ABSTRACT

Blends of linear low-density polyethylene (LLDPE)/poly(vinyl alcohol) (PVA) were prepared by conventional thermoplastic processing technique. The blends were mixed using a Haake rheometer at 150°C and 50 rpm for 10 min. The LLDPE and PVA were blended to give the following blend ratios (php): 90/10, 80/20, 60/40, 50/50 and 40/60. The effect of maleic acid via in situ cross-linking on processability, component interaction, miscibility, thermal stability, tensile properties, and morphology of LLDPE/PVA blends was investigated in this research. The results indicated that the presence of maleic acid increases the equilibrium torque of LLDPE/PVA blends. This observation may be due to better compatibility and cross-linking between LLDPE and PVA. The formation of cross-linking was confirmed by Fourier transform infrared analysis and depression of melting points of PVA and LLDPE in the blends. The thermal stability and mechanical properties such as tensile strength, elongation-at-break, and Young's modulus of the LLDPE/PVA blends also improved in the presence of maleic acid. Evidence for greater compatibility between LLDPE and PVA was confirmed by emergence of elongated fibrils extending over the surface of the PVA dispersed phases in the LLDPE matrix as revealed by scanning electron microscopy micrographs.

INTRODUCTION

Poly(vinyl alcohol) PVA is an important synthetic biodegradable polymer having excellent gas barrier properties, high strength, tear, and flexibility. However, it is found to have poor dimensional stability due to high moisture absorption. It also has relatively high price compared to other commercial polymers. Therefore, blended with renewable and abundant agro-resource based such as polysaccharides, particularly starch can be utilized to reduce the manufacturing cost. Blending with starch results in improved moisture resistance and accelerated degradation [1,2]. However, the properties of the blends deteriorated as starch content in the blend formulation increased, owing to poor compatibility between the two components and phase separation during blend preparation.

Techniques applied to improve compatibility between PVA and starch includes the following: addition of suitable plasticizers [3,4] cross-linking agents [5-7], fillers [8-10] and compatibilizers
[11,12]. Nevertheless, PVA/starch blends are found frequently prepared in solution due to their low thermoplasticity at melting temperature [13]. Solution method is not preferred due to high processing cost and low efficiency in comparison to thermoplastic processing. Furthermore, PVA/starch blends are found too weak to be used when exposed to humidity in environment. Mao et al. [14] reported that the strength of PVA/starch is decreased by 60% as the relative humidity increases from 30% to 93%. Thus, the key to widen PVA application is to reduce its moisture absorption for further thermoplastic technique processing.

Polyethylene (PE) is likely acceptable due to its low production cost and higher water resistance properties [15,16] when it is blended with PVA. Unfortunately, research in PE/PVA blend preparation by thermoplastics processing is not reported widely [17,18]. Current work by Lui and coworkers [18] shows that starch/PVA/PE blends can be processed through thermoplastic technique with incorporation of plasticizers. However, plasticizers can hinder chemical interactions between the blends and compatibilizers.

In our previous work, we successfully blended linear low-density polyethylene (LLDPE) with PVA through thermoplastics technique [19] without using any plasticizer, but the tensile strength of the blends decreased significantly due to immiscibility and compatibility between the two components. Meanwhile, maleic acid-grafted polyolefins were found to exhibit high compatibility [20]. Free radical grafting of maleic acid onto polymer blends [20] has gained acceptance since it does not require pretreatment and additional cost in comparison to maleic anhydride [21-23]. Therefore in this work, maleic acid is used as a compatibilizer to improve the interaction between LLDPE and PVA chains. The processing, miscibility, thermal stability, tensile properties and morphology of LLDPE/PVA blends are studied based on current development.

EXPERIMENTAL

Materials
Poly(vinyl alcohol) with an average molecular weight of 89,000 - 98,000 and +99% hydrolyzed, maleic acid and dicumyl peroxide were obtained from Sigma-Aldrich Sdn. Bhd. (Malaysia). Linear low-density polyethylene (LLDPE) with a melt mass flow rate (MFR) of 1.0 g/10 min (190°C/2.16 kg) and a melting temperature of 123°C was obtained from Polyethylene Sdn. Bhd. (Malaysia).

Mixing Procedure
The preparation of blends was carried out in a Haake Reomix PolyDrive at a temperature of 150°C with rotor speed of 50 rpm for about 10 min. The LLDPE was first charged to start the melt mixing. PVA was added after 2 min. Mixing was continued for another 8 min. In the compatibilized blend system, polyvinyl alcohol and 4 php of maleic acid were added after 2 min, followed by 0.1 php of dicumyl peroxide 1 min later. Mixing was continued for another 7 min. The torque development was recorded during mixing. The blends were taken out and sheeted through a laboratory two-roll mill at a 2.0 mm nip setting. The blends were compression moulded in an electrically heated hydraulic press. Hot-press procedures involved preheating at 150°C for 4 min followed by further 4 min compression at the same temperature and subsequent cooling under pressure for 3 min.

FTIR Spectroscopy
The chemical characterization was performed by Attenuated Total Reflection Fourier Infrared (ATR-FTIR) carried out using a Perkin Elmer Spectrometer (USA) in the range of 4000-600 cm⁻¹. For each spectrum, 52 consecutive scans with 4 cm⁻¹ resolution were recorded. The neat PVA, neat LLDPE and LLDPE/PVA blends without compatibilizer were dried for 24 h at 80°C using an air oven prior to testing. The LLDPE/PVA blend compatibilized with maleic acid was purified by initially immersing in acetone for 24 h and then rinsing three times with distilled water. It was then maintained in air oven for 24 h at 80°C for solvent evaporation followed by Soxhlet extraction for 10 h using distilled water to eliminate unbound PVA to the LLDPE matrix. Finally, the blend was dried for 24 h at 80°C using the air oven.

Measurement of Tensile Properties
Tensile tests were carried out according to ASTM D 638
using Instron 3366 (USA). Dumb-bell specimens (1 mm thick) were cut from the moulded sheets with a Wallace (Malaysia) die cutter. A crosshead 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. Tensile strength, Young’s modulus, and elongation-at-break data were evaluated from the stress-strain determinations.

DSC Measurements
The differential scanning calorimetry (DSC) measurements of blends were carried out by using Perkin-Elmer Pyris 1 DSC (USA) under nitrogen atmosphere. Each blend was first heated from 30°C to 170°C at a heating rate of 10°C/min, then it was annealed for 5 min at 170°C, cooled from 170°C to -50°C at a cooling rate of 10°C/min, and rescanned from -50°C to 300°C at a heating rate of 10°C/min (second scan). 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 DSC thermograms.

The degree of crystallinity (X_c) of LLDPE in the blend was evaluated from the following equation:

\[ X_c = \frac{\Delta H_{exp}}{\Delta H^*} \cdot W_f \]

where, \( \Delta H_{exp} \) is the experimental heat of fusion determined from DSC, \( \Delta H^* \) is the heat of fusion of fully crystalline LLDPE 290 J/g [24], and \( W_f \) is the weight fraction of LLDPE in the blend.

Thermogravimetric Analysis
Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (TGA 7) (USA) under nitrogen atmosphere to avoid oxidation. Each blend weighed 10 ± 0.5 mg, and heated from 30°C to 700°C at a heating rate of 20°C/min.

SEM
The blends were characterized using a scanning electron microscope (model Zeiss Supra 35VP, Germany). The fracture ends of the specimens were mounted on aluminium stubs and were sputter coated with a thin layer of gold to avoid electrostatic charge during examination.

RESULTS AND DISCUSSION
Rheology
Figure 1 shows the torque versus mixing time for LLDPE/PVA blends with and without compatibilizer containing 40 php PVA. The results show that the torque is increased drastically as the LLDPE granules are being charged into the mixer chamber. After 2 min, LLDPE which underwent melting stage produced lower torque value. When the second component (PVA with or without maleic acid) was added to the molten LLDPE (on 2nd min) it showed sudden increases in torque due to the resistance exhibited by PVA in the LLDPE matrix. Later, the torque gradually dropped and reached a steady value for LLDPE/PVA without maleic acid. However, the LLDPE/PVA blends with incorporation of maleic acid showed an opposite trend when dicumyl-peroxide was added at the 3rd min of mixing.

Figure 2 shows the effect of blend ratio on the equilibrium torque at 10 min of mixing of LLDPE/PVA blends with and without maleic acid. It is obvious that both systems (with or without maleic acid) show an upward trend of equilibrium torque to a maximum value at 40 php PVA content in the blends. The LLDPE/PVA blends with maleic acid added exhibited a higher equilibrium torque as compared to the uncompatibilized LLDPE/PVA blends. This could be attributed to the increased ester cross-linkages as maleic acid which was grafted onto LLDPE to react with hydroxyl groups of PVA. The ester cross-linkages increased with increasing PVA content in compatibilized blends, the extent of which was
Figure 2. The effect of blend ratio on the stabilization torque at 10 min of the LLDPE/PVA blends with and without maleic acid.

reflected by increased melt viscosity. The possible reaction between PVA, maleic acid, and LLDPE during blending is given in Scheme I. However, the further increase in PVA loading led to decreased equilibrium torques in both systems. This is due to the plasticizing effect caused by the hydroxyl groups of PVA for both systems.

During the reactive blending of the LLDPE/PVA blends with maleic acid, the carboxylic group of the latter could react with the hydroxyl of the former to form ester cross-linkages. Furthermore, the carbon-carbon double bond of maleic acid was grafted onto LLDPE molecule through a free radical mechanism initiated by dicumyl-peroxide. These reactions contributed to the difference in magnitudes of the torques between the LLDPE/PVA blends with and without maleic acid.

FTIR Analysis

The FTIR spectra of neat LLDPE, neat PVA, and LLDPE/PVA blends with and without maleic acid are shown in Figure 3. Spectrum a in Figure 3, shows the characteristic C-H stretching bands with two
peaks at 2915 cm$^{-1}$ and 2847 cm$^{-1}$, C-H bending at 1461 cm$^{-1}$, and C-H out-of-plane bending bands at 729 cm$^{-1}$ and 718 cm$^{-1}$. All peaks are also present in the LLDPE/PVA blend (spectrum c in Figure 3) with an additional peak at 3358 cm$^{-1}$ corresponding to the stretching vibration of the hydroxyl groups, but stretching vibrations of carbonyl groups at 1052 cm$^{-1}$ and acyclic C=C at 1658 cm$^{-1}$ correspond to PVA component (spectrum b in Figure 3). The carbonyl group is the result of incomplete removal of acetic groups during production of PVA through indirect method of hydrolysis of polyvinyl acetate. However, these peaks disappear in the LLDPE/PVA blend with the incorporation of maleic acid, suggesting to esterification reactions. Spectrum d in Figure 3 also shows new absorption bands consistent with ester bonds at 1261 cm$^{-1}$, 1095 cm$^{-1}$, and 1020 cm$^{-1}$ and similarly the carbonyl bond (C=O) from maleic acid which is being cross-linked with LLDPE at 1712 cm$^{-1}$. Furthermore, it seems that the carbon radical center of LLDPE must have attacked the unsaturated maleic acid and produced a tertiary carbon which shows a strong and high intensity peak at 800 cm$^{-1}$ [23]. The high-intensity peak at 800 cm$^{-1}$ indicates that the high concentration of tertiary carbon is formed during the grafted process.

Miscibility of the Blend

Figure 4 shows the peak melting temperature ($T_{mp}$) of the LLDPE and PVA phases in the LLDPE/PVA blends with and without maleic acid. Without maleic acid, the $T_{mp}$ of LLDPE and PVA in the blends remains practically unaffected by the variation in PVA content. However, when maleic acid is incorporated in the LLDPE/PVA blends, the $T_{mp}$ of LLDPE shows a slight decrease (1°C difference) as compared to the respective uncompatibilized LLDPE/PVA blends. Similarly, there is a decrease of about 10°C in the $T_{mp}$ of PVA. It is believed that the esterification reaction and the grafts formed through the addition of maleic acid are responsible for the decrease in $T_{mp}$s of LLDPE and PVA in the blends.

This formation may have disturbed the chain arrangement and prevented a good crystal packing, which results in depression of $T_{mp}$ of PVA. This result is compatible with a study of Yordanov et al. [26]. They reported that when a compatibilizer is incorporated in the linear low-density polyethylene/polyamide 6 blends, small decreases in the melting temperatures of both linear low-density polyethylene (1°C difference) and polyamide 6 (5°C difference) are indications of their better compatibility as compared to the uncompatibilized blends.
The melt crystallization temperatures ($T_c$) of LLDPE in the LLDPE/PVA blends with and without maleic acid are presented in Table 1. The cooling scan of the PVA phase has been excluded from the study in order to avoid the degradation of PVA during annealing. The cooling of all samples was performed from 170°C (below degradation temperature of PVA). The $T_c$ of the LLDPE phase in the uncompatibilized LLDPE/PVA blends is increased slightly with an increased PVA content. It is proposed [19] that the PVA molecules interrupt the crystallization process of LLDPE in the LLDPE/PVA blends, which induces lower thermodynamic stability and hence a higher $T_c$ of LLDPE during the cooling process. Minkova et al. [27] reported that when non-polar LLDPE is blended with polar polyamide 6, the $T_c$ of LLDPE increases due to weak interactions between the two components and the segregation of the LLDPE phase in the blends. When maleic acid compatibilizer is added into the LLDPE/PVA blends, their $T_c$s shift to lower temperatures as compared to those of the uncompatibilized blends. Interestingly, the decreases in $T_c$ occur at the blend ratio of 60/40, which is close to the $T_c$ of the neat LLDPE. No definite reason has been provided for this observation. Nevertheless, this indicates that maleic acid increases the compatibility between the

<table>
<thead>
<tr>
<th>Sample (php)</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$X_c$ (%)</th>
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<tr>
<td>LLDPE/PVA: 100/0</td>
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<td>115.57</td>
<td>60.27</td>
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<td>117.96</td>
<td>38.49</td>
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Figure 5. Degree of crystallinity of LLDPE in the LLDPE/PVA blends with and without maleic acid.

Figure 5 shows the degree of crystallinity of LLDPE as measured from the heat of fusion (ΔH) obtained from the DSC results for the second scan (Table 1). It can be seen that the degree of crystallinity of LLDPE is significantly decreased with lower LLDPE content of both systems. According to Groeninckx et al. [28], a sharp drop in the degree of crystallinity of LLDPE with its lower content in the blends is due to the immiscibility of the two components. Figure 8 also shows that with the same PVA content, the LLDPE/PVA blends with maleic acid exhibit lower degree of crystallinity compared to the LLDPE/PVA blends of no maleic acid content. This is due to the effect of cross-linking buildup between the maleic acid and LLDPE/PVA, leading to more defects in the crystallization of the LLDPE/PVA blends. Other researchers have also reported that the decrease in crystallinity upon cross-linking is due to the fact that cross-linking provides some hindrance to the ordered arrangement of the polymer chains [29-32].

Thermogravimetry Studies

Figures 6a and 6b show the thermogravimetric analysis (TGA) and its derivatives for the LLDPE/PVA blends with and without a compatibilizer. For comparison, the curves of the pure LLDPE and PVA are shown in Figure 6.

In general, both systems show a two-stage degradation process, except the pure LLDPE. The first degradation stage between 230°C to 400°C is due to water evaporation from the decomposition of hydroxyl groups [15]. The second degradation stage between 410°C to 520°C is due to chain scission of the carbon-carbon bonds in the main chain. It is clear that there is a very different trend in degradation of the LLDPE/PVA blends from that of neat LLDPE. This may indicate that PVA does not affect the degradation process of the blends due to weak interactions between the two components. For compatibilized blends, although a similar two-stage degradation is observed, but it is shifted to a higher temperature as compared to their respective uncompatibilized blends. This indicates that the LLDPE/PVA blends with maleic acid are relatively more stable compared with the uncompatibilized
Table 2. DTG$_{\text{max}}$ for the LLDPE/PVA blends with and without maleic acid.

<table>
<thead>
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<th>Sample (php)</th>
<th>$T_{\text{mp}}$ (°C)</th>
<th>$T_c$ (°C)</th>
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<td>LLDPE/PVA: 100/0</td>
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<td>501</td>
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<tr>
<td>LLDPE/PVA: 60/40</td>
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<td>499</td>
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<tr>
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<td>-</td>
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<tr>
<td>LLDPE/PVA: 60/40 and maleic acid</td>
<td>383</td>
<td>491</td>
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<tr>
<td>LLDPE/PVA: 50/50 and maleic acid</td>
<td>383</td>
<td>486</td>
</tr>
<tr>
<td>LLDPE/PVA: 40/60 and maleic acid</td>
<td>380</td>
<td>480</td>
</tr>
</tbody>
</table>

 systems. This is consistent with the proposed role of maleic acid acting as a cross-linker in the blend system by holding the two phases together, leading to the high thermal stability of the LLDPE/PVA blends.

The temperature of the maximum derivative of thermogravimetric analysis in Table 2 was extracted from the DTG derivative as shown in Figure 6b. It can be seen that for both systems, there are two separated DTG$_{\text{max}}$ which correspond to a two-stage degradation process with the exception of neat LLDPE. This indicates that a separation phase has occurred between the LLDPE and PVA components. However, with similar PVA content, the LLDPE/PVA blends with maleic acid show a higher temperature of DTG$_{\text{max}}$ on the first stage of the degradation process and a lower temperature of DTG$_{\text{max}}$ as compared to the LLDPE/PVA blends without maleic acid.

According to Jana et al. [33], the compatibilized low-density polyethylene/poly(dimethyl siloxane) rubber blends show that the higher temperatures of the degradation process and DTG$_{\text{max}}$ are indications of the better compatibility between the two components as compared to the uncompatibilized blends.

**Tensile Properties**

Figure 7 shows the effect of PVA content on the tensile strength of the LLDPE/PVA blends with and without maleic acid. It can be seen that the tensile strength of the LLDPE/PVA blends without maleic acid decreases steadily by increasing the PVA content. The reduction observed is due to the poor interfacial adhesion between the two polymers with different polarities which results in poor stress-transfer between the matrix and the dispersed phase.

It is believed that PVA formed agglomerates due to the strong intramolecular hydrogen bonds between the hydroxyl groups which result in its poor dispersion in LLDPE, particularly at higher PVA contents. However, as maleic acid was added into the LLDPE/PVA blends, up to 50 php PVA content, the tensile strength of the blends significantly increased and beyond this value it is decreased. This is again due to the capability of maleic acid to improve PVA dispersion and enhance the interaction between the LLDPE and PVA components (SEM section). As it is discussed already, Scheme I shows the proposed
chemical interactions between the LLDPE and PVA in the presence of maleic acid. Meanwhile, the decrease in compatibilized blends after the addition of 50 php of PVA content is due to the plasticizing effect that could be significant beyond this content.

The relationship between Young's modulus and elongation-at-break, and the PVA content for the LLDPE/PVA blends with and without maleic acid are shown in Figures 8 and 9, respectively. As anticipated, the Young's modulus is increased with an increase in PVA content, whereas the elongation-at-break is decreased. However, with the same PVA content, the LLDPE/PVA blends with maleic acid show higher Young's modulus and elongation-at-break compared to the LLDPE/PVA blends without maleic acid. This is due to the outcome of cross-linking and the better interactions between the LLDPE and PVA components in the presence of maleic acid.

**Morphology Studies**

The comparison of the SEM tensile fractures of LLDPE/PVA: 90/10 and 60/40 php blends with and without maleic acid at 100× magnification are shown in Figures 10 and 11, respectively. It is found that maleic acid produced an entirely different morphology in the LLDPE/PVA blends. Without maleic acid, the micrograph of the LLDPE/PVA blends (Figures 10a and 10b) exhibits several PVA phases clustered together forming big individual agglomerates with irregular shapes and sizes, and

**Figure 9.** Plots of the variation of PVA content vs. elongation-at-break of the LLDPE/PVA blends with and without maleic acid.

**Figure 10.** SEM micrographs of tensile fracture surface of uncompatibilized blends of: (a) LLDPE/PVA: 90/10 and (b) LLDPE/PVA: 60/40 at magnification 100×, and (c) LLDPE/PVA: 60/40 at magnification 300×.
several holes formed due to the detachment of the PVA agglomerates from the LLDPE matrix. The agglomerates and holes formation are evidence for increased interfacial tension and separation phase between the PVA and LLDPE components. Furthermore, LLDPE/PVA: 60/40 php, (arrows in Figure 10c) clearly shows the distinct boundaries with cavities that separate the PVA agglomerates and the LLDPE matrix, indicating the increase in interfacial tension of the blends with increased PVA content.

However, the LLDPE/PVA 90/10 php blends with addition of maleic acid (Figure 11a) have produced a smaller size PVA agglomerates which to a certain degree are covered with LLDPE. The SEM micrographs (Figures 11b and 11c) show elongated fibrils extending over the surface of the PVA agglomerates of the fractured surface which are indication of good interactions between the two polymers. Perhaps, this fibril is a grafted LLDPE that cross-link with PVA because it connects the boundaries of the two polymers. Several works have shown that the addition of compatibilizers improves interfacial adhesion through steric stabilization [34] and good wetting and lowering surface tension [35]. It is suggested that similar mechanism is operative in this system described above.

CONCLUSION

The following conclusions can be drawn from this study:
- The presence of maleic acid up to 40 php has increased the processing torque of the LLDPE/PVA blends which then it is decreased by increased maleic acid content.
- The compatibility of the LLDPE/PVA blends is enhanced by maleic acid as shown by the depression of the melting temperature of the PVA component.
- The tensile properties such as tensile strength, elongation-at-break and Young's modulus, and the thermal stability of the LLDPE/PVA blends are improved by the incorporation of maleic acid.
- The SEM tensile fracture of the blends shows that maleic acid has improved the adhesion between the PVA dispersed phase and the LLDPE matrix.
ACKNOWLEDGEMENT

One of the authors is thankful for the financial support from the Research University of Universiti Sains Malaysia, (USM-RU-PRGS), Grant No. 1001/PBAHAN/8041007.

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