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CONVERSION OF LIGNOCELLULOSE FROM OIL PALM BIOMASS INTO WATER-SOLUBLE CELLULOSE ETHER

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ABSTRACT

Cellulose, in combination with lignin and hemicellulose, is found in all plant materials. It is also the most abundant form of plant biomass. In the oil palm industry, empty fruit bunches (EFB), which are generated in large amounts at the palm oil mill, is made up of approximately 37% α-cellulose (on a dry weight basis). The use of this oil palm by-product may be expanded by the chemical modification of the cellulose into products of high value, such as cellulose ether. This study attempted to synthesise water-soluble cellulose ether, particularly sodium carboxymethylcellulose (NaCMC), from the EFB fibre. The properties of EFB-based NaCMC including the degree of substitution (DS), and viscosity were studied. In addition, the α-cellulose and NaCMC were analysed for their structural properties by Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffractometry. The properties of EFB-based NaCMC in comparison to the United States Pharmacopeia (USP) grade NaCMC (from Sigma-Aldrich) were discussed. EFB-based NaCMC exhibited viscosity of about 400 cps (2% at 25°C) while USP grade NaCMC exhibited viscosity of 500 cps (2% at 25°C), i.e. *slightly higher than EFB-based NaCMC. The infrared spectrum of α-cellulose from EFB was identical to that of commercial cellulose (from Sigma-Aldrich) with the presence of C-O-C, C-C, O-H and C-H bands. The typical absorption bands observed between 1300 cm^{-1} and 1580 cm^{-1} on the infrared spectra for both the EFB-based NaCMC and USP grade NaCMC indicated the presence of the COO group. As for the X-ray diffractogram, the profiles of both the EFB-based NaCMC and USP grade NaCMC were identical, even though the EFB-based NaCMC was less amorphous in structure compared with that the USP grade NaCMC. The results suggest chemical disruption of the cellulose crystallinity by breaking hydrogen bonds in cellulose and opening the structure to accessibility by other chemicals. These findings on NaCMC from an underutilised by-product of the palm oil industry could contribute towards the development of an oil palm-based specialty chemicals industry.*

Keywords: empty fruit bunches, cellulose, cellulose ether, sodium carboxymethylcellulose, Fourier transformed infrared spectroscopy (FTIR).

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INTRODUCTION

Oil palm empty fruit bunches (EFB) are readily available and are a renewable organic material generated at palm oil mills during the processing of fresh fruit bunches (FFB) in the production of palm oil. EFB are also a valuable biomass resource which can readily be converted to energy. Extraction of products or precursors that can lead to products of higher value from EFB is a strategy for increasing revenue.

There are many attempts to diversify the use of lignocellulose derived from oil palm biomass (Rosnah *et al.,* 2009). Biomass feedstock from the oil palm plantation and the palm oil mill has long

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been identified as a sustainable source of renewable energy, particularly in palm oil-producing countries. Besides that, other higher value products like composite for automotive parts, oil palm plywood, medium density fibreboard, fine chemicals, bio-fertiliser, pulp and paper are also produced. Studies have shown that oil palm fibre comprise important constituents such as lignin (21.2%), α-cellulose (41%), holocellulose (65.5%), ash (3.5%) and alcohol benzene extractives (4.1%) (Astimar, 2007). Cellulose is a high value compound used for industrial purposes. It is the major constituent of paper, and it also acts as a starting material for the production of regenerated fibres such as rayon and other cellulose derivatives, especially esters and ethers. Amongst the ether groups, the most important material is carboxymethylcellulose (CMC), generally prepared by adding chloroacetic acid to sodium cellulose.

In general, the primary cell wall of plants contains 10%-20% of cellulose while the secondary cell wall consists of up to 50% cellulose. These compositions, however, differ from one plant to another, and vary with age. Cellulose $(C_6H_{10}O_5)_n$ exists together with complex compounds like lignin and hemicelluloses, and is stabilised in the presence of hydrogen and ionic bondings (Allan, 1995). The characteristics of mechanical fibre and plant tissue are generally determined by the type and nature of these lignocellulosic components. In addition, they also rely on the chemical long-chain basic structure of the cellulose, which is based on the number of glucose units or cellobiose. One unit of cellobiose is made up of two glucose molecules (*D-glucopyranoside*), which combine together at position β (1→4). This combination will form a long-chain chemical branching unit and eventually determines the degree of polymerisation of the cellulose (Solomons and Fryhle, 1976).

CMC has been used in soap, detergent and body-care products, and also used as a stabiliser in the formulation of liquid nutritional products as an alternative to gellam gum and/or carragenan (Morris *et al*., 2000). CMC with degree of substitution (DS) in the range of 0.7 to 1.2 or higher is used as a thickener and flow improver for reactive printing (Kniewske *et al*., 1995). CMC with low DS of 0.05 to 1.0 is useful as a disintegrator in tablets due to its excellent binding force property (Traconis *et al*., 1997; Christoph and Roland, 1999).

The main constraint in producing value-added products from cellulose is the extraction and the purification of the cellulose itself. While the removal of lignin can be done using delignification oxidising chemicals, the crystalline cellulose hinders the derivatisation process. An increase in the crystalline region increases the rigidity of the cellulose, and this phenomenon affects the accessibility of the cellulose molecules to chemical reaction (Tripp, 1971). Alkali metal hydroxides have been commonly used as swelling agents for cellulose before conversion to cellulose derivatives.

This article reports on the attempts to produce cellulose ether, namely sodium carboxymethylcellulose (NaCMC), from EFB fibre, and on the analysis of the properties of cellulose and NaCMC prepared from the fibre. The X-ray diffraction method, Fourier transformed infrared analysis and microscopic investigations were carried out in this study.

EXPERIMENTAL

Materials

EFB fibres were obtained from Szetech Engineering, Malaysia. NaCMC of United States Pharmacopeia (USP) grade and commercial cellulose were purchased from Sigma-Aldrich, Germany (type of pulp and technique of preparation were not described).

Preparation of holocellulose and cellulose. EFB fibre measuring 0.25 mm long were used as a source of cellulose. The dried fibre were first delignified according to ASTM, D 1104-56 to produce holocellulose. In this step, about 4.0 g of the fibre were mixed with distilled water and the sample was treated with 2.0 ml acetic acid (CheMAR) and 5.0 g of sodium chlorite (R&M, United Kingdom) at 70°C for 4 hr to degrade the lignin. The homogenate was filtered, and the residue, which was holocellulose (a combination of hemicellulose and cellulose), 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 (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 NaCMC.

Preparation of EFB-NaCMC. The chemical conversion of cellulose to NaCMC employed a technique known as the one-step process. Two stages of reactions, namely, alkalisation and alkylation, were carried out one after another. In the first stage, about 2.0 g of cellulose in isopropyl alcohol (Merck, Germany) was treated with 30% (w/v) of sodium hydroxide (NaOH) for one and a half hours to produce alkali cellulose. The second stage involved alkylation or the etherification reaction of the alkali cellulose with monochloroacetic acid (Merck, Germany) under a controlled temperature of 55ºC with stirring for 18 hr to yield NaCMC. The product was ground to powder. Both

EFB-cellulose and EFB-based NaCMC were then analysed for their structural properties, together with commercial cellulose and USP grade NaCMC from Sigma-Aldrich (viscosity of 400 to 800 cps at 2% solution/25°C) as reference materials.

Analyses

Lignin content of cellulose. The acid-insoluble lignin contents of EFB fibre and cellulose were determined according to ASTM, D1106-96. About 2.0 g of EFB-cellulose were mixed with 15 ml of cold 12% H_2SO_4 (72% v/v) and allowed to stand for 2 hr at a temperature of 20°C. The mixture was then diluted to a 3% concentration of H_2SO_4 (Merck, Germany), then boiled for 4 hr and filtered, and the residue was washed with hot water before drying at 105°C for 2 hr. The lignin content in the cellulose was then calculated.

Degree of substitution of NaCMC. The degree of substitution (DS) of NaCMC powder was analysed according to ASTM, D1439-97. In this analysis, about 0.7 g of EFB-based NaCMC was mixed with 95% (v/v) ethyl alcohol (Merk, Germany). Approximately 2.5 ml of HNO_3 were added into the mixture which was then boiled for 5 min. The supernatant liquid was decanted through a Whatman filter paper number 4, and the precipitate in the beaker was transferred through the filter with 95% (v/v) ethyl alcohol. It was then washed with hot 80% (v/v) ethyl alcohol before transfer into a glass dish. The dish was heated in a steam bath until all the alcohol was completely removed, and then dried in an oven at 105°C for 2 hr. About 0.5 g of the dried NaCMC was then mixed with 50 ml of distilled water and 12.5 ml of 0.3 N NaOH solution, and boiled for 30 min. The excess NaOH was titrated against 0.3 N HCl (Merck, Germany) to a phenolphthalein end point and DS was calculated.

Viscosity. EFB-NaCMC and USP NaCMC, sigma (DS 0.7) solution of 2% concentration were prepared from their powdered forms and viscosity was measured by using an Anton Paar DV-2P viscometer at a constant temperature of 25±0.5°C.

Fourier transformed infrared spectroscopy (FTIR). Infrared spectra of the samples were recorded using a Perkin Elmer - FTIR Spectrum One spectrometer, and transmission was measured in the range of 4000-650 cm^{-1}. The samples were analysed using attenuation reflectance at a scan speed of 0.20 cm s^{-1} and a resolution of 4.0 cm^{-1}.

Scanning electron microscopy (SEM). Microscopic investigations were conducted using a Hitachi S2700 scanning electron microscope (SEM).

X-ray diffractometry. Each dried sample was placed onto a 12-mm sample holder and analysed under powder X-ray diffraction (XRD). The 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 with a time constant of 0.1 s.

RESULTS AND DISCUSSION

Approximately 37% dry weight of α-cellulose was isolated from oil palm EFB fibre. Only a small percentage of residual lignin of about 1.2% in the cellulose was detected unlike in EFB fibre which was composed of a high lignin content of about 21%. Thus, the α-cellulose content was 98.8%. The results show that by using the chlorus acid method to delignify the fibre, a significant loss of lignin and a high α-cellulose content were achieved. The presence of an oxidising agent altered the lignin portion by substitution reactions as well as oxidative reactions, and eventually the lignin was removed in the process. As a comparison to other methods that attempt to delignify the fibre, a study to prepare high purity cellulose pulp from EFB fibre was reported by Tanaka *et al*. (2001) by processes including pre-hydrolysis and ozone bleaching, and it was shown that the α-cellulose content was 95.1%. The remaining 4.9% might have included impurities including lignin. Extraction of cellulose pulp and lignin from oil palm biomass by using a solvent and soda at high temperature was also reported by Astimar *et al*. (2002), who found that pulp yield and lignin content were 45% and 3.7%, respectively. The selection of the pulping method which can produce high purity chemical cellulose is important because this cellulose is used in chemical conversion into cellulose derivatives such as alkali cellulose and various cellulose ethers and esters.

The recovery of α-cellulose from holocellulose involved the use of a slightly strong sodium hydroxide solution as mentioned in the ASTM method. Holocellulose is defined as a water-insoluble carbohydrate fraction of plant materials which consists of hemicellulose and cellulose. Theoretically, based on alkaline solubility, as at 17.5% concentration of NaOH solution, hemicellulose, β-cellulose and γ-cellulose are fractions that remain soluble in an alkaline medium. The α-cellulose is insoluble in 17.5% NaOH and is thus captured in the process. Nevell *et al*. (1985) defined the cellulose pulp, also termed as α-cellulose, as the portion that is insoluble in 10% and 18% sodium hydroxide. Hemicellulose has to be removed as much as possible from the holocellulose to produce high purity cellulose pulps otherwise its presence would adversely affect the performance of end-use product processes.

Knowing that the cellulose in the EFB fibre has a highly ordered structure, its combined crystalline and amorphous properties make it inaccessible to most reagents, including the alkylating reagent to promote the chemical reaction. For this reason, the first stage of NaCMC production was carried out in the presence of NaOH to ensure the formation of an intermediate of cellulose known as alkali cellulose which allows accessibility to the reacting agent. At the alkalisation stage the crystalline lattice of cellulose is changed by disrupting the hydrogen-bonded crystalline region and hence promoting accessibility to the alkylating agent. The formation of Na^+ widens the smallest pores down to the space between the lattice planes of cellulose. When the highest swelling ability of cellulose is achieved (Fengel and Wegener, 1984), the cellulose will have undergone complete de-crystallisation. The formation of ONa-groups increases the reactivity of the cellulose which allows for the substitution of the carboxymethyl group from the alkylating reagent, producing NaCMC. A high concentration of NaOH is recommended to allow for a peeling effect on the cellulose (mercerisation), and to ensure that all of the cellulose molecules are converted to NaCMC. Almlof (2010) reported that using a low concentration of NaOH (9%) in the mercerisation stage could result in incomplete transformation of cellulose to alkali cellulose, and finally the CMC produced when dissolved in water resulted in very thick and semi-solid gum-like gels, due to the uneven distribution of substituting groups along the cellulose backbone. However, CMC mercerised with alkali concentrations at 18.25% and 27.5% showed a total transfer of the cellulose molecules to CMC of high DS.

Approximately 59% dry weight of NaCMC was produced from EFB fibre. The EFB-based NaCMC exhibited different physical and chemical properties in comparison with its feedstock. Cellulose is characterised by its insolubility in water whereas NaCMC is a water-soluble polymer. The study on viscosity showed that USP grade NaCMC (Sigma-Aldrich) was slightly more viscous (500 cps) than EFB-based NaCMC (400 cps) (2% at 25°C). Factors such as the degree of polymerisation, the type of starting pulp, the molecular weight of the NaCMC polymer and the technique for NaCMC preparation contribute to the higher viscosity of USP grade NaCMC as compared with EFB-based NaCMC.

The FTIR analysis showed the spectrum of the EFB-based cellulose to be identical to that of commercial cellulose (Sigma-Aldrich) (*Figure 1*). The characteristic broad band of the O-H bond (ν_{OH}) was found in the range of 3200-3400 cm^{-1}. This clearly indicates the presence of the -OH groups on the glucose units. The medium peak at 2893.66 cm^{-1} was due to C-H bonds (ν_{CH}), whilst the peak at 1023.1 cm^{-1} was assigned to the C-O-C (ν_{COC}) linkage of the anhydrous repeating units. The shoulder at 1157.90 cm^{-1} was due to C-C bonds, and an absorption band at 895.62 cm^{-1} indicated the β-glycosidic linkages.

The FTIR spectra of EFB-based NaCMC and the USP grade NaCMC exhibited a similar pattern as shown in *Figure 2*. For the infrared spectrum of EFB-based NaCMC, a very strong absorption band at 3572.1 cm^{-1} was assigned to the vibrations of the intra-molecular hydrogen bonds (ν_{OH}). The broad band at 3200-3400 cm^{-1} was also a further indication of a higher proportion of water linked to NaCMC. This implies that NaCMC is very

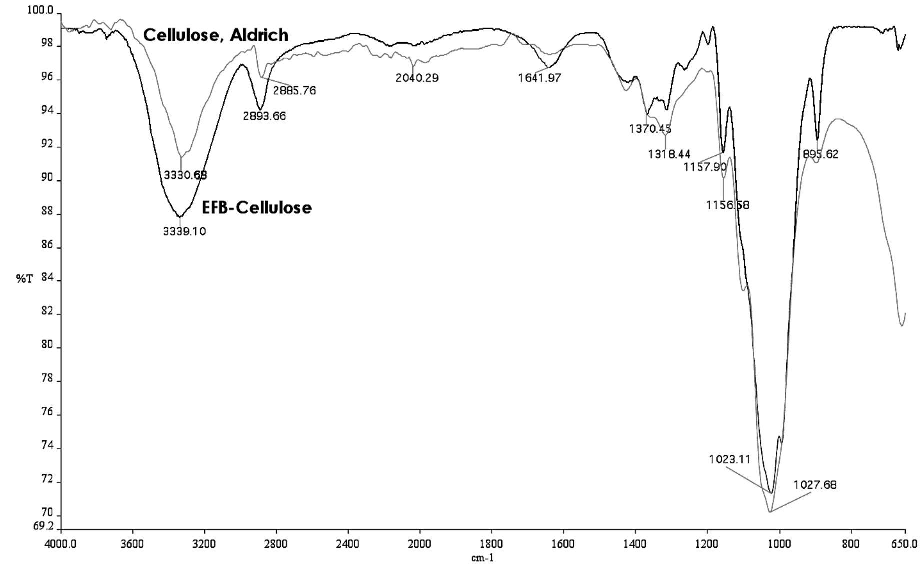


Figure 1. Fourier transformed infrared spectra of cellulose derived from empty fruit bunch (EFB) fibre and commercial cellulose (Sigma-Aldrich).

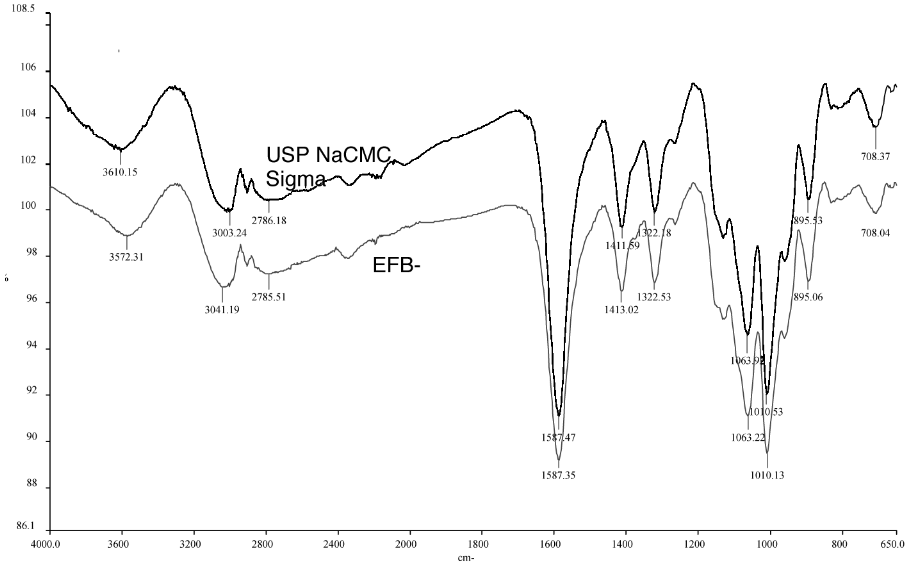


Figure 2. Fourier transformed infrared spectra of sodium carboxymethylcellulose (NaCMC) derived from empty fruit bunch (EFB) fibre and USP grade NaCMC (Sigma-Aldrich).

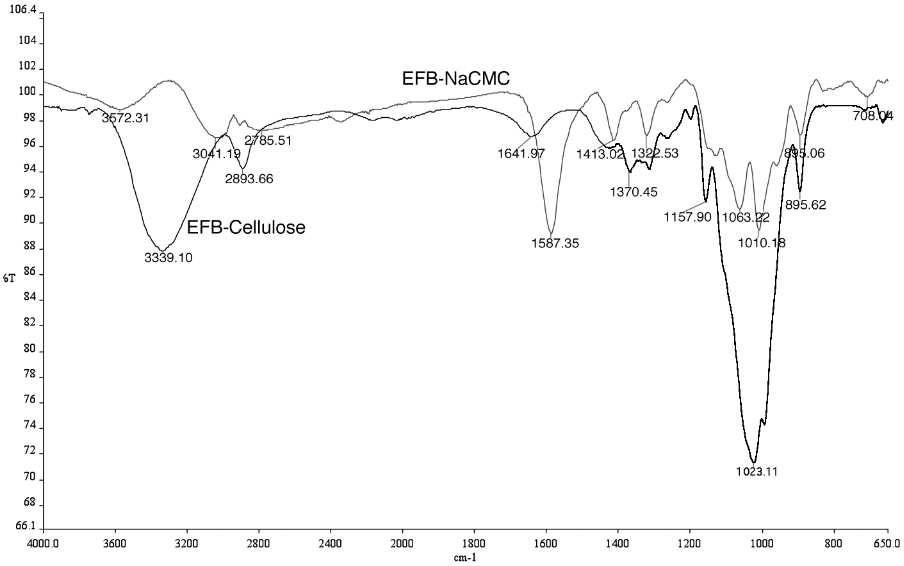


Figure 3. Fourier transformed infrared spectra of cellulose and sodium carboxymethylcellulose (NaCMC) derived from empty fruit bunch (EFB) fibre.

hygroscopic in nature. The shoulder at 3041.19 cm^{-1} was assigned to the stretching vibrations of the C-H bonds (ν_{CH}). Subsequently, the strong peak at 1587 cm^{-1} belonged to the stretching vibrations of C=O from Na carboxylate because C=O for carboxylic acid at the region of 1700-1650 cm^{-1} overlapped with the C=O ester. It also indicated the presence of alkyl ether. The strong peaks at 1413.02 cm^{-1} and 1322.5 cm^{-1} were assigned to the CH_2 group (δCH_2) and OH bending vibrations, respectively. One of the two strong peaks at 1063 cm^{-1} and 1010 cm^{-1} reflected bending vibrations of the ether glycosidic linkage ($\delta_{C\text{-}O\text{-}C}$).

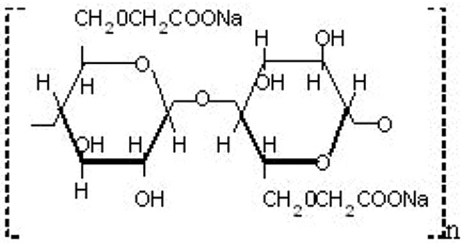
The comparison of the spectra of both the EFB-cellulose and EFB-based NaCMC (*Figure 3*) shows the likelihood that they exhibited significantly different features. The peak at 1587 cm^{-1} was indeed absent for EFB-cellulose due to the absence of carboxylic groups. On the other hand, weak peaks at 1413 and 1322 cm^{-1} were observed for EFB-cellulose; however, both became very intense in the EFB-based NaCMC infrared spectrum. These peaks might be taken as evidence for the involvement of the substitution reaction on the cellulose polymer. Equation (a) shows the formation of alkali cellulose, and Equation (b) shows the formation

$$(C_5H_7O_4.CH_2OH)_x + xNaOH \longrightarrow (C_5H_7O_4.CH_2ONa)_x + H_2O \qquad (a)$$

sodium cellulose

$$(C_5H_7O_4.CH_2ONa)_x + xClCH_2\ COOH \longrightarrow (C_5H_7O_4.CH_2O\ CH_2COONa)_x + xNaCl + H_2O \qquad (b)$$

sodium cellulose chloroacetic acid sodium carboxymethylcellulose



Source: Technical Insight Inc., (1980).

of ether links in which the hydroxyl of anhydrous glucose is replaced by the carboxymethyl group of monochloroacetic acid.

The scanning electron microscopic (SEM) analysis reveals more evidence of the morphological changes that occurred during chemical conversion from fibre to NaCMC. *Figure 4* shows that EFB fibre comprised a mixture of differently sized fibrils which were still intact. This structure was governed by the lignocellulosic compounds, especially lignin that gave strength to the fibrils and the polysaccharides, especially the cellulose and hemicellulose. On the other hand, holocellulose as observed in *Figure 5* showed the absence of a greater part of the smaller fibrils, which indicated the removal of lignin from the EFB fibre during the delignification process. Further treatment of holocellulose with NaOH activated the dissolution of hemicellulose (Huang and Chen, 1996), leaving only the cellulose with smooth uniformly sized fibrils as shown in *Figure 6*. The conversion of EFB-cellulose to EFB-based NaCMC resulted in an etherified product having a rough surface and with uniformly sized fibrils. This was due to the disruption of the crystalline features of cellulose during the chemical reaction to form NaCMC as shown in *Figure 7*.

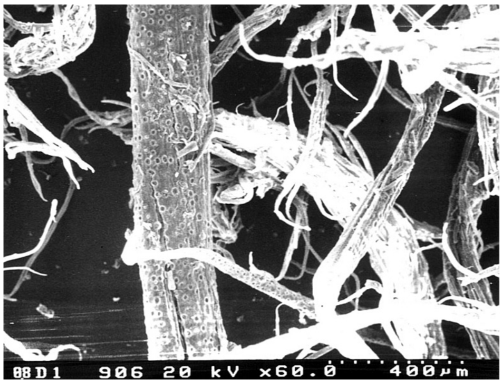


Figure 4. Scanning electron micrograph of oil palm empty fruit bunch fibre (60X).

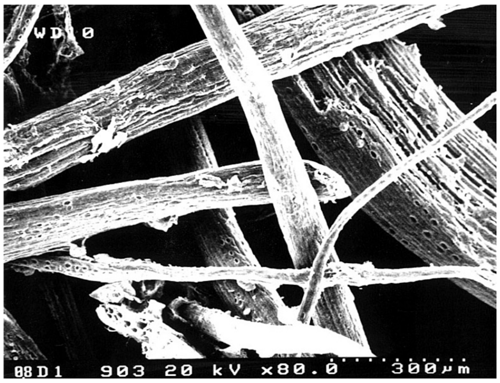


Figure 5. Scanning electron micrograph of holocellulose derived from oil empty fruit bunch fibre (80X).

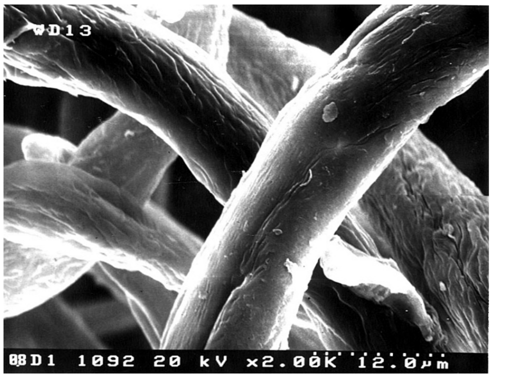


Figure 6. Scanning electron micrograph of cellulose derived from empty fruit bunch fibre (2000X).

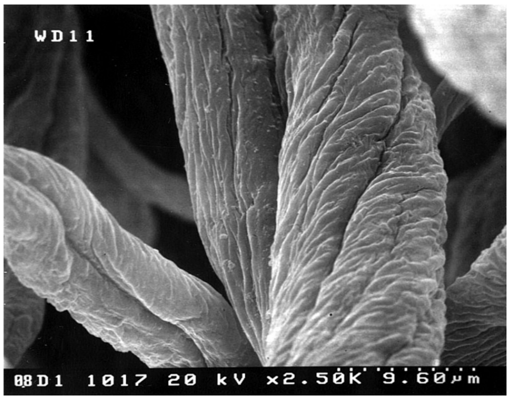


Figure 7. Scanning electron micrograph of sodium carboxymethylcellulose synthesised from cellulose of empty fruit bunch fibre (90X).

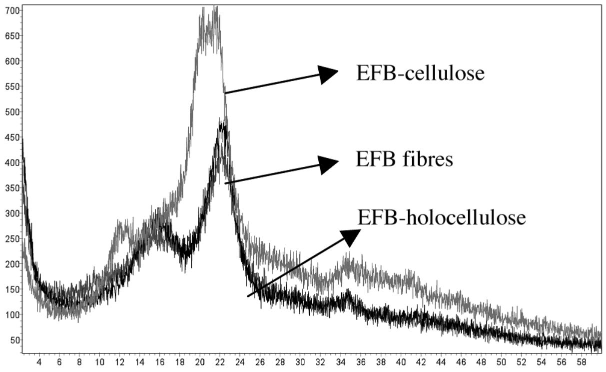


Figure 8. X-ray diffractograms of empty fruit bunch (EFB) fibre, holocellulose and cellulose.

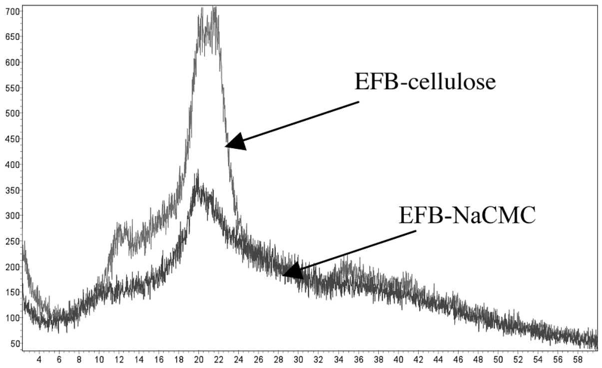


Figure 9. X-ray diffractograms of cellulose derived from oil palm empty fruit bunch (EFB) fibre and sodium carboxymethylcellulose (NaCMC) synthesised from empty fruit bunch fibre.

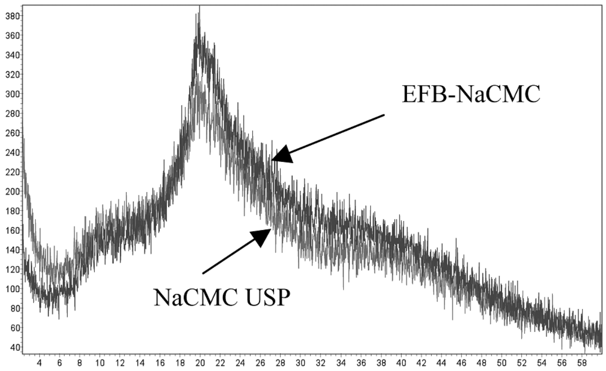


Figure 10. X-ray diffractograms of sodium carboxymethylcellulose (NaCMC) USP and sodium carboxymethylcellulose synthesised from empty fruit bunch (EFB) fibre.

The X-ray diffraction patterns for EFB fibre, EFB-holocellulose and EFB-cellulose are shown in *Figure 8*. The diffractogram profiles show the presence of both the crystalline fraction and the amorphous fraction in all the samples. The amorphous fraction produced a diffuse background, especially at a diffraction angle ranging from 14°-17° for EFB fibre and holocellulose, and from 11°-14° for EFB-cellulose. The linear peak position of cellulose was however higher in comparison with holocellulose and EFB fibre, indicating that the crystallinity of cellulose was much higher than that of holocellulose and EFB fibre. The crystalline fraction of cellulose was observed at a diffraction angle ranging from 19°-22°, whereas for EFB fibre and holocellulose, the crystalline fraction was shown at a diffraction angle ranging from 18°-24°. Quantitative measurements of the crystallite size at 22° for EFB fibre, holocellulose and α-cellulose showed that α-cellulose exhibited the largest crystallite size of 3166 nm (Lorentz), followed by holocellulose of 1456 nm (Lorentz) and EFB fibre of 6.8 nm (Lorentz). The full width half-maximum (FWHM) readings at 22° were 2.0, 2.17 and 2.78 for cellulose, holocellulose and EFB fibre, respectively. According to Fengel and Wegener (1984) and Zickler *et al.* (2007), hemicellulose and lignin are both amorphous substances, whereas cellulose has crystalline and amorphous regions. Hence, the removal of lignin and other amorphous aromatic compounds including hemicellulose from the EFB fibre and holocellulose by chemicals (Gumuskaya and Usta, 2002) contributed to the crystal behavior of cellulose.

Figure 9 shows the X-ray diffraction patterns of EFB-based NaCMC and EFB-cellulose. The crystalline structure of EFB-cellulose is associated with the inter-molecular and intra-molecular hydrogen bonds. EFB-based NaCMC having DS of 0.7 showed peak broadening with diffuse background and lower intensity in comparison with the higher linear peak position for EFB-cellulose, indicating the amorphous structure of EFB-based NaCMC. It seems that the crystalline structure of cellulose derived from EFB had been reduced during the alkalisation process at the first step of NaCMC preparation, after which the carboxymethylation process was completed. Alkalisation of cellulose changed the crystalline lattice of cellulose by disrupting the hydrogen-bonded crystalline region, thus facilitating the substitution of the carboxymethyl group into the cellulose polymers.

Figure 10 shows the X-ray diffraction patterns of EFB-based NaCMC and USP grade NaCMC (Sigma-Aldrich). The USP grade NaCMC also showed peak broadening but at a slightly lower intensity than EFB-based NaCMC which is an indication that the NaCMC USP standard was more amorphous than the NaCMC derived from EFB fibre. The FWHM readings at 22° for EFB-based NaCMC and USP grade NaCMC were 6.8 and 7.5, respectively. Factors such as DS, purity, degree of polymerisation and method of NaCMC preparation contribute to this behaviour. According to Gelman and Hawkins (1987), the type of starting pulp and the molecular weight of the pulp, as well as the ratio of various reactants applied in the process (Aurel and McArthur, 1970; Schoggen, 1972), influence DS of NaCMC, and subsequently its crystalline behaviour in comparison with USP grade NaCMC.

CONCLUSION

Water-soluble NaCMC with DS of 0.7 was successfully synthesised from EFB fibre. As anticipated, the results from X-ray diffraction, SEM and FTIR analyses show that EFB-based NaCMC had different morphological and chemical properties from those of cellulose, holocellulose and EFB fibre. The chemical reactions throughout the whole processes of transforming the EFB fibre to NaCMC that caused changes in the chemistry and morphology of the fibre were observed and discussed**.** The NaCMC produced proved to be amorphous in structure and dissolved easily in water.

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