Effect of Cobalt-60 γ Radiation on the Physical and Chemical Properties of Poly(ethylene terephthalate) Polymer

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ABSTRACT: The structural, optical, and morphological properties of Co^{60} γ irradiation on poly(ethylene terephthalate) polymer samples were studied with X-ray diffraction (XRD), ultraviolet–visible spectroscopy, scanning electron microscopy (SEM), and Raman spectroscopy. The diffraction pattern of virgin sample showed that the polymer was semicrystalline in nature. However, because of irradiation, the crystallinity decreased up to a dose level of 110 kGy and increased up to 300 kGy. The crystallite size, strain, and dislocation were calculated from the XRD data, and the crystallite size decreased from 291.07 to 346.90 Å. The absorption edge shifted from 315 to 330 nm, and the band gap of the samples decreased from 3.79 to 3.66 eV. The SEM micrographs showed radial bulging along with inhomogeneous liner exfoliation, and also, a rocky shape pattern with different sizes was observed. A significant change was found in the Raman spectra of the γ-irradiated polymer at the highest dose. The results of the structural, optical, and morphological studies show recovery characteristics at the highest dose level of 300 kGy. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: activation energy; irradiation; Raman spectroscopy; UV–vis spectroscopy

INTRODUCTION

Polymers have proven their potential in all fields of life and especially in the fields of food-packing products, medical science, electronics, and space technology.[1] Poly(ethylene terephthalate) (PET) is a soft, transparent thermoplastic with a high melting point (265°C); it has very good mechanical strength (at least up to 175°C) because of the presence of an aromatic ring in the polymer backbone. It is resistant to heat, moisture, and many chemicals and, thus, has wide applications. The use of radiation in polymers has great importance because it helps to achieve some desired improvements in the polymer properties. γ-irradiation treatment provides a unique way to modify the chemical, structural, optical, mechanical, and electrical properties of a polymer by causing irreversible changes in the macromolecular structure.[2,3] The physicochemical properties of PET have been modified by chemical treatments, the addition of various plasticizers, and interaction with ionizing radiation.[4] Numerous studies reported in past decades have demonstrated that the interaction of ionizing-radiation-induced modifications with PET poly-

mers lead to a wide variety of property changes. Steckenreiter et al.,[5] Neagu et al.,[6] Kulshrestha et al.,[7] Singh et al.,[8] Liu et al.,[9] Singh et al.,[10] Zhu et al.,[11] and Sun et al.[12] studied the effect of different energy ion-beam irradiations on the physical, electrical, and chemical properties of PET. Such irradiations cause the photons to penetrate the material, break the polymer chains, and create free radicals. These free radicals can also recombine to create crosslinks between adjacent molecules. Crosslinked materials improve the long-term performance. Different studies on the effects of ion irradiation with polymers have revealed a variety of modifications of structural, electrical, optical, and chemical compositions, including processes such as main-chain scission, intermolecular crosslinking, the creation of unsaturated bonds, the formation of volatile fragments, and the creation of carbonaceous clusters.[13,14] The dielectric properties have been found to depend strongly on the degree of crystallinity and on the manner in which a particular degree of crystallinity has been attained.[6,15,16] For ion-beam irradiation, the following aspects are well established. Energy loss by charged particles in the material medium (electromagnetic interaction, high concentration of excited and ionized target atoms) is differential in nature, and hence, the energy deposited is nonhomogenous in nature.[17] It is confined to the beam diameter only. However, γ irradiation has been found to have the ability to expose the whole area of the

sample and, hence, is expected to create homogeneous modification in the sample.

Although a lot of work has been done to investigate the effects of ion irradiation on polymeric materials, the dependence of effect parameters related to ionizing radiation is not completely understood thus far. In this article, we report the results of structural, optical, and electrical changes produced by 1.25-MeV γ-ray-induced modifications on the PET polymer. The molecular structure of the PET polymer ($[-C_{10}H_8O_4-]$) is shown as follows:
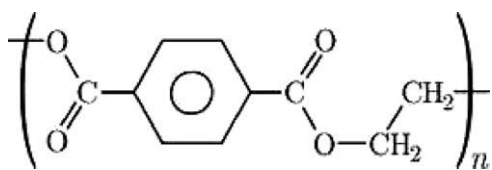
EXPERIMENTAL

PET polymer sheets with a thickness of 50 μm were obtained from Messrs Good Fellow (Cambridge, United Kingdom) and were used without any further treatment. Polymer samples with a size of 1×2 cm^2 were cut from the commercially available sheets. One sample was kept as the virgin sample, and the other five samples were subjected to irradiation. The samples were irradiated with a 1.25-MeV γ-radiation source of Co^{60} in a radiation chamber (which was in a form of cylindrical chamber 14 cm in length and 10 cm in diameter) with a dose rate of 4 kGy/h and a source strength of 2 kCi. The samples were irradiated in a dose range of 16–300 kGy at the University Grants Commission (UGC)–Department of Atomic Energy (DAE) Consortium for Scientific Research, Kolkata Centre (Kolkata, India). The irradiated samples were characterized with three analytical techniques, XRD, ultraviolet–visible (UV–vis) spectroscopy, and Raman spectroscopy, to determine the possible changes/modifications that took place in the PET polymer by irradiation. The XRD data analyses of PET samples were carried out on a powder X-ray diffractometer (PW-1830, PANalytical B.V., Almelo, The Netherlands) with monochromatic Cu Kα radiation (8.04 keV and λ = 0.154 nm). The optical changes were analyzed by UV–vis spectroscopy (UV 1601 PC) in the wavelength range 200–480 nm to observe the energy gap (E_g) variation with increasing dose.

RESULTS AND DISCUSSION

Powder XRD studies

The XRD patterns of the virgin and irradiated PET polymer samples at different doses of radiation are shown in Figure 1(A–F). The diffraction peaks occurred at 2θ = 25.245° in the virgin PET and at 16, 48, 110, 142, and 300 kGy in the γ-irradiated polymer

samples. Figure 1 shows that the peak intensity decreased up to 110 kGy and increased at 142 and 300 kGy. This indicates that the size of the crystallite decreased because of scissioning of the polymer chains, and at higher doses, crosslinking was predominant in polymer and increased the crystallite size. The full width at half-maximum (fwhm) is generally associated with the crystallite size (L), which can be obtained from Scherer's formula:

$$L = k\alpha/\beta \cos\theta \qquad (1)$$

where $k = 1$, λ is the wavelength and has a value of 1.54 Å, β is the fwhm (rad), k is constant, and θ is angle (rad).

The quantities of the increase and decrease in peak intensity, fwhm, and crystallite size with doses are provided in Table I. It was clear from our observation of the peak intensity, fwhm, and crystallite size that all of the results indicated the recrystallization of polymer, which may have been due to scissioning and crosslinking of the polymer chains with increasing radiation doses.

UV–vis spectral studies

The absorption of light energy by polymeric materials in the UV and visible regions involves the transition of electrons in the σ, π, and *n*-orbitals from the ground state to the higher energy states. The results of the absorption studies of the virgin and irradiated PET polymer samples at various doses are shown in Figure 2. It is clear from the figure that the absorption edge shifted toward the higher wavelength side from 315 to 330 nm. This shift may have been related to the formation of conjugated bonds; this showed the possibility of the formation of carbon clusters. This type of transition occurs in nonbonding electrons containing compounds and aromatic compounds.[8,15,18]

Determination of the band gap (Table II)

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:

$$E_g = hc/\lambda_g \qquad (2)$$

where h is Planck's constant, c is the velocity of light, and λ_g is the wavelength. This polymer obeyed the rule of direct transition and gave the relationship among the optical band gap, absorption coefficient, and incident photon energy ($h\nu$) as follows:

$$\alpha(h\nu) = B(h\nu - E_g)n \qquad (3)$$

where B is a constant, E_g is the value of the optical energy gap between the valance band and the
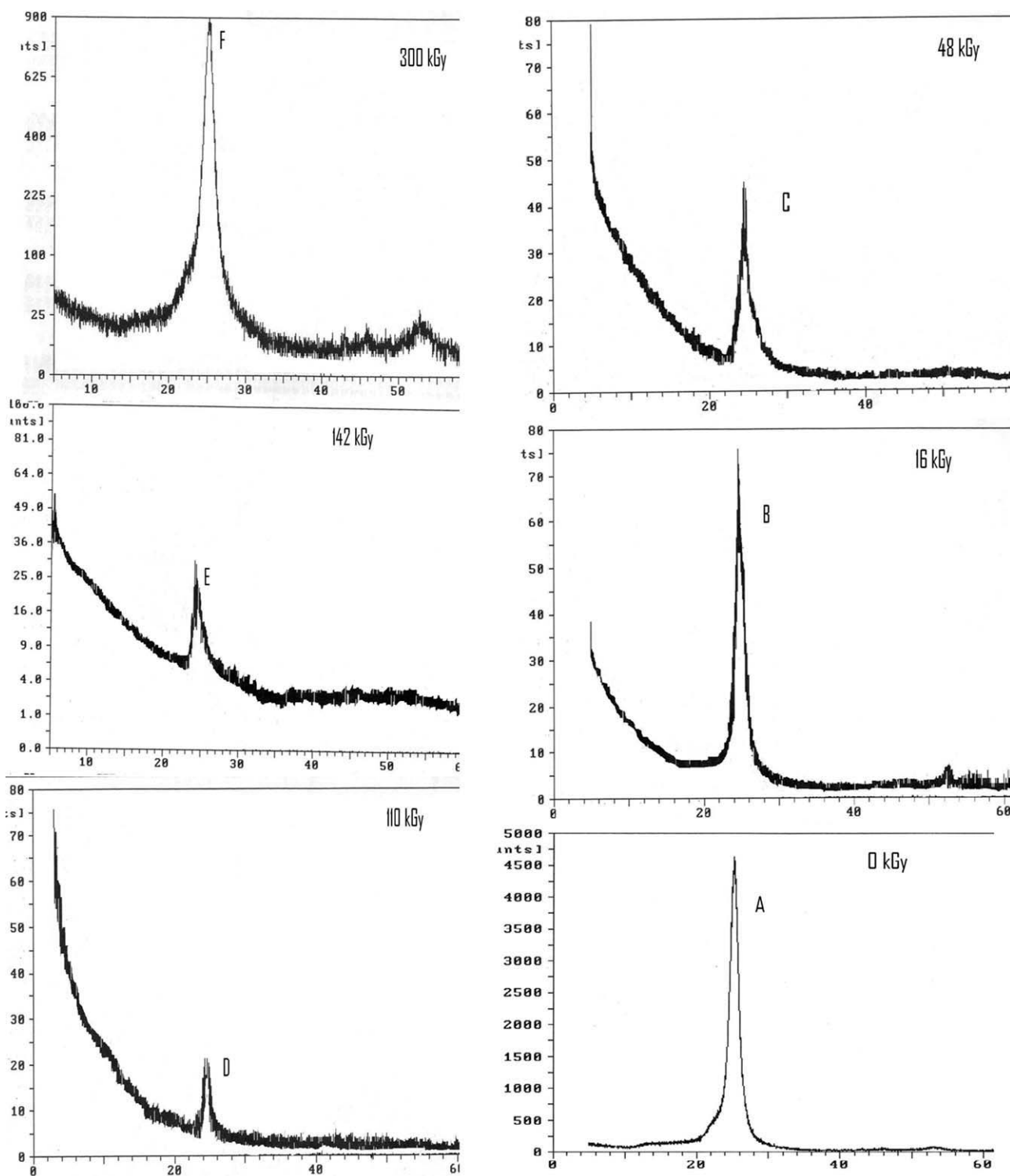
Figure 1   XRD pattern of virgin and γ-irradiated PET at various doses (16, 48, 110, 142, and 300 kGy).

conduction band, and n is the power that characterized the electronic transition, whether it is direct or indirect during the absorption process in the K space. Particularly, the n values are 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden allowed, indirect allowed, and indirect forbidden transitions, respectively.

The variation of $(\alpha h\nu)^2$ with $h\nu$ for the PET polymer is shown in Figure 3. It was clear that the value of the optical direct band gap decreased from 3.79 to 3.66 eV. In these studies, we obtained the results by plotting $(\alpha h\nu)^2$ as a function of $h\nu$. Taking into account the linear portion of the fundamental absorption edge of the UV–vis (shown in Fig. 2), we

Sample	Angle of peak (2θ)	Dose (kGy)	β (Å)	L (Å)
1.	25.245	0	0.280	291.07
2.	24.780	16	0.560	145.53
3.	25.945	48	0.580	144.95
4.	24.365	110	0.640	127.21
5.	24.630	142	0.320	254.43
6.	25.965	300	0.240	346.90

present such plots in Figure 3. By extrapolating the straight parts of this relation to the $h\nu$ axis, we determined the direct band gaps for the virgin and γ-irradiated PET polymer samples. This, in turn, clearly indicates the direct band gaps in the PET polymer samples with decreasing tendency at higher γ ray
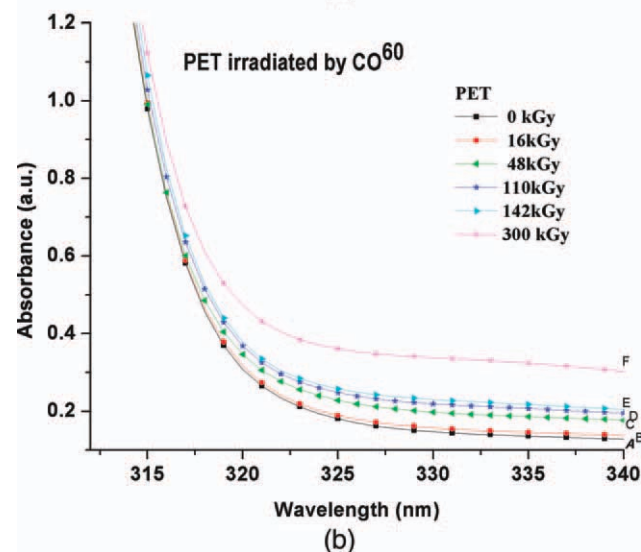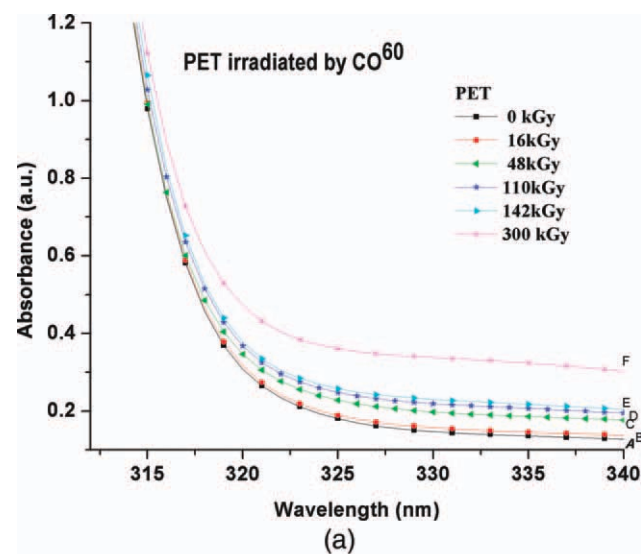
**TABLE II
Variation of the Band-Gap Energy and Urbach's Energy
in the Pristine and γ-Irradiated PETs and the Number of
Carbon Atoms (N) per Conjugated Length**

γ-Radiation dose (kGy)	Absorption edge (λ_g;nm)	Direct band-gap energy (eV)
0	319	3.79
16	320	3.78
48	321	3.76
110	322	3.72
142	323	3.71
300	324	3.66

doses. These results confirm that the irradiation produced faults in the PET polymer structure (band rupture, free radicals, etc.) that increased the electronic disorder and induced the creation of a permitted state in the forbidden (interdict) band or the deformation of the valence band.[19–22]

Surface morphology

The SEM micrographs of the virgin and γ-irradiated samples at various doses are shown in Figure 4(A–F). Figure 4(A) shows the surface morphology of the unirradiated PET polymer. The observed feature showed a smooth surface with a homogeneous pattern throughout the scanned region. Figure 4(B) shows the SEM micrograph of the same polymer irradiated at 16 kGy. We observed a small bulging in various shapes throughout the scanned region; at a dose of 48 kGy, the SEM photograph showed an entirely different feature, which was observed in previous dose. At a further dose of 110 kGy, shown in Figure 4(C), small bubble formation throughout the scanned region was observed. Figure 4(D) shows the surface morphology of the polymer irradiated at
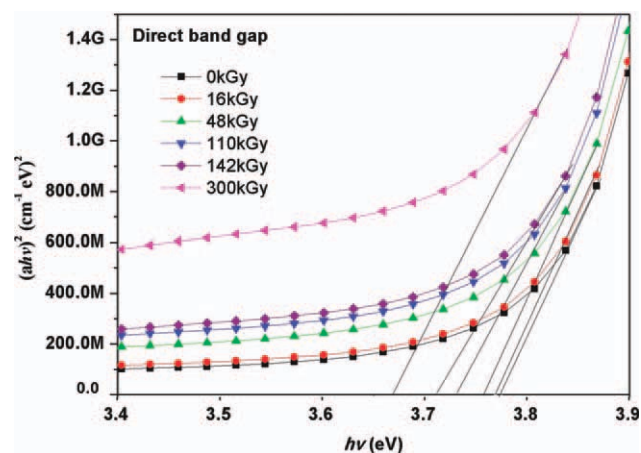

Figure 2 UV–vis spectra of pristine and 1.25-MeV-γ-irradiated PET polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 3 Dependence of $(\alpha h\nu)^2$ on $h\nu$ for the virgin and γ-irradiated PET polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]
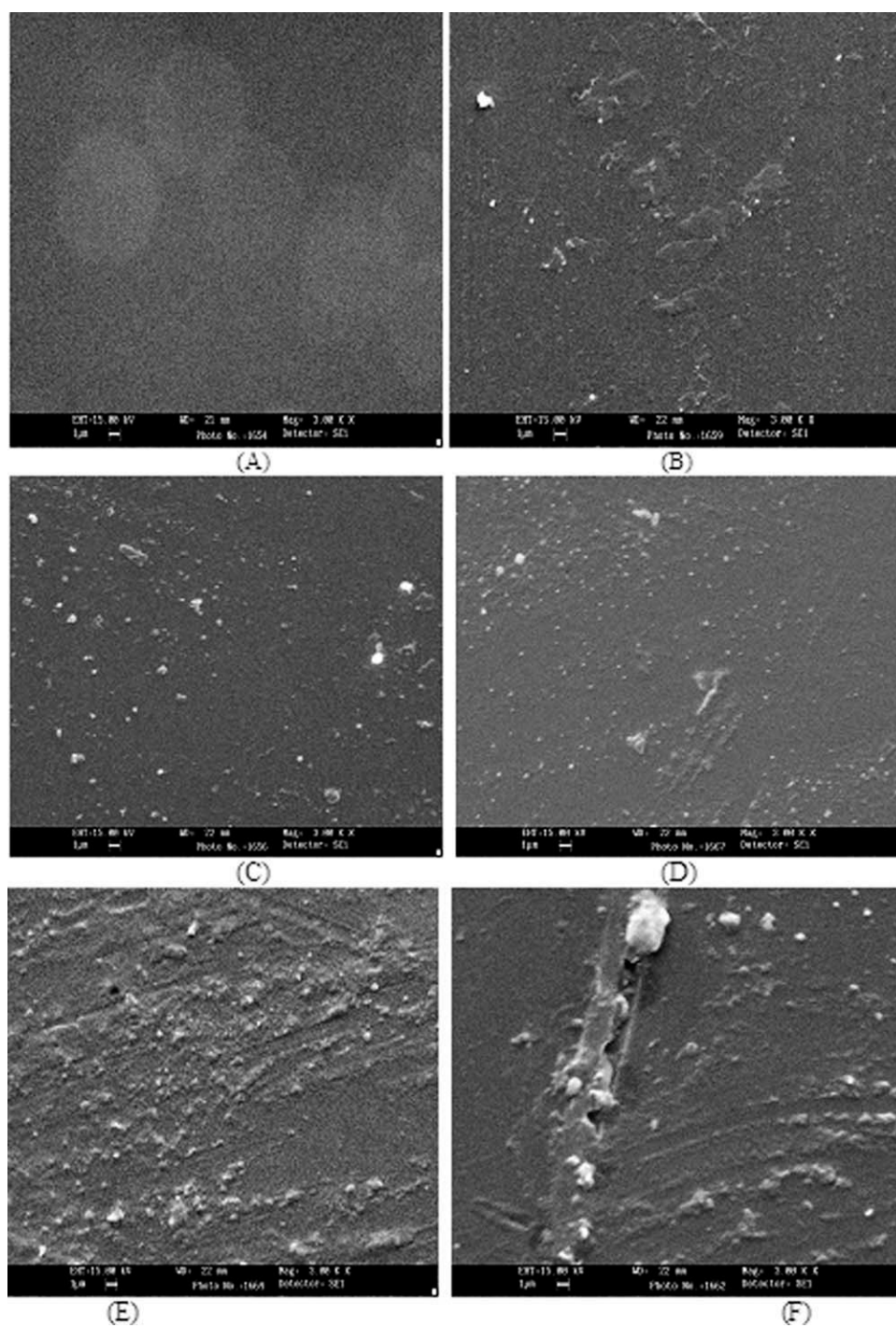
Figure 4 SEM micrographs of (A) virgin and γ-irradiated PET polymers at (B) 16, (C) 48, (D) 110, (E) 142, and (F) 300 kGy.

dose of 142 kGy; it was clear from the micrograph that at this dose, the irregular bulging of the surface along with small bubbles occurred. At the highest dose of 300 kGy, the micrograph [Fig. 4(F)] showed radial bulging along with inhomogeneous liner exfoliation, and also, a rocky shape pattern of different sizes was observed in the scanned region. They may have been due to the exfoliation of the bulging,

which formed due to evolved gases from the polymer.

Raman spectroscopy

Raman spectroscopy was used to study the composition of the track area in γ-irradiated samples, and its behavior was compared with that of virgin PET.
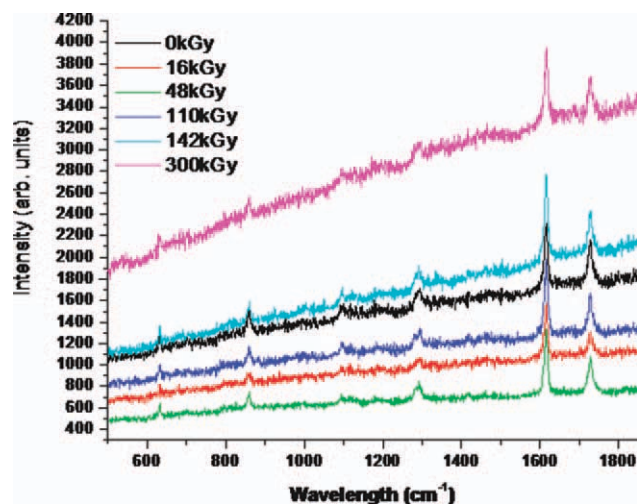
Figure 5 Raman spectra of (a) virgin and γ-irradiated PET polymers at (b) 16, (c) 48, (d) 110, (e) 142, and (f) 300 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5 shows the Raman spectra of the virgin and irradiated PET at different doses. The recorded spectrum of γ-irradiated PET had same characteristics but more distinct results at a higher dose. The intensities of the Raman band of the γ-irradiated polymer were initially lower than those of the virgin polymer, but as the dose was increased, the intensity of the irradiated PET sample at 300 kGy was greater than that of the virgin PET polymer. This probably indicated the carbonization of the track area and nucleation of carbon-rich clusters.

In the irradiated samples, a slight broadening of the characteristic spectral band was observed; this may have been due to the radiation damage. The Raman band of virgin PET observed at 1614.6 cm^{-1} was related to vibrations with C=C stretching because of the strong atomic character. Irradiation at 300 kGy, which corresponded to the maximum Raman shift (1620 cm^{-1}), indicated that microstrain decreased in the irradiated film. The intensity of Raman bands increased with increasing irradiation dose; this may have been due to ordering along the fiber molecules. The intensity for the 300-kGy irradiated sample of PET polymer was high because of its low microstrain value. The Raman active bands of PET and their associated vibrations are summarized in Table III, along with the fwhm and intensity values at different doses.

CONCLUSIONS

Modifications of PET polymer samples under a 1.25-MeV γ-radiation source of Co^{60} were studied by means of XRD, UV–vis spectroscopy, high-frequency impedance analysis, SEM, and Raman spectroscopy techniques. The following conclusions were drawn:

- An initial decrease in the crystallinity and a recovery characteristic was observed with increasing dose. The crystallite size also showed recovery characteristics with increasing dose.
- The band gap (E_g) decreased from 3.79 to 3.66 eV with increasing γ irradiation dose because of the photodegradation of PET.

TABLE III
Variation of fwhm and Intensity of the Raman Bands as a Result of Irradiation at Different Doses

Signal	Virgin PET	16 kGy	48 kGy	110 kGy	142 kGy	300 kGy	Molecular vibration
Position	629.75	629.29	629.51	629.20	629.30	631.79	Ring mode
fwhm	4.4	2.7	4.0	4.3	5.6	3.7	
Intensity	1278.7	814	572.8	1001.5	2194.1	1360.8	
Position	856.5	856.8	858.2	859.7	859.6	859.6	Ring CC and C(O)—O stretching
fwhm	6.5	6.3	7.8	7.3	11.2	10.7	
Intensity	1528.79	927.4	708.3	1134.2	2549.03	1584.08	
Position	1093.8	1093.6	1093.9	1090.8	1093.6	1094.4	Ring CC, C(O)—O, and ethylene glycol CC stretching
fwhm	10.4	9.6	8.2	6.7	3.7	7.2	
Intensity	1568.3	994.2	731.3	1244.1	2827.3	1717.1	
Position	1115.9	1115.3	1114.9	1117.5	1122.7	1120.9	C(O)—O and ethylene glycol CC stretching
fwhm	7.2	7.1	7.2	8.5	8.6	8.1	
Intensity	1003.3	1003.4	711.5	1198.7	2834.3	1690.3	
Position	1292.1	1292.3	1291.8	1294.9	1292.1	1292.1	C(O)—O stretching
fwhm	6	5.3	4.2	7.6	1.10	2.3	
Intensity	1703.2	1064.1	850	1335.5	3064.1	1980.2	
Position	1614.6	1614.6	1614.3	1614.6	1614.6	1620.4	Ring mode
fwhm	7.6	7.4	7.8	8.1	7.4	7.1	
Intensity	2295.9	1501.6	1329.6	1985.3	3942.0	2764.8	
Position	1727.3	1727.3	1728.5	1727.5	1727.5	1727.5	C=O stretching
fwhm	8.6	8.8	8.3	8.1	5.8	6.1	
Intensity	2144.4	1292.0	1054.7	1669.3	3669.9	2424.5	

- Bubble formation at lower doses and radial bulging along with inhomogeneous linear exfoliation and a rocky shape pattern of different sizes at higher doses were seen on the surface of the irradiated PET; this may have been related to the scissioning and crosslinking of the polymer chain.
- The maximum Raman shift occurred at (1620 cm^{-1}), and the intensities of the Raman band of the γ-irradiated polymer were greater than those of the virgin polymer. These increased with high dose and probably indicated the carbonization of the track area and nucleation of carbon-rich clusters.

In all the experimental studies, including XRD, UV–vis spectroscopy, SEM, and Raman spectroscopy measurements; we recorded observations of this type for the first time to the best of our knowledge. These results show recovery characteristics at higher radiation doses. This may have been due to the rearrangement, degradation, scissioning, and crosslinking of the polymer chains, which could be correlated with the recovery of the original characteristics with increasing dose.

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