Effects of Kenaf Loading on Processability and Properties of Linear Low-Density Polyethylene/Poly (Vinyl Alcohol)/Kenaf Composites

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This study was conducted to evaluate the possibility of utilizing kenaf (KNF) in LLDPE/PVOH to develop a new thermoplastic composite. The effect of KNF loading on the processability and mechanical, thermal and water absorption properties of linear low-density polyethylene/poly (vinyl alcohol)/kenaf (LLDPE/PVOM/KNF) composites were investigated. Composites with different KNF loadings (0, 10, 20, 30, and 40 phr) were prepared using a Thermo Haake Polydrive internal mixer at a temperature of 150 °C and rotor speed of 50 rpm for 10 min. The results indicate that the stabilization torque, tensile modulus, water uptake, and thermal stability increased, while tensile strength and elongation at break decreased with increasing filler loading. The tensile fractured surfaces observed by scanning electron microscopy (SEM) supported the deterioration in tensile properties of the LLDPE/PVOM/KNF composites with increasing KNF loading.

Keywords: Linear low density polyethylene; Poly(vinyl alcohol); Kenaf; Composites; Kenaf loading

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INTRODUCTION

Enthusiasm in reducing the demand for petroleum-based polymers has brought about the idea of blending polymers with synthetic and/or natural fillers or with biodegradable polymers. Examples of such include polypropylene (PP)/linear low-density polyethylene (LLDPE) filled with wood powder and low density polyethylene (LDPE)/thermoplastic sago starch (TPSS) reinforced with kenaf fiber (Dikobe and Luyt 2010; Majid et al. 2010). Polyolefins, especially polyethylene (PE), have been widely used in daily life for short term applications such as plastic bags, packaging films, healthcare products, and automobile parts (Noranizan and Ahmad 2012). Linear low-density polyethylene (LLDPE), one class of polymer under PE, is widely used in packaging applications; however, its resistance to biodegradation causes environmental pollution (Sam et al. 2009; Dikobe and Luyt 2010; Nordin et al. 2012). Poly(vinyl alcohol) (PVOH) is a water-soluble biodegradable polymer that is extensively used in packaging applications (Othman et al. 2011; Rahmah et al. 2013). It is well known for its biodegradability and strength, but with the limitation of having low water/humidity resistance and poor processability (Ismail et al. 2009; Azahari et al. 2011; Othman et al. 2011). Nordin et al. (2012) reported that blending LLDPE with PVOH is possible, but only at a suitable ratio for optimum properties. Meanwhile, research by Rahmah et al. (2013) reported a decrease
in tensile strength and an increase in tensile modulus with increasing sago starch (SS) content for hybrid films of linear low-density polyethylene (LLDPE)-sago starch (SS)-poly(vinyl alcohol) (PVOH).

Over the past few years, exploitation on the usage of natural fibers in polymer composites has gained great interest from researchers all over the world (Malkapuram et al. 2009). The benefits of natural fibers that make them attractive include their relatively low cost, light weight, environmental friendliness, and competency in terms of strength per weight of material (John and Thomas 2008; Malkapuram et al. 2009). In the 21st century, the growing awareness of avoiding destruction of forests has raised the demand of using non-wood plant fiber instead of wood plant fiber (Ashori et al. 2006). Examples of non-wood plant fibers include bagasse, bamboo, rattan, wheat, and kenaf, which have become attractive alternatives to natural fibers for use as reinforcement and/or fillers (Ashori et al. 2006). Of all the non-wood plant fibers, kenaf (Hibiscus cannabinus) has been widely used in research studies (Ismail et al. 2010; Majid et al. 2010; Akil et al. 2011; Pang and Ismail 2013; Saba et al. 2015). For instance, Pang and Ismail (2013) introduced kenaf into polypropylene/waste tire dust composites and found that the tensile modulus and thermal stability of the composite increased with the addition of kenaf.

Although kenaf fiber is a popular fiber in many polymer composites, to the best of this work’s knowledge, so far, the introduction of kenaf fiber into LLDPE/PVOH blend has not been studied or reported. Therefore, the objectives of this study are to determine the possibility of using kenaf as reinforcement in LLDPE/PVOH/KNF composites, to produce a new thermoplastic composite based on kenaf, and to investigate the effect of kenaf loading on the processability and properties (mechanical, thermal and water absorption) of LLDPE/PVOH/KNF composites.

**EXPERIMENTAL**

**Materials**

Linear low-density polyethylene (LLDPE) was supplied by PT Lotte Chemical Titan Nusantara, Indonesia, with a melt flow rate of 1 g/10 min at 190 °C and a density of 0.92 g/cm³. Poly(vinyl alcohol) (99+ % hydrolyzed) was supplied by Sigma-Aldrich (Malaysia) Sdn. Bhd., with a molecular weight of 89,000 to 98,000 g/mol and a density of 1.269 g/cm³. Kenaf (KNF) was obtained from National Kenaf and Tobacco Board (LKTN), Kelantan, Malaysia. Before treatment, the KNF was subjected to a grinding process, where KNF was ground using a mini grinder from Rong Tsong Precision Technology Co. (Taiwan) with Product Id: RT-34 to yield an average particle size of 75 µm.

**Composite preparations**

The KNF was dried in a vacuum oven at 80 °C, 24 h prior to being used in the composites preparation. The weight ratio of LLDPE/PVOH was maintained at 60:40 (by weight percent), with different KNF loadings (0, 10, 20, 30, and 40 parts per hundred). The melt compounding of a series of LLDPE/PVOH/KNF composites were performed in an internal mixer (Thermo Haake Polydrive (Germany), Model R600/610) at a temperature of 150 °C and rotor speed of 50 rpm. The LLDPE was loaded into the mixing chamber and allowed to melt for 2 min, followed by addition of PVOH and KNF after 2 min and 6 min, respectively. The processing torque was recorded for each sample. The compounded samples were then compression-molded at 150 °C into 1 mm thick sheets using an
electrically heated hydraulic press (GoTech Testing Machine (Taiwan), Model KT-7014 A).

**Methods**

*Measurement of tensile properties*

The tensile testing was done in accordance with ASTM D638 by using an Instron 3366 Universal Testing Machine. The crosshead speed was set at 5 mm/min with a constant gauge length of 50 mm. The tests were performed at 25 ± 3 °C on the 1 mm thick dumbbell-shaped specimens and an average of five readings of tensile strength, tensile modulus, and elongation at break were recorded.

*Morphological study*

A Leo Supra-35VP field emission scanning electron microscope (SEM) was used to observe the tensile fractured surfaces of the specimens. The fractured surfaces of the specimens were sputter-coated with a thin layer of gold to avoid electrostatic charging and poor resolution. The specimens were then mounted onto the aluminum stubs for examination.

*Water uptake*

The water uptake test was carried out in accordance with ASTM D570. The specimens were first dried in an oven for 24 h at 50 °C until a constant weight was obtained. The weight difference after immersion was recorded by weighing them periodically on a Sartorius balance, Model: BS224S, with a precision of 1 mg. The excess water on the specimen surfaces was removed with tissue paper before weighing. The water uptake test was performed for 30 days and the percentage of water uptake was calculated using Eq. (1),

\[ W_t(\%) = \frac{W_2-W_1}{W_1} \times 100 \]  

(1)

where \( W_t \) is the total water uptake by the specimen, and \( W_1 \) and \( W_2 \) are the weights of the specimen before and after immersion in distilled water, respectively.

*Thermogravimetric analysis (TGA)*

Thermogravimetric analysis (TGA) was performed by using a Perkin Elmer (USA) Pyris 6 TGA. TGA analysis was conducted in ramp mode from 30 to 600 °C under nitrogen at a flow rate of 50 mL/min. The heating rate was 20 °C/min.

**RESULTS AND DISCUSSION**

**Processing Torque**

Figure 1 shows the processing torque versus mixing time data for the LLDPE/PVOH/KNF composites with different KNF loadings. For all the composites, a similar trend of processing torque curves are observed. It is clearly seen that the torque increased drastically as LLDPE granules were added into the mixing chamber. Then, the LLDPE underwent a melting stage, which resulted in a lower torque value. After 120 seconds, when PVOH was added into the mixing chamber, once again the torque value
suddenly increased drastically. This sudden increase in torque can be attributed to the resistance exhibited by PVOH in the LLDPE. A similar observation was reported by Ismail et al. (2010) on the processing torque of a LLDPE/PVOH blend. The torque value then decreased gradually due to the melting of PVOH. After 360 seconds, the KNF was added to the mixing chamber causing the torque to increase due to the increase in the resistance of KNF in the LLDPE/PVOH matrix. The torque then gradually dropped and reached a steady value at the end of the mixing time of 600 seconds.

**Fig. 1.** Processing torque versus mixing time of the LLDPE/PVOH/KNF composites with different KNF loadings

Figure 2 shows the stabilization torque for the LLDPE/PVOH/KNF composites with different KNF loadings at 10 min of mixing time. The steady torque value mentioned earlier can be referred to as the stable torque or equilibrium torque value obtained at the end of the mixing stage (Pang and Ismail 2013).

**Fig. 2.** Stabilization torque for the LLDPE/PVOH/KNF composites with different KNF loadings at 10 minutes of mixing time

It is obvious that the stabilization torque value increased for the LLDPE/PVOH/KNF composites with increasing KNF loading. Higher KNF loading tends to limit the space for the movement of the LLDPE/PVOH matrix and subsequently increases the composites’ resistance to flow in the mixture; thus, the LLDPE/PVOH/KNF composites with 40 phr KNF showed the highest stabilization torque value of 17.8 Nm and
the processability was more difficult compared to the LLDPE/PVOH/KNF composites with other KNF loadings. According to Sarifuddin et al. (2013), the greater the kenaf core fiber (KCF) loading in low-density polyethylene/thermoplastic sago starch/kenaf core fiber (LDPE/TPSS/KCF) composites, the higher the torque value.

**Tensile Properties**

Figure 3 shows the tensile strength of the LLDPE/PVOH/KNF composites with different KNF loadings. The incorporation of KNF resulted in lower tensile strength, which continued to decrease with increasing KNF loading. Several other researchers have reported similar findings on natural fiber-reinforced polymer composites (Ismail et al. 2010; Balakrishna et al. 2012). The main reason for the decrease in tensile strength of the LLDPE/PVOH/KNF composites was due to incompatibility among the components; the highly hydrophilic KNF was not compatible with the hydrophobic matrix, causing the formation of weak interface between them. Consequently, stress was inefficiently transferred across the matrix-filler interface when stress was applied. The weak interface region of KNF and LLDPE/PVOH may also act as a stress concentrator (failure site), and as a result, a weakened interaction between them and debonding at the interface. Another factor that contributes to the deterioration of tensile strength at higher KNF loading is the de-wetting effect (Ismail et al. 2010). Higher KNF loading levels tend to promote more filler-filler interaction as compared to filler-matrix interaction; therefore, the wettability of KNF by the LLDPE/PVOH matrix was significantly reduced, which also resulted in poor stress transfer upon stress application.

![Fig. 3. Tensile strength of the LLDPE/PVOH/KNF composites with different KNF loadings](image)

Figure 4 shows the tensile modulus of the LLDPE/PVOH/KNF composites with different KNF loadings. Tensile modulus of a composite corresponds to its stiffness, *i.e.*, the higher the value of tensile modulus, the stiffer the composites are. According to John and Thomas (2008) and Supri and Ismail (2011), tensile modulus or stiffness of a composite also depends on the stiffness of the filler itself. In this study, the incorporation of KNF increased the stiffness of the composites, as shown by the higher tensile modulus, which gradually increased with increasing KNF loading. The presence of the KNF filler restricted the LLDPE/PVOH matrix from moving freely, thereby increasing the rigidity of the composite. This finding was in good agreement with other studies (Ismail et al. 2010; Santiagoo et al. 2011).
Figure 4 shows the elongation at break of the LLDPE/PVOH/KNF composites with different KNF loadings. From the results, the elongation at break of the composites decreased with increasing KNF loading. This is due to the incorporation of KNF, which reduced the deformability of the composites by the restriction on the matrix chain. Higher KNF loading made it difficult for composites to deform upon stress application. This was due to the poor stress transfer at the weak KNF-LLDPE/PVOH interface. Similar trends were observed in other works (Ismail et al. 2010; Pang and Ismail 2013; Sarifuddin et al. 2013).

Morphological Study

Figure 6 shows the SEM micrograph of the tensile-fractured surface of the LLDPE/PVOH matrix at a magnification of 200X. It shows that the presence of PVOH agglomerates results in phase separation between the LLDPE and PVOH. Additionally, the holes are due to the detachment of the PVOH agglomerates from the LLDPE. The formation of PVOH agglomerates and holes are evidence of the weak interfacial adhesion between the LLDPE and PVOH. This finding is in good agreement with a previous study by Ismail et al. (2009), which reported that there is poor interaction and phase separation between PVOH and LLDPE due to their incompatibility. The point of interest, however,
would be the presence of fiber debonding in the composites; therefore, in Fig. 6, there is absence of voids or fiber detachment sites due to the absence of KNF.

![Fig. 6. SEM micrograph of the tensile-fractured surface of the LLDPE/PVOH matrix (at 200x magnification)](image)

In Fig. 7a to d, the SEM micrographs show that several micro-voids and fiber detachment sites formed in the LLDPE/PVOH/KNF composites after the incorporation of KNF at all loading levels. The presence of the failure sites (voids and detachment sites) indicates the poor interfacial adhesion between the LLDPE/PVOH matrix and the KNF as a result of their incompatibility. At the lowest KNF loading (10 phr), however, the KNF seemed embedded in the matrix and less KNF detachment sites were observed (Fig. 7a). This finding justifies the higher tensile strength of the LLDPE/PVOH/10 KNF composite.
compared to the composites with other KNF loadings. Meanwhile, Fig. 7d shows that some of the KNF was damaged and there is a greater amount of KNF debonding observed. This phenomenon indicated poorer interfacial adhesion between the KNF and the LLDPE/PVOH matrix at higher KNF loading levels as a result of poor fiber wetting. Thus, the SEM findings support the results of tensile property findings.

**Water Absorption**

Figure 8 shows the percentage of water absorption as a function of immersion time for the LLDPE/PVOH/KNF composites with different KNF loadings. For the LLDPE/PVOH matrix, initially the water absorption increased rapidly for the first few days, and then remained almost constant until reaching its equilibrium point. The water uptake by the matrix is due to the presence of hydroxyl groups of the PVOH (Tan et al. 2014).

![Figure 8. Percentage of water absorption as a function of immersion time for the LLDPE/PVOH/KNF composites with different KNF loadings](image)

It can be seen that the water absorption of the LLDPE/PVOH/KNF composites initially increased, then decreased after 2 days of immersion, followed by a slight increase until the 7th day before gradually decreasing again at a very slow rate. The decrease trend in water absorption after 2 days is due to the possibility that PVOH leached out from the composites and dissolved slowly in the water (Tan et al. 2014). The leaching of PVOH tends to cause the KNF to detach from the composites and leach into the water. This is because the LLDPE/PVOH matrix, which acts as a binder and is unable to hold the KNF in the composites, thus causing the KNF to leach out and make the water become turbid with time. According to Tan et al. (2014), the reduction in water uptake of kenaf fiber-PVOH composites with time is due to the leaching of both PVOH and kenaf fiber.

Figure 8 shows that the water absorption of the composites increased with increasing KNF loading from 10 to 40 phr. The structure of KNF itself consists of hydroxyl groups, which gives KNF the hydrophilic nature and tendency to form hydrogen bonding when reacted with water; therefore, the hydroxyl groups of the KNF increased with increasing KNF loading, and, hence, impart greater water absorption due to the ability to form hydrogen bonds with water. Balakrishna et al. (2012) and Seong Chun et al. (2013)
also found that greater amounts of hydroxyl groups are available to bond with water at higher filler loading levels. The other reason for the increasing water absorption is due to the weak interfacial adhesion between the KNF and the LLDPE/PVOH matrix. The weak interfacial adhesion may cause formation of microcracks or voids that allow water to be absorbed by the composite (Demir et al. 2006). Tan et al. (2014) reported that the water absorption ability of kenaf fiber-PVOH composites comes from the water absorption properties of both the kenaf and the PVOH.

**Thermogravimetric Analysis (TGA)**

Figures 9 and 10 show the TGA and DTG curves of the LLDPE/PVOH and LLDPE/PVOH/KNF composites with different KNF loadings. The TGA data is tabulated in Table 1.

![Fig. 9. TGA curves of the LLDPE/PVOH and LLDPE/PVOH/KNF composites with different KNF loadings](image)

From Fig. 9, it can be seen that the weight loss of LLDPE/PVOH matrix occurred in a two-stage degradation process from 230 to 520 °C. This result can be confirmed by the presence of two peaks from the DTG curves in Fig. 10. The first stage of degradation happened between 230 and 400 °C and is related to the decomposition of hydroxyl groups of the PVOH. The second stage of degradation occurred from 410 to 550 °C and is due to the chain scission of the carbon-carbon bond in the main chain of the LLDPE as reported by Nordin et al. (2012).

As for all the LLDPE/PVOH/KNF composites, thermal degradation occurred in a three stage degradation process. This result is also confirmed by the presence of three peaks from the DTG curves in Fig. 10. The first stage of weight loss happened up to a temperature of 100 °C, due to gradual evaporation of absorbed moisture. The second stage of weight loss occurred in the temperature range of 250 to 400 °C, due to thermal degradation of KNF. According to Fisher et al. (2002), the weight loss that occurred approximately between 200 °C and 400 °C was due to the thermal decomposition of the three major constituents (hemicelluloses, cellulose, and lignin). Between 450 and 550 °C, the third stage of weight loss took place, corresponding to the decomposition of LLDPE.
The temperature at which 5% weight loss ($T_{5\%}$) occurred was lower for the LLDPE/PVOH/KNF composites than that of the LLDPE/PVOH for all loading levels. Meanwhile, $T_{5\%}$ of the LLDPE/PVOH/KNF composites decreased with increasing KNF loading. The incorporation of KNF resulted in early thermal decomposition of the composites at a lower temperature, due to the low thermal stability of KNF. Seong Chun et al. (2013) reported that the low thermal decomposition temperature of recycled polypropylene/coconut shell power (rPP/CSP) composites was due to the low thermal stability of hemicelluloses in CSP. The decomposition temperature at the maximum rate of weight loss ($T_{\text{max}}$) of the composites can be related to the thermal decomposition temperature of the LLDPE/PVOH matrix. From Table 1, the $T_{\text{max}}$ increased with the incorporation of KNF and gradually increased with increasing KNF loading. This observation indicates that the incorporation of KNF improved the thermal stability of the LLDPE/PVOH matrix at high temperature.

**Table 1. TGA Data of LLDPE/PVOH and LLDPE/PVOH/KNF Composites with Various KNF Loadings**

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>Char Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLDPE/PVOH</td>
<td>283</td>
<td>473</td>
<td>0.762</td>
</tr>
<tr>
<td>LLDPE/PVOH/10 KNF</td>
<td>277</td>
<td>476</td>
<td>1.308</td>
</tr>
<tr>
<td>LLDPE/PVOH/20 KNF</td>
<td>276</td>
<td>480</td>
<td>5.570</td>
</tr>
<tr>
<td>LLDPE/PVOH/30 KNF</td>
<td>235</td>
<td>483</td>
<td>5.867</td>
</tr>
<tr>
<td>LLDPE/PVOH/40 KNF</td>
<td>234</td>
<td>484</td>
<td>8.560</td>
</tr>
</tbody>
</table>

It can be seen that the percentage of char residue showed an increasing trend with increasing KNF loading. The formation of char residue provides a barrier between the heat source and the polymeric material by slowing down or inhibiting the out-diffusion of volatile decomposition products from the composites (Beyler and Hirschler 2001; Ismail et al. 2008). Thus, with increasing KNF loading, the char residue increased and hence formed a thicker barrier/layer between the heat source and polymeric material. The thick
barrier/layer of char residue resulted in a higher temperature being required for decomposition of the composites; therefore, the thermal stability of the composites increased with increasing KNF loading.

**CONCLUSIONS**

1. The processability of the composites became more difficult as the kenaf fiber (KNF) loading increased.
2. Tensile strength and elongation at break of the composites decreased with increasing KNF loading.
3. Tensile modulus increased with increasing KNF loading.
4. Water absorption of the composites increased with increasing KNF loading.
5. The thermal stability of the composites increased with KNF loading, as a higher temperature at the maximum weight loss rate ($T_{\text{max}}$) and char residue were observed for the composite with higher KNF loading.

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