STUDIES OF OPTICAL AND ELECTRICAL PROPERTIES OF GAMMA IRRADIATED POLYETHERSULFONE (PES) POLYMER

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ABSTRACT

The Optical and Electrical properties of 1.25 MeV gamma rays energy irradiation on Polyethersulfone (PES) polymer were studied by using Ultraviolet/ Visible (UV/VIS) absorption spectroscopy, and the electrical properties has been studied by using High Frequency Analyzer Impedance Techniques, The conducting behavior of Polymer were investigated by the impedance spectroscopy at ambient temperature. The variation of dielectric permittivity and dielectric loss with frequency was carried out at ambient temperature. There is an exponential increase in a.c. conductivity with log frequency and the effect of irradiation is significant at higher doses. The dielectric permittivity and dielectric loss is observed to change significantly due to irradiation. It has been found that dielectric response in both virgin as well as irradiated samples obey the Jonscher's power law. The band gap has been calculated from the UV-VIS spectra shows an appreciable change.

KEYWORDS: PES, Dielectric, UV-VIS spectroscopy, Gamma radiation**.**

INTRODUCTION

Polymers have proven their potential in all fields of life like household to space craft and also in the fields of medical sciences, electronics and Nuclear technology. Polyethersulfone (PES) is a heat-resistant, transparent, amber, non-crystalline polymer. The most characteristic feature of PES polymer is that it has better high-temperature properties than the conventional engineering plastics. Specifically, PES polymer remains in satisfactory condition in long-term continuous use without causing any dimensional change or physical deterioration at temperatures as high as 200ºC. Use of radiation in polymers has great importance because it helps in achieving some desired improvements in the polymer properties. Gamma radiation treatment provides a unique way to modify the chemical, structural, optical, mechanical and electrical properties of the polymer by causing irreversible changes in their macromolecular structure [1-6]. Numerous studies reported in the past few decades demonstrate that the interaction of ionizing radiations-induced modifications with PES polymers leading to a wide variety of property changes [7-11]. Many investigators have studied the effect of different energy ion beam irradiations on the physical, electrical and chemical properties of PES polymer. Such irradiations cause the photons to penetrate the material, breaking the polymer chains and creating free radicals. These free radicals can also recombine to create crosslinks between the adjacent molecules. Crosslinked materials have been found to improve their long term performance. Different studies of effect of ion irradiation on polymers reveal a variety of modifications of electrical, optical and chemical compositions including processes such as main chain scission, intermolecular cross linking, creation of unsaturated bonds, formation of volatile fragments and creation of carbonaceous clusters Kazuo *et al.* [12], Nilam *et al.* [13] Xianqiang et al. For ion beam irradiation, the following aspects are well established: (1) Energy loss LET (dE/dx) by charge particle in the material medium (electromagnetic interaction, high concentration of excited and ionized target atom) is differential in nature and hence energy deposited is non-homogeneous in nature. It is confined to the beam diameter only. However, the gamma irradiation have been found to have the ability to expose the whole area of the sample and hence expected to create homogeneous modification in it. Although a lot of work has been done to investigate the effect of ion irradiation on polymeric materials but the dependence of effect parameters related to ionizing radiation has not been completely understood so far. In this article, we report the results of electrical and chemical changes

produced by 1.25 MeV gamma ray irradiation induced modifications in PES polymer. The molecular structure PES polymer is shown below
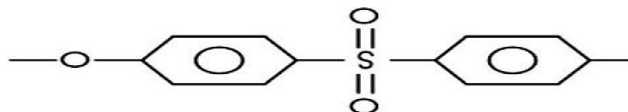
EXPERIMENTAL

The Polyethersulfone (PES) polymer sheets of thickness 200 μm were obtained from Messrs Good Fellow, Cambridge, and U.K were used without any further treatment.

Co[60]Gamma ray irradiation

The polymer samples of size (1×1) cm^2 were cut from the commercially available sheet. One sample was kept as virgin and the other four samples were subjected to irradiation. The samples were irradiated using 1.25 MeV Gamma radiation source of Co^{60} in the radiation chamber (which is in a form of cylindrical chamber of 14 cm length and 10 cm diameter) with dose rate 4 kGy/h and source strength was 2 K Curie. The samples were irradiated in the dose range of 16 kGy to 300 kGy at UGC – DAE Consortium for Scientific Research, Kolkata Centre, Kolkata. The irradiated samples were characterized by using two analytical techniques like UV-VIS spectroscopy, High Frequency Impedance Analyzer (HFIA), and to observe the possible changes/modifications that could take place in the PES polymer by irradiation.

Optical Response (UV-VIS spectroscopy)

The optical changes were analyzed by UV-VIS spectroscopy (UV 1601 PC) in the wavelength range 190–900 nm to observe the energy gap (E_g) variation with increase of dose.

Electrical Response (PSM 1735 High Frequency Impedance Analyzer)

The electrical properties of all samples (virgin and irradiated) were also studied. The dielectric loss and dielectric constant measurements were carried out by using PSM 1735 High Frequency Impedance Analyzer over the frequency range 1 mHz to 10 MHz at room temperature. The a.c. conductivity was calculated using the relation

$$\sigma = (2\pi f C_p D t) \, A^{-1} \, (\Omega^{-1} \, cm^{-1}) \tag{1}$$

The dielectric constant was calculated using the relation

$$\varepsilon = C_p / C_\infty$$

where C_p is the capacitance measured using the PSM 1735 High Frequency Impedance Analyzer, f is the frequency, D is the dielectric loss and $\varepsilon = \varepsilon_o A/t$, where ε_o is the permittivity in vacuum and A and t are the cross- sectional area and thickness of the sample, respectively.

RESULTS AND DISCUSSION

To keep the treatment simple and unambiguous, the results of the present study have been discussed separately.at 300 kGy, the blister exfoliation can be seen at the highest dose of gamma radiation.

UV-Visible Spectral Response

The absorption of light energy by polymeric materials in UV and visible regions involves transition of electrons in σ, π and n- orbital's from the ground state to the higher energy states. Ultraviolet-visible (UV/VIS) spectroscopy has become an important tool for investigating these electronic transitions. It is used to estimate the value of optical energy gap (E_g) in polymers. The results of absorption studies with UV/VIS spectrophotometer carried out on virgin as well as irradiated PES polymer samples are shown in Figures 1. The optical response of virgin and irradiated PES polymer samples at various doses is shown in figure 1. It is clear from the figure that the absorption edge is shifted towards the higher wavelength side from 415 to 450 nm. This shift may be correlated with the formation of conjugated bonds showing the possibility of

formation of carbon clusters. This type of transition occurs in non bonding electron containing compounds and also in aromatic compounds due to bond cleavage and reconstruction [8, 14-18].

Urbach Rule

The absorption coefficient near the band edge for non – crystalline materials shows an exponential dependence on the photon energy ($h\nu$) given by the expression known as Urbach formula [19]

$$\alpha(\nu) = \alpha_o \exp(h\nu/E_u) \qquad (2)$$

The exponential absorption edge (known as Urbach's rule) observed in most materials is interpreted in terms of thermal fluctuations in the band-gap energy. In eq. 2, α_o is a constant, E_u is an energy which is interpreted as the width of the tail of localized state in the forbidden band gap, ν is the frequency of radiation and h is Planck's constant. The origin of E_u is supposed to be due to thermal vibrations in the lattice [20]. The logarithm of the absorption coefficient $\alpha(\nu)$ was plotted as a function of the photon energy ($h\nu$) for irradiated PES polymer samples with different doses of gamma rays as shown in Figure 2. The value of the Urbach energy E_u in each case was calculated by taking the reciprocal of the slope of the linear portion in the lower photon energy region of these curves and is and also shown in Figure 3. The increases in Urbach's energy in the case of PES polymer may be due to decreases in the amorphous nature of the polymer at higher doses.

Determination of Band Gap

The absorption edge of semi crystalline materials gives the measure of the band strength or band gap E_g, and the position of the sharp absorption edge is

$$E_g = hc/\lambda_g \qquad (3)$$

Where h is the Planck's constant, c is the velocity of light and λ is the wavelength. The present polymer obeys the rule of indirect transition as well as direct transition [21]. The equation 4 gives the relationship among the optical band gap, absorption coefficient and incident photon energy as

$$\alpha(h\nu) = B(h\nu - E_g)^n / h\nu \qquad (4)$$

where $h\nu$ is the photon energy of the incident photons, B is constant, E_g is the value of the optical energy gap between the valance band and the conduction band, n is the power, which characterizes the electronic transition, whether it is direct or indirect during the absorption process in the k-space. Specially, n is 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The variation of $(\alpha h\nu)^{1/2}$ with photon energy ($h\nu$) for PES polymer is shown in figure 6.

ELECTRICAL RESPONSE

The ac conductivity measurement was performed for virgin and irradiated PES polymer samples and the corresponding graph is shown in figure 2. A sharp increase in conductivity has been observed in virgin as well as irradiated PES polymer samples as dose increases. The increase in conductivity at a given frequency due to irradiation may be attributed to scissioning of polymer chains, resulting in an increase of free radicals, unsaturation, etc. An ac. field of sufficiently high frequency may cause a net polarization, which is out of phase with the applied field. This results in a.c. conductivity and it appears at frequencies greater than that at which traps are filled or emptied (15, 16). Figure 3. Shows a plot of tan δ (dissipation factor) vs log frequency for virgin and irradiated PES polymer samples. It is observed that loss factor decrease as frequency increases moderately with increasing dose. The increase in loss factor with dose may be due to scissioning of polymer chains, resulting in an increase of free radicals unsaturation, etc. Figure 4. shows a plot of dielectric constant (ε) vs log frequency at ambient temperature for virgin and irradiated polymer samples. As evident from the graph, the dielectric constant remains almost constant up to 117 kHz and then decreases at higher frequencies. At lower frequency, the mobility of the free charge carriers is constant and thus the dielectric constant remains uniform. As the frequency increases the charge carriers migrate through the dielectric and get trapped against defect sites and induce an opposite charge in its vicinity. At these frequencies, the polarization of trapped and bound charges cannot take place and hence the dielectric constant decreases. The decrease in dielectric constant at higher frequency can also be explained by Jonscher's power law [15].

CONCLUSIONS

The optical and electrical properties of Polyethersulfone (PES) Polymer samples under 1.25 MeV gamma radiation source of Co^{60} have been studied by UV-VIS spectroscopy High Frequency Impedance Analyzer techniques. The following conclusions have been drawn:

- The results of ac. conductivity, dielectric loss (δ) and dielectric constant (ε) of PES polymer samples shown an increasing trend with an increase in gamma ray radiation doses.
- The optical band gap (E_g), and Urbach energy (E_u) were determined from the optical absorption spectra. It is concluded that the values of indirect band gap are lower than the corresponding values of direct band gap in virgin and gamma irradiated PES Polymer samples. Also the band gap (E_g) decreases with the increase of gamma irradiation dose, due to the photo-degradation of PES polymer and the formation of defects and clusters in the material, while the cluster size (number of carbon atoms N per conjugated length) increases with the increase of absorbed dose.
- Optical transmittance has been found to increase in visible as well as infrared regions. The increase of optical transparency indicates that it depends greatly on energy band gap and radiation dose on polymer.

In the experimental studies such as UV-VIS measurements and High Frequency Impedance Analyzer the observed modifications of Polyethersulfone (PES) polymer were found with increasing radiation dose. They attribute to scissioning and crosslinking of the polymer chains, leading to production of free radicals and unsaturated bonds in the polymer matrix upon irradiation.

ACKNOWLEDGMENTS

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Fig-1 (UV/VIS spectra of virgin and 1.25 MeV gamma-irradiated PES polymers)
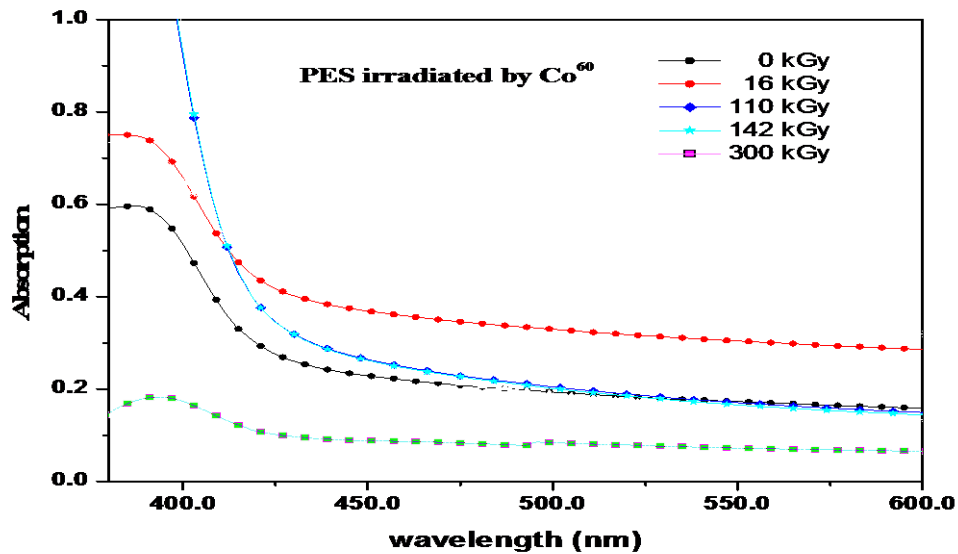
Fig 2 (The a.c conductivity vs log of frequency plot for virgin and irradiated PES Polymers)
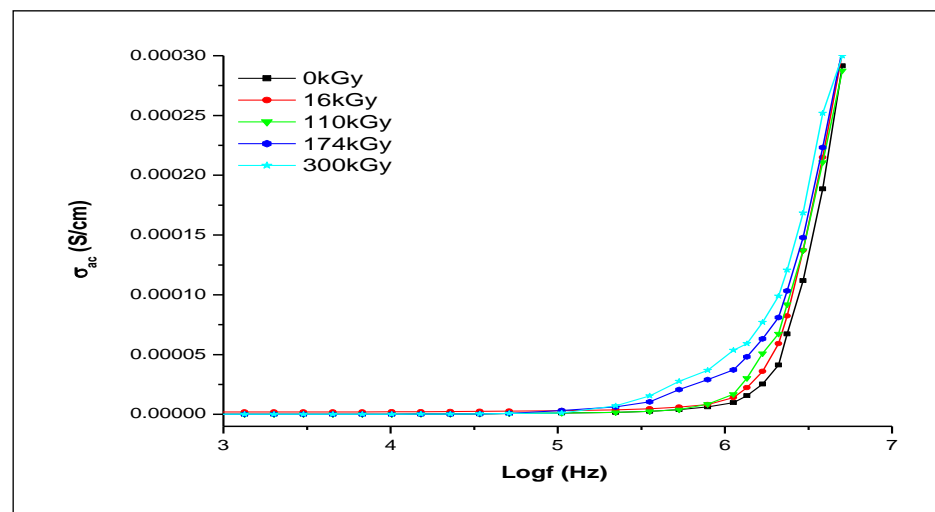
Fig 3   (Plot of dielectric constant vs log of frequency for virgin and irradiated PES   polymers)
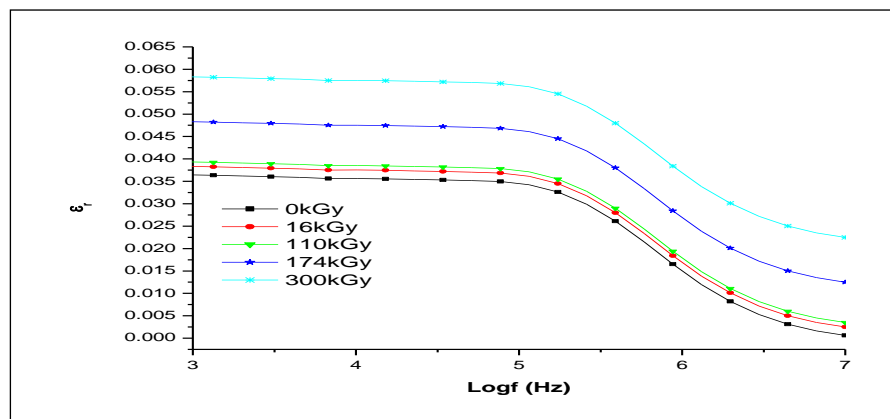
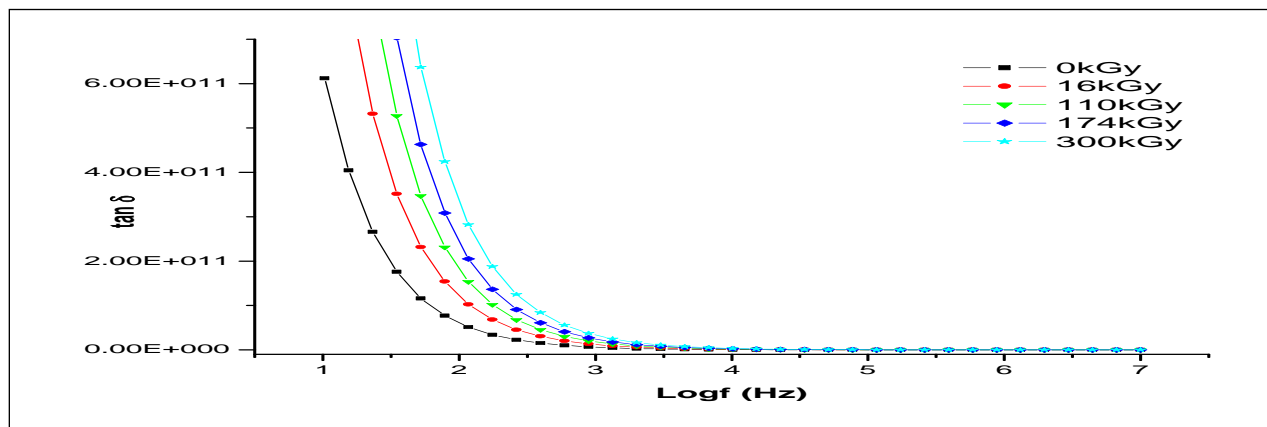**Fig- 4(** Variation of tan δ with log of frequency for virgin and irradiated PES polymers)

Fig. 5 (The dependence of $(\alpha h\nu)^{1/2}$ on photon energy (*hv)* for virgin and gamma irradiated PES polymers
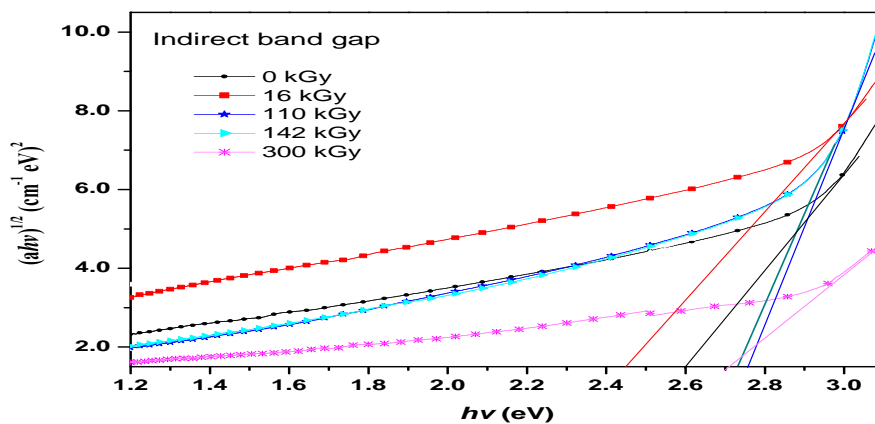
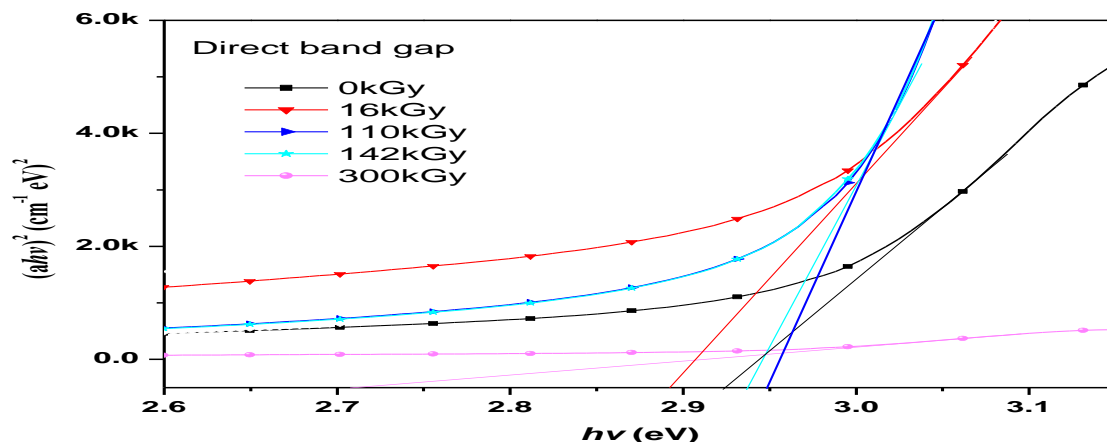**Fig .6 (**The dependence of $(\alpha h v)^2$ on photon energy (*hv)* for virgin and gamma irradiated PES polymers)

Fig. 7 (The dependence of natural logarithm of α on photon energy for virgin and gamma irradiated PES polymers)
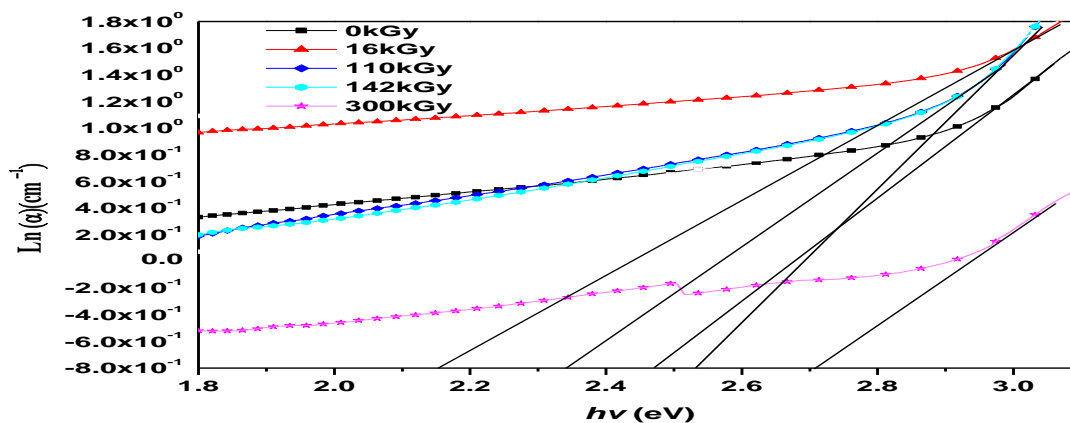

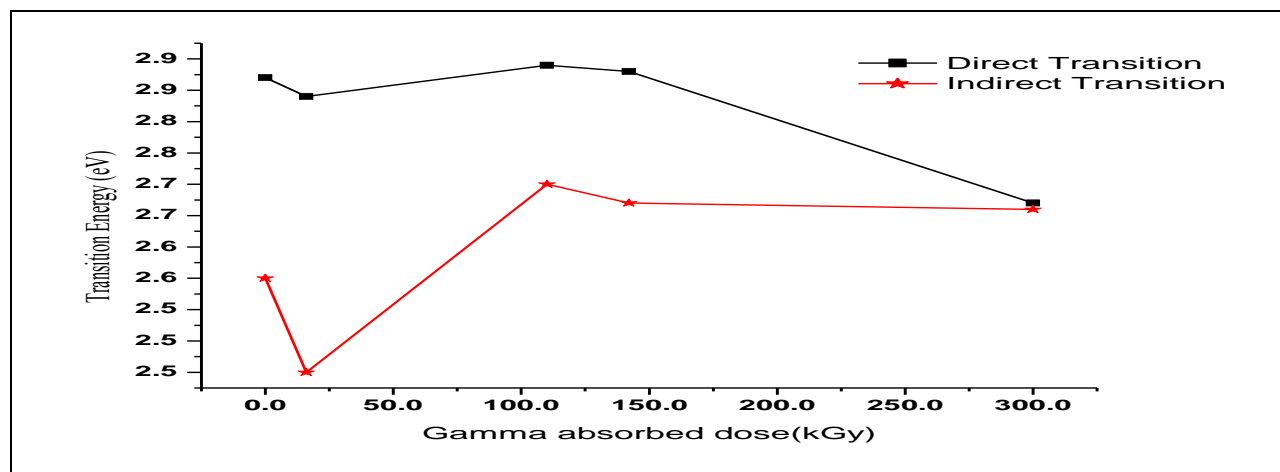**Fig 8 (**Plots for transition energy (eV) as a function of the gamma absorbed dose (kGy

Fig.9 (Gamma radiation dose dependence of optical transmittance spectra virgin and Irradiated PES polymer)