot of work in this field of ion beam treatment has been carried out to investigate the interaction of charged particles with matter. The application of ion beams nowadays range from the use of low energy ions in the field of surface technology to the application of relativistic heavy ions in radiation therapy.

1.2. POLYMERS

Polymer is a generic name given to a vast number of materials of high molecular weight. Depending on their origin they can be grouped as natural and synthetic polymers. Owing to the presence of carbon in their backbone structure they can be classified as organic and inorganic polymers. They can be divided into thermoplastic and thermosetting polymers due to their response to application of heat. According to its ultimate form and use, a polymer can be classified as plastic, elastomer, fibre or liquid resin [2].

While the chemical structure of a macromolecule depends on the chemical nature of the monomeric units, the geometrical structure depends on the spatial arrangement of the monomeric units with respect to each other. Polymers exist only as solid or liquid but never as gas as they decompose before reaching their boiling point [3]. Because of their low cost, easy processibility, low weight, high corrosion resistance, high electric resistance, durability, etc., polymers are fast replacing metals and alloys in many applications and are extensively used nowadays in the field of industries, science and technologies, particularly in space and nuclear technology.

The application of ionising radiations to polymeric materials has grown due to the fact that the physical and chemical properties of the polymers can be modified by suitable and controlled irradiation. Interest also evolved in the peculiar nature of the ion-polymer interactions. This field of polymer modification and characterisation by ion beam treatment has become a very challenging field owing to the vast technological implications.

1.3 EFFECTS OF ION IRRADIATION ON POLYMERS

The irradiation of energetic ions affects the physico-chemical properties of the polymeric materials. The primary phenomena associated with the interaction of radiation with the polymers are chain scission, chain aggregation, molecular emission and formation of double bonds [4]. 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 chains 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, plasticising the material. All these effects depend on the composition, density, molecular weight of the polymer, temperature and time of irradiation, mass, energy, charge and fluence of the ion beam.

The energy deposition by the traversing ions triggers a wide range of complicated processes and may cause permanent changes in the spatially limited regions known as latent tracks [5]. The track of a highly ionising particle in a polymer consists of a core in which intensive destruction occurs and a halo where the cross-linking of macromolecules predominate. The process of creation of cross-linked region around the track core can be described by the following scheme [6]:

i) Generation of a number of hydrogen atoms and ions in the core.

ii) Their diffusion to the surrounding space and interaction with macromolecules initiating the formation of interior radicals.

iii) Recombination of radicals.

The ultimate changes in the polymer depend on the competition between the processes as well as the effects of delta electrons.

Chemical etching is the technique for amplification of these latent tracks. This technique is based on preferential attack of the chemical solution to the region along the particle trajectory [7]. The sensitivity of polymeric track detectors is known to be affected by various factors such as purity of the monomer, the molecular structure of the polymers, polymerisation conditions, environmental conditions during irradiations and etching.

Ion irradiation leads to modification in most of the polymeric properties like optical, thermal, mechanical and electrical properties.

- ♦The solubility and molecular weight distribution are also affected by ion bombardment [8].
- ♦Ion irradiation at high fluence leads to carbonisation of the polymer and the properties of the modified polymer resembles those of amorphous carbon [9,10].
- ♦Optical properties of ion beam irradiated polymers have been characterised [11] and modification induced in the optical properties of the polymer due to energy deposition by the impinging ion beam have been reported [12,13].

- The effect of irradiation on the chemical structure of the polymer resulting in modification in the electrical properties of polystyrene, polyimide, polystersulphane have been studied [14]. Doping effects introduced by ion irradiation lead to modification in electrical conductivity of the polymers [15].
- Ion irradiation on ferroelectric polymer leads to a phase transition [16].
- The hardness, surface smoothness and wear resistance of the polymers can be improved by multiple ion beam treatment [17].
- Ion bombardment leads to a change in the refractive index of the polymer due to formation of a relatively high concentration of unsaturated bonds all along the irradiated polymer layer [18,19].
- A decrease in melting point and enthalpy of polymers has been observed by ion irradiation [20].
- Track registration properties such as the etch-rates, detection efficiency, sensitivity of the detectors, etc. can be highly influenced by ion irradiation [21-23].

1.4. IMPACT OF PROTON IRRADIATION ON POLYMERS

Three important phenomena that come into picture due to passage of a charged heavy particle through matter are:

(i) At sufficiently high velocities, the ion is stripped of all of its electrons and the energy loss is essentially through electronic excitation and ionisation of the stopping material.

(ii) At velocities comparable to the velocities of its K-shell electrons, the heavy ion starts to pick up electrons from the stopping material. The mechanism of energy loss is still essentially all electronic.

(iii) At velocities comparable to those of the valence electrons of the stopping material, the mechanism of energy loss becomes one of elastic collisions between the heavy ion and the atoms of the stopping material.

Proton is a kind of light ion and the stopping power in solids is small so that the probability of causing observable defect is small [24]. Literature survey indicates that a lot of work is going on to induce modification in polymeric materials using proton beam irradiation.

- Durrani et al. [25] gave massive doses (~10^{16} cm^{-2}) of 3 MeV protons to glass detectors both before and after their exposure to ^{252}Cf fission fragments and Fe ions. In both the cases, and particularly for the post-proton irradiations (Exposure to ^{252}Cf fission fragments and Fe ions followed by proton irradiation), a significant diminution of the etched track diameters for heavily charged particles was observed. The reduction in diameters was accompanied by a fall in registration efficiency of the heavy particles.

- For proton irradiated CR-39, the sensitivity increases with increase in proton energy, reaching a maximum at about 0.5 to 0.8 MeV and then decreases with further increase in proton energy. This finding enhances the applicability of CR-39 in neutron dosimetry [26].
- The chemical registration of 1 to 2 MeV protons in CN-85 detectors were studied and it has been found that CN-85 has very high response to low energy protons. At each energy, there was a linearity between the track diameter and etching time and the slope of the line decreased with increase in particle energy. The registration efficiency for proton decreased with increase in their energy [27].
- For Polyallyldiglycol carbonate irradiated to 200 keV proton beam the refractive index was found to be an increasing function of the dose [19].
- A number of attempts have been made to improve the detection efficiency of CR-39 for protons. A co-polymer labeled USF-3 was developed by adding a small amount of anti-oxidant to CR-39, which

could record tracks of protons up to the energy of 16 MeV [28]. Another co-polymer of CR-39 with 3wt% of NIPAAM (N-isopropylacrylamide) showed a still higher sensitivity by recording normally incident protons up to 20 MeV energy [29]. Again another co-polymer CR-39/NIPAAM/Naugard445, composed in weight ratio of 99/1/0.01 is found to be highly sensitive to low LET (linear energy transfer) particles in the region below 10keV/μm of LET_{200eV} and able to record normally incident particles of LET_{200eV} down to ~1.5 keV/μm, recording protons up to energy 27 MeV [30].

- The thermal annealing of proton tracks of 4 to 6 MeV at temperatures ranging from 150 to 240°C in CR-39 polymeric detectors have been studied and the activation energy for the annealing process was found to be 0.2 ± 0.02 eV. This work is of considerable importance in neutron dosimetry [31].

1.5. THE PRESENT WORK

In this work, an attempt to characterise the effects of proton irradiation on the physico-chemical properties of some polymeric materials using various experimental techniques has been made. It is hoped that the findings in this work would be of important relevance to material science and applications of polymers.

Dose dependent modifications in optical, structural, topographical and thermal properties of eight different polymers by four different doses of 62 MeV proton irradiation has been quantified by various characterisation techniques. The work is further extended to the study of extra surface damage due to the deposition of additional amounts of energy by fullerene destruction in one of these polymers. Also, the effect of proton irradiation through thin metal foils has been studied in one of the polymers. In this dissertation an account of the work has been presented in the subsequent chapters as follows:

CHAPTER 2 gives a detailed account of structures, properties and utilities of all the eight polymers used (Makrofol-N, Triafol-TN, Polyethylene terephthalate, Triafol-BN, Polypropylene, Polyimide, Polytetrafluoro ethylene and Polyallyldiglycol carbonate). A brief description of the work already done on these polymers has also been reported. A detailed description of the different characterisation techniques, the principles and conditions of operations and the various parameters that can be studied through these techniques are also given.

CHAPTER 3 describes the irradiation parameters and conditions for ion (proton and ^{28}Si) irradiation. A detail information about the doses used is also given. The experimental set up and conditions of the different characterisation techniques used in the present work to analyse the irradiated polymers are also discussed.

In **CHAPTER 4**, the results obtained from different technical studies showing the dose dependent modifications induced in the polymers by proton irradiation has been discussed in terms of **track registration property, activation energy for etching, optical band-gap, infra-red absorbance, surface roughness, thermal decomposition behaviour, melting, crystallisation** and **free radical formation.**

The effect of proton irradiation on fullerene, its destruction and the effect of the huge amount of energy released during the destruction process on the track registration property of the polymer Polyallyldiglycol carbonate (PADC) has been described. The effect of proton irradiation through some metal targets on the modification of track registration property has also been discussed.

CHAPTER 5 describes the important conclusions derived from the present investigation and the future perspectives. The proton-induced modifications as well as the utility of the modified polymers have been discussed in detail. A brief account is also given on the further investigations in this field and extension of the present work.