

INFLUENCE OF SULPHURIC ACID CONCENTRATION ON THE PHYSICO-CHEMICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE FROM OIL PALM EMPTY FRUIT BUNCH FIBRE

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ABSTRACT

The interest for microfibrillated cellulose (MFC) has been present within the academic sector since the 1980s, but recently this material has become commercially available as it is growing significantly in the industrial sector. Therefore, in this study the oil palm empty fruit bunch fibre (OPEFB-fibre) was selected to be synthesised into MFC. This study focused on the effect of acid concentrations on the isolation of MFC from OPEFB-fibre using the acid hydrolysis method, followed by ultrasonication. The important parameter studied was the concentration of sulphuric acid (10% to 40%) while reaction time and temperature were kept constant. The resulting MFC was analysed using Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffractometer (XRD) and scanning electron microscope (SEM). Based on the FTIR results, it was found that the structure of cellulose was retained after undergoing the acid hydrolysis process. The highest thermal stability was obtained when MFC was treated with 20% sulphuric acid which was determined by using TGA. The XRD method was used to study the structural property of the MFC and the result showed that the MFC produced had 60% of crystallinity index. The morphological features were identified using SEM. The results showed that the particle size of MFC ranged between 10 μm to 200 μm . As a result, the parameters used tend to influence the physico-chemical properties of MFC produced and it has the potential to facilitate filler increase in wood-free paper industry.

Keywords: empty fruit bunch fibre, microfibrillated cellulose, acid hydrolysis, ultrasonication, physico-chemical.

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INTRODUCTION

Oil palm empty fruit bunches (OPEFB) is a major agricultural biomass by-product in Malaysia and for each tonne of crude palm oil (CPO) produced will concomitantly give rise to approximately 1.1 t of empty fruit bunch (EFB) as waste residues (Law *et al.*, 2007). OPEFB has been classified as lignocellulosic residues that typically contain 50%

cellulose, 25% hemicellulose and 20% lignin as well as extractive in the cell wall. Besides OPEFB, lignocellulosic residues are also present in the oil palm trunks (OPT), oil palm fronds (OPF), kernel shell, EFB-fibre, pressed fruit fibre (PFF) and palm oil mill effluent (POME). Cellulose is the most abundant renewable natural bio-polymer on earth and is present in a wide variety of living species including plants, animals and some bacteria (Li *et al.*, 2009). It is the main structural constituent of plants regaining importance as a renewable chemical resource to replace petroleum-based materials (Beck *et al.*, 2011; Ma *et al.*, 2011). The annual

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production of cellulose is estimated to be over 7.5 x 1010 t (Habibi *et al.*, 2010). For economic feasibility, the cellulose extraction should be integrated with other chemicals extraction such as the hemicellulose (xylan) and the lignin.

In general, the micro- and nano-sized cellulosic materials are produced with different chemical and mechanical methods. In the literature, these materials are termed micro/nanocrystalline cellulose (MCC, NCC), micro/nanofibrillated cellulose (MFC, NFC), cellulose nanowhiskers (CNW), *etc.* MCC and NCC are needle-shaped, while MFC and NFC are similar to cobweb or spaghetti-shape (Osong *et al.*, 2016). In recent years, the scientific work has focused on two different types of celluloses; MFC and NCC. In addition, MFC is cellulose with a diameter of 0.1-1 μm with a length range of 5-50 μm in which the outer layer of the fibres, which have been stripped away by mechanical shearing, exposes the fibril bundles (Peng *et al.*, 2011). It is a white, fine, odourless crystalline powder and a biodegradable material which can be isolated from pure cellulose through acid hydrolysis method. It can be obtained through homogenisation, microfluidisation or grinding routes (Peng *et al.*, 2011). MFC is especially well suited for its strength enhancing properties in specialty papers such as filter paper, release liners, labels, decor paper, electrical paper and barrier paper among others. It also can provide strength, stiffness and barrier properties. As a rheology modifier and stabiliser, MFC is ideal for paints, coatings and adhesives (Nathalie *et al.*, 2012).

In order to reduce the cellulose crystallinity, the use of acid hydrolysis has been practiced by previous researchers (El-Sakhawy and Hassan, 2007; Sun *et al.*, 2004). Basically, strong acids are oxidising agents and would dehydrate and redistribute the biopolymers in lignocellulosic materials (Segal *et al.*, 1959). A study by Rozmarin *et al.* (1977) reveals the effect of acid hydrolysis on the crystallinity of cellulose. The results showed that the crystallinity index decreased rapidly with an increase in acid concentrations. Sulphuric acid has been preferred and widely used in the hydrolysis as compared to others due to its ability to provide a highly stable electrostatic aqueous suspension with the introduction of sulphate groups on the surface of crystallites (Brinchi *et al.*, 2013). From the literature, there is not much chemical treatment approach that was carried out using sulphuric acid hydrolysis at low concentration for environment safety concern (Jonoobi *et al.*, 2012).

The physico-chemical processes are improvement of existing chemical processes, to reduce reaction time and improve the efficiency of the process. In order to enhance the removal of lignin and increase their efficiency, physical parameters such as pressure and temperature are added to the established chemical pre-treatment (Fatihah *et al.*, 2018).

Previous studies show that ultrasonic treatment is significant in lignocellulosic biomass pre-treatment technology to enhance the extractability of main component such as hemicelluloses, cellulose and lignin. Ultrasound increases the cleavage of bonds within lignin as well as the bonds between lignin and hemicellulose. The cleavage reactions are enhanced by radicals produced by ultrasound and the shear forces from ultrasonic mixing improve the degradation of polymer (Bussemaker and Zhang, 2013).

Generally, previous studies focused on the isolation of MCC from oil palm biomass residue (Haafiz *et al.*, 2013) and other materials such as from jute cellulose (Jahan *et al.*, 2011), peel of pear fruits (Habibi *et al.*, 2010), mulberry barks (Li *et al.*, 2009), wheat and cereal straws (Alemdar and Sain, 2008), sugar cane bagasse (Bhattacharya *et al.*, 2008), and soyabean husk (Uesu *et al.*, 2000). This study had successfully isolated MFC from OPEFB instead of MCC using combination of chemical and physical processes. The objective of this study was to determine the effect of acid concentration on the physico-chemical properties of MFC obtained from OPEFB. The physico-chemical properties were characterised using Fourier transform infrared spectroscopy (FTIR) to confirm the basic structure of cellulose in MFC, the thermal stability was carried out using thermogravimetric analysis (TGA), the surface morphology of MFC was monitored using scanning electron microscopy (SEM) as well as the determination of crystallinity index using X-ray diffraction (XRD) analysis. This article reports the pioneering work on the isolation of MFC from OPEFB with different acid concentrations which has a potential to be used as bio-based fillers for environmental-friendly composites.

MATERIALS AND METHODS

Materials

Samples of OPEFB shredded fibres were collected from the Palm Oil Mill Technology Centre (POMTEC) located in Labu, Negeri Sembilan, Malaysia. The OPEFB shredded fibres were then transported to MPOB Head Office, Selangor, Malaysia for further processing.

Preparation of Holocellulose and Cellulose

The OPEFB shredded fibres were initially dried in the oven before use. Dried OPEFB shredded fibres with the average of 0.25 mm in length were used as a source of cellulose. The dried fibres were first de-lignified according to the American Society for Testing Materials (ASTM), D 1104-56 to produce holocellulose. In this step, about 4.0 g of the fibres

were soaked in distilled water and the sample was treated with 2.0 ml of 100% acetic acid (ChemAR) and 5.0 g of 99% sodium chlorite (R&M, United Kingdom) at 70°C for 4 hr to degrade the lignin. The mixture was filtered, and the solid residue, the holocellulose was washed with distilled water.

The next step was to remove the hemicellulose fraction according to ASTM, D 1103-60. About 2.0 g of holocellulose was treated with 50 ml of 17.5% sodium hydroxide solution (99% Merck, Germany). The insoluble α -cellulose was filtered and washed with 8.3% sodium hydroxide solution. The cleaned α -cellulose was used as the starting material for the preparation of microfibrillated cellulose. The detailed characteristic and morphology of α -cellulose (lignin content, FTIR, XRD and SEM) were described in previous article (Rosnah *et al.*, 2012).

Preparation of Microfibrillated Cellulose

The purified cellulose fibres were then subjected to acid hydrolysis reaction at different concentrations of sulphuric acid. The cellulose EFB-fibre (1.0 g) was mixed with 200 ml of 10%, 20%, 30% and 40% sulphuric acid (~95%-98%) solution. This mixture was then treated by the ultrasonicator at 50°C and frequency at 50-60 Hz for 3 hr. After ultrasonication process, the suspension was then washed with distilled water to reach the neutral condition and then filtered to separate the MFC from it. The MFC samples were labelled as MFC1 to MFC4 according to the sulphuric acid percentage 10% to 40%, respectively. The detailed characteristics and morphology of MFC were characterised using FTIR, SEM, TGA and XRD analysis.

Characterisation of Physico-chemical Properties

FTIR analysis. Infrared spectra of samples were recorded using a Perkin Elmer-FTIR Spectrum One Spectrometer and transmission was measured in the range of 650-4000 cm^{-1} .

TGA. TGA was performed using Mettler Toledo model to analyse the thermal behaviour of OPEFB and MFC samples. The samples were heated from 30°C to 600°C with heating rate of 10°C min^{-1} under nitrogen gas atmosphere.

SEM. A Hitachi S2700 SEM was used to evaluate the microscopic features of the samples. A piece of dry sample was put on the SEM sample lens, then the lenses were placed in a vacuum chamber to avoid obstruction and contamination by other particles. The lenses helped to direct electrons towards the sample. The electron imprint was converted into three-dimensional (3D) image. The magnification power used for the samples was 1000X.

XRD. X-ray diffraction (XRD) was carried out to study the crystallinity of the samples. The sample patterns of all the cellulosic and MFC samples were pressed to form pellets and recorded on X'Pert X-ray diffractometer (SIEMENS XRD D5000) using Ni-filtered Cu $K\alpha$ radiation (30 kV and 30 mA). The diffraction intensities were measured between Bragg angles (2θ) of 5°-69° with 0.04° min^{-1} step size. The crystallinity index (C_{ir}) was calculated by Segal's formula (Segal *et al.*, 1959) using intensity measurement at 22.5° and 18.5° (amorphous background) 2θ :

$$C_{ir} (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

where C_{ir} - crystallinity index, whereas I_{002} - maximum intensity (in arbitrary units) of the diffraction from the 002 plane at $2\theta = 22.5^\circ$ and I_{am} = intensity of the background scatter measured at $2\theta = 18.5^\circ$.

RESULTS AND DISCUSSION

Observation of MFC after Acid Hydrolysis Reaction

Figure 1 demonstrates the appearance of OPEFB fibre and cellulose OPEFB-fibre while Figure 2 shows the hydrolysed MFC fibres at different acid percentage via acid hydrolysis process. For the bleaching process to produce cellulose from OPEFB fibre, the detailed process has been discussed in the preparation of holocellulose and cellulose. The detailed characteristic and morphology of α -cellulose (lignin content, FTIR, XRD and SEM) were described in previous article (Rosnah *et al.*, 2012). The MFC fibres in varied acid concentration were hydrolysed for 1 hr reaction. After the acid hydrolysis reaction, a fine fibre structure with pale yellowish colour was observed in MFC1 to MFC3 as depicted in Figures 2a, 2b and 2c. Contrary to this observation, the fibres in MFC4 were over hydrolysed and the colour turned to dark brown as shown in Figure 2d. This indicated that the fibre structure of 40% MFC4 treatment (Figure 2d) was damaged and degraded during the acid hydrolysis. This was detected from the acid treated fibre suspension that had changed to dense dark brown sediment during washing through filtration process. In addition, it was also difficult to leach out the excess acid and neutralise as the acidic solution had incorporated deep into the hydrolysed dense sediment. Hence, the condition for MFC4 disclosed that this treated fibre failed to be further analysed using XRD analysis. Meanwhile, the MFC 10% to 30% conditions revealed that the hydrolytic reaction between sulphuric acid and treated fibres had formed a cellulose structure and suitable to be further investigated and discussed.

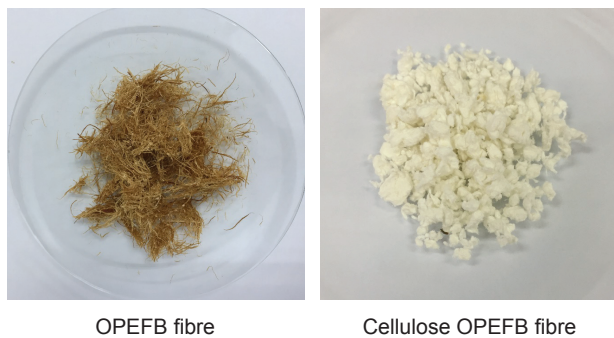
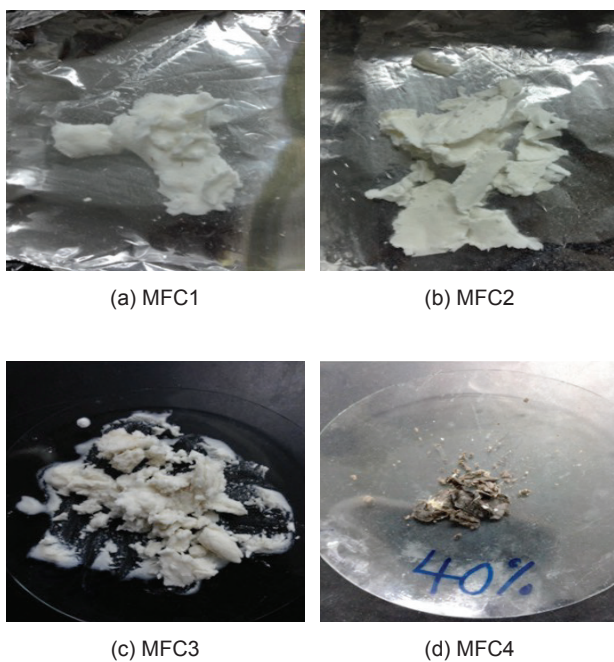


Figure 1. The appearance of oil palm empty fruit bunches (OPEFB) fibre and cellulose empty fruit bunches fibre (EFB-fibre).

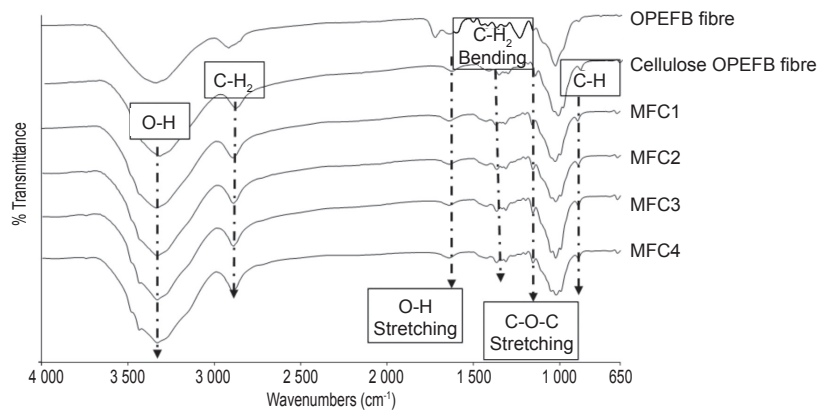


Note: H₂SO₄ - sulphuric acid.

Figure 2. The microfibrilled cellulose (MFC) with different acid concentration used. (a) MFC1 - 10% H₂SO₄; (b) MFC2 - 20% H₂SO₄; (c) MFC3 - 30% H₂SO₄ and (d) MFC4 - 40% H₂SO₄.

FTIR

FTIR spectra of raw OPEFB-fibre, cellulose OPEFB-fibre and that of MFC1 to MFC4 samples are presented in Figure 3. The peak assignments are depicted in the same figure. Comparing between the raw OPEFB and alkaline treated fibre (cellulose OPEFB), there was no detection of peak intensity at 1732 cm⁻¹ for carbonyl (C=O) stretching vibrations, suggesting the removal of pectin, hemicellulose or the ester linkage of the carboxylic group of ferulic and p-coumaric acids of lignin or hemicelluloses in the raw fibres. While, the absence of peak intensity at 1265 cm⁻¹ and 1507 cm⁻¹ in the spectra of the alkaline treated fibres indicated the removal of lignin, hemicellulose and waxes (Ireana Yusra *et al.*, 2014). The disappearing of certain peaks in the spectra of other than cellulose OPEFB-fibre indicated that the purification process was successful subject to the removal of lignin, hemicellulose and other impurities. From Figure 3, the FTIR spectra displayed similar pattern and peak position for all MFC samples. The spectral bands located at 3400-3340 cm⁻¹ and 2900 cm⁻¹ were identified in all spectra, thus, represented the O-H stretching of intermolecular hydrogen bonds and aliphatic saturated C-H stretching, respectively. The first spectral band observed represents the hydroxyl group which is related to moisture content. This is where the OH bond is bonded to the structure of cellulose, hemicellulose and lignin. The shoulders which were seen around 1510 cm⁻¹ for the untreated samples demonstrated the aromatic C=C bonds in the aromatic rings of lignin. While all peaks and shoulders between 1400-1000 cm⁻¹ for the untreated samples belonged to the typical cellulosic bonds. This indicated that the chemical structure of the cellulosic fragment of MFC have not been affected by the different acid concentrations used in the acid hydrolysis process. Inversely, their morphology and thermal stability could be affected by the high concentration of acid.



Note: H₂SO₄ - sulphuric acid.

Figure 3. The Fourier transformed infrared spectroscopy (FTIR) of oil palm empty fruit bunches (OPEFB), cellulose OPEFB-fibre and microfibrilled cellulose (MFC) with different acid concentrations: MFC1 - 10% H₂SO₄; MFC2 - 20% H₂SO₄; MFC3 - 30% H₂SO₄; MFC4 - 40% H₂SO₄.

Thermal Analysis of Cellulose and MFC

TGA is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. The thermal behaviour and thermal stability of the samples obtained before and after were studied. Figures 4a and 4b show the thermogram of cellulose OPEFB-fibre and MFC 10% to 40%, respectively. It was observed that all MFC samples displayed single step degradation in the temperature range of 200°C-400°C while the weight loss of moisture in the samples was observed at around 100°C. The thermal stability of the samples was characterised by the temperature at 50% (T_{50}) and the temperature of the maximum weight loss (T_{max}). It is noted that the MFC2 was stable until a much higher temperature up to 389°C, as compared to the cellulose OPEFB-fibre because a higher cellulose crystallinity can delay the degradation process and improve the thermal stability (Lima *et al.*, 2004). The T_{max} showed that MFC2 exhibited better thermal stability at temperature of 388°C as compared to the other MFC. This indicated that the

higher decomposition temperature obtained for MFC2 was attributed to the higher crystallinity of cellulose material (Hussin *et al.*, 2016; Osong *et al.*, 2016). From Table 1, it is concluded that the MFC isolated from OPEFB cellulose produced by acid hydrolysis at four different acid concentrations clearly reveals that the acid hydrolysis treatment affects the thermal stability of the MFC.

TABLE 1. DECOMPOSITION TEMPERATURE OF CELLULOSE OIL PALM EMPTY FRUIT BUNCHES FIBRE (EFB-fibre) AND MICROFIBRILLATED CELLULOSE (MFC)

Samples	$T_{50\%}$ (°C)	T_{max} (°C)
Cellulose OPEFB-fibre	318.9	357.9
MFC1	343.7	377.1
MFC2	351.7	388.8
MFC3	305.0	364.8
MFC4	203.2	218.4

Note: MFC1 - 10% H_2SO_4 ; MFC2 - 20% H_2SO_4 ; MFC3 - 30% H_2SO_4 ; MFC4 - 40% H_2SO_4 ; $T_{50\%}$: 50% weight loss; T_{max} : maximum weight loss.
 H_2SO_4 - sulphuric acid.

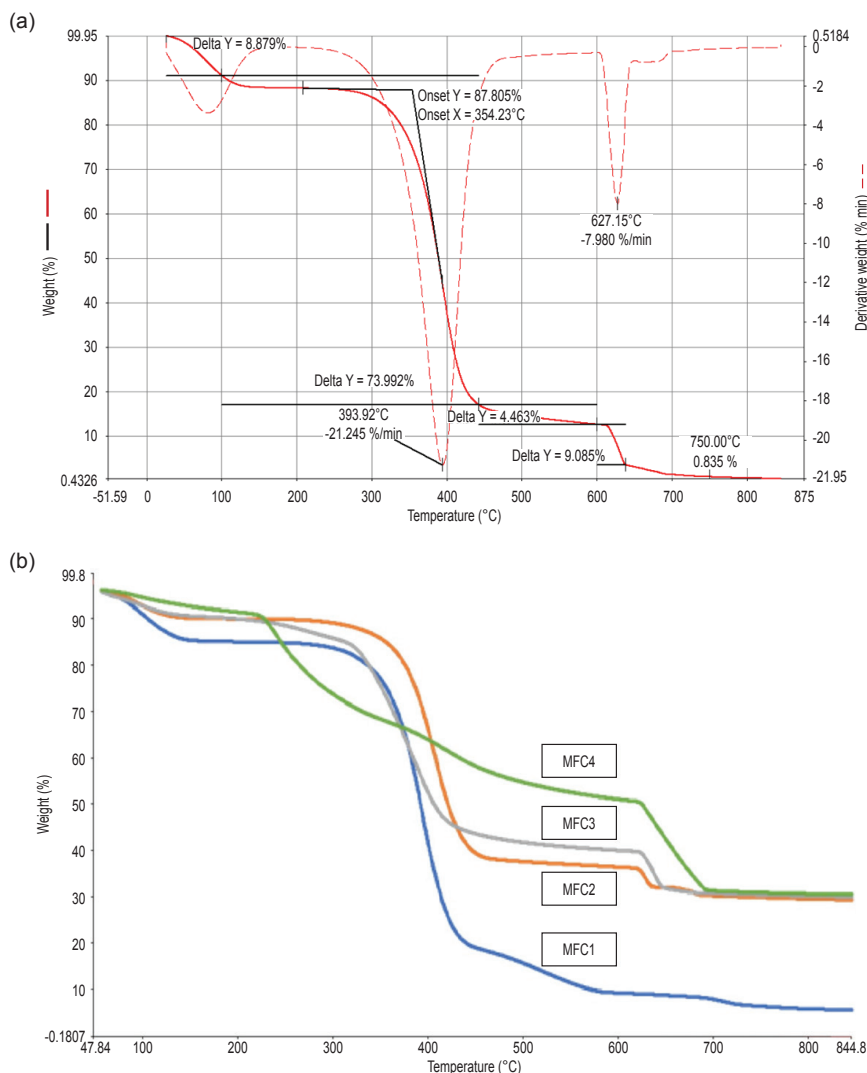
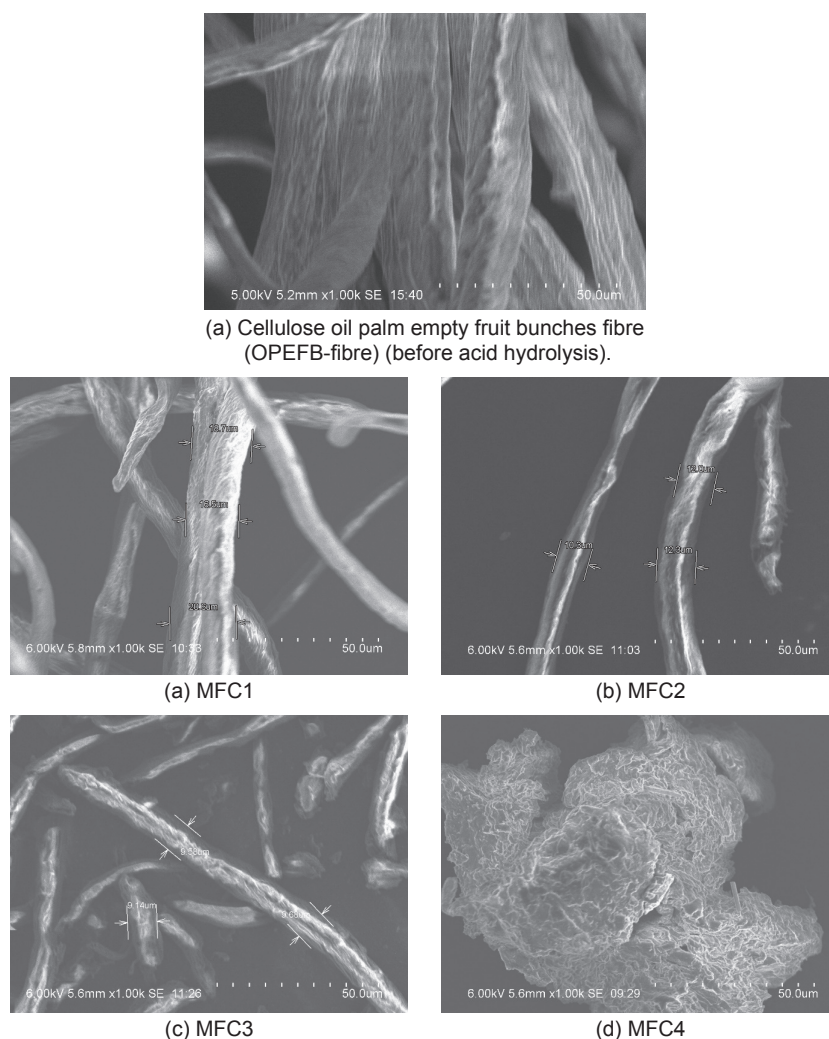


Figure 4. Thermogravimetric profile of (a) cellulose oil palm empty fruit bunches fibre (OPEFB-fibre) and (b) MFC1, MFC2, MFC3 and MFC4.

SEM Micrographs of Cellulose Before and After Acid Hydrolysis

The morphological structures of cellulose (before acid hydrolysis) and MFC (after acid hydrolysis) are presented in Figure 5. Based on the figure, it was observed that the morphology of MFC differed after the treatment process. The morphology of MFC revealed that the diameter of MFC decreased along with the shortened length of fibres when the concentration of sulphuric acid increased. The results showed that the acid treatment decreased the widths of the fibres significantly. The width of MFC was decreased from 19 μm to 9.4 μm at 30% sulphuric acid concentration (Table 2). This observation is in agreement with the study by Fahma *et al.* (2010), where it was found that the formation and diameter of the MFC produced greatly depends on the concentration of acid and acid-fibre ratio. Besides that, it can be clearly seen that the external surface of MFC exhibited a smooth surface and irregular structure

which was possibly due to the removal of silica, hemicellulose and lignin (Figure 5b). This showed a good agreement with XRD results where the MFC had higher crystallinity index than cellulose EFB-fibre. From Figures 5a, 5b and 5c, the MFC have the average size of 19, 11 and 9.4 μm , respectively, which indicated the disruption of lignocellulosic structure. Through this observation also, the lignin and hemicellulose were removed through bleaching process (Megashah *et al.*, 2018) which caused the defibrillation of fibre bundles into individual microfibrillated cellulose. The raw fibres of OPEFB before treatment is composed of bundles which are bound together by lignin and hemicellulose. The morphology possesses an irregular and rough surface of fibre bundles. Different morphology has been observed on MFC after 40% sulphuric acid treatment, where the fibres formed rough and dense agglomerated surface morphological structure due to high acid concentration used in the reaction. This similar morphology has been observed during the isolation of MCC by Rosnah *et al.* (2009).



Note: H₂SO₄ - sulphuric acid.

Figure 5. The scanning electron microscope (SEM) micrograph of cellulose (before acid hydrolysis) and microfibrillated cellulose (MFC) (after acid hydrolysis). MFC1 - 10% H₂SO₄; MFC2 - 20% H₂SO₄; MFC3 - 30% H₂SO₄; MFC4 - 40% H₂SO₄ (1000X magnification).

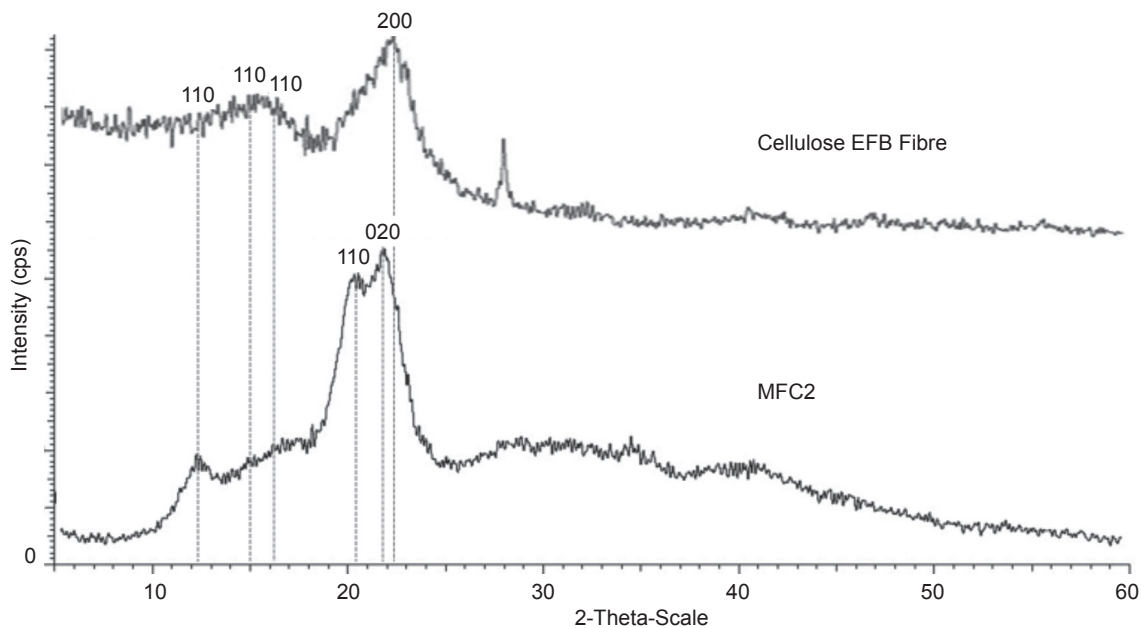


Figure 6. The X-ray diffractograms of cellulose oil palm empty fruit bunch fibre (OPEFB-fibre) and MFC2.

TABLE 2. RANGE OF DIAMETER SIZE OF CELLULOSE EMPTY FRUIT BUNCHES FIBRE (EFB-fibre) AND MICROFIBRILLATED CELLULOSE (MFC)

Samples	Range diameter size (µm)
Cellulose OPEFB-fibre	25 - 30
MFC1	18 - 20
MFC2	10 - 12
MFC3	9.1 - 9.7
MFC4	> 50

XRD Analysis of Cellulose and MFC

Generally, the degree of crystallinity of materials is evaluated using the X-ray diffraction method. The degree of crystallinity is the ratio of crystalline areas to amorphous areas in the cellulose. The X-ray diffraction patterns for cellulose OPEFB-fibre and MFC2 are shown in Figure 6. Based on the overall MFC observation, the MFC2 was found suitable and selected for its properties to be further investigated using XRD analysis. This was due to its high decomposition temperature (TGA) and it exhibited a few typical cellulose crystalline peaks in the 2θ range of 10°-40° (Ma *et al.*, 2011). The crystallinity value was calculated by using Segal's method. The crystallinity values of OPEFB-fibre and MFC2 were 51% and 60%, respectively (Table 3). As the overall extraction process started from cellulose OPEFB-fibre to the isolation of MFC, the crystallinity index kept increasing due to elimination of some hemicellulose and lignin, which existed in the amorphous regions (Chuayjuljit *et al.*, 2010). The alignment of cellulose molecules stands mostly are located at this region. Higher crystallinity is due to more efficient removal of nanocellulosic

polysaccharides and dissolution of amorphous zones. The results also confirm that hydrolysis takes place preferentially in the amorphous region as acids dissolve the amorphous regions while crystalline regions are more stable towards chemical attack. However, the interesting observation is that both samples displayed a single peak at theta 22.6° which represents the cellulose I polymorph structure. Thus, the acid hydrolysis concentration did not affect the cellulose polymorph which was similar to the observation reported by Haafiz *et al.* (2013) and Rosa *et al.* (2012).

TABLE 3. THE CRYSTALLINITY INDEX OF CELLULOSE OIL PALM EMPTY FRUIT BUNCHES FIBRE (EFB-fibre) AND MICROFIBRILLATED CELLULOSE 2 (MFC2)

Name	Crystallinity index (%)
Cellulose EFB-fibre	51
MFC2	60

CONCLUSION

In this study, MFC was successfully isolated from OPEFB with different acid hydrolysis concentration. For the analysis and description based on appearance of MFC, only MFC fibre hydrolysed at 40% sulphuric acid was over hydrolysed and turned to dark brown. The results obtained from FTIR analysis showed the chemical structure of the cellulosic fragments were not influenced by different acid concentration treatments. While, SEM analysis showed that all MFC samples have smooth, finer and less aggregated fibril-like structures except for MFC fibre hydrolysed at 40% sulphuric acid. SEM study demonstrated the smallest diameter of MFC

was around 9.4 μm . Based on the TGA results, it can be concluded that MFC treated with 20% sulphuric acid has good thermal stability as compared to others. Meanwhile the XRD analysis revealed the C_r of MFC2 increased after acid hydrolysis treatment. It is concluded that, acid hydrolysis of fibre using 20% H_2SO_4 for one hour is the optimum condition of acid pre-treatment process based on TGA, SEM and XRD analysis and it has the potential to be used in the production of environmental-friendly filler biocomposites at high temperature range (Jimat *et al.*, 2019; Rozmarin *et al.*, 1977).

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