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# SOLID-STATE CHARACTERISTICS OF MICROCRYSTALLINE CELLULOSE FROM OIL PALM EMPTY FRUIT BUNCH FIBRE

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## ABSTRACT

*Oil palm empty fruit bunches (EFB) are one of the by-products generated from palm oil mills. They consist mainly of lignocellulosic compounds, namely cellulose, hemicellulose and lignin. Cellulose, in particular, constitutes about 37% (dry weight) of the EFB, and is a compound with high value and can be exploited for the benefit of the palm oil industry.*

*In this study, an attempt to prepare microcrystalline cellulose (MCC) from the isolated EFB-cellulose was carried out. The MCC was prepared by controlled acid hydrolysis of the isolated α-cellulose which attacked the amorphous region, and was followed by the back neutralization process with alkali. The structural properties of the cellulose and MCC were studied by Fourier Transformed Infra-red Spectrometry (FTIR) and X-ray diffraction methods. The FTIR spectrum of MCC from EFB was identical to that of the commercial MCC as well as the cellulose which showed comparable presence of C-O-C, C-C, O-H, and C-H bands. However, a broad peak at 3329 cm$^{-1}$ was observed from the EFB-cellulose due to absorption vibration of the hydroxyl groups. The X-ray diffraction pattern revealed a low degree of order for EFB-cellulose and a relatively ordered structure for EFB-MCC. Two peaks of diffraction angles ranging between 19° and 23° were observed in the EFB-MCC, indicating the presence of a small percentage of cellulose II. The commercial MCC had a highly ordered structure compared to EFB-MCC as indicated by the presence of a single peak at 22.5°.*

**Keywords:** empty fruit bunches, cellulose, microcrystalline cellulose, Fourier Transformed Infra-red Spectroscopy.

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## INTRODUCTION

Oil palm empty fruit bunches (EFB) are abundantly and readily available renewable organic materials generated from the palm oil mills. In 2007, it was estimated that around 19.03 million tonnes (wet weight basis) of EFB were available in Malaysia (Astimar *et al*., 2008). EFB can be considered as a valuable biomass residue which can be converted not only into energy (which is currently its major use), but also as a raw material for products of higher value such as panelling and composites, fine chemicals, pulp and paper as well as compost and bio-fertilizer.

Studies have shown that oil palm fibre comprises lignocellulosic biochemical components which are largely made up of 18-23% (w/w) lignin, 35% (w/w) cellulose and 25% (w/w) hemicellulose (Abdul Azis *et al*., 1989; Rosnah *et al*., 2002). Cellulose, which can be obtained in the pure form from cotton, or extracted from lignocellulosic material, is a value-added compound that is being used in a wide range of industries. It is the major constituent of pulp and paper products, and is also being utilized as a starting material for the production of regenerated fibres such as rayon, microcrystalline cellulose and other cellulose derivatives, especially esters and ethers (Sixta, 2006). Microcrystalline cellulose (MCC) has many applications in structural composites,

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pharmaceuticals, food, paper, *etc*. In addition, it is a naturally derived stabilizer, texturing agent and fat replacer.

Generally, the chemical constituents that make up the cell wall of wood fibre determine its structural characteristics. Hemicellulose and lignin are both amorphous substances, whereas cellulose has crystalline and amorphous regions (Fengel and Wegener, 1984; Zickler *et al*., 2007). An increase in the crystalline region increases the rigidity of cellulose, and this phenomenon affects the accessibility of the cellulose molecules (Tripp, 1971; Bertran and Dale, 2003). Several researchers have carried out investigations on the changes in crystallinity index of cellulose during kraft and other alkaline pulping processes. Vozar (1998) used X-ray diffractometry to determine the crystallinity index in holocellulose and cellulose of selected hardwood species. He found that the crystalline phase of holocellulose is lower than that of cellulose in all the species. This method has been used by many researchers to study details on the accessibility of the cellulosic part (Oh *et al*., 2005; Zhao *et al*., 2007).

The use of acid hydrolysis to reduce cellulose crystallinity has been adopted by many researchers (Sidiras and Koukios, 1989; Sun *et al*., 2004; El-Sakhawy and Hassan, 2007). Basically, strong acids are oxidizing agents and would dehydrate and redistribute the biopolymers in lignocellulosic materials (Song and Lee, 1984). The effect of acid hydrolysis on the crystallinity of cellulose was also studied by Rozmarin *et al.* and their results showed that with an increase in acid concentrations the crystallinity index decreased rapidly. In addition, the presence of sodium hydroxide decreased the crystallinity index of α-cellulose because sodium hydroxide penetrates and swells the cellulose fibre (Rozmarin *et al*., 1977).

This article reports the structural properties of holocellulose, cellulose and MCC extracted from oil palm EFB fibre by the optimized process. Analyses by X-ray diffractometry and Fourier Transformed Infra-red Spectroscopy (FTIR) and scanning electron microscopy were carried out for the purpose of this study.

## MATERIALS AND METHODS

### Preparation of Microcrystalline Cellulose

MCC was prepared from cellulose which was earlier isolated from oil palm EFB fibre. To isolate cellulose, the dried fibre was first delignified according to ASTM, D 1104-56 to produce holocellulose, and this was followed by the removal of the hemicellulose fraction according to ASTM, D 1103-60. For the preparation of holocellulose, about 4.0 g of the ground EFB fibre strands (measuring less than 425 μm in diameter) were mixed with distilled water and treated with 2.0 ml acetic acid and 5.0 g sodium chlorite at 70°C for 4 hr. Later, 2.0 g of the holocellulose produced were treated with 50 ml 17.5% sodium hydroxide solution, and then 70 ml distilled water were added. This was to separate the hemicellulose from the holocellulose, leaving the α-cellulose. The insoluble α-cellulose was filtered and washed with 50 ml 8.3% sodium hydroxide.

Two categories of MCC were produced by hydrolyzing the α-cellulose with 1% sulphuric acid under pressurized steam for 1 hr and 3 hr: MCC A (1 hr treatment) and MCC B (3 hr treatment). The MCC was separated from the hydrolysate and washed with distilled water. The processes which followed involved alkalizing the MCC with sodium hydroxide solution, and bleaching of the MCC with hydrogen peroxide. The suspension was then washed and filtered. The holocellulose, α-cellulose, MCC A and MCC B were then analysed for their structural properties. Commercial MCC (from Sigma-Aldrich) was used as the standard.

### Fourier Transformed Infra-red Spectroscopy Analysis

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

### Scanning Electron Microscopy

A Hitachi S2700 scanning electron microscope (SEM) was used to evaluate the microscopic features of the samples.

### X-ray Diffractometry

The X-ray diffraction (XRD) measurements were conducted over a 2.3 to 60° 2θ range on a Bruker Model D8 Advance diffractometer, using CuKα X-rays. The step width was 0.025° 2θ $min^{-1}$ with a time constant of 1 s.

## RESULTS AND DISCUSSION

The flow chart and mass balance during the preparation of MCC from EFB are illustrated in *Figure 1*. The yields of MCC from EFB were 22% and 18% for MCC A and MCC B, respectively. *Figure 2* shows the X-ray diffraction patterns for EFB fibre, EFB holocellulose and EFB-cellulose. A smeared-out diffractogram was observed for all samples, especially the peaks that appeared at diffraction angles ranging from 18°-24° for cellulose and from 20°-24° for EFB fibre and holocellulose, indicating a low degree of order. However, the linear peak position of cellulose was much higher in comparison to holocellulose and EFB fibre, indicating that the crystalline behaviour of EFB fibre and holocellulose was very much lower than for cellulose. The presence of amorphous aromatic compounds such as lignin, polysaccharide polymers and many others was attributed to this behaviour (Gumuskaya and Usta, 2002).

The X-ray diffractograms of MCC A and MCC B are shown in *Figures 3* and *4*, respectively. These diffraction patterns revealed a relatively more ordered structure of the MCCs as compared to EFB-cellulose. The peak intensity of both MCCs appeared to be higher than that of EFB-cellulose indicating that the MCCs were more crystalline than cellulose. Theoretically, cellulose is composed of millions of microfibrils, and each microfibril is composed of two areas: the amorphous and crystalline regions (Marchessault, 1986). During processing to MCC, the α-cellulose which generally has the lattice of cellulose II was hydrolyzed and depolymerized to remove a large portion of the amorphous region, leaving the crystalline cellulose.

In the hydrolysis process also, the crystalline

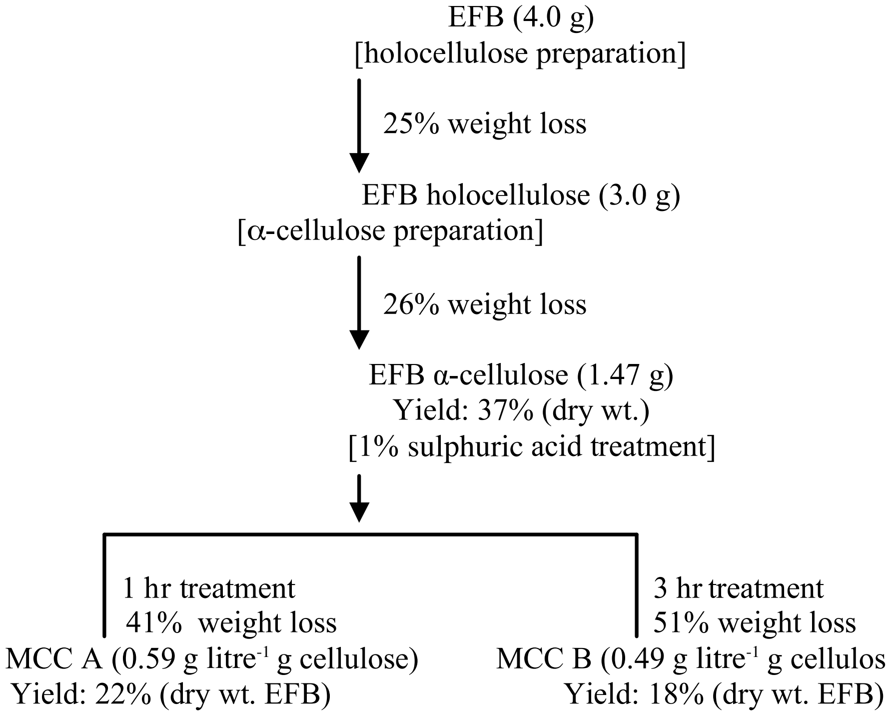


*Figure 1. Flow chart and mass balance during the preparation of microcrystalline cellulose (MCC) from empty fruit bunch (EFB) fibre.*

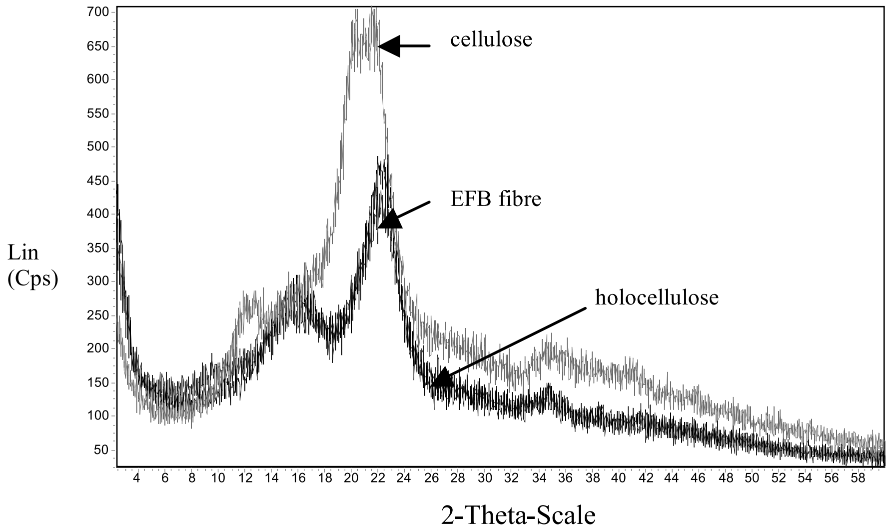


*Figure 2. The X-ray diffractograms of empty fruit bunch (EFB) fibre, holocellulose and cellulose.*

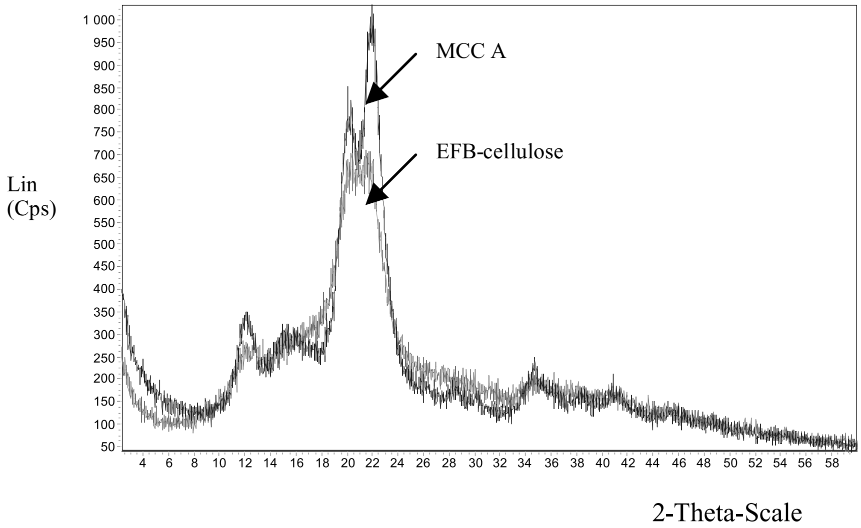


*Figure 3. The X-ray diffractograms of microcrystalline cellulose (MCC) A and empty fruit bunch (EFB)-cellulose.*

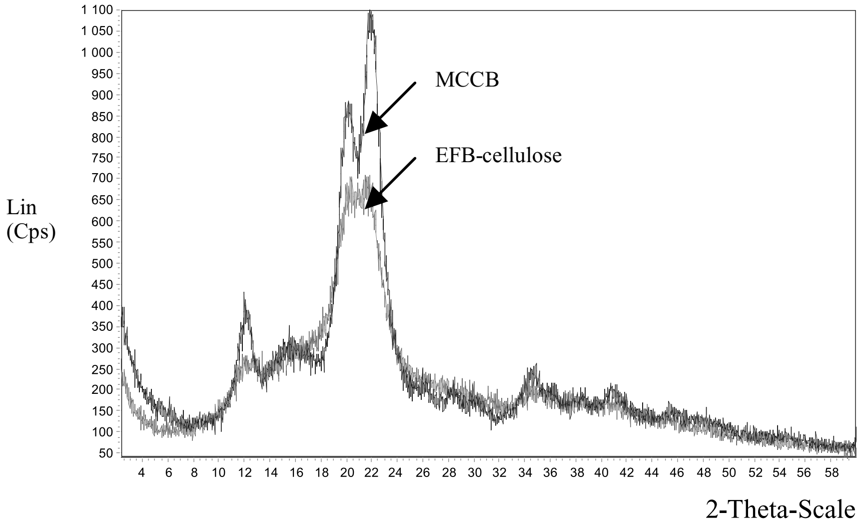


*Figure 4. The X-ray diffractograms of microcrystalline cellulose (MCC) B and empty fruit bunch (EFB)-cellulose.*

region of cellulose I tends to increase so that the crystallinity of MCC became higher than that of cellulose from EFB. The X-ray diffraction pattern of cellulose I is normally observed in native cellulose of higher plants whereby the planes are observed at 14.8°, 16.3° and 22.6°, respectively (Iijima and Takeo, 2000). The crystalline fraction is considered to be responsible for producing a sharp X-ray diffraction pattern at 22.6°. The intrinsic nature of the cellulose I microfibrils is such that all the chains are organized in a parallel fashion whereas the cellulose II is organized in an anti-parallel manner. The presence of both crystalline and semi-crystalline regions was also observed in the diffractogram curves of EFB-MCC. The presence of a noticeable peak on the shoulder of the prominent peak at the diffraction angles of 2θ ranging from 19°-23° suggests this kind of behaviour (Zugenmaier, 2007). The full-width half-maximum (FWHM) readings at 22° for MCC A and MCC B were 1.8 and 1.7, respectively, and the values were slightly higher than that of the commercial MCC. In comparison, only the crystalline peak was observed at 22.5° for the commercial MCC with an FWHM reading of 1.6 as shown in *Figure 5*. This shows that MCC produced from EFB had a slightly less crystalline behaviour than commercial MCC, and that MCC B was slightly more crystalline than MCC A.

Increasing the time of hydrolysis from 1 hr to 3 hr affected the crystallinity of MCC. The diffractogram curves of EFB MCC also showed reflections that is characteristic of a cellulose II lattice, suggesting the presence of a small percentage of cellulose II. In the case of commercial MCC, the diffractogram shows the characteristic cellulose I lattice. According to Iijima and Takeo (2000), the degree of crystallinity of MCC would not reach 100% and this was explained by considering the size of the microfibrils, the number of cellulose molecules constructing the microfibril and the surface effect on crystallinity.

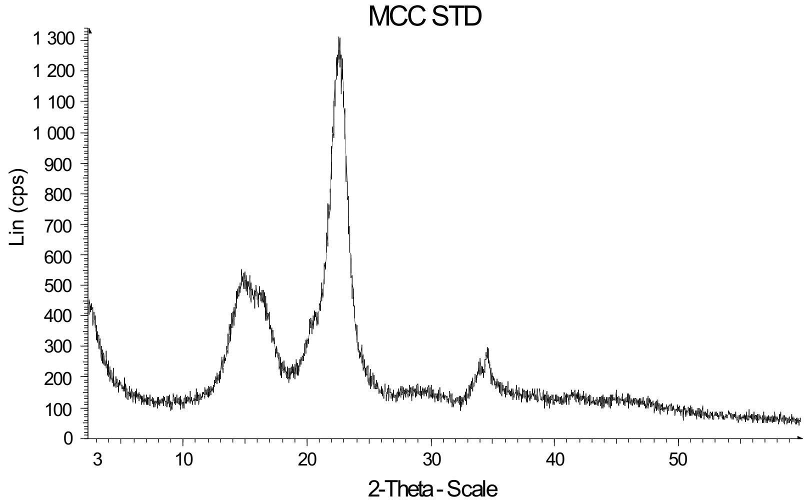


*Figure 5. The X-ray diffractogram of commercial microcrystalline cellulose (MCC).*

The degree of crystallinity would be larger than 64% when the width of the microfibril was 5 nm. If the width of the microfibril was 10 nm, the degree of crystallinity would be larger than 81%.

In the FTIR analysis, the spectra of MCC A and MCC B were identical to that of the commercial MCC as shown in *Figure 6*. In addition, the EFB-cellulose spectrum was also similar to the two MCC spectra, suggesting that the same functional groups were present in all samples. However, the characteristic intermolecular and intramolecular O-H stretching vibration band of the EFB-cellulose spectrum in the range of 3200-3400 cm$^{-1}$ appeared broader compared to the others. This suggests that the cellulose chain polymers were much longer than the MCC chain polymers. A greater number of OH groups on the glucose units of the cellulose polymers broadens the peak. The peaks at 1428 cm$^{-1}$ and 1314 cm$^{-1}$ of all samples were associated with the intramolecular hydrogen bonds at the $C_6$ group and O-H in-plane bending vibration, respectively (Vijay *et al.*, 2001). A medium peak at 2892.97 cm$^{-1}$ was due to C-H bonds. The peak at 1022-1030 cm$^{-1}$ was assigned to the C-O-C linkage of the anhydrous repeating units and the shoulder at 1157-1160 cm$^{-1}$ was due to C-C bonds. The intensity of the peak at 894.99 cm$^{-1}$ which was associated with the β-glycosidic linkages decreased as the crystallinity of the samples increased. The hydrolysis process caused the cleavage of glycosidic linkages of cellulose to produce MCC. Thus, a higher intensity of this peak was observed in cellulose compared to MCC A, MCC B and commercial MCC.

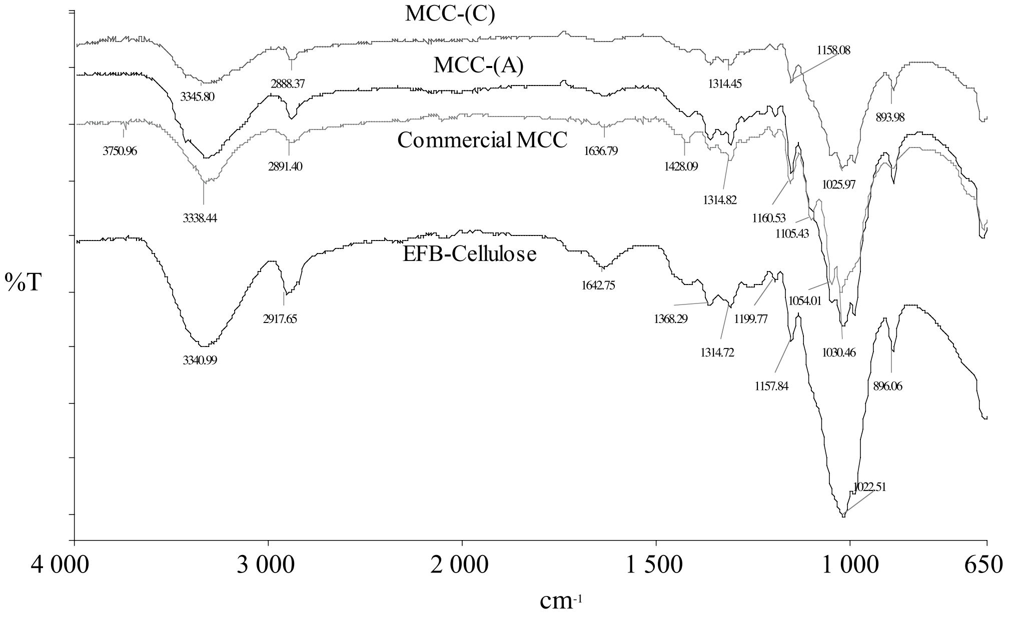
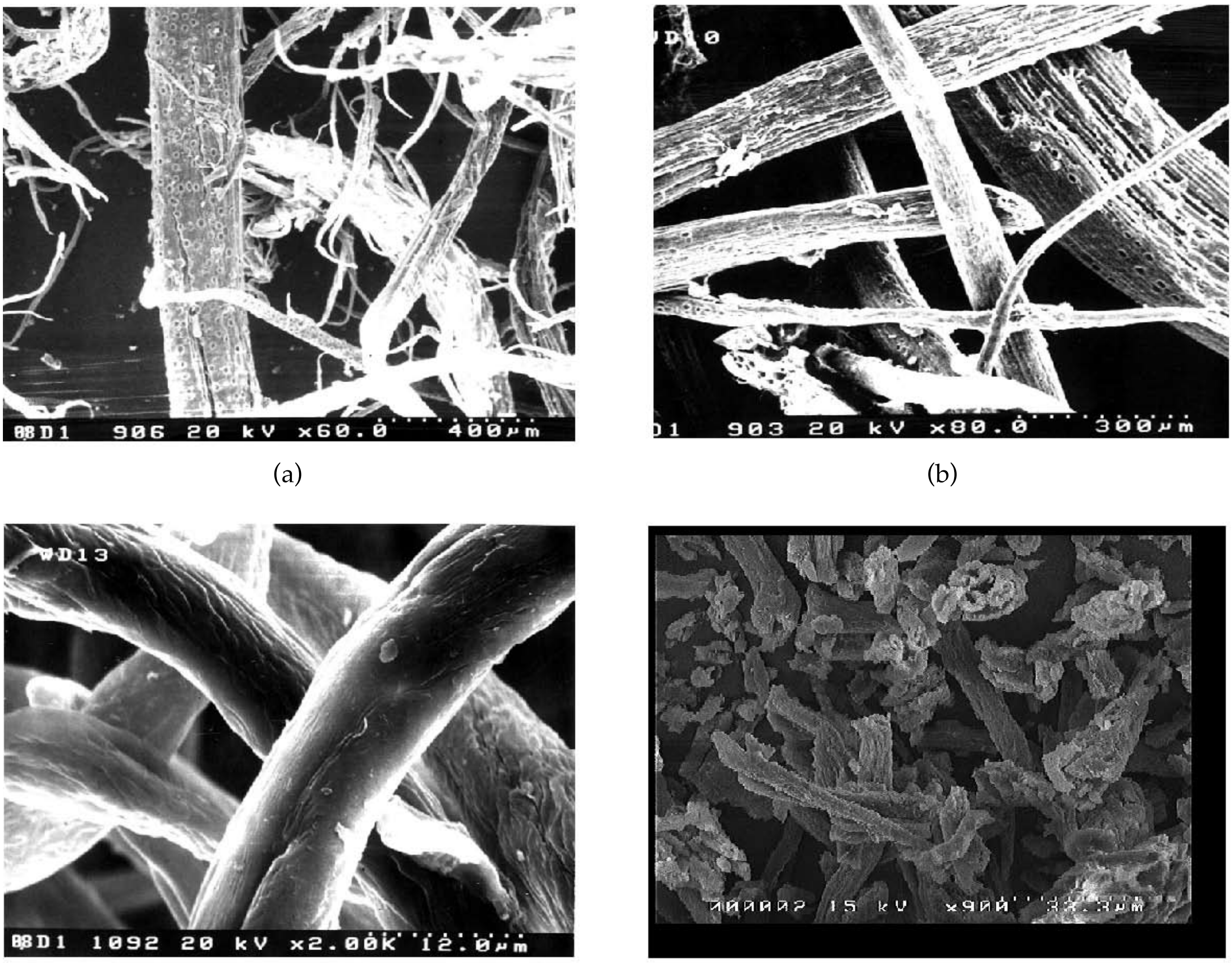


*Figure 6. Infra-red spectra of microcrystalline cellulose (MCC) A, MCC B, commercial MCC and empty fruit bunch (EFB)-cellulose.*

The SEM analysis illustrated the morphological changes which occurred during the chemical conversion of EFB fibre into EFB-MCC as shown in *Figure 7a* to *d*. *Figure 7a* shows that EFB fibre comprised a mixture of differently sized fibrils which were still quite intact. In actual fact, this structure is governed by the lignocellulosic components, especially the lignin that gives strength to the fibrils and the polysaccharides, especially the cellulose and hemicellulose. However, a greater part of the smaller fibrils seemed to be absent in the holocellulose due to the removal of lignin during the delignification process as shown in *Figure 7b*. Further down the processing of holocellulose into α-cellulose uniform sized fibrils with smooth surface were formed (*Figure 7c*), whereas treatment with 1% sulphuric acid during the preparation of MCC caused the fibrils to become shorter and have rough surfaces as shown in *Figure 7d*. The texture of EFB-MCC diverged from that of cellulose due to the depolymerization of the cellulose polymers to shorter chained MCC.



(a)

(b)

(c)

(d)

*Figure 7. Electron micrographs of the samples (a) empty fruit bunch (EFB) fibre (60x), (b) EFB-holocellulose (80x); (c) EFB-cellulose (200x), and (d) EFB-MCC (600x).*

## CONCLUSION

As anticipated, the results from X-ray analysis and microscopic investigations show that EFB-MCC exhibited different morphological properties in comparison with cellulose from EFB. The X-ray diffraction pattern showed distinctive differences in structure between EFB-MCC and the commercial MCC. The EFB-MCC was slightly less crystalline than the commercial MCC which might be due to the presence of a small portion of cellulose II. Whether the semi-crystalline feature of EFB-MCC was due to its nature or it was influenced by other factors such as the chemicals used, reaction time and others have yet to be studied in the future.

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## REFERENCES

ABDUL AZIS, A; MOHAMADIAH, B and ROSNAH, M S (1989). Preparation of alpha cellulose from palm fruit mesocarp. *Proc. of the of 14th Malaysian Biochemical Society Conference*. 4-5 September 1989, Malaysia.

ASTIMAR, A A; MOHD BASRI, W and CHOO, Y M (2008). Advanced carbon products from oil palm biomass. *J. Oil Palm Research Special Issue*: 22-32.

BERTRAN, M S and DALE, B E (2003). Determination of cellulose accessibility by differential scanning calorimetry. *J. of Applied Polymer Science, 32(3)*: 4241-4253.

EL-SAKHAWY, M and HASSAN, M L (2007). Physical and mechanical properties of microcrystalline cellulose prepared from agricultural residues. *Carbohydrate Polymers*, *67(1)*: 1-10.

FENGEL, D and WEGENER, G (1984). Carboxymethylcellulose. *Wood Chemistry, Utrastructure* (de GRUYTER, W, ed.). Berlin, New York. 78 pp.

GUMUSKAYA, E and USTA, M (2002). Crystalline structure properties of bleached and unbleached wheat straw (*Triticum aestivum* L.) soda-oxygen pulp. *Turk J Agric., 26*: 247-252.

IIJIMA, H and TAKEO, K (2000). *Handbook of Hydrocolloids* (Philips, G O and Williams, P A, eds.). Woodhead Publishing Limited. p. 333-342.

MARCHESSAULT, R H (1986). *Cellulose Structure Modification and Hydrolysis* (Young, R A and Rowell, R M, eds.). Wiley-Interscience, New York, 379 pp.

OH, S Y; YOO, D I; SHIN, Y; KIM, H C; KIM, H Y; CHUNG, Y S; PARK, W H and YOUK, J H (2005). Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydrate Research, 340(15)*: 2376-2391.

ROZMARIN, G H; UNGUREANU, V and STOLERU, A (1977). A study on the supramolecular structure of cellulose carried out by means of acid hydrolysis. *Cellulose Chem. and Technology, 11*: 523-530.

ROSNAH, M S; KU HALIM, K H and WAN HASAMUDIN, W H (2002). The potential of oil palm lignocellulosic fibres for the cellulose derivatives production. *Proc. of the Research and Consultancy Seminar*. Faculty of Mechanical Engineering, UiTM Shah Alam, Malaysia. p. 140-145.

SIDIRAS, D K and KOUKIOS, E G (1989). Acid saccharification of ball-milled straw. *Biomass, 19(4)*: 289-306.

SIXTA, H (2006). *Handbook of Pulp* (Sixta, H, ed.). Wiley-VCH Verlag GMbH, & Co.KGaA, Germany. 11 pp.

SUN, J X; SUN, X F; ZHAO, H and SUN, R C (2004). Isolation and characterization of cellulose from sugarcane bagasse. *Polymer Degradation and Stability, 84(2)*: 331-339.

SONG, S K and LEE, Y Y (1984). Acid hydrolysis of wood cellulose under low water condition. *Biomass, 6(1-2)*: 93-100.

TRIPP, V W (1971). Measurement of crystallinity. *Cellulose and Cellulose Derivatives* (Bikales, M and L. SEGA, L, eds.). Willey Interscience. New York. p. 305-323.

VIJAY, K; MARIA, L R M and DONG, Y (2001). Preparation, characterization, and tabletting properties of a new cellulose-based pharmaceutical aid. *International Journal of Pharmaceutics, 235*: 129-140.

VOZAR, M (1998). Application of x-ray analysis in the study of holocelllulose of six hardwood species. Vybrane procesy prichemickom sprac_vani dreva. II. Medzinarodne symposium. Technika Univerzita vo Zvolene, p. 85-89.

ZHAO, H; KWAK, J H; ZHANG, Z C; BROWN, H M; AREY, B W and HOLLADAY, J E (2007). Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis. *Carbohydrate Polymers, 68(2)*: 235-241.

ZICKLER, G A; WAGERMAIER, W; FUNARI, S S; BURGHAMMER, M and PARIS, O (2007). *In situ* X-ray diffraction investigation of thermal decomposition of wood cellulose. *J. Analytical and Applied Pyrolysis, 80(1)*: 134-140.

ZUGENMAIER, P (2007). *Crystalline Cellulose and Cellulose Derivatives: Characterization and Structures* (Series in Wood Science). Lavoisier, France. 360 pp.

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A 'Letter to Editor' should be concise. Please include your full name (add a pseudonym, if you like), address, gender and phone number (for reference only). You can send by e-mail, regular mail or fax (603-8922 3564). Personal information of sender will be kept confidential. Send your letter to: Malaysian Palm Oil Board, P.O. 10620, 50720 Kuala Lumpur (Attn: Publication Section) or e-mail us at: pub@mpob.gov.my

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- There will be a very short word limit, which is strictly enforced. A general guideline would be 200-250 words.
- You must not submit the same letter to more than one publication at the same time.
- The letter should refer to a specific article recently published by JOPR.
- There is a strict deadline for responding to a given article. The sooner you respond to specific article, the more likely it is that your letter will be published.

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- Short Communications are original short articles which are published with the objective of disseminating technical ideas of the originator without losing time. This will provide researchers with a venue where they can share their most current results and developments in the shortest possible time. The Short Communications, like regular papers will be reviewed by expert reviewers and evaluated by editor. Unlike regular papers, Short Communications will be published within six months of submission.
- Short communications should be prepared in a camera-ready format and limited to 2000 words and not more than four illustrations (*i.e.* Figures and Tables).
- Format: Abstract (~80 words), Keywords, Introduction, Materials and Methods, Results and Discussion, Conclusion and References.
- In order to help expedite the reviewing process, authors are advised to suggest a list of two unbiased potential reviewers to the Editor. Please include their names and e-mail addresses in the submission e-mail. These reviewers should not be related to the author, nor should they be associates or collaborators.