International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2022): 7.942

High Dose Gamma Radiation Induced Modifications in Chemical, Electrical and Morphological Properties of PES Polymer

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Abstract: ***Polyethersulfones is a high temperature amorphous engineering material with excellent thermal properties and have an ability to retain many mechanical and electrical properties up to 200^{o}C temperature. We have studied the Chemical, Electrical and Morphological properties of virgin and high dose (500-2000 kGy) γ-irradiated samples of PES polymer. The polymer samples were analysed by using Fourier transforms infrared (FTIR) spectrophotometer, with 0.5 wave number resolution in the range (4300-500 cm^{-1}). While comparing the FTIR spectra the increase in the intensity of the characteristic bands may be attributed to breakage of chemical bonds and elimination of low molecular gases due to gamma irradiation. The dielectric studies were carried out by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range of 10 Hz–30 MHz at ambient temperature. In this study it is found that with increase of radiation dose the dielectric constant increases may be due to scissioning of polymer chains and the migration of long lived radicals from crystalline region to amorphous region. The surface morphology of PES polymer was characterized by scanning electron microscope (SEM) using (JEOL, Model No. 3300) operating at 30 kV accelerating voltage. The size of the blisters are found to be increased with the increasing of irradiation dose, may be due to the increasing gas pressure near the top surface of the sample. From the SEM micrographic, significant changes observed only when the micrographs of gamma irradiated PES polymer samples are compared with the virgin sample.***

Keywords: Gamma irradiation; PES; FTIR; Frequency Impedance Analyzer; SEM

1. Introduction

PES polymer gets its name because of the presence of ether groups and sulfone group in its backbone chains as shown in Fig. 1.1. PES polymer has high glass transition temperature, possibly due to very stiff sulfone group in the structure. The crystalline property is to be expected in PES polymer because of a hard benzene ring and soft ether bonds in the structure.

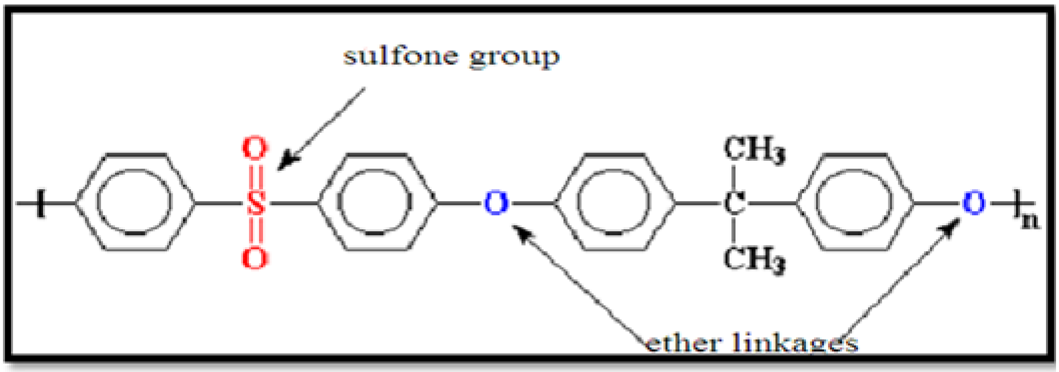


Figure 1.1: Molecular structure of PES

Due to its thermal stability and retentive nature of mechanical and electrical properties, PES is widely applicable in cooling system fans, relay and switch bodies, injection moulded printed circuit boards, lamp reflectors, hot water meters and valves, electrically heated styling brushes, laboratory centrifuges, lamps and reflectors, dental equipment’s, electrical components, weapon system components, plastic bearing cages and radomes oven components, etc.

Now a days, the effect of irradiation on polymers is one of the important fields for altering the properties of polymers like electrical, optical, chemical, mechanical, etc. [1,2]. Several methods have been used to improve the properties of the polymers like electron beam, ion bombardment and gamma irradiation [3-6]. Although a lot of work has been done to investigate the effect of ion beam irradiation on polymeric materials, but the dependence of resulting parameters related to ionizing radiations have not been completely understood so far. Gamma irradiation provides a unique way to modify the chemical, structural, optical, mechanical and electrical properties of the polymers by causing irreversible changes in their macromolecular structure [7-9]. Gamma rays irradiations lead to disruption of chemical bonds and ejection of hydrogen atoms while formation of double bonds – C= C– initiates their clustering [10, 11].

The Polyethersulfones (PES) polymer materials can also be modified to change their optical, electrical and electrochemical properties by irradiating with electromagnetic radiations such as X-rays and γ-rays through grafting and scissioning. The usefulness of these changes so formed depends upon the polymer structure and the experimental conditions of irradiation [12].

The knowledge of optical properties of polymers is needed for the fabrication of LEDs, optical sensors, antireflective coatings, etc. This justifies the need for studying the irradiation effects on the optical properties of the polymers such as optical energy band gap. The gamma radiation of heavy dose normally destroys the initial structure of the polymers and leads to chain scission, chain aggregation, formation of double bonds and molecular emissions. As a consequence of this the polymer properties are modified. The knowledge about the crystallinity of the polymers is justified as it determines the transport properties [13].

In general, the crystalline phase is regarded as resistant and the permeability in a semi-crystalline polymer is substantially lower than the amorphous, because of the reduced space available for diffusion and the winding path around the crystallite [14].

The absorption of radiation energy in sufficient amounts will affect the number of charge carriers in insulating materials to an extent as determined by its molecular structure and chemical composition. Since the dielectric property of the insulating materials depends upon the mobility of the charge carriers present in its structure, the best dielectric materials are those which contain a minimum of charge carriers. However, the potential charge carriers may be formed by the splitting of covalent, atomic or molecular bonds under the influence of the energetic ions. The dielectric response of a material provides information about the orientation and translational adjustment of mobile charges present in the dielectric medium in response to an applied electric field.

The most important property of dielectric materials is its ability to be polarized under the action of the field. The dielectric loss behaviour of polymer films is very important because of their possible applications for insulation, isolation and passivation in micro-electronic circuits [15]. Polyethersulfone (PES) is finding extensive use in electronics due to its excellent dielectric property. The dose rate effects on the electrical properties of several other polymers including that of PES have been studied by Wang et al. [16]. The reported value of chemical response of 1.25 MeV γ- irradiated PES shows that with increasing radiation dose the average free volume and intensity of the absorption band decreases [17, 18].The morphology of the polymer is also found to change with increasing radiation dose.

2. Experimental Details and Analytical Techniques

The semi-crystalline pure research grade Polyethersulfone (PES)sheets of thickness 250 µm were procured from MS Good fellow U.K. and were used without any further treatment. The polymer samples of size (2 x1) cm^2 were cut from the commercially available sheet. One sample was kept virgin and other four samples were subjected to irradiation. The samples were irradiated using 1.25 MeV Gamma radiation (the average energy of the two 60-Co photons) source of Co^{60} in the radiation chamber (which is in a form of a cylindrical chamber of 14 cm length and 10 cm diameter) with dose rate 4 kGy/h and source strength 2 K Curie from UGC– DAE Consortium for Scientific Research, Kolkata Centre, Kolkata. The irradiated samples were characterized by using the analytical techniques like, SEM, FTIR spectroscopy and High Frequency Impedance Analyzer (HFIA), to observe the possible modifications that could take place in PES polymer by irradiation.

3. Chemical Study (FTIR Spectroscopy)

Chemical modifications were evaluated using Perkin Elmer, Fourier transform infrared (FTIR) spectrophotometer, Model 1720 with 0.5 wave number resolution in the range (5000 – 500 cm^{-1}). FTIR spectroscopy was carried out to monitor scissioning of various bonds and formation of new functional groups, especially with regard to oxidation.

4. Electrical Response (High Frequency Impedance Analyzer)

The dielectric studies were carried out by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range (10 Hz–30 MHz) at ambient temperature. The impedance analyzer was equipped with a small furnace for a high temperature measurement. The data generated from the instrument were collected through an interface between instrument and the computer using data acquisition and control software PSM 1735.

5. Surface Morphology (SEM)

The surface morphology of PES polymer was characterized by scanning electron microscope (SEM) using (JEOL, Model No. 3300) operating at 30 kV accelerating voltage. Surface of the samples were coated with a thin layer of gold (3.5 nm) by using vacuum evaporation technique to minimize sample charging effects due to the electron beam of the SEM.

6. Results and Discussion

The summarized results obtained from the Fourier Transform Infrared Spectroscopy (FTIR), High Frequency Impedance Analyzer and Scanning Electron Microscope (SEM) characterizations of virgin and gamma irradiated PES polymer samples have been discussed separately as under:

6.1 Chemical Studies (FTIR)

The Fourier Transform Infrared spectrum of pristine and gamma irradiated PES polymer samples with dose level 500 kGy, 1000 kGy, 1500 kGy and 2000 kGy are shown in Fig.6.1The FTIR spectra show that the overall structure of the polymer remains same due to gamma irradiation but very small changes have been observed at higher doses. This indicates that inter-chain separation is not very much affected by the gamma dose. The peak positions remain almost unshifted, but only the absorbance values of the functional groups changes after irradiation. This kind of changes might be as a result of decrease in the concentration of already existing bonds.

The absorption bands as obtained from the unirradiated sample are identified at (a) 550 cm^{-1}, (b) 750 cm^{-1} (c) 2100 cm^{-1} and (d) 3100 cm^{-1} may be due to CH_2 absorption, C–H bending vibration, C=S stretching vibration and C=O stretching vibration, respectively. In addition to the above mentioned bands, the ring vibration of p-substituted phenyl ether shows band at 1050cm^{-1}.The aromatic bending vibration and stretching vibration respectively are also reported in some other polymers in the literature [19-20].While comparing the FTIR spectra of virgin sample with irradiated samples we observe that there is no change or shift in the spectrum of irradiated PES polymer samples, except a slight change in the intensities of some identified peaks. The results we obtained from the above study are well in agreement with the previous results [21]. The increase in the intensity of the characteristic bands may be attributed to breakage of chemical bonds and elimination of low molecular gases due to gamma irradiation. Such type of reaction might have taken place in the chamber during irradiation, as the vacuum of few micro torr is not sufficient to remove all the oxygen/H_2O (moisture) contents.

The observed results from the FTIR studies indicate that PES polymer is resistant to gamma radiation over the entire irradiation process.

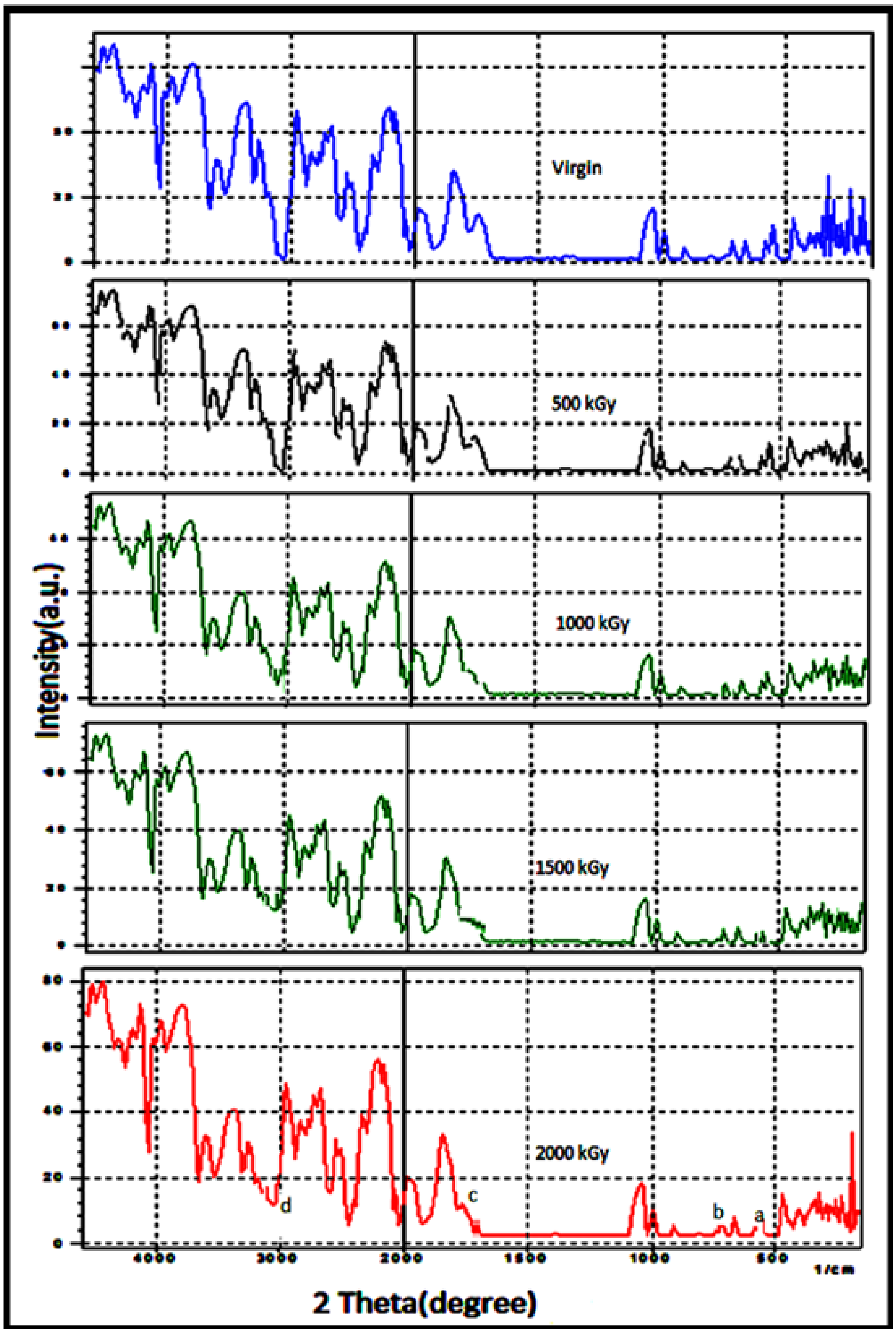


Figure 6.1: FTIR spectra of virgin and gamma irradiated PES polymer samples

6.2 Electrical studies

For the electrical measurements the virgin and irradiated polymer samples were examined for dielectric loss(δ), dielectric constant (ε_r) and A C conductivity by using High Frequency Impedance Analyzer (PSM 1735) over the frequency range (10 Hz-30 MHz) at ambient temperature. The different data obtained were plotted as a function of log of frequency as shown in Figs.6.2 to 6.5

The A C conductivity vs log of frequency plot for all the five samples are shown inFig.6.2The result shows that A C conductivity decreases in the lower frequency range due to the formation of some defects in the energy gap as a result of gamma irradiation. These defects create barriers against the motion of charge carriers already existing in virgin polymeric materials [22].

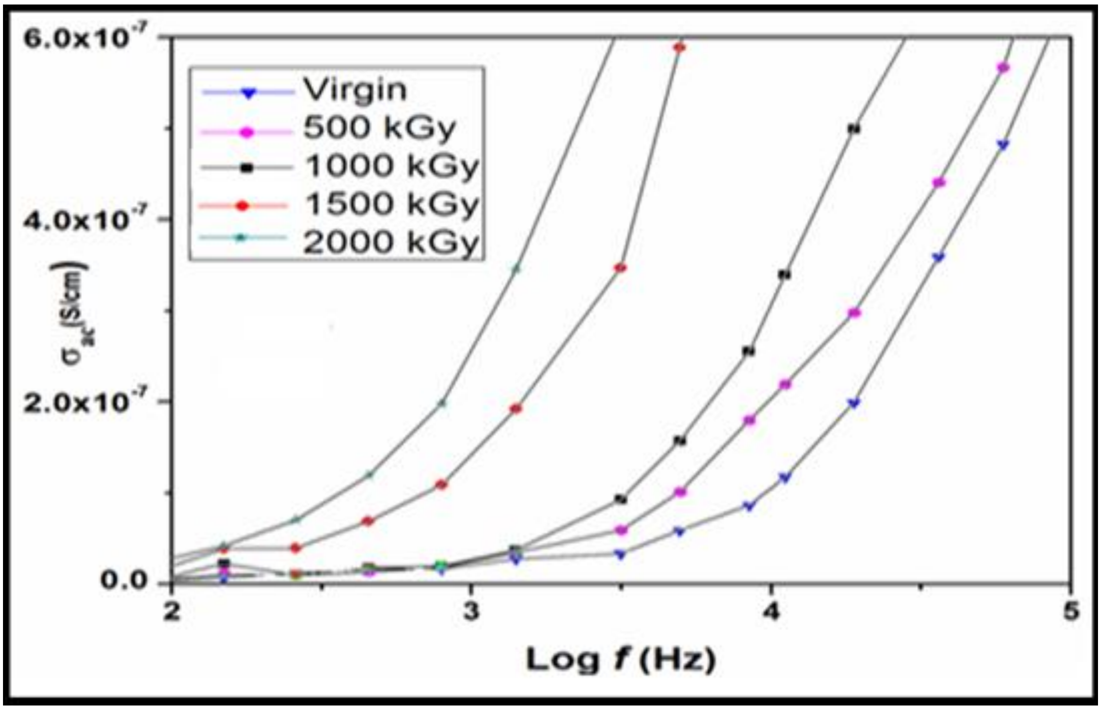


Figure 6.2: AC Conductivity vs log of frequency plot for virgin and irradiated PES polymer samples

A sharp increase in the A C conductivity between the frequency range Log 2- Log 4 has been observed in virgin as well as irradiated PES polymer samples with the increase of irradiation dose. The increase in conductivity at a given frequency due to irradiation may be attributed to scissioning of polymer chains and the migration of long lived radicals from crystalline region to amorphous region, resulting in an increase of free radicals, unsaturation, etc. The A C field of sufficiently high frequency may cause a net polarization, which is out of phase with the applied field. This results in an increase of A C conductivity at relatively higher frequency side [23].

Fig. 6.3 shows the plot of tan δ (dissipation factor) vs Log of frequency for virgin and irradiated PES polymer samples. From the graph it is observed that tan δ factor decreases as the frequency increases [24]. However, the increase in losses (with increasing dose) at low frequency (Log 3.5Hz) could be associated with the polarization due to bound/trapped space charges. With increase in frequency, polarization decreases and becomes vanishingly small at relatively higher frequency. The increase in dielectric loss as the dose increases from 500 kGy to 2000 kGyis attributed to chain scissioning.

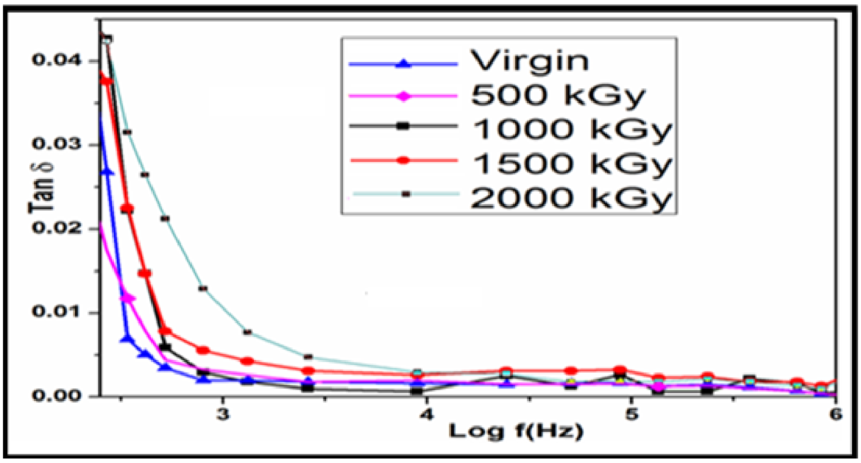


Figure 6.3: Variation of tan δ with log of frequency for virgin and irradiated PES polymer samples

Fig.6.4 shows the plot of dielectric constant vs log of frequency for virgin and irradiated PES polymer samples. The plotted graphs indicate that the dielectric constant (ϵ_r) remains almost constant at low frequency side and decreases relatively at higher frequencies [25]. The constant portion of the graph in the lower frequency range (Log 2-Log3.5), it is expected that the space charge distribution remain unaltered and thus dielectric constant is uniform. However, at relatively higher (Log 6.25) frequency, a redistribution of the bound/trapped space charge takes place, causing a decrease in the dielectric constant. The decreasing behaviour of the dielectric constant at higher frequency side was also reported earlier [26].The decrease in dielectric constant can also be explained by Jonscher's Power Law. It is also found that with increase of radiation dose the dielectric constant increases may be due to scissioning of polymer chains and the migration of long lived radicals (which are trapped mostly in crystalline region) from crystalline region to amorphous region.

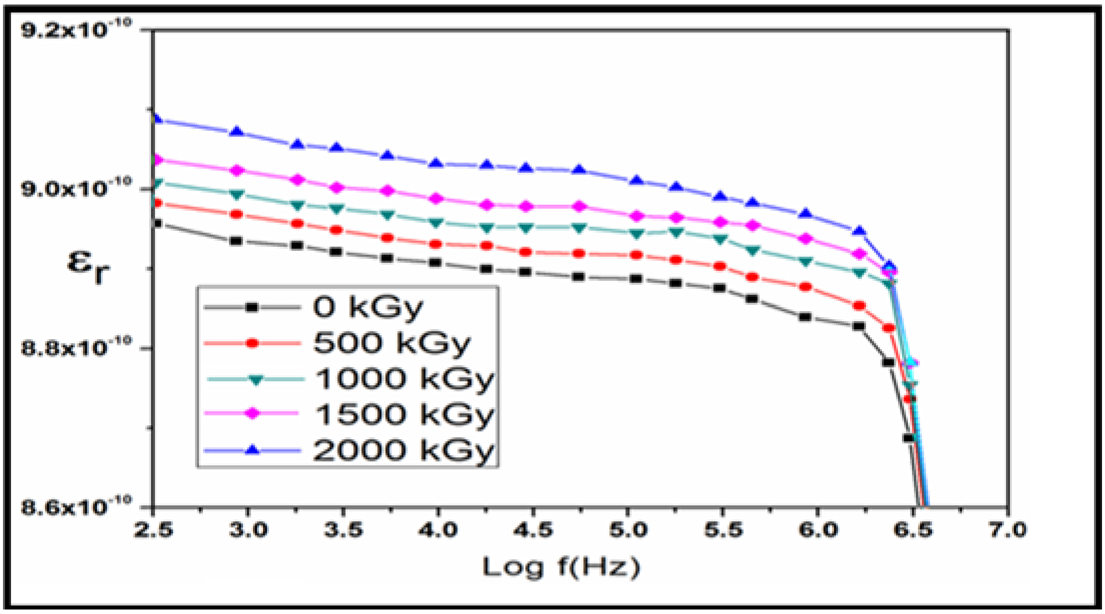
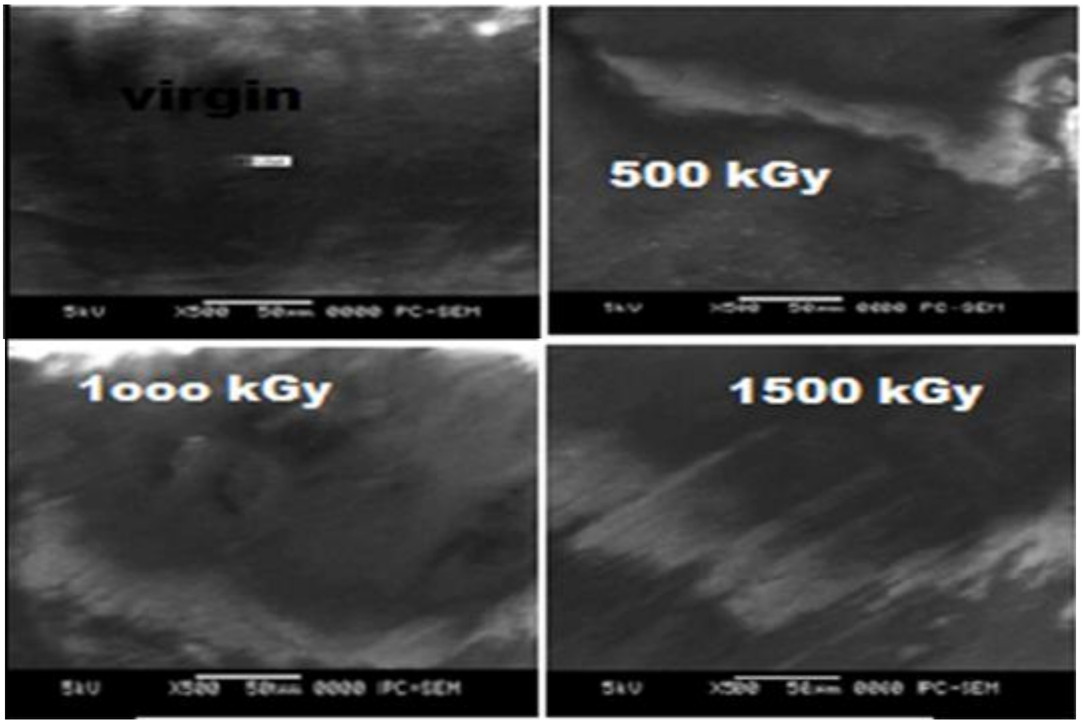


Figure 6.4: Plot of dielectric constant vs log of frequency for virgin and irradiated PES polymer samples

6.3 Surface Morphology of PES Polymer

Surface Morphology of the polymer was studied using SEM. It provides us qualitative information regarding the cross-sectional morphology of the virgin and the irradiated samples. Scanning electron microscope (SEM) cross-sectional images of virgin and irradiated PES polymer samples at dose level 500 kGy, 1000 kGy, 1500 kGy and 2000 kGy are shown in Fig. 6.5The SEM picture of the virgin PES polymer sample shows that the overall surface is smooth throughout the scanned region.



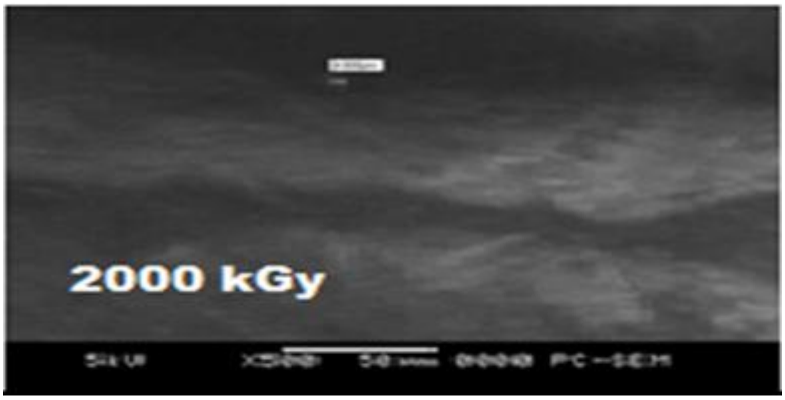


Figure 6.5: SEM images of virgin and gamma irradiated PES polymer samples

The SEM micrograph shows that the small size blisters are formed on the surface of PES polymer sample when irradiated at a dose level of 500 kGy. The size of the blisters are found to increase with increasing irradiation dose, may be due to the increasing gas pressure near the top surface of the sample. This result suggests that the nucleation density of bubbles saturates after a certain irradiation dose, and prolonged irradiation results only in their growth [27].From the SEM micrographic studies, significant changes could be observed only when the micrographs of gamma irradiated PES polymer samples are compared with the virgin sample.

7. Conclusions

Modifications induced under 1.25 MeV gamma radiations source of Co^{60} in PES polymer samples was studied by using UV-Visible spectroscopy, XRD, FTIR spectroscopy, High Frequency Impedance Analyzer and SEM techniques. The following conclusions have been drawn:

The FTIR spectrum of PES polymer shows no major change except a small increase in the intensities of some identified band due gamma irradiation. The results obtained from the FTIR spectra suggest that the inter-chain separation is not much affected by gamma irradiation.

A decrease in the lower frequency range as well as an increase at higher frequency side was observed in A C conductivity, however it was also found to increases with increasing irradiation dose. The dielectric loss increases at lower frequencies and decreases at higher frequency side was found in virgin as well as irradiated samples. The space charge remains unaltered at lower frequencies and redistributed at higher frequencies. Similar results were observed in the dielectric constant study.

The qualitative information of SEM crossectional morphology of virgin sample shows that the overall surface of PES sample is smooth. The sequential developments of blisters are shown on the surface of the irradiated polymer samples. It is possibly due to evolution of gas atoms causing plastic deformation of the surface layer. The increase in surface area of the blisters was observed due to increasing the dose level.

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