Effects of Polyethylene-g-maleic Anhydride on Properties of Low Density Polyethylene/Thermoplastic Sago Starch Reinforced Kenaf Fibre Composites

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Received 18 July 2009; accepted 25 May 2010

ABSTRACT

Effects of polyethylene-g-maleic anhydride (PE-g-MA) as a compatibilizer on tensile properties and morphology of low density polyethylene/thermoplastic sago starch (TPSS)-kenaf fibre composites were studied. TPSS was prepared by mixing the starch (65 wt%) and glycerol (35 wt%) and storing it overnight at room temperature. The mixture was then melt-compounded using a heated 2 roll-mills at 150°C for 20 min. LDPE/TPSS blend ratio was fixed at 80 wt% of LDPE and 20 wt% of TPSS. LDPE/TPSS-kenaf fibre composites with different fibre loadings, with and without the addition of PE-g-MA were prepared by using an internal mixer at 150°C. All mixings were carried out for 20 min at a rotor speed of 50 rpm. Tensile test specimens were cut out from the compression moulded sheets. Results indicated that the tensile strength and Young's modulus of LDPE/TPSS-kenaf fibre composites with the addition of PE-g-MA were greater than the composites without the addition of PE-g-MA particularly at higher fibre loading. The interfacial properties between LDPE, TPSS and fibre were improved after the addition of PE-g-MA as it is evident from the tensile surface fracture morphology using a scanning electron microscopy. Equilibrium water uptakes for LDPE/TPSS-kenaf fibre composites were higher than those of LDPE/TPSS-kenaf fibre composites with the addition of PE-g-MA due to lower abundance of hydrogen group.

INTRODUCTION

Hydrocarbon-based plastics as long lasting materials usually create problems in living environment [1]. Because of this, some alternatives have been considered to reduce the amount of plastic wastes and the two most popular ways are recycling of plastics and production of degradable and biodegradable plastics [2]. Early production of degradable plastic material focused on native starch filled thermoplastic but only low volume of starch was being used due to inherent loss in the mechanical properties at high starch loading [1-3].

Plasticization is one of the popular ways to improve the properties of starch. Starch and plasticizers that used under pressure and shear, can easily melt and flow, which allows starch to be processed by injection, extrusion and blow moulding, similar to most synthetic thermoplastic polymers.

Key Words:
kenaf; compatibilizer; composites; interfacial adhesion; chemical interaction.

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Native starch commonly exists in the form of single granules with about 15-45% crystallinity. During plasticization, hydrogen bonds are formed between plasticizers and starch, replacing the strong hydrogen bonds between the hydroxyl groups of the starch molecules [3]. Plasticizers, first destroy the native starch crystallinity and then form new morphological structures.

However, the mechanical properties of thermoplastic starch itself do not show any improvement upon plasticization. The two main disadvantages of thermoplastic starch are the low mechanical properties and low water resistance. To improve these properties, blending this thermoplastic starch with common hydrocarbon plastic material, might be the solution for these problems.

Generally, in some applications such as in automobiles, thermoplastic starch blend with hydrocarbon material does not fulfil all requirements. To preserve renewability (renewable raw material), biodegradability and to improve the mechanical properties of the final products, associations between natural fibre and the blend have been investigated [4,5]. One of the popular natural fibres being used in recent years is kenaf fibre. Kenaf fibre (*Hibiscus cannabinus*) is a species of *Hibiscus*, probably native to southern Asia, though its exact natural origin is unknown. Kenaf is one of the allied fibres of jute and shows similar characteristics.

Several studies such as Torres et al. [6] and Mondragon et al. [7] have demonstrated the attraction of using natural fibre as reinforcement in thermoplastic starch matrices but they were just several papers which focused on thermoplastic starch blend with hydrocarbon plastic material-filled with natural fibre. Hydrocarbon plastics reinforced kenaf fibre usually find application in furniture industries. This is due to good mechanical strength of the fibre that prolongs the lifetime of the products.

The purpose of this study was to produce composites of low density polyethylene (LDPE) and thermoplastic sago starch (TPSS) blend-reinforced with kenaf fibre. Most of the previous studies just focused on hydrocarbon polymer materials reinforced natural fibre. Now in this study, blend of LDPE and thermoplastic sago starch has been introduced before the reinforcement process with kenaf fibre. The hydrophilic nature of TPSS and kenaf fibre might have good effects for the composites where both materials might interact with each other due to the existence of the abundance of hydroxyl groups. LDPE has been used because it has more branches than other polyethylenes, which means that the chains do not fit well together. Branches in LDPE reduce the molecular weight of the materials, which then lead to lower intermolecular forces. The instantaneous-dipole induced-dipole attraction in LDPE also is lower due to similar effects, which results in higher degradation potential as compared to HDPE. Therefore, a compatibilizer, polyethylene-g-maleic anhydride (PE-g-MA) was added to the composites to improve LDPE/TPSS-kenaf fibre composite compatibility and also to improve the tensile properties of the composites. Tensile properties of LDPE/TPSS-kenaf fibre composite were determined as a function of kenaf fibre loading. Scanning electron microscopy (SEM) was used to examine the fracture surfaces of the composites to help in explaining the tensile properties data. Water absorption test was carried out to determine the water uptakes for the composites.

**EXPERIMENTAL**

**Materials**

Sago starch was obtained from the Land Custody Development Authority (LCDA), Sarawak (Malaysia). Its moisture content was 13 wt%. The granular sizes ranged from 9 to 35 μm, with an average granule size of 20 μm. Sago starch decomposes at 230°C. Pellets of low density polyethylene (LDPE) with melting temperature of 138°C were obtained from Titan Chemical (Malaysia). Kenaf fibre was obtained from Forest Research Institute of Malaysia (FRIM) with the average length of 5 mm. PE-g-MA was obtained from Sigma-Aldrich (M) Sdn. Bhd. (Malaysia) whereas glycerol was obtained from Ajax Chemicals (Malaysia) respectively.

**Preparation of TPSS**

Sago starch was dried in a vacuum oven for 24 h at 80°C. TPSS was prepared by premixing sago starch in
powder form with 35 wt% liquid glycerol in a kitchen blender with a capacity of 200 g. The mixture was considered ready when the starch was fully covered with the liquid glycerol after mixing for 5 min. In case of insufficient mixing, manual mixing was used with spatula. The mixture was kept in a dry place for 24 h at room temperature. After the process, the compound was melt-mixed using heated two-roll mills at 150°C for 10 min.

Preparation of LDPE/TPSS-kenaf Fibre Composite

TPSS was melt-blended with LDPE and kenaf fibre in a Haake Rheomix mixer Model R600/610. Kenaf fibre was first dried in an oven at 70°C for 3 h. Mixing was performed at 150°C and 50 rpm for 20 min. LDPE/TPSS blend ratio was fixed at 80 wt% of LDPE and 20 wt% of TPSS. LDPE was first added into the mixing chamber followed by TPSS after 3 min of mixing. After both mixtures were stabilized, kenaf fibre was added. Total mixing time was 20 min. Kenaf fibre loadings were from 5, 10, 20, 30 to 40 wt%. For composites with the addition of PE-g-MA, the amount of PE-g-MA was fixed at 10 wt% based on kenaf fibre weight. Melt temperature and mixing torque were recorded during the mixing periods.

Compression Moulding

LDPE/TPSS-kenaf fibre composites were compression moulded in an electrical heated hydraulic press. Hot press procedures involved preheating at 150°C for 6 min, followed by compression for 3 min at the same temperature. All compression moulded sheets (150 × 150 × 1 mm) were then cold pressed for 2 min.

Tensile Properties

Tensile tests were carried out with a universal testing machine Instron 3366 according to ASTM D638. Dumbbell specimens of 1 mm thickness were cut from the compression moulded sheets with a Wallace die cutter. A cross-head speed of 5 mm/min was used and the test was performed at 25 ± 3°C. Five specimens were used to obtain average values for tensile strength, elongation-at-break and Young's modulus.

Morphology Study

Studies on the tensile fracture surface of the LDPE/TPSS-kenaf fibre composites were carried out using a field emission scanning electron microscope, Supra36VP. Surfaces of the samples were mounted on aluminium stubs and sputter coated with a thin layer of gold to avoid electrostatic charging and poor resolution during examination.

Water Absorption Study

Tensile specimens were dried at 80°C in a vacuum oven until a constant weight was attained prior to immersion in distilled water at room temperature. The water absorption tests were performed until the specimens were saturated. Weight gains were recorded by periodic removal of the specimens from the water. Moisture on the surface of the sample was removed with paper towels before weighing on a balance with a precision of 1 mg. The percentage of water uptake at any time (Wt) was calculated according to the following equation:

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

where \( W_1 \) and \( W_2 \) are the weights of dried sample and the samples after exposure time, t. The percentage of equilibrium water uptake was calculated as an average value of several consecutive measurements showing no appreciable additional absorption of water.

Fourier-transform Infrared Spectroscopy Study

Fourier-transform infrared spectroscopy (FTIR, Perkin Elmer System 2000) was used to obtain some qualitative information about the functional groups and chemical characteristics of the LDPE/TPSS-kenaf fibre composite with and without the addition of PE-g-MA. For each spectrum, 52 consecutive scans with 4 cm⁻¹ resolution were recorded. Samples were measured in the form of sheets of about 1 mm thickness, prepared by hot press moulding.

RESULTS AND DISCUSSION

Processing Characteristics

Figure 1 shows the processing torque values for...
LDPE/TPSS-kenaf fibre composites with and without the addition of compatibilizer (PE-g-MA). From the figure, it is clear that LDPE/TPSS shows the lowest torque values particularly at the end of compounding. It is also observed that the torque increases as the amount of kenaf fibre loading increases in the composites with and without compatibilizer (Figures 1a and 1b). This trend may be due to the existence of kenaf fibre that is stiffer in the matrix and that will increase the viscosity of the compound during the process. As a result the torque value increases with the increase in kenaf fibre.

Figure 2 shows the stabilization torque for LDPE/TPSS-kenaf fibre composites, with and without the addition of compatibilizer. The stabilization torque values of compatibilized and uncompatibilized composites increased with increasing kenaf fibre loading. However, for compatibilized composite the values of stabilization torque at 5 to 30 kenaf fibre loadings are slightly higher than the uncompatibilized composites. Such an increase in the torque for the compatibilized composite is probably due to the reaction between the chemically reactive groups of the compatibilizer with both LDPE/TPSS blend and kenaf fibre that produce branched chains and cross-linking. This refers to the reaction between the anhydride groups of the compatibilizer and the hydroxyl groups of either the starch or kenaf. Figure 3 shows the proposed interaction that might occur during the compounding of LDPE/TPSS-kenaf fibre composites in the presence of PE-g-MA. The interaction in Figure 3 has been confirmed with FTIR analysis. With the addition of compatibilizer, kenaf interaction with the matrix can be improved as discussed in the morphological properties. According to Bikiaris et al. [8] and Abdul Majid et al. [9], the reaction produces branched chains and cross-linked macromolecules which have higher melt viscosity compared to linear macromolecules. Because of the reaction, the stabilization torque of the compatibilized composite is higher than the uncompatibilized composites.

**Tensile Properties**

Figure 4a shows the tensile strength of LDPE and LDPE/TPSS-kenaf fibre composite for the composites with and without compatibilizer. Tensile strength for pure LDPE is 9.28 MPa. From the figure, it can be seen that the tensile strength value for pure LDPE is higher compared to each composites sample except for composite with 20% kenaf fibre loading with the addition of compatibilizer. From Figure 4a, also compatibilized composites show an increase in the tensile strength with the increase of kenaf fibre.
Figure 3. (a) Esterification of PE-g-MA and starch, (b) hydrogen bonding of PE-g-MA and starch, and (c) kenaf fibre interaction with PE-g-MA.
The strength of the composite is basically due to the fibre reinforcement and good interfacial adhesion between the blend and the fibre. In these composites, kenaf fibre and thermoplastic sago starch are the hydrophilic materials, whereas LDPE is the hydrophobic material. Because of different polarities, interfacial adhesion between the kenaf fibre and LDPE is difficult to be made. Because of those factors, the compatibilized composite shows higher tensile strength values due to the addition of compatibilizer inside the composite that can improve the interfacial adhesion and interaction between fibres and matrix as observed in the proposed interaction. Without the addition of compatibilizer, the composites provided a site for a weak interfacial adhesion. A weak interfacial adhesion may be the weakest part of the composite as it provides a site for failure initiation [7-17]. At 30% and 40% of kenaf fibre loadings, the lower values in tensile strength may be due to the weak stress transfer because the fibre has reached the maximum volume. With the addition of compatibilizer the agglomeration can be reduced because PE-g-MA not only acts as a compatibilizer inside the composite, it also acts as a separator for the agglomerations that occur inside the composites. When agglomeration is reduced, fibre inside the composites can still act as reinforcement. This can be proved with the tensile values at 30% and 40% fibre loadings. Composite with the addition of compatibilizer showed better tensile strength compared to the uncompatibilized composites.

Figure 4b shows the Young's modulus for LDPE/TPSS-kenaf fibre composite with and without compatibilizer. (Tensile strength, Young's modulus and elongation-at-break for neat LDPE are 9.2844 MPa, 271.24 MPa and 133.3%, respectively).

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Figure 4b shows the Young's modulus for LDPE/TPSS-kenaf fibre composite with and without the addition of compatibilizer. For pure LDPE, the Young's modulus value is 271 MPa. The increase in Young's modulus value for the composites as compared to pure LDPE is due to the stiffening effect that occurs because of the existence of fibre inside the composites. The composites with the addition of compatibilizer show higher Young's modulus values compared to the uncompatibilized composites due to the enhancement of interfacial adhesion between the blend and the fibre. As it is evident in Figure 4, elongation-at-break for both uncompatibilized and compatibilized composites is reduced with increase in kenaf fibre. For pure LDPE, the elongation-at-break value is 133%.
Morphology Study
Figure 5 shows the SEM tensile fracture surface of LDPE/TPSS-kenaf fibre composite without the addition of compatibilizer. Figure 5a shows the blend of LDPE/TPSS and Figures 5b-5d show the dispersion of kenaf fibre in LDPE/TPSS matrix. In Figure 5 it is also evident that the fibres are not being covered by the matrix. Fibres pull out can be seen from the figure. This is attributed to a weak interaction between the fibre and matrix. There are also gaps between the fibre and matrix, which are indications of weak interfacial adhesion between the fibre and matrix.

Figure 5 also shows that kenaf does not seem to have good interactions with starch granules although they share the same hydrophilic chemical bonding [4-6]. Both these materials contain large amounts of hydroxyl groups. Theoretically, the starch and kenaf fibre can chemically interact to form either hydrogen bonds or ester bonds. This behaviour might be because of the round shape of thermoplastic starch that minimizes the interaction between kenaf and starch. In Figure 5 it is observed, that at 5% fibre loading, the thermoplastic starch granules still have some contact with the fibre, though to a very small extent. In contrast, at higher fibre loading as shown in Figure 5d the contact between thermoplastic starch and fibre is hardly noticed.

SEM micrograph in Figure 6 shows a better distribution of kenaf fibre as compared to Figure 5. The agglomeration at higher fibre loading can be minimized with the addition of PE-g-MA. In this figure, the fibre is little pulled-out because contacts between the matrix and the fibres improve with the addition of compatibilizer [5-10]. That is one of the reasons why at 40% fibre loading, tensile strength for compatibilized composite was higher than the composite at 40% fibre loading without the addition of compatibilizer.

Water Absorption Study
Figure 7 shows the water uptakes for the compatibilized and uncompatibilized LDPE/TPSS-kenaf fibre composites. From the figure, the water uptake...
Water uptakes for: (a) LDPE/TPSS-kenaf fibre and (b) LDPE/TPSS-kenaf fibre/PE-g-MA.

for both compatibilized and uncompatibilized composites increased with the increase in kenaf fibre loading. Water uptakes in LDPE/TPSS-kenaf fibre composites are mainly due to the starch particles and kenaf fibre. This may be attributed to the hydrophilic nature of the starch and fibre by virtue of the presence of an abundant hydroxyl groups which are available for interaction with water molecules. The water molecules can saturate the surface of the
LDPE/TPSS-kenaf fibre composites easily and also penetrate into the composites through voids which result in higher water uptake in a short exposure time [11,12].

The compatibilized composites showed lower percentage of water uptakes as compared to the uncompatibilized composites. Figure 8 shows that at each loading of kenaf fibre, LDPE/TPSS-kenaf fibre composites with the addition of PE-g-MA shows lower equilibrium of water uptake relative to LDPE/TPSS-kenaf fibre composite without the addition of PE-g-MA. This is probably due to the bonding which is formed between the fibre-PE-g-MA and starch-PE-g-MA as shown in previously proposed interaction that reduces the water penetration into the composites.

Fourier-transform Infrared Spectroscopy
The reason for the use of PE-g-MA as a compatibilizer is based on two factors: (1) the ester forming ability of anhydride groups with hydroxyl groups on starch and kenaf fibre, and the hydrogen-bond-forming ability between the carboxyl groups of hydrolyzed maleic anhydride and hydroxyl groups on starch and kenaf; (2) the good compatibility between grafted PE chains and the PE phase [9].

It is evident in Figure 9 and Table 1, that there are two characteristic peaks of LDPE/TPSS-kenaf fibre composites, with those at 3200 cm⁻¹ to 3400 cm⁻¹ attributed to C-O-H bond stretching, and that near 1634 cm⁻¹ attributed carboxyl/ester group formed between fibre and PE-g-MA and starch and PE-g-MA after the addition of compatibilizer. The peak shape and position of the composite with addition of compatibilizer are changed little as compared to the composite without the addition of compatibilizer. The peak area at 3200-3400 cm⁻¹ has changed, whereas the uncompatibilized composite showed higher peak area compared to the compatibilized composite. This behaviour might be due to the hydrogen bond formation occurring after the addition of compatibilizer. The peak at 1634 cm⁻¹ of the composites can only be seen for the compatibilized composite as the ester bond is formed after the addition of compatibilizer. According to Wang et al. [13-16], the better the compatibility of the polymer composite, the greater would be the correlative peaks shift and change in peak shapes. This phenomenon indicates that the composites with PE-g-MA have better compatibility between the fibre and starch than those without PE-g-MA.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>3200-3400</td>
<td>O-H stretching bond</td>
</tr>
<tr>
<td>2700-3000</td>
<td>Typical CH₂ &amp; CH bending</td>
</tr>
<tr>
<td>1634</td>
<td>Carboxyl/ester group (C=O)</td>
</tr>
<tr>
<td>1461</td>
<td>CH₂ bending</td>
</tr>
<tr>
<td>1376</td>
<td>C-H bend due to CH₂ and CH₃</td>
</tr>
<tr>
<td>1348</td>
<td>O-H in-plane bending</td>
</tr>
</tbody>
</table>

CONCLUSION

LDPE/TPSS-kenaf fibre composite is a three-medium composite. Therefore, PE-g-MA is needed to improve the compatibility between the matrix and kenaf fibre. Tensile strength and Young’s modulus of the LDPE/TPSS-kenaf fibre composites are improved with the addition of PE-g-MA. SEM Micrographs of the tensile surface fracture show better interfacial adhesion between LDPE/TPSS and kenaf fibre in the
presence of PE-g-MA as a compatibilizer. Water absorption study shows that the addition of PE-g-MA reduces the water uptake of LDPE/TPSS-kenaf fibre composites.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Research University Grant (Grant No. 1001/PBAHAN/814008).

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