Dispersion and roles of montmorillonite on structural, flammability, thermal and mechanical behaviours of electron beam irradiated flame retarded nanocomposite

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\textbf{A B S T R A C T}

In this work, the effects of montmorillonite (MMT) dispersion and electron beam irradiation on intercalation and flammability-thermal behaviours of alumina trihydrate (ATH) added low density polyethylene and ethylene vinyl acetate (LDPE–EVA) blends were investigated. MMT and ATH added LDPE–EVA blends were compounded using Brabender mixer and compression moulded into sheets. The samples sheets were electron beam irradiated in the dosage range of 0 to 250 kGy. The dispersion and intercalation of nano-MMT in LDPE–EVA matrix were investigated through X-ray diffraction (XRD) analysis. The d-spacing measurements revealed that the addition of nano-MMT has effectively intercalated into polymer matrix and this has enhanced the compatibility of ATH particles and LDPE–EVA matrix. Limiting oxygen index test (LOI) revealed that the incorporation of MMT into ATH added LDPE–EVA blends as improved the flame retardancy up to 26.5 LOI%. Besides, the application of electron beam irradiation were also improved the flame retardancy of the blends by increasing the LOI% for about 2% compared to non-irradiated samples. The application of irradiation dosage up to 250 kGy has rapidly improved the thermal stability of blends by delaying decomposition temperature and also promoting formation of char. The increasing of MMT loading level and irradiation dosage has effectively enhanced tensile strength and Young’s modulus by intercalating polymer matrix into interlayer galleries of MMT particles. Beside, the formation of crosslinking networks in polymer matrix also could further enhance the tensile strength and Young’s modulus. The intercalation effect of MMT particles and formation of crosslinking networks in polymer matrix could improve the thermal and mechanical properties. Consequently, this study has demonstrated that addition of MMT and electron beam irradiation into ATH added LDPE–EVA blends could produce better flammability, thermal and physical properties of ATH added LDPE–EVA blends.

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1. Introduction

Low density polyethylene (LDPE) and ethylene vinyl acetate (EVA) blends have been used in the wide range of engineering field due to their good physicomechanical properties. However, the application of LDPE–EVA blends as wire and cable insulation materials are limited because of its poor flame resistance. The poor flame resistance of LDPE–EVA blends is mainly attributed to their hydrocarbon origin. The flame resistance of LDPE–EVA blends could be improved by incorporating fire retardants [1–4]. Several researchers have reported that the incorporation of metal hydroxides type fire retardants (i.e. magnesium hydroxide, alumina trihydrate (ATH), zinc borate, etc.) into LDPE–EVA matrix could effectively enhance the flammability of polymer blends [5,6]. High loading levels (up to 60 wt.%) of the metal hydroxides type flame retardants are needed in order to increase the flame retardancy of the LDPE–EVA blends effectively [5]. However, the addition of high loading levels of flame retardants such as magnesium hydroxide, ATH and zinc borate, in LDPE–EVA blends tend to cause deterioration on mechanical properties of the polymer blends [7].
is one of the most commonly used mineral flame retardants for polymer materials due to its cheaper in price widely available in the market [8]. Various techniques have been applied to enhance the fire retardancy of LDPE–EVA blends without harming its mechanical properties. Incorporation of layered nano-clay or montmorillonite (MMT) into flame retarded polymer blends is one of the techniques to enhance the fire retardancy of polymer blends especially for LDPE–EVA blends. The polar group of EVA, vinyl acetate (VA) along the macromolecules chains of EVA could help in improving the polymer matrix to intercalate into the layered structure of clay or MMT particles [9,10]. The MMT intercalation effect in polymer matrix is usually detected through the changes of interlayer spacing of MMT in polymer blends [1]. The finely dispersed MMT particles could significantly enhance the flame retardancy and mechanical properties of polymer blends. For instance, the addition of 5 wt% of montmorillonite was found to improve the elongation at break of flame retarded LDPE–EVA blends by 10% to 30% [7]. On the other hand, synergistic combinations of flame retardants were also used to enhance the flame retardancy of polymer blends at lower loading while maintaining the required mechanical properties. The combinations of aluminium hydroxides with zinc borate, magnesium hydroxides with zinc borate and intumescence systems or silicates are the examples of flame retardants packages shown promising outcomes to enhance the flame retardancy of polymer blends [7]. At the mean time, the addition of combinations of montmorillonite (MMT) with fire retardants into polymer blends was also known to improve the flame resistance of polymer blends [1,11,12]. The incorporation of MMT particles could improve the flammability of polymer blends by delaying the thermal decomposition temperature while increasing the formation of char residue during combustion [12].

2. Experimental

2.1. Materials

Low density polyethylene (LDPE) and ethylene vinyl acetate copolymer (EVA) were used as polymer base in this study. LDPE with grade Titanlene LDF200GG and EVA with grade of UE6299 were purchased from Titan Chemicals Corporation Sdn. Bhd., Malaysia and USI Corporation, Taiwan, respectively. Alumina trihydrate, Al2O3·3H2O (ATH) with the grade of Micral 9400 was supplied by J.M. Huber Corporation, United States. ATH was added into polymer compound as flame retardant in this study. Zinc borate was added into polymer compound as a smoke suppressant and it was supplied by ShanDong Chuan Jun Chemical, China. Trimethylolpropane trimethacrylate (TMPTMA) containing 175 ppm monomethyl ether hydquinone was supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia. TMPTMA was used as radiation sensitizer in this polymer compound to promote the formation of free radicals in polymer matrix during irradiation process. LDPE-grafted maleic anhydride (LDPEgMAH) with grade of NG1201 was supplied by Shenghui Jianqio Plastic, China. LDPEgMAH grafted with 1% of maleic anhydride was used as a compatibilizer in this study to improve the compatibility between the polymers matrix and fillers. Calcium stearate and Irganox grade of 1010 were supplied by Industrial Resins Malaysia Sdn. Bhd and Ciba Specialty Chemicals, respectively. Calcium stearate was used as external lubricant to prevent the polymer melt from sticking on processing machine during samples compounding. Irganox grade 1010 was added as antioxidant in polymer compound to prevent pre-mature degradation caused by either melt blending or irradiation stage. Montmorillonite (MMT) with grade of Nanomer 1.3P was purchased from Nanocor, Arlington Height and used as reinforcement filler in the polymer compound to improve the mechanical properties.

2.2. Samples preparation

All the LDPE–EVA blend formulations were containing a fixed amount of 50 phr LDPE, 50 phr EVA, 25 phr ATH, 6 phr LDPEgMAH, 1 phr TMPTMA, 2.5 phr calcium stearate, 7.5 phr zinc borate and 0.05 phr Irganox 1010. Each formulation was added with different amounts of MMT (i.e. 2.5 phr, 5 phr, 7.5 phr and 10 phr). The LDPE–EVA blends were compounded using the Brabender mixer at the mixing temperature of 130 °C and rotor speed of 50 rpm for 12 min. For samples compounding process, LDPE and EVA were firstly melted in Brabender mixer at 130 °C for 4 min. Then, additives were added into LDPE–EVA melts and mixed in Brabender mixer for another 8 min. The compounded samples were further hot pressed into 1 mm thickness sheet at the heating temperature of 175 °C using a hot press machine. For the compression moulding process, the compounded samples were preheated at the temperature of 175 °C for 8 min. The preheated samples were then pressed at temperature of 175 °C and pressure of 10 MPa for 5 min. The hot pressed samples were cooled down under pressure of 10 MPa for 2 min with the cooling rate of 15 °C/min. The 1-mm sheets were irradiated at room temperature to the irradiation dosage of 50 kGy, 150 kGy and 250 kGy with dose rate of 50 kGy per pass in an electron beam accelerator. The acceleration voltage of electron beam accelerator was set to 5 MeV.

2.3. Testing methods

2.3.1. X-ray diffraction (XRD) test

The X-ray diffraction (XRD) test was conducted using X-ray diffractometer model XRD-6000 Shimadzu to evaluate the dispersion and intercalation pattern of MMT in LDPE–EVA matrix. The voltage and current of diffractometer were set at 40 kV and 30 mA. The XRD spectra were recorded with the diffractometer in step-scan mode at room temperature by using Copper irradiation (wave length of 0.1542 nm) generator at the scanning rate of 1° per min in the range of 0–2θ.
2.3.2. Transmission electron microscopy (TEM) test

TEM test was conducted to observe the dispersing and intercalation of MMT particles in polymer matrix. A transmission electron microscope (TEM) with the acceleration voltage of 100 kV was used to study the morphologies of the nano-particles of MMT and the dispersion of MMT in LDPE/EVA matrix. The specimens of samples used for TEM test were ultrathin form. The ultrathin specimens were sectioned by using a cryogenic ultra-microtome.

2.3.3. Limiting oxygen index test (LOI)

Limiting oxygen index (LOI) test was carried out using an apparatus from Rheometer Scientific, United Kingdom in accordance to ASTM D2863. The 1-mm sheets were cut into the dimensions of 150 mm × 150 mm × 1 mm and the cut specimen was placed vertically in a transparent test column. A mixture of nitrogen and oxygen was purged into the transparent column for two minutes to create an oxygen–nitrogen atmosphere inside the test column. Then, the specimen was ignited with a burner at the top. The concentration of oxygen in the mixture was increased until the concentration level was sufficient enough to support the combustion of specimen. The LOI% of each formulation was measured with nine specimens.

2.3.4. Thermogravimetric analysis (TGA)

TGA test was carried out by using Mettler Toledo thermogravimetric analyzer with unit model of TGA/SDTA851e to analyze the thermal characteristics of the samples. The samples with the weight around 2 mg and 3 mg were firstly placed in a 150 µl silica crucible. The samples were heated and scanned from temperature 60°C to 700°C at a heating rate of 20°C per min under a nitrogen atmosphere. The initial decomposition temperature and the thermal degradation weight loss (formation of char) of samples were recorded and analyzed.

2.3.5. Tensile analysis

Tensile analysis was conducted by using Instron micro tester model 5848 according to ASTM D1822. The 1 mm thickness compression moulded samples was cut into dumbbell shape by using dumbbell sample cutter. The samples were tested under a crosshead speed of 50 mm per min under the load of 2 kN at room condition. The gauge length of samples was fixed at 14 cm. The results of elongation at break, tensile strength and Young’s modulus were recorded and analyzed.

3. Results and discussions

3.1. Crystallography-structural analysis

The X-ray diffraction analysis is usually performed to investigate the dispersion and intercalation state of MMT in polymer matrix. The positions of diffraction peaks on the XRD curves of LDPE–EVA blends could be observed between 2θ = 0° to 2.52° to determine the interlayer spacing (d-spacing) of silicate layers of nano-MMT. The d-spacing of the nano-MMT into ATH added LDPE–EVA blends were calculated through the Bragg’s equation as shown below [17]:

\[ d = \frac{\lambda}{2 \sin \theta} \]  

where 2θ is the angle of diffraction peak and \( \lambda \) is the wavelength of Cu-irradiation and equals to 0.154 nm. The inter-chain separation, R was determined from Klug and Alexander equation as given below [17]:

\[ R = \frac{5 \lambda}{8 \sin \theta} \]  

Table 1

<table>
<thead>
<tr>
<th>Samples (irradiation dose)</th>
<th>XRD analysis on curves (b) in Fig. 1–3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Angle, 2θ</td>
</tr>
<tr>
<td>MMT</td>
<td></td>
</tr>
<tr>
<td>2.5M-LE (0 kGy)</td>
<td>1.285</td>
</tr>
<tr>
<td>5.0M-LE (0 kGy)</td>
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<td>7.5M-LE (0 kGy)</td>
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<td>10M-LE (0 kGy)</td>
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</tr>
<tr>
<td>7.5M-LE (50 kGy)</td>
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</tr>
<tr>
<td>10M-LE (50 kGy)</td>
<td>1.264</td>
</tr>
<tr>
<td>2.5M-LE (150 kGy)</td>
<td>1.260</td>
</tr>
<tr>
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<tr>
<td>7.5M-LE (150 kGy)</td>
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<tr>
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<td>2.5M-LE (250 kGy)</td>
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<tr>
<td>5.0M-LE (250 kGy)</td>
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</tr>
<tr>
<td>7.5M-LE (250 kGy)</td>
<td>1.254</td>
</tr>
<tr>
<td>10M-LE (250 kGy)</td>
<td>1.252</td>
</tr>
</tbody>
</table>

Fig. 1. (a), (b) and (c) XRD curve of 25 phr ATH added LDPE–EVA blends filled with various electron beam irradiation doses.
1.249 at 15,000 for non-irradiated, 25 phr ATH and 10 phr MMT added LDPE–EVA blends using TEM. The dispersing and intercalation effect of MMT particles in LDPE–EVA matrix was also depicted in Fig. 2 under TEM observation. By observing Fig. 2(a), the MMT particles were observed to disperse evenly in LDPE–EVA blends. The LDPE–EVA matrix can also be observed to effectively intercalate into the interlayer galleries of MMT particles as shown in Fig. 2(b). The intercalation effect of MMT particles could increase the distance between the interlayer galleries of MMT particles as indicated by the increment in d-spacing value of samples. This can be explained where the hydrophobic section of nano-MMT enables the molten LDPE–EVA matrix to intercalate effectively into the interlayer galleries of MMT particles with expanded d-spacing [17–19]. Such intercalation effect of the interlayer galleries of MMT particles in LDPE–EVA matrix can be confirmed as depicted in Fig. 2(b). It could be obviously seen that the MMT particles are consisted of multi layers galleries and the LDPE–EVA matrix was effectively intercalated into the interlayer galleries of MMT particles [20]. On the other hand, the typical hydrophilic characteristic at the edge of MMT layers is compatible to the alumina trihydrate. This could further enhance the intercalation of ATH particles and LDPE–EVA matrix into nano-MMT interlayer galleries [12,17,18]. Moreover, the intercalation effect of montmorillonite in polymer matrix could provide reinforcing effect to LDPE–EVA matrix by increasing the surface area of interfacial adhesion between MMT particles and polymer matrix. At low and moderate irradiation doses (0–150 kGy), the d-spacing of peak (b) were slightly increased with increasing of MMT loading level from 2.5 to 7.5 phr. This also shows that low amounts of MMT particles in LDPE–EVA matrix could promote the intercalation effect of LDPE–EVA matrix into interlayer galleries of MMT particles under low and moderate irradiation doses. However, the d-spacing was slightly decreased as the MMT loading level increased from 7.5 to 10 phr. This could be due to the MMT particles in LDPE–EVA matrix are tended to agglomerate into larger particles when a high MMT loading level is added. The agglomeration of MMT particles could reduce the effectiveness of MMT particles intercalate and disperse in LDPE–EVA matrix. This is evidently observed with the reduction of d-spacing of MMT added in the blends. At high irradiation dosage (250 kGy), the d-spacing was observed to increase when MMT loading level increased from 2.5 to 5 phr. However, the d-spacing decreased with subsequent increasing of MMT loading level. The decrement in d-spacing of 250 kGy irradiated samples with increasing of MMT was observed to occur at low MMT loading level in compared to lower irradiation dosages. The d-spacing of 250 kGy irradiated samples was continued to decrease with further increasing of MMT loading level from 5 to 10 phr.

At low MMT loading levels (2.5–7.5 phr), the d-spacing was observed to marginally increase with increasing of irradiation dose from 0 to 150 kGy. This indicates that the electron beam irradiation has enhanced the dispersion and intercalation effect of MMT particles in LDPE–EVA matrix by forming the crosslinking networks in polymer matrix. The formation of crosslinking networks in polymer matrix could further enhance the intercalation effect of polymer matrix into the interlayer galleries of MMT particles. However, the d-spacing of all LDPE–EVA blends were observed to decrease when applied to high irradiation dosages (150 kGy and 250 kGy). This is attributable to the occurrence of chains scissioning in LDPE–EVA matrix [18]. At high loading level of MMT (10 phr), the d-spacing of ATH added LDPE–EVA blends was observed to reduce marginally as the samples were irradiated to 50 kGy. However, the d-spacing of ATH added LDPE–EVA blends were increased with further increasing of irradiation dosages (from 50 to 250 kGy).

The inter-chain separation of ATH added LDPE–EVA blends were increased with the addition of nano sized MMT. The MMT particles added into matrix of ATH added LDPE–EVA blends could fit into the cavities occur between the surface of ATH particles and LDPE–EVA chains. This has led to increase the inter-chain separation of LDPE–EVA blends. For non-irradiated, 50 and 150 kGy irradiated samples, the inter-chain separation was gradually increased as the loading level of MMT increased from 2.5 to 7.5 phr. However, further increment of MMT loading level from 7.5 to 10 phr was found to slightly decrease the inter-chain separation. This might be attributed to occurrence of agglomerated particles in LDPE–EVA matrix which could reduce the intercalation effect of MMT particles into LDPE–EVA matrix. Thus, also reduce the inter-chain separation of LDPE–EVA blends. For 250 kGy irradiated samples, the inter-chain separation was increased from 8.73 to 8.86 as MMT loading level had increased from 2.5 to 5 phr. Fur-

where $R$ is the inter-chain separation of the diffraction peak. The d-spacing, change of d-spacing and inter-chain separation of nano-MMT and all the samples were calculated from Eqs. (1) and (2) as presented in Table 1.

According to Fig. 1, two diffraction peaks, which are peaks (a) and (b) were seen on the XRD curve of pristine nano-MMT. From the XRD curves of the LDPE–EVA blends filled with increasing of MMT loading level (as shown in Fig. 1(a)), the peak (a) was shifted to lower angle and nearly disappear on the XRD curves. The peak (b) also found to slightly shift from 1.285 to lower angle around 1.249° and 1.261°. Table 1 also presents the characteristic 2θ, d-spacing, change of d-spacing and inter-chain separation of peak (b) for nano-MMT filler and MMT and ATH added LDPE–EVA blends. The d-spacing for peak (b) of nano-MMT added LDPE–EVA blends shows an increment within 0.13–0.20 nm compared to pristine nano-MMT. This indicates that the nano-MMT particles were homogeneously dispersed into the matrix of LDPE–EVA blends with increasing of MMT loading level. Besides, the dispersing of MMT particles in LDPE–EVA matrix was also depicted in Fig. 2 under TEM observation. By observing Fig. 2(a), the MMT particles were observed to disperse evenly in LDPE–EVA blends. The LDPE–EVA matrix could further enhance the intercalation effect of polymeric matrix into nano-MMT interlayer galleries [12,17,18]. Moreover, the intercalation effect of montmorillonite in polymer matrix could provide reinforcing effect to LDPE–EVA matrix by increasing the surface area of interfacial adhesion between MMT particles and polymer matrix. At low and moderate irradiation doses (0–150 kGy), the d-spacing of peak (b) were slightly increased with increasing of MMT loading level from 2.5 to 7.5 phr. This also shows that low amounts of MMT particles in LDPE–EVA matrix could promote the intercalation effect of LDPE–EVA matrix into interlayer galleries of MMT particles under low and moderate irradiation doses. However, the d-spacing was slightly decreased as the MMT loading level increased from 7.5 to 10 phr. This could be due to the MMT particles in LDPE–EVA matrix are tended to agglomerate into larger particles when a high MMT loading level is added. The agglomeration of MMT particles could reduce the effectiveness of MMT particles intercalate and disperse in LDPE–EVA matrix. This is evidently observed with the reduction of d-spacing of MMT added in the blends. At high irradiation dosage (250 kGy), the d-spacing was observed to increase when MMT loading level increased from 2.5 to 5 phr. However, the d-spacing decreased with subsequent increasing of MMT loading level. The decrement in d-spacing of 250 kGy irradiated samples with increasing of MMT was observed to occur at low MMT loading level in compared to lower irradiation dosages. The d-spacing of 250 kGy irradiated samples was continued to decrease with further increasing of MMT loading level from 5 to 10 phr.

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![Fig. 2](image_url). The dispersing and intercalation effect of MMT particles in LDPE–EVA matrix for non-irradiated, 25 phr ATH and 10 phr MMT added LDPE–EVA blends using TEM at 15,000 × magnification.
Furthermore causing delay to the combustion process [7, 12, 23]. Kiewicz et al. [22] who concluded that the addition of MMT can retard the combustion process of ATH added LDPE–EVA blends from mixing with free oxygen during combustion process, thus trix could also impede the diffusion of flammable volatile gases from mixing with free oxygen during combustion process, thus retarding the combustion process of ATH added LDPE–EVA blends [24, 25].

By referring to Table 2, the LOI% of ATH added LDPE–EVA blends were slightly improved with increasing of electron beam irradiation dosage from 0 to 250 kGy at all loading levels of MMT. This showed that the formation of crosslinking networks in the matrix of ATH added LDPE–EVA blends could improve the fire resistance of the ATH added LDPE–EVA blends. The crosslinked chains in ATH added LDPE–EVA matrix could retard the combustion of LDPE–EVA matrix by reducing the melt dripping [19]. Moreover, the reduction in the dripping of samples could increase the strength of char formed during combustion and it would function as a thermal insulation layer on the surface of the polymer matrix. The char covered on the polymer surface resist the heat transfer to the inner region to vaporize the flammable polymer volatiles from supplying fuel for combustion process. Thus, it could further retard the combustion of the polymer matrix.

TGA results of 25 phr added LDPE–EVA blends filled with increasing of MMT loading levels under increasing of irradiation doses were presented in Fig. 3 and Table 2. Based on Fig. 3, all the 25 phr ATH added LDPE–EVA blends were observed to demonstrate the degradation or decomposition in two degradation steps. The first step of degradation was taken place in the temperature range of 250–420 °C, while the second step of degradation was observed to occur in the range of 420–550 °C as shown in Fig. 2. The first step degradation is attributed to the released of water vapour during ATH combustion as well as elimination of acetic acid of EVA chains by formation of double bonds and also breakage of crosslinking networks for irradiated samples [1, 7, 9]. On the other hand, the second step of degradation is mainly involved the thermal decomposition of ethylene backbone chains and also crosslinked backbone chains. The thermal decomposition of backbone chain in LDPE–EVA blends decreased the molecular mass with the formation of combustible gases and char in small mass amount [1]. By referring to Table 2, the first stage decomposition temperature was gradually increased from 318.2 to 333.3 °C as the MMT loading level increased from 2.5 to 10 phr. This also indicated that the increasing of MMT loading level from 2.5 to 10 phr could enhance the thermal stability of LDPE–EVA by delaying the decomposition temperature with 15.1 °C. As mentioned earlier in LOI results, the intercalation of LDPE–EVA matrix into MMT particles galleries could lead to prevent the diffusion of volatile gases produced during thermal degradation out from the polymer matrix [9, 26]. The MMT particles in LDPE–EVA matrix also could reduce the permeability of oxygen gas from LDPE–EVA surface into the LDPE–EVA matrix. Hence, it has enhanced the thermal properties of LDPE–EVA blends. Besides that, the increasing of MMT loading levels from 2.5 to 10 phr was also observed to increase the formation of char residue after the combustion process from 21.4% to 22.6% (as observed in Table 2). The char formed and covered on the LDPE–EVA blends could act as a protective layer that thermally insulated the LDPE–EVA matrix from combustion and also separated the polymer surface from oxygen gas.

By referring to Table 2, the increasing of irradiation dosages from 0 to 250 kGy gradually increased the first stage decomposi-

### Table 2

<table>
<thead>
<tr>
<th>Samples</th>
<th>0 kGy</th>
<th>50 kGy</th>
<th>150 kGy</th>
<th>250 kGy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limiting oxygen index (LOI), %</td>
<td>2.5M-LE</td>
<td>22.2 ± 0.29</td>
<td>22.0 ± 0.15</td>
<td>22.9 ± 0.17</td>
</tr>
<tr>
<td></td>
<td>5.0M-LE</td>
<td>23.1 ± 0.23</td>
<td>24.0 ± 0.23</td>
<td>24.6 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>7.5M-LE</td>
<td>24.0 ± 0.23</td>
<td>24.7 ± 0.23</td>
<td>25.3 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>10M-LE</td>
<td>24.9 ± 0.23</td>
<td>25.3 ± 0.23</td>
<td>26.0 ± 0.26</td>
</tr>
</tbody>
</table>

| Mid decomposition temperature of first stage degradation (T_{1,1}), °C | 2.5M-LE | 318.2 | 332.8 | 346.1 | 347.9 |
| | 5.0M-LE | 327.8 | 333.1 | 347.0 | 347.7 |
| | 7.5M-LE | 333.2 | 336.4 | 347.2 | 348.2 |
| | 10M-LE | 333.3 | 336.8 | 346.9 | 348.0 |

| Formation of char, % | 2.5M-LE | 21.4 | 22.5 | 22.9 | 23.1 |
| | 5.0M-LE | 22.0 | 22.6 | 23.0 | 23.2 |
| | 7.5M-LE | 22.5 | 22.8 | 23.1 | 23.3 |
| | 10M-LE | 22.6 | 23.0 | 23.1 | 23.2 |
tion temperature of LDPE–EVA blends with increment in the range of 14.7–29.7 °C. It is obviously seen that the irradiation crosslinking has further improved the thermal stability of LDPE–EVA blends by introducing the three dimensional crosslinking networks. This could be due to the crosslinking networks formed in LDPE–EVA matrix is more stable in resisting the formation of volatile gases during combustion [9]. Thus, the thermal stability of LDPE–EVA blends has been enhanced by the irradiation crosslinking. On the other hand, the formation of char residue after the thermal decomposition slightly increased as the irradiation dosages increased from 0 to 250 kGy. This indicates that the formation of crosslinking networks can promote the formation of char. Also, the char formed could act as a thermal protective layer of LDPE–EVA blends by preventing the oxygen gas from contact with the surface of LDPE–EVA blends. Thus, the thermal stability could be enhanced with the application irradiation crosslinking process.

3.3. Mechanical properties

According to Fig. 4(a), the tensile strength of non-irradiated LDPE–EVA blends was slightly increased as the loading level of MMT increased from 2.5 to 7.5 phr. This might be attributed the dispersion of MMT particles in LDPE–EVA matrix could provide reinforcement effect to the polymer matrix. The addition of MMT particles into ATH added LDPE–EVA matrix could finely intercalate into the cavities between the ATH particles and LDPE–EVA matrix. LDPE–EVA matrix can effectively intercalate into the interlayer galleries of MMT particles, while the ATH particles were attached to the polar section of MMT particles [26,27]. The intercalation effect of MMT particles could improve the interaction between ATH and LDPE–EVA matrix and promote stress transfer effectively from polymer matrix to the ATH and MMT particles [14]. However, the tensile strength was slightly decreased with further increment in MMT loading level from 7.5 to 10 phr. This could be due to the high amounts of MMT particles were agglomerated into larger particles and caused poor dispersion of MMT particles in polymer matrix. This also reduces the intercalation effect in polymer matrix and thus ruins the performance of tensile strength. On the other hand, the tensile strength of the LDPE–EVA blends was gradually increased with increasing of irradiation dosage at all loading levels of MMT. This also indicated that the irradiation crosslinking could further improve the reinforcement effect of MMT particles to the LDPE–EVA matrix [28]. The formation of crosslinking networks could further enhance the interfacial adhesion between the polymer matrix and ATH and MMT particles while improving the compatibility between the ATH and MMT particles and LDPE–EVA blends. This could enable the stress to be transferred effectively from polymer matrix to ATH and MMT particles, subsequently enhances the tensile strength of LDPE–EVA blends [29].

Fig. 4(b) shows the effect of MMT loading level and irradiation dosages on elongation at break of 25 phr ATH added LDPE–EVA blends. The increasing of MMT loading level from 2.5 to 10 phr has gradually decreased the elongation at break of all non-irradiated and irradiated LDPE–EVA blends. The intercalation of LDPE–EVA matrix into the interlayer galleries of MMT particles promotes formation of a restricted environment against the polymer chains to move freely. This also reduces the ability of elongation for intercalated LDPE–EVA blends. The agglomeration of MMT particles at high loading level could significantly reduce the intercalation effect of MMT particles in polymer matrix, subsequently the elongation at break was reduced. On the other hand, the increment of irradiation dosage from 0 to 150 kGy has gradually increased the elongation at break of LDPE–EVA blends at low MMT levels (2.5 and 5 phr). This is due to the formation of crosslinking in polymer matrix could improve the intercalation effect of MMT particles and LDPE–EVA matrix. This also could further enhance the interfacial adhesion between ATH particles and LDPE–EVA matrix. However, the elongation at break of LDPE–EVA blends was significantly decreased as the irradiation dosage increased up to 250 kGy. This is attributed to the high degree of crosslinking formed in LDPE–EVA matrix which can resist the matrix reorganization and restrict the mobility of polymer chains from slippage on each other when under stretching [14]. At high loading level of MMT (10 phr), the elongation at break of LDPE–EVA blends was gradually increased with increasing of irradiation dosage (from 0 to 250 kGy). This due to the formation of crosslinking networks in LDPE–EVA matrix could extent the continuities of polymer matrix. Therefore, the increment of irradiation dosage has significantly increased the elongation at break of LDPE–EVA blends.

By referring to Fig. 4(c), the addition of MMT particles into LDPE–EVA matrix has significantly increased the stiffness Young’s modulus of non-irradiated and irradiated LDPE–EVA blends. The increment of MMT loading level from 2.5 to 10 phr has gradually increased the Young’s modulus of LDPE–EVA blends under various irradiation dosages. The incorporation of MMT particles into ATH added LDPE–EVA matrix has effectively enhanced the Young’s modulus by intercalating of LDPE–EVA matrix into interlayer galleries of MMT particles. The intercalation of LDPE–EVA matrix into the interlayer galleries of MMT particles and the attachment of polar edge section of MMT particle to ATH particles with high polar behavior are played an important role in enhancing the Young’s modulus [27]. This also indicated that the MMT particles could effectively fit and intercalate into interfacial between ATH particles and LDPE–EVA matrix and enhance the interfacial adhesion of ATH particles in LDPE–EVA matrix. Therefore, the mobility of polymer chains has been restricted. At low loading level of MMT, the
MMT particles could well distribute and disperse in LDPE–EVA matrix and this could help in enhancing the intercalation effect of MMT particles in polymer matrix with minimum occurrence of agglomerated MMT particles. However, the MMT particles tended to agglomerate together into larger MMT aggregates particles at high loading level of MMT. The agglomerated MMT particles could reduce the intercalation effects of MMT particles in polymer matrix, thus reducing the Young’s modulus.

The effect of irradiation crosslinking on Young’s modulus of LDPE–EVA blends has been investigated as shown in Fig. 4(c). At low MMT loading levels (2.5 and 5 phr), the increasing of irradiation dosages was found to significantly increase the Young’s modulus of LDPE–EVA blends. This was attributed to the formation of crosslinking networks in LDPE–EVA matrix could highly restrict the mobility of LDPE–EVA chains to slippage between each other and thus enhance the Young’s modulus (stiffness) of LDPE–EVA blends. This indicated that the formation of crosslinking networks in ATH added LDPE–EVA matrix could further enhance the reinforcement effect of ATH particles in LDPE–EVA matrix by enhancing the interfacial adhesion (compatibility) within ATH particles and LDPE–EVA matrix [28]. The high restricted in the mobility of polymer chains by the crosslinking networks formed in polymer matrix and has highly improved the Young’s modulus of ATH added LDPE–EVA blends. Besides, the formation of crosslinking networks in ATH added LDPE–EVA matrix also observed to lower the agglomeration of ATH and MMT particles in polymer matrix. Then, this also could increase the total effective MMT particles in polymer matrix that reduce the continuities of polymer matrix and further enhance the Young’s modulus. However, the Young’s modulus of high MMT added LDPE–EVA blends was gradually decreased with increasing of irradiation dose as shown in Fig. 4(c). This is due to the high MMT particles in LDPE–EVA matrix are agglomerated together into larger MMT particles. The formation of crosslinking networks in polymer matrix with MMT agglomerated particles was found unable to further improve the intercalation effects of MMT particles in LDPE–EVA matrix.

4. Conclusions

The dispersion roles of MMT on intercalation and flammability-thermal behaviours of electron beam irradiated ATH added LDPE–EVA blends were investigated in this study. The XRD analysis exhibited that the MMT particles were well dispersed and intercalated in the matrix of LDPE–EVA blends. The intercalation effect of MMT has significantly improved the compatibility between the filler particles and polymer matrix producing samples with better properties. Moreover, the intercalation of MMT into LDPE–EVA matrix was effectively enhanced by electron beam irradiation with the formation of crosslinking networks. The addition of MMT has enhanced the flame resistivity of ATH added LDPE–EVA blends whereas the LOI% for non-irradiated and irradiated samples was observed to the highest at the loading level of 10 phr MMT. Meanwhile, the electron beam irradiation also improved the flame resistivity of ATH added LDPE–EVA blends. The LOI value was found to increase about 2% as the irradiation dosage as the 10 phr MMT added samples when subjected to 250 kCgy compared to non-irradiated samples.

In addition, the increasing of MMT loading level also exhibited thermal stability effect to the blends with the elevation of first stage of decomposition temperature when the MMT loading level has increased from 2.5 to 10 phr. This is due to the intercalation of LDPE–EVA matrix into MMT particles galleries can resist the permeability of volatile gases out from polymer matrix. By increasing the irradiation dosage from 0 to 250 kCgy, the first stage decomposition temperature of ATH and MMT added LDPE–EVA blends were also significantly improved. This indicates that the formation of crosslinking networks in matrix of ATH and MMT added LDPE–EVA blends is more stable in resisting the production of volatile gases when heating, thus enhancing the thermal stability of LDPE–EVA matrix. The increasing of MMT loading level and crosslinking networks also found to induce the formation of char. The char formation could enhance the flame resistance and thermal stability of LDPE–EVA blends by reducing the permeability of volatile gases while acted as thermal insulation layer to reduce the heat transfer from vaporizing the flammable volatile polymer components.

The increment of MMT loading level has slightly increased the tensile strength of LDPE–EVA blends by intercalating the polymer matrix into the interlayer galleries of MMT particles. The effective intercalation of MMT particles in LDPE–EVA matrix could improve the interaction between ATH particles and LDPE–EVA matrix by effectively transferring stress from polymer matrix to MMT and ATH particles. Thus, the tensile strength has been enhanced. On the other hand, the tensile strength of LDPE–EVA matrix also gradually increased with increasing of irradiation dosage by introducing the formation of crosslinking networks in LDPE–EVA matrix. The increasing of MMT particles has exhibited an inferior effect on the elongation at break of LDPE–EVA blends. This is due to the intercalation effect of MMT particles in LDPE–EVA matrix could improve the interfacial adhesion between ATH particles and LDPE–EVA matrix, thus reducing the elongation at break. The increment of irradiation dosage was significantly enhanced the elongation at break of LDPE–EVA blends. The formation of crosslinking networks in polymer matrix could extent the matrix discontinuities of LDPE–EVA blends.

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