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Microcrystalline Cellulose (MCC) From Oil Palm Empty Fruit Bunch (EFB) Fiber via Simultaneous Ultrasonic and Alkali Treatment

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Abstract**—**In this study, microcrystalline cellulose (MCC) was extracted from oil palm empty fruit bunch (EFB) cellulose which was earlier isolated from oil palm EFB fibre. In order to isolate the cellulose, the chlorination method was carried out. Then, the MCC was prepared by simultaneous ultrasonic and alkali treatment from the isolated α-cellulose. Based on mass balance calculation, the yields for MCC obtained from EFB was 44%. For fiber characterization, it is observed that the chemical composition of the hemicellulose and lignin for all samples decreased while composition for cellulose increased. The structural property of the MCC was studied by X-ray diffraction (XRD) method and the result shows that the MCC produced is a cellulose-I polymorph, with 73% crystallinity.

Keywords**—**Oil palm empty fruit bunch, microcrystalline cellulose, ultrasonic, alkali treatment, X-ray diffraction.

I. Introduction

OIL palm is the highest yielding edible oil crop in the world. It is cultivated in 42 countries in 11 million ha worldwide. 1 ha oil palm plantation produces about 55 ton of dry matter in the form of fibrous biomass annually [13]. Lignocellulosic fibers can be extracted from oil palm tree such as trunk, frond, fruit mesocarp and empty fruit bunch (EFB). Among the various fiber sources in an oil palm tree, EFB has potential to yield up to 73% fibers [3] and has potential to substitute the natural fibre resources. Empty fruit bunch (EFB) is obtained after the removal of oil seeds from fruit bunch for oil extraction.

Since EFB is one of the most abundant biomass materials that are regularly discharged from palm oil refineries, efforts to convert this material into value-added products have gained great interest. One of these is to extract the high value lignocellulosic materials such as hemicelluloses, cellulose and lignin, contents of which are estimated at 22-25%, 40-43% and 19-21% [8], respectively, in the dry EFB.

The most significant material in EFB is cellulose, which has a variety of potential applications in the chemical, food, and composite industries. Cellulose is a naturally occurring polymer in plants and it is comprised of glucose units joined together by β-1,4-glycosidic bonds. The linear cellulose chains are bundled together as microfibrils, and these microfibrils are composed of amorphous and crystalline regions. In comparison of internal bonding, the amorphous regions exhibit weaker internal bonding while the crystalline regions exhibit strong internal bonding.

Recently, extraction of microcrystalline cellulose (MCC) from natural fiber resources such as EFB has gain major interest due to its potential to be an effective reinforcement in polymeric composites materials. Microcrystalline cellulose (MCC) is a fine, white, odorless, crystalline powder, and a biodegradable material used especially in food, cosmetic and medical industries as a water-retainer, a suspension stabilizer, a flow characteristics controller in the systems used for final products, and as a reinforcing agent for final products such as medical tablets. MCC is typically characterized by a high degree of crystallinity, although there are variations between grades; values typically range from 55 to 80% as determined by X-ray diffraction (XRD) [12].

Different approaches have been applied to the preparation of MCC. All of them lead to different types of micromaterial, depending on the cellulose origin, its treatment condition, and the disintegration process. These factors will give differ in crystallinity, moisture content, surface area, porous structure, particle size and molecular weight [7]. Several processes have been used to extract microfibers from cellulosic materials. These methods include treatments, such as chemical hydrolysis, pulping beating [2], high pressure homogenizing [4] and cryocrushing [1]. Among all of these, acid hydrolysis methods are widely used in the production of MCC as well as in the industrial scale. However, the use of acid has a number of important drawbacks, such as potential degradation of the cellulose, corrosivity, and environmental incompatibility. Considering all the above issues, this research study focused on using a simple, low cost and environment-friendly method in order to extract the MCC.

Recently, the ultrasonic technique has been used to isolate cellulose microfibers. Ultrasonication is the application of sound energy to physical and chemical systems. The chemical effects of ultrasonication are derived primarily from hot spots the form during acoustic cavitation, which is, the formation, growth and collapse of bubbles in a liquid [9]. The effect of ultrasonication in degrading polysaccharide linkages has been well described by [10], [14] investigated the preparation of individual cellulose nanofibers from wood using high-intensity ultrasonication combined with chemical pretreatments. Reference [11] used high intensity

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ultrasonication in a batch process to isolate fibrils from several cellulose sources. Using this process a mixture of microscale and nanoscale fibrils was obtained. The results show that small fibrils with diameters ranging from about 30 nm to several micrometers were peeled from the fibers. Some fibrils were isolated from the fibers, but some were still on the fiber surface. Therefore, in this study, the assistance from alkali treatment will be more successful in the production of MCC. In this approach, this treatment will not only help in extracting the MCC, but, it also can increase the interactions between fiber and polymer as well as increases the number of reactive hydroxyl groups on the fiber surface available for chemical bonding especially in future potential applications such as composites production.

II. Materials And Methods

A. Materials

Fibrous strands of oil palm empty fruit bunch (EFB) fibers were supplied by Malaysian Palm Oil Board (MPOB), Bangi Malaysia. The important chemicals used for extracting MCC in this work were acetic acid, sodium chlorite and sodium hydroxide, purchased from Sigma-Aldrich (Ohio, USA). Commercially available MCC, with a size of ~50 μm, was used as reference which was denoted as C-MCC.

B. Methods

1. Preparation of EFB Pulp

Oil palm empty fruit bunch (EFB) fiber was ground by a grinder and then sieved to reduce the size (measuring less than 400 μm in diameter). This dried ground EFB fiber was then, kept in a desiccator at 50% relative humidity until use.

2. Pretreatment Procedures

About 4.0 g of the ground EFB fiber strands (measuring less than 400 μm) were mixed in hot distilled water and treated at 70ºC for 4 hr. A calculated amount of sodium chlorite and acetic acid were added into the mixture in order to separate lignin from fiber. The fibers then were washed many times with distilled water until the yellow color and the odor were removed. 2.0 g of the holocellulose produced were treated with 17.5% NaOH at 20ºC for about 2 hr in order to separate the hemicellulose from the holocellulose, leaving the α-cellulose as well as to activate the OH groups of the cellulose. After that, the insoluble α-cellulose was filtered and washed with 8.3% NaOH. 10% acetic acid was poured and used to neutralize the excess NaOH present in the cellulose residue. Then, the cellulose obtained was dried in an oven at 105ºC overnight.

3. Preparation of MCC

The purified cellulose fibers were then subjected to ultrasonic treatments at resonance condition, using a Daihan Ultrasonic bath. 1.0 g of the cellulose EFB fiber was mixed into 200 ml of 10% sodium hydroxide solution. This mixture was then treated by the ultrasonicator at 50ºC for 3 hr. After ultrasonication process, the suspension was then washed with distilled water and filtered to separate the MCC from it. The EFB fiber, holocellulose, α-cellulose and MCC were then analysed for their structural properties. Commercial MCC also was used as the standard.

4. Composition Analysis of Isolated Cellulose and Microcrystalline Cellulose

The chemical composition of the isolated fibers was determined by methods shown in the following sequence: holocellulose and α-cellulose (TAPPI T257 om-85), Klason lignin (TAPPI T222 om-88).

5. X-Ray Diffraction

X-ray diffraction (XRD) was carried out to study the crystallinity of the samples. The sample patterns of all the cellulosic and MCC samples were pressed to form pellets and recorded on X'Pert X-ray diffractometer (SIEMENs XRD D5000) using Ni-filtered Cu Kα radiation (30 kV and 30 mA). The diffraction intensities were measured between Bragg angles (2θ) of 5–69º. The crystallinity index (CrI) was calculated by Segal's formula [6] using intensity measurement at 22.5º and 18.5º (amorphous background) 2θ:

$$\mathrm{CrI} = (I_{002} - I_{am})/I_{002} \quad (1)$$

$$CrI\ (\%) = CrI\ 100 \quad (2)$$

where I_{002} denotes the maximum intensity of the 002 peak at about 2θ = 22.5º and I_{am} is the lowest intensity corresponding to 2θ value near 18.5º

III. Results And Discussion

A. Fiber Composition

From the analysis, it is observed that the cellulose, hemicellulose and lignin content in untreated EFB fiber were similar to that reported by [5] in which the cellulose, hemicellulose and lignin content were 51.22%28.24% and 15.19%, respectively. In actual fact, EFB fiber is governed by the lignocellulosic components, especially the lignin that gives strengths to the fibrils and the polysaccharides, especially the cellulose and hemicellulose. Thus, the most important features of an effective treatment strategy include breaking the lignocellulosic complex. In the early stage of pretreatment process, the ground EFB fiber was treated with acetic acid and sodium chlorite in delignification process in which this treatment involved the removal of lignin. Therefore, as we can see from Table I, the chemical composition of lignin for the treated EFB decreased. Further down, in the production of holocellulose into α-cellulose, a greater part of the lignin and hemicellulose were degraded and the values for cellulose content increased. This can be described as a disruption of the cell-wall matrix including the connection between carbohydrates and lignin, as well as depolymerizing and solubilizing the hemicelluloses leaving the α-cellulose content.

TABLE I
CELLULOSE, HEMICELLULOSE AND LIGNIN COMPOSITION OF TREATED AND UNTREATED EFB FIBRE

Pretreatment	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Untreated EFB fibre (Physical Treatment) - Ground EFB fiber (less than 425 µm)	51.22	28.24	15.19
Treated EFB fibre (Chemical Treatment) - Use acetic acid, sodium chlorite and sodium hydroxide	61.53	23.52	9.6

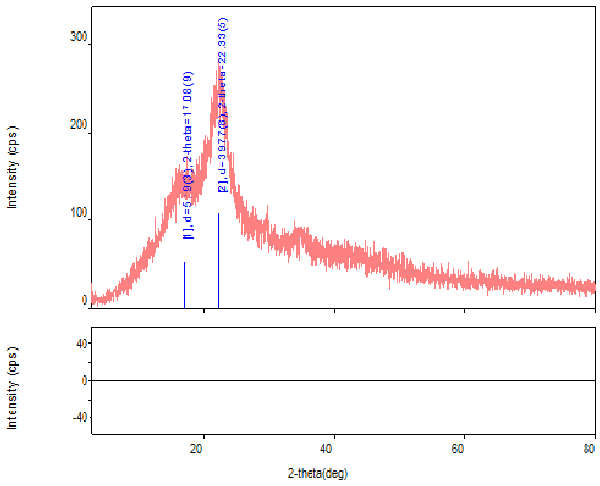

Fig. 1 X-Ray Diffractograms for EFB cellulose

B. X-Ray Diffractometry (XRD) Analysis

The crystallinity of each sample starting from raw material until the production of EFB-MCC is listed in Table II. The crystallinity values of EFB fiber, holocellulose, cellulose and EFB-MCC were 50%, 54%, 62% and 73% respectively, compared to the commercial MCC, which exhibited 79% of crystallinity. Throughout the conversion process, starting from EFB fibre into the production of cellulose, the crystallinity index is increasing due to removal of hemicellulose and lignin, which existed in amorphous regions leading to realignment of cellulose molecules. An increase in the crystallinity is also related to increases in the rigidity of the cellulose structure, which can lead to a higher tensile strength to fibers. This increase would be expected to increase in the mechanical properties for composites production. From Fig. 1, both crystalline and semi-crystalline regions can be observed in the diffractogram curves of EFB cellulose. The presence of a noticeable peak on the shoulder at the diffraction angles of 2θ ranging from 16º-24º suggests this kind of behavior because the small portion of cellulose II is still presence. In the production of MCC, ultrasonic process was carried out. During the cavitation of ultrasonic process, the potential energy of the expanded bubble is converted into the kinetic energy of a liquid jet that moves through the bubble's interior, penetrates the opposite bubble and hits the surface of the cellulose molecule. This continuous physical stresses cause the particle breakage and initiates the depolymerization of the cellulose polymers to shorter chained of MCC. With the assistance of alkali treatment, the yields of MCC production increases. The alkali treatment not only help in extracting the MCC, but, it also increases the interactions between fiber and polymer as well as increases the number of reactive hydroxyl groups on the fiber surface available for chemical bonding especially in future potential applications. The crystallinity of the MCC from EFB is slightly less crystalline in comparable with commercial MCC. This might be due to the fact that ultrasonic process is non-selective process in which it can remove both amorphous and crystalline cellulose. As the reaction time increase, the crystalline regions also might be degraded in a small portion.

TABLE II
CRYSTALLINITY OF EFB FIBRE, HOLOCELLULOSE, CELLULOSE, EFB-MCC AND COMMERCIAL MCC

Sample	Crystallinity (%)
EFB Fibre	50
Hollocellulose	54
Cellulose	62
MCC from EFB	73
Commercial MCC (C-MCC)	79

IV. CONCLUSIONS

The research findings show that the production of MCC from EFB fibre via simultaneous ultrasonic and alkali method is adequate for obtaining samples with high yields and crystallinity. The results from XRD analysis confirmed the crystallinity of MCC obtained was comparable with the MCC produced using other method. It also was slightly less crystalline than the commercial MCC although the method of production involved only used ultrasonic assisted with alkali condition.

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