Research Article

Structural and Optical Investigations of Radiation Damage in Transparent PET Polymer Films

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Effects of gamma irradiation at different doses up to 135 kGy on polyethylene terephthalate (PET) polymer films have been investigated by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and ultraviolet-visible (UV-VIS) spectroscopy. From XRD analysis, it was found that even at a high dose of gamma irradiation of 135 kGy, crystallinity of the PET samples remain unchanged. However, the FTIR peak at 871 cm$^{-1}$ (depicting C–H bending mode of out-of-plane vibration) and another at 1303 cm$^{-1}$ (representing C–H bending mode of in-plane vibration) disappear for gamma-irradiated PET. In this study, it has also been found that $\gamma$-irradiation in air enhances the optical absorption in the wavelength region 320–370 nm. This has been attributed to free radicals being produced in the polymer by the $\gamma$-radiation. Further, the free radicals react with oxygen of air to form carbonyl group and hydroxyls. With increasing $\gamma$-dose, there is a red shift of the UV—near visible cutoff for PET. XRD and FTIR observations on $\gamma$-damage have been correlated.

1. Introduction

Radiation damage to various polymers [1–12] due to irradiation by either fast ions or energetic neutrons or high energy photons is a topic of practical and theoretical interest. Theoretical effort aims to understand [1–3] topics like the relative contribution of crosslinking and chain scission to the damage and the detailed mechanisms of the damage. The practical interest in such radiation damage pertains to utility factor and various applications. PET or polyethylene terephthalate films have attracted interest as polymers due to their ample application and wide availability. The changes, due to Mo, N, O, and Kr ion irradiations [4, 12] in PET structure, have been reported, and correlation of these changes to other properties were attempted. However, many aspects of damages due to $\gamma$-radiation and fast ions are not yet clearly understood so that more experimental data are welcome.

A high energy ion affects nuclei of the target solid in addition to its electronic interaction in the solid, and its energy is very often chosen to be much higher than $\gamma$-photon energy, here, 1.25 MeV. Electronic excitation can affect polymer bonding with varied results that depend on both the nature of radiation and the nature of the polymer in a complex manner. Our DSC thermogram [9, 10] showed that radiation induced changes of melting point of PEO-salt samples are in opposite directions for 160 MeV Ne$^{6+}$ ion and 1.25 MeV $\gamma$-ray irradiations. This interesting feature hints at different mechanisms of radiation damage in two cases—chain scission predominating in the $\gamma$-radiation, while 160 MeV Ne ions must have made crosslinking of chains to be the predominant damage process. Chain scission is known to predominate [11] in $\gamma$-irradiated PET as well. Heavier high energy ions can deposit much higher energy in a lower volume [4], to form ion tracks in polymers, causing different effects. So, damage by each kind of radiation needs to be documented.

FTIR spectroscopy has been one of the most powerful among the qualitative and quantitative methods of studying molecular bonding structure and functional group analysis.
There are a host of references regarding pure structural analysis namely, silicon, germanium, carbon, oxygen and hydrogen related compounds. However, identifying and analysis of functional groups in a compound structure in a polymer like PET are rather complicated and not fully understood. In this study, we have compared and correlated changes in optical property of PET with some functional groups detected in the material.

Among photons, γ-radiation is very effective in causing damage. Abou Zeid et al. [5] found γ-radiation to be more effective than thermal neutrons and electron beam in damaging high density polyethylene. For some space applications and practical situations like sterilization of food, packed in a polymer foil or sheet, damage to the polymers by γ-irradiation needs to be experimentally studied and understood [6, 7]. In earlier efforts [8–11], we studied radiation damage in engineering polymers and also in ion conducting polymers like PEO-salt compounds. PET (poly (ethylene terephthalate)) is basically a semicrystalline polyaromatic polymer [12] with the empirical formula \( (\text{C}_10\text{H}_8\text{O}_4)n \), as detailed later. The objective of the present study is to understand gamma irradiation-induced change in molecular structure of PET polymer films, from infrared analysis, and its correlation with the radiation effects on crystallinity and optical property.

2. Experimental Outline

Our samples were cut as suitable strips from 100 micron thick PET sheets. Such strips were gamma irradiated in air at room temperature to different doses up to 135 kGy, with a 130 rads/min Co60 gamma source (gamma energy = 1.25 MeV). Its dose rate (1.3 Gy min \(^{-1}\)) was determined with the help of the Frick Dosimeter, taking \( G(\text{Fe}^{3+}) = 15.6 \). Irradiation was carried out without any further intervention on the above-mentioned PET sample. Irradiated samples have always been preserved in vacuum desiccators.

The X-ray diffraction studies were carried out using Brucker AXS diffractometer at IUCA, New Delhi, India, before and after each irradiation for different \( y \)-doses. FTIR (Fourier transform infrared) spectroscopy of the samples were recorded in the transmission mode using FTIR (PerkinElmer model RX 1) spectrometer. The scans were done in the ratio mode with a resolution of 1 cm \(^{-1}\). The number of scans was maintained at 50 for all samples.

The optical absorption spectra of the polymer films were recorded, at room temperature, before and after each gamma irradiation in the wavelength range 200–800 nm employing UNICAM UV 500 UV-VIS spectrophotometer.

3. Results and Discussion

PET, having a chemical composition of C, H, and O, can be expected to be highly infrared active. It was, therefore, decided to carry out a careful infrared spectroscopy using a FTIR spectrometer to understand the molecular bonds.

Following [4], its chemical structure is

\[
\text{O}
\begin{array}{c}
\text{O} \\
\text{C} \\
\text{H}_2
\end{array}
\]

\[
\text{Polyethylene terephthalate (PET)}
\]

In order to understand the initial crystalline or amorphous nature of the material, XRD results are shown in the consolidated graph of Figure 1. This was done prior to understanding of the molecular bonds in PET. Unirradiated as well as irradiated PET sample depicted only one crystalline peak at \( 2\theta = 26^\circ \) corresponding to (100) plane. With increase of the dose of \( y \)-irradiation, neither any significant change of the X-ray peaks (like shift in \( 2\theta \) of the peak) nor any development of new peaks were observed. This implies that there is no noticeable change, due to \( y \)-irradiations at least up to 135 kGy, of the stacking of the polymer chains. Moreover, no growth of amorphous phase at the expense of the (100) plane crystallinity was detected. This is in contrast to 4.39 MeV/u Xe ion irradiation of PET to a fluence of \( 1.0 \times 10^{12} \) ions/cm \(^2\) (implying an electronic energy loss of 11.4 keV/nm) that destroyed the crystallinity, as indicated by (100) plane, completely, and the material finally underwent amorphization [13].

The peaks in FTIR spectra for PET give dual information. Firstly, every peak position is fundamental to molecular bonding structure or functional group existing in the infrared active material. So, any shift in peak position in a spectrum directly refers to a change in bond strength or bond angle. Such a feature is highly probable in a complex structure like PET. This means any change in the network structure of PET directly influence the bonding (=CO, =CHO, =OH, etc.) of the material. The influence either weakens or strengthens bonding corresponding to a functional group. Weakening and strengthening of a bond shifts the wave number of the corresponding absorption peak to lower and higher values, respectively. Absence of a particular molecular bond relates to scission or break in the particular bonding structure. However, coexistence of various types of functional groups in PET has a combined effect, and, as a result, the infrared absorption peak positions deviate from its pure form. Secondly, variation in intensity of particular peak in a spectrum correlates to the proportion of that functional group present in the material.

Full FTIR spectrum (4000 to 450 cm \(^{-1}\)) for unirradiated PET sample has been shown in Figure 2. FTIR results for all our \( y \)-irradiated PET samples along with that for the unirradiated sample have been compiled into a composite graph (Figure 3) for easy comparison. In this figure, the FTIR spectra of PET samples with successive gamma irradiations are depicted in the region 2000 cm \(^{-1}\) to 450 cm \(^{-1}\) to focus on the main region of interest only. The usual practice of plotting transmission (in %), as a function of wavenumber (in cm \(^{-1}\)), has been followed. The minima or dips in the transmission spectra refer to absorption maxima corresponding to characteristic molecules and groups.
In polyethene terephthalate (PET), there are molecular groups (involving carbon, hydrogen, and oxygen), which are highly infrared active and have characteristic absorption peaks. The FTIR peaks, mostly marked in Figures 2 and 3, appear in the present infrared absorption spectrum, reflecting their bond strength as outlined next. The C–H stretching modes of vibration are most strong, involve carbon and hydrogen atoms, and show up at higher wavenumbers in different functional groups. These refer to functional groups such as alkyl, alkanal, alken, alken, and arene, which appear as absorption peaks in the region 3000–2700 cm\(^{-1}\). The C–H bending mode of vibration has weaker bond strength compared to their stretching modes. Such modes of vibration exist in the alkyl and alkene groups. These appear in the absorption spectra in the region 1460–1370 cm\(^{-1}\) and 990–890 cm\(^{-1}\), respectively. In arene, the C–H bending mode of vibration, both in plane and out of plane, exist in the region 1300–1000 cm\(^{-1}\) and 900–650 cm\(^{-1}\), respectively. The O–H stretching mode in alkanol (OH) and alkyl groups (CH\(_3\), CH\(_2\), and CH) exist in the infrared absorption spectra in the region 3650–3590 cm\(^{-1}\). The C=O stretching mode of vibration in aliphatic ketone or alkanal, aromatic ketone, alkanolic acid alkanoyl chloride, and alkanolate ester appears in the region 1815–1680 cm\(^{-1}\). Characteristic infrared spectra in the range 1720–1712 cm\(^{-1}\) correspond to C=O in the carbonyl group [14, 15]. The C–O stretching modes in alkanolate ester and alkoxy ether have characteristic peaks in the region 1300–1050 cm\(^{-1}\). The groups parasubstituted phenyl ring, ethylene glycol, transconfiguration-\(\nu\)(CO) and -\(\nu\)(CH\(_2\)) has signature absorption peaks at 973 and 850 cm\(^{-1}\), respectively. The wagging vibrations for aliphatic, olefinic, aromatic, and acetylenic CH groups were related to features in the range 1000–650 cm\(^{-1}\). In the aromatic rings, stretching vibrations of double bonds and CH\(_2\) bending vibration.
were linked to 1680–1430 cm$^{-1}$ [4]. The creation of alkynes was assigned to ion irradiation leading to formation of C–H stretching mode of the alkyn end group (R–C≡C–H) at 3294 cm$^{-1}$. The C≡C stretching vibration was ascribed to 2102 cm$^{-1}$. The crystalline structure of PET underwent amorphization and was attributed to transconfiguration of the ethylene glycol residue. It was stressed that alkynes were formed near ion trajectory in the ion irradiated PET samples. The aromatic rings underwent a modification from unsubstituted to monosubstituted benzene groups rather than getting destroyed. The formation of olefins, carboxylic acids, alcohols and carbon dioxide occurred when PET was subjected to electron or UV irradiation [16, 17]. Main chain scission and formation of olefins in a PET monomer led to degradation products and resulted in products such as benzoic acid residue, alcohols and alkynes. The 1614, 1504, 410 1126, 1109, 1018, and 875 cm$^{-1}$ peaks were ascribed to parasubstituted benzene rings, while mono-substituted benzene rings corresponded to 1606 and 713 cm$^{-1}$. Different mechanisms for ion-induced degradation of polymers under vacuum and in oxygen atmosphere were discussed. Vacuum irradiation resulted in formation of carboxylic acid and benzoic acid residues. On the basis of fast recombination processes of radicals, it was reasoned that the reactions favored formation of alkynes. Further, multiple radicals on the ethylene glycol residue greatly enhanced the probability for creation of alkynes. Such a phenomenon was observed for ion irradiation of PET under vacuum. However, there are reports for absence of alkynes under low ionizing radiation (e.g., gamma, electrons [18, 19], or X-rays [20–22]). Moreover, alkynes were also detected in polymers with aliphatic main chains such as poly (vinylidene fluoride), polyethylene, and polystyrene under ion irradiation above a critical energy deposition. It was also concluded that the formation of alkynes required a remarkable reorganization of molecular bonds and assumed that the formation process was strongly related to multiple excitation and ionization events on an extremely short space and time scale.

Dworecki et al. subjected PET samples to N$^{4+}$, O$^{5+}$ and Kr$^{36+}$ ion irradiation. The energy dissipation by ions in the samples caused damage which was attributed to crosslinking of unsaturated adjacent radicals, amorphization of the crystalline fraction of the polymer, scission of the chains, and oxidation [12]. They observed changes of infrared absorption bands for the methylene group in 3914–2970 cm$^{-1}$, 1683–1578 cm$^{-1}$, and 631–506 cm$^{-1}$ regions [12, 23]. The variation of the absorption spectra in the regions 1740–1660 cm$^{-1}$ and 1660–1600 cm$^{-1}$ were assigned to the bands of the carbonyl group [12].

Our γ-irradiation on PET samples did not induce any significant change in the existing C–H and O–H stretching vibration of different types of H-bonds in the PET and also no alkyn group (3294 cm$^{-1}$) was detected in the region 3600–2500 cm$^{-1}$. This is in contrast to the effect of Kr or Mo ion irradiation of PET [4], but in line with earlier reports of no alkyn group formation in γ-irradiations of PET. Further, the absorption maxima in regions ~3000 cm$^{-1}$ to ~1400 cm$^{-1}$ and ~850 cm$^{-1}$ to ~500 cm$^{-1}$ remained practically invariant with increasing γ-irradiation dose. The region from ~3000 cm$^{-1}$ to about 2000 cm$^{-1}$ is attributed to OH bond which in turn, categorically depends on hydrogen-bonding configuration [14, 15, 24–26]. This means that hydroxyl group bonding configuration in the polymer chain remains almost intact under the influence of different doses of γ-irradiation. As a result the hydroxyl group content remains almost unchanged with increase in chain length of the polymer. The FTIR absorption peak at 1716 cm$^{-1}$, representing carbonyl C=O stretching, is one of the strongest absorption peaks of the FTIR spectra. This peak does not show any significant change in peak intensity or peak position as an effect of γ-irradiation, the observed changes being minor and fluctuating. However, absorption peaks in the region 1390–1246 cm$^{-1}$ underwent some interesting changes (Table 1). For PET samples, commencing with initial γ-irradiation of 30 kGy till 135 kGy, the absorption peak shifted from 1097 cm$^{-1}$ to lower value 1089–1085 cm$^{-1}$. The C=O bond stretching mode at 1246 cm$^{-1}$ shifted to lower wavenumber 1226–1150 cm$^{-1}$ with increasing doses of gamma irradiation. The 1303 cm$^{-1}$ absorption peak in unirradiated PET, disappeared with the lowest dose (30 kGy) of γ irradiation (Table 1). The peak at 1260 cm$^{-1}$ underwent a variation till 1297 cm$^{-1}$ with increasing doses of γ-irradiation (Figure 3). These features indicate weakening of the C=O bonding modes of vibration with increased dose of gamma irradiation. While on the other hand, the C–C alkane (–H$_2$C–CH$_2$–) bond at 1328 cm$^{-1}$ and 1390 cm$^{-1}$ show almost no change with increased dose of gamma irradiation. This could mean that chemical bond strength related to C–C and CH$_2$ remains invariant. Absorption peaks at ~1303, 1246, and 1097 cm$^{-1}$, which refer to in-plane C–H bending bond and C–O stretching bonds corresponding to alkoxy (ether) or alkanoate ester groups, shifted to lower wavenumbers. It is rather clear that any shift in peak towards lower wave number value represents weakening of bonds or scission of bonds and peak shifts towards higher values indicate stronger bonds. The exact reasons for such shifts are still not very clear. It is important to observe that under the impact of lowest dose of gamma irradiation, the absorption peaks at 1302 and 871 cm$^{-1}$, representing out-of-plane C–H bending mode, disappear completely.

There are reports which indicate that crystallinity of PET, corresponding to (100) crystallographic plane, correlate with the existence of infrared absorption peak strength at 1472, 973, and 850 cm$^{-1}$ corresponding to ethylene glycol molecular groups [13, 27]. From our data (Table 1), we find that in our PET material the absorption peak nearest to 1472 cm$^{-1}$ is at 1465 cm$^{-1}$ in unirradiated PET, and it remains almost invariant with variation of gamma-radiation dose. Infrared absorption at 973 cm$^{-1}$ and 850 cm$^{-1}$ remains unchanged. It can be suggested that C–O–C and γ-(CH$_2$)$_2$ transconfiguration in the PET samples remains intact and does not undergo any change with variation in gamma radiation doses. As a consequence, the crystalline structure of PET remains unchanged with gamma-radiation doses, as found by X-ray crystallography (Figure 1).

The optical absorbance versus wavelength results from our UV-visible absorption experiment is depicted in Figure 4 for different radiation doses in the range 0–135 kGy. It can
Table 1: Our observed wavenumber values (in cm\(^{-1}\)) at the FTIR absorption peaks for unirradiated (UI) and differently \(\gamma\)-irradiated PET samples. In the symbolic names like PET\(_{135}\), the numbers in the names indicate \(\gamma\)-doses in kGy unit.

<table>
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be seen that irradiated samples have a red shift [25] for the wavelengths in ultraviolet and near visible region. As expected, absorbance is seen to increase very steeply for wavelengths below a cutoff wavelength. There is also an absorption tail on the high wavelength side. It is clear from the results in Figure 4 that the absorbance graph for our PET samples shifts upwards (i.e., towards higher absorbance) monotonically with increasing \(\gamma\)-dose. However, Moura et al. [6] observed nonmonotonic behavior for LDPE samples, for irradiation doses 20, 30, and 65 kGy, and they called it inconsistent. Absorbance in the near-UV has been observed to be more sensitive to \(\gamma\)-irradiation in wavelength range 320–370 nm, out of 200 to 800 nm spectrum actually recorded. At an arbitrarily chosen wavelength of 335 nm, for example, absorbance increases from the unirradiated value of 0.258 to 0.592 for 135 kGy, as detailed in Table 2.

The change in absorption in this wavelength region is likely to be due to formation of unsaturated groups and presence of carbonyl and hydroxyl groups in the polymer due to the irradiation in air. The main effects of irradiation are chain scissions and crosslinking, accompanied by the formation of unsaturated products in the polymer chain. Free radicals produced in the polymer by the radiation can react with oxygen in air and form such groups. There are reports [6, 13, 25] of such increase of carbonyl concentration due to \(\gamma\)-irradiation and also of formation of hydroxyl compounds.

4. Conclusions

FTIR absorption peak at \(\sim 871\) cm\(^{-1}\), representing out-of-plane C–H bending mode of PET, disappears completely under the impact of initial dose (30 kGy) of gamma irradiation. No significant \(\gamma\)-irradiation-induced change in the region from \(\sim 4000\) cm\(^{-1}\) to \(\sim 3000\) cm\(^{-1}\) (attributed to OH bonding) tends to show that the hydroxyl group bonding configuration in the polymer chain remains almost intact under the influence of different doses of \(\gamma\)-irradiation. With initial \(\gamma\)-irradiation of 30 kGy till 135 kGy, the C=C bond stretching mode at 1246 cm\(^{-1}\) shifted to lower wave numbers in the range 1226–1150 cm\(^{-1}\). Further, 1303 cm\(^{-1}\) decreased
...to 1260 cm\(^{-1}\) and varied till 1297 cm\(^{-1}\) indicated weakening of the respective carbon-carbon double bonding modes of vibration with increased dose of gamma irradiation. While on the other hand, the C=C alkane (−CH\(_2\)-) bond at 1328 cm\(^{-1}\) and 1390 cm\(^{-1}\) shows almost no change with increased dose of gamma irradiation. This could mean that chemical bond strength related to C=C, C=H, and CH\(_2\) remains invariant.

Crystalline structure in the present PET sample consists of (100) planes of atoms giving a XRD peak at \(2\theta = 26^\circ\). Our XRD analysis has shown that gamma irradiation of PET samples has no influence on this crystalline structure, at least up to 135 kGy. This can be correlated to our FTIR observations. We see that C=O–C bond at 973 cm\(^{-1}\) and \(\gamma\)-(CH\(_2\)) transconfiguration bond at 850 cm\(^{-1}\) in the PET samples are hardly affected by different gamma radiation doses. As already discussed, these infrared absorption peaks are related to (100) crystallographic planes. So, XRD and FTIR results support each other in finding no loss of crystallinity.

In ultraviolet (UV) visible (VIS) spectroscopy, change of optical density or absorbance was detected even at the lowest dose (50 kGy) of \(\gamma\)-irradiation. UV barrier improves due to irradiation. Increase of absorbance with irradiation dose at any particular wavelength has been monotonic. Enhancement of optical absorption by \(\gamma\)-irradiation has been observed to be significant in wavelength range 320–370 nm.

**Table 2: Measured absorbance of PET, at the wavelength 335 nm, for different \(\gamma\)-doses.**

<table>
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<th>(\gamma)-dose (kGy)</th>
<th>0</th>
<th>10</th>
<th>25</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
<th>100</th>
<th>135</th>
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<tr>
<td>Absorbance</td>
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<td>0.274</td>
<td>0.310</td>
<td>0.315</td>
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<td>0.412</td>
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**Figure 4:** UV-Vis absorption spectra of PET—before and after gamma irradiation to different doses as indicated.

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