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Structural studies of surface modified oil palm empty fruit bunch with alkaline pre-treatment as a potential filler for the green composite

Nur Athirah Mohamad Radzi, Azizul Helmi Sofian *, Saidatul Shima Jamari

Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, MALAYSIA.
*Corresponding author: azizulh@ump.edu.my

KEYWORDS

Alkaline pre-treatment
Oil palm empty fruit bunch
Surface modification
Adhesiveness
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ABSTRACT

A green composite consists of natural and recyclable materials has become one of the attractive topics in advanced material. The hydrophilic properties of oil palm empty fruit bunch (OPEFB) used in green composite is difficult to bind with hydrophobic polymer. Hence, the surface modification of this filler is required to increase its surface area and roughness for better adhesive purposed. In this research study, the ultrasonification method has been performed to treat the OPEFB fiber with alkaline pre-treatment (sodium hydroxide solution (NaOH)) by using different concentration (1,2,3,4 and 5 w/v%). Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX) were performed to characterize and determine the surface roughness, area and pore enlargement for the fillers. The 5w/v% of treated OPEFB fiber was found to impose a significant impact on increasing the surface roughness, area and pore enlargement of the fiber. This modified filler has a potential to improve the thermal, mechanical and adhesiveness properties with its matrix to make a good green composite.

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1.0 INTRODUCTION

The unsustainable petroleum source for making the synthetic fiber has triggered the world to use more of environmental friendly materials. Natural fiber is one of the environmental friendly materials which has a potential to replace the synthetic fiber as it is equipped with various of positive traits in term of properties compared to synthetic fiber (May-Pat et al., 2013; Mohammed et al., 2015). Hence, the interest of conducting research on replacing these materials have been increased as it will reduce the cost and increase the sustainability of the products (Pickering et al., 2016).

The researchers, engineers and scientists have massive interest in making fiber reinforced polymer (FRP) composite by using natural fiber (Ku et al., 2011). In addition, the highest crop of oil palm empty fruit bunch (OPEFB) secures the sustainability, availability of the material and preferable to be used for prolongs times (Rozman et al., 2000). One tonne of palm oil produced will dispose approximately to 1.1 tonnes of OPEFB. The percentage amount of fibers that can be obtained by OPEFB is approximately to 73% compared to the other parts of the oil palm tree (Wirjosentono et al., 2004). Thus, the huge amount of waste will be generated and create the environmental problem (Shinoj et al., 2011). Hence, utilizing the waste will be benefited to human and environment.

Despite making a good eco-friendly natural fiber reinforced polymeric composite, there are several disadvantages such as fiber degradation, moisture absorption, insufficient of toughness, less of long-term stability and capability to withstand with a different weathering condition such as temperature, humidity and UV-radiation. These drawbacks will surely give negative impact towards the life of product (Pickering et al., 2016; Balaji et al., 2014). Hence, further structural modification of OPEFB is required to make a good composite with hydrophobic and flame retardancy properties.

According to the experimental results obtained by (Latip et al., 2019), sodium hydroxide (NaOH) is one of the best alkaline solutions used for alkaline pre-treatment process for treating the natural fiber. Hence, NaOH is used as an alkaline solution to treat the OPEFB fiber. The most suitable concentration of NaOH used such as 1 w/v%, 2 w/v%, 3 w/v%, 4 w/v% and 5 w/v% was determined in this research work to obtain the best condition for OPEFB structural surface. The ultrasonication method is used for the OPEFB alkaline treatment (Beg et al., 2015). The structural studies of the OPEFB will be characterized by using Fourier-Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy - Energy Dispersive X-Ray (SEM-EDX) analysis.

2.0 EXPERIMENTAL PROCEDURE

The OPEFB was obtained from FGV Palm Industries Sdn Bhd, Kuantan, Pahang, Malaysia. Meanwhile the NaOH, pallet for analysis was purchased from Emsure.

The method of this experiment was started by preparing the untreated and treated OPEFB fiber samples. For untreated OPEFB fiber sample, the crushed OPEFB fibers were washed by using deionized water and dried at 100°C for moisture content removal. The crushed fibers were sieved to the length of between 2-5mm for ash elimination purposed.

As for treated OPEFB fiber sample preparation, the short fibers were treated by sodium hydroxide (NaOH) at various concentration (1-5 wt/v%) and soaking time (99 minutes), with fiber to solution ratio 1:20 (5g in 100ml) by using ultrasound bath (CREST-Ultrasonics) at 80°C. The fibers were washed by using deionized water continuously for neutralization process. The treated fibers were filtered and dried at 70°C for 8 hours.

Next, the characterization process were performed to determine the functional groups and structural morphology by using Fourier-Transform Infrared Spectroscopy (FTIR), spectroscopy analyser (SHIMADZU, series 8300) and Scanning Electron Microscopy Energy Dispersive X-Ray (SEM-EDX), (Cambridge S200, microscope).

3.0 RESULTS AND DISCUSSION

The functional group analysis has been performed to the untreated and treated OPEFB fibers samples as described in Figure 1 below. The broad band at 3320.09 cm^{-1} indicates the stretching of hydroxyl groups for carbohydrate (hemicellulose, cellulose and lignin) of OPEFB fibers [10,11]. As, the concentration of alkaline treatment increased, the intensity of the band increased. Hence, the stretched of hydroxyl component in 5 w/v% of treated OPEFB fiber is higher compared to untreated fiber. The high band intensity shows more of intermolecular hydrogen bonding in the cellulose structure than untreated fiber (Zulkiple et al., 2016). It is perhaps due to exposure of the hydroxyl groups on the fiber surface after undergoing the alkaline treatment (Beg et al., 2015).

Furthermore, the peak around 2900.00 cm^{-1} shows the C-H stretching vibration in cellulose and hemicellulose components for OPEFB fibers (Latip et al., 2019; Chaiwong et al., 2019; Alam et al., 2012). The peak of 2920.58 cm^{-1} and 2854.36 cm^{-1} of raw OPEFB fiber is separated after undergoing the alkaline treatment process due to the removal of some portions of hemicellulose and lignin from the fiber (Beg et al., 2015).

Then, the peak of 1731.00 cm^{-1} is only found at untreated fiber and indicator for lignin and hemicellulose components to represent the C=O acetyl carbonyl ester of *ρ-coumaric* lignin (Beg et al., 2015; Zulkiple et al., 2016). However, the peak is completely disappeared after performing alkaline treatment on OPEFB fiber to indicate the removal of large portion of lignin and hemicellulose components on the OPEFB fiber. This result is also aligned with Beg et al., 2015; Chaiwong et al., 2019 research work. Hence, from this analysis, the hemicellulose and lignin removal are effective by undergoing alkaline pre-treatment.

In addition, the presence of the peak around 1590.00 cm^{-1} for the treated OPEFB fiber represent the CH vibration of aromatic skeletal and 1642.98 cm^{-1} for untreated fiber. Meanwhile, the presence of peak around 1590.00 cm^{-1} shows the C=C aromatic bending in lignin groups lignin (Beg et al., 2015; Zulkiple et al., 2016).

The peak around 1460.00 cm^{-1} is only detected on the treated fiber to indicate the deformation of lignin fiber occurs which is corresponding to Asymmetric -CH_3 and Symmetric C-H. The presence of C-H stretching of methylene, methoxy and methyl groups of lignin is indicated at the peak around 1317.00 cm^{-1} to 1316.00 cm^{-1} on treated fiber (Beg et al., 2015).

The peak of 1240.36 cm^{-1} shows the -C-O-C functional group of aryl-alkyl ether in lignin (Chen, 2014) or stretching of the *β-glycosidic* bond of cellulose chain (Beg et al., 2015). The intensity of band for this functional group seems decreasing from raw OPEFB fiber compared to 5 w/v% of treated OPEFB fiber. It means that the lignin component for treated OPEFB fiber is reduced.

The O-C-asymmetric mode of ester group or deformation of lignin component is indicated at peak around 1030.00 cm^{-1} for treated OPEFB fibers (Beg et al., 2015: Alam et al., 2012). The intensity of the band is increasing as the alkaline concentration used is increased. It shows that, higher concentration used will make the deformation of lignin becomes higher.

Therefore, the structural changes of OPEFB is occurred based on the functional group results obtained. The alkaline treatment by using sodium hydroxide solution at various concentrations are effective method to modify the structural of the fiber. The higher the concentration used, the

higher of lignin and hemicellulose removal from the OPEFB fiber. More significant effect of structural changes is detected for the treated fiber at 5 w/v% sodium hydroxide concentration.

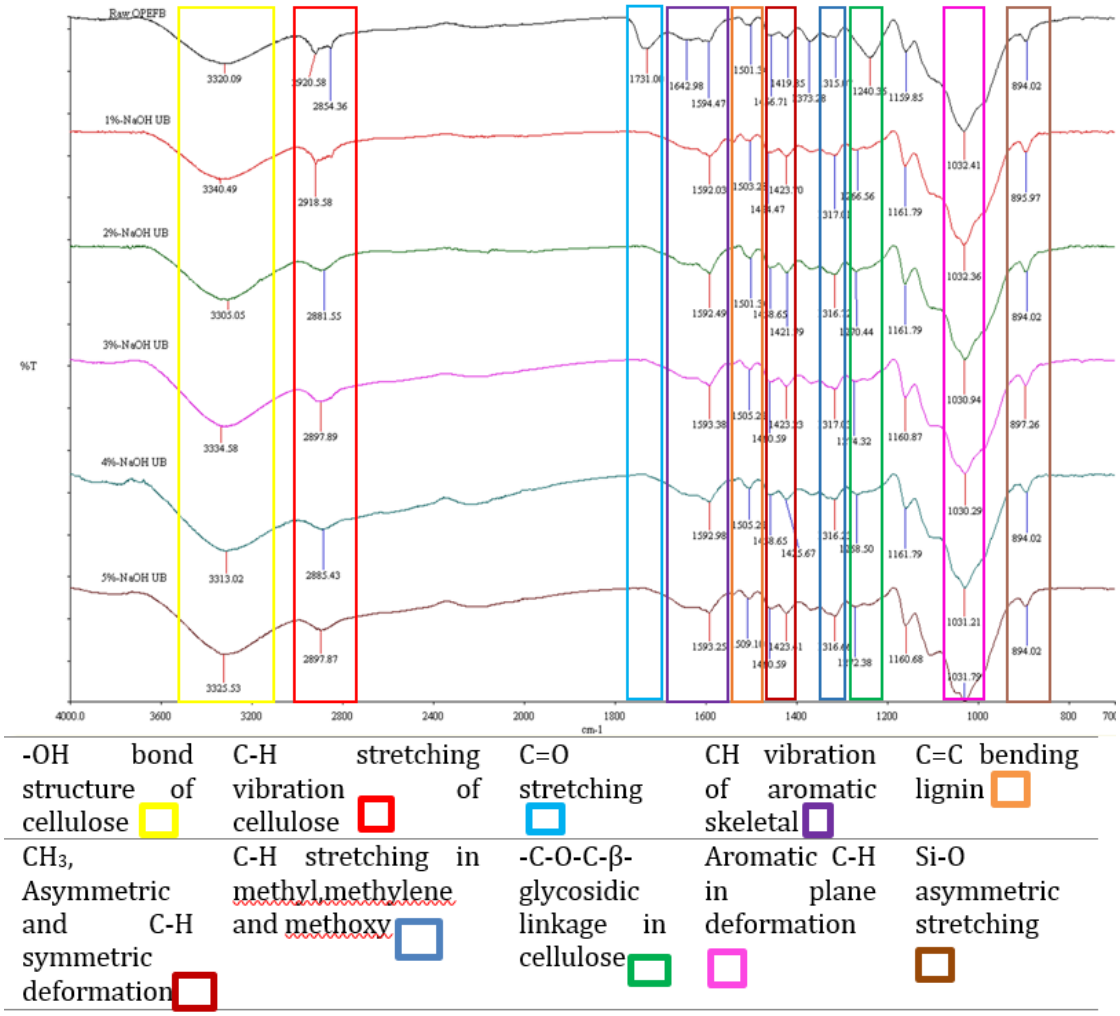

Figure 1: Comparison of functional group analysis for the raw and treated OPEFB fibers by using Fourier Transform of Infrared (FTIR) Spectroscopy.

The uneven and thick surface layer of untreated OPEFB shown in Figure 2(a) consists of hemicellulose, cellulose, lignin and silica mineral (silicon and oxygen) due to the penetration of the soil mineral into the gap of plant cell wall during the plant growth (Chaiwong et al., 2019).The presence of hemicellulose and lignin in untreated OPEFB fiber will make the rate of fiber degradation at low temperature which is not suitable for flame retardancy application. In addition, the presence of these two components will also increase the rate of moisture absorption (Mahjoub et al., 2013; Mishra et al., 2003).

Hence, the surface modification of OPEFB fiber with alkaline treatment (sodium hydroxide solution) by using ultrasound bath (CREST-Ultrasonics) were performed. The condition of

alkaline treatment was performed accordingly stated by (Beg et al., 2015; Moshiul Alam et al., 2012). The removal of large amount of hemicellulose and lignin on OPEFB fiber are confirmed by the FTIR analysis with the absence peak of 1731.00 cm^{-1} previously. This research work is aligned with (Beg et al., 2015; Chaiwong et al., 2019) as the absence of peak 1749.00 cm^{-1} and 1744.00 cm^{-1} were also confirmed in their study. However, the surface roughness, wax, pectin and the silica embedded in the fibers are varied with various sodium hydroxide concentration. The difference changes of OPEFB morphology caused by different concentration is also found in (Chaiwong et al., 2019) research work.

By using 1 w/v%,2 w/v% and 3 w/v% of sodium hydroxide concentration for fiber treatment, few of silica embedded in the fibers are removed but there is still large sum of silica presence in it. The white spot or silica embedded in the fiber is defined as impurities by Faizi et al., (2018). The treated fiber with alkaline pretreatment gives clean surface as the impurities being removed. This result is matched with the research study performed by (Faizi et al., 2018). However, for 4 w/v% and 5 w/v% of sodium hydroxide solution, the silica components are completely being removed from the fiber bodies and left with the crater marks (Chaiwong et al., 2019). The removal of silica and partial lignin decomposition makes the surface of OPEFB covered with craters is also stated by Latip et al., (2019). From these figures, the alkaline treatment with the concentration of 4 w/v% and 5 w/v% shows the best condition of fiber in term of silica removal.

However, in the matter of surface roughness, the surface of treated fiber with the concentration of 5 w/v% sodium hydroxide is rougher compared to 4 w/v% of sodium hydroxide. The roughness fiber surface for OPEFB treated with 5 w/v% sodium hydroxide is higher compare to other concentration due to the huge removal of hemicellulose components. The destruction of intra-hydrogen bonds and hydrogen bonds between hemicellulose and cellulose perhaps make the surface of fiber becomes rougher (Chaiwong et al., 2019). The new hydrogen bonding by intramolecular hydrogen bonding makes the new arrangement or rearrangement of the cellulose (Beg et al., 2015). In addition, similar roughness surface of treated OPEFB fiber is also reported in Faizi et al., (2018) work.

The opening of the pores caused by the removal of the impurities or silica on the OPEFB and exposure of cellulosic hydroxyl group give the positive traits of the physic-chemical interlock between the fiber and polymer (Beg et al., 2015). According to (Alam et al., 2012; Senawi et al., 2013), the mechanical interlocking and its bonding reaction between the fiber and its polymer matrix are caused by the exposure of hydroxyl groups obtained from the treated fiber. Enlargement of the pores and roughness of the surface fiber will produce better reinforcement condition between the fiber and its polymer matrix (Beg et al., 2015). These two factors which are the changes of surface area and porosity of the fibers will contribute to the better shear connection of the fiber and its matrix due to the best state of interfacial bonding. The tensile modulus of the treated fiber will be increased while the tensile strength decreased (Mahjoub et al., 2013). Hence, the OPEFB treated with 5 w/v% sodium hydroxide is believed to give good incorporation of the fiber with its polymer matrix. According to the result obtained by Mishra et al., (2003), the 5 w/v% concentration of sodium hydroxide also gives the best effect of interfacial surface bonding.

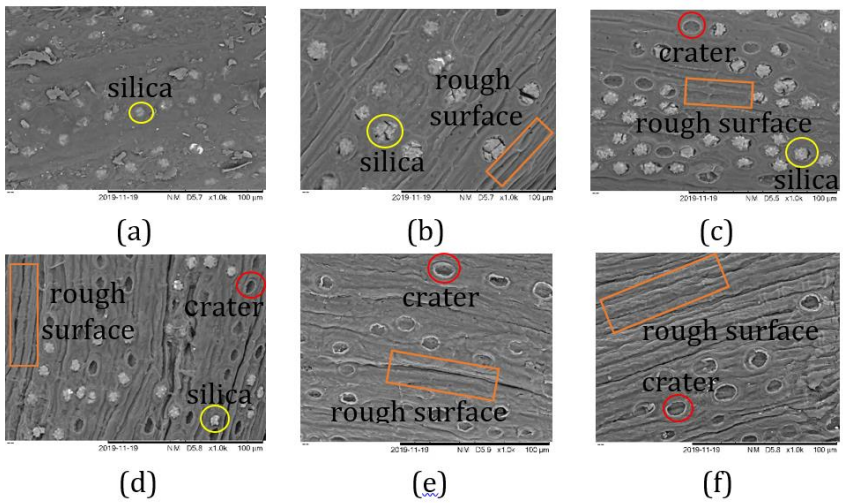

Figure 2: Surface morphology by SEM for 1000x magnificent images: (a) untreated OPEFB (b) 1w/v% (c) 2 w/v% d) 3 w/v%(e)4 w/v% (f) 5 w/v% of NaOH treated OPEFB.

Next, Figure 3 shows the electron images for the element quantification by using Energy Dispersive X-Ray (EDX) method. The list of elements quantities such as carbon, oxygen, aluminium, silicon, sulphur, calcium and platinum presented in the OPEFB fibers is tabulated in Table 1. The platinum detected in both OPEFB fibers due to the coating method for SEM analysis purposed. Hence, the quantity of platinum detected for both samples can be neglected.

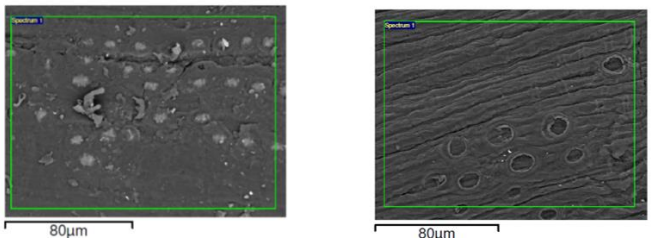

Figure 3: Electron images for Energy Dispersive X-Ray (EDX) quantification: (a) Untreated OPEFB (b) 5%-NaOH treated OPEFB.

Table 1: Weight percentages (w/w%) of elements detected on untreated OPEFB and 5 w/v% NaOH treated OPEFB**.**

Elements	**Carbon**	**Oxygen**	**Silicon**	**Calcium**	**Sulphur**	**Aluminium**	**Platinum**
Untreated OPEFB	51.294	37.679	1.933	0.255	0.067	0.411	8.362
Treated OPEFB	52.445	39.812	0.000	0.339	0.078	0.330	6.996

Based on the elements presented in Table 1, the OPEFB fiber is mainly comprises of carbonaceous material resulted from high carbon and oxygen contents with addition of silicon and aluminium elements. The presence of calcium and sulphur contents in OPEFB fiber is due to the high of OPEFB mineralogical enrichment obtained from the soil (Nyakuma et al 2019). Thus, the trend value of calcium, sulphur and aluminium contents in both untreated and treated OPEFB fibers are not being discussed in this research as the contents varies depend on the origin of the fibers itself.

The silicon content in the OPEFB fiber is one of the major elements to be discussed as it gives significant effect to reflect with the purposed of alkaline treatment. As stated in table 1 above, there is no silicon detected on 5 w/v% of treated OPEFB fiber. This quantitative analysis (EDX) has proven the qualitative surface image (SEM) from figure 2 about the removal of silica element in the 5 w/v% of treated OPEFB fiber. The pore of the OPEFB fiber is successfully enlarged due to the silicon element removal with 5% of alkaline treatment.

Another important element to be discussed along with the silicon removal is the carbon content of both untreated and treated OPEFB fibers. The carbon content for 5 w/v% of treated OPEFB fiber is higher compared to untreated OPEFB perhaps due increasing of the cellulosic components in the fiber. According to (Chen et al., 2014), the cellulose component consists of 44.44% of carbon, 6.17% of hydrogen and 49.39% oxygen. Thus, high carbon content for 5 w/v% of treated OPEFB fiber indicates more of cellulosic components presented in it. The higher cellulosic content in the OPEFB fiber will reduce the water intake hence providing desirable mechanical and weathering properties (Al-Ooqla & Sapuan, 2014). This makes the 5 w/v% of treated OPEFB fiber is preferable to be used as a filler for flame retardancy application.

4.0 CONCLUSION

As a conclusion, the removal of hemicellulose and lignin and other unwanted components by using alkaline treatment (NaOH) assisted with ultrasonic is an effective method. The evidence of effectiveness of unwanted components removal for treated OPEFB fiber is indicated by the disappearance of the 1731.00 cm^{-1} peak by using FTIR analysis. This result is supported by the structural images and quantification (SEM-EDX) analysis. The 5 w/v% of treated OPEFB fiber gives the best result and significant impact on increasing the surface roughness, area and pore enlargement compared to 1 w/v%,2 w/v%,3 w/v% and 4 w/v%. In addition, the deformation of lignin and hemicellulose components for the treated OPEFB fiber will reduce the moisture intake and increase the adhesiveness compatibility with its hydrophobic matrix (Mahjoub et al., 2013). The hydrophilic state of fiber will make a weak interaction in term of interfacial bonding with the hydrophobic polymer which is recycle polypropylene (Mohammaed et al., 2015; Mahjoub et al., 2013). Hence, the 5 w/v% of treated OPEFB fiber is a promising filler to increase the thermal and mechanical properties for the green composite (Wirjosentono et al., 2004).

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