RESEARCH ARTICLE OPEN ACCESS

Electron Beam Treatment for Enhancing the Compatibility, Thermal and Tensile Properties of LLDPE/PVA Blends: Part I, Effect of Irradiation Doses

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ABSTRACT

In this work, the effect of electron beam radiation of linear low-density polyethylene (LLDPE)/ poly (vinyl alcohol) (PVA) blends are presented. The blends were prepared by melt mixing at 150 ºC at 60/40 (php/php), of LLDPE and PVA. Gel extraction, infrared spectroscopy diffraction scanning calorimetry, thermogravimetric, tensile properties and scanning electron microcopy had been used to investigate the effect of electron beam radiation on the properties of LLDPE/PVA blends. The exposure of these blends to 200 kGy dose of electron beam radiation increased the gel content, tensile properties (tensile strength and Young’s modulus) and thermal stability due to the crosslinking formation, while, the melting temperature of LLDPE and PVA decreased as the PVA content was increased. The crosslink formation between LLDPE and PVA in the irradiated blends was demonstrated by the embedded PVA in LLDPE matrix as observed in optical images.

Keywords-Blends, Compatibility, Electron Beam Irradiation, Polyethylene

I. INTRODUCTION

Modification of polymers and polymer blends in the presence of radiation is a promising method for superior properties development [1-5]. Irradiation of pure polymer by an electron beam results in the formation of branches and three-dimensional networks through the combination of radicals generated. These radicals formed complex reactions that can in turn lead to crosslinking and /or chain scission of polymer chains. Thus it is difficult to predict the behavior of irradiated polymer blends.

Radiation causes changes in the chemical structure of polymers that later affects the electrical, mechanical, thermal and barrier properties [6-9]. The changes occur in the amorphous and crystalline region of polymers through crosslinking, chain scission, and oxidation reactions. Therefore, knowledge of the radiation reactions in complex polymeric systems is very important to correlate with product performance.

Previously, we had successfully prepared linear low density polyethylene (LLDPE) with poly (vinyl alcohol) (PVA) through melt mixing methods for packaging applications [10]. The PVA was incorporated into the blend to change non-biodegradable nature of polyethylene to biodegradable. The LLDPE/PVA blends, however, are immiscible and exhibit phase separation and poor tensile properties due to the difference in chemical makeup of LLDPE and PVA.

The compatibility and tensile properties of LLDPE/PVA blends can be improved by radiation modification. Although, electron beam modification of pure LLDPE [11-14] and PVA [15-17] are well documented, but, there is no study on the electron beam or radiation modification of LLDPE/PVA blends. Therefore, this study was basically to investigate the effect of radiation doses on the compatibility, thermal and tensile properties of LLDPE/PVA : 60/40 blends.

II. EXPERIMENTAL DETAILS

2.1 Materials

Poly(vinyl alcohol) with an average molecular weight of 89 000 – 98 000 and 99+% hydrolyzed were obtained from Sigma-Aldrich (Malaysia) Sdn. Bhd. Linear low-density polyethylene (LLDPE) with a melt index (MI) of 1.0 g/10 min (190°C, 2.16 kg) and a melting point of 123°C was obtained from Polyethylene (Malaysia) Sdn. Bhd.

2.2 Mixing procedure

Blend preparation was carried out in a Haake Reomix PolyDrive at 150°C and at a rotor speed of 50 rpm for about 10 min. The LLDPE was first added and melt-mixed for 2 min. PVA was then added to LLDPE, and the mixing continued for another 8 min. The blends were removed and sheeted through a laboratory two-roll mill at a 2.0-mm nip setting. The blend samples were compression molded into 1 mm thickness with an electrically heated hydraulic press. Samples were preheated at 150° C for 4 min, compressed for 4 min at the same temperature and subsequently cooled under pressure for 3 min.

2.3 Irradiation

The molded sheets were irradiated using a 3 MeV electron beam accelerator NHV EPS-3000 at a dose range of 0–250 kGy. The acceleration energy, beam current, and dose rate were 2 MeV, 10 mA, and 50 kGy per pass, respectively.

2.4 Gel content

The gel content of the samples was determined according to ASTM D2765. The samples were first extracted with distilled water until there was no further weight loss, and then they were extracted with xylene. The samples were placed in folded 120 mesh stainless steel cloth cages. The samples and cages were weighed before extraction. The extracted samples were then dried at 80ºC until there was no further weight loss. The gel content was calculated from the following:

Gel content = 100 percent extract (1)

$$\% \text{ Extract} = \frac{W_{LE}}{W_O - W_{PVA}} \qquad (2)$$

W_{LE} = Weight loss during extraction
W_O = Weight of original sample
W_{PVA} = Weight of PVA

2.5 Fourier Transform Infrared (FTIR)

Chemical characterization was performed by Attenuated Total Reflection Fourier Infrared (ATR-FTIR) using a Perkin Elmer Spectrum One in the range of 4000 – 600 cm^{-1}. For each spectrum, 100 consecutive scans with 4 cm^{-1} resolution were recorded. The samples were dried for 24 hrs at 80°C in an air oven prior to test.

2.6 Measurement of Tensile Properties

Tensile tests were carried out according to ASTM D 638 using an Instron 3366. Dumb bell specimens with thicknesses of 1 mm were cut from the molded sheets with a Wallace die cutter. A cross-head speed of 50 mm/min was used, and the test was performed at 25°C. Five samples of each blend were tested to obtain an average value.

2.7 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer Pyris 1 DSC under a nitrogen atmosphere. Each blend was heated from 30°C to 170°C at a heating rate of 10°C/min, annealed for 5 min at 170°C, cooled from 170°C to –50°C at a cooling rate of 10°C/min, annealed for 5 min at – 50°C and rescanned from – 50°C to 300°C at a heating rate of 10°C/min. The blend weight was 10 ± 0.5 mg. Thermal properties such as melting temperature (T_m), crystallization temperature (T_c) and heat of fusion (ΔH) were determined from the DSC thermograms. The degree of crystallinity (X_c) of the LLDPE in the blend was calculated from the following:

$$X_c = \Delta H_{exp} / \Delta H^* W_f \qquad (3)$$

where ΔH_{exp} is the experimental heat of fusion determined from the DSC scans, ΔH^* is the heat of fusion of the fully crystalline LLDPE (290 J/g) [18], and W_f is the weight fraction of LLDPE in the blend.

2.8 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (TGA 7) under a nitrogen atmosphere to avoid oxidation. The blends were heated from 30°C to 700°C at a heating rate of 20°C/min. The blend weight was 10 ± 0.5 mg.

III. RESULTS AND DISCUSSION

3.1 Gel content

Figure 1 shows the variation of gel content as a function of absorbed dose for the exposed LLDPE/PVA: 60/40 blends. Non-irradiated blends were found to be completely soluble in hot water and *p*-xylene. However, the solubility had reduced significantly due to the formation of three-dimensional networks in the irradiated blends as shown from the formation of gel. The gel content of the blends increased with absorbed dose. Examination of extracted blends with naked eyes (Figure 2, macroscopic view of extracted LLDPE/PVA: 60/40 blends) revealed that the color change from yellowish to white – featuring the characteristics of increase crosslinked formation between the LLDPE and PVA with irradiation dose. These results indicate that higher irradiation dose is necessary to enhance the radiation-induced crosslinking in LLDPE/PVA blends. This phenomenon shows that PVA is a crosslinkable polymer as reported by other researchers in different studies [1, 19-20].

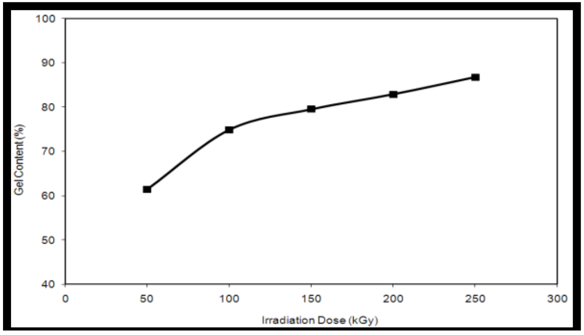

Fig. 1 - Variation of gel content as a function of absorbed dose for exposed LLDPE/PVAblends.

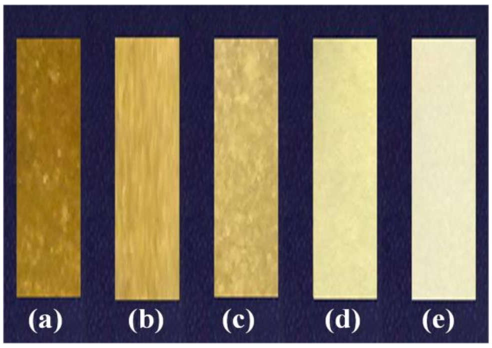

Fig. - 2 Extracted sample of LLDPE/PVAblends at: (a) 50 kGy (b) 100 kGy (c) 150 kGy (d) 200 kGy (e) 250 kGy

3.2 Mechanism of crosslinking reaction

Milosaljevis and Thomas 2001 [21] studied the radical formation of PVA induced by irradiation. They found that oxy-radicals, hydroxyl radicals and alkyl radicals were the major products. The oxy-radicals and hydroxyl radicals of PVA weremore stable than alkyl radicals (Figure 3a). Then again, allyl radicals were the mainly stable product when LLDPE were irradiated at room temperature (Figure 3b). So we propose that the crosslinking reaction occurred between the two stable radicals PVA and LLDPE, were formed on the interface when the LLDPE/PVA blends were irradiated (Figure 3c).

3.3 FTIR analysis

It was clear that after irradiation, some new absorption bands appeared which were related to chemical reaction occurred in the blends with formation of branching at 1177 cm^{-1} [22], crosslinking C–O (1080 cm^{-1}) and oxidative degradation: vinyl CH_2=CH- (908 cm^{-1}), trans vinylene –CH=CH– (965 cm^{-1}), hydroxyl containing species (like hydroperoxides –O–OH at 3550 cm^{-1}) and carbonyl groups (like ketone at 1713 cm^{-1} and esters/carboxylic acid at 1720 cm^{-1}) [23] (Figure 4). Very interestingly, the intensity band of C=O and C–O clearly increased with the increase of irradiation doses compared to CH_2=CH– and –CH=CH– bands. The C–O band was used to evaluate the level of crosslinking while C=O band was used for chain scissions. The increased C=O and C–O band were quantified in index by normalized with the absorption band at 2020 cm^{-1} to overcome the difference of samples thickness (Figure 5). The C=O index was slightly increased with the increase in irradiation doses indicated radiolytic oxidation of LLDPE matrix was minimum [24, 25]. Figure 5 also shows that there is a big difference in the level of C–O over C=O index particularly at higher irradiation doses. This explains the occurrence of more radiation-induced crosslinking over chain scission in LLDPE/PVA blends.

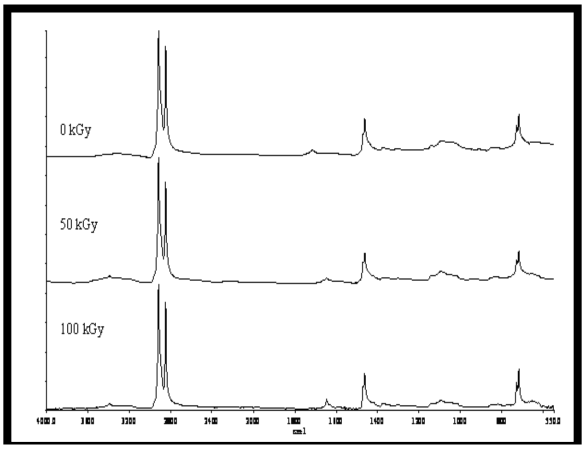

Fig. 4 - Absorption spectra at room temperature of non-irradiated and irradiated LLDPE/PVAblends.

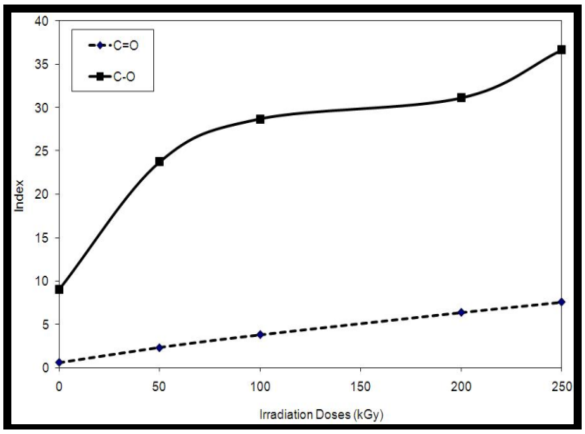

Fig. 5 - C=O and C–O index of non-irradiated and irradiated LLDPE/PVA: 60/40 blend.

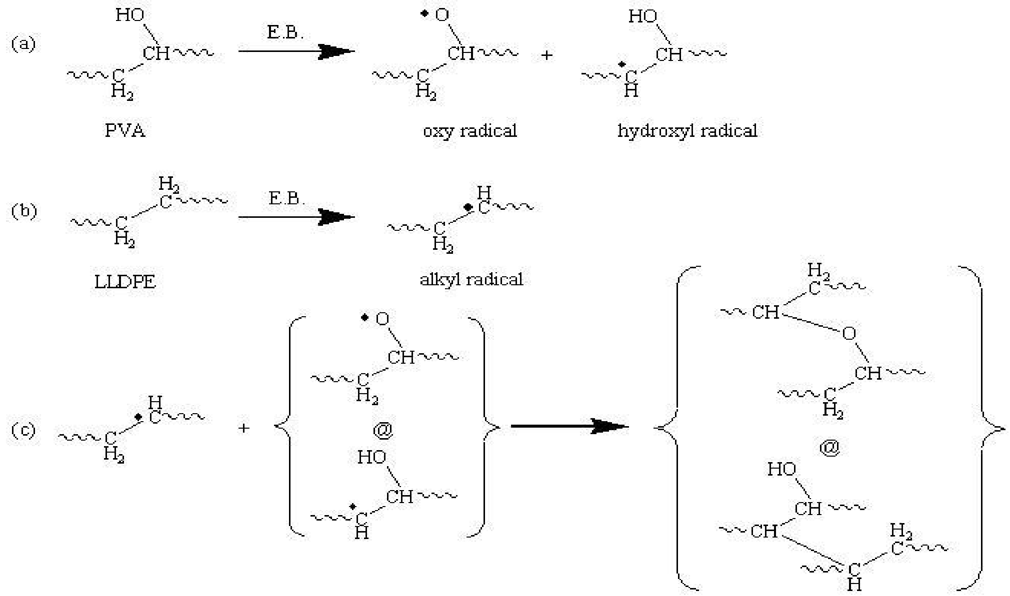

Fig. 3 - Proposed radiation induced crosslinking in LLDPE/PVA blends

3.4 DSC analysis

Due to an extremely small change in the specific heat and low value of glass transition (-135 ºC [10]) of polyethylene, the melting behavior is taken as indicative of miscibility between the two polymers in the blends. The DSC scans of the blends were used to determine two parameters signifying the melting behavior of LLDPE/PVA: 60/40 blends. The melting parameters include melting points (T_m for LLDPE and T_m for PVA) and degree of crystallinity (X_c) of LLDPE as a function of irradiation doses are presented in Table 1. The two melting peaks (T_m of LLDPE and PVA) illustrated the incompatibility between LLDPE and PVA in the blends due to different chemical makeup and polarity.

Apparently, the melting temperatures of each blend components decrease as the radiation dose increases (Table 1). This suggests that some changes occurred in polymers, probably due to the formation of more crosslinking and chain scission induced by the increase in the irradiated dose [26]. Figure 6 shows the melting endotherms of irradiated are wider due to progressive increase in chain scissions particularly at 200 kGy. The enlargement of melting endotherms also indicates broader distribution of crystal sizes.

Table 1 also indicates that the degree of crystallinity of LLDPE increases at 100 kGy and then decreases at 200 kGy. The increase in X_c is due to irradiation causing further formation of crosslinking in amorphous regions but extensive chain scission of tie molecules leads to crystal perfection [27]. Whilethe reduction of X_c at higher irradiation dose is due to the reduction of X_c at higher irradiation dose is due to melting of crystalline phase [27, 28] and formation of intermolecular crosslinks in the crystalline phase [30].

Table 1 Thermal properties of LLDPE/PVA: 60/40 blends (Second scans)

Irradiation Doses (kGy)	LLDPE			PVA
	T_m (°C)	Δ*H* (J/g)	X_c (%)	T_m (°C)
0	123.34	60.25	12.5	226.74
100	119.12	70.27	14.5	216.82
200	115.43	45.97	9.5	215.79

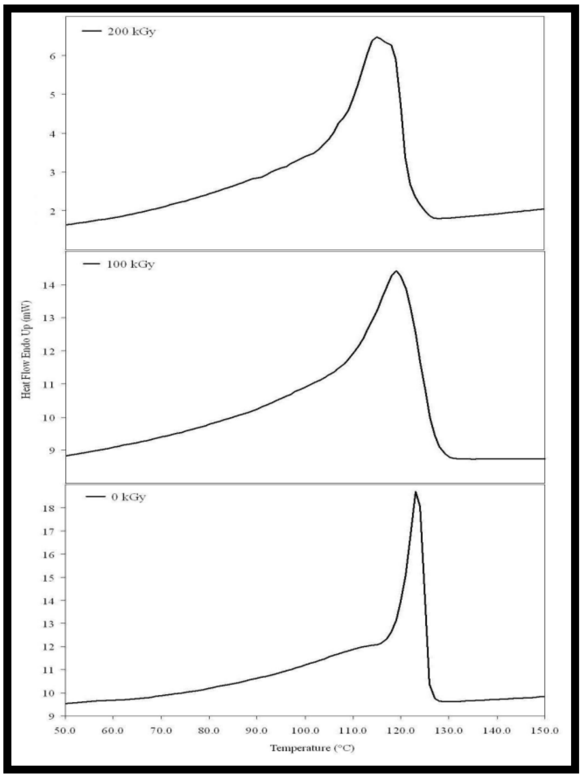

Fig. 6 - DSC second scans of non-irradiated and irradiated LLDPE/PVA: 60/40 blend

2.6 TGA analysis

The thermogravimetric curves and their derivatives for non-irradiated and irradiated LLDPE/PVA: 60/40 blends ratio is presented in Figure 7. Non-irradiated and irradiated blends showed two-step degradation process with two separate derivative curves associated to spontaneous elimination of water derived from hydroxyl group of PVA and chain scission of the carbon-carbon bonds. Irradiated blends decrease in decomposition temperature (T 5%) with irradiation dose. This was due to chain scissions that produced shorter chain with low thermal stability molecules. However, the temperature of first maximum DTG shifted to the right but the second maximum DTG remain the same with increasing irradiation doses. This confirms that the thermal stability increases in irradiated blends due to the formation of crosslinking.

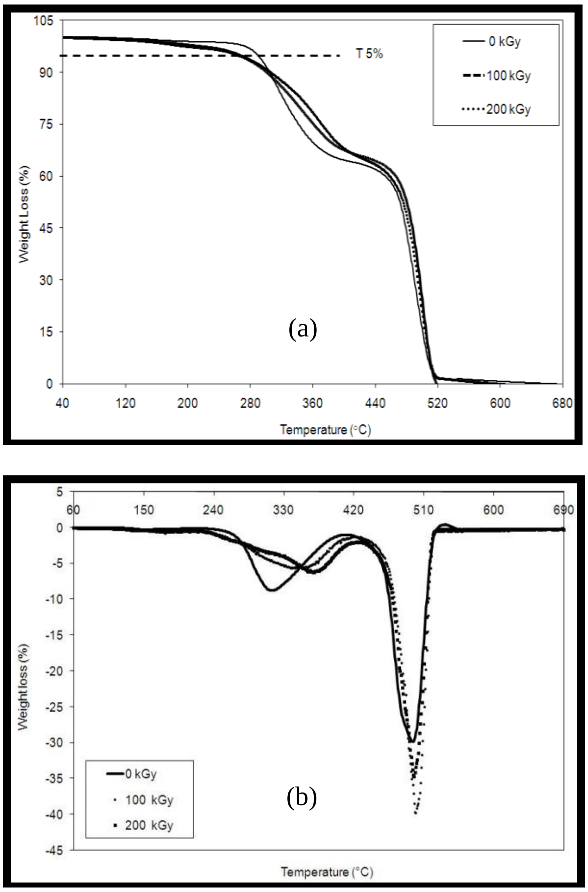

Fig. 7 - The (a) TGA and (b) DTG of non-irradiated and irradiated LLDPE/PVA: 60/40 blends.

2.7 Tensile properties

The variation of tensile properties of non-irradiated and irradiated LLDPE/PVA: 60/40 blends are shown in Figure 8. The tensilestrength increased from 9 MPa for non-irradiated to a maximum value 11 MPa, with increasing doses of irradiation up to 200 kGy and then slightly decreased with further increase in irradiation dose. The maximum tensile strength at 200 kGy is due to the effective mutual crosslinking between LLDPE and PVA components. Ali et al. 2003 [30] suggested that, the increase in tensile strength at lower doses was related to higher degree of interchain interactions by covalent crosslinking or by non-covalent interaction in polymer blends, such as those involved in the packing of crystalline domains. This can be established by observing the increase in the X_c of LLDPE blends, particularly at low level irradiation doses (Table 1). Meanwhile, the deterioration of tensile strength above 200 kGy is due to excessive crosslinking and scission of molecular chains becomes predominant. Also, as a result of crosslinking, the Young's modulus increases with irradiation doses whereas the elongation at break decreases (Figure 8b).

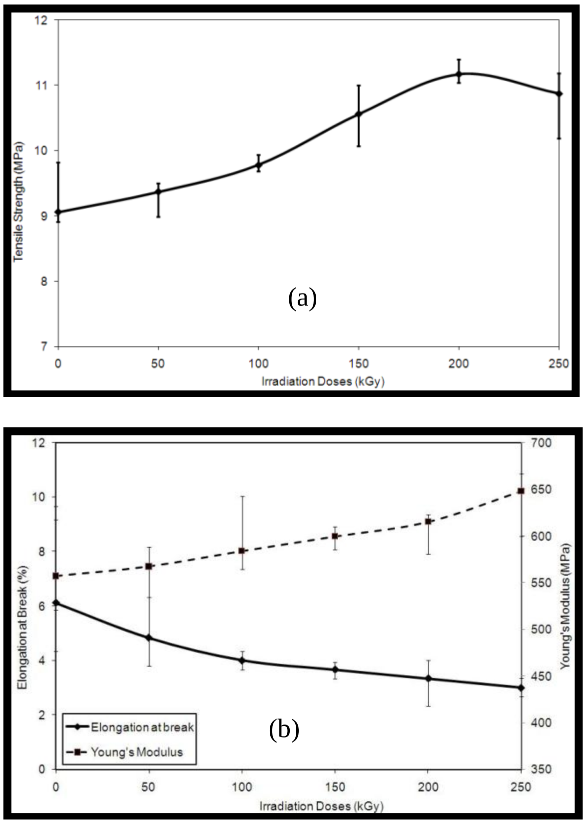

Fig. 8 - The (a) tensile strength and (b) Young's modulus and elongation at break of non-irradiated and irradiated LLDPE/PVA 60/40 blends

IV. CONCLUSION

Owing to crosslink reaction of different radicals, the compatibility of LLDPE/PVA blends was improved by the electron beam radiation crosslinking. The presence of crosslinked structure was quantified by gel content and was proven by FTIR and depression of melting temperature (LLDPE and PVA). As a result, the tensile strength and the thermal stability of the irradiated blends were enhanced compared to the non-irradiated blends. Based on tensile strength and thermal stability, the optimal absorbed dose for LLDPE/PVA blends was 200 kGy

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