Enhancement of Tensile Strength of Oil Palm Mesocarp Fiber/Poly(butylene succinate) Biocomposite via Superheated Steam-Alkali Treatment of Oil Palm Mesocarp Fiber

Yoon Yee Then[1, *], NorAzowa Ibrahim[1], Norhazlin Zainuddin[1], Hidayah Ariffin[2] and Wan MdZin Wan Yunus[3]

[1]*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

[2]*Department of Bioprocess Technology, Faculty of Biotechnology and Biomolecular Sciences, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia*

[3]*Department of Chemistry, Centre For Defence Foundation Studies, National Defence University of Malaysia, Sungai Besi Camp, 57000 Kuala Lumpur,Federal Territory of Kuala Lumpur, Malaysia*

[*]*E-mail: yoonyeetyy84@yahoo.com*

ABSTRACT

Natural fiber is incompatible with hydrophobic polymer due to its hydrophilic nature. Therefore, surface modification of fiber is needed to impart compatibility. In this work,superheated steam (SHS)-alkali was introduced as novel surface treatment method to modify oil palm mesocarp fiber (OPMF) for fabrication of biocomposites. The OPMF was first pre-treated with SHS and subsequently treated with varying NaOH concentration (1, 2, 3, 4 and 5%) and soaking time (1, 2, 3 and 4h) at room temperature. The biocomposites were then fabricated by melt blending of 70 wt% SHS-alkali treated-OPMFs and 30 wt% poly(butylene succinate) in a Brabender internal mixer followed by hot-pressed moulding. The combination treatment resulted in fiber with rough surface as well as led to the exposure ofmicrofibers. The tensile test result showed that fiber treated at 2% NaOH solution and 3h soaking time produced biocomposite with highest improvement in tensile strength (69%) and elongation at break (36%) in comparison to that of untreated OPMF. The scanning electron micrographs of tensile fracture surfaces of

biocomposite provide evident for improved adhesion between fiber and polymer after thetreatments.This work demonstrated that combination treatments of SHS and NaOH could be a promising way to modify OPMF for fabrication of biocomposite.

INTRODUCTION

Nowadays, the utilization of natural fiber in production of fiber/polymer biocomposites is of attractive, particularly because of its low density, low cost, renewability and biodegradability [1, 2]. However, the primary drawback of using natural fiber as filler in biocomposites is the incompatibility between the hydrophilic fiber and hydrophobic plastic, and oftenresults in poor interfacial interaction between them. Additionally, the hydrophilic nature of fiber also contributes to poor dimensional stability of the biocomposites as fiber tends to absorb water and swell once expose to water or humid environment [3].

These problems can be overcome by physically or chemically modifying the surface of fiber. These modifications include grafting [4],alkalization [5-11], steaming [12, 13] and silane treatment [14]. Of them, modifications of fiber by alkali and steamtreatments are of interest here due to theirlow operation cost and simplicity [9]. Hemicellulose has been shown to be alkali and heat sensitive. Therefore, it can be easily removed once fiber is exposed to alkali and steam treatments [5, 12]. According to Hosseinaei *et al.*[15], the removal of hemicellulose from the wood fiber is able to reduce the fiber hydrophilicity. This will then increases the compatibility between fiber and polymer, and subsequently leads to biocomposite with enhanced mechanical properties [5, 6]. A thorough literature study revealed that no work has been done so far on modifications of OPMF by using combinations of SHS and NaOH treatments for fabricating biocomposite.

OPMF is a biomass left behind in the oil palm mill after screw-pressing of oil palm fruits during the production of crude palm oil. It is normally burnt as solid fuel to self-supply steam and electricity required for the operation of the mill [16]. Recently, our research group has successfully utilized it as filler for biocomposites fabrication [4, 5, 12,17, 18]. Poly(butylene

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succinate) (PBS), a biodegradable thermoplastic polyester has mechanical properties similar to those of the conventional plastics such as polyethylene and polypropylene [19].Currently, it is commercially available at price lower than that of polylactic acid, a plant based biodegradable thermoplastic [6].

In this work, OPMF was surface treated by combinations of SHS and NaOH treatments. The treated fiber was characterized by Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The effect of the treated fiber on the tensile properties and morphology of OPMF/PBS biocomposite was evaluated and reported.

MATERIALS AND METHODS

Materials

OPMF was collected from FELDA Serting Hilir Oil Palm Mill, Malaysia. It was first washed by soaking in distilled water for 24hthen rinsed with hot water (60 °C) and acetone prior to drying at 60 °C in an oven. This process was carried out to remove dirt adhered to the fiber surface. The dried fiber was then ground, sieved into particle size of 150 to 300 μm and stored in a sealed polyethylene bag. The details properties of OPMF can be found in our previous work [20]. PBS, under commercialized name of BIONOLLE 1903MD was purchased from Showa Denko, Japan. It has a density of 1.26 g/cm^3 and melting point of ~115 °C.

Modification of OPMF by SHS treatment

Modification of OPMF was carried out in a superheated steam oven (QF-5200C) under normal atmospheric pressure following the method described by Then*et al.* [12]. Normal tap water was used to produce the SHS. Prior to treatment, OPMF was dried in an oven at 60 °C. The dried OPMF was then treated in a SHS oven at temperature of 220 °C for 1h. Once treatment has completed, fiber was removed immediately from the heating chamber, cooled in a desiccator and finally stored in the sealed polyethylene bag. This treated fiber was designated as SOPMF.

Modification of SOPMF by NaOH treatment

The modification of SOPMF was carried out according to the method described previously by Then*et al.* [5]. In brief, the previously obtained SOPMF was soaked in 1, 2, 3, 4 and 5% NaOH

solution for 3h at room temperature. The weight ratio of SOPMF to NaOH solution was fixed at 1:20. After the treatment process, fibers were filtered, washed several times with water and finally dried in an oven at 60 °C. The treated fibers were then used to fabricate biocomposites, and it was noted that the SOPMF treated at 2% NaOH solution produced biocomposite with highest tensile strength, tensile modulus and elongation at break in comparison to those of OPMF, SOPMF and others NaOH concentration. Therefore, 2% NaOH solution was selected to conduct another experiment with the same procedure as above except the SOPMF was soaked for 1, 2 and 4h at room temperature in order to select the best soaking time for the treatment.

Fabrication of biocomposites

PBS, OPMF, SOPMF and NaOH treated-SOPMFs were oven dried at 60 °C prior to processing. Biocomposites were fabricated by melt blending of PBS and OPMF, SOPMF or NaOH treated-SOPMFs in a Brabender internal mixer at 120 °C with a rotor speed of 50 rpm. The weight ratio of fiber to PBS was fixed at 70:30 because this is the maximum loading of fiber that can be loaded into this system as reported in our previous work [17]. In brief, PBS pellet was first melted in the Brabender mixing chamber for 2 min. Next, fiber was added slowly into the mixing chamber and continued mixing for another 13 min. The compounded material was compressed into sheet of15 mm x 15 mm x 1 mm by hydraulic hot-press also at 120 °C under pressure of 150 kg/cm^2 for 5 min, followed by cold pressing at 30 °C for 5 min.

FTIR spectroscopy

The functional groups and chemical components of OPMF, SOPMF and SNOPMF (SOPMF treated at 2% NaOH solution for 3h) were identified by a Perkin Elmer Spectrum 100 series Spectrophotometer equipped with attenuated total reflectance (ATR). The FTIR spectra of the samples were recorded in the range of frequency of 400-4000 cm^{-1}.

SEM

The scanning electron micrographs of OPMF, SOPMF, SNOPMF and tensile fracture surfaces of biocomposites were recorded by a JEOL JSM-6400 scanning electron microscope operated at 15 kV accelerating voltage. Before viewing, the oven dried samples were stuck on the metal holder

with doubled side sticky carbon tape and coated with gold by a Bio-Rad coating system for 3 min to ensure good conductivity.

Tensile properties measurement

Tensile test was carried out on the biocomposites by an Instron Universal Testing Machine, model 4302 equipped with a 1 kN load cell. The test specimens were cut into dumbbell shape from 1 mm sheet, according to ASTM D638-5. The test was conducted at 25 °C with a crosshead speed of 5 mm/min. The results were expressed in terms of tensile strength, tensile modulus and elongation at break. Five specimens were tested for each formulation. Their average values and standard deviations were reported.

RESULTS AND DISCUSSION

In our previous work [12], biocomposite with optimum tensile properties was obtained with fiber treated at the SHS temperature of 220 °C and 1h treatment time. Therefore, OPMF treated at this condition was usedto study the effect ofsubsequent NaOH treatment on the tensile properties and morphology of its corresponding biocomposites.

Characteristics of fibers

FTIR can give a quick and qualitative indication about the changes in the chemical components of fiber after treatment. The FTIR spectra of OPMF, SOPMF and SNOPMF are shown in Figure 1. Several changes are observed on the spectra after treatments. First, the absorbance of peak at 1730 cm^{-1}, assigns to a C=O stretching vibration of carboxylic acid or ester, is reduced for SOPMF and disappeared for SNOPMF due to the removal of hemicellulose [11]. Second, the absorbance of peak at 1245 cm^{-1}, corresponds to the C-O vibration of esters, ethers and phenol groups of waxy substances is reduced, indicatingwaxy substancesare partly removed [21]. Third, the absorbance of peak at 2925 cm^{-1}, belongs to the C-H stretching vibration in cellulose and hemicellulose, is further decreased after subsequent alkali treatment indicating that part of the hemicellulose is removed. These results all indicate that combinations of SHS and NaOH treatments of fiber lead to the partial removal of waxy substances and hemicellulose.In addition, the hydrophilicity of SOPMF and SNOPMF is also reduced after treatments, which is verified by

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a decrease in the absorbance of peaks at 3391 and 1645 cm^{-1},correspond to OH stretching and OH bending of absorbed water, respectively [13].
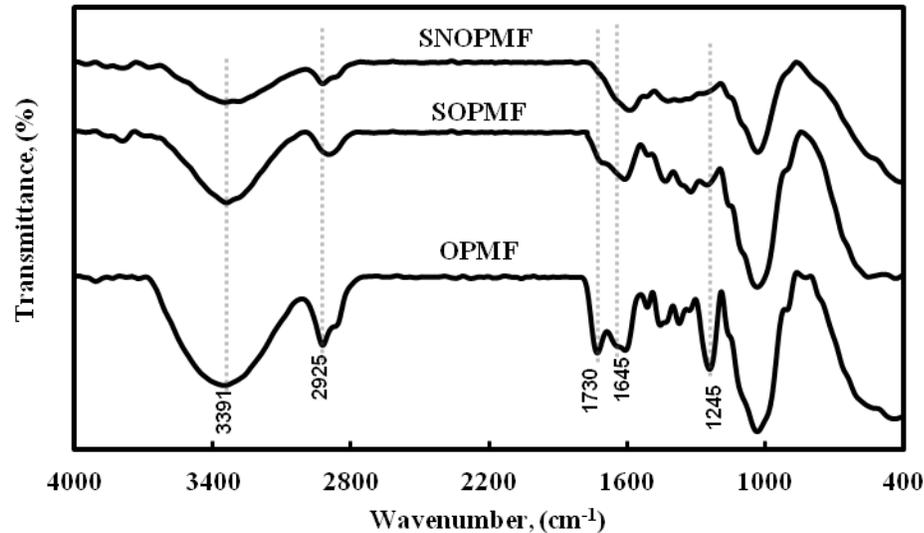

Figure 1: FTIR spectra of OPMF, SOPMF and SNOPMF.

The morphological changes of the OPMF before and after treatments are viewed under scanning electron microscope. As shown in Figure 2a, the surface of the OPMF is completely covered by non-cellulosic membranes, which mainly consistof oily and waxy substances. After pre-treatment with SHS, the non-cellulosic components have been partly removed to clearly reveal the morphology of the microfiber (Figure 2b) [7]. Some of the residual non-cellulosic components are observed to remain on the surface of fiber.However, the subsequent NaOH treatment of SOPMF has removed completely the non-cellulosic materials and lead to the greater exposure of microfibers (Figure 2c). This observed morphology could be expected to increase (i) the interfacial interaction between the fiber and matrix, (ii) the effective surface area available of contact with the matrix, and (iii) the load transfer efficiency between the matrix and the fiber. As a result, biocomposites with enhanced properties can be produced.
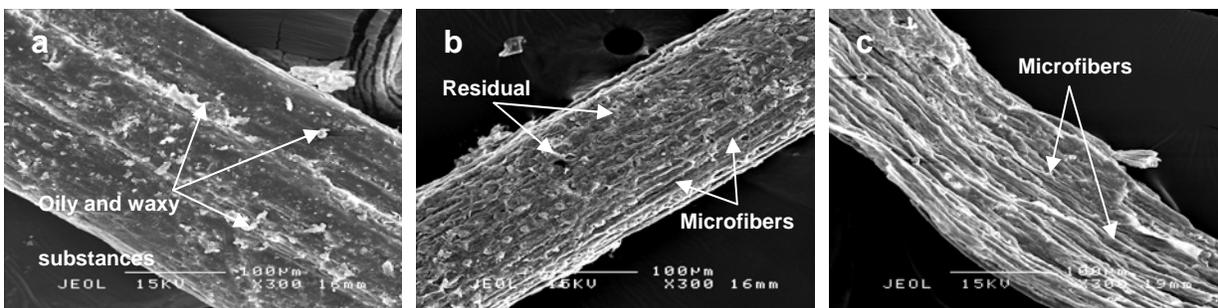
Figure 2: SEM micrographs of (a) OPMF, (b) SOPMF and (c) SNOPMF.

Characteristics of biocomposites

The tensile properties of OPMF/PBS, SOPMF/PBS and NaOH treated-SOPMF/PBS biocomposites are presented in Table 1. The OPMF/PBS biocomposite is taken as a standard material for comparison.

Table 1: Tensile properties of OPMF/PBS, SOPMF/PBS and NaOH treated-SOPMF/PBS biocomposites

Biocomposite	NaOH concentration (%)	Time (h)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
OPMF/PBS	-	-	13.86 ± 0.73	94.80 ± 7.60	2.50 ± 0.29
SOPMF/PBS	-	-	19.42 ± 0.45	552.50 ± 42.27	3.15 ± 0.35
NaOH treated-SOPMF/PBS	1	3	20.49 ± 0.61	640.10 ± 15.56	3.21 ± 0.14
	2	1	21.67 ± 0.23	700.60 ± 27.50	3.23 ± 0.36
		2	21.29 ± 0.18	662.95 ± 25.24	3.26 ± 0.28
		3	23.44 ± 0.25	670.80 ± 25.60	3.40 ± 0.14
		4	19.13 ± 0.60	154.00 ± 24.90	2.85 ± 0.19
	3	3	21.85 ± 0.62	164.90 ± 34.22	3.40 ± 0.07
	4	3	19.99 ± 0.31	128.30 ± 16.90	3.15 ± 0.07
	5	3	19.62 ± 0.87	85.55 ± 26.23	3.10 ± 0.28

As shown in Table 1, the tensile strength (TS) of the OPMF/PBS biocomposite is 13.86 MPa and it has increased to 19.42 MPa after pre-treatment with SHS. The TS of the biocomposite is further improved by subsequent NaOH treatment. At 3h treatment time, the TS of NaOH treated-SOPMF/PBS biocomposites increases with increasing NaOH concentration of up to 2%, showing an increment of 69% from OPMF/PBS, and decreases at 3, 4 and 5%.The increase in TS is attributed to the presence of rough surface and microfibersforSNOPMF (shown in Figure 2c) which can facilitate both mechanical interlocking and increase effective surface area available for adhesion of PBS,and subsequently improved the fiber/polymer interfacial adhesion [5]. It is noticeable that at NaOH concentration of 1%, the improvement in TS is rather low. This may attributes to the poor adhesion between fiber and polymer, resulting from inadequate removal of oily and waxy substances, as well as hemicellulose from the fiber [7]. In contrast, at high concentration of NaOH (3-5%), degradation and rupture of fiber may occur and lead to decrease in the TS [7].

The SHS treatment also increases the tensile modulus (TM) of OPMF/PBS biocomposite from 94.80 MPa to 552.50 MPa for SOPMF/PBS biocomposite, showing an increment of 483%. The TM of the SOPMF/PBS biocomposite is further enhanced by subsequent NaOH treatment of SOPMF. At 3h treatment time, highest value of TM is obtained at 2% NaOH solution or an improvement of 21% when compared to that ofSOPMF/PBS biocomposite.On the other hand, 26% improvement in elongation at break (EB) is recorded for SOPMF/PBS biocomposite relative to OPMF/PBS biocomposite. The EB of the SOPMF/PBS biocomposite is further enhanced by 8% in thesubsequent treatment of SOPMF by 2% NaOH solution for 3h. The increment in TM and EB is resulted from the improved interfacial adhesion between fiber and PBS which in turn facilitate better stress transfer [14].

The NaOH concentration of 2% was chosen for determining the optimum soaking time for the treatment of SOPMF as fiber treated at this concentration yielded biocomposite with highest TS, TMand EB in comparison to those of others NaOH concentration at 3h treatment time. As illustrated in Table 1, it is evident that the soaking time also gives an effect on tensile performance of the biocomposites. The TS and EB increase with increasing soaking time of up to 3h and decrease thereafter. From the tensile test result, it can be deduced that NaOH concentration of 2% and treatment time of 3h is sufficient to treat the SOPMF in order toproduce biocomposite with balance performance in TS,TM and EB.

The tensile fracture surfaces of biocomposites were investigated under SEM to evaluate the adhesion at the fiber/polymer interface, and the SEM micrographs of OPMF/PBS, SOPMF/PBS and SNOPMF/PBS biocomposites are shown in Figure 3. The adhesion between PBS and OPMF is weak with visible gap at their interface region as illustrated in Figure 3a. Besides, the OPMF is seen to be loosely packed with PBS due to lack of compatibility between these two phases.As a result, fibers are easily pulled out once stress is applied and resulted in cavities. This observation implies poor interfacial adhesion between OPMF and PBS. However, after SHS treatment, a drastic change of fracture surface morphology is noted as shown in Figure 3b. The SOPMF is closely packed together with PBS and fewer cavities are present. This indicates that the adhesion between SOPMF and PBS is improved. Meanwhile, no cavities are seen on the tensile fracture surface of SNOPMF/PBS biocomposite. Fiber breakage is observed instead of fiber pulled out. This indicates stronger interfacial adhesion is present between SNOPMF and PBS. This observation explains the reason of SNOPMF/PBS biocomposite exhibits better tensile properties than those of OPMF/PBS and SOPMF/PBS biocomposites.
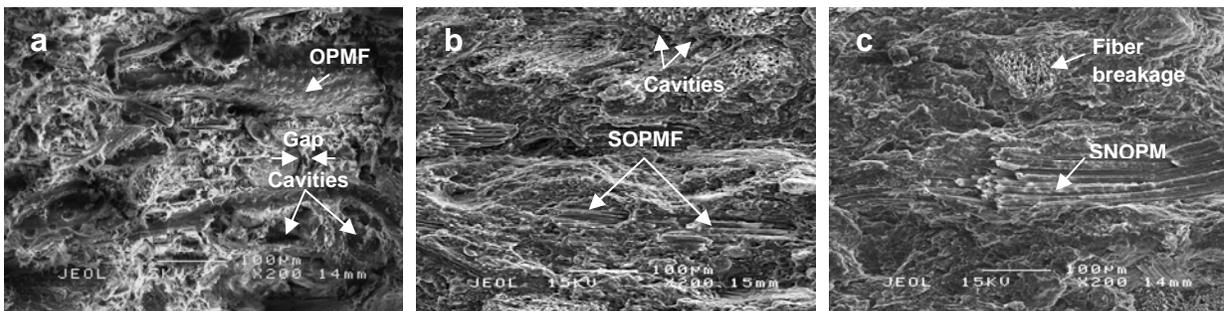

Figure 3: SEM micrographs of tensile fracture surfaces of (a) OPMF/PBS, (b) SOPMF/PBS and (c) SNOPMF/PBS biocomposites.

CONCLUSIONS

The surface of OPMF was successfully modified by combinations of SHS and NaOH treatments and later utilized for biocomposite fabrication. The oily and waxy substances on the fiber surface were partly removed afterpre-treatment with SHS. Those substances were completely removed bythe subsequent NaOH treatment and resulted in fiber with relatively clean and rough surfaces, as well asincrease in exposure of microfibers. The presence of rough surface and microfibersfor

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SNOPMF has promoted the adhesion between fiber and polymer as proven by SEM. The use of SNOPMF, which was treated by 2%NaOHsolutionfor 3h, has produced biocomposite with optimum performance in tensile strength, tensile modulus and elongation at break.

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