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Research Article

Gamma Rays Induced Modification in Ultrahigh Molecular Weight Polyethylene (UHMWPE)

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Modifications taking place in ultrahigh molecular weight polyethylene (UHMWPE) films due to gamma ray radiation-induced and investigated in correlation with the applied doses. Films were irradiated in a vacuum at room temperature by a 1.25 MeV Co^{60} a source with doses ranging from 0 to 300 kGg. The optical, chemical, structural, and surface morphological properties of the irradiated and unirradiated UHMWPE films were investigated by UV-Visible, FTIR, XRD, and SEM, respectively. The band gap E_g decreases with increasing radiation dose and coloration effects have been seen at higher doses. FTIR spectra show an oscillatory behavior in the transmittance intensities without affecting in their peak positions. Number of small absorption peaks can be seen clearly which may be due to the cross-linking of the polymeric chain. No significant change in crystalline peak has been found in the X-ray diffraction pattern indicating the structural stability of the polymer. The morphology of the smooth topography of the polymer samples to change rougher one polymeric sample shows the formation of microvoids on the surface of the polymeric materials with the increase of the doses from 0 to 300 kGy.

1. Introduction

UHMWPE (ultrahigh molecular weight polyethylene) is a polymer commonly known as high modulus polyethylene. Nowadays, the polymer materials are very useful in defense and biotechnology due to its unique and valuable properties s of UHMWPE such as semicrystalline, good biocompatibility, and mechanical stability in industrial as well as biomedical applications. The linear homopolymer produced in UHM with molecular weights of 3,000,000 to 6,000,000 atomic units, as opposed to 500,000 atomic units for HDPE. Structurally, UHMWPE (-CH_2-CH_2-)n is similar to high-density polyethylene (HDPE) differing primarily in the average length of molecular chains. The polyethylene chain forms a planer zigzag in space. The distance between two adjacent carbon atoms in the polymeric chain is 1.54 Å and valence angles formed by the C-C-C bonds are about 109.5^0. The macromolecules of polyethylene form an orthorhombic unit cell which is characterized by the following constraints: $a = 7.40$ Å, $b = 4.93$ Å, and $c = 2.534$ Å. The polymeric chains in polyethylene crystals are arranged parallel to one another and are directed along the axis "c". The hydrogen atoms are arranged in planes parallel to the plane "ab" of the unit cell.

UHMWPE has a great importance as a shielding material for space application due to its high hydrogen content, simple elemental composition, and nucleus not susceptible to release neutrons through a nuclear reaction. In addition, the availability of high molecular mass PE could lead to further enhancement of shielding and structural properties. To protect astronauts and sensitive devices during space missions, it is necessary to use them without undergoing significant changes in their physical and chemical properties due to energy deposition [1, 2]. In order to understand the effect of irradiation on polymer, its final structure must be studied.

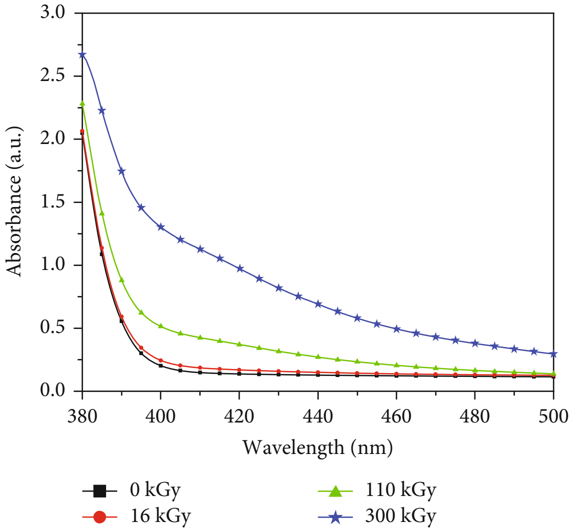


Figure 1: The spectra of optical absorption UHMWPE polymer at 0 kGy, 16 kGy, 110 kGy, and 300 kGy radiation doses.

Table 1: Absorption edge and energy gap variation in virgin and irradiated samples of UHMWPE at different doses.

Dose (kGy)	Absorption edge (λ_g) (nm)	Energy gap (E_g) (eV)	Urbach's energy (eV)
0	387	2.54	0.071
16	390	2.53	0.061
110	389	2.10	0.94
300	397	1.73	0.40

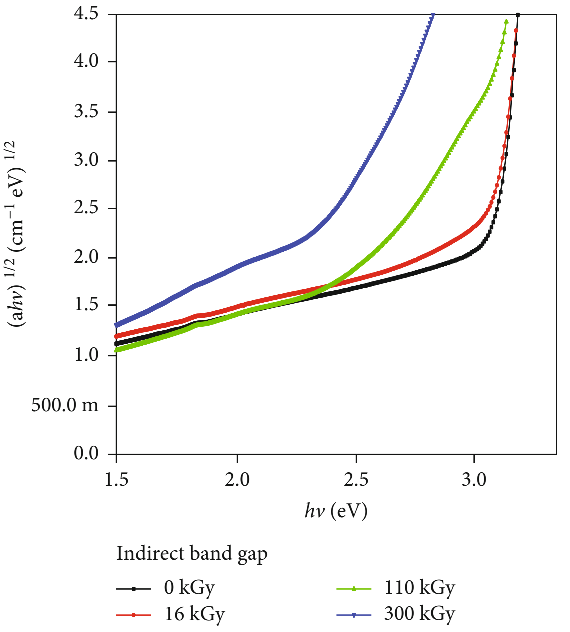


Figure 2: The optical E_g (eV) of UHMWPE polymer at 0 kGy, 16 kGy, 110 kGy, and 300 kGy radiation doses.

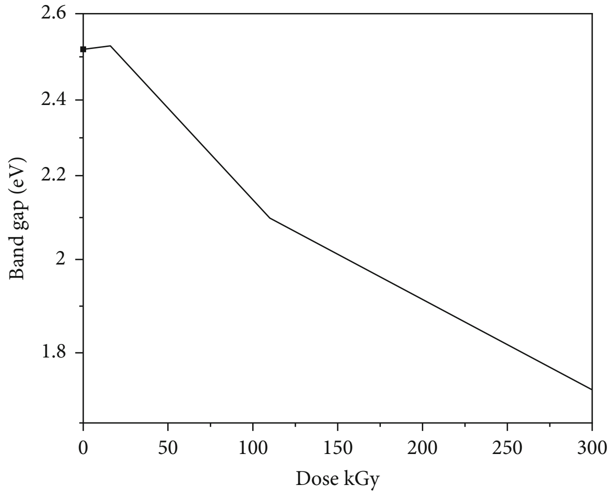


Figure 3: Difference of band gap with radiation dose of UHMWPE polymer.

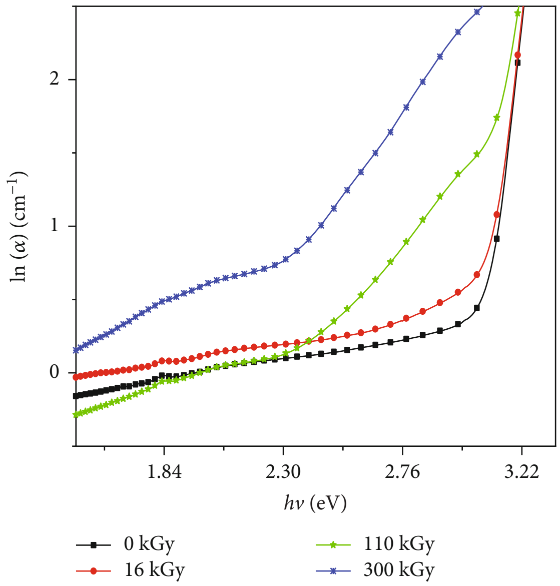


Figure 4: The dependence of natural logarithm of α on photon energy for virgin and gamma-irradiated UHMWPE polymer.

The main applications are for the modification of the polymer surface through radiation cross-linking and grafting. The surface can be coated with a cross-linkable material and then cross-linked by radiative curing. Thus, the ability of radiation to cause molecular rearrangement has proven to be valuable in making polymer more stable. Currently, gamma-irradiation and other ionising radiations are used as surface and bulk modifications/cross-linking of UHMWPE which is then further utilized in various industrial applications.

The radiation process improves the important properties of polymer material, such as mechanical properties, thermal stability, and chemical resistance, melt flow, and surface properties significantly. Radiation processing using gamma

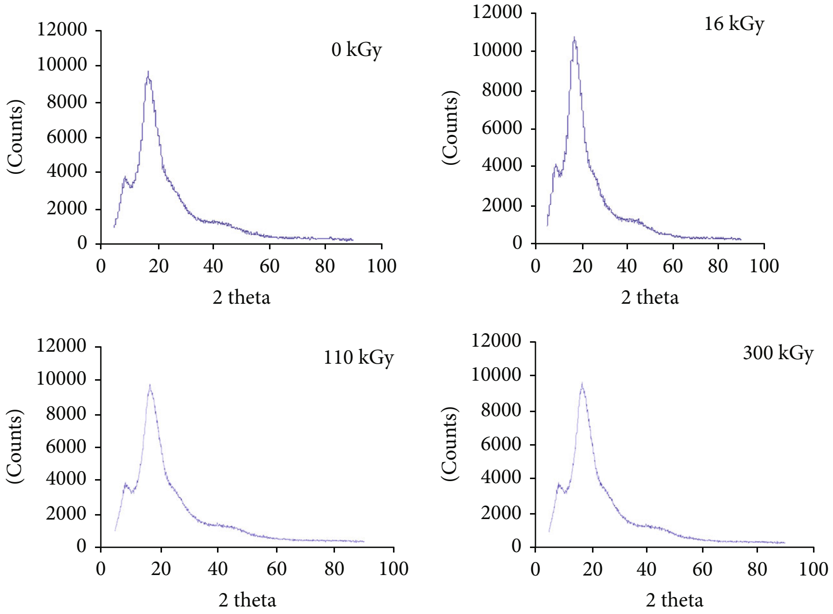


Figure 5: XRD patterns of virgin and gamma-irradiated UHMWPE polymer at various doses.

rays has been demonstrated on a large commercial scale to be a very effective means of improving the various properties of the polymers. When polyethylene is irradiated with high-energy radiation, such as gamma ray or electron beam, it will lead to chain breakage and radical formation. The nature of these changes depends on the nature of the polymer. In general, three main reactions can occur; these are cross-linking, scission, and molecular rearrangement. Cross-linking and scission processes are simultaneous, but one of them predominates depending on the molecular structure, type of irradiation, and the dose [3]. Gamma irradiation causes the photons to penetrate the material, breaking the polymer chains and creating free radicals. These free radicals also recombine to create cross-links between adjacent molecules. Cross-linked materials improve the long-term performance [4]. Basically, the irradiation of the polymers involves two competing processes: chain scission and cross-linking. Both scission and cross-linking processes affect the physical, chemical, and morphological properties of the polymer. Fundamental studies have explained how the cross-linking of the polymeric chain due to gamma irradiation becomes the main mechanism to explain most of the chemical and physical properties [5]. It has been therefore decided to further investigate the interaction of gamma irradiation with UHMWPE polymer.

2. Experimental Procedure

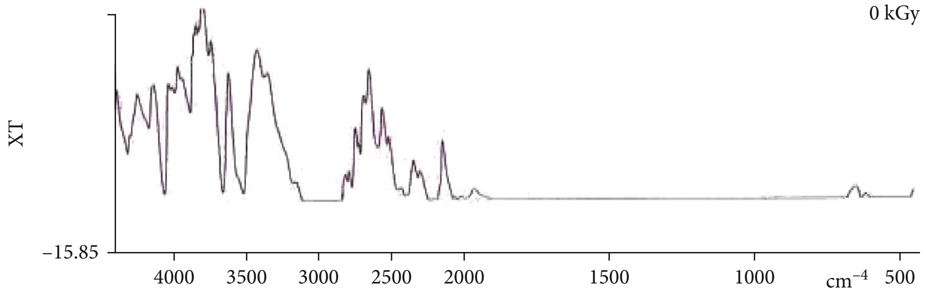
The pure UHMWPE sheet of thickness 500 μm was obtained from MS Goodfellow, U.K. The size of polymer samples ($1 \times 1\,\mathrm{cm}^2$) were prepared and irradiated with 1.25 MeV Co^{60} gamma rays with a dose rate of 4 kGy/h. 2K, Gamma irradiation facilities were conducted at UGC-DAE Consortium for Scientific Research, Kolkata Centre. The samples of UHMWPE films were irradiated to gamma rays with 16, 110, and 300 kGy doses. The samples were analyzed by four different analytical techniques to analyze the gamma-induced irradiation on UHMWPE polymers such as optical, structural, chemical, and morphology. UV-Visible spectrophotometer to observe the energy gap (E_g) variation with the increase of radiation dose. Chemical modifications were analyzed by using the FTIR technique and structural studies were analyzed using a powder X-ray Diffractometer. XRD measurements were taken by using monochromatic CuK_α (8.04 keV and $\lambda = 0.154$ nm. The surface modifications of the polymer samples were characterized by SEM. The samples were coated with a thin layer of gold (3.5 nm) by the vacuum evaporation technique to minimize sample charging effects due to the electron beam.

Table 2: XRD parameters for virgin and irradiated UHMWPE polymer at various doses.

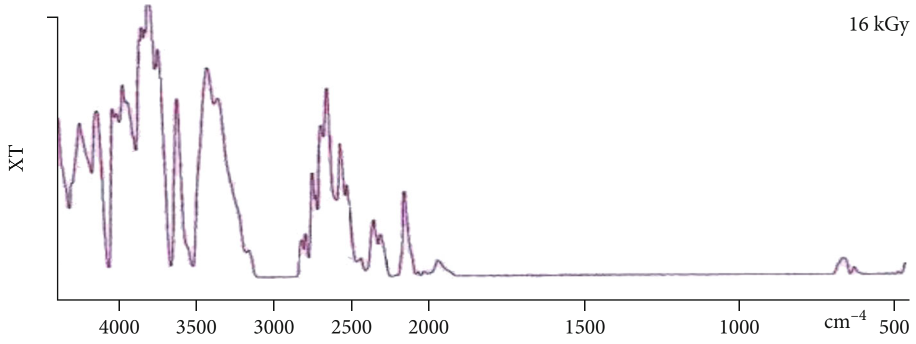
Gamma dose (kGy)	XRD 2θ (^{0})	FWHM β (^{0})	$\beta \cos \theta$	Crystallite size (Å)
0	16.7	4.05	4.00	0.385
16	16.8	4.00	3.92	0.390
110	16.9	3.90	3.85	0.400
300	17.0	3.00	2.96	0.520

3. Optical Absorption Studies

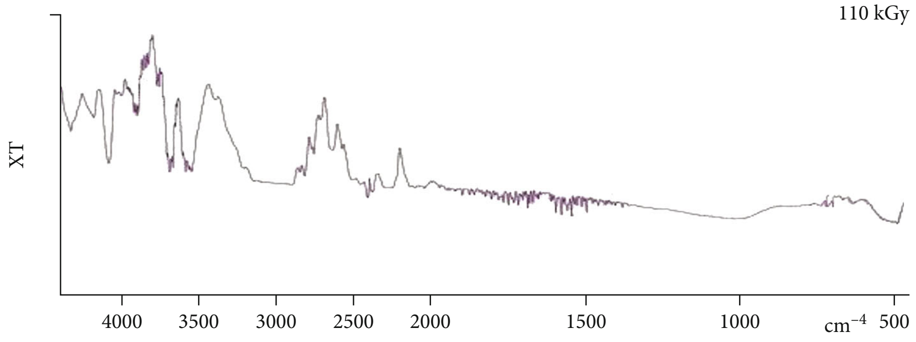
In the polymeric materials, the optical absorption of light energy in the UV and VIS region involves the promotion of electrons in σ, π, and n-orbitals from the ground state to a higher energy state [6]. The optical absorption spectra of pristine and gamma-irradiated polymer samples of UHMWPE have been shown in Figure 1. The growth of absorption due to gamma irradiation has been found in the region from 380 to 500 nm, and this absorption shifts from



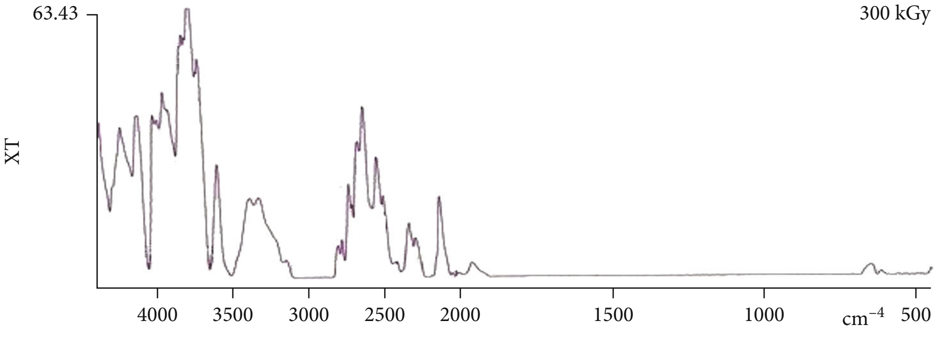
(a) 0 kGy



(b) 16 kGy



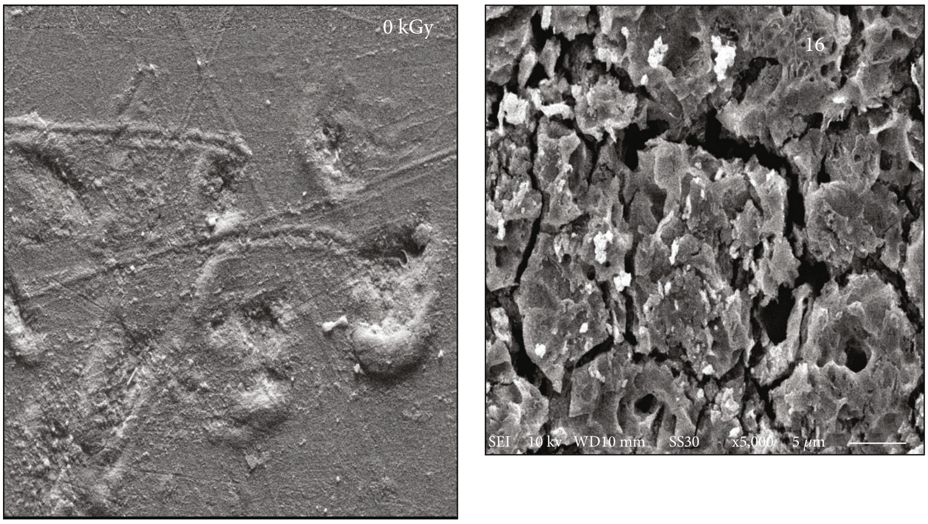
(c) 110 kGy



(d) 300 kGy

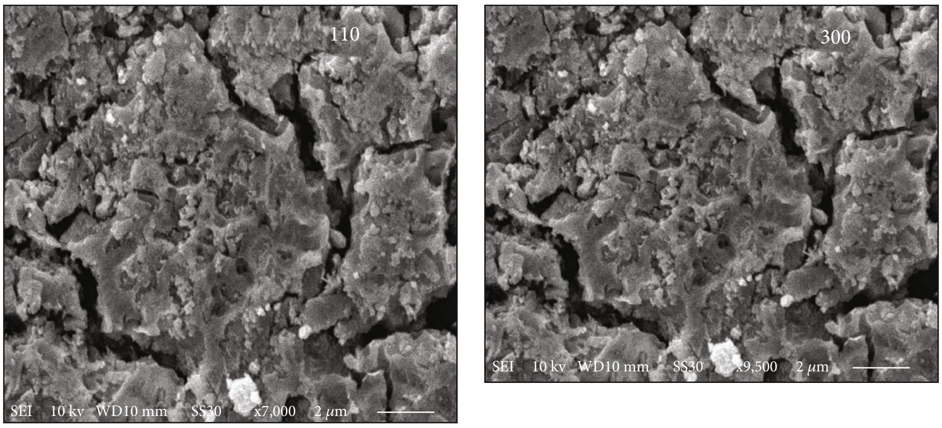
Figure 6: FTIR of (a) pristine and gamma-irradiated UHMWPE at 0 kGy, 16 kGy, 110 kGy, and 300 kGy radiation doses.

the ultraviolet-visible region towards the visible region for irradiated polymer samples. However, a gradual increase in the absorption has been found with increasing irradiation dose up to 110 kGy but a strong increase in the absorption has been observed at 300 kGy. This modification is perceived due to transition from $n \longrightarrow \sigma^*$ orbits; due to this, a single bond between carbon and hydrogen is present in the polymer. The increase in the absorption with irradiation may also be attributed to the formation of a conjugated system (-C=C-) of bands due to band cleavage and reconstruction. The observed increase in the magnitude of optical absorption due to gamma irradiation may be explained due to cross-linking of polymer samples. The irradiated polymer surfaces show a change in color from yellowish to almost yellow at the



(a) 0 KGy

(b) 16



(c) 110

(d) 300

FIGURE 7: SEM Micrographs of UHMWPE. (a) Pristine. (b) 16 kGy. (c) 110 kGy. (d) 300 kGy.

highest dose of 300 kGy. Many of the optical transitions which result from the presence of impurities have energies in the visible part of the spectrum; consequently, the defects are referred to as color centers [7]. The formation of new defects and the new charge state are generated by the interaction of gamma rays in the polymers.

3.1. Determination of Band Gap. The shift in the absorption edge is correlated with the optical energy gap, E_g by Tauc's relation [8]:

$$\boldsymbol{\omega^2 \varepsilon_2(\lambda) = \left(\hbar\omega - E_g\right)^2}, \tag{1}$$

where $\varepsilon_2(\lambda)$ is the imaginary part of complex refractive index, i.e., the optical absorbance and λ is the wavelength and $\omega = 2\pi v$ the angular frequency of the incident radiation.

Solving Eq. (1), one gets

$$\frac{\sqrt{\varepsilon_2}}{\lambda} = \frac{\mathrm{h}}{2\pi\lambda} - \frac{\mathrm{E_g}}{2\pi c}. \tag{2}$$

Therefore, the plot of $\sqrt{\varepsilon_2}/\lambda$ versus $1/\lambda$ must be a straight line with an intercept of $-E_g/2\pi c$. If θ is the inclination of the straight line with x-axis, the slope of the straight line should be $\tan\theta$ and we have

$$\frac{h}{2\pi} = \frac{E_g/2\pi c}{1/\lambda_g}, \tag{3}$$

where $1/\lambda_g$ (λ_g, being the gap wavelength) represents the abscissa of the point of intersection of the straight line with the x-axis and

$$\boldsymbol{E_g = \frac{hc}{\lambda_g}}. \tag{4}$$

The values of λ_g and corresponding results of energy gap (E_g) for virgin as well as irradiated samples have been reported in Table 1. The increase in the absorption method can be used for the investigation of the optically induced transitions and can provide information about the bond structure and energy gap in crystalline and noncrystalline materials [9]. The decrease in optical band gap (E_g) from 2.54 to 1.73 eV with the increasing dose has been observed. It has been calculated that the optical energy gap decreases by 32% at the highest dose of 300 kGy. Carbon-enriched domains created in polymers due to irradiation may be responsible for the decrease in band gap as indicated by earlier studies [10–14]. The variation of $\sqrt{\varepsilon_2}/\lambda$ with $1/\lambda$ for UHMWPE polymer is shown in Figure 2. Variation of band gap with a radiation dose of UHMWPE polymer has been given in Figure 3. It is clear from the graph that the value of the optical band gap decreases with increasing dose.

3.2. Determination of Urbach Energy. The absorption coefficient is given by the equation known as the Urbach formula [15].

$$\alpha(\nu) = \alpha_o \exp\left(\frac{h\nu}{E_u}\right). \tag{5}$$

In Eq. (5), α_o is a constant, E_u is an energy which is interpreted as 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 [16]. The logarithm of the absorption coefficient $\alpha(\nu)$ was plotted as a function of the photon energy ($h\nu$) for UHMWPE irradiated with different doses of gamma rays as in Figure 4; 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 listed in Table 1. The decrease in Urbach's energy in the case of UHMWPE may be due to the decrease in the crystalline nature of the polymer.

4. Structural Properties

The theory of crystallinity in the polymer is quite different from that of other materials [17]. The elucidation of the detailed structure of polymers by X-ray diffraction methods is a rather complicated task. This is because one has to use polycrystalline samples, which always contain amorphous regions, instead of single crystals which are too small for the XRD analysis. The X-ray photographs of even highly crystalline polymers contain a considerably smaller number of reflections than those of low-molecular-mass solids. Besides, the presence of an amorphous halo and the reflections strongly diffused because of the small size of the crystallites are the factors that considerably complicate the determination of the structure of polymers [18].

However, the increase in radiation dose and shift in angular position can be explained by a decrease in lattice spacing. The diffraction patterns of the virgin and irradiated UHMWPE are presented in Figure 5. A significant peak at $2\theta = 16.7^\circ$ has been observed in the diffraction pattern of the virgin sample clearly indicates that it is semicrystalline in nature.

It is observed in diffraction patterns of irradiated UHMWPE at 16, 110, and 300 kGy that no major change has been found in the FWHM of observed peaks.

The Scherrer equation [19] relates FWHM (β) of an XRD peak to the size of crystallites L as

$$\beta = \frac{K\lambda}{L\cos\theta}, \tag{6}$$

where β is in radians, λ is wavelength of X-ray beam (1.5444 **Å**) L (crystallite size) is in Å and K is a constant usually equal to 1. The structure of polycrystalline materials is investigated by means of the Debye-Scherrer method. The essence of this method is as follows. A beam of monochromatic X-radiation is incident on a polycrystalline sample; there will always be a proportion of small crystals in the sample that are under the conditions for which the Bragg formula is satisfied. Since these tiny crystals (crystallites) are oriented randomly in the sample, upon reflection from each set of parallel planes inside such crystallites for which Bragg's formula is satisfied and a cone of diffracted X-rays is produced. The axis of this cone coincides with the direction of the primary beam [18].

The values of FWHM (β) and corresponding results of crystallite size (L) for virgin as well as irradiated samples have been reported in Table 2. It has been observed that crystallite size increases with increasing irradiation dose and it increases by 35% at the highest dose of 300 kGy. This increment in the crystallite size may be due to the cross-linking of the polymeric chain of UHMWPE polymer.

5. Chemical Response of UHMWPE

Figures 6(a)–6(d) show FTIR spectra of virgin and gamma-irradiated UHMWPE at various doses. The polyethylene has a very simple molecular structure that contains two different kinds of bonds: H-C and C-C. In Figure 6(a), absorption peaks at 3672 and 3533 $\mathrm{cm^{-1}}$ represent C-H stretching of UHMWPE polymer. Transmittance was found to be constant in the range 3088-2800 $\mathrm{cm^{-1}}$. Absorption peaks at 2716, 2590, 2411, and 2051 $\mathrm{cm^{-1}}$ can also be seen in the spectrum, but they are unassigned in the literature. Again, transmittance intensity is found to be constant in the region 1800 to 700 $\mathrm{cm^{-1}}$. Figure 6(b) represents the FTIR spectrum of gamma-irradiated UHMWPE at 16 kGy. Peak positions are similar to Figure 6(a) with decreasing transmittance intensity. However, a decrease in the transmittance or increase in the absorbance may be due to cross-linking of the polymeric chain in UHMWPE. At 110 kGy, an interesting change has been observed in Figure 6(c). Number of small absorption peaks can be seen clearly between 1700 and 1400 $\mathrm{cm^{-1}}$.

Absorption peaks at 1773, 1734, 1685, and 1618 $\mathrm{cm^{-1}}$ represent C=C stretching and peaks at 1560, 1542, 1508, and 1458 $\mathrm{cm^{-1}}$ assigned to C-H deformation. Transmittance intensity has been shifted upwards indicating that transmittance increases with increasing radiation dose. At 300 kGy, FTIR spectrum shifted downwards in Figure 6(d) which shows that transmittance decreases with increasing radiation dose. Absorption peaks have been disappeared in Figure 6(d) which were present in Figure 6(c) in the region 1700-1400 $\mathrm{cm^{-1}}$. This spectrum shows its original characteristic of UHMWPE in which transmittance intensity was found to be constant in the region 1800-700 $\mathrm{cm^{-1}}$.

6. Morphological Study

The scanning electron microscope technique is widely used to investigate the internal structure or morphology of biodegradable polymers like UHMWPE. SEM study has been performed on UHMWPE virgin as well as gamma-irradiated surfaces with a magnification power of 5 kx. Figure 7(a) shows the SEM micrograph of a pristine sample of UHMWPE. This micrograph presents a rough surface of pure UHMWPE, while Figure 7(b) presents a micrograph of rock type of feature with microvoids at 16 kGy.

The energetic gamma irradiation produces a large amount of atomic displacements leading to polymer degradation at lower doses.

Further, with increasing gamma radiation dose, Figure 7(c) shows SEM images of polymer sample at 110 kGy. A mixture of cloudy and rock-type formation can be seen at this dose. It seems that free radicals in the form of clouds are evaporating from the rocky surface of the polymer sample. Free radicals produced by the gamma irradiation process can either react with oxygen, causing chain scission, or react internally, leading to cross-linking. Cross-linking is the predominant feature in low doses [20]. Figure 7(d) shows the SEM micrograph of polymer sample at 300 kGy. Cloudy portion with microvoids can be seen clearly. These results suggest that gamma energy dose modifies the surface morphology of the polymeric material and causes the allotropic modification of the sample to change into a rougher one with an increasing number of microvoids.

7. Conclusion

UHMWPE polymer shows substantial modifications in its optical, structural, chemical, and morphological characteristics when it is subjected to gamma radiation at different doses. The coloration effect has been found in polymer samples after irradiation which could be the possibility of the formation of new defects in the polymer. The optical E_g decreases by 32% at the highest dose of 300 kGy may also be associated with the formation of a conjugated system (-C=C-) of bands because of band cleavage and reconstruction. In addition to the above, for photosensitizers, it highly required modifications in the optical properties of the polymer. Optical properties of UHMWPE at commercially available laser wavelengths are needed [21].

XRD studies show that the virgin UHMWPE is semicrystalline in nature and crystallite size increases by 35% at the highest dose of 300 kGy. No significant change has been found in XRD patterns of virgin and irradiated UHMWPE which shows the structural stability of the polymer. Oscillatory behavior in transmittance intensities has been found in FTIR analysis. The number of small absorption peaks has been observed at 110 kGy due to irradiation which may be due to the cross-linking of the polymeric chain. Further, these peaks are found to disappear at 300 kGy. The SEM results suggest that the energy of irradiation modified the surface of the polymeric material and causes the smooth topography of the sample to modify into a rougher one with an increased number of microvoids. This describes why for due to gamma rays the polymer samples were irradiated initial oxidation was very low and increases over the years [22].

Data Availability

The XRD data from Powder XRD measurements were made on PW-1830 machine by using monochromatic CuKa (8.04 keV) and l¼0.154 nm used to support the findings of this study are included in the article. All experimental data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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