STRUCTURAL AND THERMAL PROPERTIES OF ULTRASOUND TREATED OIL PALM EMPTY FRUIT BUNCH (OPEFB) FIBER

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Abstract: In this study, surface modification of oil palm empty fruit bunch fiber (OPEFB) was carried out through treatment with ultrasound in 2% sodium hydroxide solution. Surface morphology of the fiber was studied by scanning electron microscope (SEM) analysis, and structural changes to the fiber with respect to treatment were investigated through Fourier transforms infrared spectroscopy (FTIR) analysis and X-ray diffraction (XRD) analysis. Furthermore, thermal stability of the treated fiber was investigated through thermogravimetric (TGA) analysis. Morphological changes in form of opened pore spaces and structural changes through disappearance, reduction and shifting of functional group intensities were observed for the fiber after ultrasound treatment as revealed by SEM and FTIR analysis. Density measurement revealed increased density of OPEFB fiber with respect to ultrasound treatment and also increased crystallinity was confirmed by XRD studies. Moreover, thermal stability of the fiber was found to increase after ultrasound treatment.

Keywords- Ultrasound, Surface Morphology, Structural Analysis, Oil Palm Empty Fruit Bunch Fiber.

I. INTRODUCTION

Recently, the use of lignocellulosic fibers in more diversified forms as in composite fabrication had received increased attention. This development was based on the ready availability, cheap cost, environment friendliness and renewability of natural fibers compared to the synthetic fibers. Also, natural fibers are desirable in most applications due to its light weight, nonabrasive and biodegradable properties. However, the incorporation of natural fiber in certain product especially in polymer composites often lead weak interface because of poor interfacial adhesion of the hydrophilic fibers surface and their hydrophobic polymer matrix counterparts. To overcome this challenge, physical and chemical treatments can be used to modify natural fiber surfaces through surface cleansing as well as increased surface roughness.

Fiber surface modification could involve mere activation of the fiber cellulosic hydroxyl groups, or the incorporation of new functional groups onto the fiber surface which can enhance its bonding to the matrix. Surface modification of natural fibers often offer enhanced properties to the fiber reinforced materials. However, most of the conventional methods of fiber treatment like acrylation, mercerization, coupling agents, acetylation, and peroxide treatment do involve the use of organic solvents and this could lead to release of toxic substances into the environment.

One alternative non-conventional fiber treatment method which is environmental friendly could be through the use of ultrasound energy. Ultrasound treatment technique had been largely accepted in separation technology but was recently noticed to offer several advantages for natural fiber purification. Some of the notable advantages include better purification at low alkali concentrations, shorter exposure period in the reaction chamber, reduced treatment temperature as well as enhanced mechanical strength because of reduction in degree of fiber damage. Ultrasound involves the creation of extreme and unusual chemical environment within a solution through the generation of certain small cavities which are able to enlarge and implode. This phenomenon often produces great quantum of heat as a series of ultrasonic waves are made to flow through the solution. Ultrasound treatment could lead to fiber refinement, controlled residual compressive stress as well as reduction in fiber size, all of which are desirable perquisite for enhanced mechanical strength of natural fiber reinforced materials. The effect of ultrasound comprises of both physical and chemical, but the chemical effect is often more evident. Although the chemical effect influences most of the noticeable changes to the fiber, this chemical effect usually occur through some physical processes on the fiber. The physical processes are usually in form of the formation, expansion and implosion of certain gaseous and vaporous cavities when the fiber is kept in the liquid medium. It is these physical processes that ultimately produce the desired long term chemical effect when cavitation from the ultrasonic wave helps to agitate the fiber. Fiber agitation could therefore lead to generation of strict forces on the adhered dirt particles on the fiber surface, such that rougher surface morphology with opened pore spaces could be observed on the fiber surface.

In this research, ultrasound treatment was conducted on oil palm empty fruit bunch (OPEFB) fibers in alkali medium containing 2% (w/v) NaOH. Functional group analysis, surface morphology, and structural analysis of the fiber was investigated with respect to ultrasound treatment. Furthermore,

comparisons were also drawn between thermal properties of the fiber before and after ultrasound treatment.

II. EXPERIMENTAL DETAILS MATERIALS

Oil palm empty fruit bunch (OPEFB) fibers used for this research were obtained as industrial wastes form LKPP oil palm Sdn. Berhad., Kuantan, Malaysia. Other notable chemicals which were used include analytical grade sodium hydroxide and acetic acid which were procured from Merck, Germany.

III. FIBER TREATMENT

Raw oil palm empty fruit bunch (OPEFB) fibers gotten from the industry contained several adhering substance like stones, sand particle, ash, mud, palm kernel, and other debris. The fibers were washed in flowing water remove the adhering substances, and thereafter dried in air for 3 days. After drying, the fibers were cut with the help of a plastic crusher machine after which they were sieved using a mechanical sieve shaker to separate ash and at the same time to obtain uniform size of 2-5 mm. Chemical treatment was applied through treatment of fibers with ultrasound. Weighed fibers were soaked in 2% (w/v) NaOH solution and placed in ultrasound bath (CREST- ultrasonics) running at 90^{o}C and 9 Watts. Treatment was continued for about 100 min. Optimization of ultrasound working condition was initially carried. For ultrasound treatment, weight of fiber to solution was maintained at 1:20 (w/v). Treated fibers were thereafter washed continuously in distilled water to remove excess alkali. Few drops of very dilute acetic acid was added and washing was continued until the water no longer indicate any sign of alkalinity i.e. pH of 7 attained. After this, the fibers were dried in air for 24 hr and in oven for 8 hr at 70^{o}C.

IV. SCANNING ELECTRON MICROSCOPY (SEM) ANALYSIS

Surface morphologies of OPEFB fibers before and after ultrasound treatment were studied with the help of a scanning electron microscope (ZEISS, EVO 50, Germany). Samples were coated with platinum using a sputter-coater, before observing them under the SEM apparatus. The SEM images of untreated and treated OPEFB fibers are shown in Figure 1. Surface of the untreated fiber (Figure 1a) can be seen to be smooth and even.

This indicates the presence of sizing substances like waxes, lignin and hemicellulose on the fiber surface. The image for the treated fiber can however be seen to be uneven, coarse and with surface with many revealed pore spaces. This suggests that ultrasound treatment was effective at removing considerable amount of the cementing substances from the fiber surface. Cleaning of the fiber surface through removal of certain percentage of these binding and sizing structures might have led to increased porosity and effective surface area of the fiber through the opening up of the pore spaces (Figure 1b). Moreover, opening up of pore spaces further indicate that some structural changes had occurred on the fiber surface after treatment with ultrasound. This could be in the form of disruptions to the hydrogen bonding in the structural framework of the fiber. Whenever natural fibers like OPEFB are to be used as reinforcing fillers in polymer composite materials, these changes are highly desirable in order to ensure good mechanical interlocking between the polymer matrix and fiber during composite fabrication as reported in literature.

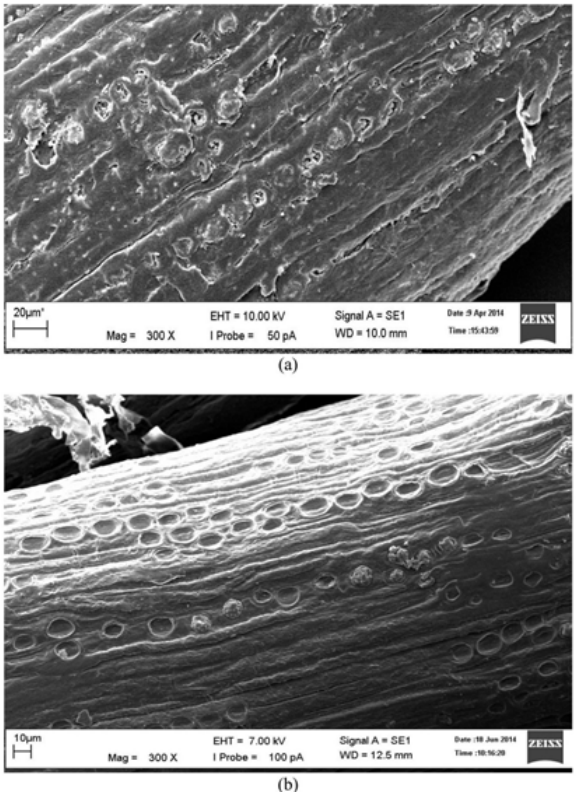

Figure 1:SEM images of (a) untreated and (b) treated OPEFB fiber.

V. FOURIER TRANSFRORMS INFRARED SPECTROSCOPPY (FTIR) ANALYSIS

Bonding structures of OPEFB fibers before and after treatment was investigated through FTIR analysis with the help of an FT-IR spectrometer (Model-Thermo scientific Nicolet 6700, Germany). The analysis was done using the standard KBr method, and wavenumber range was taken from 4000-700 cm^{-1}. From the FTIR spectra illustrated in Figure 2, it can be seen that spectrum for both untreated and treated fiber looks similar. Much needed information could not be gotten from the region around 4000-1900 cm^{-1}. This had been associated with the fact that this region is usually due to characteristic vibrations of –OH and aliphatic C-H stretching of the fiber components. In

general, the major observed peaks are 3500-3200 cm^{-1} which represents broad band for the stretching vibrations of hydrogen bonged –OH groups. The peak around 2900 cm^{-1} is due to stretching vibrations of the methylene and methyl components in cellulose and hemicellulose of OPEFB fiber. Some little structural destabilization can be found to the spectra of treated fiber at this region, in form of peak splitting which suggests structural modification of the fiber after ultrasound treatment. The other region from 1900-700 cm^{-1} seems to provide more information. Notable peaks in this region include at 1749 cm^{-1} which represents carbonyl (C=O) stretching of acetyl and carboxylic portions of hemicellulose and lignin. The disappearance of this peak from the spectra of treated fiber indicates perfect removal of the non-cellulosic components like lignin and hemicellulose from the fiber through ultrasound treatment. The peaks at 1644 cm^{-1} and 1514 cm^{-1} are assigned to =CH vibrations of aromatic skeletal and –C=C bending in lignin components of the fiber respectively. This peak at 1644 cm^{-1} can be seen to appear at a lower wavelength in treated fiber spectrum, indicating some structural changes to the fiber after treatment with ultrasound. Structural changes to fibers with respect to fiber treatment were also noticed by other researchers. The peak at 1422 cm^{-1} is assigned to asymmetric $–CH_3$ and symmetric C–H deformation of fiber lignin whereas C=H stretching of methylene, methyl and methoxy groups of lignin can was noticed at 1318 cm^{-1}. The reduced intensity and little upward shift of the peak at 1422 cm^{-1} suggests the removal of considerable proportion from the lignin and hemicellulose of the fibers after treatment as reported elsewhere. The observed structural changes for the treated fiber can serve as great incentives during composite production from natural fibers and polymer matrices.

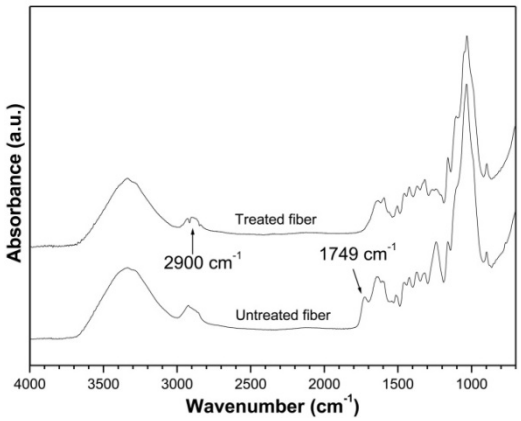

Figure 2: FTIR spectra for untreated and ultrasound treated OPEFB fiber

VI. STRUCTUAL ANALYSIS BY X-RAY DIFFRACTION (XRD)

XRD analysis was performed to investigate the crystalline structure of the fiber with respect to ultrasound treatment as well as to obtain the crystallite size, using an XRD goniometer. Analysis was carried out at a scanning range 3-30°,sampling step of 0.02°,scanning speed of 1deg min^{-1}, at a wavelength of 0.541 nm. The XRD diffractograms of untreated and ultrasound treated fiber are illustrated in Figure 3. The observed peaks of interest are at $2\theta \approx 22.2^{o}$ and $2\theta \approx 16.2^{o}$ which signifies the crystalline and amorphous portions of the fiber cellulose respectively. Analysis of theses peaks was done and the result is included in Table 1. For untreated OPEFB fiber, the conspicuous peak at $2\theta = 22.17^{o}$ represents the crystallographic (002) planes of the OPEFB fiber cellulose. This peak can be seen have shifted towards the higher angle after treatment with ultrasound which is an indication of reduced interplanar spacing of the (002) planes, which can also be seen from the d-spacing data included in Table 1. Moreover, reduction in the FWHM value suggests closer packing of the cellulose crystal structure after treatment, which could perhaps be as a result lignin and hemicellulose removal from the fiber. This could make the cellulose to rearrange through formation of new chains via hydrogen bonding. This could also explain the reason for increased crystal size and crystallinity of treated fiber perhaps as a result of possible transcrystallinity via hydrogen bonding of OPEFB fiber cellulosic hydroxyl groups of the treated fiber as reported in literature.

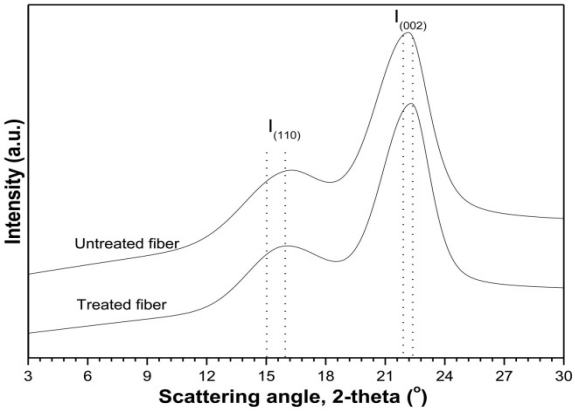

Figure 3: XRD diffractograms for untreated and ultrasound treated OPEFB fiber

Table 1
Summary of XRD parameters and density of OPEFB fiber before and after ultrasound treatment

Parameters	Untreated	Treated
Peak position (2θ)	22.17	22.47
FWHM (2θ)	3.19	2.63
d ( )	4.01	3.954
Crystallite size (nm)	26.50	32.20
CrI (%)	37.27	44.17

VII. DENSITY MEASUREMENT

Density measurement was carried out untreated and treated fibrin order to obtain the mass occupied by a unit volume of the sample. This was done using a gas pycnometer (MODEL- mycromeritics, AccuPyc 11 1340). Inert helium gas was allowed to pass through each sample weighing about 2-4 g. Density values obtained for the fiber before and after ultrasound treatment are 1.3910 g/cc and1.4916 g/cc respectively. The higher density with respect to treated fiber could be associated with removal of non-cellulosic components like lignin, hemicellulose and waxes from the fiber. This might have led to some structural changes that favoured the rearrangement of the fiber crystalline cellulose, causing it to attain a well ordered structural arrangement. This could increase the bulk density through reduced surface volume as reported elsewhere.

VIII. THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was conducted using a TA analyser (TGA Q500 V6.4, Germany). Samples weighing about 5 ± 2 mg were placed in a platinum crucible under nitrogen atmosphere at a flow rate of 40 mL min^{-1}. Heat was applied at 20^{o}C min^{-1} in the range from 25-600^{o}C. Figure 4a and b shows the TGA and DTG curves for untreated and ultrasound treated fibers respectively. From the TGA curve, a general initial weight drop can be seen for both fiber types from room temperature to around 150^{o}C. This could be due to the release of preabsorbed moisture from the fiber as a result of water vaporization heat. Thermal decomposition of lignocellulosic materials generally take place at temperatures around 200-400^{o}C. In this range, the early decomposition often occurs in the amorphous regions of the material whereas the crystalline region most often decomposes at the higher temperature within this range. However, lignin portions of natural fibers would only begin to decompose at temperatures above 400^{o}C. From Figure 4 a, the onset of thermal decomposition for untreated fiber can be seen to be at 255-369^{o}C perhaps due to decomposition of hemicellulose in the amorphous region of the fiber. For ultrasound treated fiber the initial decomposition temperature started from 272-385^{o}C which is higher than for untreated fiber. Reason for this higher initial temperature value could be associated with removal of hemicellulose from the fiber after ultrasound treatment.

This could lead to the reduction of the amorphous portions, thus favouring higher degree of crystallinity such that the initial decomposition temperature becomes mainly dependent on the crystalline cellulose decomposition. Furthermore, the residue after 550^{o}C further depicted ultrasound treated OPEFB fibers as more stable with 21.80% residue whereas untreated fiber has 13.03% residue. The thermal degradation temperature (T_d) can be gotten from the DTG curve in Figure 4 b, it is however customary to consider the decomposition temperature at 50% weight loss of a material as a pointer to its structural destabilization. Summary of the thermal parameters with the T_d values for untreated and treated fiber are included in Table 2.

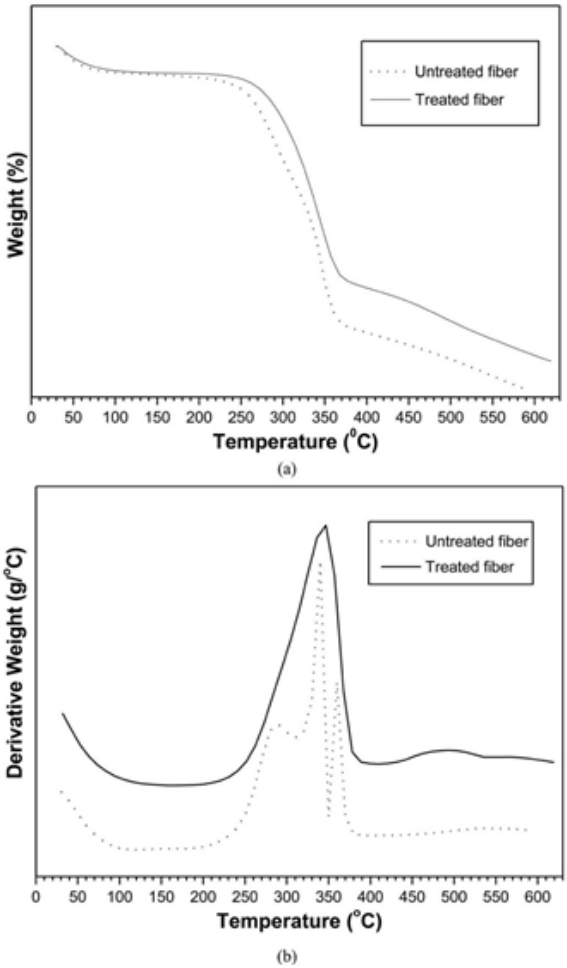

Figure 4: TGA and DTG curves for untreated and treated OPEFB fibers

Table 2
Temperature parameters for OPEFB fiber before and after ultrasound treatment

Fiber Type	$T_{\geq 5\%}$ (°C)	$T_{\geq 10\%}$ (°C)	$T_{\geq 50\%}$ (°C)	T_{max} (°C)	Residue % at ≥550°C
Untreated	96	255	335	340	13.03
Treated	105	272	342	346	18.80

CONCLUSION

Oil palm empty fruit bunch fibers were effectively treated with ultrasound in alkali medium of low concentration. Obvious modifications at both morphological and structural levels were observed for the treated fiber, which was accrued to the removal of less significant and non-cellulosic components from

the fiber surface. Density as well as thermal degradation temperature was also found to increase after the fibers were treated with ultrasound, coupled with increased crystallinity as confirmed through XRD analysis. These were associated to the rearrangement and close packing of the fiber cellulosic components after the non-cellulosic binding structures have been removed through ultrasound treatment. Thus ultrasound treatment of OPEFB fibers led to improved properties which suggests that ultrasound treated fibers can offer reasonable enhancement to its reinforced plastic composite.

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