

# Dielectric Spectroscopy of Makrofol KG Using Heavy Ion Irradiation

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## Abstract

High energy heavy ion irradiation of polymers affects their dielectric constant and loss factor. Structural changes produced in the polymer owing to the breaking of its long molecular chains by heavy ions are responsible for such modifications in the polycarbonate plastic. Dielectric constant and loss factor are studied by irradiating samples with 85 MeV <sup>16</sup>O and 80 MeV <sup>28</sup>Si ions with the fluence which varied from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The study is carried out for different frequencies of the applied electrical field ranging from 1 kHz to 100 kHz both for the pristine and ion irradiated samples. In comparison, we find that the  $\epsilon'_{r(\omega)}$  values for <sup>16</sup>O irradiation sample decreases than those with the  $\epsilon'_{r(\omega)}$  values for the <sup>28</sup>Si irradiated sample at the same dose and temperature series. This indicates that various kind of chemical species are formed in polycarbonate on irradiation with Oxygen and Silicon ions. Activation energy in the case of pristine, 85 MeV <sup>16</sup>O and 100 MeV <sup>28</sup>Si ion irradiated samples are respectively found to be 102.1 kJ/mol, 214.4 kJ/mol and 127.6 kJ/mol.

## Keywords

Activation Energy, Dielectric Loss, Pelletron Accelerator

## 1. Introduction

Polycarbonate (PC) film having a brand name Makrofol KG (chemical name: bis-phenol-A-polycarbonate) is a semi-crystalline thermoplastic material. Makrofol is widely used for ion track recording and to prepare track etched membrane as micro filters. Three different types of widely used polycarbonate are Makrofol-KG, KL and N. All these three types of polycarbonates have the same chemical formula (C<sub>16</sub>H<sub>14</sub>O<sub>3</sub>) and were purchased from the same company (Farbenfabriken Bayer A G, Leverkusen, Germany). Only the difference is in etching parameters. The polycarbonates, like Makrofol, are insensitive to X-rays and light charged particles. However, they can conveniently detect heavy ions in the study of heavy ion nuclear reactions, cosmic rays. They can also explore the super heavy elements and also acts as most suitable for microfilter technology

Polymers irradiation with protons, neutrons and gamma rays produces significant changes in their chemical structure

like degradation of chemical bonds, backbone structure, cross linking, chain scission and end-linking at different ionic energy densities. Such changes have been studied in recent past by many workers [1], [2], [3], [4], [5], [6], [7] and [8]. The track produced by Swift heavy ion irradiation (SHI) in Makrofol KG polycarbonate after etching is found in the nanometer range [9], [10] and [11].

When Makrofol is irradiated with swift heavy ions, large-scale lattice defects have been created due to breaking of its long molecular chains, which leads to the formation and transport of reactive species that can permanently change the physico-chemical properties of these materials [12].

To characterize the electrical property impedance spectroscopy (IS) is used. IS is an effective method it can resolve the grain and grain boundary contribution to the system and calculate the conductivity and dielectric constant [13]. The impedance analysis gives the maximum possible information about the material [14].

Earlier Rajesh et al. showed that as the frequency increases,

dielectric constant decreases up to a certain limit and then remain constant when the Makrofol KG polycarbonate film was irradiated with 145 MeV  $\text{Ne}^{6+}$  and 100 MeV  $\text{Si}^{8+}$  ions by varying the fluence from  $1 \times 10^{10}$  to  $1 \times 10^{12}$  ions/cm<sup>2</sup> [15].

Motivated by the above earlier results; we have exposed Makrofol KG polycarbonate with 85 MeV  $^{16}\text{O}$  and 80 MeV  $^{28}\text{Si}$  ions with the fluence which varied from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions/cm<sup>2</sup>. The dielectric constant measurements were done for the better understanding of chain scission and end linking in the polycarbonate at different energy densities. Such changes are studied by measuring real and imaginary parts of complex dielectric constant  $\epsilon_{r(\omega)}^*$  and the loss tangent,  $\tan \delta$ . The important new results obtained in this work are: scission takes place in  $^{28}\text{Si}$  irradiated samples while end linking might be taking place in  $^{16}\text{O}$  irradiated samples. The dielectric relaxation is used to calculate the apparent activation energy of the relaxation process [16, 17, 18]. The dielectric constant (or relative permittivity)  $\epsilon_{r(\omega)}^*$  of a dielectric solid placed in alternating electric field of frequency  $\omega$ , is a complex quantity because the orientational polarization lags behind the polarizing electric field as the frequency of the applied field is increased. The complex dielectric constant can be written in the form

$$\epsilon_{r(\omega)}^* = \epsilon'_{r(\omega)} - i\epsilon''_{r(\omega)} \quad (1)$$

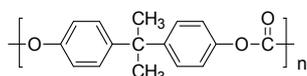
where  $\epsilon'_{r(\omega)}$  is the real dielectric constant and characterizes the most important electrical property of the dielectric material. The imaginary part  $\epsilon''_{r(\omega)}$  characterizes the dissipation of energy of electric oscillation in a dielectric subjected to the action of an alternating electric field. In this way there is a phase lag between the electric displacement vector  $\vec{D}$  and the electric field vector  $\vec{E}$  because at high frequencies the dipoles do not faithfully follow the rapidity of the applied alternating field. This phase lag is described by the so-called dielectric loss tangent or dissipation factor given by

$$\tan \delta = \frac{\epsilon''_{r(\omega)}}{\epsilon'_{r(\omega)}} \quad (2)$$

The magnitude of the real dielectric constant  $\epsilon'_{r(\omega)}$  of the polymer is determined by the chemical constitution, structure and composition. The dielectric losses (viz.,  $\epsilon''_{r(\omega)}$  and  $\tan \delta$ ) depend upon the molecular motion and charge carrier motion.

## 2. Experimental Details

A sheet of Makrofol-KG with thickness of 20  $\mu\text{m}$  was obtained from Bayer AG, Lever Kussen, Germany. This sheet is manufactured by a casting process. The chemical structure of Markafol-KG is given below:



The samples were of size  $1.5 \times 1.5 \text{ cm}^2$  was irradiated using swift heavy ion beams from the 16 MV Van de Graff accelerator (Pelletron) facilities at the Inter University Accelerator Centre, New Delhi. During the irradiation the samples were kept inside a chamber with pressure maintained at  $1 \times 10^{-6}$  Torr. The ion beam used was  $^{16}\text{O}$  (85 MeV) and  $^{28}\text{Si}$  (100 MeV), having a current density of 1- 2 pA/cm<sup>2</sup> corresponding to a flux of about  $1.25 \times 10^{10}$  ions/cm<sup>2</sup> per sec (pA stands for particle nano ampere, 1pA =  $6.25 \times 10^9$  particle/s/cm<sup>2</sup>). The fluence range was varied from  $1 \times 10^{11}$  to  $1 \times 10^{13}$  ions/cm<sup>2</sup>.

SRIM (stopping range in materials) program of version SRIM 2008.04 were used to calculate  $S_e$  (electronic energy loss),  $S_n$  (nuclear energy loss) and projected area inside the material of PC having density  $1.2 \text{ g/cm}^3$ ; containing  $9.3781 \times 10^{22}$  atoms/cm<sup>3</sup>. The electronic energy loss of the  $^{16}\text{O}$  ion beam having energy 85 MeV in the PC film i.e.  $(dE/dx)_e$  is  $50.38 \text{ eV/\AA}$ . The depth profile calculations of the beam in 20 $\mu\text{m}$  thick films at the entrance and exit of the ion beam are respectively found to be  $(dE/dx)_{0\mu\text{m}} = 49.88 \text{ eV/\AA}$  and  $(dE/dx)_{20\mu\text{m}} = 50.38 \text{ eV/\AA}$ . The value of projected range of the ion beam inside PC is 23.01  $\mu\text{m}$ , which is greater than the sample thickness. Hence, the ion beam will pass through the material. The value of nuclear energy loss  $(dE/dx)_n$  is  $2.146 \text{ eV/\AA}$ . Since the energy of ion beam is 85 MeV, at such high energy, energy transferred to the PC material is due to  $S_e$ , therefore the effect of  $S_n$  is negligible. Similarly, the electronic energy loss of the  $^{28}\text{Si}$  ion beam having energy 80 MeV in the PC film i.e.  $(dE/dx)_e$  is  $72.32 \text{ eV/\AA}$ . The depth profile calculations of the beam in 20 $\mu\text{m}$  thick films at the entrance and exit of the ion beam are respectively found to be  $(dE/dx)_{0\mu\text{m}} = 71.56 \text{ eV/\AA}$  and  $(dE/dx)_{20\mu\text{m}} = 72.32 \text{ eV/\AA}$ . The value of projected range of the ion beam inside PC is 25.21  $\mu\text{m}$ , which is greater than the sample thickness. Hence, the ion beam will pass through the material. The value of nuclear energy loss  $(dE/dx)_n$  is  $2.232 \text{ eV/\AA}$ . Since the energy of ion beam is 80 MeV, at such high energy, energy transferred to the PC material is due to  $S_e$ , therefore the effect of  $S_n$  is negligible (Rajesh Kumar, 2009). The role of the energy loss thus tells about the general evolution of materials modification as a function of energy loss.

## 3. Result and Discussions

*Dielectric Studies:* The dielectric properties of a material depend upon different types of polarization that is bipolar, electronic, atomic and space charge polarization.

The variation of dielectric constant ( $\epsilon'$ ) and tangent loss ( $\tan \delta$ ) versus  $\log(f)$  in the temperature range of  $75^\circ\text{C}$  to  $150^\circ\text{C}$  for the pristine samples is shown in Fig. 1. The value of  $\epsilon'_{r(\omega)}$  in our case of pristine polycarbonate varied from 11.0 to 11.8 with temperature. Figs. 2 and 3 show a plot of dielectric constant  $\epsilon'_{r(\omega)}$  versus  $\log(f)$  and tangent loss ( $\tan \delta$ ) versus frequency in the temperature range of  $75^\circ\text{C}$  to  $125^\circ\text{C}$  for the  $^{28}\text{Si}$  irradiated samples at fixed dose  $1 \times 10^{12}$  ions/cm<sup>2</sup>. The value of  $\epsilon'_{r(\omega)}$  in the case of  $^{28}\text{Si}$  irradiated samples varied from its pristine value 11.0 to 15.8 at a fixed dose. The  $\epsilon'_{r(\omega)}$

values for the  $^{28}\text{Si}$  irradiated samples are found to be more than those for the pristine and appear to increase with increasing temperature. It is clear from Fig.2 that at a particular dose, the  $\epsilon'_{r(\omega)}$  value remains constant from  $\log(f)$  2.5 to 4.25 (i.e. from 316 Hz to 17.8 kHz) and then decreases with increase in frequency.

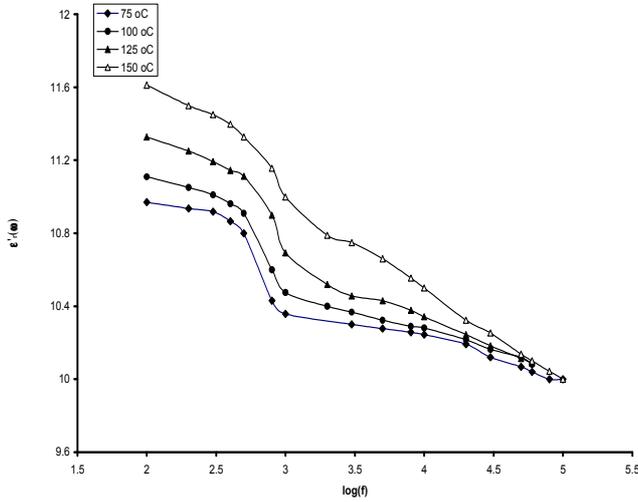


Fig. 1. A plot of dielectric constant  $\epsilon'(\omega)$  versus frequency for pristine Makrofol KG at various temperatures.

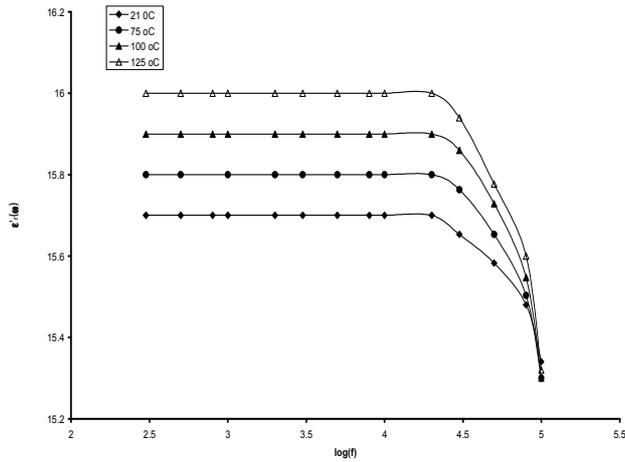


Fig. 2. A plot of dielectric constant  $\epsilon'(\omega)$  versus  $\log(f)$  for  $^{28}\text{Si}$  irradiated Makrofol KG at various temperatures and at fluence of  $1 \times 10^{12}$  ions/cm $^2$ .

Fig.4 shows a plot of dielectric constant  $\epsilon'_{r(\omega)}$  versus frequency at fixed temperature (75 °C) of different doses for the  $^{16}\text{O}$  irradiated samples. We observed that at a particular dose, the  $\epsilon'_{r(\omega)}$  value remains constant from  $\log(f)$  2.4 to 4.3 (i.e. from 280 Hz to 20 kHz) and then decreases with the increase of frequency.

The dielectric relaxation may be used to calculate the apparent activation energy of the relaxation process. The magnitude of activation energy values for the Pristine, polycarbonate irradiated with (85 MeV ) and  $^{28}\text{Si}$  (100 MeV ) samples are shown in Fig.5. The slope of the graph is used in following equation to find activation energy [19, 20].

$$U = \text{slope} \times 2303 \times k \quad \text{where } k \text{ is the Boltzmann's constant}$$

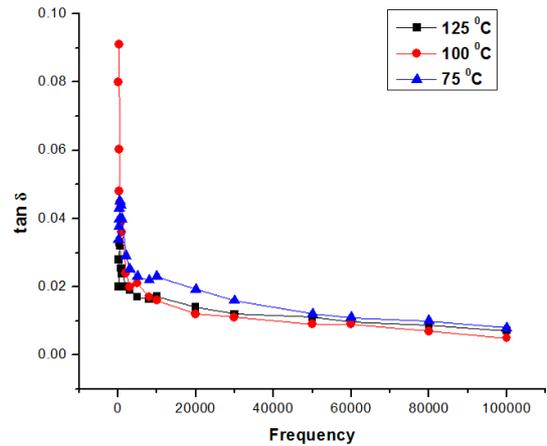


Fig. 3. A plot of dielectric loss  $\tan \delta$  versus frequency for  $^{28}\text{Si}$  irradiated Makrofol KG at various temperatures and at fluence of  $1 \times 10^{12}$  ions/cm $^2$ .

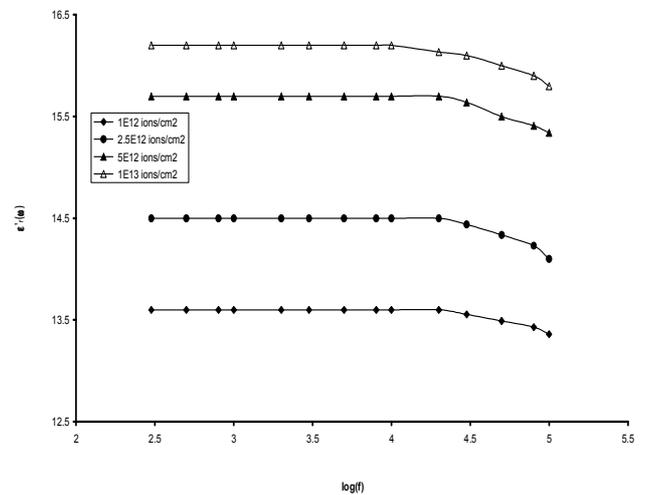


Fig. 4. A plot of dielectric constant  $\epsilon'(\omega)$  versus frequency for  $^{16}\text{O}$  irradiated Makrofol KG at different fluences and at temperature of 75 $^{\circ}$  C.

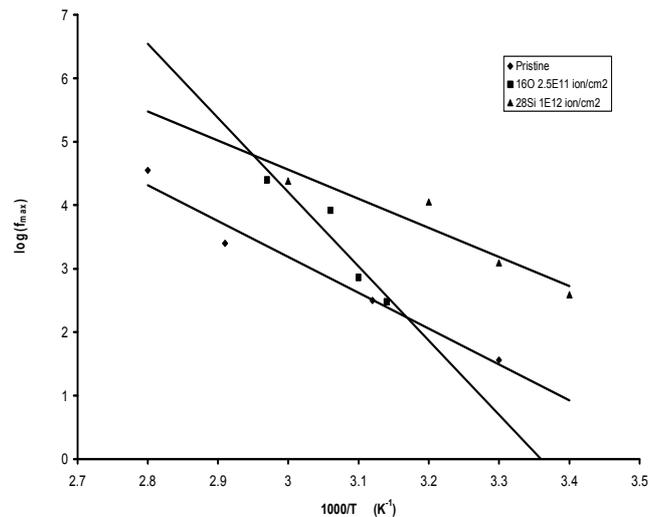


Fig. 5. A plot of  $\log(f_{max})$  versus  $1000/T$  for (a) Pristine (b)  $^{28}\text{Si}$  irradiated Makrofol KG and (c)  $^{16}\text{O}$  irradiated Makrofol KG.

Accordingly, this value for the Pristine, polycarbonate irradiated with  $^{16}\text{O}$  (85 MeV) and  $^{28}\text{Si}$  (100 MeV) samples are found to be 102.1 kJ/mol, 214.4 kJ/mol and 127.6 kJ/mol respectively.

At frequency up to 17.8 kHz, the dielectric constant is high due to the accumulation of charge at grain boundary and the sample and electrode interface with each other also called space charge polarization. As the frequency increases the dielectric constant decreases due to the space charge polarization, which diminishes gradually hence the electronic and atomic contribution dominates.

#### 4. Conclusion

Heavy ion irradiation of polycarbonate leads to chemical changes in the polymer chain, namely, chain scission and cross linking. The dielectric constant of heavy ion irradiation of Makrofol-KG polycarbonate sheet decreases with increase in frequency, whereas in the high frequency region it shows the frequency independent behavior. The dielectric loss is constant at high frequency. Thus, this material exhibit high dielectric constant and low dielectric loss with variation in frequency implying that the material is suitable for high frequency microelectronic device applications. Dielectric spectroscopy, we found that the dielectric constant,  $\epsilon'_{r(\omega)}$  values for  $^{16}\text{O}$  irradiation sample decreases than those with the  $\epsilon'_{r(\omega)}$  values for the  $^{28}\text{Si}$  irradiated sample at same dose and at same temperature. This indicates that various kinds of chemical species might have formed in polycarbonate on irradiation with Oxygen and Silicon ions.

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