EFFECT OF FIBER LOADING ON PROPERTIES OF THERMOPLASTIC SAGO STARCH/KENAF CORE FIBER BIOCOMPOSITES

Norshahida Sarifuddin, Hanafi Ismail, and Zuraïda Ahmad

Growing attention has been paid to the innovation of ecological products, prompted by rising environmental concerns. As a natural polymer, thermoplastic sago starch has been regarded as an alternative material to petroleum-based plastic owing to its availability, cost, and biodegradability. In order to produce thermoplastic starch materials with enhanced structural and functional stability during use, kenaf fibers were incorporated as the reinforcing filler. In this work, thermoplastic sago starch (TPSS)/kenaf core fiber (KF) biocomposites were prepared at different fiber loadings (0 to 35 wt.%), and the effects of fiber loading were analyzed by mechanical tests, TGA, FTIR, SEM, and water absorption behavior. The tensile analysis showed a linear increase in strength and modulus upon increasing fiber content until it reached an optimum at 30 wt.% fiber loading. The thermal stability of biocomposites was improved slightly by the incorporation of kenaf fibers into TPSS matrices. FTIR results indicated a change in the functional group of the biocomposites. Moreover, the interfacial adhesion properties of biocomposites were evident from morphological studies of tensile fracture surfaces. It is interesting to note that water absorbed by the biocomposites was reduced by the addition of fiber, and it seems that the hydrophilic character was decreased especially for the glycerol-plasticized sample. The results obtained clearly illustrate the potential use of these fiber and biopolymers to establish their suitability as alternative biocomposite materials.

Keywords: Thermoplastic sago starch; Kenaf fiber; Biocomposites

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INTRODUCTION

Synthetic polymers are widely used in daily life, and increasingly they are being used in more diverse areas due to their ease in processing, permanent stability, and antibacterial properties. These benefits of synthetic polymer products, however, in turn cause environmental problems when they are discarded, buried in the sea, or thrown in riverside soil. With the increasing interest in environmental issues, the sustainability or biodegradability of resources is becoming increasingly important (Lee et al. 2010).

The biodegradable polymer polyactic acid (PLA) is the most promising biodegradable polymer and currently the subject of many studies. This polymer can...
provide good strength and is easy to process in most equipment; however, it is expensive and it needs further modification for many practical applications (Yussuf et al. 2010).

Among other biodegradable materials, starch has drawn great attention due to its abundant supply and low cost. In nature there are basically two types of starch polysaccharides structures: the linear amylase and the highly branched amylpectin. The intermolecular and intramolecular hydrogen bonds between hydroxyl groups of starch molecules lead to the crystallinity in native starch (Lin and Tung 2009). Unfortunately, these materials still have poor mechanical properties and remarkable sensitivity to moisture, which limit their applicability (Gomez and Aguilerast 1983; Davidson et al. 1984). However, various approaches can be used to design starch materials with enhanced structural and functional stability during use, which then could broaden their application range. In the presence of plasticizers at high temperature and under shear, starch can readily melt and flow, allowing for its use as an extruded or injected material, similar to most conventional synthetic thermoplastic polymers.

Thermoplastic starch (TPS) has two main drawbacks when compared to most plastic materials currently in use; it is mostly water-soluble and has poor mechanical properties. One approach that has been considered to improve the properties of TPS is the use of fibers as reinforcement (Curvelo et al. 2001). Natural fiber is the preference in light of the fact that it can be completely biodegraded in the natural environment and it is fully sustainable. Recently, many studies have investigated biodegradable polymers filled with natural fibers. For instance, natural fibers such as kenaf, hemp, jute, bamboo, flax, pineapple, and cordenka have been used with PLA as fiber-reinforced biocomposites due to their good mechanical properties, lower cost, and lower weight. Different natural fibers (flax, ramie, jute, palm, and sisal, among others) are described in the literature as reinforcement of starch-based thermoplastic polymers (Wollerdorfer and Bader 1998; Kaith et al. 2010; Alvarez and Vazquez 2004). Most natural fibers are composed of cellulose, hemicellulose, and lignin in different relative amounts (Bismarck et al. 2005). When natural fibers are mixed with thermoplastic starch and its blends, their mechanical properties become notably enhanced. This fact has been attributed to the chemical similarity of starch and fibers, providing good compatibility between them (Puglia et al. 2003). It should be noted that good adhesion between the natural fiber and polymeric matrix is necessary to define a good fiber/matrix interface.

Starch from various sources has been studied as TPS, including corn starch, potato starch, cassava starch, and wheat starch (Prachayawarakorn et al. 2010). However, very few publications are available on thermoplastic sago starch. Sago starch comes from Southeast Asia, where it is produced by the sago palm. Sago starch has its own unique characteristics; it is easy to gelatinize, has high viscosity, and is easily molded. As a cheap and abundantly available resource, sago starch becomes a useful source for foodstuffs and industrial raw materials. Although there are different natural fibres described in the literature as reinforcement of starch-based thermoplastic polymers, few reports exist about kenaf fiber as reinforcing materials of starch. Kenaf, a natural fiber, is a cellulose-containing plant that is mainly grown in Southeast Asia. It grows fast, can be harvested at a very low cost with many environmental advantages, and has good mechanical properties (Rudnik 2007).
Several researchers have studied the mechanical properties of PLA/kenaf composites. Huda et al. (2008) investigated the effect of fiber surface treatment on the mechanical properties by using a laminated PLA/kenaf composite, and found that mechanical properties of PLA/kenaf composites were significantly better than those of the PLA matrix itself. A similar observation was reported by Ochi (2008), who investigated the mechanical properties of PLA/kenaf composites. However, there is little literature regarding the combination of thermoplastic starch and kenaf fibers. To the best of our knowledge, no reports on thermoplastic sago starch/kenaf fibers biocomposites are available in the literature. Therefore, this work focuses on the investigation of the mechanical, thermal, and morphological properties of these biocomposites. Likewise, the properties were determined by means of several parameters: plasticization of sago starch, fiber loading, and processing factors.

**EXPERIMENTAL**

**Materials**

Sago starch was obtained from the Land Custody Development Authority (LCDA), Sarawak, Malaysia. Kenaf core fiber was obtained from Forest Research Institute of Malaysia (FRIM) with the average length of 5 mm and ground using a table-type pulverizing machine (Rong Tsong Precision Technology, RT-34) into short fibers (flour), 30 to 40 μm in diameter before use. The chemical compositions of kenaf core fibers are listed in Table 1. The fibers were then sieved using a shaker with pass 70 mesh. Fibers were used as received in the original form and not chemically treated prior to processing. Glycerol was an analytical grade reagent, purchased from Merck Chemicals (Malaysia).

**Table 1. Chemical Composition of Kenaf Core Fiber (Ashori et al. 2006)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holocellulose</td>
<td>75.8</td>
</tr>
<tr>
<td>Alpha-cellulose</td>
<td>46.1</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>29.7</td>
</tr>
<tr>
<td>Lignin</td>
<td>22.1</td>
</tr>
<tr>
<td>Pentosan</td>
<td>20.7</td>
</tr>
<tr>
<td>Hot water</td>
<td>3.9</td>
</tr>
<tr>
<td>Ash</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**Processing**

Sago starch powder was dried in a vacuum oven for 24 hr at 80 °C. Then, the powder was premixed manually with glycerol at a weight ratio of 65:35 in accordance with a previous study (Abdul Majid et al. 2010a,b). The mixture was further stirred vigorously by a high speed mixture for approximately 2 min. Kenaf fiber was first dried in an oven at 70° C for 3 hr before being added to the thermoplastic sago starch. TPSS was melt-blended with kenaf fiber at different fiber loading (0 to 35 wt.%) in a twin screw extruder (Thermohaake Rheomix, 557-5501). Zone temperatures of 150°C were
selected collectively for the feed, metering, compression and die sections. The screws were operated at 100 rpm. The mixtures were then granulated in a polymer crusher equipped with a strainer. The pellets were compression molded in an electrically heated hydraulic press (Kao Tieh Go Tech Compression Machine). Hot press procedures involved preheating at 150°C for 6 min, followed by compression for 3 min at the same temperature. All compression molded sheets (150 × 150 × 1 mm) were then cold pressed for 2 min.

**Mechanical Testing**

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 molded sheets with a Wallace die cutter. A crosshead 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.

**Fourier Transform Infrared (FTIR)**

The functional groups and chemical characteristics of TPSS/KF biocomposites were obtained by Fourier Transform Infrared Spectroscopy (FTIR, Perkin Elmer System 2000) with a resolution of 4 cm⁻¹ in a spectral range of 4000 to 600 cm⁻¹ using 32 scans per sample.

**Thermogravimetric (TG) Analysis**

TPSS/KF biocomposite samples were cut into small pieces (5 to 10 mg), which were then tested using thermogravimetric instruments (Perkin Elmer, Pyris Diamond TG/DTA) under nitrogen atmosphere within a temperature range from room temperature to 450°C at a heating rate of 15°C/min. Thermal degradation temperature was reported by the onset degradation temperature where the weight loss started to occur.

**Water Absorption**

Water uptake measurement was carried out as per ASTM D570. The samples were first dried in an oven at 70°C for 24 hr until a constant weight was attained and then dipped in the distilled water at ambient temperature. After soaking for a specific interval, the samples were then removed from the water, gently dried by wiping with a clean cloth, and immediately weighed to the nearest 0.001 g. The percentage of water absorption was calculated as follows,

\[ WA (%) = \left[ \frac{(M_1 - M_0)}{M_0} \right] \times 100 \] (1)

where \( M_0 \) and \( M_1 \) were the dried weight and final weight of the sample, respectively.

**Morphology**

Scanning electron micrographs of tensile fracture surfaces of TPSS/KF composites were obtained by using a Scanning Electron Microscope (SEM, model ZEISS Supra 35 VP). The samples were sputter coated with a thin layer of carbon to avoid
electrostatic charging during the examination. The image results were analyzed to investigate the distribution of natural fibers in polymer matrix and their interaction.

RESULTS AND DISCUSSION

Mechanical Properties

Tensile properties of TPSS/KF at different fiber loadings are shown in Fig. 1(a)-Fig. 1(c). It can be seen that the tensile strength and Young’s modulus were higher for the TPSS/KF composites compared to those of the unreinforced starch, in agreement with literature results (Dias et al. 2011; Mueller et al. 2009). Tensile strength of TPSS/KF composites was 1.12, 2.01, 4.94, and 10.53 times that of the unreinforced starch when the fiber loading was 5, 10, 20, and 30 wt.%, respectively. The enhancement indicates the effectiveness of the reinforcing materials. The strength of composites, however, increased until it reached the maximum fiber loading and optimum tensile strength at 30 wt.% fiber content. The results suggest that kenaf fibers may reinforce the TPSS matrix due to their similar chemical structure, which increases the hydrogen bonding between both constituents.

It is worth noting that the tensile strength and Young’s modulus of composites are influenced by the nature of matrix and the adhesion between fiber and matrix (Wan et al. 2009). Due to the fact that both kenaf fibers and thermoplastic starch are hydrophilic materials, good interfacial adhesion takes place. However, the drop in tensile strength becomes more drastic at higher loading due to the fact that there is greater formation of fiber-fiber interaction than fiber-matrix interaction with increasing fiber content. The applied force cannot be transferred from polymer matrix to rigid fiber particles due to the reduction in the effective cross-sectional area of the composites caused by fiber particles. At higher loadings, fibers tend to agglomerate, subsequently resulting in weak stress transfer, as shown later in a morphological study.

![Fig. 1a. Tensile strength for TPSS/KF biocomposites](image-url)
The tensile strength and modulus increased with increasing kenaf fiber content, whereas the elongation decreased (Lee et al. 2010). It can be observed that kenaf fiber caused the decrease in elongation at break of the TPSS matrix gradually (Fig. 1 (c)). The addition of fibers (5 to 35 wt.%) to the starch matrix brought about a drop from 32.35% to 1.239% in the elongation at break. This effect is expected, since the fiber incorporation imparts rigidity and restrains the deformation on the matrix, which leads to an inevitable decrease in degree of the ductility of the material (Belhassen et al. 2009).
IR Spectroscopic Study

The FTIR spectra of composites were examined with respect to characterizing the chemical bonds between fibers and starch. The major observed peaks could be identified as the functional groups of starch and fiber; however, there were some slight changes in band positions and intensities. It is known that if two polymers are compatible, a distinct interaction (hydrogen bonding or dipolar interaction) exists between the chains of one polymer and those of the other, causing the IR spectra of composites to change. It is evident in Fig. 2 that characteristic peaks appeared at 3200 cm\(^{-1}\) to 3500 cm\(^{-1}\), which can be attributed to C-O-H bond stretching. This behavior might be due to hydrogen bond formation occurring after the addition of fiber. In order to confirm the increase in intermolecular hydrogen bonding, it can be observed that the band at 3200 cm\(^{-1}\) to 3500 cm\(^{-1}\) was slightly broadened after the addition of kenaf fiber. It is also worth noting that the difference in IR spectra between TPSS and TPSS/KF at 1260 cm\(^{-1}\) is that the C-O stretching peak is narrower in TPSS/KF, possibly due to the rearrangement of hydrogen bonds between starch and fiber. The change in IR spectra indicates a distinct interaction and compatibility between the chains of polymers. It also can be seen that pure TPSS exhibits IR main peak positions in the range of 1475 to 1450 cm\(^{-1}\), 1275-1070 cm\(^{-1}\), and 1200-1000 cm\(^{-1}\), representing C-H asymmetric stretching of -CH\(_2\)-, -CH\(_2\)- deformation, C-O-C stretching, and C-O-H stretching, respectively (Prachayawarakorn et al. 2010). The peak position at approximately 1646 cm\(^{-1}\) is due to the bound water present in the starch (Prachayawarakorn et al. 2010).

![Fig. 2. FTIR spectra of TPSS/KF composites at different fiber loading](image-url)
Thermal Properties

Thermogravimetric analysis of the composite was carried out to assess its thermal stability and degradation temperature. The onset degradation temperature and thermogravimetric (TG) curves for different TPSS/KF samples are shown in Table 2 and Fig. 3, respectively. It can be observed that thermal degradation of TPSS occurred in three steps: 1st region (250 to 280 °C), 2nd region (335 to 400 °C), and 3rd region (above 400 °C). Similar behavior was observed for TPSS-filled kenaf fiber biocomposites. However, it is envisaged that the major mass loss will start at temperatures above 300 °C for unreinforced matrix as well as for biocomposites because it has been reported that dehydration and depolymerization are the two main processes associated with the degradation mechanism (Rudnik 2007). The maximum degradation step in the 2nd region is assigned to the degradation of starch. This is in agreement with reports elsewhere (Moriana et al. 2010). It can be seen that TPSS showed an onset decomposition temperature ($T_d$) of approximately 337.8° C, and the addition of fibers caused an increase of $T_d$. The $T_d$ values of TPSS were 349.7° C and 386.9° C by the use of 10 and 30 wt.% of fiber, respectively. TPS-reinforced fiber caused an increase in the onset decomposition temperature of starch. This could be explained by the fact that the TPS is phase compatible with fiber by increasing hydrogen bond linkage, as shown by FTIR spectra in Fig. 2.

Table 2. Onset degradation temperature of different TPSS/KF biocomposites

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_d$ (°C) (onset)</th>
<th>1st</th>
<th>2nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPSS + 0 % KF</td>
<td>275.1</td>
<td>337.8</td>
<td></td>
</tr>
<tr>
<td>TPSS + 10 % KF</td>
<td>243.5</td>
<td>349.7</td>
<td></td>
</tr>
<tr>
<td>TPSS + 30 % KF</td>
<td>254.5</td>
<td>386.9</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. TGA thermogram of different TPSS/KF biocomposites
The addition of even low amounts of fibers to TPS resulted in a significant increase in the thermal stability, while the effect of fiber content on mass loss at the onset temperature will not be obvious (Ma et al. 2005). It is known that the fiber has a vacant structure that leads to a low thermal conductivity (Lee et al. 2010). The fiber component will decrease the mass loss of plasticizer, and therefore the thermal stability of TPSS materials will be improved (Lee et al. 2010). Fiber went through the last degradation step at the temperature of approximately 400°C, which was associated with the thermal decomposition of hemicelluloses, pectin, and cellulose.

**Water Absorption**

Figure 4 shows the water uptake of TPSS/KF composites with varying fiber loading as a function of time. It can be observed that the water uptake of the composites increased linearly within the initial stage of absorption process, then the increasing rates slowed down and finally approached a plateau corresponding to the water uptake at equilibrium. It took about 5 hours for different TPSS and TPSS/KF samples to reach absorption equilibrium. Starch is known to take up large amounts of water, which is further exacerbated by glycerol plasticization (Duanmu et al. 2010). However, it was found that the very high degree of moisture absorption of TPSS was reduced after the inclusion of fibers. This behavior was related to the less hydrophilic character of the fibers in comparison to starch’s hydrophilic property (Prachayawarakorn et al. 2010). Note that the unreinforced starch showed the highest percentage of water uptake due to its hygroscopic nature. The greater the fiber content, the less the water was absorbed. The fiber seems to operate as a buffer to decrease the tendency of the thermoplastic starch to absorb water. This can be attributed to the fact that starch has lower crystallinity and is more bio-susceptible than fiber (Wan et al. 2009). The overall reduced water absorption can be ascribed to the presence of strong hydrogen bonding between the matrix phase and the fiber phase.

![Figure 4. Water absorption of TPSS/KF biocomposites](image-url)
The chemical similarity may result in good interfacial adhesion between the two components, which, to some extent, resists diffusion of water molecules. It is also worth noting that the fiber could absorb the excess glycerol and produce a network that hinders the swelling of the matrix, consequently obstructing the absorption of water (De Carvalho et al. 2002). Thus, it is believed that the addition of fiber is an effective way to decrease its sensitivity to moisture, thus improving the stability of mechanical properties (Wan et al. 2009).

**Morphology**

SEM micrographs at 300X magnification of the fractured surface of TPS filled with different fiber contents are shown in Fig. 5, which revealed the dispersion of fiber in TPS matrix. A spot of starch granules plasticized with glycerol can be observed in Fig. 5(a). For the TPSS reinforced by 10 wt.% of kenaf fiber, the SEM micrograph in Fig. 5(b) revealed the kenaf fiber was well embedded into the TPSS matrix; however it is possible to see isolated fibers coming out of the fracture surface of the composites. The microstructure of fracture surface illustrates the occurrence of ductile tearing of the matrix with some fibers breakage. This is ascribed to weak interfacial adhesion between fiber and matrix.

**Fig. 5.** SEM micrographs of TPS/Kenaf fiber composites at (a) 0 wt.% fiber loading (b) 10 wt.% fiber loading (c) 30 wt.% fiber loading and (d) 35 wt.% fiber loading.
On the contrary, Fig. 5(c) shows intimate mixing of the fiber with the matrix. Kenaf fibers were perfectly wetted by the TPSS, which corroborates the presence of chemical bonding between fiber and starch matrix, probably due to the presence of hydrogen bonding (Canigueral \textit{et al.} 2009). This phase morphology is evidence of phase compatibility, and it is well accepted that tensile strength and modulus of composites are influenced by the nature of matrix and the adhesion between fiber and matrix (Wan \textit{et al.} 2009). Figure 5(d) however, exhibits a debonding of fiber from matrix. Breaking of fibrils and fiber strand with small particles adhered to the fiber surface is well visualized, which indicates lower dispersion efficiency when the fiber content exceeded 30 wt. %.

**CONCLUSIONS**

1. Biocomposites could be prepared from sago starch and kenaf core fiber. The inclusion of kenaf fiber as reinforcement showed higher stress at maximum load and Young’s modulus compared to unreinforced TPSS.

2. Thermal degradation temperatures and thermal stability of TPSS were also improved by reinforcing fibers.

3. The inclusion of kenaf fiber in the thermoplastic starch matrix results in a decrease of its hydrophilic character and capacity of water uptake.

4. The best optimum properties were obtained from TPSS with 30 wt.% kenaf fibers.

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**REFERENCES CITED**


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