APPLICATION OF SWIFT HEAVY ION IRRADIATION (SHI) ON POLYMERS AND DEVELOPMENT OF NANO AND MICRO PORES AND ELECTRODES FOR DEVICES USING PLASTIC TRACK DETECTORS

ABSTRACT

THESIS

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IN

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BY

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Abstract

Polymeric solids (plastics) are known to be sensitive to register the material damage caused in their matrix by heavy ionizing charged particles (protons and above). These damaged regions are usually 50-100 Å around the particles trajectory. Since they can not be seen by naked eye or optical microscope, they are called 'Latent' tracks. The diffraction contrast images of latent tracks can however be observed only with the help of electron microscope. The usual method of seeing the particle tracks in plastics using optical microscopes is to first enlarge the latent tracks to sizes comparable to the wavelength of visible light by using the 'selective chemical etching'.

The plastic track detectors have found innumerable applications in nuclear physics, cosmic ray, radiation physics, geophysics, biomedical technology and what not. In fact, today there is hardly any branch of science and engineering where these detectors do not have actual or potential applications. But still the cause of damage and types of defects produced by heavy ions in polymers is not well understood.

Keeping this in mind the characterization of damaged regions in plastic (Makrofol KG) with heavy ion beams has been done by us. In this thesis I have
studied the possibility of applications of Swift heavy ion irradiation (SHI) of polycarbonate plastic (polymer) for the development of micro and nano pores and electrodes by making through-etched holes in thin plastic foils and filling them with conductor and insulator materials.

The ions generated pores are not only used for filtration of bacteria of micron sizes but also used for track engineering by filling materials inside the pores. I have succeeded in depositing copper in the etched pores in the polymer matrix and produced copper needles of micronsizes on the copper substrate using template techniques. These fine pores and electrode structures have applications in electronics, optical and biomedical sciences. I have also developed microstructures of potassium iodide in the etched pores in the polymer matrix. Such microstructures can be used in the fabrication of miniature electronic components and new composite materials. In order to understand the damage caused by the SHI in the polymer, I have carried out experimental measurements of the dielectric response (i.e. variation of dielectric constant) of unirradiated and irradiated plastic foils with Swift heavy ions of different kinds (\(^{7}\text{Li},^{16}\text{O},^{24}\text{Si}\) and \(^{59}\text{Ni}\)) having different fluences and energy. Calculations have been made for the dielectric loss factors and results
have been interpreted theoretically. Further insight about damages caused by the SHI has been gained by using an Ultraviolet and Visible spectrophotometer. The variation of UV-Vis absorbance in terms of wavelength of light has been interpreted, variation of carbonaceous clusters with fluences, their size estimation and the optical band gap calculations using different heavy ions have been made. The entire work done by me is presented in the five chapters of the thesis.

Chapter 1 describes the two basic processes of energy loss i.e. electronic energy loss and nuclear energy loss and the two models of formation of tracks, which are related to our work.

Chapter 2 relates the instrumentation and equipments used. It describes briefly the 15 MV pelletron accelerator of NSC, low and high fluence-irradiation setup, microscope, scanning electron microscope and spectrophotometer, which were used in this work.

Chapter 3 contains the characterization of pores in polymer using SEM, fabrication of copper needles/electrodes on copper substrate using template technique and developments of microstructures of potassium iodide at the site of through etched pores in the polymer matrix.
Chapter 4 discusses in detail, the dielectric response measurements and calculation of loss factor, which reveal chemical and electrical changes caused by SHI irradiation.

Chapter 5 deals with the use of UV-Vis spectrophotometer to our work and the details of calculations of number of carbon atoms present in the carbonaceous clusters formed in the damaged regions and also the estimation of optical energy gap of the irradiated foil for various ions.

The work described in chapter 3, 4 and 5 are claimed to be the original contributions of the author and they have several applications and implications for future work.
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Certificate

Certified that the work reported in this thesis submitted for the DEGREE OF DOCTOR OF PHILOSOPHY (Ph.D.) in Applied Physics is the original work carried out by Mr. Mohammad Mujahid under our supervision on the topic “Application of Swift Heavy Ion Irradiation (SHI) on Polymers and Development Of Nano and Micro Pores and Electrodes for Devices Using Plastic Track Detectors”. Also certified that this thesis did not form the basis of the award of any previous degree.

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Chapter 1

Swift Heavy Ion Irradiation of Polymers
1.1 Introduction

Heavy ion having energy \( \geq 1 \text{ MeV/nucleon} \) and moving with velocity \( \sim 2 \times 10^8 \text{ m/s} \) is known as Swift Heavy Ion (SHI). The study of modification of materials by SHI attracted attention of researchers due to the fact that the irradiation by SHI causes such effects in the macromolecule which are not possible by any other means. SHI irradiation causes a number of chemical changes in polymers like cross linking, chain scission, formation of \( \text{C} = \text{C} \), formation of alkyne group, depletion of \( \text{H} \) and hetero atoms (e.g. \( \text{N} \), \( \text{S} \), or \( \text{O} \)) and changes in physical properties like change in resistivity and dielectric response. It is the high value of the electronic stopping power of the ions, which induces an unusual high density of electron-hole pairs in insulating materials close to the ion path. Some of the technological applications of the SHI irradiation based studies [1-2] are optical wave guide and cavities and lithography (a method of defining patterns of devices processing) etc.

The modification induced by the highly energetic heavy ions in insulating materials may be understood, if the energy loss transfer from the ion to the targets is known. The following processes are involved in energy loss of the particle:

1. Electronic stopping \( 'S_e' \) (inelastic collision of incident ion with target atomic electrons resulting in excitation and ionization of the target atoms).

2. Nuclear stopping \( 'S_n' \) (elastic collision with screened target nuclei, resulting in displacement of target nuclei, resulting in displacement of target atoms).

The complete energy loss process can be viewed in the (fig. 1.1).
FORMATION OF ION TRACKS IN POLYMERS BY SHI

Fig 1.1: FORMATION OF ION TRACKS IN POLYMERS BY SHI
1.2 Electronic stopping

Electronic energy loss arises from electromagnetic interaction between the positively charged ion and the target electrons. One mechanism is called glancing collision (inelastic scattering, distant resonant collisions with small momentum transfer). Both glancing and knock-on collision transfer energy in two ways: electronic excitation and ionization. Electronic excitation is also the process in which an orbital electron is raised to a high energy level, whereas, in ionization, an orbital electron is ejected from the atom. Glancing collisions are quite frequent but each collision involves a small energy loss (<100 eV). On the other hand, knock-on collisions are very infrequent but each collision imparts a large energy to a target electron (>100 eV). These knock-on electrons are often known as δ-electrons. The range of atomic collision cascade defines the core of the tracks and has a diameter of less than 10 nm. The track is surrounded by a halo region corresponding to maximum range of the δ-electrons of about 100-1000 nm (Fig 1.2), given by Chatterjee and Magee 1980[3]. In polymer track halo plays an important role, since the δ-electron cascade further damage such as strand breaks or cross links of polymer chain.

The electronic stopping of the ion on the target is treated within the local density approximation wherein each infinitesimal volume element of the solid is considered to be an independent plasma[4]. A mathematical expression for the electronic stopping cross-section is given by

\[ S_e \propto \int (v,\rho) (Z'(v))^\gamma p dV \]
Fig. 1-2. Atomic collision cascade called Track core and track Halo.
Where $I$ is the stopping interaction function of a particle of unit charge with velocity $v$, with a free electron gas of density $\rho$, $Z'$ is the effective charge of an atom having atomic number $Z$, and $dv$ is a volume element. $I(v, \rho)$ varies with the particle velocity and plasma frequencies of the electrons in the stopping medium. The effective charge of an atom having atomic number $Z$ is given by

$$Z'(v) = 1 - a \exp\{-b (v Z^{2/3} / v_B)\}$$

Where $a$ and $b$ are fitting constants, $v_B$ is the Bohr velocity (a typical velocity of outer shell electron ~$2 \times 10^8$ m/s) of the particle.

Electronic energy loss in the material can be varied from a level of eV/A° to a very high value, say 10 keV/Å° by choosing the mass and energy of the ion. Early belief that $S_e$ affects only insulators and not conductors has been proved wrong[2]. Heavy ions offer possibility of modifying any type of solid structure. At sufficiently high energy highly charged ions may induce amorphization, crystallization, viscous flow and plastic deformation in metals. There are thresholds involved in the value of $S_e$ which depend on the material beyond which properties of materials are modified.

1.3 Nuclear Stopping

Nuclear energy loss arises from the collision between the energetic particle and target nuclei, which causes atomic displacements and phonons. Displacement occurs when the colliding particle imparts energy greater than certain displacement threshold energy, $E_A$
to a target atom. Otherwise, knock-on- atoms can not escape their sites and their energy dissipates as atomic vibration (phonons). $E_A$ is the energy that a recoil requires to overcome the binding forces and to remove the atoms from its original site. Since the nuclear collision occurs between two atoms with electron around protons and neutrons, the interaction of an ion with a target nucleus is treated as the scattering of two screened particles.

Nuclear stopping is derived with consideration of the momentum transfer from ion to target atoms and the interatomic potential between two atoms. Thus nuclear stopping varies with ion velocity as well as the charges of two colliding atoms. Nuclear stopping becomes important when an ion slows down to approximately the Bohr velocity. For this reason the maximum nuclear energy loss occurs near the end of the ion track.

Nuclear stopping is given by equation given by Bohr and Wilson[5].

$$S_n = s_n \frac{8.462 Z_1 Z_2 M_1}{(M_1 + M_2) (Z_1^{2/3} + Z_2^{2/3})^{1/2}}$$

Where $s_n$ is the reduced nuclear stopping, which depend upon reduced energy of the ions. $Z_1$ and $Z_2$ are the charges and $M_1, M_2$ are the atomic masses of the ion and target.

### 1.4 Track Formation Mechanism

The basic mechanism of formation of defects in the inorganic and organic insulating materials is different but the end results are same. The physical and chemical properties of the damaged regions surrounding the trajectory of the charged particle in the insulating material become much more different from that of the bulk material. This makes the
damage tracks chemically more etchable whereby they can be enlarged to be finally visible under optical microscope when their size becomes several times more than the wavelength of visible light.

The insulating materials register tracks only if the incident ion produces a primary ionization along its trajectory at a rate greater than a certain critical value—the characteristic of the material.

1.5 Track Formation Models

The primary mechanism by which the kinetic energy of a high velocity heavy ion is deposited is electronic stopping. The process involves an intense series of electronic ionization, excitation and dissociation events. The characteristic time for energy absorption is $10^{-17}$ to $10^{-15}$ s. There are two models for track formation:

1.5.1 Coulomb explosion model: When heavy ion passes through the matter, it knocks electrons out of the atoms in the crystal lattice, leaving behind positive ions. These ions thereupon repel each other violently due to Coulomb forces, disturbing the regular lattice and thus tracks are formed. In polymers by passing of heavy ions the molecular chains are broken and new species are formed. Based on this mechanism[6], the requirements of latent track formation would be the following

(a) The pressure due to Coulomb repulsive forces inside the ionized channels must be greater than that due to coherent attractive forces in the atomic lattice.
(b) The positive ions in the channels should not recombine within $10^{-13}$ s, for approximately so much time is needed for the ions to be removed from the lattice points.

(c) The time required by the hole to diffuse a distance must be greater than the lattice vibration time required for the ions to be displaced from their sites.

(d) There must be at least one ionization per atom plane crossed by the incident charged particle.

### 1.52 Thermal Spike model:

: Thermodynamic evolution of lattice system of material in pico second time scale due to ion irradiation is known as thermal spike. Spreading of electronic energy in a large volume due to electron-electron and electron-phonon interaction induces a significant increase in lattice temperature ($10^3$ K to $10^4$ K) followed by a rapid quench ($10^{14}$ K/sec) due to heat conduction. As a result of this heating episode, various atomic processes are activated and damage of the lattice is produced[7].

### 1.6 Goal of our experiments

The aim of our work was to study the effects of SHI irradiation on polymers leading to their applications in the development of micro/nano electrodes for devices. With this objective in mind we have generated heavy ion tracks of micron size in polymers and
deposited metals and crystals of potassium iodide in the pores and studied the electrical properties i.e. dielectric response and loss factor for pristine and ion irradiated polymers. The optical changes were studied by UV-Vis Spectrophotometer and from this we have calculated cluster size and energy gap. Our work has some very important applications as discussed in sequence below.

1.6 Importance of studying tracks in polymers: The exact physical mechanism by which high energy heavy ions produce damage in polymer is still an unsolved problem. Etching process does not provide exact information about the initial structure and real nature of ion tracks, since a large amount of material is removed and many other physical and chemical properties are changed, therefore we planned to study the early stages of track etching using SEM. Etched channels with diameters in the micron and sub micron range are applied as microfilters in filtration of micro/ultramicro bacteria for use of clinical applications and industries. Fischer and Spohr [8] have suggested many newer applications viz., new electronic devices (point contact diodes), field emitters, microcomposite materials and characterization of ultramicroelectrode ensembles. Martin and co-workers [9] are also actively engaged in exploring more applications in this field. Possibilities of other developments are volcano field-ion sources, metal-semiconductors junctions, polymers microwave antenna etc. One can also get idea of track engineering through the work of Eyal et al [10] how through hole formed in the irradiated polymide of 20 nm showed chemical activity in the time scale of month and one can also try the through hole formation in other sample at different thickness.
1.62. Importance of growth of micro/nano structures using Nuclear Track Filters (NTF): Method of filling the pores with material is called Track engineering. The technique of NTF is used for synthesizing organic and metallic microtubules[11] and metal-semiconductor heterostructures which have applications in microelectronics, field emission electrodes, tunneling diodes[12], electrochemistry, conductive polymer, nanofibre fabrication, transparent metal structures, biological substitutes. Nano and micro materials also have wide-ranging implications to a variety of areas, including chemistry, electronics, optics, and biomedical sciences and their application include use in electronic, optical, and mechanical devices, drug delivery[13] and bioencapsulation. Microcrystals are used for fabrication of miniature electronic components and new composite materials[14].

1.63 Importance of dielectric response: Study of dielectric response reveals, how non-polar molecule induces dipole moment when placed in electric field. This study is also useful as dielectric capacitors can store more electric charge due to polarization. Better understanding about the competition between chain scissioning and end linking in the polycarbonate at different ionic energy densities is obtained by observing the modification induced in polycarbonates by SHI using dielectric measurements[15].

1.64 Importance of photospectrometry in our study: Evidence for the existence of three categories of compounds in heavy ion irradiated polycarbonate is obtained from analysis of UV-Vis spectrophotometer. The first kind is formed from intermolecular
combination of the phenoxy-phenyl and phenoxy-phenoxy radical pairs, which show UV absorbance in the 275-350 nm region. The second kind is formed by the reaction of the radical with a neighboring H, O₂ or H₂O molecule. The presence of such compounds leads to chain ruptures and as a result, a decrease in the molecular weight. The third kind is formed by intermolecular radical combination. Such a group may provide branching centers and eventually lead to crosslinking.

Information about carbonaceous clusters, optical band gap, E₇, in ion irradiated polymer films is obtained using UV-Vis spectroscopy. These clusters which are responsible for electrical conductivity in ion irradiated polycarbonate films is also characterized using UV-Vis spectroscopy[16].

This chapter describes the two basic process of energy loss i.e. electronic energy loss and nuclear energy loss and the two models of formation of Tracks which are related to our work. The objectives of the present work are apelled out.
1.8 References

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Chapter – 2

Instruments and equipments
2.1 Introduction

This chapter deals with brief description of the equipment with their relevant details and specification used in the experiments carried out and various techniques for the offline measurements employed in this thesis. The present experimental work involves the following stages:

[1] Irradiation of polymers using 15 MV Pelletron Accelerator at NSC
[2] Use of low and high fluence irradiation set up
[3] Preparation of etched track membranes and then revealing of the micro structures by SEM.
[5] Off-line measurements to study di-electric study and loss factor of pristine and various ion irradiated polymers.
[6] Spectro photometry of pristine and various irradiated samples

In the following sections, it is aimed to present the details of the various experimental techniques and equipments employed.

2.2 Pelletron Accelerator

The 15-MV Pelletron accelerator at Nuclear Science Center (NSC) [1] belongs to a class of particle accelerators known as Van de Graaff electrostatic accelerator. It is capable of accelerating almost any ion beam from hydrogen to uranium to energies from a few MeV (million electron volts) to hundreds of MeV. A schematic diagram showing the basic principle of acceleration is shown in Fig. (2.1). In this machine, negative ions are
**Fig 2.1:** A schematic diagram showing the basic principle of acceleration in 15UD pelletron
produced and re-accelerated to ~400 keV, mass analyzed and are then injected into strong
electrical field inside the accelerator. At the Centre of the accelerator tank there is a
terminal shell, which is maintained at high voltage (up to 15 million volts). The negative
ions on travelling through the accelerating tube from the top of the tank to the positive
terminal get accelerated. On reaching the terminal, they pass through a stripper that strips
the ions off their electrons, thus transforming them to positive ions. These positive ions
are repelled from the terminal (due to positive potential) and thus are again accelerated to
ground potential to the bottom of the accelerator, i.e. the same terminal potential is used
twice to accelerate the ions. On exiting from the accelerator, the ion beam corresponding
to a particular energy is selected and bent by an analyzing magnet.

Negative ions injected into the accelerator column are accelerated to the terminal and
gain an energy V MeV, where V is the terminal potential. The terminal has a foil stripper
assembly (thin carbon foil) as well as a gas stripper (nitrogen gas at low pressure). As the
ions pass through the stripper, it strips off some of the electrons to become positive ions.
Depending on the foil thickness (or gas pressure), the incident energy and type of the
ions, the charge state distribution of the emerging positive ions will vary. The most
probable charge state and other charge states after stripping can be calculated by semi-
empirical formulae. These ions are further accelerated while travelling to the high-energy
end of the accelerator and gain energy equal to qV where q is the charge state. As a result
the ions emerging out of the accelerator [2] column gain energy given by

\[ E_i = [ E_{inj} + (1 + q) V ] \text{ MeV} \]
Where, $E_i$ the energy of the ion having a charge state $q$ after stripping. $V$ is the terminal potential in MV (million volts) and $E_{\text{inj}}$ is the energy of injected particle in MeV. The ion beam emerging from the accelerator is focussed at the object point of the analyzing magnet by means of magnetic quadrupole triplet lens placed at the accelerator exit.

The Pelletron ion beam is generally composed by several components, each with different charge state and energy. However, for the experimental purpose[3] precise monoenergetic ions are required. So the Pelletron high energy beam line following the main accelerating tube includes an energy dispersive, homogeneous dipole magnet, which can be set such that all unwanted ion beam components are filtered out leaving only the selected component for onward transmission to the beam lines. For an ion beam having mass $M$, energy $E$, and charge state $q$, the analyzing field required for selection of such a beam is governed by the relation

$$B = K \left( ME \right)^{1/2} / q$$

Where $K$ is constant. Setting different magnetic field strengths ($B$), one can choose the different $M$, $E$ and $q$ of the ions.

The entire beam transport system of the 15 UD Pelletron accelerator is maintained under a clean ultra high vacuum condition i.e. at pressure below $1 \times 10^{-9}$ Torr. This is achieved by the use of different types of vacuum pumps distributed all along the beam line from the ion source to the irradiation chamber.

The ion beam of a desired energy ($E$) and mass ($M$) is transported into any one of the seven beam lines of the beam hall by means of a switching magnet. The beam is kept centered and focussed by means of steering magnet. The beam is visually
monitored by beam profile monitors and the beam current is measured by means of Faraday cups[4].

2.3 Low fluence irradiation setup

The general purpose scattering chamber (GPSC) which is used for our work is low fluence irradiation setup (Fig. 2.2). It is of 1.5m in diameter and of 0.6m in height. Samples which require ion dose up to $10^6$ ions/cm$^2$ are irradiated in this chamber. It is used to irradiation of the samples equipped with a target ladder arm. The ladder has four faces. Each face can accommodate at least five samples, they are controlled by `remote’ and can be watched on the TV screen. The sample mounting ladder can be rotated around the ladder with 0.05° precision. The vacuum inside the chamber during the experiment was $1 \times 10^{-6}$ mbar using a Difstack pump having a speed of 2000 l/s.

GPSC is situated at angle of 45° to the beam line. A collimator arrangement has been provided at the entrance and a Faraday cup has been provided at a distance of 1.65m away from the exit of the chamber. Beam falls normally on the quartz or gold target and scattered at angle 45° and falls on the samples to be irradiated. Firstly the beam is allowed to fall on the quartz, which starts glowing. This we can view on TV screen. We use quartz to see the location and position of the beam, whether the beam is coming on the sample or falling somewhere else, if the beam is not falling within the desired area of samples to be irradiated, it is adjusted with the help of magnetic steerar. For irradiation of our samples we have used $^{28}$Si beam having energy 100 MeV which falls normally on the thin Au foil having thickness 1mg/cm$^2$ and the scattered beam falls normally to the
FIG. 28 Schematic diagram showing General Purpose Scattering Chamber for low flux irradiation.
polymers. Detector which is connected to pre-amplifier, amplifier and multichannel analyzer (MCA) gives idea about counts/sec for the number of particles scattered. When irradiation of one side is over, ladder containing samples were rotated and then watch the vacuum of the chamber to come about $5 \times 10^{-6}$ m bar. Scattering of the beam in the GPSC is the Rutherford Scattering given by

$$Y = Q \times t \times \frac{d\sigma}{d\Omega} \times d\Omega$$

Where $Y$ = no. of particle scattered.

$Q$ = no. of particle incident

$t$ = thickness of the target

$d\sigma/d\Omega$ = Rutherford Cross section

$d\Omega$ = Solid angle

$2.4$ Material Science Chamber for high fluence irradiation

This high vacuum chamber (38 cm diameter) has a facility for temperature controlled (liquid cooled) multiple sample holders having provision for linear movement of 120 mm and a rotation of 360°. A vacuum of $10^{-7}$ mbar is maintained by using a diffusion pumping system filled with a LN$_2$ trap. A remote controlled target holder can be positioned perpendicular to the beam line for irradiation. Various samples can be irradiated in an experiment using bellow-sealed linear movement of the holder by 140
mm. Material science beam line (Fig. 2.3) is used for ion fluence up to $10^{13}$ ions/cm$^2$. For irradiation we have to see whether beam is falling at the desired place on the quartz or not, then we allow the beam to fall on the irradiated samples. The rectangular ladder used to fix up seven samples contains four faces and its position can be changed by auto control switches. ACCTV camera was also attached to one of the ports of chamber for viewing the sample position.

2.5 Optical microscope

The tracks formed by chemical etching can be easily counted under optical microscopes using ordinary magnification (200X-1000X). In case of normal or near normal incidence the microscope can be focused on the surface of the detector where the intersection of the track with the surface is seen as a dark circular spot. By little defocussing one can also look into depth of the track hollow. In case of grazing incidence, the etched tracks can be easily distinguished from the background scratches etc. When the track density is small it can be easily evaluated by counting under optical microscope using ordinary magnifications (200 X – 1000 X). The tracks then appear as black dots or conical channels against white background. With the help of microscope under magnification of 400X-500X we can see the tracks easily whose pore diameter is of the order of microns. Picture of the track can also be seen through a microscope (Olympus-HT3) in which light falls normally on the sample surface and have magnification of 10X, 20X and 30X respectively and connected to computer. The picture of pore of the track can be stored in the Imaging of Microsoft-Promt and using calibrated slide picture, one can calculate
Fig. 2.3 High vacuum chamber for material Science Experiment.
diameter of the pore. Using fine adjustment at the sight of the microscope, surface morphology can be studied.

2.6 Scanning Electron Microscope

Analysis of the surface topography developed due to ion impact is invariably done today with scanning electron microscopes. Seeing small atoms at atomic resolution has always been a challenge, because they don’t strongly scatter the electrons in the microscope’s beam and when light atoms are close to heavy ones, it has been virtually impossible to resolve them. Heavy atoms scatter electrons much more, and as a result the interference pattern is just too complex to resolve. SEM overcomes this difficulty by making a through-focal series of images, each with the scattered electrons interfering with different relative phases and then uses computer processing to unscramble the electron waves and combine them into a single high resolution image in which all electrons are in phase. It allows large tilt angles, large depth of focus and high lateral resolution. In this microscope an energetic beam of electrons is focussed on the specimen and is scanned in a rectangular raster. Electron beam energies can be varied over a range of few keV and beam size from few tens of angstrom to few hundred angstroms. When incident electrons strike the target, a number of processes occur. Usually back scattered primary electrons or emitted secondary electrons are used to produce geometrical image of the surface. These electrons are properly collected (by focussing onto a detector) and detected. The signal produced by the detector is used to modulate the brightness of an oscilloscope spot which traverses a raster in exact synchronism with the beam at the specimen surface. Thus an image of the surface on the screen is produced. The contrast is adjusted by
varying beam current, its energy and spot size. The magnification is adjusted by simply varying the ratio of scanned specimen area to the display screen area. A schematic lay out of a scanning electron microscope is shown in Fig. (2.4). SEM, LEO 440 used for the study of our sample is fully computerised and having about lakh of magnification.

2.7 Cell for Template Synthesis

Template Synthesis[5] provides an unique way of micro/nano structure fabrication using the pores of track etched membranes i.e. nuclear track filters. The methodology is based upon the extensive work done by several authors [6]. The simplest and well known underlying concept of electrodeposition of metals through electroplating is described as an electrochemical process in which metallic ions in a supporting solution are reduced to the metallic state at the cathode, which, if closely covered by track etched membrane, would lead to the formation of growth of plated film as embodiment of micro or nano-structure. The etched pores of the membrane used would act as templates. The technique is shown schematically in Fig. (2.5). After the pores are filled with the desired material, galvanic process is interrupted and the replica is separated from the membrane matrix either by peeling it off mechanically or by dissolving the membrane itself in suitable solvent. Electrodeposition of the metal takes place in a template cell, the detailed structure of the cell is described in Reference [5] but we have fabricated our own cell with the same basic concept.

The design of the cell used in the present work, is shown in fig. (2.6). This is a 80 mm long cylindrical structure made of perspex. Cathode and anode are made of copper and are detachable. The NTS covers the cathode and is sealed thoroughly by an O-ring, which
Fig 2-4 Block diagram of a Scanning microscope.
ION IRRADIATION

TRACK ETCHING

TEMPLATE SYNTHESIS

CONDUCTING COAT

MICRO STRUCTURE ON SUBSTRATE

FIG. 25 Template synthesis to produce micro structures.
Fig 2-6 Cell for Template synthesis.
is 20 mm in the present case. Base area of the anode is 30 mm and the inner length of the cell, which is used for electrolyte, is 45 mm long. The cell before use is thoroughly rinsed with Milli Q 10 MΩ water, ethanol in succession and then air-dried. A small piece (1 cm × 1 cm) of thoroughly cleaned copper electrical tape with conducting adhesive layer at the backing was used as a cathode, affixed to the copper electrode. The distance between cathode and anode is adjustable in this design. The cathode, after being rinsed with H₂SO₄ (5-15 vol. %) or HCl (20-30 vol. %) to remove the oxide layer[6], is covered with the given NTF which is also thoroughly cleaned, washed and rinsed with Milli Q water and ethanol. In order to secure close contact, the NTF should be wetted by the electrolyte solution before use [7]. The electrolyte used here was CuSO₄.5H₂O (195-250 g/l, i.e. 0.78-1 M) + H₂SO₄ (30-75 g/l).

2.8 Apparatus for dielectric measurement

Dielectric Constant and loss factor are measured with the help of Hewlett Packard (HP 4284 A) LCR meter. It requires a power source of 220 V ac and is a general purpose LCR meter for incoming inspection of components, quality control, and laboratory use. The HP 4284 A is used for evaluating LCR components, material, and semiconductor devices over a wide range of frequencies (20 Hz to 1 MHz). It offers C-D measurements with a basic accuracy of ± 0.05 % (C and D) where C and D represents capacitance and dielectric loss factor at all frequencies with six digit resolution (the dissipation factor resolution is 0.000001) on every range. With its built in comparator, the HP 4284 A can output comparison/decision results for sorting components into a maximum of ten bins.
Sample holder: Diagram of the sample holder, which is about 1.7 m long can be seen in the figure(2.7).

Heater: Heating of the sample is carried out with the help of a 35 W heater connected to a contractor and a variac.

The setup for dielectric response measurement is given in fig.(2.8).

2.9 Spectrophotometer
Spectrophotometer used for our work is HITACHI 3000 double beam spectrometer(8).
An apparatus designed for optical absorption, phosphorescence and radioactive decay measurements are called spectrophotometer. In optical absorption spectrophotometer electromagnetic radiation in the near-UV, visible, or near IR regions is used to excite the transition between the electronic states. Whereas atom at low pressure gas discharges exhibit very sharp lines, electronic centres in molecules and condensed matter display a variety of different bandshapes. In consequence, the absorbed intensity is a function of the photon wavelength (or energy). The first essential of an absorption spectrophotometer is a broadband source viz. xenon lamp which have usable light output in the range 270 to 1100 nm. In the arc lamp, radiation is due to the collision of Xe atoms with electrons which flow across the arc. Complete separation of the excited electrons from the atoms leads to ionization and the continuum output. The formation of Xe atoms in excited states leads to the sharp lines in the output from Xe arc lamps.
Accurate measurements of the absorption at different wavelength [8] are best made using a double-beam spectrometer (Fig2.9) when the signal is processed using computer and when these data are converted to microcal origin 41, we get the desired graph.
Fig 2.7 Apparatus diagram for Sample holder used for Dielectric measurement.
Fig. 2.8 Set-up for Dielectric measurement
Fig 2.9 Block diagram of a double beam Spectrophotometer.
References


Chapter –3
Creation of Micro Pores and Microstructures by Template Technique
3.1 Introduction:

Charge particles are slowed down when passing through the matter. If heavy ions with a kinetic energy in MeV range penetrate a solid, their energy is dissipated and absorbed and this can cause structural change in the material. Thus, depending upon the specific properties of the solid, the ions cause continuous tracks in a narrow region along their trajectories [1-2]. In polymers as well as in other insulators, energetic heavy ions create continuous damage trails along their paths. Under ion irradiation polymer molecular chains usually break apart into shorter chains that alter the structure in the affected area. The material in the track left by the ion passage is normally heavily amorphosized. Under normal conditions, a latent track can exist for a long time. Due to different chemical bonds in the damaged region, the latent tracks can be etched with a higher rate than the bulk unaffected material. The etching of latent tracks in polymers is commonly used for production of membranes that contain channels with diameters in the micron and sub micron range. Membranes of that kind are applied as microfilters or can be used for fabrication of various metallic microstructures [3-4].

In insulating material, it is possible to visualize the latent ion tracks by several techniques like microscope, SEM, TEM, HRSEM, SFM, Xray diffraction and gas diffusion experiment. Recently, high-resolution electron microscopic imaging of track cross-sections, for example in zircon, in germanium sulphide crystals or in high temperature superconductors was carried out [5]. The diameter of the latent tracks observed in polymers and their cross-sections were estimated indirectly from neutron diffraction and gas diffusion experiments. In both cases, an average value of 10 nm was obtained.
However, high resolution SEM imaging of latent tracks in polymers should give direct information about radiation damage produced by energetic particles in these materials [6, 7].

The exact physical mechanism by which high energy heavy ions produce damage in different materials is still an unsolved problem. Etching process leads to the enlargement of heavy ion damaged trails and make them visible under optical microscope. This approach does not provide exact information about the initial structure and real nature of ion tracks, since a large amount of material is removed and many other chemical properties are changed. In the present experiment the characterization of pore diameter is carried out with microscope and with SEM. Applications of track filling may involve fabrication of track-structure nano/micro components for mechanical and electronic devices. The fully computerized SEM (Model, LEO 440) is used in this work for analysis of tracks. The sample before analysing is coated with iodine to prevent charging up problems. After characterization we have deposited copper metal in the pores and succeeded in the growth of Potassium iodide microstructures in the polymer matrix, which leads to microtechnology.

Micro/Nano technology is an emerging field having great potential for bringing in revolution in the development and advancement of sensors and devices. In recent years, there has been tremendous interest in nanopores and micropores in polymers generated by swift heavy ions (SHI) for vast variety of applications. These pores are created by controlled chemical etching of ion irradiated thin polymer foils, so as to produce Nuclear Track Filters (NTFs). Physical properties of a material can change significantly in the transition between the macroscopic scale and nanoscale. Therefore, nanophysics
fabrication is very important both for its technological applications and fundamental interest. Recent advances in electrodeposition technique make possible the growth of well defined periodic structures, such as magnetic multilayers with layer thickness as small as few nanometers. Martin et al. [8] have fabricated nanoelectrode ensemble using template technique and Chakravarti et al. [3] have also employed this technique to grow microstructure junctions using the novel material system Cu-Se in the chemically etched pores of polycarbonate foils. Recently, Biswas et al. [9] have fabricated and tested resonant electron tunneling in single quantum well heterostructure junction and its characteristics using Nuclear Track Filters. Most of the workers have been reporting mainly on the use of Nuclear Track Filters in filtration of micro/ultramicro bacteria for use of clinical applications and industries [10,11]. Fischer and Spohr [12] have suggested many newer applications viz., new electronic devices (point contact diodes), field emitters, microcomposite materials and characterization of ultramicroelectrode ensembles. Martin and co-workers [13-15] are also actively engaged in exploring more applications in this field. Possibilities of other developments are volcano field-ion sources [16], metal-semiconductors junctions[17], chemical sensors[18], conducting polymers[19], microwave antenna etc.

3.2 Experimental Details:

Experimental Parameters

Ion $^{28}$Si
Energy 100 MeV
Fluence $1 \times 10^6$ ions/cm$^2$

Irradiation setup GPSC

Thickness of sample 20 μm

Etchant used 6N NaOH at 60°C

Time of etching zero minute, 1.5 minutes, 2.5 minutes, 5 minutes, 10 minutes, 30 minutes and 90 minutes respectively

3.3 Irradiation Details:

Our aim was to generate micro/nano structures using SHI. This requires the exposure of polymers by ion beam of ion dose up to $10^8$ ions/cm$^2$ preferably with uniform density and low ion straggling. After this ion dose, overlapping of pore (micro size) will begin. One requires large ion dose up to $10^{12}$ ions/cm$^2$ so as to get the nano pores without their overlapping. Low fluence irradiation set up was carried out in general purpose scattering chamber (GPSC). Most of the NTFs used in the present work were of Makrofol KG (Polycarbonate from Bayer AG), 20 μm thick, having an average pore diameter of 800 nm with pore density $10^6$ cm$^{-2}$. These were prepared by irradiating the foils with heavy ions $^{28}$Si, 100 MeV with ion fluence of $10^6$ ions/cm$^2$ at the 15 MV Pelletron accelerator of the Nuclear Science Centre (NSC), New Delhi, India, using the general purpose scattering chamber (GPSC). Low flux irradiation set up. We established optimum experimental parameters from Pelletron accelerator by putting the gold/quartz foil scatter and measured the beam current which was found to be 95 nA at accelerator entrance. The scattered ions were detected by Si surface barrier detector coupled to MCA (multi channel analyzer) and beam current by Faraday cup. With the help of data
we can estimate better pulse from the scatter used, its % resoluton and dose. Faraday cup gives the counts/sec for the number of particle coming directly to the target and MCA gives the counts/sec for the number of particles scattered.

3.4 Copper Deposition on Copper Substrate

The NTFs used in the present work were of Makrofol KG (Polycarbonate from Bayer AG), 20 μm thick, with pore density 10^6 cm^-2. These were prepared by irradiating the foils with heavy ions ^28Si, 100 MeV with ion fluence 10^6 ions/cm^2 and beam current of 5-6 pnA (1pnA = 6.2 × 10^9 ions/sec) at the 15 MV Pelletron Accelerator of the Nuclear Science Centre (NSC), New Delhi, India, using the general purpose scattering chamber (GPSC) facility and followed by chemical etching of the latent tracks in 6N NaOH, at 60 °C for 90 min. These were found to be the optimum conditions to produce etched through pores. For electrodeposition, a suitable cell was designed and fabricated by NSC team. The design of the cell used in the present work, is shown in Chapter2 (Fig. 2.6). This cell has a 80 mm long cylindrical structure made of perspex cathode and anode are made of copper and are detachable. The NTF covers the cathode and is sealed thoroughly by an O-ring, which is 20 mm in the present case. Base area of the anode is 30 mm and the inner length of the cell, which is used for electrolyte, is 45 mm. The cell before use is thoroughly rinsed with Milli Q 10 MΩ water, ethanol in succession and then air-dried. A small piece (1 cm x 1 cm) of thoroughly cleaned copper electrical tape with conducting adhesive layer at the backing was used as a cathode, affixed to the copper electrode. The distance between cathode and anode is adjustable in this design. The rate of deposition of metallic films also depends on current density, interelectrode distance, cell voltage, electrolyte's concentration and flow conditions, temperature etc. The cathode, after being
rinsed with H₂SO₄ (5-15 vol. %) or HCl (20-30 vol. %) to remove the oxide layer, is covered with the given NTF which is also thoroughly cleaned, washed and rinsed with Milli Q water and ethanol. In order to secure intimate contact, the NTF should be wetted by the electrolyte solution before use [14]. The electrolyte used here was CuSO₄·5H₂O (195-250 g/l, i.e. 0.78-1 M) + H₂SO₄ (30-75 g/l), with a current density of 0.1-1 A/cm²/6V. In our experiment, we have used 115 W Elnova power supply of HYTEK (Model 61) with maximum voltage range 0-30 V and maximum current range 0-2 A having various functions like set voltage and current limit function. An ammeter having maximum range of 1 A is used in series with the cell to limit the current during electrodeposition process. Temperature of the electrolyte is recorded using SONIT digital thermometer. In our experiment we applied 4 V across the electrode and a current of 0.9 A through the electrolyte for 1 hour. Inter electrode distance was 1.0 cm and composition of the electrolyte used in our experiment is of 7.5 g cupric sulfate (CuSO₄·5H₂O) in 40 ml Milli Q water + 0.5 ml of 25% dilute H₂SO₄. After the electrodeposition was over, the electrolyte was drained out and cathode flushed with 3% dilute H₂SO₄ and air-dried. The NTF was carefully removed, washed with distilled water, ethanol and air dried. On the respective sides of the NTF, metallic structure of copper could be seen using computerized SEM (Model LEO 440).

3.5 Growth of Potassium Iodide Micro Structure using Template Technique

We have also filled pores of polymer matrix with crystal of potassium iodide using template technique (fig.3.1). The samples used for this work were Makrofol KG 26 μm.
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Potassium iodide crystal grown in the polymer matrix
thick. These foils were irradiated with $^{238}\text{U}$, 11.2 MeV/n and with fluence of $5 \times 10^5$ ions/cm$^2$ at the GSI, Germany. The foils were etched in 6N NaOH solution at 60 °C for 5-6 hours to produce pores of 3-4 µm in the temperature-controlled bath. The crystals of KI were taken in the petridish and the etched Makrofol film was kept between the Crystal for 20 hours at room temperature (30 °C). The etched film was then taken out from petridish and kept on the filter paper. The growth of the crystal could be observed under optical microscope. The polymer matrix is then dissolved in the CH$_2$Cl$_2$ and the sample is left for 10 minutes. CH$_2$Cl$_2$ dissolved the polymer matrix and only needle like structures were obtained. Sample containing KI crystals were then analyzed under SEM at NPL, New Delhi.

3.6 Results and Discussion

3.6.1 Ion Track Characterization

Etching of the polycarbonate was performed for different times for the measurement of variation in pore sizes. For higher etching time, the pore size were measured using optical microscope but for lower etching time it was difficult to measure tracks or pore size using an optical microscope. Therefore, we availed SEM facility of NPL, New Delhi, India. From the Characterization curve (fig. 3.2) we found that our sample consists of four damaged zone and for this brand which uses a particular irradiation parameters, up to 350 nm the track-etch rate was initially fast , from 350 nm to 550 nm track etching is slow, from 550 nm- 620 nm etching is slower and then from 620 nm onwards it became constant i.e. equal to the bulk etch rate of the polycarbonate(fig. 3.3). Following the
Fig. 32 Characterization curve
-350 nm etching is fast

~350 - 550 nm etching is slow

~550 - 620 nm etching is slower

-620 nm onwards etching is constant

Fig. 33 Idea of Etching Rate of a Polymer (Makrofol KG) Under SHI
characterization curve we have analyzed SEM picture at higher etching time, which is shown in fig. 3.4

3.62 Copper Deposition Using NTF

Top and lateral views of SEM photographs of copper deposition using NTF on the copper substrate are shown in fig. 3.5 and fig. 3.6. Latter reveals deposition of solid copper structure on the copper substrate having diameter 2.2 μm. Better result is expected using chemical in the purest form, proper choice of cell voltage and current. Proper inter electrode distance would also lead to better deposition.

3.63 Growth of KI Micro Structures

KI crystal has a face-centered lattice. The SEM picture of KI crystals that are grown in the polymer matrix is shown in fig. 3.7. Since the polymer matrix is being put in contact with Potassium Iodide crystal for 20 hours, hence by evaporation at room temperature KI crystals exist there in the channels. The shape of the microstructure depends on the diameter of the pore size of the channels. In this figure, one can easily see some grouping of crystals of KI because the grain that has the most favourable orientation will overgrow the rest of the grains, and finally the most loosely packed direction will predominate.
Fig. 3.4 SEM picture of Makrofol KG at high magnification, etching is carried out for 2 hrs
Fig. 3. Top view of Scanning electron micrographs of the copper deposited on copper substrate.
Fig. 3: Late view of SEM picture of copper microstructure (2.2 μm) grown on copper substrate.
Fig. 3: Potassium Iodide microstructures grown in the polymer matrix.


References:


Chapter 4
Dielectric constant measurements of irradiated polymers
4.1 Introduction

Substances like oil, mica or plastic which are insulators and have no free electrons are called dielectric. How the swift heavy ion irradiation affects the electrical properties of polymers, tempted us to study the variation of dielectric constant of pristine and irradiated polymers. Study of dielectric response reveals the types of chemical species present in the sample and resulting chemical changes caused by SHI irradiation. Its study also sketches the atomic picture, viz. how non-polar molecule induces dipole moment when placed in electric field.

In fact, SHI causes a number of chemical changes in polymers like cross-linking, chain scission, formation of C= C, formation of alkyne group, depletion of heteroatoms (e.g. H, N, S or O) [1-5]. Radiation induced modifications in polycarbonate have been studied in the past extensively [6-8]. The effect of any radiation (electron, neutron, γ-rays or ion beams) on polycarbonate is primarily chain scission. However, at increased doses active sites or branching points created by scission may lead to intermolecular crosslinks. High Performance Liquid Chromatography (HPLC) and UV analysis in the past have provided evidence for the existence of three categories of compounds in heavy ion irradiated (128MeV Ar\textsuperscript{9+}) polycarbonate [6]. The first kind is formed from intramolecular combination of the phenoxy-phenyl and phenoxy-phenoxy radical pairs, which show UV absorbance in the 275-350 nm region. The second kind is formed by the reaction of the radical with a neighboring H, O\textsubscript{2} or H\textsubscript{2}O molecule. The presence of such compounds leads to chain ruptures and as a result, a decrease in the molecular weight. The third kind is formed by intermolecular radical combination. Such a group may provide branching centers and eventually lead to crosslinking. At low to moderate doses, the first two
categories of compounds predominate, whereas at high doses the yield of the third
category of compound is sufficiently high to control the process.

Several theories have been given to explain why scission predominates in some polymers
and crosslinking in others under irradiation [9]. It has been observed that scission takes
place in polymers having the structure as shown in Fig. 4.1 (a) (from Reference [9]).
This is because \( R_1 \) and \( R_2 \) produce a steric strain that weakens the bonds of the backbone
chain. Such polymers also have low heats of polymerization, leading to the formation of
monomer on pyrolysis and also chain scission during irradiation. Such a process usually
leads to lower molecular weight of the polymer. A process of ‘end linking’ is also
possible during scission. At least one of the fragments may link to the main chain of a
neighboring molecule to give a branched molecule of a higher molecular weight. This is
shown in Fig. 4.1(b). The physical properties of an end-linked polymer would be
essentially identical to those of a crosslinked polymer. Polycarbonate has the structure
shown in Fig. 4.1(c). In this case both \( R_1 \) and \( R_2 \) are \(-\text{CH}_3\) groups. The steric hindrance
due to them causes chain scission.

\subsection*{4.2 Dependence of dielectric loss on frequency}

The capacitance \((C_p)\) and \(\tan\delta\) measurements were carried out using a parallel plate
configuration of electrodes on both sides of the polymer film using a HP4284A LCR
meter over the frequency range 100 Hz-1MHz. \(\varepsilon'\) was calculated from the measured
capacitance

\[ \varepsilon' = \frac{C_p}{C_0} \]

Where

\[ C_0 = \frac{\varepsilon_0 A}{d} \]  \hspace{1cm} (1)
Fig. 4. (a) Structure of polymers that undergo chain-scission

(b) (1) Free polymer chains; (2) End-linked; (3) Cross-linked

(c) Structure of polycarbonate
Here, $\varepsilon_0$ is the permittivity of vacuum, $A$ is the cross-sectional area and $d$ is the thickness of the sample.

The complex dielectric constant or relative permittivity $\varepsilon^*$ of a solid is given by the following expression:

$$\varepsilon^* = \varepsilon' - i\varepsilon''$$  \hspace{1cm} (2)

Where $\varepsilon'$ is the real dielectric constant and $\varepsilon''$ is the dissipation of the energy of electrical oscillations in the dielectric when subjected to an ac field. There also arises a phase lag between the electric displacement and the electric field strength, described by the dielectric loss tangent, $\tan\delta$.

$$\tan\delta = \frac{\varepsilon'}{\varepsilon''}$$  \hspace{1cm} (3)

The dissipation factor, $\tan\delta$, was measured directly with the LCR meter. The magnitude of $\varepsilon'$ depends on the chemical constitution, structure and composition of the polymer, and $\varepsilon''$ and $\tan\delta$ depend upon molecular motion in the polymers\cite{10}.

4.3 Dependence of Dielectric Constant on Frequency

In a polymeric dielectric placed in a sinusoidal electric field the electric displacement vector must take account of the past history of the material in some way, thus relaxation processes become important. The expressions for $\varepsilon'$ and $\varepsilon''$, taking into account the relaxation process (single relaxation) becomes \cite{10}:
\[ \varepsilon' = \varepsilon - \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2} \]  
\[ \varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2} \]  

\[ \tan \delta = 2 \tan \delta_m \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \quad \text{where} \quad 2 \tan \delta_m = \frac{\varepsilon_0 - \varepsilon_\infty}{\sqrt{\varepsilon_0 \varepsilon_\infty}} \]  

where \( \varepsilon_0 \) is the dielectric constant at \( \omega \to 0 \) and \( \varepsilon_\infty \) is the value at \( \omega \to \infty \) and \( \tau \) and \( \tau_1 \) are the relaxation times for the two processes.

Thus \( \varepsilon'' \) passes through a maximum at \( \omega \tau = 1 \) and \( \tan \delta \) has a maximum at \( \omega \tau_1 = 1 \).

### 4.4 Temperature dependence of the dielectric

The temperature dependence of the dielectric properties can be found using the expression

\[ \tau = \tau_0 e^{U/RT} \quad \text{(where} \tau \text{is the dipole relaxation time).} \]

### 4.5 Experimental Details

Polycarbonate, \([-\text{OC}_6\text{H}_4-4-\text{C (CH}_3_2 \text{C}_6\text{H}_4-4-\text{OCO-}]_n \) (PC) which exists in the semi-crystalline form with a density of 1.2 g/cm\(^3\), was used in the form of 20\( \mu \)m thick films. The films were obtained from Goodfellow Corporation (UK).

The samples were irradiated using swift heavy ion beam from the 15 MV Van de Graff accelerator (Pelletron) facility at the Nuclear Science Centre, New Delhi. During the
irradiation the samples were kept inside a chamber with pressure maintained at 1x10^-6 Torr. The ion beams used were 45 MeV \(^{7}\)Li, 98 MeV \(^{59}\)Ni, 100 MeV \(^{16}\)O and 100 MeV \(^{28}\)Si, having a current density of 2 pA/cm\(^2\) corresponding to a flux of about 1.25x10\(^{10}\) ions/cm\(^2\) per sec. The fluence range was from 10\(^{11}\) to 10\(^{13}\) ions/cm\(^2\). The electronic stopping power of the \(^{7}\)Li beam in the film, i.e. \((dE/dX)_{e}\) is 7.205 eV/Å, \(^{59}\)Ni is 546.3 eV/Å, \(^{16}\)O is 50.38 eV/Å and that of the \(^{28}\)Si is 169.4 eV/Å. The depth profile calculations of 45 MeV Li ions in 20μm thick polycarbonate using the TRIM code yielded \((dE/dx)_{0\mu m}=6.88\) eV/Å and \((dE/dx)_{20\mu m}=7.04\) eV/Å at the entrance and exit of the ion beam in the polymer film, respectively. Thus a change of 2.3% in the value of \((dE/dx)\) as the ion beam passes through the sample is insignificant. Corresponding to the fluences used, the transferred energy densities, range from 7x10\(^{-4}\) eV/Å\(^3\) to 7x10\(^{-3}\) eV/Å\(^3\) for Li and 5.5x10\(^{-2}\) eV/Å\(^3\) for Ni beam as shown in Table 1.

### 4.6 Results and Discussion

#### 4.6.1 Effect of Irradiation on Dielectric Constant

The effect of ion irradiation on the dielectric properties of polymers has been reported earlier [11-14]. Gamma rays and neutron irradiation of ceramics have been known to increase the value of loss factor (tanδ) [15]. In our case the value of \(\varepsilon'\) in the case of pristine and irradiated polycarbonate varied from 1.2 to 1.4. Fig. 4.2 shows a plot of \(\varepsilon'\) vs frequency for the pristine and irradiated polycarbonates. The \(\varepsilon'\) values for the irradiated samples are more than those for the pristine, and appear to increase with increasing dose. At a particular dose, the \(\varepsilon'\) value remains constant for low frequencies.
Effect of Irradiation on $\varepsilon$

Fig 4.2. A plot of dielectric constant ($\varepsilon$) versus Frequency for the pristine polycarbonate and those irradiated with $^7$Li at fluences of $2.5 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$.

- The $\varepsilon'$ values for the irradiated samples are more than those for the pristine, and appear to increase with increasing dose.
- At a particular dose, the $\varepsilon'$ value remains constant for low frequencies (1kHz to 50 kHz) and then decreases.
- The increase in the $\varepsilon'$ values on irradiation has been attributed to the increase in rigidity of the polymer in the past.
(1kHz to 50 kHz) and then decreases. This is obvious from Eq. (4). At low frequencies (i.e. $\omega \tau \rightarrow 0$), the dielectric constant $\varepsilon'$ can be approximated to $\varepsilon' = \varepsilon_0$. At high frequencies (i.e. $\omega \tau \rightarrow \infty$) the expression becomes $\varepsilon' = \varepsilon_\infty$ which is lower than $\varepsilon_0$. The increase in the $\varepsilon'$ values on irradiation has been attributed to the increase in rigidity of the polymer in the past [14]. Dielectric response of Oxygen and silicon irradiated sample shows similar types of behaviour.

4.62 Effect of temperature on tan$\delta$

An extensive study on the Thermally Stimulated Depolarization Current (TSDC) spectrum of Bisphenol-A-Polycarbonate (1mm thick sheets obtained by compression moulding of an amorphous powder) in the temperature range 77-470 K, by Laredo et al [16] indicated two major relaxations. The $\beta$-relaxation, a broad band ranging from 80-250 K, was due to local motions of the small polar groups (e.g. $-\text{CH}_3$), restricted carbonate groups or carbonate groups accompanied by the phenyl groups in the main chain. The $\alpha$-relaxation, at 425 K, was the dielectric manifestation of the primary glass transition in the TSDC experiment. The $\alpha$-relaxation peak values, $T_\alpha$, varied with the degree of crystallinity, all crystallized samples showed $\alpha$-relaxation at lower temperature than the amorphous ones. The normalized peak area was found to be a measure of the mobile amorphous content of the polymer, i.e. the number of molecules participating in the motion. The higher the amorphous content of the polymer, the greater the area under the peak. In our study the polycarbonate (PC) films were 20$\mu$m thick and highly crystalline, hence it is not surprising that the $T_\alpha$ values are much lower.
Fig. 4. 3 and Fig. 4. 4 show the plot of tanδ versus Temperature for the pristine, $^7$Li irradiated and $^{59}$Ni irradiated polycarbonate samples in the temperature range 280-450 K. The tanδ values for the irradiated samples are much higher than that for the pristine polycarbonate. The plots for the pristine and $1 \times 10^{12}$ ions/cm$^2$ Li irradiated sample show one relaxation maximum. The values of $T_\alpha$ and peak area are shown in Table 1. The peak area and hence the amorphous content of the irradiated polymer increases with increased transferred energy density, showing a maximum at the $^{59}$Ni irradiated sample. The increase in amorphous fraction may be correlated to the process of crosslinking in irradiated polymers. Crosslinking results in the formation of an insoluble network or gel i.e. an amorphous fraction in the irradiated polymer film.

Thus, we may conclude that crosslinking is the predominant process in the $^{59}$Ni irradiated sample. However, the trend in the $T_\alpha$ values is slightly different. The $T_\alpha$ value decreases for the $^7$Li ($1 \times 10^{12}$ ions/cm$^2$) irradiated sample from that of the pristine. Adam and Gibbs[17] have proposed the decrease in $T_g$ (glass temperature) corresponding to a decrease in the size of the “cooperatively rearranging” region in their Configurational Entropy Model. Such a shift may be correlated with the process of chain scission, where the polymer chain fragments into smaller pieces. Thus it may be concluded that chain scission predominates in the $^7$Li ($1 \times 10^{12}$ ions/cm$^2$) irradiated sample. However, chain scission may lead to a process of end-linking (akin to crosslinking) at higher doses. For the PC irradiated at a fluence of $5 \times 10^{12}$ ions/cm$^2$, the end-linking process slowly takes over from scission and the $T_\alpha$ value shifts to higher temperatures. There is thus a competition between chain scission and end-linking in the ion-irradiated polycarbonate. A Hitachi U3300 UV-VIS spectrophotometer was used for the optical absorption
Fig 4.3 A plot of tanδ versus Temperature for the pristine and ⁷Li irradiated polycarbonate at two fluence ($1 \times 10^{12}$ and $5 \times 10^{12}$ ions/cm²).
Fig 4.4 (a) A plot of tanδ versus Temperature for the pristine and $^{59}$Ni irradiated polycarbonate at a fluence of $1 \times 10^{12}$ ions/cm$^2$. 
Table I. Transition temperatures for the Polycarbonate samples in the tanδ-T plots at 1kHz.

<table>
<thead>
<tr>
<th>Sample details</th>
<th>Fluence (ions/cm²)</th>
<th>Energy Density (eV/Å³)</th>
<th>Tα (K)</th>
<th>Peak Area (arb. Units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PC</td>
<td>0</td>
<td>0</td>
<td>348</td>
<td>0.3806</td>
</tr>
<tr>
<td>⁷Li irr. PC</td>
<td>1x10¹²</td>
<td>7.25x10⁻⁴</td>
<td>328</td>
<td>2.1778</td>
</tr>
<tr>
<td>⁷Li irr. PC</td>
<td>2.5x10¹²</td>
<td>1.81x10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>⁷Li irr. PC</td>
<td>5x10¹²</td>
<td>3.625x10⁻³</td>
<td>363</td>
<td>7.9205</td>
</tr>
<tr>
<td>⁷Li irr. PC</td>
<td>1x10¹³</td>
<td>7.25x10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>⁶⁰Ni irr. PC</td>
<td>1x10¹²</td>
<td>5.46x10⁻²</td>
<td>348</td>
<td>15.7738</td>
</tr>
</tbody>
</table>
measurements. In order to ensure that the oxidation and corrosion processes come to saturation, the samples were stored for two months after irradiation. This is not surprising as the UV spectra of the $^7$Li and $^{59}$Ni irradiated samples show the existence of different chemical species in the two different cases (Fig 4.4(b)).

4.6.3 $^7$Li versus $^{59}$Ni irradiation

It may be concluded from UV graph that the chemical species formed in polycarbonate on irradiation with these two different ions are different. It has been mentioned earlier that three different categories of compounds are formed during the course of irradiation of PC (see Introduction). One of them leads to chain scission and another to end-linking. Since the chemical species present in the $^7$Li and $^{59}$Ni irradiated samples are different, it may be concluded that chain scission predominates in one and crosslinking (or end-linking) in the other.

4.6.4 Effect of Frequency on tanδ

Every dielectric relaxation process is associated with an activation energy, which may be calculated from the variation of the relaxation process with frequency. Fig 4.5(a), (b), (c) and (d) show the tanδ-T curves at various frequencies for the pristine and irradiated polycarbonate samples. The relaxation peaks are found to shift to higher temperatures with the increase in frequency for all the samples. This shift may be used to calculate the apparent activation energy of the relaxation process using the linear equation [18]:

$$\log f = \log f_0 + \frac{\Delta E}{2.303RT_{max}}$$
Li versus Ni irradiation

![Graph of optical absorbance versus wavelength](image)

**Fig. 4.4** A plot of optical absorbance versus λ (wavelength) for the pristine, $^7$Li and $^{59}$Ni irradiated polycarbonate samples.
Fig. \( \tan \delta - T \) plots at various frequencies (1kHz, 3kHz, 5kHz, 10kHz and 60kHz) for the (a) pristine (b) \(^7\)Li irradiated at a fluence \(1 \times 10^{12}\) ions/cm\(^2\) (c) \(^7\)Li irradiated at a fluence \(5 \times 10^{12}\) ions/cm\(^2\) (d) \(^{59}\)Ni irradiated at a fluence of \(1 \times 10^{12}\) ions/cm\(^2\).
A plot of $1/T_{\text{max}}$ versus log $f$ for the pristine, $^7$Li irradiated at two fluence ($1 \times 10^{12}$ and $5 \times 10^{12}$ ions/cm$^2$) and $^{59}$Ni at a fluence of $1 \times 10^{12}$ ions/cm$^2$. 
where \( f \) is the frequency, \( f_0 \) is a constant, \( \Delta E \) is the apparent activation energy, \( R \) is the gas constant and \( T_{\text{max}} \) is the absolute temperature corresponding to the maximum tan\( \delta \) value \( (4.5\,^\circ) \). The activation energy values for the pristine and irradiated polycarbonate are indicated in Table II. The \( \Delta E \) value for the \(^7\)Li, \( 1 \times 10^{12} \) ions/cm\(^2\), irradiated sample is much lower than that for the pristine. This is because scission breaks down the size of the polymer chain and facilitates the movement of the functional groups. However, the \( \Delta E \) value for the \(^7\)Li, \( 5 \times 10^{12} \) ions/cm\(^2\), irradiated sample is much higher than that for the pristine. The loss tangent values for this sample have been found to be very much higher (as shown in Fig. 4.3). Both these facts may be correlated to the increased rigidity of the polymer chain as the end-linking process begins. The activation energy for the \(^59\)Ni \( (1 \times 10^{12} \) ions/cm\(^2\)) irradiated sample is very low, although end-linking is the predominant process here. A closer look at Fig. 4.5 (d) shows that the magnitude of relaxation has actually shifted to a higher frequency.

The magnitude of relaxation also varies with frequency, but shows a different trend for different samples. In the case of the pristine polycarbonate, Fig. 4.5(a), the magnitude decreases with increase in frequency from 1kHz to 10kHz, and totally disappears at 60 kHz. For the \(^7\)Li \( (1 \times 10^{12} \) ions/cm\(^2\)) irradiated sample the magnitude falls drastically from 1 kHz to 3 kHz, and slowly increases upto 60kHz. It was then observed to fall again at 100kHz (not shown here). The relaxation process has become much faster i.e. spans over a short frequency range. This is in agreement with the low activation energy observed earlier. The magnitude of relaxation for the \(^7\)Li \( (5 \times 10^{12} \) ions/cm\(^2\)) irradiated sample show the same trend as the pristine, i.e., the relaxation progressively dies down from 1 kHz-60kHz, though the values of tan\( \delta \) are much higher. For the \(^59\)Ni \( (1 \times 10^{12} \) ions/cm\(^2\)) sample
Table II. Relaxation Characteristics as a function of Frequency for the Polycarbonate samples

<table>
<thead>
<tr>
<th>Sample details</th>
<th>1kHz</th>
<th>3kHz</th>
<th>5kHz</th>
<th>10kHz</th>
<th>60kHz</th>
<th>ΔE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PC</td>
<td>T(°C)</td>
<td>80</td>
<td>85</td>
<td>90</td>
<td>95</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>tanδ_max</td>
<td>7.8x10^-3</td>
<td>6.5x10^-3</td>
<td>5.8x10^-3</td>
<td>4.5x10^-3</td>
<td>-</td>
</tr>
<tr>
<td>7Li 1x10^{12} irr. PC</td>
<td>T(°C)</td>
<td>55</td>
<td>70</td>
<td>75</td>
<td>80</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>tanδ_max</td>
<td>4.2x10^-2</td>
<td>2.1x10^-2</td>
<td>2.4x10^-2</td>
<td>3.2x10^-2</td>
<td>3.8x10^-2</td>
</tr>
<tr>
<td>7Li 5x10^{12} irr. PC</td>
<td>T(°C)</td>
<td>85</td>
<td>88</td>
<td>89</td>
<td>90</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>tanδ_max</td>
<td>1.5x10^-1</td>
<td>9.1x10^-2</td>
<td>6.1x10^-2</td>
<td>4.8x10^-2</td>
<td>-</td>
</tr>
<tr>
<td>59Ni 1x10^{12} irr. PC</td>
<td>T(°C)</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>tanδ_max</td>
<td>-</td>
<td>-</td>
<td>5x10^-1</td>
<td>2.5x10^-1</td>
<td>2.5x10^-2</td>
</tr>
</tbody>
</table>
the magnitude of the relaxation dies down from 5kHz-60kHz. It appears that the
relaxation frequency has shifted from 1 kHz (for the other samples) to 5 kHz. The span is
also reduced, and hence the decrease in the activation energy (Table II). This can be
explained by the fact that a totally different kind of motion is taking place here. This is
not surprising as the UV spectra of $^7$Li and $^{28}$Ni irradiated samples(fig. 5.1) show the
existence of different chemical species in the two different cases.

4.6 Variation of $\tan \delta$ with frequency for the $^7$Li, $^{59}$Ni, $^{16}$O and $^{28}$Si
irradiated polycarbonate at one fluences ($1x10^{12}$)

The graph 4.6(a), (b), (c) loss in $^{59}$Ni sample is greater over the rest due to the high
value of dE/dx and opposite trend in the $^{16}$O and $^{28}$Si irradiated polycarbonate at fluence
($1x10^{12}$). From Fig 4.7(a), (b), (c), (d), (e) and Fig 4.8 (a), (b), (c), (d) we
find that loss in $^{28}$Si irradiated sample decreases and loss in $^{16}$O irradiated samples
increases with frequency because thermal orientations of segments or groups of the
polymeric material are facilitated due to bond dissociation [13] in $^{16}$O irradiated sample
while cross-linking effect decreases molecular motion in $^{28}$Si irradiated samples.

4.7 Conclusions

Heavy ion irradiation of polycarbonate leads to chemical changes in the polymer chain,
namely, chain scission and crosslinking. Which of the two processes will predominate
depends upon the ion dose. At low ion doses chain scission is the major process. At
higher doses fragmented chains link to the main chain of a neighbouring molecule,
A plot of tan\(\delta\) versus Temperature for the \(^7\)Li, \(^{59}\)Ni, \(^{60}\)O and \(^{28}\)Si irradiated polycarbonate at one fluence \((1 \times 10^{12})\)
Fig 4.6(b): A plot of $\tan \delta$ versus frequency for the $^{18}O$ irradiated polycarbonate at three fluence levels.
A plot of tanδ versus frequency for the $^{28}\text{Si}$ irradiated polycarbonate at three fluence ($1 \times 10^{12}$, $2.5 \times 10^{12}$ and $1 \times 10^{13}$ ions/cm$^2$).

**Fig 4.6c9**
Fig 4.7(a) tanδ-T plots at various frequencies (1kHz, 3kHz, 5kHz, 10kHz and 30kHz) for the pristine sample.
Fig 4.7  \( (c)^{16}O \) irradiated at a fluence \( 1 \times 10^{12} \) ions/cm\(^2\).
Fig. 4. $^7\text{Li}^6\text{O}$ irradiated at a fluence of $5 \times 10^{12}$ ions/cm$^2$. 
$1 \times 10^{13}$ ions/cm²

- 3k Hz
- 5k Hz
- 10k Hz
- 20k Hz
- 30k Hz

Oirradiated at a fluence of $1 \times 10^{13}$ ions/cm²

TEMPERATURE °C
Fig 4.8 (a) tanδ-T plots at various frequencies for the (a) $^{28}$Si irradiated at a fluence=$(1\times10^{12})$ ions/cm$^2$
\( \text{Temperature °C} \)

\( \tan \delta \)

- **Si, \( 1 \times 10^{12} \text{ cm}^{-2} \)**
  - ■ 5k
  - ▲ 8k
  - ■ 10k
  - ○ 20k
  - ■ 30k

**Fig 4.8** (b) \( ^{28}\text{Si} \) irradiated at a fluence \( 2.5 \times 10^{12} \)
(c) $^28$Si irradiated at a fluence of $5 \times 10^{12}$ ions/cm$^2$. 
Fig 4.8 (d) \textsuperscript{28}Si irradiated at a fluence of $1 \times 10^{13}$ ions/cm$^2$. 

$\text{Si, } 1 \times 10^{13} \text{ cm}^{-2}$

- $3k$
- $8k$
- $10k$
- $20k$
leading to an ‘end-linked’ product with a high molecular weight. The physical properties of this end-linked product are similar to that of a crosslinked polymer. In this case the scissioned product (polymer irradiated by $^7$Li at a fluence of $1 \times 10^{12}$ ions/cm$^2$) had lower loss tangent values than the end-linked one (polymer irradiated by $^7$Li at a fluence of $5 \times 10^{12}$ ions/cm$^2$). The polymer film irradiated with $^{59}$Ni ($1 \times 10^{12}$ ions/cm$^2$) had loss tangent values much higher than that of the $^7$Li, $^{16}$O and $^{28}$Si irradiated polycarbonate samples and opposite trend in the $^{16}$O and $^{28}$Si irradiated polycarbonate at fluence ($1 \times 10^{12}$) is observed. One dielectric relaxation peak was observed in the temperature range 300-423 K for all the samples. The activation energy for the relaxation process was lowest in the case of the sample in which chain scission occurred on irradiation.
References:


Chapter 5

Optical Study of Irradiated Polycarbonate using UV-Vis Spectroscopy
5.1 INTRODUCTION

UV-Vis spectroscopy, which gives us an idea about the value of optical band gap, $E_g$, is an ideal tool for the investigation of the carbonaceous clusters (that are supposed to be the carriers in electric conductivity) formed along latent tracks of energetic ions in polymers. The formation of these clusters in polymer films on ion irradiation has been investigated extensively [1-3]. The very first optical studies of the so called ‘blackening’ of polymer films irradiated with heavy ions were on polyimide, which has been known to show a marked increase in conductivity on irradiation. Measured depth profiles of optical absorption in polyimide when compared to those calculated using the Monte Carlo code TRIM95[4], show that the blackening profile resembles the effects due to the ‘nuclear energy transfer’ rather than the ‘electron energy transfer’. Thus the blackening was correlated with the release of carbon atoms from polymer chains during irradiation; such atoms could then form graphite like precipitation or clusters. In fact, the shape of the optical spectrum of 150 MeV Xe$^+$ [5-7] irradiated polyimide was found to resemble that obtained for pure graphite. The irradiated film was found to contain upto 40% of graphite inclusions. Amorphous carbon or graphite is known to consist of compact clusters of fused six-fold rings. The number of such rings in a cluster may be obtained from the optical band gap, $E_g$, using the Robertson’s relation [9]. According to Robertson et al. this band gap depends upon the ratio of sp$^2$ hybridized carbons to sp$^3$ hybridized carbon atoms in a cluster. In the case of a six membered benzene ring type structure, $E_g \approx 5.3$ eV[8], whereas for a buckminsterfullerene type structure $E_g = 4.9$ eV [3].

The optical absorption spectra of irradiated polymers are characterized by a tail followed by an absorption edge in the 200-800 nm wavelength region. Several such studies on
polymer films (polymethylmethacrylate PMMA, polystyrene PS, polyimide PI, polyethylterephthalate PET etc.) irradiated with ion beams (He, Ne, Ar, Au, Li etc.) have been reported in the past[9-11]. The other techniques used to probe these carbonaceous clusters are small angle X-ray or neutron scattering (SAXS and SANS) and temperature dependence of electric conductivity [12]. The various experimental techniques are sensitive to different properties of the clusters. For example the UV-Vis spectroscopy is sensitive to the optically active cluster region i.e. visible cluster size, SAXS is sensitive to the amorphous phase and thus the electron enriched cluster size. Thus there may be discrepancies in the values of the cluster size as determined by these three techniques. The following information about these carbonaceous clusters have been obtained from these studies:

(a) In case of high energy heavy ion impact, the cluster formation sets in at a minimum transferred electronic energy density of around $10^3 \text{ eV/Å}^3$. However, the threshold energy density for low energy heavy ion impact is $10^1 \text{ eV/Å}^3$ [9].

(b) Highly energetic heavy ions form small clusters along single ion tracks. The cluster size does not exceed the track diameter (10 nm). But in the case of overlapping tracks of light low energy particles, the cluster size is not limited by the track diameter, and giant clusters are formed, exceeding 100nm size. For example in the case of PMMA irradiated with 35 MeV Li of fluence $1\times10^{12}$ cm$^{-2}$, large fractal structures are produced whereas 2 GeV Au of fluence $5\times10^{10}$ in PMMA produces small clusters of size 5-6 nm.

(c) Cluster growth is known to increase for transferred energy densities of maximum 20 eV/Å$^3$, above which it comes to a saturation.
(d) Electronic conductivity in these irradiated polymers results from electron hopping between these ‘giant’ aggregates.

5.2 EXPERIMENTAL DETAILS

Polycarbonate, [-O-C₆H₄-4-C(CH₃)₂C₆H₄-4-OCO-]ₙ, which exists in the semi-crystalline form with a density of 1.2 g/cm³, was used in the form of 20µm thick films. The films were obtained from Goodfellow Inc., USA.

The samples were irradiated at the 15 MV tandem Van de Graff accelerator (Pelletron) facility at the Nuclear Science Centre, New Delhi, inside a material science chamber with pressure maintained at 1x10⁻⁶ Torr. The ion beam used were 45 MeV ⁷Li, 85 Mev ¹⁶O, 100 MeV ²⁸Si with current densities of 1-5 pnA/cm². A Hitachi U3300 UV-Vis spectrophotometer was used for the optical measurements. In order to ensure that the oxidation and corrosion processes come to a saturation, the samples were stored for two months after irradiation. The UV absorption analysis was carried out thereafter.

5.3 Results and Discussion

Fig.5.1, 5.2 and 5.3 compare the absorption edge of the UV-VIS spectra of pristine and irradiated polycarbonate. This lies in the 200-800 nm region. This is attributed to the π→π' transitions in the aromatic compounds and is very sensitive to the change in the environment around the phenyl ring. It has been observed in the past that the absorption edge in the UV spectrum increases with increasing irradiation dose. The degree of sharpness of the spectra decreases with increase in dose, indicating the increased damage in the films as the fluence is
Figure 5.1 UV-Vis spectra of polycarbonate (20 μm thick) irradiated with 45 MeV Li ion at $0, 1 \times 10^{12}, 2.5 \times 10^{12}, 5 \times 10^{12}, 1 \times 10^{13}$ ions/cm$^2$. 
Fig 5.2 A plot of absorbance Vs wavelength for $^{16}\text{O}$
Fig 5.3 A plot of absorbance Vs wavelength for $^{28}\text{Si}$
increased. The creation of chemical defects in polymer films on irradiation has been studied by many workers[10]. This optical band edge can be correlated to the optical band gap $E_g$ by the Tauc’s equation[7]:

$$\omega^2 \varepsilon_2 = (\hbar \omega - E_g)^2$$

Which on readjustment becomes

$$\sqrt[2]{\varepsilon_2} \lambda = \frac{\hbar \lambda - E_g}{2\pi c}$$

Here $\varepsilon_2 (\lambda)$ is the optical absorbance and $\lambda$ is the wavelength. A plot of $\sqrt[2]{\varepsilon_2} \lambda$ Vs $1/\lambda$ gives the value of $E_g$. The intersection of the extrapolated spectrum with the abscissa yields the gap wavelength $\lambda_g$, from which the gap energy is derived to be $E_g = h\omega/\lambda_g$. The number of carbon hexagon rings in the cluster, $M$ is then found from the relation given by Robertson et al [9].

$$E_g = 2! |\beta| M^{-0.5}$$

where $2\beta$ is the band structure energy of a pair of adjacent $\pi$ sites, $\beta = -2.9$ eV for a six membered carbon ring. Fink et al[6] have shown that the Robertson equation underestimates the cluster size in irradiated polymers. So they assumed the structure of the clusters to be like buckminsterfullerene i.e. $C_{60}$ ring instead of $C_6$, arriving at the relation

$$E_g = 34.3 / \sqrt{N}$$
where \( N \) is the number of carbon atoms per cluster. We have used this relation to obtain the number of carbon atoms per cluster in irradiated polycarbonate.

A shift is observed in the absorption edge towards higher wavelengths on irradiation. Fig. 5.4, 5.5 and 5.6 show the plot of \( \sqrt{E_g} \) versus \( 1/\lambda \) for the polymer films. \( E_g \) values were estimated by extrapolating these plots to the x-axis and using Eq. 2. These values have been used to obtain the cluster size using Eq. (3). Table 1 lists these values. The value of \( E_g \) showed a decreasing pattern with increase in fluence. However, an increase in fluence by one order of magnitude leads to a decrease of only 0.02 eV in \( E_g \), which is in agreement with results reported in the past [3-4]. It pointed out by [3-4] that the enhancement in cluster size for PMMA irradiated with a fluence of \( 1 \times 10^{14} \) ions/cm\(^2\) is very large. The cluster size for the various irradiated polycarbonate samples vary from 60 - 62\( \AA \). The cluster size in pristine polymer refers to density fluctuations in the polymer structure. The cluster growth begins only at fluences greater than \( 2 \times 10^{12} \) cm\(^2\). Typical track diameter for irradiated polymers have been reported to be 6nm[14], indicating that ion track overlapping begins at a fluence of \( \sim 3 \times 10^{12} \). For example at a fluence of \( 1 \times 10^{12} \) cm\(^2\) the cluster size is almost same as the pristine sample. This indicates that cluster size growth takes place only after the ion tracks start overlapping. These values are much lower than those for the irradiated PMMA samples reported in
Figure 2. A plot of $(\varepsilon_2/\lambda)^{1/2}$ vs $1/\lambda$, representing the Tauc's relation to derive the optical band gap energy $E_g$. The value of $h\nu^{-1}$ is obtained by extrapolating the straight line portion of the absorption edge to the $1/\lambda$ axis.
Fig 5.5 A plot of $\varepsilon_2$ Vs $1/\lambda$ for $^{16}$O
Fig 5.6 A plot of $\varepsilon_2$ Vs $1/\lambda$ for $^{28}\text{Si}$.
literature. It has been reported that the cluster size increases with increasing complexity of the monomeric units. The variation of the cluster size with the transferred energy density, obtained from the relation (dose x stopping power) is shown in Table 1. The increase in cluster size occurs after about $10^{-3}$ eV/Å$^3$ of transferred energy density which is in accordance with the previous results [12, 14]. In our work we find that size of cluster formed increases with electronic energy loss and for $^{28}$Si ion irradiation, cluster size increases with fluence.

5.3 Conclusions

The growth of carbonaceous clusters in polycarbonate on irradiation with 45 MeV $^7$Li, 85 MeV $^{16}$O, 100 MeV $^{28}$Si was observed. It begins with the onset of ion track overlapping, and the threshold fluence as per our measurement is $2.5 \times 10^{12}$ particles cm$^{-2}$. This corresponds to an energy density of $10^{-3}$ eV/Å$^3$. Polymeric conductivity and loss factor (tan $\delta$) are measured (discussed in Chapter 4) and the observations are correlated with the growth in cluster size. In our work we find that size of cluster formed increases with electronic energy loss and we also find that for $^{28}$Si ion irradiation, cluster size increases with fluence.
Table 1. Optical band gap, $E_g$ and cluster sizes for polymer films irradiated at different fluences.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Ion,energy</th>
<th>Dose (cm$^2$)</th>
<th>$E_g$ (eV)</th>
<th>Cluster size (No. of carbons)</th>
<th>$S_c$ (eV/A°)</th>
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</thead>
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<tr>
<td>PC</td>
<td>45 MeV Li</td>
<td>0</td>
<td>4.39</td>
<td>61</td>
<td>7.205 eV/A°</td>
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<td></td>
<td></td>
<td>1x10$^{12}$</td>
<td>4.41</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.5x10$^{12}$</td>
<td>4.38</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5x10$^{12}$</td>
<td>4.37</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10$^{13}$</td>
<td>4.35</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>85 MeV O</td>
<td>0</td>
<td>3.04</td>
<td>127</td>
<td>50.38 eV/A°</td>
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<tr>
<td></td>
<td></td>
<td>5x10$^{11}$</td>
<td>3.38</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1x10$^{12}$</td>
<td>3.38</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>5x10$^{12}$</td>
<td>2.98</td>
<td>132</td>
<td></td>
</tr>
<tr>
<td>PC</td>
<td>100 MeV $^{28}$Si</td>
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<td>3.04</td>
<td>127</td>
<td>169.4 eV/A°</td>
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<td>264</td>
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<td>1.0x10$^{13}$</td>
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References

In this thesis I have carried out the SHI irradiation on polymers. Since the cause of damage and types of defects produced by heavy ions in polymers is not well understood. Keeping this in mind the characterization of damaged regions in plastic (Makrofol KG) with heavy ion beams has been done by us and idea of various damage zones is extracted from the rate of etching. In this thesis I have also studied the possibility of applications of Swift heavy ion irradiation (SHI) of polycarbonate plastic (polymers) for the development of micro and nano pores and electrodes by making through-etched holes in thin plastic foils and filling them with conductor and insulator materials.

The ions generated pores are not only used for filtration of bacteria of micron sizes but also used for track engineering by filling materials inside the pores. I have succeeded in depositing copper in the etched pores in the polymer matrix and produced copper needles of micronsizes on the copper substrate using Template Techniques. These fine pores and electrode structures have applications in electronics, optical and biomedical sciences. I have also developed microstructures of potassium iodide in the etched pores in the polymer matrix. Such microstructures can be used in the fabrication of miniature electronic components and new composite materials. In order to understand the damage caused by the SHI in the polymer, I have carried out experimental measurements of the dielectric response (i.e. variation of dielectric constant) of unirradiated and irradiated plastic foils with
Swift heavy ions of different kinds (\(^7\)Li, \(^{16}\)O, \(^{24}\)Si and \(^{59}\)Ni) having different fluences and energy. Calculations have been made for the dielectric loss factors and results have been interpreted theoretically. Further insight about damages caused by the SHI has been gained by using an Ultra violet and visible spectrophotometer. The variation of UV-Vis absorbance in terms of wavelength of light has been interpreted, variation of carbonaceous clusters with fluences, their size estimation and the optical band gap calculations using different heavy ions has been made. The entire work done by me is presented in the five chapters of the thesis.

Chapter 1 describes the two basic processes of energy loss i.e. electronic energy loss and nuclear energy loss and the two models of formation of tracks, which are related to our work.

Chapter 2 relates the instrumentation and equipments used. It describes briefly the 15 MV pelletron accelerator of NSC, low and high fluence irradiation setup, microscope, scanning electron microscope and spectrophotometer, which were used in this work.

Chapter 3 contains the characterization of pores in polymer using SEM, fabrication of copper needles/electrodes on copper substrate using Template Technique and developments of microstructures of potassium iodide at the site of through etched pores in the polymer matrix.
Chapter 4 discusses in detail, the dielectric response measurements and calculation of loss factor, which reveal chemical and electrical changes caused by SHI irradiation.

Chapter 5 deals with the use of UV-Vis spectrophotometer to our work and the details of calculations of number of carbon atoms present in the carbonaceous clusters formed in the damaged regions and also the estimation of optical energy gap of the irradiated foil for various ions.

The work described in chapter 3, 4 and 5 are claimed to be the original contributions of the author and they have several applications and implications for future work.
List of publications


1. Study of Chin Scission versus Crosslinking in MeV Ion Irradiated Polycarbonate using Dielectric Spectroscopy
   
   M. Mujahid, Shiuli Gupta, Padam Singh, D. Kanjilal, D.K. Avasthi and D.S. Srivastava

**Papers accepted in the National Symposium**

1. Paper accepted in the 42nd DAE –Solid state Physics Symposium (December 20-24, 1999) at Kalpakkam

   1.1 Dielectric Constant Measurement of MeV Ion Irradiated Polycarbonates
       M. Mujahid, Shiuli gupta, D.K. Avasthi and D.S. Srivastava,
   1.2 Growth of Potassium Iodide micro/nano structures using Template Method

2. Paper accepted in XI Nat. Symp. SSNTD oct 12-14, 1998 at Amritsar

   Control Production of submicron or nanometer pores in plastic foils
   M. Mujahid, Padam Singh and D.S. Srivastava
Study of Chain Scission versus Crosslinking in MeV Ion Irradiated Polycarbonate using Dielectric Spectroscopy

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PACS: 61.82.Pv ; 61.80.Jh ; 77.22.Gm ; 81.05.Lg
Keywords: Polymers, ion irradiation, dielectric loss, relaxation, glass transition

Abstract

Swift heavy ion irradiation of polycarbonate (PC) causes both, chain scission and crosslinking. Dielectric spectroscopy was used to verify these chemical changes in $^7$Li (fluence: $1\times10^{12}$ ions/cm$^2$ and $5\times10^{12}$ ions/cm$^2$) and $^{59}$Ni irradiated PC films. The dielectric constant $\varepsilon$ and tan$\delta$ values were found to increase with increased fluences. The tan$\delta$ versus temperature ($T$) plots showed one relaxation peak ($T_\alpha$) in the temperature range 300-423 K for all the samples. $T_\alpha$ was found to shift to lower temperature for the polycarbonate irradiated using $^7$Li at a fluence of $1\times10^{12}$ions/cm$^2$, for the PC irradiated at a higher fluence ($5\times10^{12}$ ions/cm$^2$) the peak shifted to higher temperature. This indicated that in the first case chain scission had occurred and in the second case end-linking. For the $^{59}$Ni irradiated samples the relaxation peak shifts to higher temperature indicating that end-linking has taken place. The activation energies for the relaxation process have also been determined using the tan$\delta$ versus temperature plots at various frequencies (1 kHz, 3kHz, 5kHz, 10kHz and 60kHz).
Study of Chain Scission versus Crosslinking in MeV Ion Irradiated Polycarbonate using Dielectric Spectroscopy

1 Introduction

Swift heavy ion irradiation causes a number of chemical changes in polymers like: cross linking, chain scission, formation of C=C, formation of alkyne group, depletion of heteroatoms (e.g. N, S or O) \(^1\)–\(^5\). Radiation induced modifications in polycarbonate have been studied in the past extensively \(^6\)–\(^8\). The effect of any radiation (electron, neutron, γ-rays or ion beams) on polycarbonate is primarily chain scission. However, at increased doses active sites or branching points created by scission may lead to intermolecular crosslinks. High Performance Liquid Chromatography (HPLC) and UV analysis in the past have provided evidence for the existence of three categories of compounds in heavy ion irradiated (128MeV Ar\(^{9+}\)) polycarbonate \(^6\). The first kind is formed from intramolecular combination of the phenoxy-phenyl and phenoxy-phenoxy radical pairs, which show UV absorbance in the 275-350 nm region. The second kind is formed by the reaction of the radical with a neighbouring H, O\(_2\) or H\(_2\)O molecule. The presence of such compounds leads to chain ruptures and as a result a decrease in the molecular weight. The third kind is formed by intermolecular radical combination. Such a group may provide branching centers and eventually lead to crosslinking. At low to moderate doses the first two categories of compounds predominate, whereas at high doses the yield of the third category of compound is sufficiently high to control the process.
Several theories have been given to explain why scission predominates in some polymers and crosslinking in others under irradiation \(^9\). It has been observed that scission takes place in polymers having the structure Fig. 1(a). This is because \(R_1\) and \(R_2\) produce a steric strain that weakens the bonds of the backbone chain. Such polymers also have low heats of polymerization, leading to the formation of monomer on pyrolysis and also chain scission during irradiation. Such a process usually leads to lower molecular weight of the polymer. A process of ‘end linking’ is also possible during scission. At least one of the fragments may link to the main chain of a neighboring molecule to give a branched molecule of a higher molecular weight. This is shown in Fig. 1(c). The physical properties of an end-linked polymer would be essentially identical to those of a crosslinked polymer. Polycarbonate has the structure shown in Fig. 1(b). In this case both \(R_1\) and \(R_2\) are \(-\text{CH}_3\) groups. The steric hindrance due to them causes chain scission.

In this work, we have observed the modification induced in polycarbonates by swift heavy ions, namely, \(^7\text{Li}\) (45 MeV) and \(^{59}\text{Ni}\) (98 MeV), using dielectric measurements and UV spectroscopy. There is clearly competition between the chain scission and the ‘end-linking’ phenomenon as the ion dose is increased.

II Experimental

Polycarbonate, \([\text{C}_6\text{H}_4\text{-4-CH}_2\text{C}_6\text{H}_4\text{-4-OCO}_2\text{-}]_n\), which exists in the semi-crystalline form with a density of 1.2 g/cm\(^3\), was used in the form of 20\(\mu\)m thick films. The films were obtained from Goodfellow Inc., USA.
The samples were irradiated at the 16 MV tandem Van de Graff accelerator (Pelletron) facility at the Nuclear Science Center, New Delhi, inside a chamber with pressure maintained at $1 \times 10^6$ Torr. The ion beam used was 45 MeV $^7$Li and 98 MeV $^{59}$Ni, with current density of 2 pA/cm$^2$. The fluence range was from $10^{12}$ to $10^{13}$ ions/cm$^2$. The electronic stopping power of the $^7$Li beam in the film, i.e. $(dE/dX)_e$ is 7.205 eV/Å and that for $^{59}$Ni is 546.3 eV/Å. The depth profile calculations of 45 MeV Li ions in 20μm thick polycarbonate using the TRIM code yielded $(dE/dx)_{0\mu m} = 6.88$ eV/Å and $(dE/dx)_{20\mu m} = 7.04$ eV/Å. Thus a change of 2.3% in the value of $(dE/dx)$ as the ion beam passes through the sample is insignificant. Corresponding to the fluences used, the transferred energy densities, obtained from the relation (fluence x stopping power), range from $10^{-4}$ to $10^{-2}$ eV/Å$^3$.

The capacitance ($C_p$) and tan δ measurements were carried out using a parallel plate configuration of electrodes on both sides of the polymer film using a HP4284A LCR meter over the frequency range 100 Hz-1MHz. $\varepsilon'$ was calculated from the measured capacitance using the relation:

$$\varepsilon' = \frac{C_p}{C_0} \quad \text{where} \quad C_0 = \frac{\varepsilon_0 A}{d} \quad (1)$$

Here, $\varepsilon_0$ is the permittivity of vacuum, $A$ is the cross-sectional area and $d$ is the thickness of the sample. The dissipation factor, tan δ, was measured directly with the LCR meter. A Hitachi U3300 UV-Vis spectrophotometer was used for the optical measurements. In order to ensure that the oxidation and corrosion processes come to saturation, the samples were stored for two months after irradiation. The UV absorption analysis was carried out thereafter.
III Results and Discussion

The complex dielectric constant or relative permittivity \( \varepsilon^* \) of a solid is given by the following expression:

\[
\varepsilon^* = \varepsilon' - i\varepsilon''
\]  

(2)

Where \( \varepsilon' \) is the real dielectric constant and \( \varepsilon'' \) is the dissipation of the energy of electrical oscillations in the dielectric when subjected to an ac field. There also arises a phase lag between the electric displacement and the electric field strength, described by the dielectric loss tangent, \( \tan \delta \).

\[
\tan \delta = \frac{\varepsilon'}{\varepsilon''}
\]  

(3)

The magnitude of \( \varepsilon' \) is determined by the chemical constitution, structure and composition of the polymer, and \( \varepsilon'' \) and \( \tan \delta \) depend upon molecular motion in the polymers. In a polymeric dielectric placed in a sinusoidal electric field the electric displacement vector must take account of the past history of the material in some way, thus relaxation processes become important. The expressions for \( \varepsilon' \) and \( \varepsilon'' \), taking into account the relaxation process (single relaxation) becomes 10:

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2 \tau^2}
\]  

(4)

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega \tau}{1 + \omega^2 \tau^2}
\]  

(5)

\[
\tan \delta = 2 \tan \delta_m \frac{\omega \tau_1}{1 + \omega^2 \tau_1^2} \quad \text{where} \quad 2 \tan \delta_m = \frac{\varepsilon_0 - \varepsilon_\infty}{\sqrt{\varepsilon_0 \varepsilon_\infty}}
\]  

(6)
Thus $\varepsilon''$ passes through a maximum at $\omega \tau = 1$ and $\tan \delta$ has a maximum at $\omega \tau = 1$.

The temperature dependence of the dielectric properties can be found using the expression $\tau = \tau_0 e^{U/RT}$. Thus a plot of $\varepsilon''$ versus $1/T$ shows a maximum at temperature $T_{\text{max}}$.

A. Effect of Irradiation on $\varepsilon$

The effect of ion irradiation on the dielectric properties of polymers has been reported earlier $^{11-14}$. Gamma rays and neutron irradiation of ceramics have been known to increase the value of loss factor (tan $\delta$) $^{15}$. The value of $\varepsilon'$ in the case of pristine and irradiated polycarbonate varied from 1.2-1.4. Fig.2 shows a plot of $\varepsilon'$ vs frequency for the pristine and irradiated polycarbonates. The $\varepsilon'$ values for the irradiated samples are more than those for the pristine, and appear to increase with increasing dose. At a particular dose, the $\varepsilon'$ value remains constant for low frequencies (1kHz to 50 kHz) and then decreases. At low frequencies the motion of the free charge carriers is constant and so $\varepsilon$ is constant. As the frequency increases the charge carriers migrating through the dielectric get trapped against a defect site and induce opposite charge in its vicinity, as a result of which they slow down and the value of $\varepsilon$ decreases. The increase in the $\varepsilon'$ values on irradiation has been attributed to the increase in rigidity of the polymer in the past $^{14}$.

B. Effect of temperature on tan $\delta$

Fig.3 shows the plot of tan $\delta$ versus temperature for the pristine and $^7$Li irradiated polycarbonate. The tan $\delta$ values for the irradiated samples are much higher than that for the pristine polycarbonate. The plots for the pristine and $1 \times 10^{12}$ ions/cm$^2$ $^7$Li irradiated
samples show one relaxation maximum. The polymer film irradiated at a higher-dose (5x10^{12} ions/cm^2) shows two peaks. The glass transition temperature (T_g) for pristine polycarbonate is 150 °C. Hence, the peak observed at 80 °C for the pristine polycarbonate film is associated with a sub-glass transition β relaxation, and is referred to as T_β. This T_β is observed to shift towards lower temperatures (53 °C) for the 1x10^{12} ased 7Li irradiated. T_α also shifts to lower temperatures with increased dose, however, in this temperature range the peaks for the pristine and 1x10^{12} ions/cm^2 irradiated samples cannot be observed. Irradiation causes chain scission and as a result there is a decrease in the molecular weight, which leads to a decrease in T_β.

Fig. 4 shows the plot of tan δ versus temperature for the pristine and 59Ni irradiated polycarbonate. The magnitude of tan δ increases considerably on 59Ni irradiation. The increase in the loss factor is much more that that observed in the case of 7Li irradiation. For example, the maximum value of tan δ for 5x10^{12} ions/cm^2 irradiated with 7Li is 0.125 whereas that for 59Ni 1x10^{12} ions/cm^2 irradiated is 0.200. The maximum in the tan δ plot has shifted to higher temperature on irradiation.

It can be seen from Table 1 that the energy density transferred in the case of 59Ni, 1x10^{12} ions/cm^2, is much more than that for the 7Li irradiated samples. As mentioned earlier, in such a case the third category of intermediate compounds dominate, leading to end-linking. In such a case there will be a fraction of insoluble high molecular weight compounds. This leads to the shift of T_β to higher temperatures. Thus, the effects of 59Ni and 7Li irradiation are different, one leads to end-linking and the other leads to scission.

Fig. 5 shows the UV absorption spectra for the pristine, 7Li irradiated and 59Ni irradiated samples. In the case of the 7Li irradiated sample there is no shift of the 275nm
peak, but there is a considerable increase in absorbance in the 280-290nm region. Whereas in the case of the \(^{59}\)Ni irradiated sample the peak at 275nm shifts to lower wavelengths and there is not much change in the 280-290nm region. Thus, it may be concluded that the chemical species formed in polycarbonate on irradiation with these two different doses are different.

C. Effect of Frequency on \(\tan \delta\)

Most theories of relaxation phenomena in polymers rest on the fundamental assumption that the functional groups in the polymer undergo internal rotation around a chemical bond. The pre-glass transition relaxations are often associated with a crank-shaft mechanism of motion around the C-C bond\(^{10}\). Such rotations are thermally activated and involve the jump of atoms over a potential-energy barrier from one equilibrium position to another. This process is associated with an activation energy, which may be calculated from the variation of the relaxation process with frequency. Fig 5 (a), (b), (c) and (d) show the \(\tan \delta\)-T curves at various frequencies for the pristine and irradiated polycarbonate samples. The relaxation peaks are found to shift to higher temperatures with the increase in frequency for all the samples. This shift may be used to calculate the apparent activation energy of the relaxation process using the linear equation\(^{16}\):  

\[
\log f = \log f_0 + \frac{\Delta E}{2.303RT_{\text{max}}}
\]

where \(f\) is the frequency, \(f_0\) is a constant, \(\Delta E\) is the apparent activation energy, \(R\) is the gas constant and \(T_{\text{max}}\) is the absolute temperature corresponding to the maximum \(\tan \delta\) value. The activation energy values for the pristine and irradiated polycarbonate are
indicated in Table II. The $\Delta E$ value for the $^7$Li, $1\times10^{12}$ ions/cm$^2$, irradiated sample is much lower than that for the pristine. This is because scission breaks down the size of the polymer chain and facilitates the movement of the functional groups. However, the $\Delta E$ value for the $^7$Li, $5\times10^{12}$ ions/cm$^2$, irradiated sample is much higher than that for the pristine. The loss tangent values for this sample have been found to be very much higher (as shown in Fig.3). Both these facts may be correlated to the increased rigidity of the polymer chain as the end-linking process begins. The activation energy for the $^{59}$Ni ($1\times10^{12}$ ions/cm$^2$) irradiated sample is very low, although end-linking is the predominant process here. A closer look at Fig. 6(d) shows that the magnitude of relaxation has actually shifted to a higher frequency.

The magnitude of relaxation also varies with frequency, but shows a different trend for different samples. In the case of the pristine polycarbonate, Fig. 6(a), the magnitude decreases with increase in frequency from 1 kHz-10kHz, and totally disappears at 60 kHz. For the $^7$Li ($1\times10^{12}$ ions/cm$^2$) irradiated sample the magnitude falls drastically from 1 kHz to 3 kHz, and slowly increases upto 60kHz. It was then observed to fall again at 100kHz (not shown here). The relaxation process has become much faster i.e. spans over a short frequency range. This is in agreement with the low activation energy observed earlier. The magnitude of relaxation for the $^7$Li ($5\times10^{12}$ ions/cm$^2$) irradiated sample show the same trend as the pristine, i.e., the relaxation progressively dies down from 1 kHz-60kHz, though the values of $\tan \delta$ are much higher. For the $^{59}$Ni ($1\times10^{12}$ ions/cm$^2$) sample the magnitude of the relaxation dies down from 5kHz-60kHz. It appears that the relaxation frequency has shifted from 1 kHz (for the other samples) to 5 kHz. The span is also reduced, and hence the decrease in the activation energy (Table II).
This can be explained by the fact that a totally different kind of motion is taking place here. This is not surprising as the UV spectra of the $^7$Li and $^{59}$Ni irradiated samples (Fig.5) show the existence of different chemical species in the two different cases.

**IV Conclusions**

Heavy ion irradiation of polycarbonate leads to chemical changes in the polymer chain, namely, chain scission and crosslinking. Which of the two processes will predominate depends upon the ion dose. At low ion doses chain scission is the major process. At higher doses fragmented chains link to the main chain of a neighboring molecule, leading to an ‘end-linked’ product with a high molecular weight. The physical properties of this end-linked product are similar to that of a crosslinked polymer. In this case the scissioned product (polymer irradiated at $^7$Li $1 \times 10^{12}$ ions/cm$^2$) had lower loss tangent values than the end-linked one (polymer irradiated at $^7$Li $5 \times 10^{12}$ions/cm$^2$). The polymer film irradiated with $^{59}$Ni ($1 \times 10^{13}$ions/cm$^2$) had loss tangent values much higher than that of the $^7$Li irradiated samples. One dielectric relaxation peak was observed in the temperature range 300-423 K for all the samples. The activation energy for the relaxation process was lowest in the case of the sample in which chain scission occurred on irradiation.
Table 1. Transition temperatures for the Polycarbonate samples in the tan δ-T plots at 1kHz.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluence (ions/cm²)</th>
<th>Energy Density (eV/Å³)</th>
<th>T₀ (°C)</th>
<th>T₉ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PC</td>
<td>0</td>
<td>0</td>
<td>150</td>
<td>80</td>
</tr>
<tr>
<td>Li irr. PC</td>
<td>1x10¹²</td>
<td>7.25x10⁻⁴</td>
<td>145</td>
<td>52</td>
</tr>
<tr>
<td>Li irr. PC</td>
<td>5x10¹²</td>
<td>3.625x10⁻¹</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>Ni irr. PC</td>
<td>1x10¹²</td>
<td>5.46x10⁻²</td>
<td>-</td>
<td>88</td>
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Table II. Relaxation Characteristics as a function of Frequency for the Polycarbonate samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>1kHz</th>
<th>3kHz</th>
<th>5kHz</th>
<th>10kHz</th>
<th>60kHz</th>
<th>ΔE (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine PC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>167</td>
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<tr>
<td>T(°C)</td>
<td>80</td>
<td>85</td>
<td>90</td>
<td>95</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Tan δ&lt;sub&gt;max&lt;/sub&gt;</td>
<td>7.8x10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>6.5x10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>5.8x10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>4.5x10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>7Li 1x10&lt;sup&gt;12&lt;/sup&gt; irr. PC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>79</td>
</tr>
<tr>
<td>T(°C)</td>
<td>55</td>
<td>70</td>
<td>75</td>
<td>80</td>
<td>110</td>
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</tr>
<tr>
<td>Tan δ&lt;sub&gt;max&lt;/sub&gt;</td>
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<td>2.4x10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>3.2x10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>3.8x10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>7Li 5x10&lt;sup&gt;12&lt;/sup&gt; irr. PC</td>
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<td>T(°C)</td>
<td>85</td>
<td>88</td>
<td>89</td>
<td>90</td>
<td>-</td>
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<td>Tan δ&lt;sub&gt;max&lt;/sub&gt;</td>
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<td>4.8x10&lt;sup&gt;-2&lt;/sup&gt;</td>
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<td></td>
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<tr>
<td>59Ni 1x10&lt;sup&gt;12&lt;/sup&gt; irr. PC</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>77</td>
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<td>70</td>
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<td>100</td>
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</tr>
<tr>
<td>Tan δ&lt;sub&gt;max&lt;/sub&gt;</td>
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<td>-</td>
<td>5x10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>2.5x10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>2.5x10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>
Fig 1

(a) Structure of polymer that undergo chain extension
(b) Structure of polymeric alkane
(c) 1st free polymer chain (2) End linked (3) Cross-linked
Figure 2.
Loss at 1kHz

Pristine

\[1 \times 10^{-8}\]

\[5 \times 10^{-8}\]

\(\tan \delta\)

Temperature (°C)
Figure A
Fig 7
References:


Dielectric Constant Measurement of MeV Ion Irradiated Polycarbonates

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1. Introduction

The dielectric response of solids provides information about the orientational and translational adjustment of mobile charges present in the dielectric medium in response to an applied electric field. The energy transferred to an alternating field is a function not only of the field but it also depends upon the physical characteristics of the material. The most important property of the dielectric material is its ability to be polarized under the action of the field. The study of the dielectric response before and after heavy ion irradiation can give significant insight to the modification of the bulk properties responsible for the dielectric response [1,2]. In this paper results of the dielectric response and loss factor as a function of frequency of field and temperature for pristine and various irradiated samples are presented. This gives better understanding of the track formation mechanism on the basis of microstructure so formed due to passage of heavy ions through the polymer material.

2. Experiments

The samples used in the present work were of Makrofol Kg, 25 µm thick. These foils were irradiated with ions 7Li, 50 MeV with ion fluences of \(1 \times 10^{12}, 2.5 \times 10^{12}, 5 \times 10^{12},\) and \(1 \times 10^{13}\) ions/cm² at the 15 MV Constant and loss factor (\(\tan \delta\)) measurement were carried out using the Hewlett Packard LCR meter over the frequency range 100 Hz – 1 MHz. The dielectric constant was calculated using the relation \(\varepsilon = C_p/C_0\) where \(C_p\) is capacitance measured using the LCR meter and \(C_0 = \varepsilon_0 A/d\), where \(\varepsilon_0\) is the permittivity of vacuum and \(A\) and \(d\) are the cross-sectional area and thickness of the sample. \(\tan \delta\) was measured directly with the LCR meter.

3. Results and Discussion

Fig 1. Shows a plot of dielectric constant (\(\varepsilon\)) versus Frequency at room temperature for pristine and \(7\)Li irradiated polycarbonate samples.
The $\varepsilon$ values for the irradiated samples are more than those for the pristine, and appear to increase with increasing dose. At a particular dose, the $\varepsilon$ value remains constant for low frequencies (1KHz to 50 KHz) and then decreases. At low frequencies the motion of the free charge carriers is constant and so $\varepsilon$ is constant. As the frequency increases the charge carriers migrating through the dielectric get trapped against a defect site and induce opposite charge in its vicinity, as a result of which they slow down and the value of $\varepsilon$ decreases.

Fig 2 represents a plot of loss factor $\tan \delta$ Vs Temperature at 1 kHz for pristine and irradiated polycarbonate samples at various doses. The measurements were taken from room temperature to 150 °C. The value of $\tan \delta$ is found to increase with increasing dose. Two relaxation peaks are observed in this temperature range. They may be associated with pre-glass transition ($\beta$) and glass transition ($\alpha$) motion of the polymeric chain. Both the peaks show shifts to the low temperature side with increase of ion dose. Ion irradiation leads to chain scission and subsequently reduction in the molecular weight. As a result the molecular motion is facilitated and the glass transition shifts to lower temperatures.

![Fig. 2. Plot of $\tan \delta$ Vs Temperature for the pristine and irradiated polycarbonate samples at 1 kHz.](image)

**References**


**4. Conclusion**

Swift heavy ion irradiation of polycarbonates leads to chain scission and as a result there are changes in the dielectric properties. The value of the dielectric constant and loss factor increases with increase of irradiation dose.
Growth of potassium Iodide micro/nano structures using template method

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1. Introduction

Micro/Nano technology is an emerging field having a vast potential for bringing in revolution in the development and advancement of the techniques involved in the fabrication of miniature electronic components, new composite materials and devices. In recent years, there has been tremendous interest in etched nano/micro pores generated by SHI in polymers, called Template method. Therefore nano/micro physics fabrication is very important both for its technological applications and fundamental interest. The unique growth behavior and crystal structure of KI may be used as 1D-quantum wires. These nano/micro structures generated in the pores can be short, long needles like fibril, tubules, tapered conical (single or double cones) shaped etc. depending on the pore size and geometry. In the present work, the growth of KI crystal is demonstrated in etched polymer matrix, which served as template. KI is a salt that forms a regular crystal. It is very well soluble in water and readily crystallizes at normal conditions, therefore, its growth behavior was chosen in this paper.

2. Experiments
The samples used in present work were Makrofol KG 25 \( \mu \text{m} \) thick. These foils were irradiated with \( ^{238}\text{U} \), 11.2 MeV/n and with fluence of \( 5 \times 10^5 \) ions/cm\(^2\) at the GSI, Germany. The foils were etched in 6N NaOH solution for 5-6 hours to produce pores of 3-4 \( \mu \text{m} \) in the temperature-controlled bath. The crystals of KI were taken in the petri dish and the etched Makrofol film was kept between the Crystal for 20 hours. The etched film was then taken out from petridish and kept on the filter paper. The growth of the crystal could be observed under optical microscope. The polymer matrix is then dissolved in the \( \text{CH}_2\text{Cl}_2 \) and the sample is left for 10 minutes. \( \text{CH}_2\text{Cl}_2 \) dissolved the polymer matrix and only needle like structures were obtained. Sample containing KI crystals were then analyzed under SEM at NPL, New Delhi.

3. Results and discussion
KI crystal has a face-center lattice. The relative density of crystallographic planes of this lattice is (111), (100), (110) etc. The SEM picture of KI crystal that is grown in the polymer matrix reveals about the orientation of the crystallographic planes. This oriented growth can occur due to various reasons. If the initial crystallization in the polymer matrix starts from randomly oriented nuclei, the geometrical selection will take place due to the anisotropy of the crystal growth. The grain that has the most favorable orientation will over grow the rest.
our work is obviously of epitaxial nature. Their orientations entirely depend on the KI crystals that are first formed on the surface of the polymer matrix.

4. Conclusion.

The growth of microstructure involves the orientation of the crystallographic planes and one can observe short and long needles like fibril and tubules depending on the pore size. These structures are used in the fabrication of miniature electronic components and new composite materials.

5. Acknowledgments

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Fig.1. Growth of KI crystal having diameter of 20μm inside etched pores in Makrofol.

6. References

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CONTROLLED PRODUCTION OF SUBMICRON OR NANOMETER PORES IN PLASTIC FOILS

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ABSTRACT

The plastic track detectors have found innumerable applications in the field of nuclear physics, geophysics, cosmic-ray studies, environmental radiation physics and microanalysis of trace elements etc. over the last 30 years. One of the latest applications of plastic track detectors is to make through etched-holes at the sites of charged particle tracks thus produce Nuclear Track Filters with holes of diameters of the order of few microns or even of nanometer size. Such nuclear track filters can be employed for the filtration of cancer blood cells, and also filtration of bacteria in beer industry and for the studies on water flow, aerosol mass determination from quartz crystal and separation of two different liquid phase etc. This paper describes the first successful attempt made by us in producing such nuclear track filters using the heavy ion beams from accelerators in India.

1. EXPERIMENTAL PROCEDURE

Polycarbonate plastic Makrofol having thickness 30 μm was irradiated with heavy ion beams like Si\(^{7+}\) of energy 100 Mev (coded as \(A_{\text{M}}\)) and Ag\(^{15+}\) having energy 200 Mev (coded as \(A_{\text{p}}\)) with a beam current of about 5pnA (coded as \(A_{\text{c}}\)) giving fluence of \(10^4-10^6\) ions/cm\(^2\) for micro and nano pore production. The ion beam facilities available at the 15 UD pelletron in Nuclear Science Centre, New Delhi, India was used for this purpose.

Etching of the foil was done in an etching cell designed indigenously as shown in fig. 2. In this cell the irradiated plastic foil having latent damage tracks separates the two plexi-glass chambers filled with 6N NaOH solution which serves both as the track etchant and also as conducting medium. The temperature of the solution was controlled at 70°C. The diameter of the holes could be controlled by etching time and ion masses, while the density of holes (no. of tracks per cm\(^2\)) is controlled by particle fluence. During the etching process the resistance of the cell was continuously recorded by measuring current through pores. The instant of break-through is characterized by sudden increase of current within minutes (fig. 1). Average no. of through etched holes counted by microscope in 1 cm\(^2\) and the foil for \(A_{\text{M}}\) & \(A_{\text{p}}\) are found to be 12576 & 10395 respectively.
Fig. 1 shows that pore radius increases linearly with time. The value of slope (dr/dt) for series A and series B are found to be 0.016 nm min$^{-1}$ and 0.0125 nm min$^{-1}$ respectively.
2. RESULTS AND DISCUSSION

Until the track is etched through the foil represents a nearly infinite resistance and the current is of the order of nanoampere, but the instant of break through is characterized by sudden increase of current within minutes with the assumption if a cylindrical pore geometry, the radius of the pore is given by

$$r = \frac{1}{\sqrt{n \pi R}}$$

where \( l \) is thickness of the plastic left after break through.
\( n \) is the number of tracks per cm\(^2\) at the instant of breakthrough
\( R \) is the resistance of Makrofol at the time of break through (1.5x 10\(^9\) ohm)
\( K \) is the specific conductivity or the 6N NaOH solution at 70\(^\circ\)C after calibration it with 0.1 N KCl solution at 60\(^\circ\)C=27.6 mhos/m.

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