



Effect of γ -irradiation on the thermal properties of UHMWPE/MWCNTs nanocomposites: a comparative study of incorporating unmodified and γ -ray-modified MWCNTs

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Abstract. The efficacy of defective sites in MWCNTs as free radical scavengers was investigated on the basis of thermal analysis of ultra-high molecular weight polyethylene (UHMWPE)/MWCNTs and UHMWPE/ γ -MWCNTs nanocomposites. Homogenized composites of polyethylene (PE) with MWCNTs and γ -MWCNTs (0.5% by weight) were prepared by the ball milling process for 2 h at a speed of 200 rpm. Thereafter, micron-sized sheets were prepared (by hot pressing) and subjected to γ -dose ranging from 25 to 150 kGy. To investigate the thermal properties and thermal stability, differential scanning calorimetric (DSC) and thermo-gravimetric analysis (TGA) measurements were performed in an inert atmosphere. The results showed that peak melting temperature (T_m) and lamellae thickness (L_c) remained unaltered for UHMWPE/MWCNTs composites; however, for UHMWPE/ γ -MWCNTs composites the values varied from 138 to 141°C. This behaviour was attributed to chain scission close to crystalline lamellae due to radiation-induced free radicals, thus reducing the percentage of inter-phase contents within the polymer matrix and enhancing the percentage crystallinity for composites. Furthermore, TGA revealed the higher thermal stability of composites as compared with pristine ones and significant increase in residues percentage for composites, i.e., from \sim 3 to 7%. These results confirmed the importance of defective sites within the MWCNTs as free radical quenchers, and stopping the chain scission, particularly close to crystalline lamellae, thus preventing loss of the important interphase region of UHMWPE.

Keywords. UHMWPE; DSC; TGA; nanocomposites; MWCNTs.

1. Introduction

Ultra-high molecular weight polyethylene (UHMWPE), due to its high wear resistance, suitable fitness, low friction coefficient, biocompatibility and fatigue resistance, is considered as the most reliable material for bio-implants such as tibial inserts, acetabular liners, etc. However, subsequent to its use for a year or so, generation of wear debris because of its continuous articulation against the metallic parts results in osteolysis and aseptic loosening of the implant, which is the major factor in prosthesis failure [1–5]. To address this problem, crosslinking of UHMWPE using energetic radiations such as γ , e-beam, X-rays, etc., is employed. UHMWPE components treated with high-energy radiations result in significant increase of crosslink density within the amorphous phase of polymer, thus enhancing the wear resistance of UHMWPE [6–9]. However, the major concern is initiation of oxidation reaction in the presence of molecular oxygen, converting UHMWPE into a brittle polymer, which significantly

affects the material's structural, mechanical and thermal properties are concerned [6,10,11]. To stabilize and enhance physical properties of aforementioned materials, particularly thermal ones, addition of various fillers as radiation-induced free radical quenchers is currently in practice. In addition to this, researchers are working on figuring out new and smarter fillers (organic/inorganic/nano-scale) to enhance the thermal stability of UHMWPE [12–15].

Although gamma irradiation does enhance the thermal stability of UHMWPE components, it is reported that residual free radicals and/or long-lived oxygen-induced free radicals [16] pose an everlasting threat for longevity of components and their thermal stability. Natural antioxidants like α -tocopherol (commonly known as Vitamin E) have proven to be efficient and suitable fillers to quench residual free radicals and thus enhance the mechanical, thermal and wear properties of UHMWPE components [17–19]. In another study, Shafiq *et al* [20] reported that irradiating UHMWPE in the presence of organo-silanes like vinyl-tri-ethoxy silane

results in significant increase of its thermal properties, including the increase in onset thermal degradation temperature (T_{on}), peak melting temperature (T_m) and crystalline lamellae thickness (L_c). They attributed this behaviour to quenching of radiation-induced polyethylene (PE) free radicals by silane via silane grafting extension and siloxane linkages reactions. Recently, Martínez-Morlanes *et al* [21] studied the effect of gamma irradiation on the thermal properties of UHMWPE/MWCNTs nanocomposites. They found that incorporation of unmodified MWCNTs had almost negligible effect on the melting temperature of pristine UHMWPE, and an increase in thermal stability was observed in UHMWPE/MWCNTs nanocomposites as compared with pristine UHMWPE. However, unfortunately, they observed and reported a decrease in degree of crystallinity for UHMWPE/MWCNTs due to reduction of crystalline lamellae density of UHMWPE.

According to our knowledge, after a comprehensive literature review on the subject matter of interest and PE radiation chemistry and physics as well as MWCNTs, this reduction in crystalline lamellae density might be due to defective sites already present within the MWCNTs; these sites are responsible for quenching primary alkyl radicals [22], which play the main role for enhancing the crosslinking yield, percent crystallinity and average crystallite size [20]. Therefore, this particular study is designed to compare the effect of gamma irradiation on the thermal properties, including T_m , T_c , L_c , T_{on} and thermal stability of UHMWPE nanocomposites with unmodified MWCNTs and gamma-ray-modified MWCNTs, i.e., UHMWPE/MWCNTs and UHMWPE/ γ -MWCNTs. The modification of MWCNTs has been performed by treating the MWCNTs with 100 kGy of gamma dose because it has been reported by Safibonab *et al* [23] that irradiating the MWCNTs with ≤ 100 kGy dose results in eliminating already present defective sites within the MWCNTs.

2. Materials and methods

2.1 Materials

The materials/chemicals used during this study are UHMWPE ($d = 0.940 \text{ g cm}^{-3}$), pure and γ -irradiated MWCNTs, methanol (99% pure) and acetone (99% pure). UHMWPE, methanol and acetone were purchased from Sigma Aldrich Chemie, Steinheim, Germany, and used as such without any further purification/treatment. MWCNTs were gifted by a goodwill fellow from Korean Atomic Energy Agency for this particular research work.

2.2 Sample preparation and irradiation

Appropriate concentrations (0.5 and 1.0) of pure and γ -irradiated MWCNTs were dispersed in methanol (100 ml) by sonification for approximately 45–50 min. The blends

of UHMWPE and dispersed MWCNTs (in methanol) were prepared by wobbling the admixture. The methanol was then evaporated from the slurry by heating the mixture at 60–70°C overnight in an oven (Mettler, GmbH). Afterwards, ball milling of samples was performed for 2 h at 200 rpm using the facility available at Pakistan Institute of Engineering and Applied Sciences, Islamabad, Pakistan. The homogenized UHMWPE/MWCNTs and UHMWPE/ γ -MWCNTs composites were then subjected to hot pressing (Gibitre Instruments Laboratory Press) and moulded into sheets of micron size.

The compression moulding of composites was carried in three systematic steps as follows.

- Step-1:* The composites in powder form were preheated at 150°C for 5 min. It is worth mentioning here that during this preheating period the pressure was kept as low as possible.
- Step-2:* The pressure and temperature were gradually raised to 200 bar and 190°C, respectively; on achieving the required pressure and temperature, samples were further heated for the next 15 min.
- Step-3:* After combined heating and pressing treatment, samples were cooled to room temperature (i.e., 25°C) under 40–50 MPa pressure.

After preparation of composite sheets, all the samples were divided into five groups. One of these five groups was kept in a shelf and categorized as the control sample, while other four groups were sent to Pakistan Radiation Services (PARAS), Lahore, for γ -irradiation and were irradiated in air at room temperature for total dose values of 25, 50, 100 and 150 kGy.

All the samples were labelled with various codes for their identification based on the treatment (i.e., pure or irradiated), concentration and category (i.e., whether un-modified or γ -ray modified) of MWCNTs involved. The sample codes are given in table 1.

Table 1. Samples codes used for identification within the text of this manuscript.

Sample code*	MWCNTs nature	MWCNTs concentration (%)
P	—	—
PP-A	Pure/un-irradiated	0.5
PP-B	Pure/un-irradiated	1.0
PI-A	Gamma irradiated	0.5
PI-B	Gamma irradiated	1.0

*Note: To represent the absorbed dose of composite, subscript with sample codes is used, e.g., PP-A₂₅ represents the UHMWPE composite containing 0.5% of pure MWCNTs and irradiated for 25 kGy of gamma dose.

2.3 Measurements

2.3a Differential scanning calorimetric (DSC) analysis:

For DSC measurements, an Indium-calibrated Mettler Toledo thermo-gravimetric analysis (TGA)/DSC-1 star system (Schwarzenbach, Switzerland) Instrument was used. The temperature accuracy and temperature precision of the DSC machine calibrated with the In standard are ± 0.10 and $\pm 0.050^\circ\text{C}$, respectively. Each sample of approximately 5 mg weight was placed in an aluminium pan and heated non-isothermally in nitrogen atmosphere of 50 ml min^{-1} from room temperature to 200°C and then brought back to room temperature at constant heating and cooling rate of 10°C m^{-1} . Heat flow as a function of temperature was recorded and analysed for each sample. The analysis includes the calculation of percentage crystallinity X_c (%), lamellae thickness (L_c), peak melting (T_m) and re-crystallization temperature (T_c). For the estimation of X_c and L_c , following well-known relations were used [14,15,24–28]:

$$X_c (\%) = (\Delta H_m^\circ / \Delta H_m) \times 100, \quad (1)$$

$$T_m = T_m^\circ (1 - 2\sigma / L_c \rho_c \Delta H_m^\circ), \quad (2)$$

where ΔH_m° is melting enthalpy of 100% crystalline PE (290 J g^{-1}), ΔH_m is melting enthalpy of the sample, T_m is melting temperature of the polymer, T_m° is equilibrium melting temperature of the best crystalline PE, which is 145.7°C , $\sigma = 95.7 \times 10^{-7}\text{ J cm}^{-2}$ is specific surface energy, $\rho_c = 1.005\text{ g cm}^{-3}$ the crystalline phase density and L_c is lamellae thickness.

2.3b TGA: In order to perform a comparative study and analyse the effect of γ -irradiation on thermal stability of pristine UHMWPE and its nanocomposites with MWCNTs and γ -MWCNTs, TGA measurements were performed in an inert atmosphere using the thermogravimetric analyzer (model: TGA/SDTA851e, Schwarzenbaclz, Switzerland) available at the Institute of Space Technology (IST) Pakistan. The details of the TGA instrument are as follows: temperature range—ambient to 1500°C ; temperature accuracy— $\pm 1^\circ\text{C}$; furnace heating rate $0.1\text{--}100^\circ\text{C min}^{-1}$; furnace cooling time from 1000 to $100^\circ\text{C} < 15$ min; balance measuring range up to 1 g with sensitivity of $1.0\text{ }\mu\text{g}$. Each sample of approximately 10 mg weight was placed in the alumina pan and the test was run from 25 to 800°C at the constant heating rate of $20^\circ\text{C min}^{-1}$ in the continuous purge of nitrogen (40 ml min^{-1}). The weight loss as a function of temperature was recorded and plotted against temperature for the analysis of thermal degradation of pristine UHMWPE and its composites with MWCNTs and γ -MWCNTs. It is worth mentioning here that in order to confirm the reproducibility of TGA data, four readings were taken for samples irradiated to 50 kGy, i.e., P₅₀, PP-A₅₀ and PP-B₅₀. These particular samples were chosen because it has been reported that UHMWPE suffers

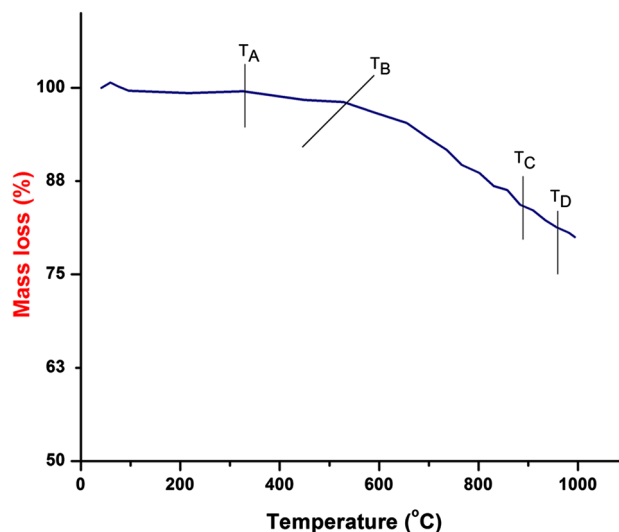


Figure 1. TGA curve of MWCNTs with marked points of T_{on} , $T_{5\%}$, $T_{10\%}$ and $T_{20\%}$.

more due to free radical chain scission oxidation reactions at intermediate doses [6]. On finding that total standard deviation in overall thermal behaviour is $\leq 5\%$, only one or two of the other samples were tested with the assumption that standard deviation will remain $\leq 5\%$.

3. Results and discussion

This particular study has the main aim of exploring and comparing the effect of incorporating modified MWCNTs on thermal properties and thermal stability in post-irradiated UHMWPE nanocomposites (whether UHMWPE/MWCNTs or UHMWPE/ γ -MWCNTs). Therefore, it is of particular importance to have insight of thermal properties (i.e., on X_c (%), T_m , T_c and L_c) and thermal stability of UHMWPE/MWCNTs and UHMWPE/ γ -MWCNTs nanocomposites prior to radiation treatment. The following section briefly sums up the effect of incorporating modified and unmodified MWCNTs on the aforementioned thermal properties and stability; figure 1 shows the thermal decomposition behaviour of pure MWCNTs.

3.1 DSC and TGA of UHMWPE and its composites before irradiation

The values of X_c (%), T_m , T_c and L_c of pristine UHMWPE and its nanocomposites with MWCNTs and γ -MWCNTs are presented in figure 2 and table 2. As expected, all samples exhibit the characteristics endothermic and exothermic peaks with melting peak varying by $1\text{--}2^\circ\text{C}$ from the value of pristine sample, i.e., 137°C , re-crystallization peak varying by $1\text{--}2^\circ\text{C}$ from the pristine value, i.e., 113°C and lamellae thickness varying by $1\text{--}2$ nm from the pristine value, i.e., 12.9 nm. The aforementioned thermal properties in

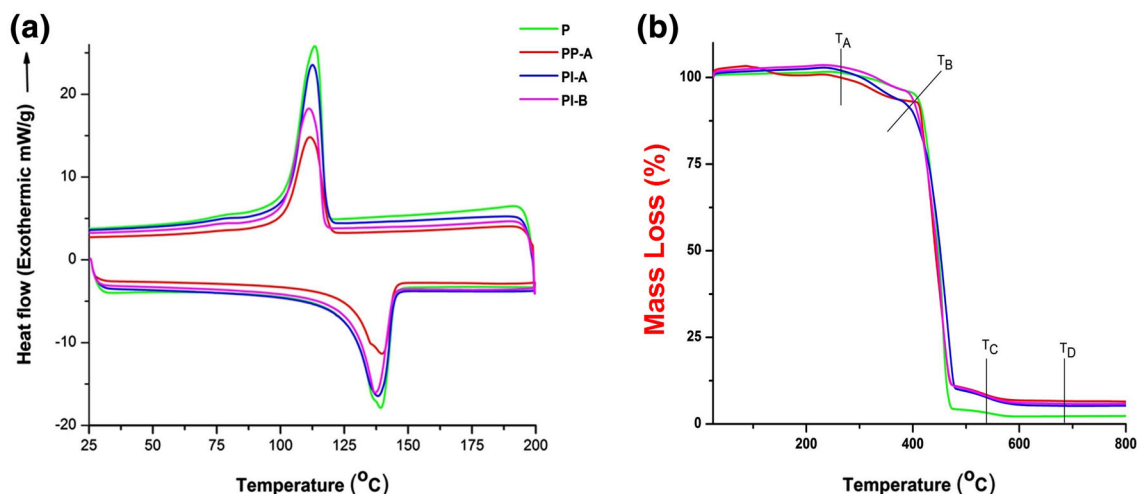


Figure 2. (a) DSC and (b) TGA thermo-grams of UHMWPE, UHMWPE/MWCNTs and UHMWPE/ γ -MWCNTs.

Table 2. DSC and TGA data of UHMWPE, UHMWPE/MWCNTs and UHMWPE/ γ -MWCNTs.

Sample	DSC data				TGA data			
	T_m (°C)	L_c (nm)	X_c (%)	T_c (°C)	T_{on} (°C)	T_{20} (°C)	T_{40} (°C)	Residue (%)
P	138.37	12.9	43	113.52	366.10	412.80	443.20	2.38
PP-A	139.16	14.5	41	111.53	292.05	422.35	434.85	6.60
PI-A	137.61	11.8	40	112.92	256.73	418.50	441.82	6.00
PI-B	136.29	10.1	43	111.71	287.15	421.63	451.20	6.00

UHMWPE/MWCNTs nanocomposites show an increasing trend, while a decreasing trend for UHMWPE/ γ -MWCNTs nanocomposites (as compared with UHMWPE) is evident from table 2. Already present defective sites within MWCNTs and elimination of these defective sites on γ -irradiating the MWCNTs with a total dose value of ≤ 100 kGy [23] might be the reason for aforementioned behaviour in thermal properties of UHMWPE/MWCNTs and UHMWPE/ γ -MWCNTs nanocomposites as compared with UHMWPE. These defective sites may be responsible for additional heat absorption and higher melting point, lower set temperature and higher values of enthalpy change, i.e., ΔH_m (measured from the area under the endothermic absorption peak). The further decrease in melting temperature and ΔH_m and the values of re-crystallization temperature T_c for PI-B sample (see table 2) also support our argument here. However, the values of X_c (%) show the mixed trend which is due to its dependence on the values of ΔH_m .

TGA measurements were performed to investigate the thermal degradation behaviour of UHMWPE and its composites. The weight loss as a function of temperature, shown in figure 2b, gives the picture of thermal stability of pristine and filler-added UHMWPE samples. The single-step mass loss behaviour of UHMWPE remains unaffected with the incorporation MWCNTs (whether they are irradiated or un-irradiated); however, nanocomposites are found to be more

thermally stable as compared with pristine UHMWPE in spite of lower values of T_{on} (onset degradation temperature) of nanocomposites concerned. Furthermore, residue (%) values of nanocomposites are higher as compared with pristine values (see table 2 for details). As far as the thermal behaviour is concerned, the trend of weight loss as a function of temperature can be clearly divided into four steps: (1) T_A —primary weight gain, (2) T_B —rapid weight loss, (3) T_C —secondary weight gain and (4) T_D —final volatilization temperature (see figure 2b). Diffuse oxygen and its reaction with PE radicals are mainly responsible for the initial weight gain (T_A) and weight gain before final volatilization, i.e., T_C . The readers are referred to the literature for a detailed discussion on this weight gain during thermal degradation of UHMWPE [4,20].

3.2 DSC and TGA of UHMWPE and its composites after irradiation

3.2a DSC and TGA of post-irradiated UHMWPE: In order to study the effect of γ -irradiation on the thermal properties of pristine UHMWPE, DSC measurements were performed, and heat flow as a function of temperature for each sample is plotted as shown in figure 3. All the samples exhibit the characteristic endothermic and exothermic peaks; the peak melting (T_m) and re-crystallization (T_c) temperature varied, respectively, from 138 to 141 and from 113 to 107°C

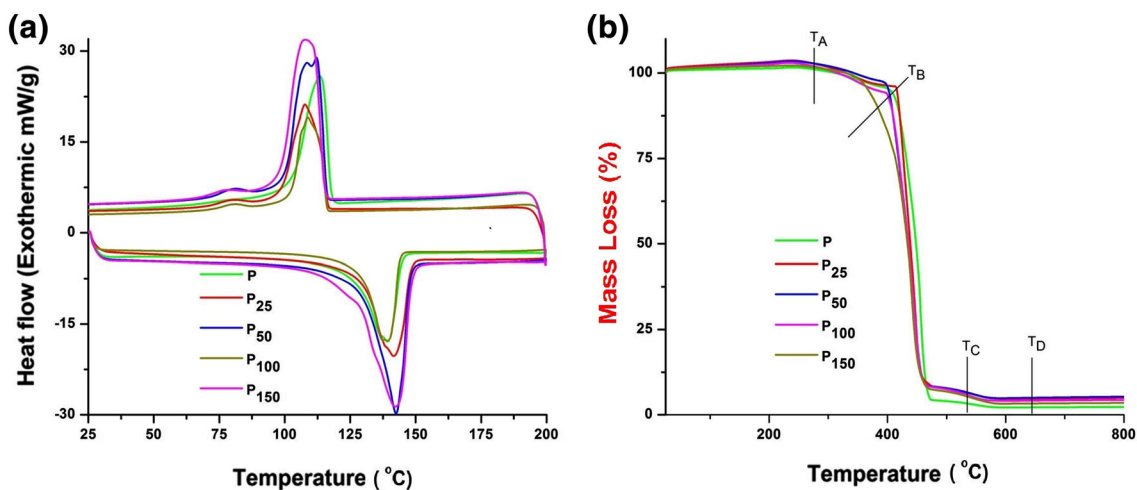


Figure 3. Radiation dose vs. (a) peak melting temperature (T_m), (b) average crystalline lamellae thickness (L_c), (c) percentage values of crystallinity and (d) re-crystallization temperature (T_c) of pristine UHMWPE and UHMWPE nanocomposites containing 0.5% of un-irradiated (PP-A) and irradiated (PI-B) MWCNTs.

Table 3. DSC and TGA data of γ -irradiated UHMWPE composites.

Sample	DSC data				TGA data			
	T_m (°C)	L_c (nm)	X_c (%)	T_c (°C)	T_{on} (°C)	T_{20} (°C)	T_{40} (°C)	Residue (%)
P	138.37	12.9	42.73	113.52	366.10	412.80	443.20	2.38
P ₂₅	140.76	19.3	53.22	107.21	269.20	424.7	434.1	4.90
P ₅₀	141.16	20.9	55.96	112.13	289.66	411.2	426.2	5.32
P ₁₀₀	138.54	13.3	50.33	108.59	270.91	414.4	428.6	4.92
P ₁₅₀	141.05	20.5	68.17	107.45	320.19	405.70	427.80	3.22

(see figure 3). The calculated values of percentage values of crystallinity (X_c), T_m , T_c and lamellae thickness (L_c) using equations (1) and (2) are summarized in table 3. It can be seen from figure 3 that T_m increases with increase in absorbed dose and has the maximum value for the sample irradiated to 100 kGy. The value of peak melting temperature was found to decrease slightly for the 150 kGy sample. In addition to this, sharpness of endothermic peaks increased with the increase in absorbed dose. A plausible explanation for this increase in T_m is radiation-induced crosslinking and/or chain scission near the crystalline lamellae boundaries due to PE free radical radiation oxidation chain reactions. These phenomena are mainly responsible for the kinetic confinement of PE melting process [12,21,29]; as result, increase in values of X_c (%) and T_m with radiation is observed (see table 3). Higher the role of PE free radicals in chain scission, higher the increase in X_c (%), T_m and L_c . However, in samples where PE radicals play their major role in crosslinking, the values of X_c (%), T_m and L_c are lower, e.g., for 100 kGy sample the values of X_c (%), T_m and L_c are lower as compared with 25, 50 and 150 kGy values.

Now, coming to exothermic behaviour of these samples, figure 3 clearly shows a decrease in peak values of T_c with

absorbed gamma doses. Along with this decrease, a significant reduction in exothermic peak area has been observed for 25 and 50 kGy radiation doses, which are found to follow the reverse trend of 100- and 150-kGy-irradiated samples. Furthermore, an exothermic hump around 80°C had been observed for all samples, which might be due to absorbance of heat by PE to recover its *all-trans* interphase contents [16]. However, further investigations are in progress to correlate this exothermic hump with the interphase contents (%) of UHMWPE.

As far as the dependence of percentage crystallinity X_c (%) and average crystallite sizes of pure/pristine UHMWPE on absorbed gamma dose is concerned, increase from 40 to 68% and ~ 13 to ~ 21 nm has been observed in X_c and L_c , respectively (see table 3 for details). Similarly, it can be seen that thermal stability of UHMWPE gets seriously affected with irradiation; as a whole, irradiated samples lost their weights at lower temperatures as compared with un-irradiated ones, with higher values of residue (%). Chain scission close to crystalline lamellae immediately after irradiation, which reduces the *all-trans* interphase contents of UHMWPE [16], is responsible for the aforementioned experimentally observed increase in X_c , L_c and decrease in thermal stability.

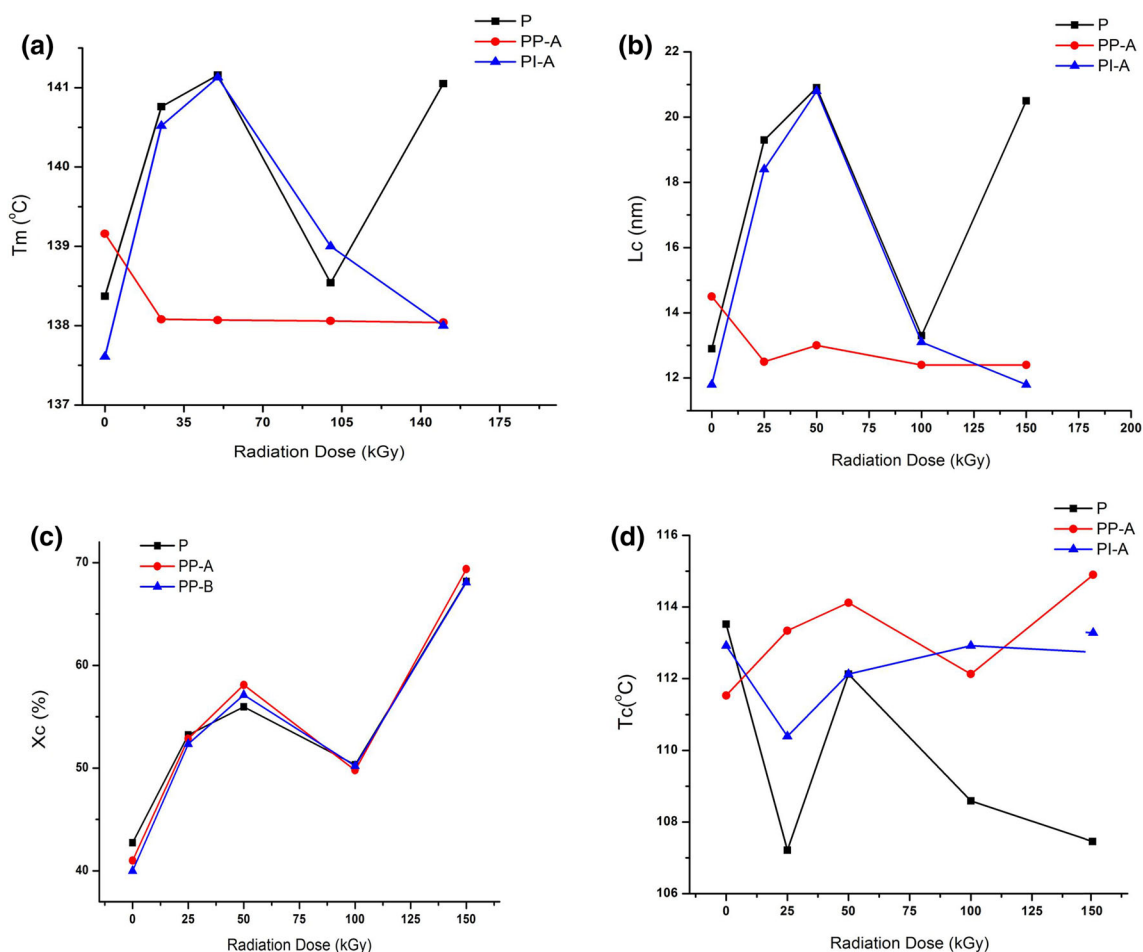


Figure 4. Radiation dose vs. (a) peak melting temperature (T_m), (b) average crystalline lamellae thickness (L_c), (c) percentage values of crystallinity and (d) re-crystallization temperature (T_c) of pristine UHMWPE, UHMWPE nanocomposites containing 0.5% of un-irradiated (PP-A) and irradiated (PI-B) MWCNTs.

Furthermore, initial gains at T_A and secondary weight gain T_c due to radiation oxygen uptake [4] during thermal degradation are also evident in irradiated alone sample as well.

3.2b DSC and TGA of UHMWPE and its composites:

Figure 4a and b shows the dependence of T_m and L_c of pristine UHMWPE (P) and its nanocomposites with un-irradiated and γ -irradiated MWCNTs, i.e., PP-A and PI-A, on absorbed radiation dose. Increasing trends in the values of T_m and L_c are evident for pristine UHMWPE and its composites with γ -MWCNTs, whereas the values for PP-A samples remain almost unaffected. The oxidation reactions of PE free radical [2,22] and free radicals scavenging ability of MWCNTs due to defective sites [21] within the matrix of CNTs can be used to explain aforementioned trends for samples labelled as P, PP-A and PI-A. In PP-A samples, defective sites in MWCNTs are responsible for scavenging the majority of radiation-induced free radicals, thus limiting their role in oxidation chain reaction and degradation; however, in sample PI-A the role of PE free radicals in oxidation chain reactions is more dominant because it is

well established and experimentally reported understanding that γ -irradiation of MWCNTs with a dose value of ≤ 100 kGy improves their quality by eliminating the already present defective sites within MWCNTs matrix [23]. Therefore, the trend for PI-A is almost similar to that of pristine UHMWPE. Furthermore, abrupt decrease of T_m and L_c for 150 kGy PI-A sample is also in accordance with our argument here because treating MWCNTs with a dose value of ≥ 100 kGy increases the defective sites as reported by Safibonab *et al* [23]. The trend for percent crystallinity X_c (%) is almost the same for pristine UHMWPE and its composites with MWCNTs and γ -MWCNTs. Re-crystallization temperature T_c values as a function of absorbed dose are higher for composites as compared with the pristine sample (see figure 3d). Higher chain mobility due to the presence of MWCNTs within PE matrix might be responsible for this behaviour.

Figure 5 shows the weight loss as a function of temperature and dependence of onset degradation temperature, 20% weight loss temperature and 40% weight loss temperature on the MWCNTs (whether irradiated or un-irradiated) and

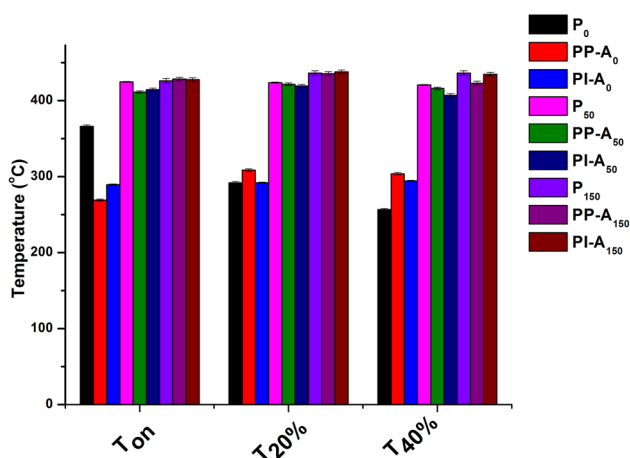


Figure 5. TGA graph showing the dependence of onset degradation temperature.

irradiation. The degradation temperatures at different weight losses increase with irradiation for P, PP-A and PI-A. The enhancement of crosslink density with irradiation along with the further action of kinetic hindrance offered by MWCNTs for the motion of long chain within this dense crosslink network [17,18] is responsible for higher thermal stability of irradiated samples and composites. Composites of UHMWPE with un-irradiated MWCNTs have shown lower thermal stability as compared with UHMWPE/ γ -MWCNTs. Once again, free radical scavenging ability of MWCNTs due to defective sites is responsible while limiting their role for maximum contribution to PE crosslinking.

4. Conclusion

UHMWPE nanocomposites were prepared successfully with various concentrations of un-modified and γ -ray-modified MWCNTs. The prepared composites were then subjected to hot pressing and irradiated with gamma radiation of different doses ranging from 25 to 150 kGy. The results from DSC data showed that peak melting temperature (T_m) was increased from 138 to 141°C for UHMWPE/ γ -MWCNTs samples irradiated with ≤ 100 kGy. However, for sample irradiated with 150 kGy, abrupt decrease in T_m was observed, which was attributed to the increase of defective sites in γ -MWCNTs present inside the polymer matrix on irradiating the composites for gamma dose ≥ 100 kGy. A similar trend was observed for average crystalline lamellae thickness, i.e., L_c . Furthermore, TGA showed an increase in thermal stability by an increase in experimentally observed values for 20% weight loss temperature from 303 to 461°C. In addition to this, significant increase in percentage residue was seen due to incorporation of MWCNTs in both un-modified or γ -ray-modified samples. These results revealed that thermal stability of UHMWPE can be enhanced with incorporation

of MWCNTs mainly due to interactive effect of MWCNTs with UHMWPE and further crosslinking encouraged by γ -irradiation.

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