

Superheated Steam Treatment of Oil Palm Mesocarp Fiber Improved the Properties of Fiber-Polypropylene Biocomposite

Noor Ida Amalina Ahamad Nordin,^{a,b} Hidayah Ariffin,^{a,c,*} Mohd Ali Hassan,^a Yoshihito Shirai,^d Yoshito Ando,^d Nor Azowa Ibrahim,^e and Wan Md Zin Wan Yunus^f

The effect of fiber surface modification by superheated steam (SHS) treatment and fiber content (30 to 50 wt.%) was evaluated relative to the mechanical, morphology, thermal, and water absorption properties of oil palm mesocarp fiber (OPMF)/polypropylene (PP) biocomposites. SHS treatment of OPMF was conducted between 190 and 230 °C for 1 h, then the SHS-treated fiber was subjected to melt-blending with PP for biocomposite production. The biocomposite prepared from SHS-OPMF treated at 210 °C with 30 wt.% fiber loading resulted in SHS-OPMF/PP biocomposites with a tensile strength of 20.5 MPa, 25% higher than untreated-OPMF/PP biocomposites. A significant reduction of water absorption by 31% and an improved thermal stability by 8% at $T_{5\%degradation}$ were also recorded. Scanning electron microscopy images of fractured SHS-OPMF/PP biocomposites exhibited less fiber pull-out, indicating that SHS treatment improved interfacial adhesion between fiber and PP. The results demonstrated SHS treatment is an effective surface modification method for biocomposite production.

Keywords: Superheated steam treatment; Surface modification; Fiber-matrix bond; Biocomposite; Mechanical properties

Contact information: a: Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, 43400 UPM Serdang, Selangor, Malaysia; b: Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Pahang, Malaysia; c: Laboratory of Biopolymer and Derivatives (BADs), Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia; d: Department of Biological Functions and Engineering, Graduate School of Life Science and System Engineering, Kyushu Institute of Technology, 2-4 Hibikino, Wakamatsu, Fukuoka 808-0196, Japan; e: Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia; and f: Department of Defence Science, Faculty of Defence Science and Technology, National Defence University of Malaysia, 57000 Kuala Lumpur, Malaysia; *Corresponding author: hidayah@upm.edu.my

INTRODUCTION

In recent years, hybrid materials that combine petroleum-based polymers with biodegradable (Mohan and Kanny 2012), low cost (Then *et al.* 2013), and renewable natural fibers (Gomes *et al.* 2007) have been developed. In Malaysia, the palm oil industry is the biggest contributor to agricultural waste. Empty fruit bunch (EFB) and oil palm mesocarp fiber (OPMF) are two important fibrous materials generated as biomass at palm oil mills, where both biomasses are generated after the oil extraction. OPMF is used as biomass fuel and is inefficiently burnt for energy generation by steam boiling (Ali *et al.* 2015; Zakaria *et al.* 2015). Oil palm mesocarp fiber, found in nature, has similar characteristics to EFB in terms of chemical composition; OPMF has potential for other uses, such as biosugar production (Mahmud *et al.* 2013; Zakaria *et al.* 2015) and as a

reinforcing material in biocomposites (Sreekala and Thomas 2003; Then *et al.* 2013).

Oil palm mesocarp fiber, like other natural fiber, has low compatibility with polymer matrices due to its hydrophilicity. The surface modification of fiber, such as silane treatment (Sawpan *et al.* 2011), alkaline treatment (Gomes *et al.* 2007; Sgriccia *et al.* 2008; Mohan and Kanny 2012), and the addition of compatibilizer (Arbelaiz *et al.* 2005; Hosseinaei *et al.* 2012) can improve the interaction between the two materials, thus enhancing the mechanical properties of the biocomposites.

In lignocellulosic material, hemicellulose is the most hydrophilic and thermally unstable polymer (Arbelaiz *et al.* 2005; Sgriccia *et al.* 2008). The interfacial bonding of fiber-polymer can be improved by diminishing the hemicellulose component in the fiber (Han *et al.* 2009; Eslam *et al.* 2011; Hosseinaei *et al.* 2012; Kaewkuk *et al.* 2013). Hydrothermal and steam treatments such as superheated steam (SHS) (Bahrin *et al.* 2012; Mahmud *et al.* 2013; Then *et al.* 2014), hot-water extraction (Eslam *et al.* 2011; Hosseinaei *et al.* 2012), and steam explosion (Ando *et al.* 2000; Han *et al.* 2009) reduce the hemicellulose content of fiber.

A previous report showed that OPMF became more hydrophobic after SHS treatment due to the reduced content of hydroxyl groups, mainly from the removal of hemicellulose (Nordin *et al.* 2013). It was also shown that SHS-OPMF had higher crystallinity and thermal stability compared with untreated OPMF. These results may lead to improvement in the properties of biocomposites produced from SHS-treated OPMF. In this study, the effects of SHS treatment temperature and fiber loading on the characteristics of OPMF/polypropylene (PP) biocomposites were clarified. Results from this study revealed the potential of SHS-OPMF as a reinforcement material in biocomposites.

EXPERIMENTAL

Material

OPMF was kindly provided by FELDA Serting Hilir Palm Oil Mill, Negeri Sembilan, Malaysia. Raw OPMF was prepared as described by Nordin *et al.* (2013). The fiber had an average length of 20 to 30 mm, and there was no further mechanical treatment prior to the SHS treatment. The selected matrix was polypropylene (PP) pellets supplied by Polypropylene Malaysia Sdn. Bhd. (Pahang, Malaysia) with a code of 606251 G 112. The melt flow index (MFI) of the PP at 230 °C was 18 g/10 min, and the density was 0.91 g/cm³.

Superheated Steam Treatment

The SHS oven (QF-5200C, Naomoto Corporation, Osaka, Japan) was used to perform the extraction of hemicellulose at different temperatures (190, 200, 210, 220, and 230 °C) over a time period of 60 min under ambient pressure. The treatment and selected conditions were based on a previous study (Nordin *et al.* 2013).

Preparation of OPMF/PP Biocomposites

Prior to blending, fiber samples were ground using a Wiley mill (model CW-1, Taipei, Taiwan) and sieved using a sieve shaker (Minor 200, Endecotts, London, UK) to isolate the fiber size of 150 µm. Ground OPMF was mixed with PP by melt-blending in a twin screw internal mixer (Thermo Haake Rheomix Polydrive, Waltham, MA, USA) at

170 °C and 50 rpm rotor speed for 10 min as described by Ibrahim *et al.* (2011). The total sample weight of the PP and fiber inside the mixing chamber was 40 g. In order to determine the effect of the SHS treatment temperature, biocomposites were prepared from OPMF treated at 190 to 230 °C for 60 min with 30 wt.% fiber loading. The effect of fiber loading on biocomposite properties was tested by varying the fiber loading from 30 to 50 wt.%.

Biocomposite sheets (10 × 10 cm) were prepared by heat compressing 10 g of the OPMF/PP blend (untreated and SHS-treated biocomposites) in a hot compression molding machine (electrically-heated platen press, Hsin-Chi Machinery Co. Ltd., Hsinchu, Taiwan). Biocomposite samples were preheated in the mold at 160 °C for 10 min to allow complete melting at atmospheric pressure. The molten compound was then pressed at the same temperature under a pressure of 110 kg/cm² for 5 min to form biocomposite sheets with 1 and 3 mm thickness. The molded sheets were then transferred to a cold press and pressed for another 5 min. The sheets were used for mechanical, morphological, thermal, and water absorption analyses.

Mechanical Properties of Biocomposites

The mechanical properties of OPMF/PP biocomposites were studied considering the effect of SHS temperature and fiber loading. Tensile and flexural tests were carried out using an Instron universal testing machine (Instron 4302, Norwood, MA, USA) according to ASTM D638-5 (2000) and ASTM D790 (2000), respectively. Specimens for tensile and flexural tests were cut according to these standards. A load cell of 1 kN was used, and the tests were performed at 25 °C. A crosshead speed of 5 mm/min was used for the tensile test. A crosshead speed of 1.3 mm/min and a support span length of 48 mm were used for the flexural test. An un-notched IZOD impact test for the biocomposites was carried out according to the ASTM D256 (2000) using an IZOD impact tester (Mumbai, India) equipped with a 7.5 J pendulum at 25 °C. Five specimens were tested for each test, and the average values were reported.

Differential Scanning Calorimetry

Thermal analysis of the biocomposites was investigated using differential scanning calorimetry (DSC) (TA Instruments Q20, Waters-LLC, New Castle, Delaware). A test sample of 7 to 9 mg was used. All samples were heated from 40 to 200 °C at a heating rate of 10 °C min⁻¹. The percentage of crystallinity (X_c) of the biocomposites was determined from the DSC analysis, as shown in Eq. 1. X_c of the biocomposites was calculated as the ratio of the melting enthalpy (ΔH_m) to the specific heat of fusion of 100% crystalline PP, taken as 190 J g⁻¹ (Hristov and Vasileva 2003), as shown in Eq. 1.

$$X_c = \frac{\Delta H_m}{\Delta H_m^{*PP}} \times 100 \quad (1)$$

Scanning Electron Microscopy

The surface morphology of the fractured samples after the tensile test of OPMF/PP biocomposites was observed using scanning electron microscopy (SEM) (LEO 1455 VPSEM, Electron Microscopy Ltd., Cambridge, England). For SEM analysis, oven-dried OPMF samples were mounted on the stub and gold-coated for 180 s prior to SEM observation. The micrographs were obtained with an acceleration voltage of 20 kV.

Water Absorption

Dumbbell-shaped specimens were used to standardize the sample size for the water absorption test (Hosseinaei *et al.* 2012). The samples were oven-dried at 60 °C for 24 h, weighed, and soaked in water at 25 °C for 90 days. Water absorption was checked periodically by removing the sample from the water, weighing, and immersing it in the water again. The amount of water absorbed (M_t) was calculated as in Eq. 2,

$$M_t \% = \frac{(W_t - W_o)}{W_o} \times 100 \quad (2)$$

where w_o is the initial weight of the specimens, and w_t is the weight of the specimens at t time.

Thermogravimetric Analysis

The thermal stability of biocomposites was determined by thermogravimetric analysis (TGA). Approximately 6 to 8 mg of samples were heated from 50 to 600 °C using a nitrogen air flow of 50 mL/min and a heating rate of 10 °C/min in a TGA instrument (TA Instruments Q500, Waters-LLC, New Castle, DE, USA).

Statistical Analysis

All data were analyzed with one-way analysis of variance (ANOVA) followed by Duncan's multiple range test for comparing means. Results of five replicates for each parameter analyzed were used to perform the statistical analysis. The ANOVA was performed on Mstat software (Michigan State University, East Lansing, MI, USA), and the probability was set at 0.05 ($p < 0.05$). Mean values for each set of data were compared to determine if the parameter demonstrated a significant or insignificant effect. Significant differences between parameters analyzed are denoted by different superscripts (A – C).

RESULTS AND DISCUSSION

Effect of SHS Treatment Temperature on the Properties of OPMF/PP Biocomposites

The effect of SHS temperature on the mechanical properties of OPMF/PP biocomposites was determined, as shown in Table 1. The mechanical properties of SHS-OPMF/PP biocomposites improved compared with the untreated-OPMF/PP biocomposite, up to a treatment temperature of 210 °C.

The mechanical properties of SHS210-OPMF/PP improved by 25% for tensile strength, 18% for tensile modulus, 45% for flexural strength, 3% for flexural modulus, and 83% for impact strength when compared with untreated-OPMF/PP. Table 1 shows that SHS210-OPMF/PP biocomposite gave the highest tensile strength at 20.5 MPa. In terms of tensile modulus, the increment was significant for SHS-OPMF/PP biocomposites compared with the untreated-OPMF/PP biocomposite, regardless of the temperature used. Statistical analysis showed that there was no significant difference in flexural modulus for all samples. In contrast, the impact strength of SHS-OPMF/PP biocomposites (*i.e.*, the 190 °C sample) increased to 96% higher than untreated biocomposites. The results obtained were in agreement with a report by Hosseini *et al.* (2012), which exhibited that impact strength of biocomposite with the incorporation of flax fiber in polyurethane (PU) matrix

was higher compared to neat PU. However, upon addition of fiber treated at temperatures over 220 °C, the impact strength decreased to as low as 47 J/m.

Table 1. Mechanical Properties of OPMF/PP Biocomposite Samples^{a,b}

Treatment Temperature (°C)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
Untreated	16.32±1.87 ^B	448.56±10.49 ^B	23.02±2.27 ^C	1329±283 ^A	44.10±7.34 ^C
190	17.45±0.54 ^B	524.94±23.58 ^A	30.90±1.55 ^{AB}	1327±130 ^A	86.85±10.35 ^A
200	17.72±1.03 ^B	522.92±48.70 ^A	32.15±1.54 ^{AB}	1428±103 ^A	82.52±6.35 ^A
210	20.47±1.44 ^A	531.46±44.91 ^A	33.44±0.91 ^A	1370±112 ^A	80.92±5.37 ^A
220	19.92±0.29 ^A	539.08±9.62 ^A	29.67±1.26 ^{AB}	1338±142 ^A	61.17±7.54 ^B
230	19.28±0.75 ^A	540.36±13.97 ^A	29.15±1.18 ^B	1273±107 ^A	46.55±8.27 ^C

^aStandard deviation shown in parentheses

^bIn superscripts, different letters in the same column indicate a statistical difference ($p < 0.05$) among the sample

Scanning electron microscopy micrographs of fractured samples from the tensile test can further explain fiber-polymer physical interaction (Fig. 1). Untreated OPMF in a PP matrix was easily visible, and many of the fibers were pulled from the PP matrix during the tensile test (Fig. 1a). This result implied that there was poor interfacial adhesion between the polymer and untreated fiber, which explains the low mechanical properties of the biocomposites. Distinct gaps between the fiber and the matrix were also observed, which may explain the low mechanical properties of biocomposites.

In contrast to SHS-treated fiber, there was less fiber pull-out observed from the PP matrix. Figure 1b, which represents SHS190-OPMF/PP biocomposite, shows less pulled-out fibers and fewer voids compared to untreated-OPMF/PP. For biocomposites prepared from SHS210-OPMF and SHS230-PMF, fractured fibers can be clearly observed, as shown in Figs. 1c and 1d, respectively. Both samples also exhibited less fiber pull-out and formation of voids. Figure 2a shows untreated biocomposite failure caused solely by matrix tearing. However, for SHS-OPMF/PP biocomposites shown in Fig. 2b, massive failures of both the fibers and matrix in the form of fiber splitting and tearing were observed.

The improved or decreased trends of the mechanical properties of the biocomposite can be controlled mainly by altering the composition of fiber chemicals after SHS treatment. Nordin *et al.* (2013) reported that SHS treatment removed some hemicellulose, silica bodies, and moisture from OPMF. The reduction of the hemicellulose content increased the hydrophobicity of the fiber. Improved hydrophobicity of the fiber increased the mechanical properties of the biocomposite due to stronger physical interaction between the fiber and polymer matrix (Sinha and Rout 2009; Then *et al.* 2014). This improved hydrophobicity explains why the SHS-treated-OPMF/PP biocomposites had higher mechanical properties compared with untreated-OPMF/PP. Removal of silica bodies, on the other hand, gave rougher surface topography of the fiber, consequently increasing the effective surface area to which PP could adhere on the fiber surface. This decrease in adhesive surface agreed with Kaewkuk *et al.* (2013), whose report included the term “mechanical interlocking” to explain the phenomenon.

Another explanation for the improved mechanical properties of the SHS-treated biocomposites relates to fiber dispersion within the polymer matrix. Fiber with improved hydrophobicity is more compatible with the polymer and easily disperses within the matrix (Hosseinaei *et al.* 2012). Hydrophilic untreated-OPMF tends to agglomerate due to fiber-fiber interactions, making it difficult to disperse in a hydrophobic polymer matrix. However, mechanical properties were slightly reduced, especially impact strength for biocomposites prepared from fiber treated at temperatures above 210 °C. The decreased mechanical properties of the biocomposites can be explained as being due to the disruption of fiber structure especially cellulose when treated at high temperature. This is supported by Han *et al.* (2009), who reported that cellulosic component tends to disrupt at temperatures above 220 °C. The disruption of cellulosic component may affect the strength of the fiber and hence led to the reduction of biocomposites mechanical properties.

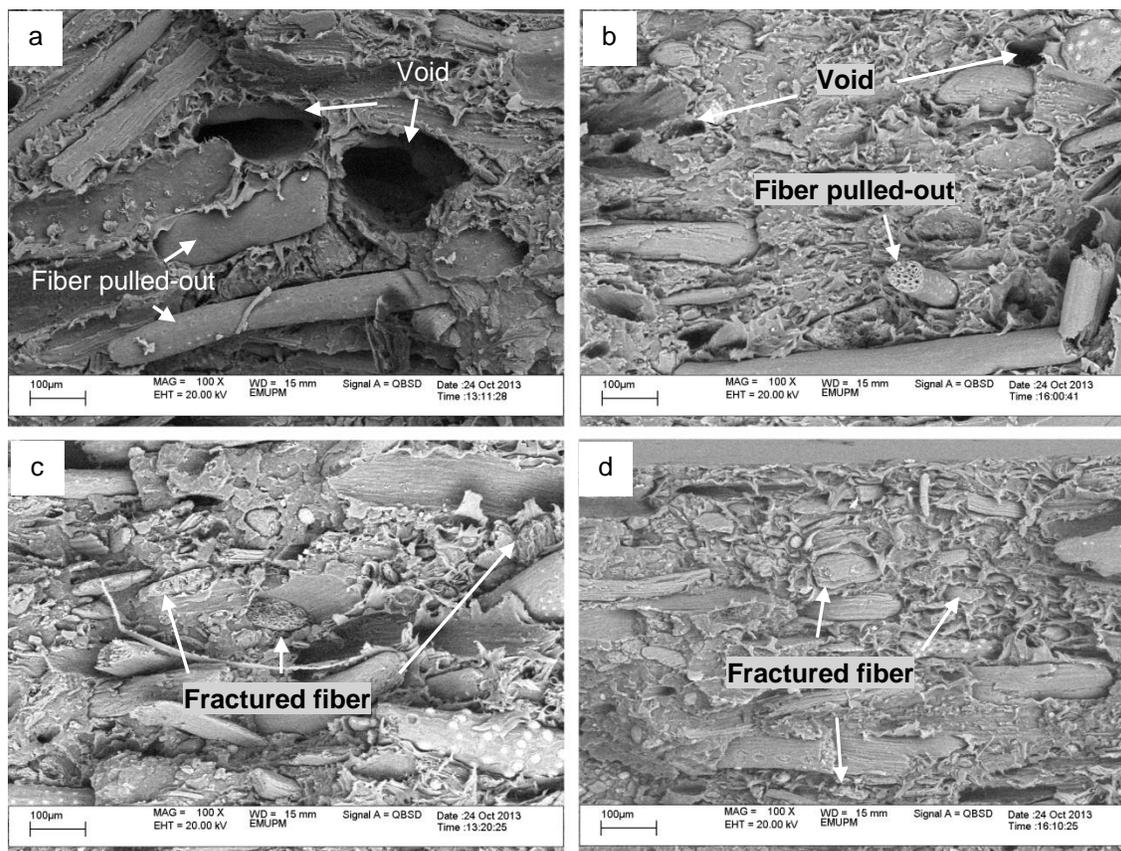


Fig. 1. Fractured samples after the tensile test of (a) untreated-OPMF/PP; pulled-out fibers, voids, and a gap between the fibers and the PP can be easily observed; (b) SHS190-OPMF/PP; less pulled-out fibers and fewer voids; (c) SHS210-OPMF/PP; fractured fibers can be observed; and (d) SHS230-OPMF/PP; showed fewer voids and gaps

Table 2 shows the melting point and crystallinity of the OPMF/PP biocomposites. There was a trend of increasing melting point temperature, which reached 169.2 °C, near the T_m of neat PP (169.5 °C). This increase showed that SHS-treated OPMF had better compatibility with PP compared with untreated-OPMF. Notably, the increment in melting point was consistent with the increase in SHS treatment temperature. This similarity can be explained by the improved compatibility between fiber and PP at higher SHS temperatures, as more hemicellulose was removed at higher temperatures.

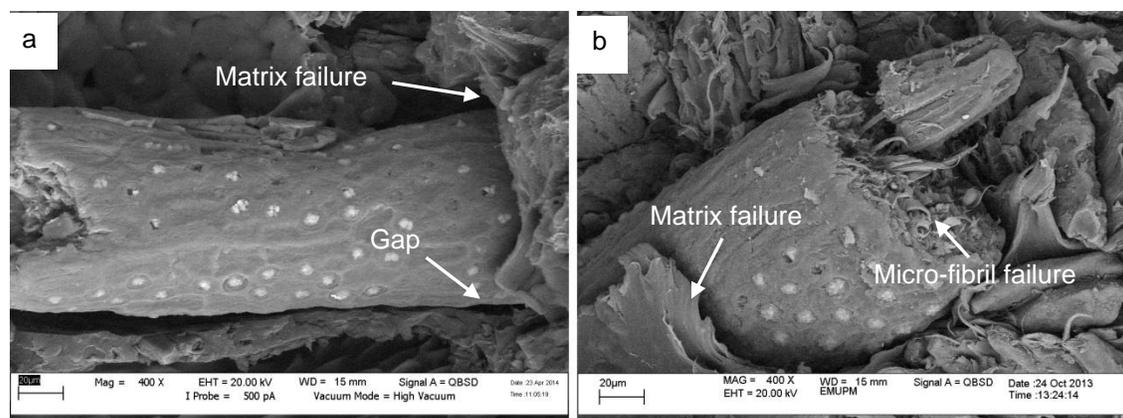


Fig. 2. (a) Untreated-OPMF/PP biocomposite showed only matrix failure, and (b) SHS-OPMF/PP biocomposite had poor fiber-matrix adhesion, indicated by micro-fibril and matrix failure

The crystallinity of the OPMF/PP biocomposite increased when the samples were prepared from SHS-OPMF, up to the treatment temperature of 210 °C. The highest crystallinity was found in SHS200-OPMF/PP biocomposites, where an improvement of almost 20% was recorded, compared with that of untreated-OPMF/PP biocomposites. An increase in the crystallinity can occur due to the removal of amorphous hemicellulose and low molecular weight lignin in SHS treatment. However, biocomposites prepared from OPMF treated with SHS at high temperatures (above 210 °C) showed reduced crystallinity. This result agreed with study reported by Nordin *et al.* (2013) that showed that the alteration of the cellulose crystalline region occurred at high treatment temperatures, subsequently affecting the biocomposite crystallinity.

Table 2. Melting Point (°C) and Crystallinity (%) of OPMF/PP Biocomposite

Sample	T_m (°C)	ΔH_m (J g ⁻¹)	X_c (%)
PP	169.5	95.7	50.3
Untreated-OPMF/PP	162.9	49.7	24.3
SHS190-OPMF/PP	164.6	51.7	27.2
SHS200-OPMF/PP	165.1	55.0	28.9
SHS210-OPMF/PP	166.7	53.3	28.0
SHS220-OPMF/PP	167.0	45.5	23.9
SHS230-OPMF/PP	169.2	44.3	23.3

Effect of Fiber Loading on the Mechanical Properties of OPMF/PP Biocomposite

The effect of fiber loading (30 to 50 wt.%) on the mechanical properties of SHS-OPMF/PP biocomposites was studied using samples of untreated OPMF and SHS-treated OPMF at 210 °C for 1 h (SHS210-treated OPMF), as shown in Table 3. It was found that biocomposite prepared from fiber treated at temperature 210 °C for 1 h gave the highest mechanical properties. Thus, this sample was used in order to study the effect of fiber loading. Overall, increased fiber loading caused decreased tensile strength, tensile modulus, flexural strength, and impact strength in biocomposites prepared from both untreated and SHS210-treated OPMF. In contrast, the flexural modulus improved for both samples as the fiber loading increased.

Table 3. Mechanical Properties of Untreated-OPMF/PP and SHS210-OPMF/PP Biocomposites at Different Fiber Loading^{a,b}

Sample	Fiber Loading (wt.%)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	Impact Strength (J/m)
Untreated-OPMF/PP	30	16.32±1.87 ^A	449±10 ^A	23.02±2.27 ^A	1329±283 ^B	44.10±7.34 ^A
	40	14.89±0.89 ^B	429±15 ^B	22.58±4.27 ^A	1596±133 ^A	46.60±6.61 ^A
	50	13.43±1.26 ^B	375±18 ^B	20.97±0.81 ^B	1706±69 ^A	44.18±4.80 ^A
SHS210-OPMF/PP	30	20.47±1.44 ^A	531±45 ^A	33.44±0.91 ^A	1370±112 ^B	80.92±5.37 ^A
	40	16.92±1.27 ^B	525±71 ^B	27.63±0.92 ^B	1382±49 ^B	72.64±11.02 ^B
	50	13.99±1.06 ^C	442±26 ^C	23.83±0.62 ^C	1737±58 ^A	69.32±5.30 ^B

^aStandard deviation shown in parentheses

^bIn superscripts, different letters in the same column indicate statistical difference ($p < 0.05$) among the samples; statistical differences were analyzed between the fiber loading only for the same group of OPMF/PP biocomposite

Low mechanical properties for both biocomposites at high fiber loading can be explained by insufficient fiber wetting of the PP matrix, which led to poor stress transfer. There have been similar reports that the mechanical properties of biocomposites decreased when more fiber was added (Mir *et al.* 2013; Etaati *et al.* 2014). The lower mechanical properties of biocomposites at high fiber loading was also caused by fiber agglomeration, which creates voids in the biocomposites.

Fiber agglomeration at high fiber loading results from strong fiber-fiber interaction (Kaewkuk *et al.* 2013; Then *et al.* 2013). Based on these results, the effect of fiber loading on the mechanical properties of biocomposites was similar for both untreated and SHS-treated biocomposites. Even though compatibility of the PP fiber was increased after SHS treatment, at higher fiber loading both agglomeration and poor wettability were the strongest reasons for failure.

The flexural modulus was improved for both untreated and SHS-treated biocomposites when the fiber content was increased. When fibers were incorporated into the polymer matrix, the biocomposites became stiffer and their flexural moduli improved (Lee *et al.* 2013). Other studies also showed an increment of flexural modulus as fiber content increased, due to the stiffness of the fiber that may positively contribute to the overall stiffness of the biocomposite (Then *et al.* 2013).

Water Absorption of OPMF/PP Biocomposites

Untreated-OPMF/PP and SHS-OPMF/PP biocomposites were examined for their water absorption, and the results are presented in Fig. 3. Overall, the percentage of water absorption was the highest for untreated OPMF biocomposite, followed by SHS190-OPMF/PP and SHS200-OPMF/PP biocomposite. A trend can be observed for SHS-treated OPMF biocomposites, whereby biocomposites that contained OPMF treated at a lower temperature range showed higher water absorption compared with biocomposites with OPMF treated at higher temperatures.

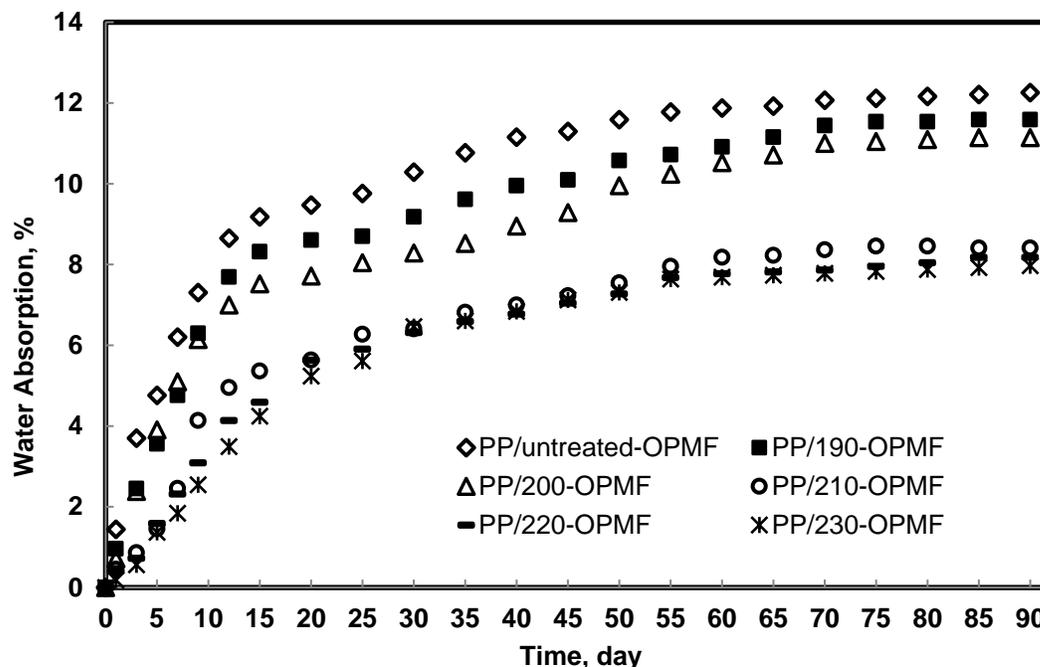


Fig. 3. Water absorption of untreated-OPMF/PP and SHS-OPMF/PP biocomposites with the addition of 30 wt.% fiber loading at different SHS temperatures

To elucidate the water absorption property in relation to SHS treatment, the maximum water absorption results are tabulated in Table 4. In our previous study, it was shown that hemicellulose content decreased with the increase in SHS treatment temperature (Nordin *et al.* 2013). It was expected that the removal of hemicellulose caused the fiber to lose some hydroxyl groups, making it less hydrophilic. In order to demonstrate that, a water absorption study was conducted. As shown in Table 4, water absorption was lower for biocomposites prepared from fiber treated at higher SHS treatment temperature. This clearly shows that water absorption property of the biocomposites is highly dependent on the hemicellulose content (hydroxyl groups) in OPMF.

Table 4. Maximum Water Absorption (%) of OPMF/PP* Biocomposites after 90 Days of Soaking in Water

Biocomposite	Water Absorption _{max} (%)
untreated-OPMF/PP	12.26
SHS190-OPMF/PP	11.59
SHS200-OPMF/PP	11.14
SHS210-OPMF/PP	8.41
SHS220-OPMF/PP	8.18
SHS230-OPMF/PP	7.97

*Fiber size of <math><150\ \mu\text{m}</math> and 30 wt.% fiber content

Overall, it is seen that untreated OPMF biocomposite was the most hydrophilic as being exhibited by the water absorption value. Apart from hemicellulose content,

additional reason for water absorption could be due to fiber poor adhesion with hydrophobic polymer, causing the biocomposite sample to have voids, as shown by the SEM micrograph in Fig. 1a. These voids may have contributed to water penetration and hence higher water absorption, especially for less compatible biocomposites.

Thermal Stability of Untreated-OPMF/PP and SHS-OPMF/PP Biocomposites

Biocomposite decomposition temperature was analyzed by TGA to determine its thermal stability; the results are shown in Fig. 4. Generally, both of the TG curves showed multiple degradation steps, indicating the difference in decomposition temperature of components in the biocomposites. Polypropylene decomposition temperature ranges from 350 °C to 450 °C, while lignocellulosic components (*i.e.*, lignin, hemicellulose and cellulose) degraded at temperature ranges of 160 to 900 °C, 220 to 315 °C, and 315 to 400 °C, respectively. Overall, the SHS210-OPMF/PP biocomposite had higher thermal stability than untreated-OPMF/PP. The comparison can be seen clearly from the magnified TGA curve in Fig. 4. Untreated OPMF biocomposite started to degrade at 150 °C, and SHS210-OPMF/PP biocomposite degraded at approximately 250 °C.

In contrast, the DTG thermogram of the biocomposites (Fig. 5) showed three distinct peaks for untreated-OPMF/PP and two peaks for SHS210-OPMF/PP. As reported earlier (Nordin *et al.* 2013), the lower thermal stability of untreated OPMF was due to the presence of thermally unstable hemicellulose. This was shown by the first peak in the DTG thermogram at approximately 220 to 300 °C. The higher thermal stability of the SHS210-OPMF/PP biocomposite was due to the partial removal of hemicellulose, seen by the incomplete disappearance of the first peak in the DTG thermogram (shown as a shoulder peak). Higher lignin composition in the SHS-OPMF was due to hemicellulose removal which contributed to increased residue at 550 °C.

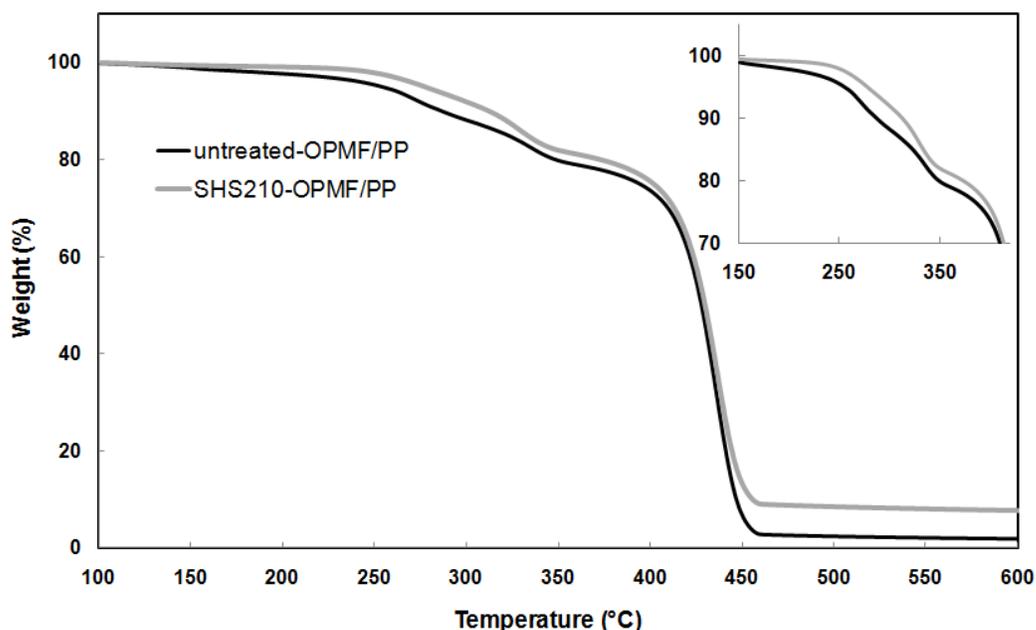


Fig. 4. Thermogravimetric analysis of untreated-OPMF/PP and SHS210-OPMF/PP biocomposite (30 wt.% fiber loading). Magnified TG curve for temperature range 150 to 400 °C is included in order to clearly show the thermal stability difference of the two samples.

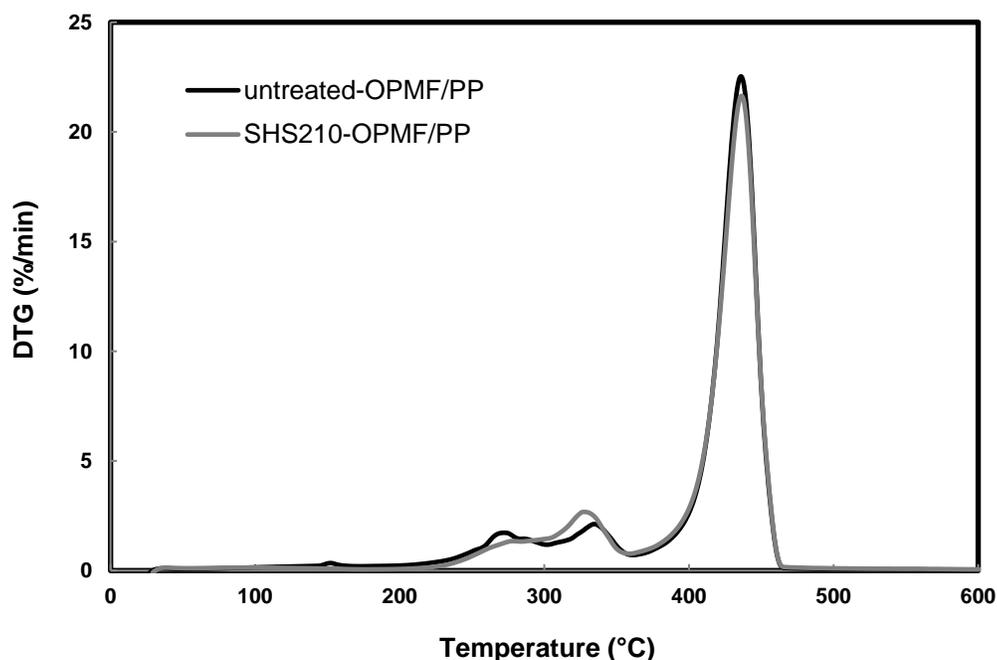


Fig. 5. DTG thermogram of untreated-OPMF/PP and SHS210-OPMF/PP biocomposite

CONCLUSIONS

1. SHS210-OPMF/PP biocomposite had higher tensile strength, tensile modulus, flexural strength, and impact strength by 25%, 18%, 45%, and 83%, respectively, compared with untreated-OPMF/PP. These results can be explained by the removal of hemicellulose, which improved the fiber hydrophobicity and led to better compatibility with the PP matrix compared with untreated OPMF. However, silica removal caused the formation of craters and provided an anchor for PP on the fiber, which caused better surface interaction between PP and OPMF.
2. For the biocomposite prepared from SHS210-OPM, water absorption was significantly reduced by 31%, and thermal properties at $T_{5\% \text{ degradation}}$ and crystallinity were increased by 8% and 15%, respectively, were also recorded in comparison with untreated-OPMF. These observations were mainly related to hemicellulose removal during SHS treatment.
3. Fiber loading had a significant effect on the mechanical properties of the biocomposites, whereby increased fiber loading from 30 to 50 wt.% reduced the mechanical properties of both SHS210-OPMF/PP and untreated-OPMF/PP biocomposites.
4. Overall, SHS treatment is an effective treatment method for surface modification of natural fiber to improve biocomposite properties.

ACKNOWLEDGEMENTS

The authors thank the Ministry of Higher Education (MOHE), Malaysia for the SATREPS research grant (vote no: 6300156) and financial support (SLAB) to the first author. The authors also thank Prof. Dr. Haruo Nishida from Kyushu Institute of Technology, Japan, for his valuable advice in data analysis, and FELDA Seriting Hilir Palm Oil Mill, Negeri Sembilan, for supplying the raw materials.

REFERENCES CITED

- Ali, A.A.M., Othman, M.R., Shirai, Y., and Hassan, M.A. (2015). "Sustainable and integrated palm oil biorefinery concept with value-addition of biomass and zero emission system," *Journal of Cleaner Production* 91, 96-99.DOI: 10.1016/j.jclepro.2014.12.030
- Ando, H., Sakaki, T., Kokusho, T., Shibata, M., Uemura, Y., and Hatate, Y. (2000). "Decomposition behavior of plant biomass in hot-compressed water," *Industrial and Engineering Chemistry Research* 39(10), 3688-3693.DOI: 10.1021/ie0000257
- Arbelaiz, A., Fernandez, B., Cantero, G., Llano-Ponte, R., Valea, A., and Mondragon, I. (2005). "Mechanical properties of flax fibre/polypropylene composites. Influence of fibre/matrix modification and glass fibre hybridization," *Composites Part A: Applied Science and Manufacturing* 36(12), 1637-1644.DOI: 10.1016/j.compositesa.2005.03.021
- ASTM D256. (2000). "Standard test methods for determining the Izod pendulum impact resistance of plastics," ASTM International, West Conshohocken, PA.
- ASTM D638-5. (2000). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA.
- ASTM D790. (2000). "Standard test method for flexural properties of unreinforced and reinforced plastics," ASTM International, West Conshohocken, PA.
- Bahrin, E. K., Baharuddin, A. S., Ibrahim, M. F., Razak, M. N. A., Sulaiman, A., Abd-Aziz, S., Hassan, M. A., Shirai, Y., and Nishida, H. (2012). "Physicochemical property changes and enzymatic hydrolysis enhancement of oil palm empty fruit bunches treated with superheated steam," *BioResources* 7(2), 1784-1801.DOI: 10.15376/biores.7.2.1784-1801
- Eslam, H. K., Saieh, S. E., and Rajabi, M. (2011). "Effect of steaming treatment on the physical and mechanical properties of WPC made of cotton flour and polypropylene," *Australian Journal of Basic and Applied Science* 5(6), 1143-1150.
- Etaati, A., Pather, S., Fang, Z., and Wang, H. (2014). "The study of fibre/matrix bond strength in short hemp polypropylene composites from dynamic mechanical analysis," *Composites Part B: Engineering* 62, 19-28.DOI: 10.1016/j.compositesb.2014.02.011
- Gomes, A., Matsuo, T., Goda, K., and Ohgi, J. (2007). "Development and effect of alkali treatment on tensile properties of curaua fiber green composites," *Composite Part A: Applied Science and Manufacturing* 38(8), 1811-1820.DOI: 10.1016/j.compositesa.2007.04.010
- Han, G., Cheng, W., Deng, J., Dai, C., Zhang, S., and Wu, Q. (2009). "Effect of pressurized steam treatment on selected properties of wheat straws," *Industrial Crops and Products* 30(1), 48-53.DOI: 10.1016/j.indcrop.2009.01.004

- Hosseinaei, O., Wang, S., Enayati, A. A., and Rials, T. G. (2012). "Effects of hemicellulose extraction on properties of wood flour and wood-plastic composites," *Composites Part A: Applied Science and Manufacturing* 43(4), 686-694. DOI: 10.1016/j.compositesa.2012.01.007
- Hosseini, N., Ulven, C., Webster, D., and Nelson T. J. (2012). "Utilization of flax fibers and glass fibers in a bio-based resin," *The 19th International Conference on Composite Materials* 7 pages. DOI: 10.1115/IMECE2014-39393
- Hristov, V., and Vasileva, S. (2003). "Dynamic mechanical and thermal properties of modified poly(propylene) wood fiber composites," *Macromolecular Materials and Engineering* 288(10), 798-806. DOI: 10.1002/mame.200300110
- Ibrahim, N. A., Hashim, N., Rahman, M. Z. A., and Yunus, W. M. Z. W. (2011). "Mechanical properties and morphology of oil palm empty fruit bunch-polypropylene composites: Effect of adding ENGAGE™ 7467," *Journal of Thermoplastic Composite Materials* 24(5), 713-732. DOI: 10.1177/0892705711401549
- Kaewkuk, S., Sutapun, W., and Jarukumjorn, K. (2013). "Effects of interfacial modification and fiber content on physical properties of sisal fiber/polypropylene composites," *Composite Part B: Engineering* 45(1), 544-549. DOI: 10.1016/j.compositesb.2012.07.036
- Lee, J. M., MohdIshak, Z. A., Mat Taib, R., Law, T. T., and Ahmad Thirmizir, M. Z. (2013). "Mechanical, thermal and water absorption properties of kenaf-fiber-based polypropylene and poly(butylene succinate) composites," *Journal of Polymers and the Environment* 21(1), 293-302. DOI: 10.1007/s10924-012-0516-4
- Mahmud, N. A. N., Baharuddin, A. S., Bahrin, E.K., Sulaiman, A., Naim, M. N., Zakaria, R., Hassan, M. A., Nishida, H., and Shirai, Y. (2013). "Enzymatic saccharification of oil palm mesocarp fiber (OPMF) treated with superheated steam," *BioResources* 8(1), 1320-1331. DOI: 10.15376/biores.8.1.1320-1331
- Mir, S. S., Nafsin, N., Hasan, M., Hasan, N., and Hassan, A. (2013). "Improvement of physico-mechanical properties of coir-polypropylene biocomposites by fiber chemical treatment," *Materials and Design* 52, 251-257. DOI: 10.1016/j.matdes.2013.05.062
- Mohan, T. P., and Kanny, K. (2012). "Chemical treatment of sisal fiber using alkali and clay method," *Composites Part A: Applied Science and Manufacturing* 43(11), 1989-1998. DOI: 10.1016/j.compositesa.2012.07.012
- Nordin, N. I. A. A., Ariffin, H., Andou, Y., Hassan, M. A., Shirai, Y., Nishida, H., Yunus, W. M. Z. W., Karuppuchamy, S., and Ibrahim, N. A. (2013). "Modification of oil palm mesocarp fiber characteristics using superheated steam treatment," *Molecules* 18, 9132-9146. DOI: 10.3390/molecules18089132
- Sawpan, M. A., Pickering, K. L., and Fernyhough, A. (2011). "Effect of various chemical treatments on the fibre structure and tensile properties of industrial hemp fibres," *Composite Part A: Applied Science and Manufacturing* 42(8), 888-895. DOI: 10.1016/j.compositesa.2011.03.008
- Sgriccia, N., Hawley, M. C., and Misra, M. (2008). "Characterization of natural fiber surfaces and natural fiber composites," *Composites Part A: Applied Science and Manufacturing* 39(10), 1632-1637. DOI: 10.1016/j.compositesa.2008.07.007
- Sinha, E., and Rout, S. K. (2009). "Influence of fibre-surface treatment on structural, thermal and mechanical properties of jute fibre and its composite," *Bulletin of Materials Science* 32(1), 65-76. DOI:10.1007/s12034-009-0010-3

- Sreekala, M. S., and Thomas, S. (2003). "Effect of fiber surface modification on water-sorption characteristics of oil palm fibers," *Composites Science and Technology* 63(6), 861-869. DOI: 10.1016/S0266-3538(02)00270-1
- Then, Y. Y., Ibrahim, N. A., Zainuddin, N., Ariffin, H., and Yunus, W. M. Z. W. (2013). "Oil palm mesocarp fiber as new lignocellulosic material for fabrication of polymer/fiber biocomposites," *International Journal of Polymer Science* 4, 1-7. DOI: 10.1155/2013/797452
- Then, Y. Y., Ibrahim, N. A., Zainuddin, N., Ariffin, H., Yunus, W. M. Z. W., and Chieng, B. W. (2014). "Surface modifications of oil palm mesocarp fiber by superheated steam, alkali, and superheated steam-alkali for biocomposite applications," *BioResources* 9(4), 7467-7483. DOI: 10.15376/biores.9.4.7467-7483
- Zakaria, M. R., Norrrahim, M. N. F., Hirata, S., and Hassan, M. A. (2015). "Hydrothermal and wet disk milling pretreatment for high conversion of biosugars from oil palm mesocarp fiber," *Bioresource Technology* 181, 263-269. DOI: 10.1016/j.biortech.2015.01.072

Article submitted: August 22, 2016; Peer review completed: October 25, 2016; Revised version received and accepted: November 2, 2016; Published: November 7, 2016.
DOI: 10.15376/biores.12.1.68-81