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Effects of gamma irradiation on the crystallization, thermal and mechanical properties of poly(L-lactic acid)/ethylene-co-vinyl acetate blends

Hossam M. Said^{a,b,*}^aJAZAN University (JU), Faculty of Science, Chemistry Department, Saudi Arabia^bRadiation Chemistry Department, National Center for Radiation Research and Technology, P.O. Box 29 Nasr City, Cairo, Egypt

ARTICLE INFO

Article history:

Received 25 June 2013

Accepted 6 August 2013

Keywords:

Poly(L-lactic acid) blends

Microstructure

Rheological

Crystallization

Mechanical properties

Gamma irradiation

ABSTRACT

Poly(L-lactic acid)/ethylene vinyl acetate polymer blends (PLLA/EVA) with various blend ratios were prepared through melt blending process. The structural-property behavior of the polymer blends before and after they had been exposed to gamma irradiation was investigated. The hydrolytic degradation was investigated. The interfacial interaction between PLLA and EVA was visualized by Mechanical testing and FTIR. The crystallization behaviors of the blends were investigated by Differential scanning calorimetry (DSC), and the thermal stability was studied by thermogravimetric analysis (TGA). The results show that the hydrolytic degradation rate of PLLA/EVA blend can be widely controlled by exposing the PLLA/EVA to gamma-irradiation and also by EVA content. In alkaline solution, the hydrolytic degradation rate of the blends exposed 100 kGy and whose EVA content is higher than 50 wt% was decelerated while the rate of the unirradiated blends whose EVA content is lower than 20 wt% was accelerated. The tensile strength and modulus of the PLLA–EVA blend were increased by increasing PLLA content in the polymer blends and irradiation dose. FTIR spectra showed that some modifications occurred, after they had been exposed to gamma irradiation. The crystallization behavior was studied with differential scanning calorimetry and the composition-dependent changed of degree of crystallinity (X_c) of the PLLA phase indicated that PLLA and EVA were immiscible over the composition range investigated. However, there is a sharp decrease in the crystallinity with increasing EVA and irradiation dose. The TGA thermograms showed that the irradiated blends were less thermally stable than the unirradiated blends, at higher temperatures, the opposite situation was seen.

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* Radiation Chemistry Department, National Center for Radiation Research and Technology, P.O. Box 29 Nasr City, Cairo, Egypt.

E-mail address: hossam_int@yahoo.com.

Peer review under responsibility of The Egyptian Society of Radiation Sciences and Applications



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1. Introduction

Recently, much attention has been paid to poly(L-lactide) (PLLA) and its copolymers not only because they are biodegradable but also they can be made from renewable natural resources such as corn starch. Therefore, utilization of PLLA will be one of the methods to reduce consumption in fossil fuels. PLLA has various advantages such as high mechanical property and transparency, somehow its brittleness and low heat resistance are shortages of PLLA in the case of being used as commodity materials. Polymer blend has been widely utilized for the control of biodegradation as well as the improvement for the mechanical properties and the heat resistance (Ma et al., 2012). The blends of PLLA with biodegradable polymers such as poly(D-lactide) (PDLA) (Mauduit, Perouse, & Vert, 1996; Tsuji, 2003), poly(3-caprolactone) (PCL) (Tsuji & Ikada, 1998; Tsuji & Ishizaka, 2001), poly(3-hydroxybutyric acid) (PHB) (Blumm & Owen, 1995; Yoon et al., 2000), poly(ethylene oxide) (PEO) (Nijenhuis, Colstee, Grijpma, & Pennings, 1996), and poly(vinyl alcohol) (PVA) (Tsuji & Muramatsu, 2001) were studied because the biodegradability and the biocompatibility were required for some applications such as medical materials. But in some cases and in other applications such as some part of car and electronic products, non-biodegradability is required. Poly(L-lactide) (PLLA) is one of the biodegradable and biocompatible polymers and has received increased attention in the decades due to its comprehensive mechanical properties. Similar to other semicrystalline polymers, the properties of PLLA, including the mechanical behavior, thermal properties, and degradation profile, are strongly dependent on the degree of crystallinity [X_c (%)] and crystalline morphology (Kulinski & Piorkowska, 2005; Pluta, 2004; Tsuji & Ikada, 1995). However, the crystallization of PLLA is very slow to develop significant crystallinity, especially, during the normal processing involved the non-isothermal conditions, such as extrusion and injection molding, it is hard to achieve high X_c (%) in PLLA. In this case, the amorphous content of PLLA plays a very important role on the final properties of the particles. Consequently, the fracture toughness is very poor, and the particles are brittle and very sensitive to the environment stress and other impact load. On the other hand, the processability of PLLA is inferior to that of the polyolefin. Thus, the wide application of PLLA in packaging, which needs a certain degree of ductility, is greatly limited. Blending with plasticizer is now widely adopted in modification of PLLA materials due to the dual effects of plasticizer in PLLA. Plasticizer can greatly improve the mobility of PLLA chain segments, and consequently, the glass transition temperature (T_g) of PLLA is decreased, and the crystallization is improved greatly on the one hand (Martin & Averous, 2001; Xiao, Lu, & Yeh, 2009; Yu et al., 2008). On the other hand, the presence of plasticizer improves the processability and ductility of PLLA greatly (Li & Shimizu, 2009). However, large reduced tensile strength and Young's modulus have been reported simultaneously due to the decrease of the macromolecular chain cohesion density (Anderson, Schreck, & Hillmyer, 2008; Lemmouchi et al., 2009).

Recently, blending PLLA with other polymers has been the main subject of many researches. Most research is mainly

focused on PLLA blends miscibility (Li & Woo, 2008; Sakai, Nishikawa, Inoue, & Yazawa, 2009; Zhang, Goh, & Lee, 1998) and rheological properties (Gu, Zhang, Ren, & Zhan, 2008; Ko et al., 2009; Wu, Zhang, Zhang, & Zhou, 2008; Zhang, Wu, Zhang, Zhou, & Xu, 2009). However, few works have been done to investigate the toughening of PLLA by elastomers. In this regard, four different elastomers into PLLA and it was found that the smaller the dispersed particles are, the better the impact strength is (Ishida, Nagasaki, Chino, Dong, & Inoue, 2009). They also suggested that elastomers with a high polarity are more suitable for toughening PLLA. The toughening effect of acrylonitrile–butadiene–styrene copolymer on PLLA was studied and it was found that the blends exhibit poor mechanical properties with low elongation at break and decreased impact strength due to the poor miscibility (Li & Woo, 2008; Tsuji & Ikada, 1995). Other work has proved that linear low-density polyethylene exhibits toughening effect for PLLA to a certain extent (Anderson & Hillmyer, 2004; Anderson, Lim, & Hillmyer, 2003). It is well known that the biodegradability of PLLA is strongly related to its crystallinity, higher-order structure and morphology. It is also known that the crystallinity and structure of polymer blend are largely influenced by its blend ratio. That is biodegradability of PLLA/EVA blend is varied depending on these two factors, i.e. crystalline structure and blend ratio. Because the two factors are not independent, the biodegradability of crystallized PLLA/EVA blends is difficult to discuss.

Irradiation can, and is well known to, induce crosslinking to polymers. It is a very powerful technique that has been widely used in both product manufactures and research laboratory (Gehring, 2000; Oshima, Ikeda, Seguchi, & Tabata, 1997). Our recent work on the effects of gamma irradiation on the PLLA/EVA blends has extended the understanding of irradiation-induced crosslinking and enhanced compatibility at the inter-phase boundaries of the two phases in the blends.

2. Experimental

2.1. Materials

Poly(L-lactic acid) was used as biodegradable polyester, with $M_w = 3.2 \times 10^5$ was supplied by Aldrich. The melt index of the PLLA is 0.63 g/10 min and the optical purity is 98.3%. EVA with 18 wt% VA contents was purchased from DuPont Industrial Polymers, Wilmington, USA.

2.2. Preparation of PLLA/EVA blends

The pellets of both polymers were dried in a vacuum oven at 60 °C for 24 h before use. Blends of EVA and PLLA were prepared (containing different ratios of the two individual polymers (20/80), (50/50) and (80/20) wt%) by melt mixing in a laboratory mixer (Brabender Plasticorder PL2100), equipped with two rotors running in a counter-rotating way. The rotor speed was 60 rpm and the set temperature was 160 °C. The blends were prepared using the following sequence: first EVA pellets were introduced into the hot mixer, after melting, PLLA was added. The polymer mixture was immediately transferred from the mixer to an open roll-mill to make into a sheet.

Sheets of 1.0 mm thickness were obtained by pressing under hot press at 165 °C for 5 min (2 min preheating and 3 min at 15 MPa). The molded plastic sheet was then immediately transferred to a water-cooled press at the same pressure.

2.3. Gamma irradiation

Irradiation was carried out in a ^{60}Co cell (made in Russia) at the National Center for Radiation Research and Technology, Cairo, Egypt. Irradiation was carried out at a dose rate 6.92 kGy h⁻¹.

2.4. Hydrolytic degradation test

Alkaline hydrolysis test was performed using the films of $0.5 \times 10 \times 10 \text{ mm}^3$ in 10 mL of 0.5 N NaOH aqueous solution of pH 12. The films were placed in vial filled with NaOH solution. The hydrolysis of the films was performed at 37 °C for a pre-determined period of time. After hydrolyzes, films were washed twice in distilled water at room temperature and wipe the NaOH solution off from the film surface, then it was dried for a few hours at room temperature followed by being dried in vacuum for 2 days and weighed (W_{t-dried}). The weight loss (W_{loss}) calculated by following equation:

$$W_{\text{loss}}(\%) = \frac{W_0 - W_{t\text{-dried}}}{W_0} \times 100$$

where W₀ is the initial weight and W_{t-dried} is the weight of degraded film after drying in vacuum.

2.5. Mechanical properties

Tensile strength and elongation at break were examined from stress–strain curves measured by using a tension meter carried out with use of (H10KS Hounsfield Co. UK), tension speed was 25 mm min⁻¹, load range 1000 N and extension range 1500 N. Samples in a dumbbell shape of 50 mm long and 4 mm neck width of different degrees of grafting were used for mechanical testing.

2.6. FTIR spectroscopic analysis

A Mattson, Genesis series I (USA) Fourier transform infrared (FTIR) spectrophotometer was used for scanning and measuring the absorption spectra at resolution of 16 cm⁻¹. The IR spectra were over the range 400–4000 cm⁻¹.

2.7. Differential scanning calorimetry (DSC)

The DSC thermograms were carried out on Shimadzu DSC-50 calorimetry at a heating rate of 10 °C min⁻¹ under flowing nitrogen gas (20 mL min⁻¹) was used to investigate melting behaviors of the samples. A sample of about 5 mg was heated directly from room temperature to 200 °C at a heating rate of 10 °C min⁻¹.

2.8. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) study was carried out on Shimadzu-30 (TGA-60) at a heating rate of 10 °C min⁻¹ under

nitrogen atmosphere from room temperature to 600 °C. The initial TGA data were used to determine the different kinetic parameters of thermal decomposition reaction. The derivative of the TGA thermograms (DTGA) or the rate of reaction (dw/dt) was determined by taking the weight loss every 2 min. The rate of reaction (dw/dt) was plotted against temperature from which the T_{max} temperatures can be determined.

3. Results and discussion

3.1. Hydrolysis behavior of PLLA/EVA blends

Fig. 1 shows the weight losses (W_{loss}) of unirradiated PLLA, EVA, and PLLA irradiated at 50 and 100 kGy respectively. The degradation of unirradiated PLLA was completed after treatment of time of 170 h (weight loss = 100%), while EVA was not hydrolyzed at all. The weight loss of unirradiated PLLA can be explained as follows. PLLA is polyester that is easy to degrade into small fragments of PLLA due to breakdown of PLLA chains in alkaline solution (0.5 N NaOH). Then the small fragments of PLLA continue to degrade into smaller fragments or lactic acid units which are soluble in water. They cause the weight loss of PLLA samples (Saha & Tsuji, 2006; Tsuji & Ikarashi, 2004). The weight loss values for PLLA irradiated at 50 kGy achieved with 75% after treatment time of 170 h, while the weight loss of PLLA irradiated at 100 kGy achieved 60% after treatment time of 170 h. The present results showed that the degradation rate became slower as the irradiation dose was increased. These differences could be attributed by the formation of radiation-induced crosslinking in the PLA (Tsuji & Ikarashi, 2004).

Fig. 2 shows the weight loss (%) of polymer blends {(80/20) and (50/50)} before and after exposed to different doses of gamma irradiation as a function of exposed time in hydrolysis test. The PLLA/EVA blend was hydrolyzed slower than neat PLLA as expected. The weight loss of PLLA/EVA blends reached the ultimate values of 75% and 43% for the 80/20 and 50/50 blends, respectively. This means that most of PLLA molecules in the PLLA/EVA blends were degraded and eluted. It is well

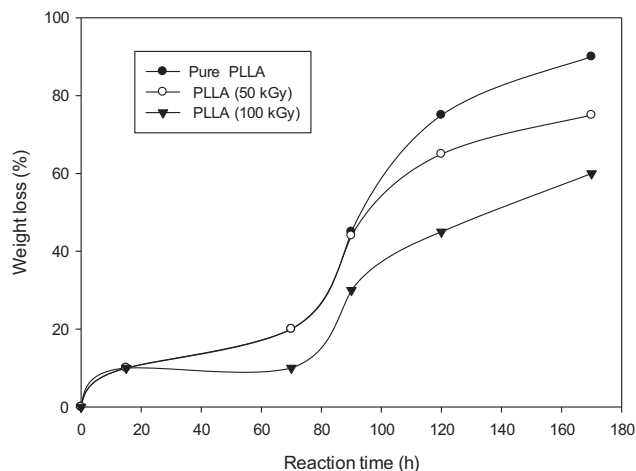


Fig. 1 – Weight loss (%) of PLLA before and after exposed to gamma irradiation.

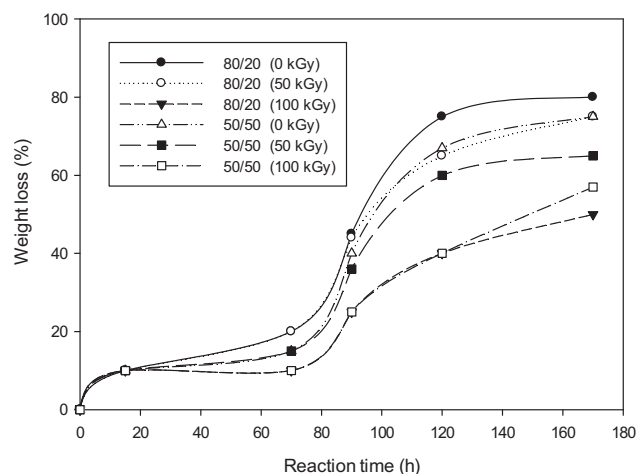


Fig. 2 – Weight loss (%) of polymer blends PLLA/EVA before and after exposed to gamma irradiation.

known that crosslinking is hardly formed in the crystalline phase, but it occurs in the amorphous state. When temperature increases to above glass transition during mixing, molecular mobility becomes active. Hence, occurrence of some crosslinking (still there is a poor adhesion between of PLLA chains and EVA (immiscibility), so the molecules of water and sodium hydroxide penetrate into the samples of polymer blends and cause the hydrolysis of polymer blends). The hydrolytic degradation rate of PLLA/EVA blends decreases as the increased in the EVA content. Thus, it is concluded that the hydrolytic degradation rate of PLLA/EVA blend can be widely controlled by EVA content. The hydrolytic degradation decreases by increasing irradiation dose from 50 kGy to 100 kGy. The weight loss values for polymer blend (PLLA/EVA) (80/20) irradiated at 50 kGy were 70% after treatment time of 170 h, while the weight loss values for the polymer blend at 100 kGy achieved 60% after treatment time of 170 h. Also the weight loss values for polymer blend (PLLA/EVA) (50/50) irradiated at 50 kGy were 40% after treatment time of 170 h, while the weight loss values for the polymer blend at 100 kGy achieved 30% after treatment time of 170 h. The decreasing of polymer blends degradation modified through gamma irradiation may be explained on the basis of formed graft copolymerization between PLLA and EVA through peroxy and radical formation. (The interaction of ionizing radiation with PLLA produces different types of radical intermediate (Nugroho, Mitomo, Yoshii, & Kume, 2001).)

3.2. Mechanical properties

The tensile strength, elongation at break and tensile modulus of PLLA/EVA polymer blends before and after being exposed to gamma-radiation were measured, and the results are shown in Table 1. As expected, the presence of EVA induces the decline of the tensile strength and tensile modulus. The properties of PLLA alone were similar to those reported by Hiljanen-Vainio, Varpomaa, Seppala, and Tormala (1996) and Tsuji and Ikada (1995). The tensile properties are greatly dependent on the ratio of EVA content in the blend. 80% PLLA/20% EVA polymer blend exhibits maximum tensile strength and ductility compared with other blends possibly due to the relative interaction between PLLA and EVA at this ratio. As the EVA content was increased, modulus began to decrease sharply, which was followed by a rather slower decrease. On the other hand, strain-at-break was gradually increased up to 50 wt% of EVA and then suddenly increased at 80 wt% of EVA. After being irradiated by 50 kGy, the tensile strength and modulus are enhanced greatly, whereas the elongation at break is reduced slightly. For example, irradiated 80% PLLA/20% EVA sample exhibits higher modulus compared with the untreated pure PLLA, suggesting the improvement of stiffness and toughness simultaneously. It can be seen that increase in modulus and decrease in the elongation at break occurred with increasing PLLA content. This observation indicates that incorporation of EVA into the PLLA improved the stiffness of PLLA/EVA blends. Once again, the results related to elongation at break of the polymer blends (PLLA/EVA) indicate plasticization role of EVA for PLLA. This is common observation with almost all filled polymer systems. Reduction in elongation at break is due to the decreased deformability of a rigid inter-phase between the filler and matrix material.

3.3. FTIR spectroscopic analysis

FTIR spectroscopy is a powerful tool for investigating the structure of polymer blends. It is known that, if two polymers form completely immiscible there should be no appreciable changes in the IR spectrum of the blends with respect to the condition of each component spectrum. However, if the polymers are immiscible interactions in the blends will result in differences (peak position and shapes) blends, was applied, and the results are shown in Figs. 3–5. The IR spectra of the polymer blends containing different ratios PLLA and EVA show the absorption band characteristic of both PLLA and EVA. Fig. 3 shows their spectra of unirradiated thin films of 80%, 50% and 20% of PLLA, one can see that, with the presence

Table 1 – Mechanical properties of PLLA and PLLA/EVA blends before and after being radiated at 50 kGy.

Composition ratio of PLLA/EVA	Tensile strength (MPa)		Elongation at break (%)		Elastic modulus (MPa)	
	0 kGy	50 kGy	0 kGy	50 kGy	0 kGy	50 kGy
100% PLLA	61.2	75.7	6.67	7.56	1801	2345
80% PLLA/20% EVA	33.77	55.8	11.6	9.8	1377	1842
50% PLLA/50% EVA	18.81	22.34	223.8	200.2	1234	1597
20% PLLA/80% EVA	10.65	15.3	632	609	1114.8	1558
100% EVA	19.37	23.33	712	621.4	27.6	29.6

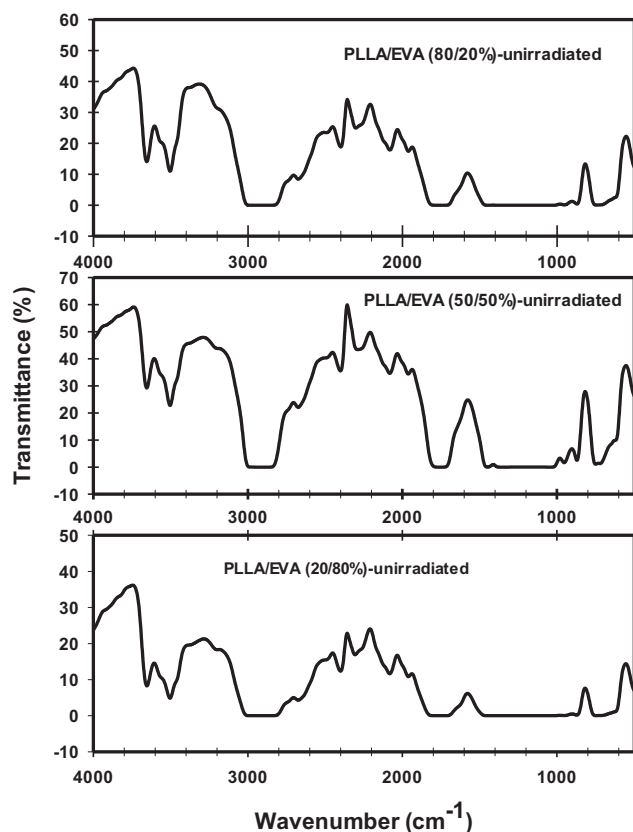


Fig. 3 – IR spectra of thin films of unirradiated PLLA/EVA blends.

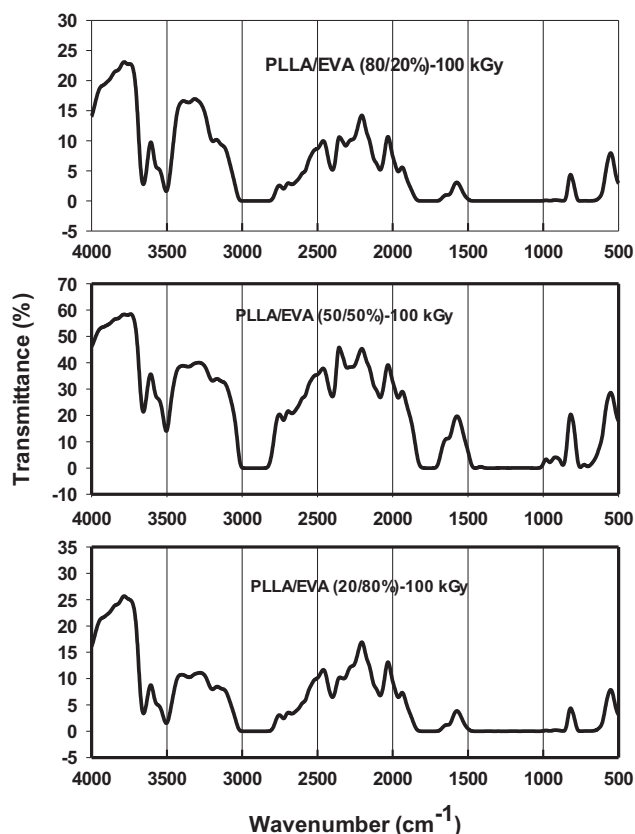


Fig. 5 – IR spectra of PLLA/EVA blends gamma irradiated at a dose of 100 kGy.

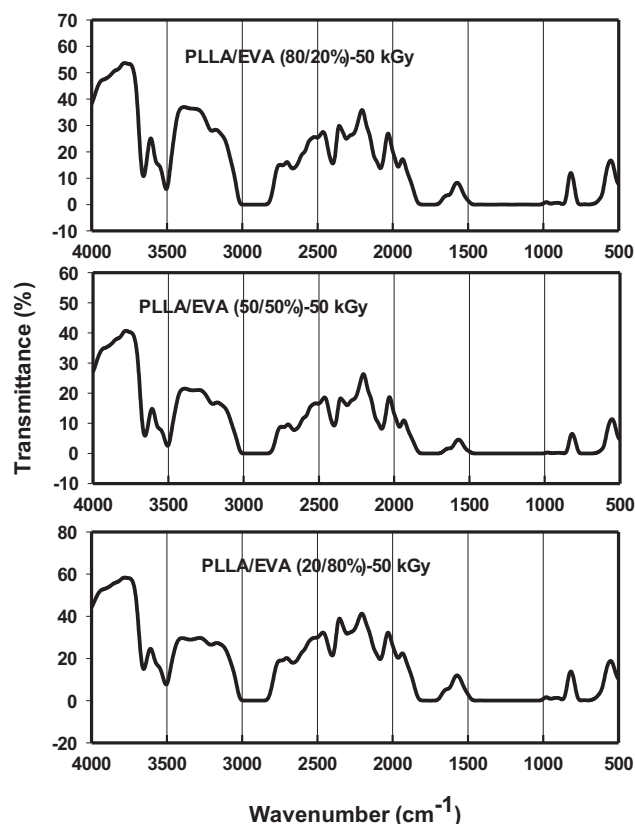


Fig. 4 – IR spectra of PLLA/EVA blends gamma irradiated at a dose of 50 kGy.

of EVA, the absorption peak of $\text{CH}_3 + \text{C}-\text{C}$ (913 cm^{-1}) of PLLA disappears and the shape of absorption peaks of $\text{C}=\text{O}$ (1751 cm^{-1}), symmetric CH_3 (1373 cm^{-1}), and asymmetric COC (1180 cm^{-1}) changes (Shirahase, Komatsu, Tominaga, Asai, &

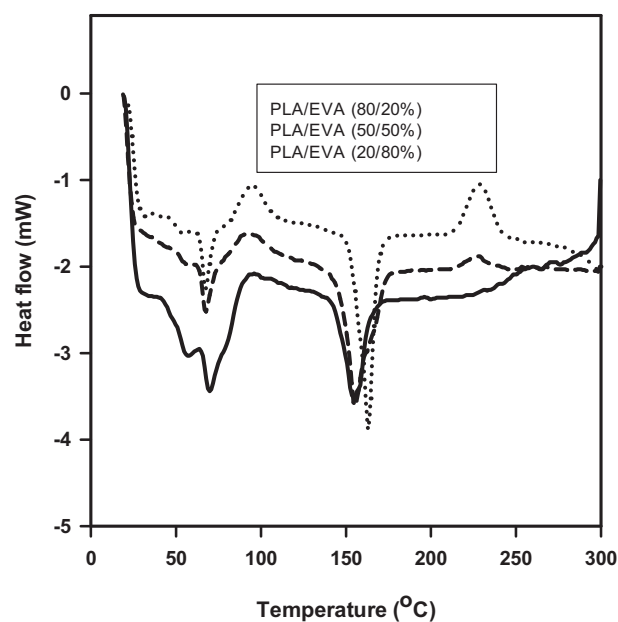


Fig. 6 – DSC thermograms of different ratios of PLLA/EVA polymer blend before exposed to gamma radiation.

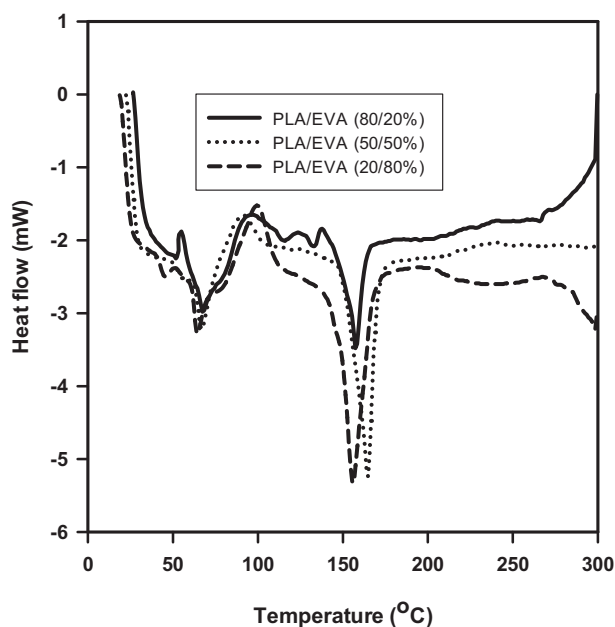


Fig. 7 – DSC thermograms of different ratios of PLLA/EVA exposed to (50 kGy) gamma radiation.

Sumita, 2006) indicating the interaction between PLLA and EVA. However, Fig. 3 does not show the degree of the interaction of PLLA/EVA blends with the variation. The IR spectra of the same polymer blends after they had exposed to 50 kGy and 100 kGy as shown in Figs. 2 and 3. Irradiation in the presence of air or oxygen leads to oxidized products, which are often undesirable, being thermally less stable and also detracting from the degree of crosslinking by reacting with polymer radicals. Although it would be expected to observe some modification on functional groups of the irradiated PLLA and

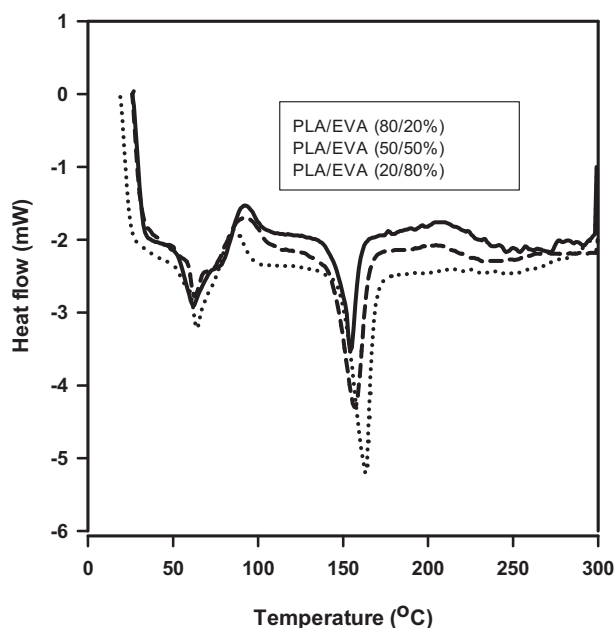


Fig. 8 – DSC thermograms of different ratios of PLLA/EVA exposed to (100 kGy) gamma radiation.

Table 2 – Cold crystallization and subsequent melting parameters of PLLA obtained from DSC measurement.

Polymer blend composition	Irradiation dose (kGy)	T_c (°C)	T_m (°C)	H_m (J g ⁻¹)	X_c (%)
PLLA(80%)/EVA (20%)	0	94	164.2	23.2	31.22
PLLA(50%)/EVA(50%)	0	96	159.6	10.26	22.4
PLLA(20%)/EVA(80%)	0	94	159.6	–	20.2
PLLA(80%)/EVA (20%)	50	90	166	22.4	30.1
PLLA(50%)/EVA(50%)	50	96	158.5	10.3	22.1
PLLA(20%)/EVA(80%)	50	98	158.5	–	18.2

EVA homopolymers and blends by FTIR, it is very difficult to detect minor chemical changes occurring on the polymer chain. This can be due to the fact that IR bands of polymers are inherently broad and weak. It would be necessary to eliminate from the observed spectrum the interfering absorptions of the unreacted functional groups present in the polymer. For polymer blend rich in PLLA polymer irradiated to 50 kGy, the decrease in specific characteristic bands of EVA is not as much as those having low contents of PLLA.

3.4. Differential scanning calorimetry (DSC)

The results of the DSC measurements of unirradiated and irradiated PLLA/EVA polymer blends at 50 and 100 kGy are shown in Figs. 6–8. The crystallinity of PLLA in the PLLA–EVA blends was obtained by utilizing the heat of fusion of the blend

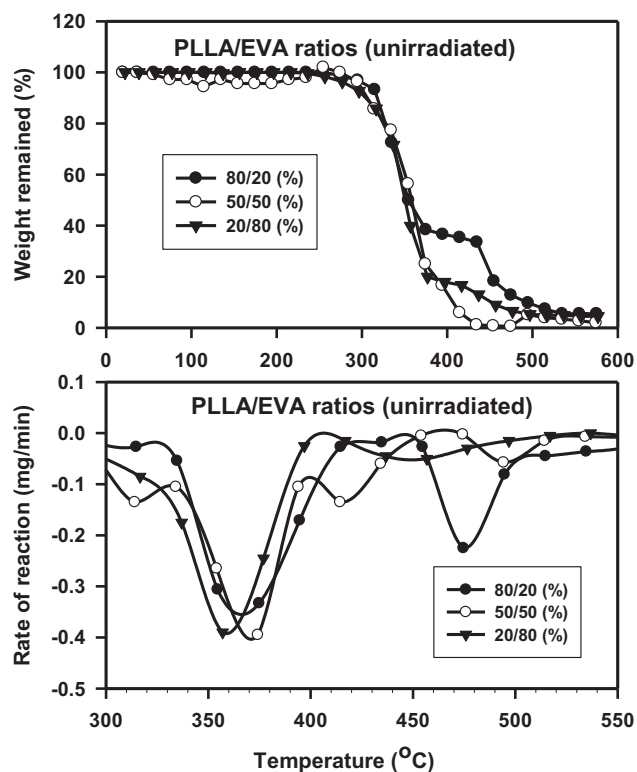


Fig. 9 – TGA thermograms and the corresponding derivatives of the TGA curves (rate of decomposition reaction (dw/dt)) for unirradiated PLLA/EVA blends at different compositions.

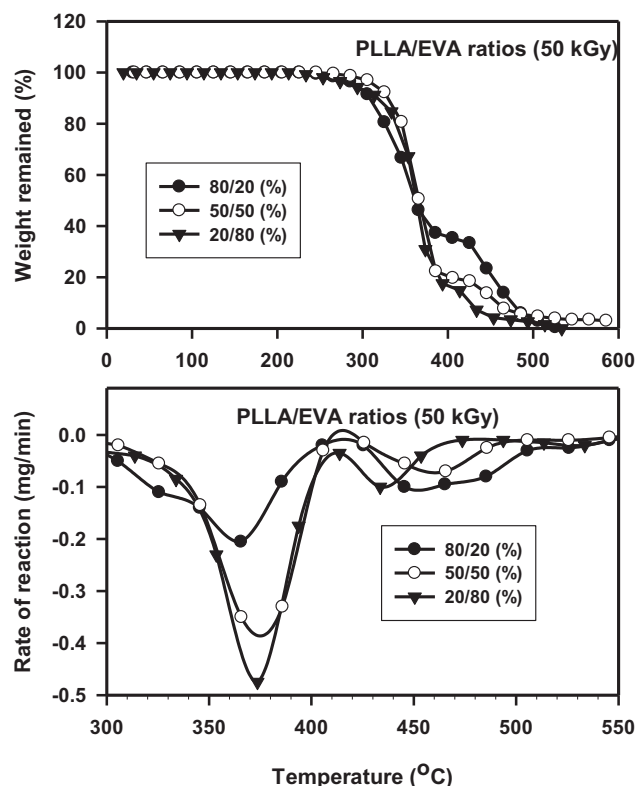


Fig. 10 – TGA thermograms and the corresponding derivatives of the TGA curves (rate of decomposition reaction (dw/dt)) for PLLA/EVA blends at different compositions after exposure to a dose of 50 kGy of gamma irradiation.

and the obtained data was plotted in Fig. 4. As the content of EVA in the blend was increased, the crystallinity of PLLA was reduced. According to the literatures, pure PLLA has three peaks at roughly 62, 120 and 173–178 °C, corresponding to glass transition (T_g), recrystallization (T_c) and melting temperature (T_m) of PLA, respectively (Kister, Cassanas, & Vert, 1998). Figs. 4–6 show the DSC heating curves of the samples before and after exposed to gamma radiation. It can be seen that there is an overlap between the glass transition temperature (T_g) of PLLA and the melting temperature (T_m) of EVA so that it is difficult to determine the T_g of PLLA in the blend. Table 2 shows the DSC measurement results of the blends PLLA/EVA. The degree of crystallinity (X_c) of PLLA is calculated by the following equation:

$$X_c = H_f / (H_f^0 W)$$

where H_f is the apparent enthalpy of fusion (indicated in DSC thermograms as the melting enthalpy per gram of blends) corresponding to the component, W is the weight fraction of the component, and H_f^0 is the enthalpy of fusion per gram of the component in its completely crystalline state (93 J g⁻¹ for PLLA) (Li et al., 2010). From the data in Table 2, for PLLA/EVA blends, the endothermic peaks (T_m -EVA) observed at relatively low temperatures (60–94 °C) are attributed to the fusion of EVA lamellae. On the other hand, one can observe an exothermic peak (T_c -PLLA) at about 90–95 °C and an

endothermic peak (T_m -PLLA) at about 158–162 °C, indicating the cold crystallization and subsequent fusion of PLLA crystallites, respectively. With the increase of EVA content, the exothermic peak weakens and shifts to higher temperatures slightly, which means that the cold crystallization of PLLA becomes more difficult, and less PLLA can transform into crystalline state. Consequently, the X_c (%) of PLLA decreases with the increase of EVA content. The effects of EVA content on cold crystallization behavior of PLLA can be explained as follows. During the heating process, EVA melts first and possibly promotes the mobility of chain segments in the interface between PLLA and EVA, showing the role of plasticizer in promoting the cold crystallization of PLLA. However, the effect becomes inconspicuous with high content of EVA monomer in EVA phase possibly due to the enhanced adhesion between PLLA and EVA phases, which prevents the migration of PLLA chain segments out from EVA phase, limits the crystallization of PLLA at this temperature and heating rate (Zhang, Zhang, Zhou, & Shen, 2003).

3.5. Thermal gravimetric analysis (TGA)

The thermal stability of any polymeric material is largely determined by the strength of the covalent bonds between the atoms forming the polymer molecules. The dissociation energies of the different covalent bands C–H, C–C, C–O, C=O, O–H and C=C were reported to be 414, 347, 351, 741, 464 and 611 kJ mol⁻¹, respectively. On the basis of these values, the

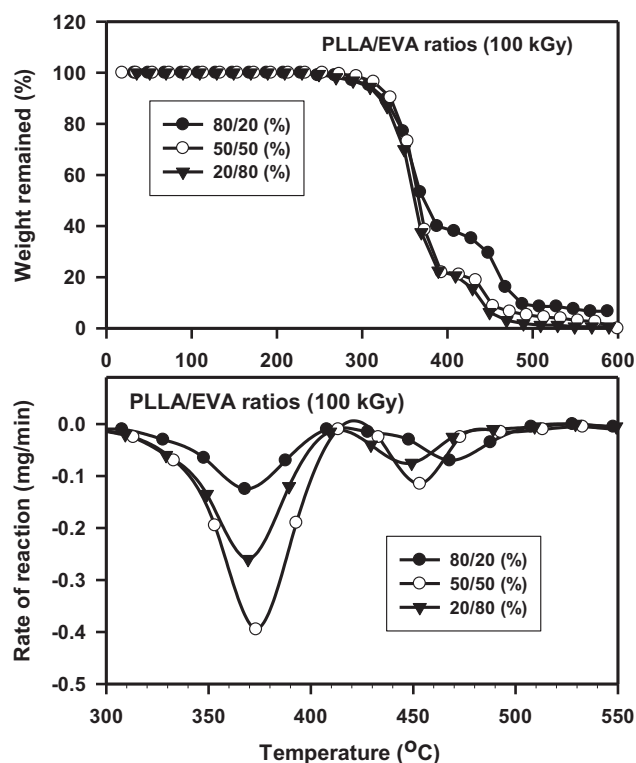


Fig. 11 – TGA thermograms and the corresponding derivatives of the TGA curves (rate of decomposition reaction (dw/dt)) for PLLA/EVA blends at different compositions after exposure to a dose of 100 kGy of gamma irradiation.

Table 3 – Weight loss (%) at different decomposition temperatures for polymers blends (PLLA/EVA) before and after exposed to gamma irradiation.

Polymer blend composition	Irradiation dose (kGy)	Weight loss (%)				
		275 (°C)	315 (°C)	355 (°C)	395 (°C)	435 (°C)
PLLA/EVA(80/20)	0	1.22	6.71	50	63.42	66.5
	50	1.5	8.46	33.34	62.69	66.67
	100	0.39	4.77	22.86	60	65
PLLA/EVA(50/50)	0	0	14.3	43.7	83.3	98.8
	50	0	3.01	19.34	77.7	81.55
	100	0	1.32	9.7	61.5	78.5
PLLA/EVA(20/80)	0	3.7	14.2	60.2	82.12	86.9
	50	1.1	5.73	15.3	69.1	85.12
	100	1.88	5.63	30	77.5	83.38

average complete dissociation energy of PLLA and EVA is calculated to be 430 and 422 kJ mol⁻¹, respectively. Thus it may be concluded that the blending of EVA with PLLA will improve the thermal stability of the polymer blend. The TGA peak temperature is the temperature at the beginning point of the most weight loss, while the final is the temperature at the end of the degradation. These two points can be determined easily using the derivative graph. Under high-energy radiation, radicals are formed at high concentrations in close proximity to one another so that second-order crosslinking reactions are favored compared with first-order chain scissions. This explanation seems to be true in the case of PLLA/EVA polymer blend, because typical thermal degradation route does not change significantly upon irradiation with gamma rays for PLLA/EVA blends. It can be said that both chain scission and crosslinking take place simultaneously during irradiation with gamma rays. The TGA and derivative TGA curves of these samples are shown in Figs. 9–11 for PLLA/EVA polymer blends before and after irradiated by different doses of gamma radiation. The derivative of the TGA thermograms, rate of thermal decomposition reaction, (dw/dt) was also plotted against temperature as shown in the same figures. A very clear phenomenon can be observed, the rate of thermal decomposition reaction of all the polymer blends goes through two maxima. The appearance of the two maxima is attributed to (1) the occurrence of phase separation between PLLA and EVA components inside the blend (the first

one is attributed to de-acetylation and due to degradation of PLLA and the second one is due to the degradation of the EVA backbone) (2) or the appearance of the two maxima is attributed to the mechanism by which the free radicals acts as a compatibilizer between the two phases. As shown in Table 3, the effect of the irradiation dose on the thermal stability was found to depend on the PLLA/EVA ratio. The weight loss (%) increased as the ratio and the irradiation dose decreased. However, the weight loss (%) decreased as the ratio increased, especially beyond 330 °C. The increase in thermal stability associated with an increasing ratio is due to the increased (crosslinking) that occurs upon the removal of acetic acid.

The weight losses (%) at different temperatures for those materials, as taken from the TGA thermograms, are summarized in Tables 3 and 4. Most of the weight loss (30–77%) observed for the unirradiated and irradiated blends occurred within the temperature range 300–400 °C, where the irradiated blends were less thermally stable than the unirradiated blends. At higher temperatures, the opposite situation was seen.

4. Conclusion

The following results were obtained on the hydrolytic degradability and structural property of the PLLA/EVA polymer blends before and after exposed to different doses of gamma irradiation.

Table 4 – Temperature of the maximum values of the rate of reaction of PLLA/EVA polymer blends before and after exposed to gamma irradiation.

Polymer blend composition	Irradiation dose (kGy)	Temperatures of maximum rate of reaction (°C)	
		First peak	Second peak
PLLA/EVA(80/20)	0	366	437
	50	365	445
	100	367	467
PLLA/EVA(50/50)	0	370	414
	50	375	464
	100	372	452
PLLA/EVA(20/80)	0	356	456
	50	373	433
	100	369	449

- 1 The hydrolytic degradation rate of PLLA/EVA blend can be widely controlled by exposing the PLLA/EVA to gamma irradiation and also by EVA content. In alkaline solution, the hydrolytic degradation rate of the blends exposed to 100 kGy and whose EVA content is higher than 50 wt% was decelerated while the rate of the unirradiated blends whose EVA content is lower than 20 wt% was accelerated.
- 2 The tensile properties are greatly dependent on the ratio of EVA content in the blend. 80% PLLA/20% EVA polymer blend exhibits maximum tensile strength and ductility compared with other blends possibly due to the relative interaction between PLLA and EVA at this ratio.
- 3 The strain-at-break was gradually increased up to 50 wt% of EVA and then suddenly increased at 80 wt% of EVA. After being irradiated by 50 kGy, the tensile strength and modulus are enhanced greatly, whereas the elongation at break is reduced slightly.

- 4 FTIR spectra confirm the microstructural configuration changes occurring in polymeric chain due to gamma irradiation with the increasing the radiation dose from 0 kGy to 100 kGy, the absorption peak of $\text{CH}_3 + \text{C}=\text{C}$ (913 cm^{-1}) of PLLA decays and the shape of absorption peaks of $\text{C}=\text{O}$ (1751 cm^{-1}), symmetric CH_3 (1373 cm^{-1}), and asymmetric COC (1180 cm^{-1}) changes, indicating the interaction between PLLA and EVA.
- 5 The degree of crystallinity (X_c) of the PLLA phase indicated that PLLA and EVA were immiscible over the composition range investigated. However, there is a sharp decrease in the crystallinity with increasing EVA and irradiation dose.
- 6 The effect of the irradiation dose on the thermal stability was found to depend on the PLLA/EVA ratio. The weight loss (%) increased as the ratio and the irradiation dose decreased. However, the weight loss (%) decreased as the ratio increased, especially beyond 330°C . The increase in thermal stability associated with an increasing ratio is due to the increased (crosslinking) that occurs upon the removal of acetic acid.

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