5.1 Introduction

The high energy radiations bring extensive changes to a variety of materials and their properties including chemical, optical, morphological, structural etc. Sterilization by ionizing radiations (X-rays, γ-rays, ultraviolet light) is considered to be a useful technique to produce sterile drug-polymer-matrices for clinical uses and also cause essential changes in its optical, structural and morphological characteristics. As the influence of γ-irradiation, the degradation of PLGA occurs. PLGA nanocomposites can extend the properties and potential applications of the biodegradable polymer by adjustment of the nanoclay content. Biodegradation of PLGA nanocomposites was retarded with increasing dose due to the introduction of crosslinking during irradiation. The biocompatibility, non-toxicity and non-inflammatory properties have been found in gamma irradiated PLGA which have been frequently used in bone repair applications (Nelson et al., 1997; Hollinger, 1983; Kleinschmidt et al., 1993; Levy et al., 1994).

The present chapter deals with the interaction of gamma rays with PLGA, PLGA/Clay nanocomposites and the modifications induced by these rays. The gamma irradiation has been performed using $^{60}$Co source with gamma energy of 1.25 MeV and the irradiator dose rate 7.5 kGy/h at Inter University Accelerator Centre (IUAC), New Delhi, India. The present chapter aims to study the effect of these radiations on PLGA and its nanocomposites with various irradiation doses by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FSEM), Fourier Transform Infrared (FTIR) and UV-Visible Spectroscopy. The influence of organically modified nanoclay (Cloisite®30B) on the durability of the nanocomposite samples is also reported. The results for various studies performed have been discussed on the basis of some basic mechanisms involved during gamma irradiation.

5.2 UV-Visible Analysis

The changes in optical band gap energy and absorption edge of polymer upon irradiation can be studied using absorption spectrometer. The wavelength of absorption is a measure of the separation of the energy levels of the orbitals concerned. Absorption
in polymer in near ultraviolet and visible region have been used to calculate the optical energy gaps and the width of the energy tail. The optical band gap energy and Urbach’s energy for the PLGA and its nanocomposites before and after gamma irradiation were calculated by using equations 3.1 and 3.2, and the variations in these values with gamma dose have been discussed. The increase in the absorbance due to irradiation indicates the formation of defects/degradation. Values of the optical energy gap and the width of the energy tails, i.e. Urbach energy, have been measured before and after irradiation.

The results of absorption studies with UV-Visible spectrophotometer carried out in pristine and irradiated PLGA and PLGA/Clay nanocomposites with gamma rays have been discussed. Figures 5.1-5.4 shows the changes in the absorption spectra of PLGA and PLGA/Clay nanocomposites upon gamma exposure in the dose range of 0–50 kGy. It can be seen that the optical absorption edge is not sharply defined, thus clearly indicating the amorphous nature of the PLGA and its nanocomposites film samples. From the absorption spectra, the indirect band gap, \((\alpha h\nu)^{1/2}\) were plotted as a function of photon energy \((h\nu)\). The values of indirect band gap \((E_g)\) for pristine and gamma irradiated samples were determined by extrapolation of the straight part of the Tauc’s plot (Figure 5.5-5.8) and measuring the intercept value in \(h\nu\) axis are enlisted in Table 5.1 and Table 5.2.

Sterilization by \(\gamma\)-radiation is known to cause chain scission in PLGA polymer (Yang et al., 2011; Lee et al., 2003). At dose of 10 kGy \(\gamma\)-radiations, band gap decreases due to deterioration of polymer chains as a result of chain scission. But at higher doses up to 50 kGy there was a small increase in optical band gap energy (Table 5.1). This may be attributed to the fact that, for gamma irradiation upto 50 kGy, recombination of free radicals which are produced by ionizing radiations or intermolecular cross-linking takes place within the polymer. The absorbance difference of pristine and irradiated polymer indicates that gamma irradiation enhances the UV absorbance and leads to formation of new chemical species as a result of energy transfer by the incidence of gamma rays.
It is also observed from Table 5.2, that there is a variation in band gap of PLGA nanocomposites with increasing dose of $\gamma$-radiation. With increasing dose rate, the values of the indirect band gap of nanocomposites samples containing 1 wt% and 3 wt% clay contents have been found to be decrease however for 5 wt% clay content the values are increasing. The decrease in band gap in 1 wt% and 3 wt% nanocomposites samples indicates that random chain scission is not the primary mechanism. The decrease in band gap implies that due to impact of radiation treatment the nanocomposites samples containing small clay content got nicely distributed without any aggregation of clay layers. In case of 5 wt% clay content, the band gap increases from 4.70 to 4.83 eV. This increase in band gap for 5 wt% nanocomposites is probably due to the partial aggregation of clay layers in the polymer matrix as compared to nano level dispersion in 1 wt% and 3 wt% nanocomposites.

The irregularities in the band gap of the thin films was measured in terms of Urbach energy ($E_u$) and is determined from the inverse of the slope of the plots $\ln(\alpha)$ versus $h\nu$ (Mott and Davis, 1979; Tauc, 1974; Urbach, 1953). The width of the band tails of the localized states are described by Urbach energy. The value of Urbach energy increases in 1 wt% and 3 wt% nanocomposite samples with increase in gamma dose but at 5 wt%, $E_u$ decreases with increase in fluence which may be due to recovery of irregularities in the band gap of polymer with crosslinking at high content of clay loading or decrease in the amorphicitcity of polymer.
Figure 5.1. UV-Visible spectra of pristine and gamma irradiated PLGA samples.

Figure 5.2. UV-Visible spectra of pristine and gamma irradiated PLGA nanocomposites samples containing 1wt% clay content.
Figure 5.3. UV-Visible spectra of pristine and gamma irradiated PLGA nanocomposites samples containing 3wt% clay content.

Figure 5.4. UV-Visible spectra of pristine and gamma irradiated PLGA nanocomposites samples containing 5wt% clay content.
**Figure 5.5.** Extrapolation of Tuac’s plot of the pristine and irradiated PLGA samples.

**Figure 5.6.** Extrapolation of Tuac’s plot of the pristine and irradiated PLGA nanocomposites samples containing 1wt% clay content.
Figure 5.7. Extrapolation of Tuac’s plot of the pristine and irradiated PLGA nanocomposites samples containing 3wt% clay content.

Figure 5.8. Extrapolation of Tuac’s plot of the pristine and irradiated PLGA nanocomposites samples containing 5wt% clay content.
Table 5.1. The variation of optical band gap energy and Urbach’s energy in pristine and gamma irradiated PLGA samples.

<table>
<thead>
<tr>
<th>Gamma dose (kGy)</th>
<th>Band gap energy ((E_g)) (eV)</th>
<th>Urbach’s energy ((E_u)) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>4.81</td>
<td>0.22</td>
</tr>
<tr>
<td>5</td>
<td>4.70</td>
<td>0.23</td>
</tr>
<tr>
<td>10</td>
<td>4.62</td>
<td>0.48</td>
</tr>
<tr>
<td>15</td>
<td>4.80</td>
<td>0.36</td>
</tr>
<tr>
<td>25</td>
<td>4.84</td>
<td>0.30</td>
</tr>
<tr>
<td>50</td>
<td>4.92</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 5.2. The variation of optical band gap energy and Urbach’s energy in pristine and gamma irradiated PLGA/Cloisite\textsuperscript{®} 30B nanocomposites samples.

<table>
<thead>
<tr>
<th>Gamma Dose (kGy)</th>
<th>1wt%</th>
<th>3wt%</th>
<th>5wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Band gap energy ((E_g)) (eV)</td>
<td>Urbach energy ((E_u)) (eV)</td>
<td>Band gap energy ((E_g)) (eV)</td>
</tr>
<tr>
<td>0</td>
<td>4.88</td>
<td>0.20</td>
<td>4.69</td>
</tr>
<tr>
<td>5</td>
<td>4.89</td>
<td>0.18</td>
<td>4.66</td>
</tr>
<tr>
<td>10</td>
<td>4.85</td>
<td>0.19</td>
<td>4.62</td>
</tr>
<tr>
<td>15</td>
<td>4.83</td>
<td>0.18</td>
<td>4.58</td>
</tr>
<tr>
<td>25</td>
<td>4.80</td>
<td>0.25</td>
<td>4.47</td>
</tr>
</tbody>
</table>
5.3 Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier transforms infrared spectroscopy (FTIR) concerns the detection of transition between energy levels in the molecules for the polymer characterization. It is sensitive to the molecular environment, chain conformation and morphology (Constantini et al., 2005; Rufino and Monterio, 2000; Campbell and White, 1989). It provides the information about functional groups within the polymer samples.

The changes in chemical structure of pristine PLGA and PLGA-based nanocomposites containing 1wt% and 5wt% of Cloisite® 30B induced by gamma irradiation were determined using FTIR spectroscopy. Representative FTIR spectra of non-irradiated and irradiated PLGA samples at 5, 15, 25 and 50 kGy, recorded in the carbonyl and hydroxyl regions are shown in Figure 5.9. The intensity of absorbed peak appeared at 1750 cm⁻¹ in pristine and irradiated samples is related to carbonyl group of ester linkage. The relative intensity of this characteristic peak regularly decreases with radiation dose. This means that as a result of gamma irradiations, the radiation induced oxidation reaction of ester groups occur which leads to the formation of free radicals and inducing the formation of hydroxyl and carbonyl compounds (Zaidi et al., 2013). The absorption band appearing in region 3400-3600 cm⁻¹ is attributed to OH groups in alcohols or carboxylic acids. Upon irradiation with gamma dose, no significant changes have been observed. Similar results are deduced for the non-irradiated and irradiated nanocomposite samples at 5, 15 and 25kGy. FTIR spectra for PLGA/Clay nanocomposites containing 1wt% and 5wt% clay content are shown in Figure 5.10 and Figure 5.11, respectively. The different FTIR spectra of pristine PLGA and irradiated nanocomposite samples reveals that there is shift of the band position of the irradiated nanocomposite samples in the presence of Cloisite® 30B in comparison with pristine PLGA. It is expected that the modifier will form hydrogen bond with epoxy in nanocomposites.
Figure 5.9. FTIR spectra of pristine and gamma irradiated PLGA samples.

Figure 5.10. FTIR spectra of pristine and gamma irradiated PLGA nanocomposites samples containing 1wt% clay content at doses 5kGy, 15kGy and 25kGy.
Figure 5.11. FTIR spectra of pristine and gamma irradiated PLGA nanocomposites samples containing 5wt% clay content at doses 5kGy, 15kGy and 25kGy.
5.4 X-ray Diffraction (XRD) Analysis

The structural arrangement of atoms and molecules in polymer and polymer nanocomposites can be studied by X-ray diffraction methods.

XRD analysis was conducted on pristine and irradiated film samples to understand the effect of gamma dose on the structure of PLGA and PLGA/Clay nanocomposites. XRD spectrum of pristine and gamma irradiated PLGA samples does not show any crystalline peaks but a characteristic broad amorphous peak for all film samples as shown in Figure 5.12. As can be seen from Figure 5.12, absence of Brag’s diffraction peak but a broad hump appears at 2θ~21.35° in the pristine PLGA sample, confirming the amorphous nature of the sample. The broadening of the diffraction peak was also observed in PLGA samples after irradiation. The reason of broadening of peak is the formation of defects after irradiation. Such defects, which may creates the new energy levels and leads to the broadening of peaks (Kumar et al., 2012). The irradiated samples also exhibit the same diffraction patterns except that peak shifts by a smaller angle. The diffraction pattern of Cloisite® 30B displays a diffraction peak at 2θ=4.8, corresponding to d_{001} (Figure 4.1). The interlayer spacing is calculated from the d_{001} peak position using Bragg’s law:

$$d_{00n} = n\lambda / 2\sin \theta$$

Where n is an integer, θ is the angle of incidence of the X-ray beam, and λ=0.154 nm is the X-ray wavelength. In Figure 5.13 and Figure 5.14, PLGA/Clay nanocomposites film samples with different loading of nanoclay i.e. 1wt% and 5wt%, after γ-irradiation have been observed. In the case of Cloisite® 30B based nanocomposites, the characteristic peak of irradiated samples does not show any d_{001} spacing. This may be due to extensive polymer penetration resulting in disruption of parallel stacking of the organoclay, causing in disordered and eventual delamination of the silicate layers in polymer matrix producing exfoliated morphology of nanocomposites, which consist of individual silicate layers dispersed in polymer matrix (Giannelis et al., 1999; Krikorian and Pochan, 2003). The XRD pattern of the PLGA shows a lack of intergallery clay diffraction due to complete exfoliation in pristine as well as those irradiated samples.
Figure 5.12. X-ray diffraction pattern for pristine and gamma irradiated PLGA samples.

Figure 5.13. X-ray diffraction pattern for pristine and gamma irradiated PLGA nanocomposites samples containing 1wt% clay content at doses 5kGy, 15kGy and 25kGy.
Figure 5.14. X-ray diffraction pattern for pristine and gamma irradiated PLGA nanocomposites samples containing 5wt% clay content at doses 5kGy, 15kGy and 25kGy.
5.5 Morphological Analysis

For morphological characterization, the PLGA and PLGA/Clay nanocomposites were observed with scanning electron microscope. The morphological changes induced by γ-irradiation in the PLGA and PLGA/Clay nanocomposites samples are examined by SEM. Figure 5.15(a-c) shows the SEM micrographs of the smooth surface of pristine PLGA and fractured surfaces of PLGA samples after γ-irradiation. No significant defects are visible on the surface of pristine PLGA samples but it displayed some small voids on the surface probably due to air pockets formed during preparation. These structures are present in both pristine PLGA as well as PLGA/Clay micrographs, thus, confirming that these are not clay agglomerations. The micrographs reveal also that no cracks are detected on the pristine PLGA surface. At 50 kGy of gamma exposure, considerable defects are observed on the fractured surface of sample (Figure 5.15(c)). These exposed samples are obviously degraded, as evidenced by a rough surface, the appearance of microcavities of different sizes and shapes and the formation of cracks. The number and the size of the microcavities have increased considerably with dose rate of gamma radiation.

Figure 5.16 and Figure 5.17 exhibit the SEM micrographs of surfaces for PLGA/Clay nanocomposites (containing 1wt% and 5wt% clay content) before and after γ-irradiation. The SEM analyses reveal that significant changes in the morphology of PLGA/Clay nanocomposites have been induced by the γ-irradiation treatment in which higher level of dispersion is expected with the radiation dose. The effects are much less pronounced in the PLGA nanocomposite samples, containing different clay content as compared to irradiated PLGA samples. In Figure 5.17, the fractured surface of the PLGA nanocomposites containing 5wt% clay content exhibit a slightly rough surface before exposure, in which nanoparticles of Cloisite® 30B in the PLGA matrix are homogeneously dispersed. Gamma irradiated PLGA nanocomposites film samples do not lead to significant degradation in contrast to previous observation for pristine PLGA. With increasing irradiation dose, the orientation of silicate layers seems to be completely destroyed, and an exfoliated morphology occurs due to random distribution.
of clay layers into polymer matrix. According to Lu et al. (2005), upon irradiation the species such as free radicals and ions generated with high mobility, they may diffuse in and/or out from the clay galleries. This rate of diffusion depends upon the irradiation dose rate, which may support the improvement of the steric interaction between clay layers and making exfoliated structure within the polymer (Koo et al., 2006). The morphology of irradiated nanocomposites clearly indicates better dispersion of the clay particles of Cloisite® 30B in the PLGA matrix. The SEM observation also suggests that the PLGA/Clay nanocomposites containing different amounts of nanoclay have shown an exfoliated morphology.
Figure 5.15. SEM micrographs of pristine PLGA (a) before irradiation and (b) after gamma irradiation of 25 kGy, (c) 50 kGy.
Figure 5.16. SEM micrographs of fractured surface for PLGA/Cloisite® 30B (1wt%) (a) before irradiation and (b) after gamma irradiation of 25 kGy.
Figure 5.17. SEM micrographs of fractured surface for PLGA/Cloisite® 30B (5wt%) (a) before irradiation and (b) after gamma irradiation of 25 kGy.
Conclusion

The results reported in the present study show that PLGA and PLGA/Clay nanocomposites prepared by ultrasonication method and exposed to γ-irradiation exhibit significant changes in properties of the materials. The nature and extent of changes in morphology of irradiated nanocomposites are strongly affected by the presence of clay. Irradiation helps in a nano dispersion of clay layers in polymer matrix, and results in an exfoliated morphology especially at higher dose. The remarkable changes are obtained in the optical properties which may be attributed to a formation of cross-linking/chain scission or recombination of the defects, which leads to an increase in the band gap energy. XRD and FTIR investigations also confirm the intermolecular interactions between clay and polymer chains after γ-radiations. The damage caused by γ-irradiation is found to be much more in PLGA samples as compared to irradiated PLGA nanocomposites. The present study of γ-irradiation of PLGA and PLGA/Clay nanocomposites has important implications for drug delivery and biomedical applications.