Chapter 2

A Comparative Study on Mechanical, Optical and Structural Properties of Co-60 Gamma Ray-Irradiated Polypropylene and Polyimide

This chapter describes a comparative study on physicochemical properties of Co-60 gamma irradiated polypropylene and polyimide. These polymers were irradiated with Co-60 gamma radiation at the doses from 0 to 230.4 kGy. The stress-strain analysis indicates that polypropylene suffers a significant degradation in its stress-strain based mechanical properties, while polyimide irradiated at the same doses under similar conditions shows remarkable stability in mechanical properties. The percentage elongation, a sensitive parameter for evaluating radiation effects, shows 90 % decrease in case of polypropylene and only a 7 % decrease for polyimide. The gamma ray induced degradation in polypropylene is mainly attributed to the extensive chain scissioning, decrease in molecular weight, oxidative embrittlement and defects whereas, the stability of the polyimide at similar doses is due to its aromatic, and complex monomer, CTC based extraordinarily strong inter- and intra-molecular interactions and oxidation resistance. This interpretation is very well supported by wide range of characterizations. The results of FTIR, UV-Visible, EDS and SEM analysis confirm that polypropylene undergoes scissioning of C-H, C-C bonds, formation of carbonyl groups, 26 % decrease in the band gap and increase in the surface roughness. But for the gamma irradiated polyimide, the scissioning of bonds, increase in of roughness and oxidation could not be noticed. This confirms that the excessively aromatic and complex monomer, CTC based extraordinarily strong inter and intra-molecular interactions and oxidation resistance have made the polyimide network substantially stable against gamma radiation up to dose of 230.4 kGy.
2.1 Introduction and Literature Survey: The applications of polymers in high and moderate radiation fields such as nuclear installations, space missions, radiation sterilization etc. need techniques to explore the effects of various radiations on their physicochemical properties. These techniques not only facilitate in understanding the fundamental radiation physics and chemistry of polymers, but also provide information required for designing radiation stable polymeric systems such as blends and composites, radiation processing of polymers, radiation enhanced diffusion, tailoring the properties and radiation assisted synthesis of polymer-nanocomposites. This requires a comprehensive and thorough understanding of effects of various particulate as well as non-particulate radiations on both radiation resistant as well as radiation sensitive polymers [1-11].

The exposure of polymers to radiation results into several physicochemical changes, a few of which include scissioning, crosslinking, unsaturation/conjugation, oxidation, embrittlement, formation of radiolysis products (hydrocarbons, carboxyl, hydroxyl and hydroperoxide etc.), evolution of gases and coloration. These changes mainly depend upon the type, structure, morphology and purity of the polymer as well as the type of radiation, dose level and its environment. In general, such changes lead to the significant modifications in mechanical, thermal, electrical and optical properties of polymers [11-13].

There are number of reports dealing with the effects of low and high-energy electrons, ions and gamma radiation on various properties of polymers. The important properties of the polymers such as mechanical, optical, thermal and electrical have been characterized and studied by the techniques such as FTIR, UV-Visible, TGA, XPS, DSC etc. However, in this literature, the focus is either on an individual polymer or polymers belonging to similar class like either aliphatic or aromatic [1, 3, 4-6, 8, 10-15]. Moreover, these studies have been carried out with radiation having different types, energies, dose rates, dose levels and environments. Therefore, a comprehensive and systematic analysis of the effects of radiation on the polymers belonging to different categories, but irradiated with same radiation under identical conditions is crucial and desirable since it can elucidate the structure-property relations of irradiated polymers in a better and generalized manner.

Polypropylene and polyimide belong to two entirely different families of polymers namely, aliphatic and aromatic respectively. Both these polymers are commercially important and are invariably exposed to radiation for various applications.
Polypropylene is a lightweight, versatile, low cost, chemically stable polymer and effectively used in medical-pharmaceutical components, food packaging and cosmetics, where it is subjected to radiation sterilization [1, 11, 15]. Polyimide (Kapton) is an important aromatic polymer known for its outstanding mechanical strength, excellent insulating properties, high glass transition temperature, light weight, low density and has superior thermal stability. It is used in spacecrafts and nuclear, aerospace and microelectronic industry [4, 5, 9, 16, 17]. In particular, polyimide gets exposed to radiation in nuclear and aerospace applications.

The radiation processing can be achieved by non particulate radiations such as microwave, infrared, laser, cold and thermal plasma, x rays, and gamma rays and non-particulate radiations such as low and high energy electrons, protons, light and heavy ions, neutrons etc. At present two most common radiation types in laboratory and industrial use are gamma and electron beam. The gamma facilities are mainly based on cobalt-60. The advantages of gamma radiation include the fact that gamma rays are very penetrating, they can be used to process the samples having relatively large dimensions and can deposit the energy uniformly. Further, the technology is extremely simple and it is not sensitive to electricity prices. Gamma rays are generally obtained from Co-60 gamma sources and carry energies 1.17 MeV and 1.33 MeV [18-20].

Therefore, in this chapter, the effects of Co-60 gamma radiation on the mechanical, optical and structural properties of polypropylene and polyimide have been studied and their respective radiation resistance has been compared. The mechanical properties based on stress-strain curves like Young's modulus, tensile strength, percentage elongation and strain energy are characterized along with optical and structural properties using techniques such as FTIR, UV-VIS, EDS, XRD and SEM. These characterizations are used to interpret the radiation-induced changes in terms of physical and chemical structure of these polymers. The objective is to correlate and compare the radiation damage induced by gamma irradiation with the structure and morphology of polypropylene and polyimide.

In the following paragraphs, the Co-60 gamma source and interaction of gamma rays with the matter are discussed in detail.
2.2 Co-60 Gamma Source: Cobalt-60 ($^{60}$Co) is a radioactive isotope of cobalt, with a half life of 5.27 years. $^{60}$Co decays by negative beta decay to the stable isotope Nickel-60 ($^{60}$Ni). In the process of decay, $^{60}$Co emits one electron with energy of up to 315 keV and then two gamma rays with energies of 1.17 and 1.33 MeV, respectively. The decay scheme Co-60 is shown below in figure 2.1.

![Decay Scheme of Co-60; Emission of Gamma Rays](image)

Figure 2.1: Decay Scheme of Co-60; Emission of Gamma Rays

2.2.1 Gamma Radiation: Gamma rays are the radiations having shortest wavelength (below about 10 picometers) and highest energy (around 100 keV) in the electromagnetic spectrum. These are the most energetic amongst all the electromagnetic radiations. Due to shortest wavelength gamma rays have the greatest ability to penetrate through any gap, even a subatomic one.

2.2.2 Co-60 Gamma Facility in Department of Chemistry, University of Pune: In this work the gamma ray facility was used from Department of Chemistry, University of Pune. The geometry of pencils in the source is arranged in such a fashion that it provides uniform dose throughout the irradiation cavity. The design of the source is as shown in figure 2.2

2.3 Interaction of Gamma Rays with Matter: When gamma rays pass through the matter, their intensity decreases exponentially. The interaction of gamma rays with the matter is governed by the density and thickness of the absorber as well as atomic absorption
coefficient ($\mu_a$). While passing through the matter, gamma rays deposit their energy by ionization and excitation of the molecules. This occurs by three important processes: Photoelectric effect, Compton scattering and pair production. The atomic absorption coefficient is the sum of cross sections of these three processes.

$$\mu_a = \tau_a + \sigma_a + \pi_a$$ \hspace{1cm} ...(2.1)

Where $\tau_a$, $\sigma_a$ and $\pi_a$ are the atomic cross sections for photoelectric absorption, Compton scattering and pair production respectively.

(i) **Photoelectric Effect:** In this process, gamma ray is completely absorbed and transfers all of its energy to the atomic electron (mostly k shell electron) resulting in its ejection. The ejected photoelectron carries kinetic energy equal to the difference between the energy of the incident gamma ray photon and the binding energy of the electron. This process is dominant for the low energy gamma ray photons with energies in the range 10-100 keV. This process is less probable for gamma rays of higher energies. The atomic cross section for the photoelectric effect is given by

$$\tau_a = CZ^4 \lambda^3$$ \hspace{1cm} ...(2.2)
Where $C$ is a constant having value $2.6 \times 10^{-30} \text{ m}^2$, $Z$ is the atomic number of the absorber and $\lambda$ is the wavelength of the gamma ray. This indicates that probability of photoelectric effect increases with the atomic number, and decreases with the energy of photon.

(ii) **Compton Scattering:** In this process, the gamma ray transfers its energy to a free or loosely bound electron resulting its ejection and a photon of reduced energy is scattered in a direction different from that of incident photon. This process is dominant for the gamma rays in the energy range 100 keV-10 MeV. The atomic cross section for Compton scattering is given by

$$\sigma_c = \frac{8\pi}{3} \left( \frac{e^2}{4\pi\varepsilon mc^2} \right) \frac{3}{8\varepsilon} \ln \left(2\varepsilon + \frac{1}{2}\right) \quad \ldots(2.3)$$

Where $\varepsilon = \hbar \nu/mc^2$.

(iii) **Pair Production:** When gamma ray passes across the nucleus, its energy is converted to a pair of electron and positron due to the electric field of the nucleus. Energy in excess of the equivalent rest mass of the two particles (1.022 MeV) appears as the kinetic energy of the pair and the recoil nucleus. At the end of its range, positron combines with the free electron. The entire mass of these two particles is then converted into two gamma rays each having energy 0.51 MeV. Though the minimum energy needed is $2m_0c^2$ i.e. 1.022 MeV, this process is more probable for photons with energy greater than 10 MeV. The atomic cross section for the pair production is given by

$$\pi_p = \frac{Z^2}{137} \left( \frac{e^2}{4\pi\varepsilon mc^2} \right)^2 \left( \frac{28}{9} \ln \frac{183}{\sqrt{Z} - \frac{2}{27}} \right) \quad \ldots(2.4)$$

The photoelectric effect dominates at low energies and high $Z$, Compton effect dominates at medium energies and low $Z$, and the pair production effect dominates at high energies and high $Z$. The source of gamma rays used in the present study was Co-60, which is the most frequently available gamma rays source. This source emits the gamma rays of energies 1.17 MeV and 1.33 MeV, which means that the most probable process by which gamma ray has transferred the energy to the polymers, is Compton scattering.

While the charged particles like $\alpha$ rays loose their energy in many encounters, the gamma ray photons are absorbed or scattered in a single event. All along their passage
through matter, the gamma ray photon may pass through an indefinite distance through matter without interacting i.e. without loosing any energy, and suddenly in a single encounter with an atomic electron, or in the nuclear field, it may loose all its energy by being captured or lose a fraction of its energy and get scattered as a photon of reduced energy. In view of this unpredictable behavior, gamma ray photons do not have a specific range in the matter as the charged particles. The secondary electrons ejected in the above-mentioned processes take part in the further ionization. A fraction of the energy of gamma ray lost during the interaction appears in the form of heat. The damage caused by radiation depends upon energy dissipated rather than the total energy incident [21-23].

2.4 Defects Produced by Gamma Rays: As discussed earlier, the most likely process in the interaction of high energy radiation with polymers is ionization. The ejected electron being lighter takes away the energy; this electron with gained energy can take part in further ionization process. During ionization rest of the atom gets recoil and is displaced from its position. The displacement of an atom requires a threshold energy $E_d$ for its displacement. If impinging particle possesses this much energy, the atom is displaced. This displaced atom acts as interstitial atom and is located between lattice sites, and the empty lattice site forms the vacancy. Introduction of vacancies and interstitials change the band structure of the material due to change in bond length and the distance between the atoms and thus produce defects. The gamma radiation being electromagnetic can not produce the displacement directly. They transfer their energy to the electrons of the target atom. These electrons can displace the atoms if their energy is greater than the energy of the displacement, $E_d$. The processes which produce displacement are of three types...Compton Scattering, photoelectric effect and production of electron hole pairs close to the nucleus.

Consider a photon of energy $E_\gamma$ incident on a solid, and assume that any atom receiving energy in excess of $E_d$ is displaced, while those receiving energy less than $E_d$ are not. Thus the cross-section per atom $\sigma_d(E_\gamma, E_d)$ for producing a primary displaced atom by photon of energy $E_\gamma$ is

$$\sigma_d(E_\gamma, E_d) = \int \frac{d\sigma}{dT}(E_\gamma, T)dT \quad \text{ ...(2.5)}$$
However as more than one process are involved in the displacement, the cross-section 
\( \frac{d\sigma}{dT} \) can be written as

\[
\frac{d\sigma}{dT} = \frac{d\sigma^c}{dT} + \frac{d\sigma^{p.e.}}{dT} + \frac{d\sigma^{p.p.}}{dT} \quad \ldots (2.6)
\]

Where \( \frac{d\sigma^c}{dT} \) is the cross-section for the displacements produced due to Compton scattering, 
\( \frac{d\sigma^{p.e.}}{dT} \) is the displacement cross-section due to photoelectric effect and \( \frac{d\sigma^{p.p.}}{dT} \) is the cross-section corresponding to process of pair production. In case of photoelectric effect the photoelectrons are produced with nearly the same kinetic energy as that of incident photon therefore it appears that this process may contribute largely towards displacement of atoms. However as discussed earlier, the cross-section for the photoelectric effect decreases rapidly for the photon energies beyond 0.1 MeV. Furthermore long lived isotopes which emit high energy photons to have appreciable cross-section for pair production are rarely found. For example widely used Co-60 gamma source emits photons of 1.17 and 1.33 MeV energies and therefore the processes of photoelectric effect and pair production do not contribute much towards displacing the target atoms.

The cross-section for displacement of atoms due to Compton scattering is given by the following relation

\[
\sigma^c = \pi r_0^2 Z \left( \frac{\alpha - 3(\alpha + 1)}{\alpha^3} \ln(1 + 2\alpha) + \frac{2(5\alpha^2 + 9\alpha + 1)}{\alpha^2(1 + 2\alpha)^2} - \frac{8\alpha^2}{3(1 + 2\alpha)^3} \right) \quad \ldots (2.7)
\]

In case of Compton scattering the energy of ejected electron varies with emission angle as per the following relation

\[
T_e = E_\gamma \frac{2\alpha(\cos^2\theta)}{(1 + \alpha)^2 - \alpha^2\cos^2\theta} \quad \ldots (2.8)
\]

Where \( T_e \) is the energy of the struck electron emitted at an angle of \( \theta \), with respect to direction of incident photon of energy \( E_\gamma \) and \( \alpha = \frac{E_\gamma}{m_e c^2} \). The energy decreases with the angle. It can be shown that for Co-60 gamma rays, the electrons emitted beyond 50° are not useful in producing atomic displacements. The advantages of Co-60 source are:
availability, radiation dose is almost constant for tens of hours, dose rate can be varied by positioning the sample with respect to the source position [24].

2.5 Experimental:

2.5.1 Sample Preparation: Samples of Polypropylene (C\textsubscript{3}H\textsubscript{6}, density = 0.91 gm/cm\textsuperscript{3}, isotactic) and polyimide (PMDA-ODA, Kapton, C\textsubscript{22}H\textsubscript{10}N\textsubscript{2}O\textsubscript{5}, density = 1.43 gm/cm\textsuperscript{3}) having dumbbell shape and thin films were used for specific characterizations. Especially, the polypropylene samples used for mechanical measurements were dumbbell shaped, obtained by injection molding. Thin films having 15 mm × 15mm × 500 μm size obtained by compression molding were used for other characterizations, whereas the polyimide (Kapton) samples were used in the form of as received films having dimensions 150 mm × 20 mm × 50 μm for mechanical measurements and 15 mm × 15mm × 50 μm for other characterizations. The sizes and shape of polypropylene and polyimide samples for stress-strain measurements were selected according to ASTM D638 and ASTM D882 respectively.

2.5.2 Irradiation: A few polyimide and polypropylene samples were kept in polyethylene bags separately and irradiated with Co-60 gamma radiation having dose rate 20 Gray per minute. (Dose: energy deposited per unit mass, 1 Gray = 100 rad and 1 rad = 1 J/kg). The irradiation was carried out under normal environmental conditions (at room temperature and in air). The total dose was varied from 57.6 to 230.4 kGy.

2.5.3 Characterizations: The pre and post irradiated samples were characterized with number of techniques as mentioned in chapter 1. The stress-strain measurements were performed as per ASTM D638 and ASTM D882 techniques. The strain rate was 10 mm/min in case of polypropylene and 20 mm/min in case of polyimide. The load used in both the cases was 500 N. The measurements were performed at room temperature and average of 3 measurements was taken. The tensile strength, percentage elongation, strain energy and Young’s modulus were calculated as per the procedures explained in chapter 1. The effects of radiation on the bond structure and functional groups were analyzed by FTIR spectroscopy. The relative oxygen contents of the samples were measured using EDS technique. The optical properties, particularly the band gap was measured by UV-Visible
spectroscopy. The crystalline properties were analyzed by XRD technique, while the radiation induced changes in surface texture and chemistry of the samples were analyzed using SEM and contact angle measurements. Finally the thermal properties of pre and post irradiated samples were examined by TGA (Thermogravimetric Analysis) technique.

2.6 Results and Discussion:

2.6.1 Mechanical Properties: The results of stress-strain curves, tensile strength, percentage elongation, Young’s modulus, and strain energy per unit volume for polypropylene and polyimide are shown in figures 2.3 to 2.8. From figures 2.3 and 2.4 it is observed that the stress-strain curve for polypropylene becomes successively weak as gamma dose increases and this reveals substantial loss in mechanical properties up to the maximum dose level of 230.4 kGy, while in case of polyimide, the stress strain curves are almost retained, which signifies that its mechanical properties are stable up to the maximum dose of gamma radiation. The figures 2.5, 2.6, 2.7, and 2.8 show that the

![Figure 2.3: Stress-Strain Curves of Pristine and Gamma Irradiated Polypropylene](image1)

![Figure 2.4: Stress-Strain Curves of Pristine and Gamma Irradiated Polyimide](image2)
degradation in the tensile strength, percentage elongation, Young’s modulus and strain energy per unit volume for polypropylene is from 22 MPa to 16 MPa, 40% to 4.25%, 550 MPa to 137.5 MPa and 10.88 MJ/m³ to 0.38 MJ/m³ respectively, whereas in case of polyimide, the percentage elongation and strain energy per unit volume show only a marginal decrease from pristine values of 17.7% to 16.5% and 15 MJ/m³ to 13.8 MJ/m³ and the tensile strength and Young’s modulus show marginal increase from 104 MPa to 111 MPa and 2464.5 MPa to 3364 MPa at the maximum dose level of 230.4 kGy. Out of these mechanical properties, the percentage elongation is considered as a sensitive
parameter for evaluating the radiation effects in polymers [15, 25]. So, the decrease in percentage elongation is observed to be conspicuous in case of polypropylene (90 %) as compared to polyimide (7%) at the dose level of 230.4 kGy. These results indicate that the degradation in polypropylene is significant as regards to all its mechanical properties, while polyimide not only shows remarkable radiation stability as regards to the strain energy and percentage elongation, but also a small improvement in its tensile strength and Young’s modulus. This drastic difference attributes to chemical structure and physical morphology of polypropylene and polyimide. In general, both scissioning and crosslinking can occur when the polymer gets exposed with radiation. The mechanism of radiation induced scissioning and crosslinking is schematically shown in figure 2.9.

![Figure 2.9: Radiation Induced Crosslinking and Scissioning](image)

The scissioning or crosslinking may be the dominant effect, depending upon the chemical structure, morphology and oxidation resistance of the polymers. However, the observed degradation in polypropylene attributes to extensive chain scissioning, decrease in average molecular weight, radiation induced tracks and defects and oxidative embrittlement [1, 3, 13, 14, 15]. The radiation chemical yields i.e. G-Value of reaction (This is radiation yield i.e. number of reaction events such as scissions or crosslinks per 100 eV energy absorbed) for polypropylene are G(X) = 0.16 for crosslinking and G(S) =0.24 for scissioning. Thus the ratio G(S)/G(X) is roughly 1.5, which indicates that in polypropylene the scissioning dominates over crosslinking [26]. The dominance of
scissioning over crosslinking in polypropylene is due to its specific chemical structure and morphology. In polypropylene, the backbone chain consists of C-C bonds. Thus the radiation stability depends upon the stability of C-C bonds, which depends upon number of functional groups in the C-C chain. Because of presence of methylene unit (CH₃), the C-C bond is relatively less stable [27].

Another reason for dominance of scissioning over crosslinking is a consequence of abundance of tertiary carbon atoms which favor scission of the main chain in polypropylene [11, 28]. Polymers with a high concentration of tertiary carbon atoms along the chain undergo primarily scission. This may be due to steric inhibition of radical-radical recombination following chain break leading to an increased yield of chain scission. Moreover, the drastic decrease in the percentage elongation clearly indicates the decrease in flexibility and increase in brittleness of polypropylene [15, 25]. Polypropylene has relatively high degree of crystallinity which indirectly enhances the degradation processes, as the radiation induced free radicals are trapped inside the crystalline zones. The free radicals thus have less mobility in the crystalline zones which prevents their cross-linking.

In case of polyimide, the tensile strength and Young’s modulus shows overall marginal increase whereas, strain energy and percentage elongation show a marginal decrease as the gamma radiation dose increases. The percentage elongation, which is considered to be a sensitive parameter to evaluate irradiation effects on polymers, is observed to decrease only by 7% as compared to the 90% decrease in case of polypropylene at the maximum dose level of 230.4 kGy. Moreover, the results indicate that except Young’s modulus, all other properties are found to increase marginally up to gamma dose of 115.2 kGy and then further decrease slightly as the gamma radiation dose increases. This behavior may be interpreted as a balance between scission on the surface and crosslinking in the bulk of polyimide and thus the increase at the intermediate dose levels may be due to crosslinking or increase in inter-chain and intra-chain interaction or reorganization of polymer chains [8].

In general, it is observed that as compared to polypropylene, polyimide has shown overall radiation stability against gamma radiation up to dose levels of 230.4 kGy. This is
due to typical chemical structure and morphology of polyimide, which has relatively heavy, bulky and complex monomer, high molecular weight and significant proportion of aromatic units and imide group in the monomer. Aromatic groups are known to have low radiochemical yields of radicals [3, 25, 29]. The heterocyclic ring (aromatic units) have ladder like structures. Due to such ladder structure, breaking of one or a few bonds cannot sever the chains. Secondly, for the breaking of chain, at least two bonds have to be broken, which has far less probability than single rupture breaking of single chain polymer. Another major reason behind the observed radiation stability of polyimide is the strong intra-molecular and inter-molecular interaction which exists due to charge transfer complexes (CTC). In polyimide, both imide linkages are attached to the central aromatic ring of the Pyromellitic dianhydride (PMDA), which becomes electron deficient due to electron-withdrawing effect of four adjacent carbonyl groups. On the other hand, the diamine phenyl rings become electron rich due to electron donating effects of the lone pair of electrons on the nitrogen and oxygen of the diphenyl ether (ODA) group. This causes transfer of electrons from electron donating nitrogen containing ODA groups to electron deficient carbonyl containing PMDA groups. This relationship causes polarization and consequently, formation of an intra-molecular charge transfer complex (CTC) between the polymer chains. The formation of Charge Transfer Complexes (CTC) is shown in figure 2.10. These Charge Transfer Complexes (CTC) impart extraordinary strength to the inter and intra-molecular interactions between the polyimide chains [5, 16]. The amber color of polyimide is the consequence of CTC [10], which unlike polypropylene, was not affected due to irradiation. This indicates that the CTC based intra and intermolecular interactions are extremely strong and have not been noticeably affected. Furthermore, the observed radiation resistance of polyimide also strongly attributes to its high oxidation resistance, which is the consequence of high oxidation state of its monomer due to presence of large concentration of electron abstracting carbonyl groups [16].
65

Figure 2.10: Charge Transfer Complexes (CTC) Responsible for Strong Inter-Molecular and Intra-Molecular Forces

2.6.2 FTIR Analysis:

The degradation of polypropylene and the remarkable stability of polyimide against gamma radiation are well supported by FTIR characterizations, which are shown in figures 2.11 and 2.12 for polypropylene and polyimide respectively. The graphs in both the figures are appended for comparison. From figure 2.11, the peaks observed near 1170 cm\(^{-1}\), 999 cm\(^{-1}\)-977 cm\(^{-1}\) confirm that the polypropylene used in the present case is isotactic [30]. Various peaks in the region 2800-3100 cm\(^{-1}\) correspond to CH\(_3\), CH\(_2\), CH stretching, while CH\(_3\) and CH\(_2\) bending are found around 1450-1480 cm\(^{-1}\). Various weak, medium and strong lines in the region 809-1369 cm\(^{-1}\) correspond to CH\(_3\), CH\(_2\), CH
bending, wagging, twisting and C-C stretching [30, 31]. It is observed that intensity of these peaks decreases with the gamma dose, which indicates that these bonds are scissioned. The decrease in the absorbance at 1170 cm\(^{-1}\), 999 cm\(^{-1}\)-977 cm\(^{-1}\) indicates that the isotactic arrangement of polypropylene is distorted after irradiation. Furthermore, characteristic bands at 1718-1725 cm\(^{-1}\) and 1650 cm\(^{-1}\) appear at all the gamma dose levels and their respective intensity is pronounced with radiation dose. Out of these lines, the 1718-1725 cm\(^{-1}\) band corresponds to carbonyl groups and this particular aspect signifies about oxidation, while the peak around 1650 cm\(^{-1}\) signifies conjugation (double bond formation).

The irradiation of polymer leads to excitation and ionization of polymer molecules. The electrons thus liberated take part in the further ionization, excitation and generation of free radicals. The excited molecules may de-excite in many ways, one out of which is generation of ionized species or free radicals. The interactions involving free radicals and ionized species may lead to many reactions such as energy transfer, evolution of gases, crosslinking etc. If irradiation occurs in presence of oxygen, then this mechanism is significantly dominated by oxidation process. The ionized species and free radicals then react with ambient and the residual oxygen in polypropylene matrix which leads to the formation of oxygen based functional groups, out of which carbonyl (C=O)
groups are the most dominant ones [1, 11, 30]. Two out of several possible reaction mechanisms which lead to oxidation are shown below

\[
\text{CH}_2-\text{CH}•-\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_2-\text{CH}-\text{CH}_3 + \text{OO•}
\]

\[
\text{CH}_2-\text{CH}-\text{CH}_3 \rightarrow \text{CH}_2-\text{CH}=\text{O} + \text{•O-CH}_2
\]

• \(\Rightarrow\) free radical (active site created due to irradiation)

OR

\[
\begin{align*}
R & \xrightarrow{\gamma} R• & \text{Initiation} \\
R• & \xrightarrow{\text{O}_2} \text{RO}_2• & \text{Propagation} \\
\text{RO}_2• & \xrightarrow{\text{RH}} \text{ROOH} + R• \\
\text{ROOH} & \rightarrow R• + \text{•OH} \\
\text{RO•} & \xrightarrow{\text{RH}} \text{ROH} + R• \\
\text{•OH} & \xrightarrow{\text{RH}} \text{H}_2\text{O} + R• \\
\end{align*}
\]

\(R \Rightarrow\) Polymer

\(R•/\) \(\Rightarrow\) Free radical/(active site created due to irradiation)

It can also be observed that the peak corresponding to carbonyl groups is broadened at higher doses and a broad and weak band is observed in the range 3375-3600 cm\(^{-1}\), which indicates the appearance of OH species. This is the indication of formation of COOH i.e. carboxylic acid at higher doses. The absorption corresponding to hydroxyl (OH, 3400 cm\(^{-1}\)) group is relatively very weak as compared to carbonyl groups. This may indicate relatively lesser concentration of OH groups which may be due to evolution of hydrogen gas (dehydrogenation) during irradiation [11].
The reaction of free radicals with oxygen does not allow the polymer chains to crosslink, due to which chain scissioning predominates over crosslinking in polypropylene. This aspect mainly leads to degradation in the mechanical properties of polypropylene.

The band around 1650 cm\(^{-1}\) corresponds to the conjugated double bonds. The scissioning of bonds and free radical formation also leads to the formation of conjugated double bonds, which is confirmed by appearance and subsequent growth of peak at 1650 cm\(^{-1}\) [32, 33]. The introduction of unsaturation sites (double bonds) into the irradiated polymer structures can be postulated to occur as follows. It can be observed that double bond formation and dehydrogenation/carbonization are related with each other.

\[
\begin{align*}
\text{OR}
\end{align*}
\]
Thus, the breaking of C-H, C-C bonds, formation of double bonds and the oxidation, are consistent with observed mechanical degradation of polypropylene. The polypropylene samples were observed to become successively yellowish and then brownish after irradiation, and this attributes to three factors such as formation of C=O groups which are known to be chromophoric [1], formation of radiolysis products [11] and conjugation [32, 33].

Figure 2.12 shows the FTIR spectra of pristine and gamma irradiated polyimide; where almost no change is observed. A detailed FTIR spectrum of polyimide showing all possible peaks and their assignments is shown in figure 1.13 and table 1.1 in chapter 1. A few prominent peaks in the spectrum are N-H stretching and bending (3486 cm$^{-1}$, 1602 cm$^{-1}$ respectively), O-H stretching (3630 cm$^{-1}$), C-C stretching of aromatic phenyl rings (ODA) (1500-1598 cm$^{-1}$) as well as aromatic C=C bonds (1456, 1500 and 1601 cm$^{-1}$), =C-N, i.e. nitrogen-aromatic ring stretching (1376-1390 cm$^{-1}$), C-H deformation in phenyl ring (823 cm$^{-1}$). [5, 9, 34-36]. It is seen that position and the intensity of almost all the lines in the FTIR of polyimide remains same. Moreover, there is no appearance of new spectral lines. Thus, it is found that the complex and bulky monomer, aromatic imide groups, CTC based strong inter-molecular and intra-molecular bonding and cross-linked arrangements of polymer chains have made the polyimide network extraordinarily strong against gamma radiation due to which all the bonds have remained almost intact up to the dose level of 230.4 kGy. It is also observed that the absorbance corresponding to the oxygen containing groups such as O-H stretching (3630 cm$^{-1}$), C=O i.e. carbonyl groups in PMDA (1725-1781 cm$^{-1}$) and C-O-C asymmetric stretch in ODA (1260-1289 cm$^{-1}$) shows no change after irradiation. This indicates that unlike polypropylene, polyimide
has not undergone oxidation after irradiation. The resistance of polyimide to bond breaking must have prevented the formation of free radicals. Secondly, the presence of electron abstracting carbonyl groups in the monomer of polyimide is responsible for its higher oxidation state and hence prevented polyimide network to undergo oxidation [16] which is another major reason for observed stability of polyimide against radiation. Unlike polypropylene samples, which were observed to become successively yellowish and then brownish after irradiation, the amber color of polyimide remained unaffected even up to maximum dose level of 230.4 kGy. This confirms that the percentage of carbonyl groups as well as the CTC based strong intra- and inter-molecular bonding in polyimide has remained almost unaffected after gamma irradiation.

### 2.6.3 UV-Visible Analysis:

The UV-Visible absorption spectra for polypropylene and polyimide are shown in figure 2.13 and 2.14 respectively.

![UV-Visible Absorption Spectra of Pristine and Gamma Irradiated Polypropylene](image1.jpg)

![UV-Visible Absorption Spectra of Pristine and Gamma Irradiated Polyimide](image2.jpg)

The absorption edge of pristine polypropylene is around 300 nm and that in case of polyimide is around 440 nm. This difference may be due to existence of carbonyl groups and charge transfer complexes in pristine polyimide and their absence in polypropylene. The absorption in UV-Visible region by polymers is mainly due to the excitation of electrons in n, σ and π orbitals from ground states to higher energy states [36]. As mentioned in chapter 1, the absorption edge and the band gap are related by
Tauc’s expression [30]. From figure 2.13 it is found that there is a red shift in the absorption edge of polypropylene from pristine value of 300 to 408 nm at the maximum dose level of 230.4 kGy; consequently, the reduction in the band gap is from 4.13 to 3.04 eV (26 %). This red shift and the decrease in the band gap mainly attribute to two reasons; one is carbonization and the other is conjugation. Carbonization is the consequence of evolution of hydrogen after irradiation, which increases the C:H ratio. The conjugation i.e. double bond formation, which is also related with dehydrogenation, has been discussed in the previous section. The energy deposited in a single primary ionization and excitation process (20-30 eV) is much higher than that of bond energies of any of the bonds present in the simple organic molecules (3-5 eV). Therefore, the energy available largely exceeds the amount required to cleave any bond. One could conclude from such considerations that bonds are broken at random. This is not the case, however. Certain selectivity rules apply that are not always well established. In linear hydrocarbons C-H bonds break more frequently than C-C bonds, in spite of lower bonds energies of the latter [37]. Due to the breaking of C-H bonds polymer is dehydrogenated/carbonized. A few additional possible mechanisms of dehydrogenation/carbonization are shown below.

i. Free radical formation: \( \text{PH}^+ + \text{PH} \rightarrow \text{P}^* + \text{PH}_2^+ \)

ii. Gas evolution: \( \text{P}^* + \text{PH}_2^+ + e^- \rightarrow \text{P}^* + \text{P} + \text{H}_2 \)

iii. Gas evolution: \( \text{H}^* + \text{PH} \rightarrow \text{P}^* + \text{H}_2 \)

\( \cdot \Rightarrow \text{Free radical/active site} \)

The migration of the free radicals may also propagate through successive hydrogen abstraction process. This process may also enhance the carbonization. This is shown below.

\[
\begin{align*}
\{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \} & \rightarrow \{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \} \rightarrow \{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \} \\
\{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \} & \rightarrow \{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \} \\
\{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \} & \rightarrow \{ \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \}
\end{align*}
\]

\( \cdot \text{CH} \Rightarrow \text{Unsaturation} \)
It has been seen earlier that the dehydrogenation and unsaturation (double bond formation) are consistent with each other. Thus unsaturation is also due to loss of adjacent substitutions on the chain or side group such as hydrogen atom or even CH$_3$ units. Thus irradiation increases the conjugation i.e. double bonds. Due to this the spacing between the energy levels decreases. As a result the $\lambda_{\text{max}}$ shifts to higher value (bathochromatic shift). The energy gap becomes progressively smaller on increasing the length of conjugation. The conjugation, which is the consequence of scissioning and subsequent rearrangements of bonds, is also confirmed by appearance, and growth of peak at 1650 cm$^{-1}$ in the FTIR spectrum [32, 33, 38].

Another explanation for decrease in the band gap is graphitization. The residual carbon formed due to dehydrogenation in the various domains of polymer matrix is known to have graphite like form. As graphite is a zero band gap material, such graphitization leads to decrease in the band gap [39, 40].

It is also found that the absorbance increases at almost all the wavelengths with dose. This is consistent with the coloration of the polypropylene samples which were observed to become yellowish and then brownish after irradiation. This is due to the oxidation i.e. formation of carbonyl groups (C=O) which are known to be chromophoric. (their appearance has been confirmed by appearance and growth of peaks at 1718-1725 cm$^{-1}$ in FTIR spectra) [39], evolution of gases, formation of radiolysis products [11], conjugation [33], formation of defects and color centers and creation of new charge states [41].

Figure 2.14 shows that there is no change in the UV-Visible spectrum of pristine and gamma irradiated polyimide. The absorption is not changed with the dose and there is no shift in the absorption edge. This confirms that the gamma radiation has not disrupted the charge transfer complexes and the concentration of carbonyl groups in polyimide up to the dose level of 230.4 kGy. It also appears that there is no carbonization, conjugation, formation of color centers and change in aromatic cluster size after irradiation. These results are also found to be consistent with FTIR analysis of both the polymers.
2.6.4 EDS Analysis: The oxidation effects observed in FTIR and UV-VIS spectra are further confirmed in EDS (Energy Dispersive X ray Spectroscopy) analysis. EDS analysis was mainly used to measure the relative percentages of oxygen in polypropylene and polyimide before and after irradiation and are shown in figures 2.15 and 2.16 respectively. The EDS spectrum of pristine polypropylene indicates some residual oxygen in the polymer matrix, however, the oxygen contents are found be in greater amount in irradiated samples. This confirms oxidation, which has been observed in FTIR and UV-VIS spectra. The EDS spectra of polyimide show more or less same oxygen contents in case of pristine as well as irradiated samples indicating oxidation resistance of polyimide. This is also consistent with FTIR and UV-VIS spectra, where no change is observed.

![Figure 2.15 Atomic Percentage of Oxygen in Pristine and Gamma Irradiated Polypropylene at Various Gamma Doses.](image1)

![Figure 2.16 Atomic Percentage of Oxygen in Pristine and Gamma Irradiated Polyimide at Various Gamma Doses.](image2)

2.7.5 XRD Analysis: In general, the morphology of polymers is semi-crystalline and the degree of crystallinity may be affected after irradiation. The change in crystallinity not only affects the overall mechanical strength of polymer, but also the mobility of radiation-induced free radicals and the diffusion of oxygen in the matrix of polymer. Thus XRD analysis may provide useful insights in the structural properties of polymers after irradiation. The height of crystalline peaks in the XRD spectrum signifies the overall
crystallinity; FWHM gives average size of the crystallites and the Bragg angles indicate the crystal type/symmetry [28]. The XRD spectra for pristine and gamma irradiated polypropylene and polyimide are shown in figure 2.17 and 2.18 respectively. The graphs are appended for comparison. From both the figures, it is observed that the polypropylene has greater degree of crystallinity as compared to polyimide. The absence of any sharp peak in the range 10-60° in the XRD spectrum of polyimide may be mainly due to its complex, bulky and aromatic monomer and the crosslinked arrangement of polymer chains. The XRD spectrum of polypropylene confirms its α-monoclinic form [13, 28]. The crystalline peaks observed at 2θ values of 14.50°, 17.5°, 19° and 22° are due to (110), (040), (130) and (041) planes respectively [15, 42]. The XRD spectra of polypropylene indicate that overall crystallinity is almost unaffected with gamma irradiation [13] except that the height of the (110) peak at 2θ = 14.50° is found to increase up to a dose level of 172.8 kGy and then decrease slightly. The FWHM of the peak is found to decrease on an average from 0.8° to 0.6° at the maximum dose. According to Debye-Scherrer formula, this decrease in FWHM indicates increase in crystallite size from 200 to 267 Å. This reveals that the gamma irradiation does not affect all the regions of polymer to same extent. This is because in polymers, the amorphous zones and the tie molecules, which join crystallites, are more
sensitive to radiation, while the crystalline zones are relatively less affected [14, 43]. In such case the scissioning of polymer chains in amorphous zones and scissioning of tie molecules joining crystalline zones may facilitate the reorganization of crystalline and amorphous zones to some extent. The breaking of tie molecules can also relieve the local stress on crystalline zones. Secondly, the breaking of molecules in amorphous zones makes them shorter, which makes their re-orientation easy. This may have caused the minor thickening of crystalline zones at the expense of amorphous zone resulting in a small increase in the height and decrease in the width of crystalline peak [13, 42, 43]. However, it may be noted that the overall crystallinity of irradiated polypropylene has not been significantly affected and yet its mechanical properties have shown substantial degradation. Thus, it may be concluded that the crystalline zones of polypropylene have remained relatively intact after irradiation and the polymer chains in amorphous zones and tie molecules joining crystalline zones have been mainly degraded [15].

In case of polyimide, the XRD spectrum shown in the figure 2.18 is observed to be not considerably affected with gamma radiation. This may be because the complexity and bulkiness of monomer and the crosslinked arrangements of polymers chains in polyimide have remained almost unaffected up to dose level of 230.4 kGy. This is in consistence with the observed mechanical stability of polyimide against gamma irradiation. Furthermore, the XRD spectrum corresponding to 115 kGy is observed to be marginally sharp and intense as compared to XRD spectra of other doses. This is also consistent with observed relative improvement in the percentage elongation and the strain energy at 115 kGy as discussed in section 2.6.1.

2.7.6 Surface Morphology: Scanning Electron Microscopy (SEM) Analysis: The effects of radiation on the surface as well as bulk morphology of pristine and gamma irradiated polypropylene and polyimide have been studied using three techniques. XRD technique has been used to study the effects of radiation on overall bulk morphology and the SEM and contact angle technique has been used to study radiation induced changes in surface morphology and surface chemistry.
Figure 2.19 and 2.20 show the SEM images of virgin and gamma irradiated polypropylene and polyimide samples. The magnification used was ×30000 in both the cases.

**Figure 2.19: SEM Images of Pristine and Gamma Irradiated Polypropylene at Various Doses**

- (a) Pristine
- (b) 57.6 KGy
- (c) 115.2 KGy
- (d) 172.8 KGy
- (e) 230.4 KGy

**Figure 2.20: SEM Images of Pristine and Gamma Irradiated Polyimide at Various Doses**

- (a) Pristine
- (b) 57.6 KGy
- (c) 115.2 KGy
- (d) 172.8 KGy
- (e) 230.4 KGy

The comparison of SEM images of virgin and gamma-irradiated polypropylene indicates that as dose increases, the degree of smoothness of polymer surface is decreased or degree of roughness/imperfection increases with the gamma dose. The surface of gamma-irradiated polypropylene is found to be consisting of defects, cavities/voids, cracks, globules and blisters of different sizes. This roughening can be attributed to various factors which are related to breaking of bonds as well as formation of new one. The radiation-induced free radicals undergo chemical reactions with themselves and with oxygen. This leads to evolution of gases from the surface (i.e. sputtering of surface particles/erosion) as well as oxidative embrittlement. The evolution of gases (i.e. the erosion rate of surface particles) takes place to different extent in different regions over the surface. Radiation also induces surface defects and change in free volume fraction over the surface. This leads to creation of globules and cavities of varying sizes over the
surface due to which the surface is roughened [7, 9, 44]. This surface degradation is also in agreement with the observed mechanical degradation of polypropylene. The evolution of gases and the formation of cavities is one of the factors responsible for the observed mechanical degradation of polypropylene.

In case of polyimide, it is seen that the surface roughening is quite less as compared to polypropylene. This is also consistent with the observed mechanical stability as well as oxidation resistance of polyimide against irradiation effects as mentioned in earlier sections. In other reports, it has been confirmed that polyimide shows comparatively lowest yields of evolution of gases in case of gamma irradiation [6].

2.7.7 Contact Angle Analysis: The surface analysis of gamma irradiated polymers was carried out by using an additional technique called as contact angle method. Contact angle is related with the surface chemistry and the surface morphology. As gamma irradiation has affected both surface chemistry and morphology, contact angle measurements can further clarify the radiation induced changes on the surface of polymers. Figure 2.21 shows the images of a 10 micro liter-drop of distilled water on the surface of pristine and gamma irradiated polypropylene at the dose of 230.4 kGy. The resolution of the instrument was 1°. It is observed that the contact angle decreases from 85.2° to 62.2°. This decrease is almost 27% and can be attributed to two reasons. One is surface oxidation and another is surface roughening. It has been observed in the FTIR and EDS analysis that polypropylene is significantly oxidized after irradiation. The FTIR has also clearly revealed that oxygen based functional groups such as carbonyl (C=O), hydroxyl (OH) and carboxylic acid (COOH) have been produced after irradiation. These groups are known to be polar. As a result the surface polarity increases after irradiation. This increases the work of adhesion which results in decrease in the contact angle [45-47]. As mentioned in chapter 1, the work of adhesion is given by

\[ W_a = \gamma_{LG}(1 + \cos \theta) \]  

Where, \( \gamma_{LG} \) = surface tension of liquid gas interface = 72.8 mJ/m². The work of adhesion as calculated from above formula is found to increase from 78.89 to 105.8 mJ/m². Another factor responsible for decrease in the contact angle is increased roughness [47,
According to Wenzel equation as mentioned in chapter 1 \((\cos \theta_w = r \cos \theta_y)\), if the surface is hydrophilic \((\theta < 90^\circ)\), the increase in the roughness \(r\) results in decrease in the contact angle \([49]\). The increase in the roughness, as calculated from Wenzel equation is from 1 to 3.44. This is quite consistent.

**Figure 2.21:** Images of a 10 Micro-Liter Drop of Distilled Water on the Surface of Pristine and Gamma Irradiated Polypropylene at the Dose of 230.4 kGy

**Figure 2.22:** Images of a 10 Micro-Liter Drop of Distilled Water on the Surface of Pristine and Gamma Irradiated Polyimide at the Dose of 230.4 kGy

With the SEM images of pristine and gamma irradiated polypropylene which has shown a substantial increase in the roughness after irradiation.

From figure 2.22, it is observed that, the contact angle of polyimide decreases from the pristine value of 70.8° to 67.6°. This decrease is only 5%. Thus polyimide continues to show its radiation stability in its surface properties also.

**2.7.8 Thermogravimetric Analysis:** TGA is considered as an important technique to evaluate thermal properties as well as composition of polymers. In this technique the sample is burnt in a furnace and its weight loss is recorded with temperature. A graph of
weight Vs temperature is called as TGA curve of the sample. TGA curve can be used to analyze the composition (in terms of highly volatile, medium volatile, combustible, and ash contents) as well as thermal stability of material. The thermal properties of polymers are governed by strength of covalent bonds within polymeric chains. As irradiation of polymers induces chain scissioning as well as crosslinking and since many polymers are oxidized after irradiation, the thermal properties of polymers are expected to show considerable changes after irradiation [50, 51]. Figure 2.23 and 2.24 show the TGA curves of virgin and gamma irradiated polypropylene and polyimide respectively. The thermograms of both polymers show two zones, the first one is stable zone and the second is fast decomposition zone. In case of polypropylene, the decomposition starts at about 100° C and is completed at about 425° C, while in case of polyimide, the decomposition starts at about 525° C at ends at about 725° C. The higher temperature of decomposition for polyimide is mainly due to its CTC based strong bonding and oxidation resistance.

Table (2.1) shows the temperatures corresponding to 5% and 10% weight loss and inflexion points calculated from TGA curves of virgin and gamma irradiated polypropylene and polyimide. It is seen that polyimide has excellent thermal stability at virgin level itself. This is consistent with its observed mechanical strength and oxidation resistance. Further, it is observed that in case of polypropylene, the temperatures corresponding to 5%, 10% weight loss and inflexion show a considerable overall
crease after irradiation. This indicates that thermal stability of polypropylene is decreased after gamma irradiation. Thus gamma irradiated polypropylene shows faster thermal decomposition. This can be attributed to radiation-induced scissioning of chains, formation of defects (such as chain ends, crosslinks, radicals, branch points, nonisotactic sequences, excess free volume, unsaturation etc.) and oxidation [52]. The scissioning of bonds, oxidation and defects are confirmed in FTIR, EDS spectroscopy and SEM analysis. It is also seen that this thermal degradation is consistent with the observed mechanical degradation of polypropylene. The TGA curves can also be used to evaluate the compositional details of material. A compositional analysis based on highly volatile, medium volatile, combustible and ash contents is shown in figures 2.25 and 2.26 for polypropylene and polyimide. In case of polypropylene the percentage of medium volatile products, which usually degrade after 200°C, is found to be increasing with the fluence. This increase is from pristine value of 70% to 92%. These medium volatile products are irradiation induced low molecular weight species and the oxidation products such as CH, CH₂, CH₃, COCH, CH₂CO, CO₂, CO aldehyde, peroxide, acetate, carbonyl, ketone, carboxylic acid, isobutene, acetone, phenol, benzoic acid, stearic acid etc. The increased percentage of such volatile products is another cause of decrease in the thermal stability of polypropylene [11]. It can be seen that in case of polyimide the TGA curves

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Polypropylene</th>
<th>Polyimide (Kapton)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T₅% (°C)</td>
<td>T₁₀% (°C)</td>
</tr>
<tr>
<td>Virgin</td>
<td>243</td>
<td>281</td>
</tr>
<tr>
<td>57.6</td>
<td>250</td>
<td>287</td>
</tr>
<tr>
<td>115.2</td>
<td>227</td>
<td>257</td>
</tr>
<tr>
<td>172.8</td>
<td>188</td>
<td>271</td>
</tr>
<tr>
<td>230.4</td>
<td>120</td>
<td>266</td>
</tr>
</tbody>
</table>

Table 2.1: Temperatures Corresponding to 5% and 10% Weight Loss and Inflexion Point Calculated from TGA Curves of Pristine and Gamma Irradiated Polypropylene and Polyimide
Figure 2.25: TGA Curves of Pristine and Gamma Irradiated Polypropylene

and corresponding characteristic temperatures show almost no change after irradiation even at the maximum dose. Further, in case of polyimide the relative percentage of highly volatile, medium volatile, combustible matter is found to be almost unaffected due to irradiation. This further signifies its thermal stability against gamma irradiation. This indicates the excellent radiation stability of polyimide as compared to polypropylene as regards to their thermal properties. This is also consistent with the observed radiation stability in other physicochemical properties as reported in earlier sections. The complex, heavy, bulky and aromatic monomer of polyimide, its CTC based strong inter- and intramolecular bonding, crosslinked arrangements of polymer chains and particularly oxidation resistance (as observed in FTIR, UV-VIS and EDS studies) seem to be responsible for the observed thermal stability of polyimide. The stability of TGA curves further confirm that polyimide is not oxidized after irradiation.

2.7 Conclusion: Polypropylene has shown substantial degradation against gamma irradiation in the dose range 57.6 kGy to 230.4 kGy, while polyimide irradiated at the same dose levels under the same conditions has shown remarkable resistance as regards to mechanical, optical and structural properties. The mechanical properties of polypropylene such as tensile strength, percentage elongation, Young’s modulus, strain energy degrade due to extensive chain scissioning, decrease in molecular weight,
oxidative embrittlement, formation of tracks and defects while in optical properties 26 % decrease in band gap, increase in absorbance is observed which is due to conjugation, carbonization and oxidation. This is confirmed by decrease in absorbance corresponding to C-H and C-C bonds and appearance and growth of peak corresponding to carbonyl groups in FTIR spectra and increased oxygen contents in EDS spectra. The bulk morphology does not show drastic change except a marginal increase in height and decrease in FWHM of (110) peak and this indicates that degradation and bond scissioning has occurred to greater extent in amorphous regions and tie molecules. SEM analysis shows degradation in surface smoothness. The contact angle shows a 27 % decrease which is attributed to surface oxidation and surface roughening. Interestingly, polyimide irradiated at the same dose levels and under the same conditions has shown almost no change in mechanical properties, FTIR, UV-Visible, EDS, XRD spectra and in the SEM images. This remarkable radiation stability of polyimide can be attributed to its complex, bulky, heavy and aromatic monomer, CTC based strong inter-molecular and intra-molecular bonding, crosslinked arrangements of polymer chains and oxidation resistance. This comparative study highlights that the radiation induced physicochemical changes in polymers under identical irradiation conditions are governed by some important physical and chemical structural parameters such as presence or absence of aromatic groups, presence or absence of charge transfer complexes (CTC), strength of intra-molecular and inter-molecular bonds, crosslinked arrangement of polymer chains and oxidation resistance.

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