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Synthesis and Characterization of Carboxymethyl Cellulose from Cellulose of Empty Fruit Bunches (EFB)

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ABSTRACT

Empty fruit bunches (EFB), a substantial agricultural waste, offer great potential for value. This study aimed to use cellulose of EFB as a source of carboxymethyl cellulose (CMC) is considerable because cellulose-based waste is categorized as the most abundant waste in nature and is easy to obtain. Cellulose was then converted to the CMC process in several steps, including cellulose alkalization, and carboxymethylation. The resulting CMC was characterized to determine its degree of substitution, viscosity, and other physicochemical properties. Characterization with Fourier Transform Infrared Spectroscopy (FTIR) verified the effect of NaOH concentration on this property. The highest degree of substitution (DS=1.34) was observed in 50 % NaOH of carboxymethylation. Cellulose can be correctly extracted from EFB and converted to CMC. Based on the cellulose of the EFB characteristic, the proper amount of NaOH was found to get a high DS. CMC has considerable features for application on biodegradable polymer materials.

Keyword: cellulose, carboxymethyl, empty fruit bunches, degree of substitution.

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INTRODUCTION

Plant waste is a significant global problem. Despite its abundance abundant and renewable, many of it is underutilized (Paranjape & Sadgir, 2023). Converting plant waste into valuable products can help reduce environmental problems (Vorobyova et al, 2019). Plant waste mainly consists of carbohydrate polymers, which can be modified to produce various products such as starch, cellulose, bagasse fiber and cotton fiber (Galiwango et al, 2019). Empty fruit bunches (EFB) are agricultural waste produced in large quantities by the palm oil industry(Permana et al, 2024). Managing this waste is often a challenge because it can pollute the environment if not managed properly (Windiastuti et al, 2022). On the other hand, demand for biopolymer-based products is increasing along with awareness of the importance of developing environmentally friendly and sustainable products.

EFB contains cellulose, hemicellulose, lignin and other components (Ngadi & Lani, 2014). Cellulose as the main source for producing carboxymethyl cellulose

(CMC) has a high molecular weight and a linear homopolymer of repeating β-D-glucopyranosyl units (Palamae et al, 2017). Large numbers of hydrogen bonds together hold crystalline regions (Ng & Amelia, 2021). Cellulose can be applied in various forms, namely derivative forms such as carboxymethyl cellulose and methylcellulose (Ching & Ng, 2014).

The cellulose from EFB has great potential to be converted into value-added products, such as CMC. CMC is a cellulose derivative that has a carboxymethyl group (-CH_2COONa) attached to its main chain (Kukrety et al, 2018; Yeasmin & Mondal, 2015). On the other hand, CMC was synthesized by treating alkali cellulose with monochloroacetic acid or its sodium salt in an aqueous NaOH solution containing an excess of organic solvent (Huang et al., 2017). Molecular weight and degree of substitution (DS) are important usability parameters of CMC(Candido & Gonçalves, 2016). The hydroxyl groups in cellulose were substituted with carboxymethyl groups primarily at the C-2, C-6, and C-3 positions (Haleem et al, 2014). Its hydrophilic properties, gel-forming ability, and adjustable viscosity make CMC versatile. CMC is widely applied in various industries such as food, pharmaceuticals, textiles, oil drilling and paper (Yeasmin & Mondal, 2015).

Therefore, the purpose of this study was to produce CMC from the cellulose of EFB and an attempt to increase the Ds of CMC produced. Synthesis of CMC from the cellulose of EFB and study the effect of NaOH concentration on the characteristics of CMC synthesized from cellulose of EFB.

METHODS

Equipment and Materials

The cellulose of EFB from PT. Damai Sejahtera Kolaka was produced by Pemana et al (Permana et al., 2024). Methanol and ethanol were provided from the local market. Sodium mono chloroacetate, Isopropanol, and Sodium chlorite were purchased from Sigma-Aldrich, USA. Natrium hydroxide, glacial acetic acid, and potassium hydroxide were prepared from Merck Chemical Co, Germany. Cellulose and CMC materials were characterized using X-ray Diffraction (XRD, XPert MPD), Fourier Transform Independent Spectrophotometer (FTIR, 8400S Shimadzu). The DS of CMC was determined by using the acid-wash method**.** A Rapid Visco Analyzer (Model: RVA-4, Germany) was used to measure the viscosity of CMC

Synthesis of CMC

The process for preparing CMC from cellulose was taken by Asl et al (Asl et al, 2017). 9 grams of Cellulose powder from EFB, 30 ml of NaOH concentration (20, 30, 40, 50, and 60 % w/v), and 270 ml of solvent isopropanol, due to its good ability in cellulose etherification based on Pushpamalar et al (Pushpamalar, 2006). At room temperature, the sample was continually swirled for an additional 30 minutes. 10.8 grams of solid sodium monochloroacetic acid were added to the mixture, and it was stirred for 90 minutes before being covered with aluminum foil and baked for 180 minutes at 55 °C. The material was then submerged for one night in 100 mL of methanol (70%). The sample was filtered and neutralized with 90% acetic acid the following day, bringing the pH down to a neutral level. The finished product underwent three ethanol washes, first in 300 mL of ethanol (70%) for 5 minutes, and then in 100 mL of 100% ethanol. Once a consistent weight was achieved, the generated CMC was dried in an oven at 55 °C.

Determination of DS

The method of measurement described in the literature was used to calculate the DS of the prepared CMC by Sophonputtanaphoca et al

(Sophonputtanaphoca et al, 2019). 250 mL of 95% ethanol was used to dissolve about 1 gram of CMC. 5 mL of 2 M nitric acid was then added. After 10 minutes of stirring and boiling the solution, the sample was five times rinsed with anhydrous methanol and then 100 mL of 95 % ethanol at 60 °C. Following filtering, the sample was dried for 3 hours at 90 °C in an oven and then cooled to room temperature. After dissolving around 0.5 g of dry CMC in 100 mL of distilled water and stirring, the liquid was brought to a boil for 20 minutes with the addition of 25 mL of 0.3 M NaOH solution. PP indicator was added after adding the sample and titrating it with a 0.3 M HCl solution. The determination of the DS was conducted using Equations (2) and (3):

$$\%CM=\frac{[V_0-V_n]\times M\times 0.059\times 100}{m} \quad (1)$$

$$DS=\frac{162\%\times\%CM}{[5900-(58\times\%CM)]} \quad (2)$$

where:
DS = degree of substitution
% CM = carboxymethyl content
Vo = the volume of blank titration (mL)
Vn = volume of sample titration (mL)
M = molarity of HCl
M = mass of sample (gram)

Determination of Viscosity

The determinant of viscosity CMC was followed by Sophonputtanaphoca et al (Sophonputtanaphoca et al., 2019) 3 g of CMC were dissolved in 25 mL of water (4% w/v) and stirred for 10 minutes at 45 ^oC to generate the sample solution. Viscosity analysis was done in two stages. The speed was set for 10 seconds at 960 rpm in the first step. The temperature was varied to 20, 30, 40, 50, and 60 ^oC for five minutes in the second step. Intervals running at 160 rpm. Every measurement was done three times.

Characterization of FTIR and XRD

Pellets were made from cellulose of EFB and CMC samples (~2 mg) with KBr (~800 mg). Trans mission was measured at the wave number range of 4000-400 cm^{-1}. The sample of cellulose of EFB and CMC are characterized by X-ray diffractometer. XRD was run at 30 mA, 40 keV, and 1.54 A^o, Cu Ka wavelength. The scan rate used to record the spectra was 0.028 2θ/s.

RESULTS AND DISCUSSION

Determination of DS

The highest level of CMC was synthesized by the NaOH. Fig. 1 illustrates the impact of various NaOH concentrations on CMC production and the DS of CMC. The DS of CMC increased when NaOH concentration increased from 20 to 50%. Nevertheless, at 60 % NaOH concentration, the DS dropped. The carboxymethylation process as reported by Pushpamalar et al (Pushpamalar et al., 2006). can explain this phenomenon. Simultaneously, the two competing reactions took place. The first process involved the hydroxyl reaction of cellulose with sodium monochloroacetate (NaMCA) and isopropyl alcohol (IPA) to produce CMC. CMC was in the range of 0.5–2.9 after cellulose was alkalized and following that carboxymethylation was carried out using NaMCA (Rani st al, 2014). CMC is swellable but insoluble when the DS is less than range, the DS increases the hydroaffinity of the CMC, making it fully soluble (Adinugraha et al, 2005). The characteristics of CMC as a polymer host are affected by the DS determination The best DS of CMC from this work was 1.34 and synthesized using 50% NaOH concentration. Comparing the DS value acquired in this work to commercial CMCs on the market, which range from 0.7 to 1.2 (Rani et al., 2014), the DS value obtained in this work is higher. Meanwhile, the synthetic polymers used in

commercially accessible CMC are unfavorable to long-term environmental sustainability. The use of synthetic polymers may be decreased by using CMC made from EFB.

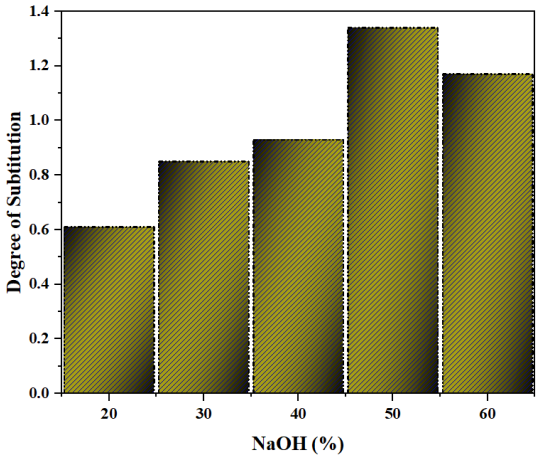

Figure 1. Effect of various NaOH concentrations in the alkalization reaction on DS of CMC synthesized from cellulose of EFB

Determination of Viscosity

It is well known that the concentrations of sodium monochloroacetate (NaMCA), NaOH, and CMC all have an impact on the viscosity of CMC. According to Adinugraha et al., the DS of CMC increased as the concentration of NaMCA increased. When the NaOH concentration increased over 20%, the DS of CMC increased and leveled off (with 3-5 g NaMCA) (Adinugraha et al., 2005). Nevertheless, in our investigation, the viscosity of CMC increased as NaOH concentration increased (Figure. 3) due to additional carboxymethyl groups replacing the hydroxyl groups in cellulose polymers and acting as hydrophilic groups. Thus, the ability of CMC to immobilize water in a system was enhanced by an increase in its DS. The aggregation of CMC most likely caused the viscosity of CMC to increase, despite the DS slightly decreasing at 60% NaOH. More research should be performed to investigate this behavior.

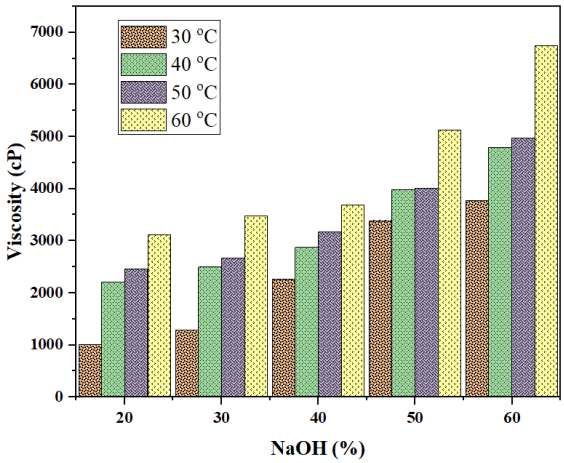

Figure 2. Effect of various NaOH concentrations on the viscosity of CMC synthesized from EFB at different temperatures

Furthermore, the impact of temperature on CMC viscosity was investigated as well. As the temperature increased, CMC viscosity dropped. Increasing the temperature of a CMC solution has a double impact of decreasing cohesive forces and increasing molecular exchange. Shear stress tends to increase with the latter impact whereas it usually decreases with the former(Haleem et al., 2014; Rahman et al., 2021; Yeasmin & Mondal, 2015). As a result, liquids exhibit a decrease in viscosity as temperature increases.

FTIR Characterization

Figure 3 shows the infrared spectroscopy spectra of cellulose from EFB and CMC that were produced at a 50% NaOH concentration. The data is not shown since the CMC results at different NaOH concentrations were comparable to those at 50% NaOH. Spectra of cellulose (Figure 3) and spectra of CMC (Figure 3) spectra provided similar functional groups, including ether (-O-), hydrocarbon (CH_2), carbonyl (C=O), and hydroxyl (-OH) groups. O-H stretching is the result of the broad band at 3200–3600 cm^{-1}(Gómez et al, 2017). (-O-) stretching and (-CH_2) scissoring are the causes of the bands at 1450 and 1000–1200 cm^{-1}, respectively (Heinze & Pfeiffer, 1999; Rani et al., 2014). The C-H stretching vibration is the result of

the band at 3000 cm^{-1}. The band at 1625 cm^{-1} is the result of stretching of C=O. When compared to the spectra of cellulose (Figure 3), the carbonyl group (C=O), methyl group ($-CH_2$), and ether group (-O-) in the spectra of the CMC sample (Figure 3) significantly increased, but the hydroxyl group (-OH) band dropped (Adinugraha et al., 2005; Candido & Gonçalves, 2016; Sophonputtanaphoca et al., 2019). This outcome showed that the cellulose molecules undertook carboxymethylation. Previous reports have reported similar observations.

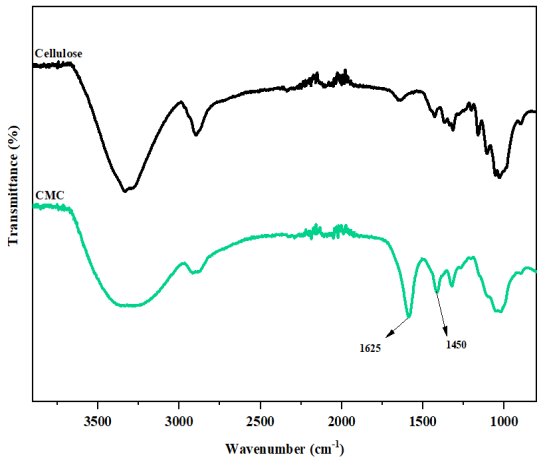

Figure 3. FTIR spectra of cellulose and CMC

XRD Characterization

As seen in Figure 4, the cellulose and CMC X-ray diffraction patterns are similar. The crystallographic planes (-110), (110), (200), and (400) correspond to the overlapping signals at 2θ = 14.39 (-110), 16.48 (110), 22.59 (200), and 34.57 (400), which form the peaks and planes of cellulose (Kedang et al, 2023). The diffraction pattern shown in Figure 4 has similarities to the cellulose field characteristic signal, and it exhibits good agreement with the standard spectrum (JCPDS No. 50-2241) (Gómez et al., 2017). Meantime, the amorphous phase is shown by the CMC diffraction peak at 2θ = 19.88. On the other hand, the CMC diffraction peaks widened and weakened, suggesting either an amorphous dominant phase or a reduction in crystallinity. It is a byproduct of the material's decreased crystallinity during the CMC production process. Typically, the CMC polymer utilized in this investigation is an amorphous substance (Kedang et al., 2023).

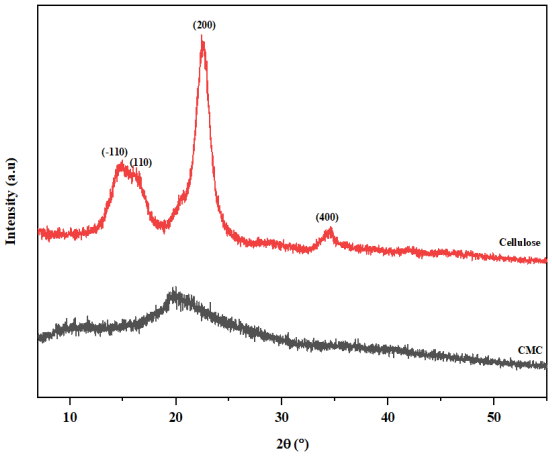

Figure 4. XRD Diffactogram of Cellulose and CMC

CONLUSIONS

The results of this research showed that EFB could be effectively utilized as a raw material in a variety of NaOH concentrations to produce carboxymethyl cellulose. This demonstrates that the primary parameter that correlates with the CMC characteristics is the NaOH content. When CMC synthesis was carried out, the DS of CMC increased as NaOH concentration rose (20–50%) and decreased at 60% NaOH concentration. CMC was used polymer material, the results shown here may be helpful. Knowing how to modify cellulose, like varying the NaOH concentrations discussed in this article, can help you think of new and possibly advantageous applications for CMC made from empty fruit bunches.

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