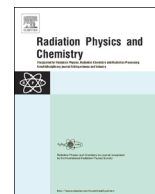




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# The influence of $\gamma$ -ray irradiation on the thermal stability and molecular weight of Poly(L-Lactic acid) and its nanocomposites

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## HIGHLIGHTS

- The gamma radiation effects of PLLA and its MK10 clay nanocomposites were studied.
- The thermal degradation of the PLLA and its nanocomposites occurred in one stage.
- The  $E$  values of the irradiated polymer seem to be smaller than those of unirradiated.
- Dioxane is more reactive against PLLA and its nanocomposites than THF and chloroform.
- The polymer structure was less stable to radiation compare to its nanocomposites.

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## ABSTRACT

The gamma ( $\gamma$ ) radiation effects on the thermal properties of Poly(L-Lactic acid) (PLLA), and three PLLA nanocomposites containing 1, 3 and 5% montmorillonite MK10 clay were investigated in different solvents such as tetrahydrofuran, chloroform and 1,4 dioxane. The polymers were irradiated by gamma radiation at low absorbed doses of 1, 5, and 10 kGy. The thermal properties and molecular weight of the unirradiated and irradiated PLLA and its nanocomposites were characterized by Thermogravimetry (TG) and Gel Permeation Chromatography (GPC), respectively. The TG curves showed that the thermal degradation of the unirradiated PLLA and its nanocomposites occurred in only one stage. The activation energies of thermal degradation ( $E$ ) for irradiated and unirradiated PLLA and its nanocomposites were determined by the Flynn–Wall–Ozawa (FWO) method. The  $E$  values of the polymer irradiated with gamma radiation seem to be smaller than those of unirradiated sample due to polymer bond scission. In addition, the calculated  $G$  values of the polymer and nanocomposites showed that the polymer structure was less stable when exposed to radiation with increasing % MK10 content.

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## 1. Introduction

Biodegradable polymers from renewable resources have importance in polymer chemistry due to increasing environmental concern and decreasing fossil resources. These polymers can be used instead of synthetic polymers from petrochemical products to solve the ecological problem of plastic waste accumulation (Ray and Bousmina, 2005; Bastioli, 2005; Rhim and Ng, 2007; Vert et al., 1995; Hyon et al., 1997). Poly(L-Lactic acid) (PLLA) is a biodegradable polymer with useful mechanical properties, applications in the biomedical industry and as replacement thermoplastic from renewable resources such as corn and potatoes (Burke

et al., 1997). Because of its bio-characteristics, thermal and physical properties, it has been used for surgical implant materials and drug delivery systems as well as ecological materials. PLA is one of the most potential candidates for plastic industries (Garlotta, 2001).

In order to improve the properties of polymers, polymer nanocomposites were prepared. Recently, works about the enhancement of physical properties of PLA by addition of clay have been reported in the literature (Ray et al., 2002; Pluta et al., 2002; Maiti et al., 2001; Ogata et al., 1997; Wu and Chiang, 2005). Various methods have been developed to prepare polymer-clay nanocomposites. In situ polymerization method among them is the most effective method for the exfoliation of clay platelets in the polymer matrix (Oral et al., 2009). The field of polymer nanocomposites is primarily based on layered silicates, such as montmorillonite. These layered silicates have platelets with a high aspect ratio (with a ca. 1 nm thickness and lateral

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dimensions varying from 100 nm to 1 mm) (Chen et al., 2002). Montmorillonite-K10 (MK10) is an acid treated clay that forms layered structures consisting of negatively charged aluminosilicates with a catalytic proton, and it has a surface area of 220–270 m<sup>2</sup>/g. MK10 is also suitable for the chemical recycling process of PLA (Okamoto et al., 2005). Dispersion of the clay platelet has a high aspect ratio in polymer matrix; therefore, polymer-montmorillonite nanocomposites have shown significant improvement in its optical properties and in the fields such as viscoelasticity, stress, strain, yield stress etc. It has proved beneficial in the production of fire retardant and gas barrier and especially at low clay loading levels, in comparison with microcomposites (Sengupta et al., 2007; Xie et al., 2012; Kasirga et al., 2012).

The radiation chemistry of polymers can be considered as a section of a more general field of the radiation chemistry of organic substances. Thus, the most important modifications observed in irradiated polymers, i.e. radiation-induced cross-linking and degradation, are closely related to the condensation and scission reactions produced by irradiation of low molecular weight substances. Although the earliest report on the effects of radiations on polymer solutions dates back to 1941, when Khenokh subjected gelatin solutions to gamma-rays, this field of the radiation chemistry of polymers has received much less attention than the irradiation of polymers in the solid state. Ionizing radiation is a well-known technique for modification of polymers. The use of ionizing radiation in the polymer area is employed to induce several chemical processes such as polymerization, crosslinking, grafting and degradation of particular polymer components (Dole, 1972; Clegg and Collyer, 1991). These processes depend on several factors, including the chemical structure of the polymer, the amount of dosage, the rate of dosage, and the environment of the material during irradiation of polymerization (Fawzy et al., 2011). The degradation of the polymer results in reduction in the activation energy of thermal degradation and molecular weight (Kalsi and Ramaswami, 2009).

The effects of interaction of ionizing radiation with PLLA and its nanocomposites containing 1, 3 and 5% montmorillonite MK10 have not been studied. In the present study, the thermal degradation kinetics and molecular weights of the PLLA and its nanocomposites irradiated with gamma radiation were investigated to compare their radiation resistance since their thermal properties and molecular weights are very important from the viewpoint of their usages. For this purpose, the apparent activation energies for thermal degradation of the polymers were determined by using the FWO method.

### 1.1. Flynn–Wall–Ozawa (FWO) method (Flynn and Wall, 1966; Ozawa, 1965)

This is one of the integral methods determines the activation energy without considering the reaction mechanism. Pre-exponential factor ( $A$ ) and activation energy ( $E$ ) does not depend on the degree of conversion, while they do on the temperature. This method uses Eq. (1).

$$\log g(\alpha) = \log \left( \frac{AE}{R} \right) - \log \beta + \log p \left( \frac{E}{RT} \right) \quad (1)$$

Doyle's approximation is used and Eq. (2) can be obtained

$$\log \beta = \log \left( \frac{AE}{R} \right) - \log g(\alpha) - 2.315 - 0.4567 \left( \frac{E}{RT} \right) \quad (2)$$

where the plot of  $\log \beta$  vs.  $1000/T$  should give a straight line with the slope  $E/R$  whence  $E$  is obtained.

## 2. Experimental

### 2.1. Materials

Montmorillonite-K10 (MK10), L-Lactic acid (LLA) (Jollands and Gupta, 2010), Methanol (MeOH), p-toluenesulfonic acid, tetrahydrofuran (THF), chloroform and dioxane were purchased from Sigma-Aldrich and dichloromethane (DCM) from Acros. All chemicals were used as received.

### 2.2. Instrumentation

Molecular weights were determined by GPC instrument; Agilent Model 1100 consisting of a pump, a refractive index detector and four Waters Styragel columns as HR 5E, HR 4E, HR 3, HR 2, and THF were used as eluent at a flow rate of 1 mL/min at 30 °C. Molecular weights were calibrated using polystyrene standards.

TG measurements of powder polymer samples were obtained on Perkin-Elmer Diamond TA/TGA from 30 to 600 °C at different heating rates (5, 10, 15, and 20 °C/min), under constant flow of 100 mL/min of nitrogen atmosphere. The sample weights for all the experiments were taken in the range of 8–10 mg.

The polymers and nanocomposites were irradiated in Co-60 gamma cell 220 of Sarayköy Nuclear Research & Training Center of Turkish Atomic Energy Authority with a 1.02 kGy/h dose rate at room temperature. The dose rate is determined by standard Fricke dosimeter and tolerance in each absorbed doses is about 1%.

### 2.3. Synthesis of PLLA and its nanocomposites

LLA polymerization with various amounts of MK10 as the catalyst was carried out according to procedure (Hyon et al., 1997). A schlenk tube was connected to vacuum system through silica gel moisture trap and schlenk was placed in an oil bath. 2 mL of (13.2 mmol) LLA and 1, 3, and 5% MK-10 were added in the schlenk tube and heated from room temperature to 180 °C and stirred for 5 h under 33 mbar vacuum. After the reaction at the same pressure, the reaction vessel was cooled down to room temperature. Then, the product was dissolved in DCM and precipitated in MeOH. The resulting polymer was filtered and dried at room temperature for 24 h and then dried in vacuum oven at 40 °C for 3 days.

The PLLA and three PLLA nanocomposite containing 1, 3 and 5% MK10 were irradiated in tetrahydrofuran (THF), chloroform and 1,4 dioxane solvents at the various absorbed doses such as 1, 5, and 10 kGy. The polymer and its nanocomposites concentration in solution were prepared as 2 mg/1 mL.

## 3. Results and discussion

The gamma radiation effects on the molecular weight and thermal properties of the PLLA and three PLLA nanocomposites have been investigated in different solvents such as THF, chloroform and 1,4 dioxane solvents. The results obtained for the PLLA and its nanocomposites samples related to their molecular weight and the thermal properties are as follows.

### 3.1. Radiation effects of thermal properties of PLLA and its nanocomposites

#### 3.1.1. Thermal degradation of unirradiated PLLA and its nanocomposites

Fig. 1a shows the respective TG thermograms of unirradiated PLLA and its nanocomposites containing 1, 3 and 5% MK10 under nitrogen atmosphere over a temperature range from 30 to 600 °C

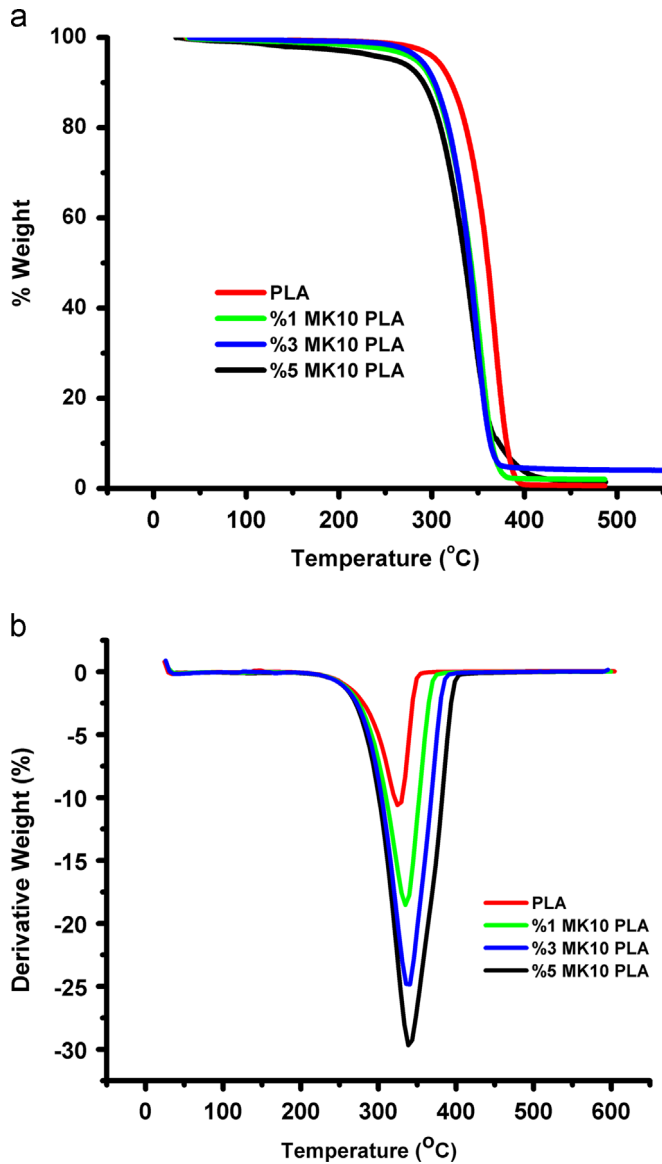


Fig. 1. The TG thermogram of PLLA and its nanocomposites (a) 0% MK10, (b) 1% MK10, (c) 3% MK10 and (d) 5% MK10.

at a heating rate of 10 °C/min. It is shown in Fig. 1a that there is only one degradation stage for those of PLLA and its nanocomposites.

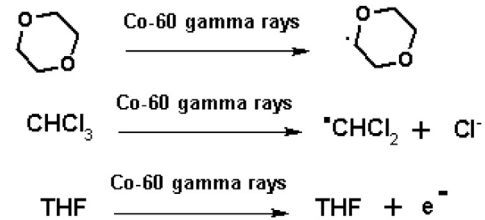
In addition, the derivative of the thermogram with respect to temperature, also known as a differential thermogram or DTG, indeed shows the maximum rate of polymer decomposition ( $T_{max}$ ). The DTG thermograms of unirradiated PLLA and its nanocomposites containing 1, 3 and 5% MK10 are shown in Fig. 1b. The maximum degradation temperatures ( $T_{max}$ ) are 359, 343, 338 and 343 °C for 0, 1, 3 and 5% MK10, respectively. It can be concluded that thermal stability of the polymers decreases significantly when the MK10 content is increased.

According to the model given by McNeill and Leiper, cyclic oligomers, lactide, acetaldehyde and carbon monoxide are final products of PLLA thermal degradation (McNeill and Leiper, 1985a). Clay particles have Brønsted and Lewis acid sites that are constituted by the lattices (Bellucci et al., 2007; Camino et al., 2005; Hiltunen et al., 1997). Thermal stability of the PLLA decreased due to these sites in nanocomposite (Kasirga et al., 2012). Moreover, MK10 in the PLA matrix accelerates the thermal degradation (Okamoto et al., 2005). Thermal degradation is dictated by the

final OH groups that “attack” the basic chain, which bends under the influence of thermal energy. Such a reaction can start at temperatures higher than 500 K (McNeill and Leiper, 1985b). In each of these reactions, the OH group regenerates and the process continues. Depending on the basic chain spot “attacked” by the OH group, different products are obtained. As a consequence of the decrease in the thermal stability of the PLLA component, induced by irradiation, the PLLA chains become more mobile, therefore, thermally less stable in MK10/PLLA composite.

### 3.1.2. Radiation degradation of PLLA in different solvents

The effects of solvent on the radiation-induced degradation have been subjected to study because the solvent is one of the obvious factors affecting not only the degradation degree but also the location of degradation. The thermal degradation behavior of the PLLA irradiated that 10 kGy absorbed doses in different solvents such as THF, chloroform and 1,4 dioxane are shown in Fig. 2. The thermal stability of irradiated PLLA polymer in 1,4 dioxane was found to be much smaller than THF and chloroform. The general degradation mechanisms of the solvents are as follows:



The apparent decrease in thermal stability may be attributed both to a decrease in the stability of the polymer and to a lack of polymer backbone. The radiation-induced degradation of the various polymers such as Poly(methyl methacrylate) (PMMA), Poly(styrene), Poly(methacrylic acid), Poly(isobutylene), Poly(vinyl acetate) and so on in a large number of solvents was investigated in the literature (Okamura et al., 1959; Henglein et al., 1957; Suljovrujić et al., 2007). Henglein et al. and Okamura et al. studied the influence of solvent on the radiation degradation of Poly(methyl methacrylate). Irradiations of PMMA were carried out in various solvents such as benzene, acetone, ethyl acetate, chloroform, dioxane, and carbon tetrachloride for influence of the viscosity molecular weight (Okamura et al., 1959). They found that maximum degradation occurred in dioxane and carbon tetrachloride as solvents. Henglein also reported about Poly(vinyl acetate) dissolved in various solvents. It was found that viscosity decreased in 1,4

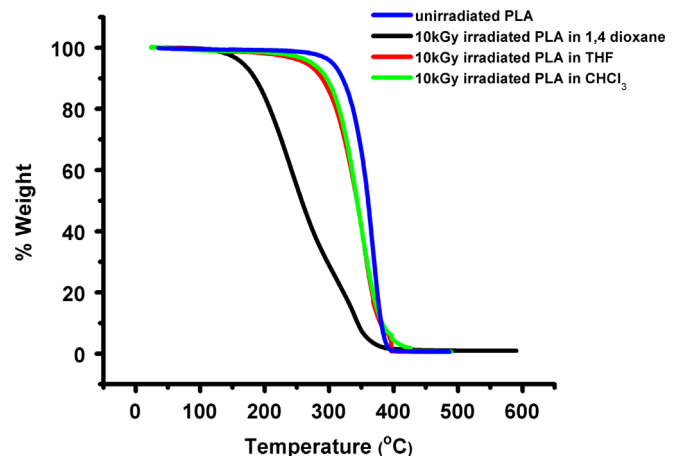
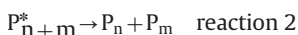


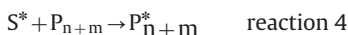
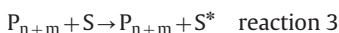
Fig. 2. The TG thermograms of PLLA at 10 kGy absorbed dose in different solvents.

dioxane, toluene, dimethylformamide, ethylbenzene, ethyl acetate, propionitrile and chloroform (Henglein et al., 1957).

The radiation-induced degradation occurs in two different pathways. First, the chain degradation results from the scission of polymer molecules which are directly excited by irradiation and not from the attack of the polymer by free radicals generated in the solvent. The scheme is as follows:



Secondly, degradation is caused by the attack of the polymer chain by free radicals generated in the radiolysis of the solvent. These mechanisms, based on “indirect effect” of irradiation, have been suggested for the radiation degradation of other polymers in solution. Consequently, our results indicate that the indirect effect is more dominant and prominent in 1,4 dioxane solvent than those in others.



According to literature, an additional chemical degradation occurs in chlorinated solvents. This process is initiated by the chlorine atoms liberated in the radiolysis of the solvent. In contrast, it appears from our results that the lowest degradation yield is obtained in chloroform. With THF as solvent, the results are very close to those obtained in chloroform at similar conditions. It may be pointed out that the polymer was found to cross-link when irradiated in the solvents at higher concentration. It follows that chain branching and intramolecular cross-linking occurred in the dilute solutions (Chapiro, 1962). Consequently, the radiation-induced degradation of PLLA and its nanocomposites containing 1, 3 and 5% MK10 was found to be solvent-dependent. This behavior can be understood based on the fact that the 1,4 dioxane solvent leads to more radical generation in the degradation system. 1,4 dioxane, which only absorbs low energy gamma radiation, leads to a high degradation yield because reaction 3–5 are favored in this solvent.

### 3.1.3. Radiation degradation of PLLA and its nanocomposites in 1,4 dioxane

The TG thermograms of PLLA and its nanocomposites in 1,4 dioxane irradiated at 10 kGy absorbed doses taken under nitrogen atmosphere at a temperature range from 30 to 600 °C at the heating rate of 10 °C/min are shown in Fig. 3. The individual degradation behavior of each PLLA and its nanocomposites were analogous, as seen from Fig. 3.

In previous papers, Milicevic et al. examined the influence of irradiation and post-irradiation treatments on the morphology, crystallinity, thermal and mechanical properties of PLLA and HAp/PLLA composite (Milicevic et al., 2010; Suljovrujić et al., 2003; Suljovrujić et al., 2007). They found that initial differences in the apparent activation energy of PLLA and HAp/PLLA became more pronounced with absorbed dose. Furthermore, they reported that the gamma radiation can be used not only for sterilization but also for tailoring desirable end use properties of these biomaterials (Suljovrujić et al., 2003).

### 3.1.4. Absorbed radiation dose effect of PLLA in 1,4 dioxane

The TG thermogram of irradiated PLLA at different absorbed doses such as 1, 5, 10 kGy is shown in Fig. 4. It was taken under nitrogen atmosphere at a temperature range from 30 to 600 °C at a heating rate of 10 °C/min. Loo et al. has studied the e-beam

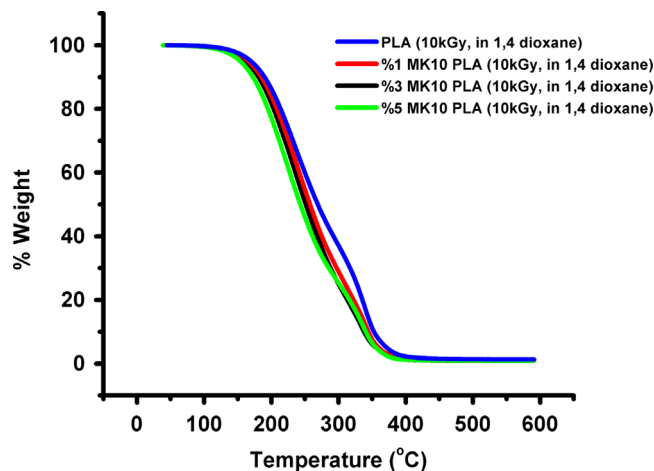


Fig. 3. The TG thermograms of PLLA and its nanocomposites at 10 kGy absorbed dose in 1,4 dioxane solvent.

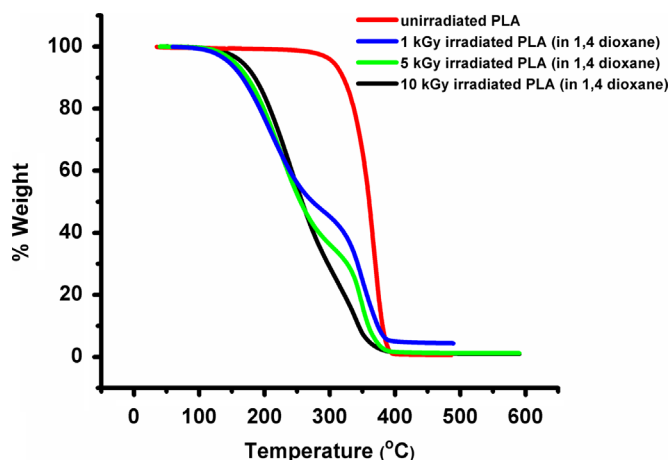


Fig. 4. The TG thermograms of PLLA at different absorbed doses in 1,4 dioxane solvent.

radiation effects on molecular weight of PLLA and PLGA (Loo et al., 2004). They found that the molecular weight of PLLA decreased with increasing radiation dose, which indicates that chain scission is the dominant process upon irradiation. Radiation degradation is a process in which the polymer suffers random chain scissions. Thus, the molecular weight and thermal stability steadily decrease with increasing radiation dose, and in some cases, the final product is a low molecular weight liquid.

The thermal stability of irradiated PLLA at different absorbed doses such as 1, 5, 10 kGy decreases with increasing radiation dose as seen in Fig. 4. Consequently, thermal stability results show that the influence of gamma radiation on the PLLA at different absorbed doses may tend to cease in polymer bonds resulting in a lower molecular weight.

### 3.1.5. Thermal degradation kinetic of the PLLA and its nanocomposites in 1,4 dioxane

Evaluation of the activation energy of thermal degradation is useful for studying the thermal stability of the materials. To calculate the activation energy of irradiated and unirradiated PLLA and its nanocomposites containing 1, 3 and 5% MK10, the TG measurement of the polymers were performed at various heating rates such as 5, 10, 15, and 20 °C/min in a temperature range from 30 to 600 °C. Various thermogravimetric methods based on either the degree of conversion or the heating rate have been reported to

determine the activation energies of thermal degradation. The method proposed by FWO (Flynn and Wall, 1966; Ozawa, 1965) has been used in the present study to calculate the activation energies. In order to obtain detailed information related to the thermal stability of the unirradiated and 10 kGy irradiated PLLA nanocomposite, the activation energies were calculated using the FWO method.

The calculated results from the FWO method of irradiated and unirradiated with 10 kGy absorbed dose of PLLA and its nanocomposites containing 1, 3 and 5% MK10 are shown in Fig. 5. The mean activation energies calculated for the unirradiated PLLA and its nanocomposites were found to be 162 kJ/mol, 160 kJ/mol, 156 kJ/mol and 150 kJ/mol, while those for irradiated were 64 kJ/mol, 60 kJ/mol, 58 kJ/mol and 54 kJ/mol for the PLLA, 1, 3 and 5% nanocomposite, respectively. It was found that the activation energies of unirradiated samples were about two and a half fold higher than those of the irradiated. The thermal behavior is dependent on the molecular weight of the polymer; for example, the higher the molecular weight, the higher the  $T_g$  (Sperling, 1986). So we examined molecular weight for 10 kGy irradiated PLLA and its nanocomposites.

### 3.2. Radiation effects of molecular weight of PLLA and its nanocomposites in 1,4 dioxane

$M_w$  (weight-average molecular weight) of the PLLA and its nanocomposites for unirradiated and irradiated with 10 kGy

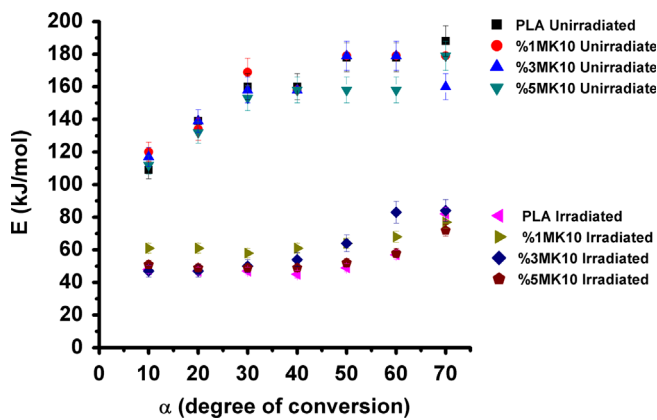


Fig. 5. The plot of activation energy ( $E$ ) vs. the degree of conversion ( $\alpha$ ) for unirradiated and irradiated with 10 kGy of PLLA and its nanocomposites.

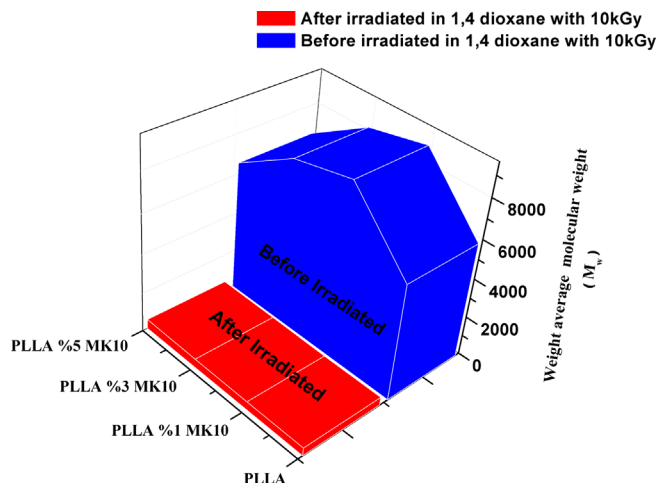


Fig. 6.  $M_w$  value of PLLA and its nanocomposites at unirradiated and irradiated with 10 kGy absorbed dose.

absorbed dose in 1,4 dioxane solvent were measured by GPC and the results are shown in Fig. 6. Rapid decrease in  $M_w$  clearly indicated that the only mode of action of radiation on PLLA and its nanocomposites was degradation. In the case of PLLA, the dominant effect is chain scission, which occurs through two main degradation mechanisms, i.e. backbone chain scission and chain scission by hydrogen abstraction. After the PLLA irradiated with gamma radiation, a decrease in molecular weight was observed (Montanari et al., 1998; Loo et al., 2005) caused by chain scission due to radical formation (Sintzel et al., 1997).

The polydispersity index (PDI) [(weight average molecular weight/number average molecular weight) ( $M_w/M_n$ )] of PLLA and its nanocomposites before and after irradiated with 10 kGy in 1,4 dioxane solvent were summarized in Table 1. The PDI values show that the irradiation has an important influence both on the PLLA molecular weight and on the polydispersity of the irradiated MK10/PLLA composite. Consequently, the irradiated PLLA and its nanocomposites samples have heterogeneous molecular weight distribution compared to the unirradiated ones.

The data for the change in the average molecular weights ( $M_n$ ) for 10 kGy absorbed dose may be used to estimate the  $G$  values. When a system is irradiated, the radiation yield is often expressed in terms of the  $G$  value, which is defined as the number of radiolysis events caused by the absorption of 100 eV of radiation (Charlesby, 1960). If scission is the only mode of action of radiation, then the radiation-chemical yield of degradation (scission)  $G$  is determined from the Alexander–Charlesby–Ross equation (Charlesby, 1960):

$$\frac{1}{M_n} = \frac{1}{M_{n,o}} + 1.04 \times 10^{-7} G(s) \times D$$

Table 1

Polydispersity index ( $M_w/M_n$ ) of PLLA and its nanocomposites at unirradiated and irradiated with 10 kGy absorbed dose.

Polymers	PDI Before irradiated	PDI After irradiated with 10 kGy
PLLA	1.382	2.601
PLLA 1% MK10	1.418	2.642
PLLA 3% MK10	1.411	2.414
PLLA 5% MK10	1.431	2.397

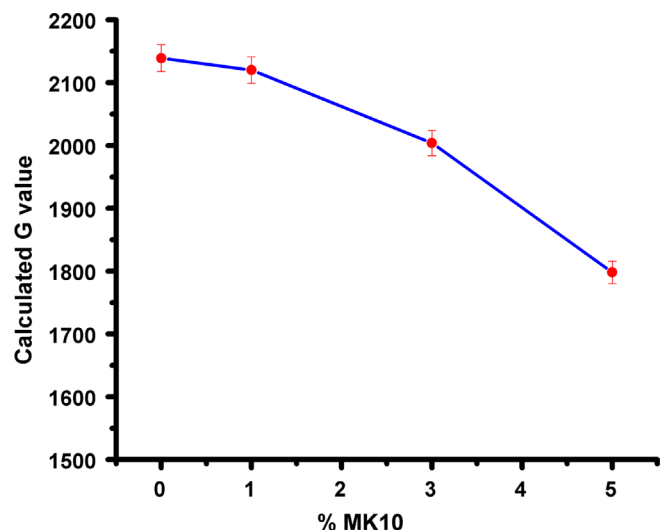


Fig. 7. The plot of calculated  $G$  values vs. the PLLA and its nanocomposites (1, 3, and 5% MK10).

where  $M_{n,0}$  and  $M_n$  are the number of average molecular weights of initial and final PLLA and its nanocomposites at certain absorbed dose ( $D$ ), respectively.

Fig. 7 shows the calculated  $G$  values for irradiated PLLA and its nanocomposites in 1,4 dioxane solvent. As seen in Fig. 7, the results of the  $G$  value with increasing % MK10 content was attributed to the increase of radical–radical recombination reactions due to the nature of MK10 structure. The decrease in  $G$  value of the polymer and nanocomposites between 0% and 5% MK10 may be attributed to the fact that the amount of montmorillonite in the polymer decreases polymer degradation.

#### 4. Conclusion

The present study investigated the effect of low absorbed doses (0–10 kGy) of gamma radiation on molecular weight and thermal behavior at room temperature in different solvents such as THF, chloroform and 1,4 dioxane on PLLA and its nanocomposites containing 1, 3 and 5% MK10. It can be concluded from the thermal degradation properties that 1,4 dioxane solvents was more reactive against PLLA and its nanocomposites than THF and chloroform under the same irradiating conditions. When 1,4 dioxane was used as solvent, thermal degradation increased slightly with the increase in dose; however, the doses used were much smaller than those commonly used with gamma rays. The activation energy was calculated using the Flynn–Wall–Ozawa method. The results showed that the activation energy slightly decreased as the MK10 content increased. According to  $G$  values related to the PLLA and its nanocomposites in 1,4 dioxane solvent, the radiation-induced degradation decreased with increasing MK10 content while the thermal stability was not affected.

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