Ultrasound Enhanced Structural Modification of Oil Palm Empty Fruit Bunch (OPEFB) Fiber/Poly(Lactic) Acid Composites

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A b s t r a c t

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Effective surface modification of natural fibers with little or no damage to the fibers had been a prominent challenge to natural fiber reinforced polymer composites. Alkali treatment had been a very efficient technique for fiber treatment. However, environmental concerns make it necessary to as much as possible reduce the concentration of alkali for any fiber treatment. In this study, ultrasonic treatment in an alkali medium of low concentration was used to modify the surface of oil palm empty fruit bunch (OPEFB) fibers. Surface morphology of fibers due to treatment was studied by scanning electron microscopy (SEM) while its structural changes were studied by Fourier transforms infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Composites were fabricated from oil palm empty fruit bunch fiber and poly (lactic) acid (PLA) through extrusion followed by injection moulding. Characterization of composites was done by mechanical testing such as tensile and flexural. Composite structural analysis was done by XRD analysis. Result showed that treatment of OPEFB fibers with ultrasound offered great structural changes which produced composites with highly desirable properties.

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1. Introduction

Recently, natural fiber reinforced thermoplastic composites have experienced enormous growth based on their many desirable properties which include reasonable stiffness and strength, reduced abrasiveness and light weight. Desirability of natural fiber in composites had been associated to its nontoxic, combustible, renewable, light weight, nonabrasive and biodegradable properties [1, 2]. However, incorporation of natural fiber into polymer composites often led to composites with poor interface due the poor interfacial interaction at the surfaces of the fiber which is hydrophilic and that of the polymer matrices which are hydrophobic in nature. Effective modification of the fiber surface can be achieved by cleaning the fiber surface as well as increasing its roughness through chemical and physical treatments [3-5].

Fiber treatment would either activate the cellulose hydroxyl groups of the fiber, or introduce new moieties unto to the fiber surface which can bond effectively to with the matrix [6]. Through fiber treatment, composites with highly desirable properties had been fabricated with natural fibers like kenaf, bamboo, ramie, flax, coir, jute, wood and most importantly oil palm fibers. Most of the conventional treatment methods were however found to involve the use of organic solvents which often led to exposure of the environment to hazardous substances [7].

A non-conventional environmental friendly alternative method for fiber treatment is through the use of ultrasound energy. Ultrasound is one extreme way of creating an unusual chemical environment within a solution by the generation of some little cavities which are capable of enlarging and imploding. This process produces enormous heat when series of ultrasonic waves are permitted to flow through the solution [8]. Ultrasound treatment being a modern environmentally-friendly treatment technique was initially exploited for separation processes. Recently, it has been noted that ultrasound treatment of natural fibers provides many advantages for fiber purification [1, 2]. Some of these includes great modification with little alkali concentration, short time of exposure in the reaction chamber, reduced treatment temperature, fiber refinement, fiber size reduction and increased mechanical strength due to the lower degree of damage [2].

Oil palm empty fruit bunch fiber (OPEFB) is one natural fiber, among several other natural fibers that had been used to reinforce polymers in different applications and at varying degrees. Notable among these are incorporation of natural fibers into thermoplastics like PLA. However, a vast majority of these studies show that there is apparently poor adhesion between the fiber and the PLA matrix interface, hence the need for further modifications to improve the surface interaction of OPEFB fibers and PLA matrix [4, 5, 9]. In this study, ultrasound treatment was carried out on oil palm empty fruit bunch (OPEFB) fibers in alkali medium containing 2% (w/v) NaOH. Composites were fabricated from untreated and treated OPEFB fibers and comparisons were drawn between the treated and untreated fiber based composites as well as between composites and pure PLA.

2. Experimental procedures

2.1. Materials

The oil palm empty fruit bunch (OPEFB) fibers used for this study was collected as waste raw materials form LKPP oil palm Sdn. Bhd., Kuantan, Malaysia. The polymer matrix which is thermoplastic poly(lactic) acid was supplied by Unic Technology Ltd, China. It is a Natureworks Ingeo^{TM} Biopolymer 3051D grades, with a melt flow index of 30-40g / 10 min (190°C/2.16kg), density of 1.24 g/cm^3 and melting temperature between 160-170°C. Other chemicals used include analytical grade sodium hydroxide and acetic acid which were procured from Merck, Germany.

2.2. Methods

Fiber treatment

Raw oil palm empty fruit bunch fibers collected from the oil palm industry contained several impurities like sand particle, stones, palm kernel, mud, ash and other debris. The fibers were washed in water flow to remove these adhering particles, after which it was left to dry in air for 3 days. Dried fibers were cut using plastic crusher machine and sieved with a mechanical sieve shaker to remove ash as well as to obtain uniform size between 2-5 mm. After this, ultrasound treatment of fibers was done by soaking the fibers in 2% (w/v) NaOH solution and placed in ultrasound bath (CREST- ultrasonics) maintained at $90^{o}C$ and 9 Watts for about 100 min. Optimization of ultrasound working condition was initially carried out as described in literature [2], while the weight of fiber to solution was kept at 1:20 (w/v) during treatment. After treatment, the OPEFB fibers were washed in distilled water continuously to remove excess alkali. This was continued and few drops of very dilute acetic acid was added until the water no longer show signs of alkalinity i.e. pH of 7 attained, after which the fibers were dried in air for 24 hr and in oven for 8 hr at $70^{o}C$.

Composite fabrication

The compounding of poly(lactic) acid (PLA) with untreated and treated OPEFB fibers was done using a twin screw extruder (model - THERMO SCIENTIFIC PRISM EUROLAB-16), fitted with a fixed length pelletizer. Preparation of samples for testing was done by initially drying the pellets in oven at $70^{o}C$ until it was moulded with an injection moulding machine (model- DR BOY 22M). Temperature parameter for extrusion and injection moulding of samples is presented in Table 1. Composites were fabricated from untreated OPEFB fibers and PLA with 0, 10, 20, 30 and 40 wt% fiber loading. Mechanical testing showed that 30 wt% fiber produced the highest mechanical properties. Other composites were prepared with treated fiber and PLA maintaining the 30 wt% fiber content. Samples which were prepared for further analysis are untreated fibers (UF), ultrasound treated fibers (TF), pure poly(lactic) acid (PLA), untreated OPEFB/PLA composites (UFC) and treated OPEFB/PLA composites (TFC).

Table. 1. Operation parameters for Extrusion moulding (EM) and Injection moulding (IM) of OPEFB and PLA

EM Conditions		IM Conditions	
Temperature Profile:		Temperature Profile:	
Zone	Temp.	Section	Temp.
Feeding zone:	110 ^{o}C	Feeding section:	160 ^{o}C
Mixing zone:	175-185 ^{o}C	Compression section:	175-185 ^{o}C
Metering zone:	190 ^{o}C	Metering section:	190 ^{o}C
Die:	185 ^{o}C	Nozzle:	180-185 ^{o}C
		Mould:	25-30 ^{o}C
Screw speed:	100-110 rpm	Screw speed:	155 rpm
Torque:	55-60 (%)	Screw position:	28.5 mm
		Injection time:	0.45 sec
		Cooling time:	25 sec

Mechanical testing of composite

Tensile testing of composites

Tensile test samples were prepared according to ASTM 638- 08: Standard Test Method for Tensile Properties of Plastics. Testing was carried out using a Shimadzu universal tensile machine (model- AG-1) fitted with load cell of 5 KN, operated at crosshead speed of 10 mm min^{-1} on tensile samples with 65 mm gauge length.

Three points bend testing of composites

Three points bend test was carried out on test specimens according to ASTM D790-97: Standard. Testing was done using a Shimadzu universal tensile machine (model- AG-1) with static load cell of 5 KN. The dimensions of test sample were 125 x 3.3 x 12 mm. The cross head speed was set at 3 mm min^{-1} with support kept at 50 mm apart. Testing was done at room temperature.

For both tensile testing and three point bending tests, seven samples for each batch were tested out of which five replicates specimens were presented as an average of tested specimens.

Surface morphological analysis (SEM)

The surface morphology of untreated and treated were analysed by a ZEISS, EVO 50 scanning electron microscope. Prior to SEM observation test sample were coated with gold using a vacuum sputter-coater to make them conductive.

Fourier transforms infrared spectroscopy (FTIR) analysis

Fourier transform infrared spectroscopy (FTIR) analysis was done for untreated and treated fibers. This functional group analysis was carried out by a Fourier Transforms Infrared Spectrophotometer (model-THERMO) using the standard KBr technique after which spectrum for each fiber type was taken with the help of OMNIC software.

Structural analysis with XRD

X-ray diffraction analysis was carried out in order to determine the crystalline structure of untreated and treated OPEFB fibers as well as composites. Analysis was done at a scanning speed of 1deg min^{-1}, sampling step of 0.02^0 and scanning range 3-30^0, using an X-ray diffractometer.

3. Results and discussion

Morphology of fiber

SEM images of untreated and treated OPEFB fibers are shown in Fig. 1. It can be seen that the surface of the untreated fiber seem smooth and even perhaps due to the presence of cementing substances like lignin, hemicellulose and waxes on the fiber surface. On the other hand, image for the treated fiber reveals uneven and coarse surface with many opened pores. This is an indication of effective removal considerable amount of cementing substances from the fiber surface after ultrasound treatment. Removal of these binding and sizing structures therefore led to increased effective surface area and porosity of the fiber by revealing the pore spaces as seen in Fig. 1(ii). Exposure of the pores spaces also is an indication of the structural changes that ultrasound treatment might have caused to the fiber perhaps by disrupting the hydrogen bonding in the structural framework of the OPEFB fiber. These changes are good incentives for improved mechanical interlocking of the fiber with polymer matrix during composite fabrication as reported in literature [2, 10].
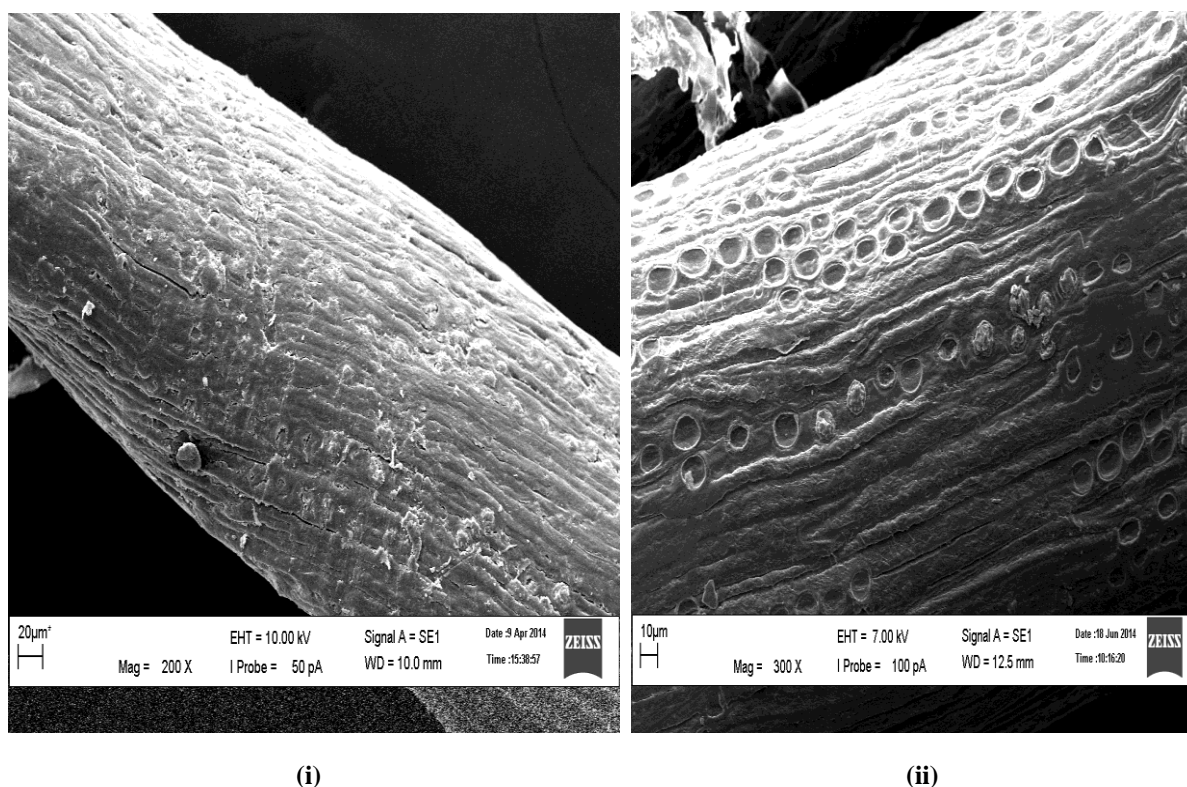
(i) **(ii)**

Fig. 1. Surface morphology of OPEFB fiber (i) before and (ii) after treatment with ultrasound

Fourier transforms infrared spectroscopy (FTIR) analysis

The FTIR spectra of OPEFB fiber before and after treatment are illustrated in Fig. 2. For both untreated and treated, the region from around 4000-1900 cm^{-1} does not really provide much information. This is because this region is usually a characteristic of vibrations from the –OH and aliphatic C-H stretching of the fiber components [11]. Other major observed peaks in this region are 3500-3200 cm^{-1} which represents broad band for stretching vibrations of hydrogen bonged –OH groups. The peak around 2900 cm^{-1} is due to vibrations coming from stretching of the methyl and methylene moieties in cellulose and hemicellulose components of OPEFB fiber. The other region from 1900-700 cm^{-1} seems to be more informative. The peaks in this region include at 1749 cm^{-1} which represents the stretching of carbonyl (C=O) of ester and carboxylic components of lignin and hemicellulose [12]. The peaks at 1644 cm^{-1} and 1514 cm^{-1} are due to =CH vibrations from aromatic skeletal and –C=C bending in lignin components of the fiber respectively. The peak at 1422 cm^{-1} represents –CH_3 asymmetric and C–H symmetric deformation of fiber lignin. Representations of the C=H stretching in methyl, methylene and methoxy groups of lignin was noticed at 1318 cm^{-1}, whereas aromatic C–H in-plane deformation of lignin is evident at 1034 cm^{-1}. The peak at 1241 cm^{-1} represents asymmetric stretching of –C-O-C- in the β-glycosidic bond of cellulose chain [2]. In general, the major difference between spectrum for untreated and treated OPEFB fiber is the weakening and sharpening of peaks

at certain points, as well the disappearance of peaks at some other point. Conspicuous among these is the disappearance of the peak at 1749 cm^{-1} for untreated fiber. This indicates an effective removal of significant portions of the fiber hemicellulose and lignin due to ultrasound treatment of OPEFB fibers, as reported elsewhere [2]. Also the peak at 1644 cm^{-1} for untreated fiber can be seen to appear at a lower wavelength in treated fiber spectrum, indicating some structural changes to the fiber after treatment with ultrasound and alkali. Structural changes to fibers with respect to fiber treatment were also noticed by other researchers [10, 13]. Other observable changes to the spectrum of treated fiber include the reduced absorption intensity and also little upward shifting of the peak at 1422 cm^{-1}. This suggests effective removal of considerable amount hemicellulose and lignin from fibers after treatment as reported elsewhere [1]. This was further confirmed by the sharpness of the peak at 1318 cm^{-1} for treated fibers. Summary of the observed peaks is presented in Table 2.
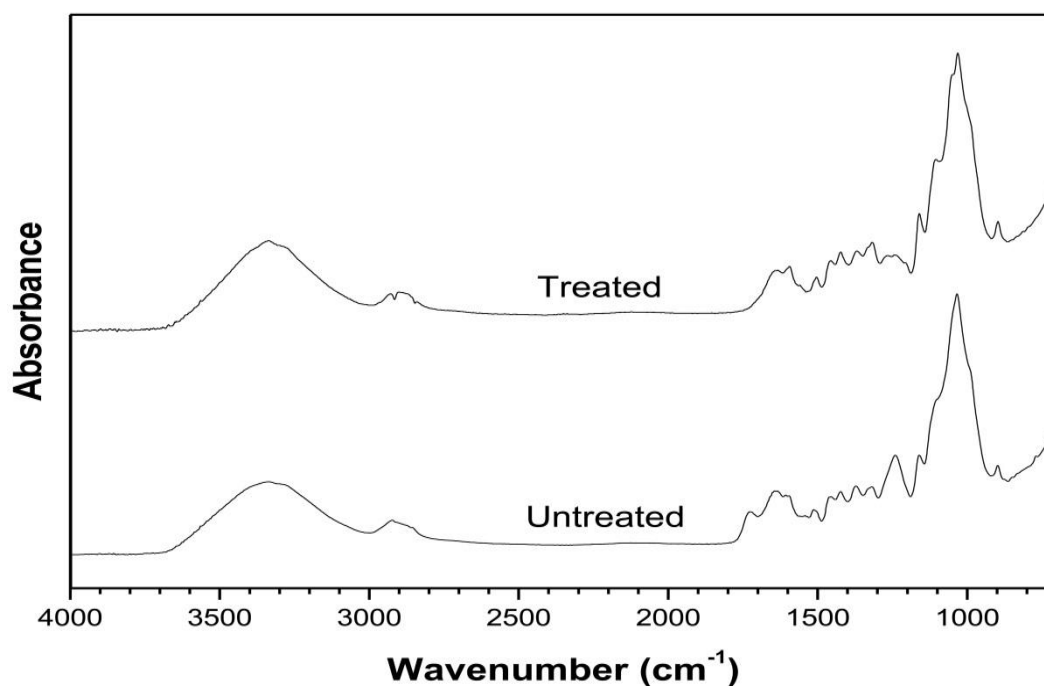

Fig. 2. FTIR spectra of OPEFB fiber before and after treatment

Table. 2. Summary of FTIR spectra for untreated and treated OPEFB fibers

Position of bands (cm^{-1})		
Untreated	**Treated**	**Functional group representation**
3335	3385	-OH bond structure of cellulose
2924	2922	C-H stretching vibration of cellulose
1749	-	C=O stretching
1644	1595	=CH vibration from aromatic skeletal
1514	1509	-C=C bending in lignin
1422	1424	-CH$_3$ asymmetric and C-H symmetric deformation
1318	1317	C=H stretching in methyl, methylene and methoxy groups
1241	1240	-C-O-C- β-glycosidic linkage in cellulose
1034	1031	Aromatic C-H in plane deformation
898	986	Si-O asymmetric stretching

Structural analysis with XRD

The XRD diffractograms of untreated and treated OPEFB fiber as well as the diffractograms for PLA, UFC and TFC are illustrated in Fig. 3i and ii. The conspicuous peaks observed for fibers and the composites is at 2θ ≈ 22.2^o and 2θ ≈ 16.2^o which represent the crystalline and amorphous components of the fiber cellulose respectively. These peaks were analysed and the result is presented in Table 3. For untreated OPEFB fiber, the conspicuous peak at 2θ = 22.17^o represents the crystallographic (002) planes of the OPEFB fiber cellulose [12]. This peak can be seen to shift towards the higher angle after fiber treatment indicating a reduced interplanar spacing of the (002) planes as confirmed by the d-spacing data in Table 3. Moreover, the reduced FWHM value suggests a closer packing of cellulose crystal structure after fiber treatment perhaps due to removal of hemicellulose and lignin from the fiber, causing the cellulose to rearrange and form

new chains through hydrogen bonding [1, 14]. This might be responsible for the increased crystal size and crystallinity of treated fiber perhaps through transcrystallinity via hydrogen bonding of OPEFB fiber cellulosic hydroxyl groups as reported elsewhere [1].

On the other hand for PLA and OPEFB/PLA composites, comparing the diffractograms in Figure 3ii reveals the diffused peak observed for PLA which is different from the diffractograms of the composites. This diffused peak of PLA indicates a poorly ordered chain with low degree of crystallinity most likely as a result of the rapid cooling process of injection moulding. This similar peak was reported for injection moulded PLA in literature [2]. From Table 3, the crystalline peak position can be seen to be shifted to the higher angle after the incorporation of OPEFB fiber into PLA. This might be due to macro stress effect, leading to a reduced molecular distance as well as reduced amorphous nature of the PLA molecules [2]. Crystallite size and

crystallinity of the composites can also be seen to be higher than for pure PLA, with treated fiber composite (TFC) having the highest. This suggests that combined ultrasound and alkali treated OPEFB fibers are capable of acting as

nucleating agents for the crystallization of PLA. This also is an indication of improved fiber-matrix interfacial adhesion of ultrasound and alkali treated OPEFB fibers with PLA as reported by other researchers [15, 16].
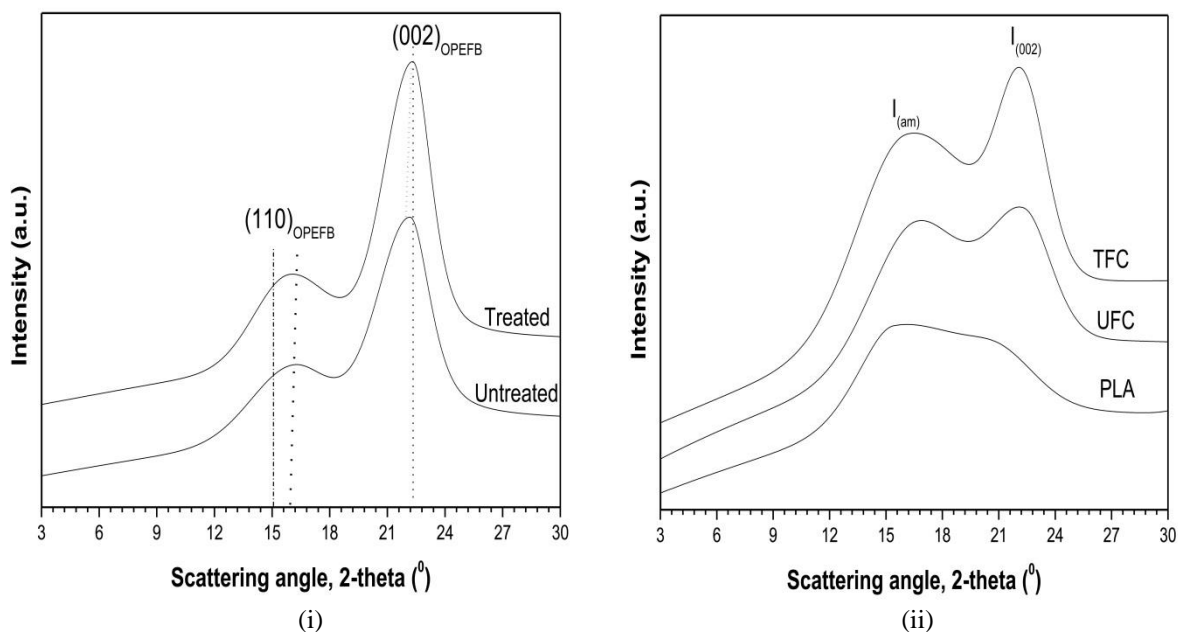

Fig. 3. XRD diffractograms of (i) untreated and treated OPEFB fiber and (ii) pure PLA, untreated OPEFB fiber composite (UFC) and treated OPEFB fiber composite (TFC).

Table. 3. Crystalline XRD parameters of untreated OPEFB fiber (UF), treated OPEFB fiber (TF), pure PLA, untreated OPEFB fiber composite (UFC) and treated OPEFB fiber composite.

Parameters	Fiber		Composites		
	UF	TF	PLA	UFC	TFC
Peak position (2θ)	22.17	22.47	21.20	22.22	22.34
FWHM (2θ)	3.19	2.63	4.20	3.87	2.96
d (Å)	4.01	3.954	4.19	3.99	3.97
Crystallite size (nm)	26.50	32.20	20.00	21.90	28.60
CrI (%)	40.27	44.17	41.23	44.59	63.44

Mechanical properties of composites

The variation of tensile strength (TS), tensile modulus (TM), flexural strength (FS) and flexural modulus (FM) of untreated OPEFB/PLA with fiber loading is presented in

Fig. 3i and ii. It can be seen that the TS, TM, FS, and FM all increased as the fiber loading increased up to 30 wt% loading. After 30 wt% fiber loading, these properties can be seen to reduce at 40 wt%. The initial increase in

mechanical properties of OPEFB/PLA composites with respect to fiber loading can be attributed to the highly desirable individual mechanical properties of OPEFB fibers as reported elsewhere [2]. Below 30 wt%, the low improvement observed could be as a result of insufficiency quantity as well as uneven distribution of fiber within the matrix, leading to ineffectiveness in stress transfer from the PLA matrix to fibers. The highest values for TS, TM, FS and FM were obtained at 30 wt% fiber loading perhaps due to even distribution of fibers within the matrix at 30 wt% fiber loading, making load transfer between fiber

and matrix more efficient. The observed decreases when the fiber loading exceeded 30 wt% could be a result of overloading effect of fiber on the matrix at 40 wt%. Excessive fiber loading could lead to fiber agglomeration within the composite, thereby leading to poor wettability of the fiber by the PLA matrix as well as creation of stress transfer breaks [1, 17]. The improvement in properties of OPEFB/PLA composite at 30 wt% fiber loading above pure PLA is 5%, 31%, 19%, 57% and 2% for TS, TM, FS, FM and IS respectively.
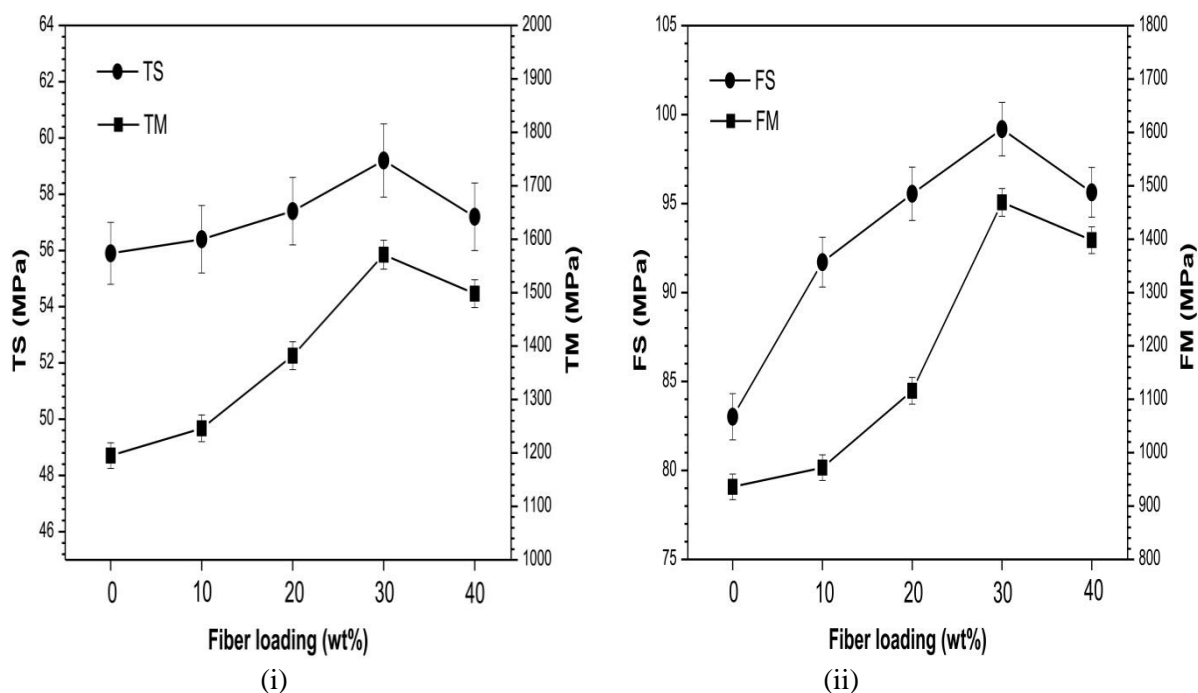

(i)   (ii)

Fig. 3. Effect of fiber loading on mechanical properties of untreated oil palm empty fruit bunch fiber and PLA (OPEFB/PLA) composite

Fig. 4i and ii represents the comparison of mechanical properties between pure PLA, untreated fiber composite (UFC) and treated fiber composite (TFC). The values are TS of 55.9. 59.2 and 73.1 MPa, TM of 1195, 1571 and 2099 MPa, FS of 83, 99, and 116 MPa and

FM of 936, 1469 and 1758 MPa respectively for PLA, UFC and TFC. Clearly, it can be seen that treated fiber composites produced the highest mechanical properties. The enhancement in properties of TFC over UFC are 23.5%, 33.6%, 16.8% and 19.6%

respectively for TS, TM, FS and FM. These figures denote reasonable values to enhance materials properties and selection. The improved performance of TFC over UFC can be associated with increased fiber-matrix interfacial adhesion [2]. These enhancements were brought about by effective delignification of OPEFB fibers through the cavitation effect of ultrasound treatment on the fibers in alkali medium. A comprehensive mechanism for

lignin and other non-cellulosic components removal from OPEFB fiber with respect to treatment can be found in literature [12]. The improved fiber-matrix interfacial adhesion therefore led to effective stress transfer between the PLA matrix and OPEFB fiber, and invariably produced composites with improved mechanical properties, as also reported elsewhere [18].
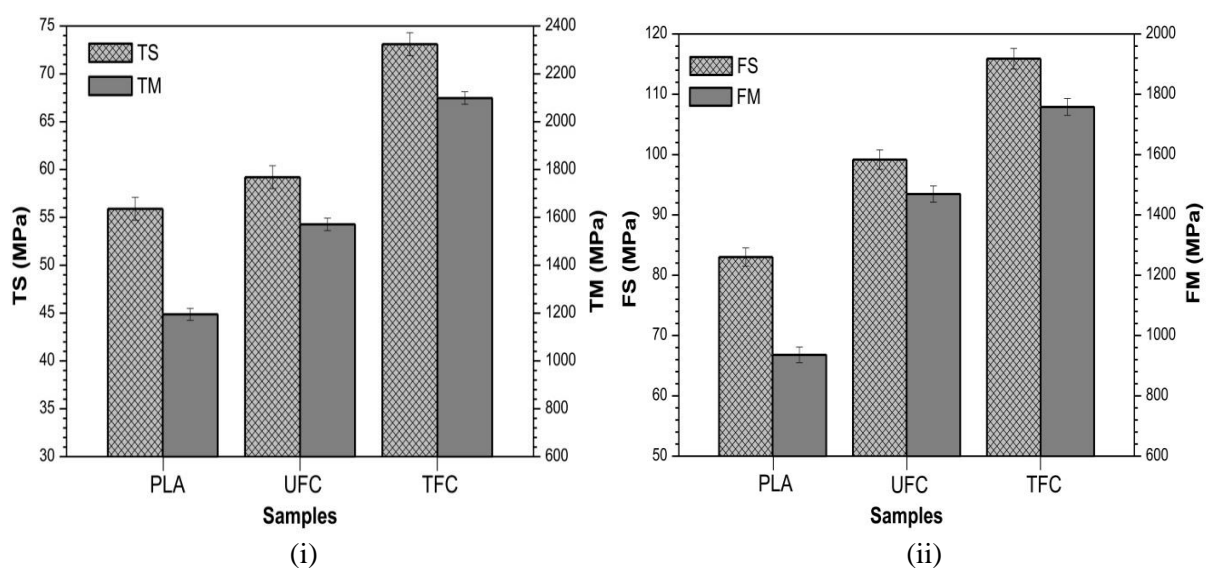

Fig. 4. Comparison of (i) TS, TM (ii) FS, FM and (iii) IS of pure PLA, untreated OPEFB fiber composite (UFC) and treated OPEFB fiber composite (TFC).

4. Conclusions

Treatment of OPEFB fibers with ultrasound in alkali medium of low concentration was able to produce considerable modifications to the fiber morphological functional and structural properties. Inclusion of ultrasound treated OPEFB fiber into PLA matrix led to production of composites with highly desirable mechanical and structural especially when compared with pure PLA and also untreated fiber composites. The improvement in mechanical properties of treated fiber composites over untreated fiber composites is

23.5%, 33.6%, 16.8% and 19.6% for TS, TM, FS and FM respectively. Thus ultrasound treatment of OPEFB fibers led to better improved properties as well as reasonable enhancement to the treated fiber reinforced PLA composite.

Acknowledgments

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