Effect of electron beam exposure on Virgin and Gamma irradiated Polyethersulfone (PES) Polymer

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Abstract: Thispaperintroducesthe useof electronbeam ofscanning electronmicroscope (SEM)toevaluate and asses the change in optical properties ofPolyethersulfone (PES) Polymerunder electron bombardment.The SEMmaybeusednotonlytoobserveasurface imagebut alsotoobtainafine electronbeamforchargingaPES polymersurfacesimultaneously. The optical properties of virgin and gamma irradiated Polyethersulfone (PES) polymer samples exposed by electron beam from SEM were studied by Ultraviolet/ Visible absorption (UV/VIS) spectroscopy. The recorded UV-VIS spectra shows maximum absorption around 395nm of gamma irradiated samples and the maximum absorption is decreases upto 385nm after expose to electron beam, however, the nature of the spectra shows the change and a shift in absorption edge towards the higher wavelength side with increasing γ irradiation dose, but as compare to electron beam effect. The band gap calculated from the optical of both gamma irradiated and electron beam irradiated data shows an appreciable change (decreases of 1eV). The values of electron beam irradiated PES polymer samples band gap have been found to be lower then the corresponding values of gamma irradiated PES polymer samples band gap. Inthisarticle, effect of an electron beam on gamma irradiated Polyethersulfone (PES) polymer samples undera15 keVprimaryelectronbeamenergy of SEMandforamagnification of15 kx.
**Key Words:** PES, Electron Beam, UV-VIS, Gamma radiation.

INTRODUCTION

Polymers have proven their potential in all fields of life and specially in the fields of medical science, electronics and space technology. Polyethersulfone (PES) is a heat-resistant, transparent, amber, non-crystalline polymer. The most characteristic feature of PES polymer is that it has much 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 [1-4]. Numerous studies reported in the past decades demonstrate that the interaction of ionizing radiations-induced modifications with PES polymers leading to a wide variety of property changes. [5-8] 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 improve the long term performance. Different studies of effect of ion irradiation on polymers, reveal a variety of modifications of structural, electrical, optical and chemical compositions including processes such as main chain scission, intermolecular crosslinking, creation of unsaturated bonds, formation of volatile fragments and creation of carbonaceous clusters Kazuo *et al*.[9], Nilam *et al*.[10]. For ion beam irradiation, the following aspects are well established: (1) Energy loss (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 Suveda *et al*. [4]. 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 optical changes/modification produced by electron beam of SEM on 1.25 MeV gamma irradiated PES polymer. The molecular structure PES polymer is shown below
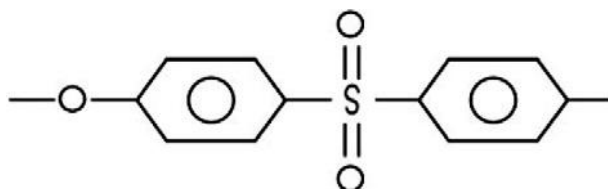
Molecular structure of Polyethersulfone

EXPERIMENTAL DETAILS

The Polyethersulfone (PES) polymer sheet of thickness of 250 μm were obtained from M/S Good Fellow, Cambridge, U.K and were used without any further treatment. The polymer samples of size (1 × 2) 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 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 subjected to a analytical technique like UV-VIS spectroscopy to observe the possible changes/ modifications that could take place in the PES polymer by gamma irradiation and again theses samples irradiated by electron beam of SEM. The electron irradiated samples were again subjected to an analytical technique like UV-VIS spectroscopy to observe the possible changes/ modifications that could take place in the gamma irradiated PES polymer samples by electron beam irradiation. The Optical changes were analysed by UV-VIS spectroscopy (UV 1601 PC) in the wavelength range 200–900 nm

to observe the energy gap (E_g) variation with increase of dose. The morphology of the surface of polymer was characterized by scanning electron microscope using (JEOL, Model No. 3300) operating at 30 kV accelerating voltage. Surface of the samples were coated with a very thin layer of gold (1.5 nm) by using the vacuum evaporation technique to samples and charging effects due to the electron beam has been observed.

RESULT AND DISCUSSION

To keep the treatment simple and unambiguous, the results of the present study have been discussed separately.

UV-VIS Spectral Studies

The absorption of light energy by polymeric materials in UV and visible regions involves transition of electrons in σ, π and n- orbitals 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 gap energy (E_g) in polymers. The results of absorption studies with UV/VIS spectrophotometer carried out on virgin as well as irradiated PES polymer samples as shown in Figures 1, 2 and 3, respectively.
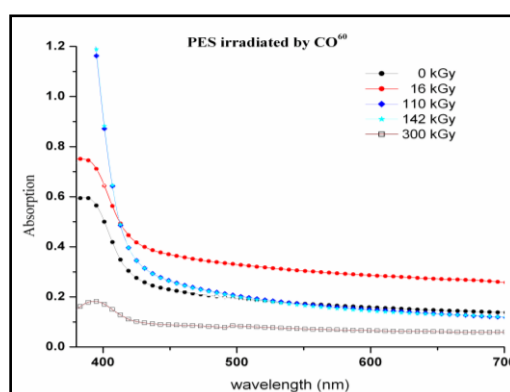

Fig. 1. UV/VIS spectra of virgin and 1.25 MeV gamma-irradiated PES polymers

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, 11-15].
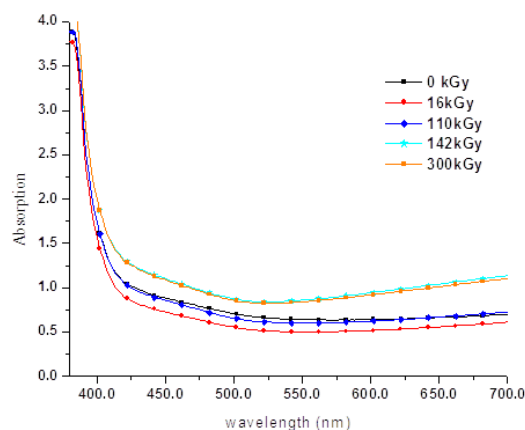
Fig. 2 (SEM irriated)UV/VIS spectra of virgin and 1.25 MeV gamma-irradiated PES polymers

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 [16]

$$\alpha(\nu) = \alpha_o \exp (h\nu/E_u) \qquad\qquad (1)$$
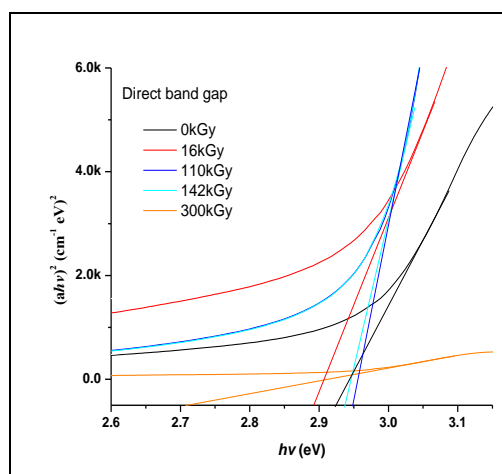

Fig. 3. The dependence of $(\alpha h\nu)^{/2}$ on photon energy ($h\nu$) for virgin and gamma irradiated PES polymers
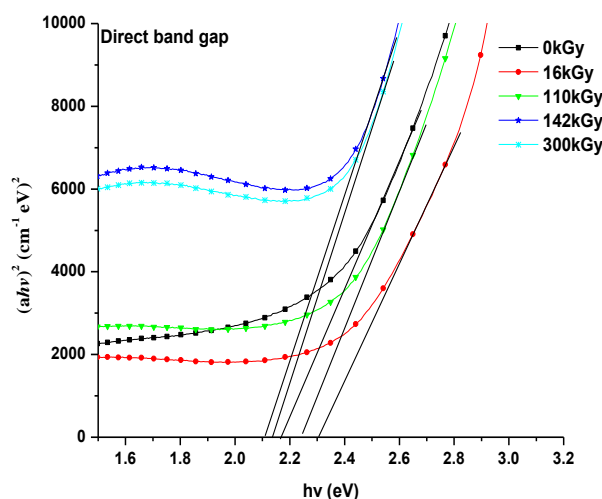
Fig.4

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. 1, 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 [17]. 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 7. 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 listed in Table 1. and also shown in Figure 9. The increases in Urbach's energy in the case of PES polymer may be due to increase in the crystalline nature of the polymer at higher doses.
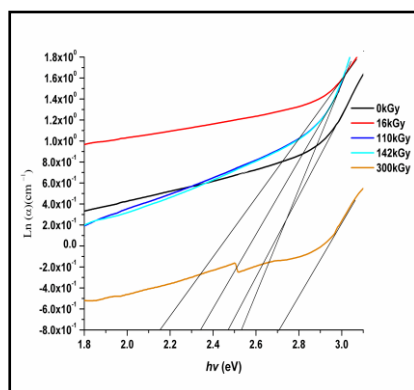
Before Electron beam (Exposed in SEM)

Fig.5

After Electron beam   **(Exposed in SEM)**
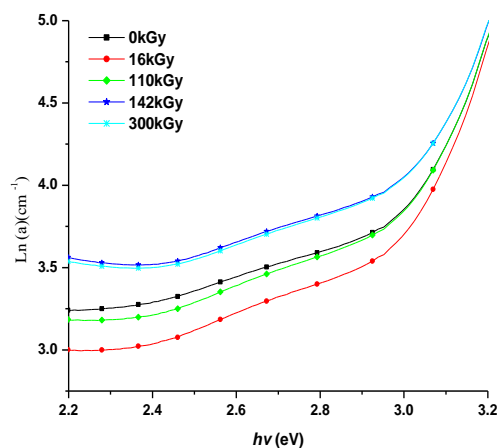

Fig.6

Determination of Band Gap

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

$$E_g = hc/\lambda_g \tag{2}$$

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 [18]. The equation 3 gives the relationship among the optical band gap, absorption coefficient and incident photon energy as

$$\alpha\,(h\nu)=B\,(h\nu-E_g)^n\,/\,h\nu \tag{3}$$

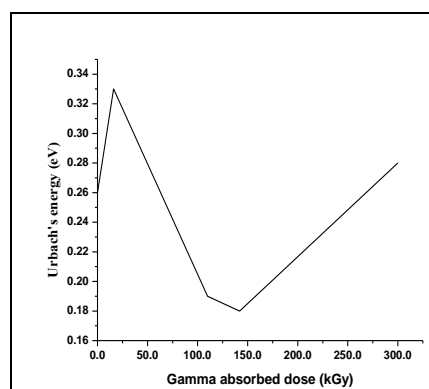**Before Electron beam (Exposed in SEM)**

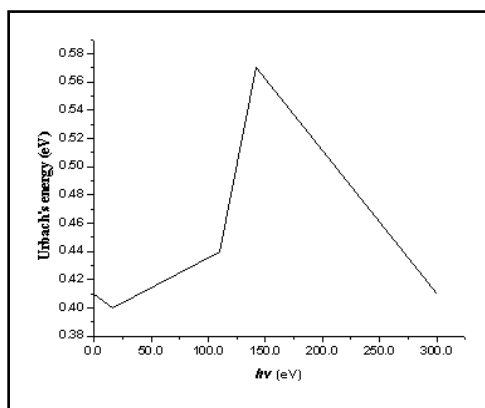**Fig.7**

After Electron beam (Exposed in SEM)

Fig.8

where hν 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 (hν) for PES polymer is shown in figure 2. The value of band gap has been determined by taking the intercept on the x-axis. It is clear that the value of optical indirect band gap decreases at 16 kGy and increases at 142 kGy and again decreases from 142 kGy to 300 kGy. The variation of energy gap with the irradiation dose is provided in Table 1.

The variation of $(\alpha h\nu)^2$ with photon energy (hν) for PES polymer is shown in figure 3.

It is clear that like the value of optical indirect band gap the value of optical direct band gap also decreases at 16 kGy and increases at 110 kGy and again decreases from 142kGy to 300 kGy. In these studies, the results were obtained by plotting $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ as a function of the photon energy (hν), respectively. Taking into account the linear portion of the fundamental absorption edge of the UV/VIS (shown in Figures 1) such plots have been presented in Figures 2 and 3, respectively. By extrapolating the straight parts of this relation to the hν axis, indirect and direct band gaps have been determined for virgin and gamma irradiated PES polymer samples. The different transition energies are shown in figure 11 and are also provided in Table 1. This, in turn, clearly indicates the simultaneous existence of indirect and direct band gaps in the PES polymer samples with decreasing tendency at higher gamma ray dose. These results confirm that the irradiation produces faults in PES polymer structure (band rupture, free radical, etc.) which increase the electronic disorder inducing the creation of a permitted state in the forbidden (interdict) band or the deformation of valence band.

Furthermore, the values of the indirect band gap have been found to be lower than the corresponding values for direct band gap as given in Table 1. The coexistence of indirect and direct band gaps in the PES polymer has not been reported so far, but such results have been observed in some other materials [19-21].

The number of carbon atoms per conjugation length N (i.e. the number of carbon hexagonal atoms in a cluster) can be calculated by Robetson relation Robertson *et al.* [22].

$$N = 2\beta\pi \ E_g \ (4)$$

Before Electron beam (Exposed in SEM)
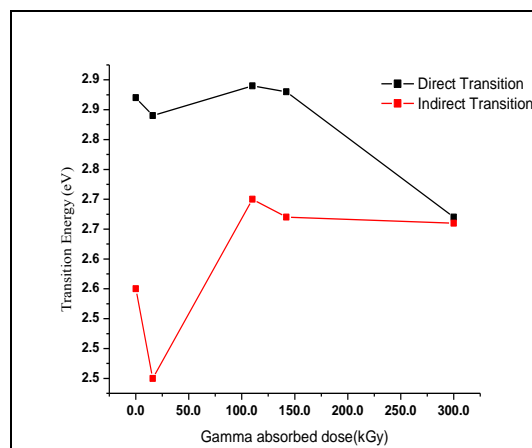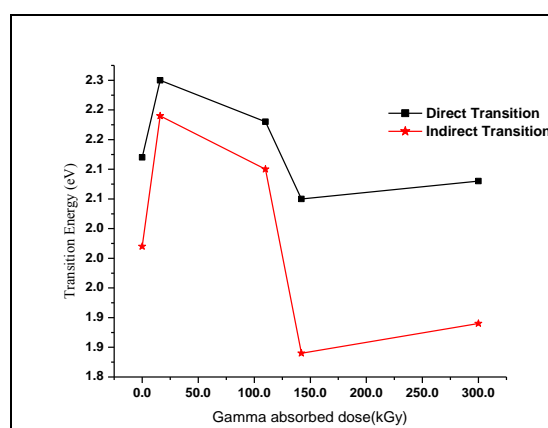

Fig 9

After Electron beam (Exposed in SEM)

Fig.10

Here 2β gives the band structure energy of a pair of adjacent π sites. The value of β is taken to be -2.9 eV as it is associated with $\pi \to \pi^*$ optical transitions in -C=C- structure. A shift in the absorption edge can be attributed to an increase of the conjugation length. The number of carbon atoms per conjugation length is found to increase up to 7 at the highest dose i.e., 300 kGy. The increase of unsaturated conjugation length in polymer samples results in their discoloration i.e., the PES polymer samples turn light yellow from transparent with increasing gamma radiation dose. Gamma radiation can induce the formation of unsaturated bonds in polymers and contribute to coloration, since as a rule, the conjugated double bonds are responsible for the colour of most organic compounds [10, 23].

Before Electron beam (Exposed in SEM)

Table 1

γ-radiation dose (kGy)	Absorption edge(λ_g) (nm)	Direct Band Gap Energy (eV)	Indirect Band Gap Energy (eV)	Urbach's energy (eV)	(N) Direct	(N) Indirect
0	421	2.92	2.60	0.56	6~	7~
16	416	2.89	2.45	0.67	6~	7~
110	428	2.94	2.75	0.41	6~	7~
142	428	2.93	2.72	0.43	6~	7~
300	416	2.72	2.71	0.61	7~	7~

After Electron beam (Exposed in SEM)

Table 2

γ-radiation dose (kGy)	Absorption edge(λ_g) (nm)	Direct Band Gap Energy (eV)	Indirect Band Gap Energy (eV)	Urbach's energy (eV)	(N) Direct	(N) Indirect
0	411	2.17	2.02	0.41	8~	9~
16	413	2.30	2.24	0.40	8~	8~
110	418	2.23	2.15	0.44	8~	8~
142	413	2.10	1.84	0.57	9~	10~
300	413	2.13	1.89	0.41	9~	10~

UV-VIS Spectral Studies after SEM (electron beam effect)

The results of absorption studies with UV/VIS spectrophotometer carried out on virgin as well as irradiated gamma PES polymer samples and further expose to electron beam as shown in Figures 4, 5 and 6, respectively. It is clear from the figure that the absorption edge is shifted towards the higher wavelength in figure 4.

The value of the Urbach energy E_u in each case was calculated and is listed in Table 2. and also shown in Figure 8 and 10. The increases in Urbach's energy in the case of PES polymer may be due to increase in the crystalline nature of the polymer at higher doses.

The value of indirect and direct band gap after the irradiation of electron beam expose in SEM. This, in turn, clearly indicates the simultaneous existence of indirect and direct band gap of PES polymer with decreasing tendency   after electron beam irradiation are shown in figure 12 and are also provided in Table 2

CONCLUSIONS

The effect of electron beam on irradiated Polyethersulfone (PES) Polymer samples under 1.25 MeV gamma radiation source of Co^{60} have been studied by means of UV-VIS techniques. The following conclusions have been drawn:

- 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 expose to electron beam 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.

In the experimental studies such as UV-VIS measurements, the results show characteristic with radiation dose. This may be due to scissioning and crosslinking of the polymer chains which can be correlated with the decreases of band gap

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