

# Swift Heavy ion irradiation effects on dielectric constant and dielectric loss in poly (ether ether ketone) (PEEK)

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DOI: 10.5185/amp.2018/986

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## Abstract

The dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of pristine and  $C^{5+}$  (70 MeV) ion irradiated samples of the PEEK have been investigated with the variation of temperature at different frequencies (100 Hz, 1 kHz, 10 kHz and 100 kHz). The maxima are obtained around 170 °C in dielectric constant ( $\epsilon'$ ) vs. temperature (T) curve. This relaxation is linked with the movement of ketone ( $>C=O$ ) dipoles linked to the main chain. The irradiation of polymers increases the orientational polarization due to increase in number of dipoles with fluence. The increase in dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) is attributed to chain scissioning at higher fluence which results in an increase of free radicals and unsaturations. Copyright © 2018 VBRI Press.

**Keywords:** Dielectric constant, dielectric loss, poly (ether ether ketone) (PEEK),  $C^{5+}$  ion, irradiation.

## Introduction

The dielectric constant and dielectric loss investigations give a better understanding of the molecular dynamics associated with the various relaxation processes in polymeric materials [1-5]. The Thermally Stimulated Depolarization Current (TSDC) technique is widely used for investigating the various relaxation processes in polymers. Further, dipolar relaxation process can be studied in detail using the TSDC technique. The comparison of the TSDC and dielectric measurements might be helpful in understanding the origin of the TSDC relaxations. In the TSDC measurements, the time and temperature are varied simultaneously to measure dielectric relaxations, while in dielectric measurements either frequency or temperature is kept constant. Basically, in the dielectric measurements, the current response of a sample to the applied voltage is observed. The dielectric constant ( $\epsilon'$ ) is based on the capacitive and resistive energy components arising from the dipolar displacement current. In addition to its relevance to electrical applications of materials, it is also a tool for investigation of molecular motions and for certain aspects of morphology and structure. Dielectric analysis is sensitive only to internal motions, which involve the reorientation of electrical dipoles. In thermoplastic like PEEK, the orientational polarization is due to conformational motion of polymeric chain. The complete orientation of molecular movement depends upon the frequency of alternating electric field.

The polar molecules exhibit high power losses at certain frequencies. At very low frequencies, the orientation of dipoles is in phase with the changes in electric field and the power losses are low. As the frequency is increased, the dipole orientations cannot be completed in the available time and the dipoles become out of phase. Therefore, the current is found to lag behind the voltage [6-7].

In this paper, the dielectric constant and dielectric loss measurements are done in pristine and irradiated samples of poly (ether ether ketone) (PEEK).

## Material and method

Polyetheretherketone (PEEK) is an organic polymer as well as a thermoplastic with high performance. The PEEK films of thickness 50  $\mu$ m [EK301050] are procured from Good Fellow, UK. The films are transparent with pale amber color. The glass transition temperature of PEEK is around 143°C and melting temperature is ~ 343°C. The samples were irradiated with  $C^{5+}$  ion beam having energy 70 MeV for fluence  $1 \times 10^{10}$  ions/cm<sup>2</sup>,  $1 \times 10^{11}$  ions/cm<sup>2</sup>,  $1 \times 10^{12}$  ions/cm<sup>2</sup> and  $1 \times 10^{13}$  ions/cm<sup>2</sup> (Current ranging from 1 to 3 pA) using the 15 MV Pelletron at Inter University Accelerator Center (IUAC), Delhi. The dielectric measurements were made at frequencies ranging from 1 kHz to 1 MHz using Agilent 4284A, a precision LCR meter. The sample placed in two probe setup was kept in a digital temperature controlled furnace

for heating in steps i.e. at a certain temperature sample was kept for almost 10 minutes and the corresponding measurements of capacitance (C) and dissipation factor (D) were made.

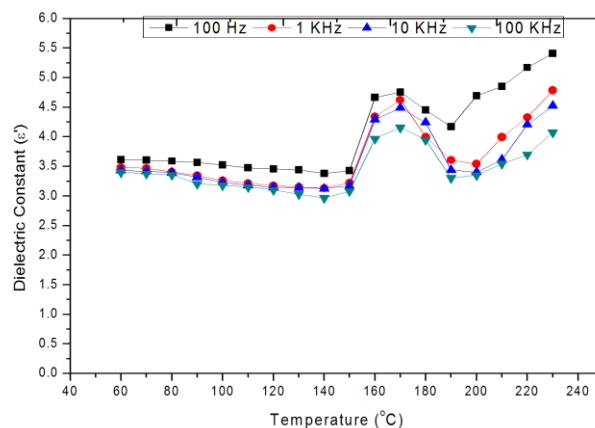
## Results and discussion

### Pristine samples

The variation of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) with temperature for pristine poly (ether ether ketone) (PEEK) samples at different frequencies (100 Hz to 100 kHz) in the interval 60°C to 230°C, have been illustrated in **Fig. 1** and **Fig. 2** respectively. It is observed from dielectric constant ( $\epsilon'$ ) vs. temperature (T) curve (**Fig. 1**), that, between temperature range 60°C to 150°C, the dielectric constant ( $\epsilon'$ ) is decreasing with temperature at all frequencies. There is a rapid increase in dielectric constant ( $\epsilon'$ ) with temperature around 150°C which is start of  $\alpha$ -relaxation and the maxima are obtained around 170°C. The dielectric constant ( $\epsilon'$ ) is decreasing with increase in temperature in the temperature range 170°C to 200°C and beyond 200°C, the dielectric constant again starts increasing very rapidly. The dielectric loss is very small below the glass transition temperature ( $T_g \sim 143^\circ\text{C}$ ) and a sharp peak is obtained above the glass transition temperature i.e. at  $\sim 160^\circ\text{C}$ . The dielectric loss is increasing sharply beyond 200°C.

The low temperature variation of dielectric constant ( $\epsilon'$ ) is usually governed by Kirkwood model [8-9]. According to Kirkwood model, in working temperature range, if the molecular configuration and the inter and intra molecular interactions are not changed, the dielectric constant is determined by  $1/T$  rule i.e. with increasing temperature dielectric constant ( $\epsilon'$ ) should decrease. The similar trend below 150 °C has been observed following the Kirkwood's model [8].

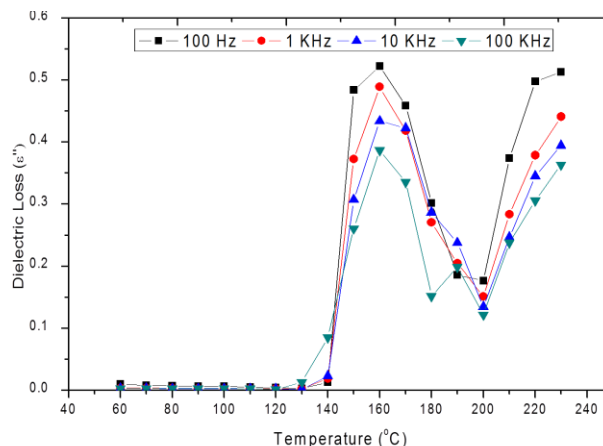
At the temperature above 150°C, there is a sudden and sharp rise in dielectric constant with temperature and that can be linked to onset of  $\alpha$ -relaxation. The existence of this relaxation process is also confirmed by TSDC analysis of PEEK and supports that this relaxation is taking place because of the movement of ketone ( $> \text{C}=\text{O}$ ) dipoles linked to the main chain [10]. In the polymers where the dipoles are directly attached to main chain, movement of the dipoles will depend on the ability of main chain segment to move. Thus, the polarization of dipoles will be less significant below the glass transition temperature than above glass transition temperature. The PEEK is an example of such polymers. In PEEK, the movement of ketone group provides the polarizability of the polymer. Hence, it is expected that the dielectric loss will have a significant increase directly after glass transition temperature [7]. The dielectric loss peak shown in **Fig. 2** starts around 140 °C, that is also confirmation of the  $\alpha$ -relaxation due to polar group attached to the main chain of PEEK [10]. The value of dielectric constant for amorphous and semi crystalline the PEEK below 150°C reported by Huo and Cebe is 3.26 [9] and our results are in agreement with their results. Besides  $1/T$  dependence,



**Fig. 1.** Variation of dielectric constant ( $\epsilon'$ ) with temperature for pristine samples of PEEK at frequencies: 100 Hz, 1 kHz, 10 kHz and 100 kHz.

there is another term which comes from cooperativity (autocorrelation) of the dipoles, and this term may also be temperature dependent [8]. Zou et al [11] observed a rapid decrease in the dipolar relaxation of the amorphous PEEK than  $1/T$  decrease, which indicates that the cooperative interaction decreases with an increase of temperature. The similar sharp decrease in dielectric constant is observed with temperature beyond 170 °C in the pristine samples of semi crystalline PEEK. The electric field and temperature have different effects on the orientation of dipoles for dielectric measurement above the glass transition temperature. The orientational polarizability of dipoles reduces as the dipoles are randomized by the thermal energy. The electric field is no longer effective in dipole alignment, and result of increasing temperature further above  $T_g$  is to randomize the dipoles more, causing a decrease in dielectric constant and dielectric loss.

The dielectric constant increases sharply with temperature beyond 200 °C due to strong ionic conductivity and space charge polarization in this region. It is clear from **Fig. 2** that dielectric loss is also increasing sharply with temperature in this region due to migration of charges and this is accordance with the work of Dova et al [12].



**Fig. 2.** Variation of dielectric loss ( $\epsilon''$ ) with temperature for pristine samples of PEEK at: 100 Hz, 1 kHz, 10 kHz and 100 kHz.

The decrease of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) with increasing frequency at a fixed temperature may be attributed to relaxation or inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipoles and that of applied field [13-14]. The dielectric relaxation involves the orientation polarization which depends upon the molecular arrangement of dielectric material. So, at higher frequencies, the rotational motion of the polar molecules (ketone group) of PEEK is not sufficiently rapid for the attainment of equilibrium with the field. As the frequency increases the ionic and orientational source of polarizability decreases [15-17].

### Irradiated samples

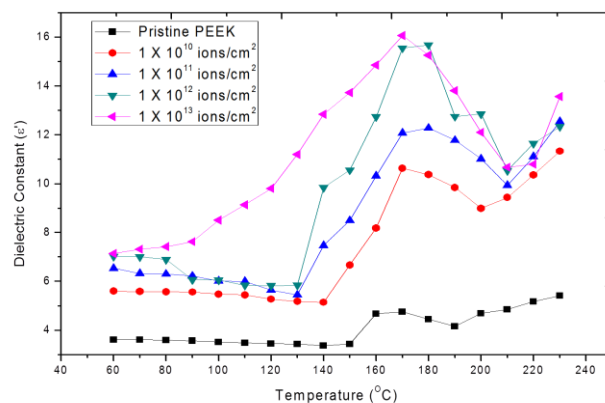
The temperature dependence of dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) for pristine and  $C^{5+}$  (70 MeV) ion irradiated samples of PEEK is illustrated by **Fig. 3** to **Fig. 10**. The samples were irradiated at different fluences [ $1 \times 10^{10}$  ions/cm<sup>2</sup>,  $1 \times 10^{11}$  ions/cm<sup>2</sup>,  $1 \times 10^{12}$  ions/cm<sup>2</sup> and  $1 \times 10^{13}$  ions/cm<sup>2</sup>]. The magnitude of dielectric constant and dielectric loss maxima are increased as compared to pristine samples of the PEEK and also increase with the increase in fluence. Also, there is a shift in maxima of dielectric constant towards higher temperature as compared to pristine one. The onset of maxima for dielectric constant shifts to lower temperature with the increase in fluence i.e. there is broadening in maxima of dielectric constant with increasing fluence.

The dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) are decreasing with increasing frequency which is due to dielectric dispersion. The polymeric materials when irradiated with ionizing radiation (gamma rays, X rays, accelerated electrons, ion beams), the very reactive intermediates products like; excited states, ions and free radicals are formed which result in rearrangements and formation of new bonds. The effects of these reactions are the formation of oxidized products, grafts, scission of main chain (degradation) or cross-linking. Often the two processes i.e. chain scissioning and cross-linking, occur simultaneously and the outcome of the process is determined by a competition between these reactions. Oxidation and degradation occur gradually with increasing fluence [18-20]. The C-C strength decreases with increase in fluence [21]. Due to this radiation and thermal aging disintegrates the molecules in PEEK and promotes cross-linking reactions at the same time and increasing the number of dipoles so that the samples have larger values for dielectric constant ( $\epsilon'$ ). In other words the irradiation of polymers increases the orientation polarization due to increase in number of dipoles with fluence [22]. The increase in maxima or peak height with increasing fluence suggests that shallow energy traps have been created having a transition in the vicinity of  $\alpha$ -relaxation. The increase in maxima or peak height of  $\alpha$ -relaxation is also supported by TSDC analysis [23].

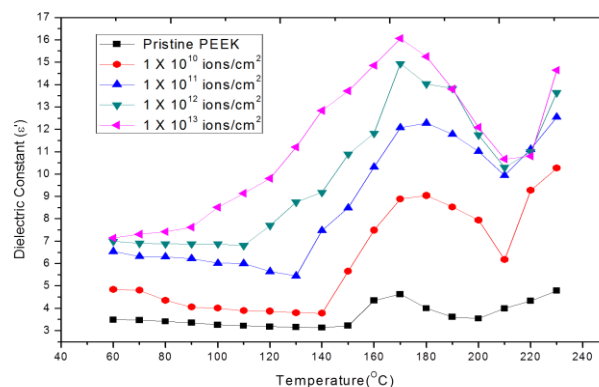
The presence of cross-linking strongly affects the segmental relaxation properties of polymers. Various workers have investigated the segmental constraint and

dynamic heterogeneity which arise due to cross links in polymer networks, and the influence of varying crosslink density on the measured glass transition temperature ( $T_g$ ) [24-29]. The introduction of cross-links leads to a decrease in the conformational freedom of the chains and results in areas of restricted mobility in the vicinity of the cross-link junctions due to this there is increase in glass transition temperature ( $T_g$ ) with increasing cross-link density [30-31]. So, there is a shift in maxima of dielectric constant towards higher temperature as compared to pristine samples of PEEK.

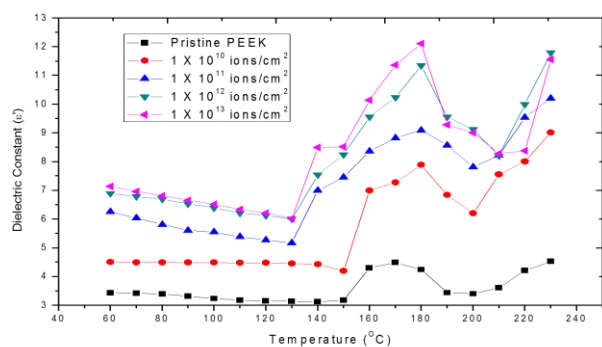
Broadening of peak of dielectric constant with increasing fluence indicates the overlapping of a large number of different relaxation periods of segmental motions of the polymer chain or of dipoles that are rigidly coupled to main molecular chain [33]. The dielectric loss ( $\epsilon''$ ) increases with increasing fluence because it is associated with electronic transitions that are more pronounced when more electrons participate in electron-hopping process between the amorphous zones created upon polymer destruction [34]. Also, it is observed that dielectric loss ( $\epsilon''$ ) and capacitance increase with the increase in ion fluence. The increase in dielectric loss ( $\epsilon''$ ) and capacitance is attributed to chain scissioning at higher fluence which results in an increase of free radicals and unsaturations [34-35]. This increase in capacitance in turn increases the dielectric constant ( $\epsilon'$ ) with the increase in fluence.



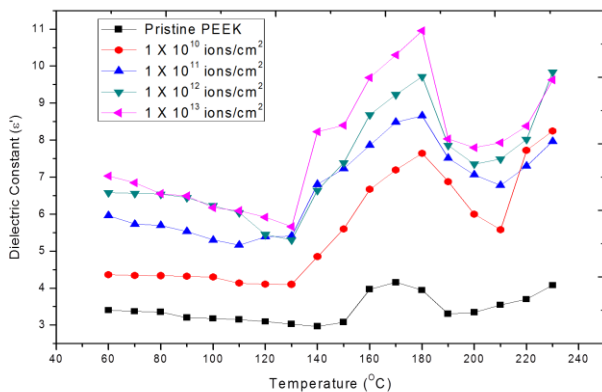
**Fig. 3.** Variation of dielectric constant ( $\epsilon'$ ) with temperature for Pristine PEEK and  $C^{5+}$  (70 MeV) irradiated samples of PEEK at frequency 100 Hz.



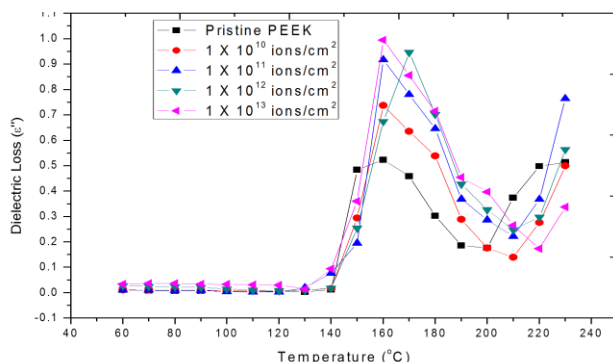
**Fig. 4.** Variation of dielectric constant ( $\epsilon'$ ) with temperature for Pristine and  $C^{5+}$  (70 MeV) irradiated samples of PEEK at frequency 1kHz.



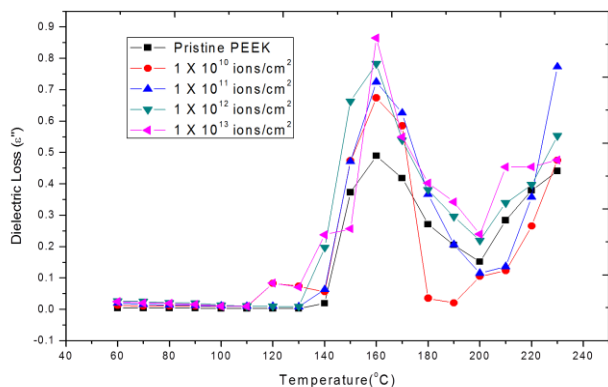
**Fig. 5.** Variation of dielectric constant ( $\epsilon'$ ) with temperature for Pristine and  $C^{5+}$  (70 MeV) irradiated samples of PEEK at frequency 10 kHz.



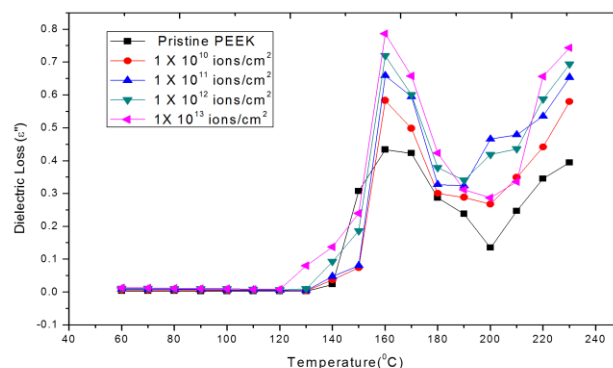
**Fig. 6.** Variation of dielectric constant ( $\epsilon'$ ) with temperature for Pristine and  $C^{5+}$  (70 MeV) irradiated samples of PEEK at frequency 100 kHz.



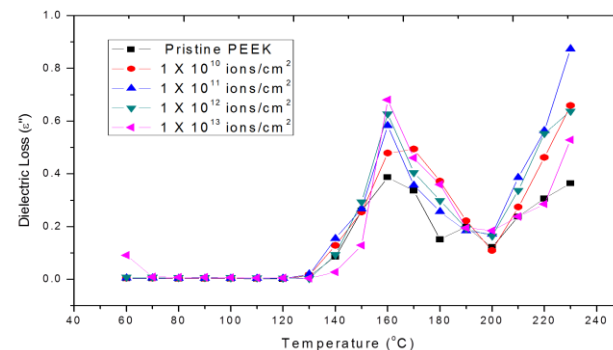
**Fig. 7.** Variation of dielectric loss ( $\epsilon''$ ) with temperature for pristine and irradiated and  $C^{5+}$  (70 MeV) samples of PEEK at frequency 100 Hz.



**Fig. 8.** Variation of dielectric loss ( $\epsilon''$ ) with temperature for pristine and  $C^{5+}$  (70 MeV) irradiated samples of PEEK at frequency 1 kHz.



**Fig. 9.** Variation of dielectric loss ( $\epsilon''$ ) with temperature for pristine and  $C^{5+}$  (70 MeV) irradiated samples of PEEK at frequency 10 kHz.



**Fig. 10.** Variation of dielectric loss ( $\epsilon''$ ) with temperature for pristine and irradiated samples of PEEK at frequency 100 kHz.

## Conclusion

The dielectric constant ( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) of pristine and  $C^{5+}$  ion irradiated samples of the PEEK have been investigated with the variation of temperature at different frequencies (100 Hz, 1 kHz, 10 kHz and 100 kHz). The dielectric constant is found to decrease with the increase in temperature (60 °C to ~ 150 °C) in accordance with the Kirkwood model. The sharp increase in dielectric constant with temperature above 150 °C is indicating the onset of  $\alpha$ -relaxation process supports the results by TSDC analysis of the PEEK samples. The maxima are obtained around 170 °C. This relaxation is linked with the movement of ketone ( $>C=O$ ) dipoles linked to the main chain. The dielectric constant ( $\epsilon'$ ) decreases with the increase in temperature in the range 170 °C to 200 °C due to decrease in cooperative interaction. The dielectric constant increases sharply with temperature beyond 200 °C due to strong ionic conductivity and space charge polarization in this region.

The dielectric loss peak starts around 140 °C, that is also confirmation of the glass transition temperature and  $\alpha$ -relaxation due to polar group attached to the main chain of the PEEK. The movement of ketone group provides the polarizability of the polymer. Hence, it is expected that the dielectric loss will have a significant increase directly after glass transition temperature. The electric field is no longer effective in dipole alignment, and result of increasing temperature further above  $T_g$  is to randomize the dipoles more, causing a decrease in dielectric constant

and dielectric loss. The decrease of dielectric constant( $\epsilon'$ ) and dielectric loss ( $\epsilon''$ ) with increasing frequency at a fixed temperature may be attributed to relaxation or inability of dipoles to rotate rapidly leading to a lag between frequency of oscillating dipoles and that of applied field.

The irradiation of polymers increases the orientational polarization due to increase in number of dipoles with fluence. The increase in maxima or peak height with increasing fluence which is also supported by the TSDC analysis, suggests that shallow energy traps have been created having a transition in the vicinity of  $\alpha$ -relaxation. Broadening of peak of dielectric constant with increasing fluence indicates the overlapping of a large number of different relaxation periods of segmental motions of the polymer chain or of dipoles that are rigidly coupled to main molecular chain. The dielectric loss ( $\epsilon''$ ) increases with increasing fluence because it is associated with electronic transitions that are more pronounced when more electrons participate in electron-hopping process between the amorphous zones created upon polymer destruction. The introduction of crosslinks leads to a decrease in the conformational freedom of the chains and results in areas of restricted mobility in the vicinity of the crosslink junctions. The increase in dielectric loss ( $\epsilon''$ ) and dielectric constant ( $\epsilon'$ ) is attributed to chain scissioning at higher fluence which results in an increase of free radicals and unsaturations.

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