FACILE SYNTHESIS OF CARBOXYMETHYL CELLULOSE (CMC) FROM AGRICULTURAL RESIDUES

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Cellulose derivative products, such as carboxymethyl cellulose (CMC), which are used in the food, cosmetics, and pharmaceutical industries, but still rely on cotton-derived cellulose, can be made from oil palm fruit empty bunches (OPEFB) and rice straw. This study examined how sodium monochloroacetic acid (NaMCA) concentration (3, 6, and 9 g) affected the simple synthesis and characteristics of CMC from OPEFB and rice straw cellulose. OPEFB-derived CMC produced with NaMCA (9 g) had the lowest of brightness, while rice straw CMC was brighter. NaMCA modifications altered the onset temperature (T_{onset}), but not maximum degradation temperature (T_{max}), according to thermal analysis. The onset temperatures of OPEFB and rice straw CMC were 40–62 °C and 67–183 °C, respectively. Commercial CMC has an onset temperature of about 27 °C. The EDX analysis showed that rice straw CMC had a higher degree of substitution (DS) of 0.34–1.37 than OPEFB CMC, which had 0.30-0.70. Oil palm empty fruit bunch (OPEFB) cellulose and rice straw cellulose offer a viable carboxymethyl cellulose (CMC) alternative. This process turns agricultural waste into valuable products and enables for their usage in numerous applications.

Keywords: cellulose, etherification, rice straw, oil palm, agricultural waste

INTRODUCTION

The ever-increasing pace of industrialization and rapid growth of the human population have led to the modernization and expansion of various sectors, which has resulted in a significant increase in the needs and demands of individuals. This, in turn, has given rise to a substantial amount of waste being generated by human activities, particularly in the food industry, thereby leading to the accumulation of agro-industrial waste. This phenomenon is particularly noticeable in the palm oil processing industry, where palm oil production generates a considerable amount of residues. Oil palm empty fruit bunches (OPEFB) are lignocellulosic solid wastes generated by the palm oil processing industry, accounting for approximately 23% of processed fresh fruit bunches per ton.[1] According to

data from the Indonesian Oil Palm Statistics, the total production of crude palm oil (CPO) in Indonesia amounted to 45.1 million tons in 2021.[2] CPO production begins with the processing of fresh fruit bunches of oil palm, which results in the production of 230 kg of OPEFB for 1 ton of fresh fruit bunches.[3] Rice straw is another common agro-industrial waste – a residual product of rice production – approximately 1.35 tons of rice straw being produced per ton of harvested rice.[4] Notably, Indonesia's total rice production is estimated to be around 54.75 million tons of dry-milled grain, corresponding to approximately 73.9 million tons of rice straw. The vast abundance of agro-industrial residues, such as OPEFB and rice straw, has given rise to significant environmental concerns. These

issues include fouling, pest attraction, greenhouse gas emissions, and soil acidification, all of which pose severe threats to both humans and the environment.[5] Moreover, the growing stringency of waste disposal laws has led to higher costs and increased energy requirements for traditional waste treatment methods, prompting a demand for alternative approaches.[6]

In recent years, the valorization of agro-industrial waste into value-added products has emerged as a waste management approach. OPEFB and rice straw contain significant amounts of cellulose, hemicelluloses and lignin. OPEFB is composed of 43-65% cellulose, 17-33% hemicelluloses, and 13-37% lignin,[7] whereas rice straw consists of 38.3% cellulose, 31.6% hemicelluloses, and 11.8% lignin.[8] Cellulose from agro-industrial waste biomass can be extracted and utilized for various applications in the fields of food, materials, and biomedicine. Cellulose, the most abundant natural polymer on earth, is a polysaccharide composed of $\beta(1\rightarrow4)$ linked D-glucose units arranged in a linear chain.[9] It plays a vital role as a structural component in the primary cell walls of green plants, algae, and oomycetes.[10] The hierarchical structure of cellulose allows it to exhibit flexibility, functionality, and exceptional specific strength.[11,12] Furthermore, cellulose is notable for its biodegradability, low density, and affordability.[13] However, cellulose is not soluble in water and, for this reason, cellulose derivatives have been developed and produced to expand the applicability of cellulose in many applications. Cellulose derivatives, such as cellulose acetate, cellulose butyrate, hydroxypropyl methylcellulose (HPMC), and carboxymethyl cellulose (CMC), can be synthesized by chemical processing. CMC is particularly important due to its advantageous properties and industrial importance.

Carboxymethyl cellulose (CMC) is a polyanionic cellulose ether derived from chemical modification of pristine cellulose.[14] Sodium carboxymethyl cellulose (Na-CMC) is a frequently used form of CMC. CMC is a substance that is both safe and biodegradable, making it suitable for consumption, without any adverse effects on the body. The information may be challenging to comprehend, but it does not present any potential health hazards. Microorganisms and enzymes are more effective at degrading CMC compared to natural cellulose, making it a more environmentally friendly option.[15–18] CMC finds application in diverse industries, such as the food, pharmaceutical, biomedical, and cosmetics industries. For instance, CMC plays a multifunctional role in the food industry, serving as a thickener, emulsifier, moisture retainer, stabilizer, preservative, and rheological agent.[19] In the pharmaceutical field, CMC is used as a viscosity enhancer in topical, oral, and parenteral drug formulations. Additionally, it functions as a binder and disintegrant in tablet formulations.[20] In the biomedical field, CMC and its composites are extensively used for tissue and bone engineering, wound dressing, 3D scaffolds, and other applications.[21]

CMC is primarily synthesized from cellulose obtained from cotton fibers.[22] However, cellulose from agro-industrial waste, such as OPEFB and rice straw, may offer a cost-effective alternative. In addition, the utilization of cellulose from such waste may reduce the environmental impact associated with agro-industrial waste. Previous studies have shown that CMC can be synthesized from various by-products and agro-industrial wastes, such as corn husk,[23] sagoo waste,[24] cacao pod husk,[25] sugarcane stalk,[26] waste paper,[27] corncobs,[28] corn stalks,[29] durian rind,[30] banana pseudo-stem,[31] OPEFB,[22] and residual mushrooms baglog.[32] Although the production of CMC from OPEFB and rice straw has already been reported, there is a need to investigate the technological processing of OPEFB and other agricultural residues to produce CMC. Additionally, it is important to analyze the characteristics of the CMC that is manufactured internally with the commercially available CMC. In practice, CMC synthesis involves the etherification of hydroxyl groups using sodium monochloroacetate (NaMCA) or monochloroacetic acid in the presence of an aqueous alkali to substitute the hydroxyl groups of cellulose at positions O-2, O-3, or O-6.[24,33] By optimizing the etherification step, CMC with desired properties can be produced. The synthesis of CMC from agricultural waste typically involves the use of a significant amount of methanol,[24] ultrasonicators, and relatively high concentrations of NaOH.[34] Additionally, steam explosion was used to extract cellulose;[35] microwave-assisted synthesis and refluxed with nitrogen purge were employed at a temperature of 50 °C for a duration of 3 hours.[36]

Thus, the objectives of this study were to modify the CMC processing protocol using cellulose extracted from OPEFB and rice straw by varying the NaMCA concentration, which is generally regarded as a simpler alternative to the previously mentioned methods, and to analyze the characteristics of the resulting CMCs.

EXPERIMENTAL

Materials

The materials employed in this research included OPEFB and rice straw. OPEFB were obtained from oil palm plantations in West Java, Indonesia. The rice straw residues were acquired from local farmers in the Serang region of Banten province, Indonesia. Both materials underwent a process of drying and cleaning to remove impurities, after which they were finely crushed using a blender. Once the material was dried and pulverized using a blender, it was placed in plastic containers along with silica gel for storage, and subsequently utilized in the following phase.

Chemical reagents, such as sodium hypochlorite (NaOCl), sodium hydroxide (NaOH) (Merck), glacial acetic acid (Merck), ethanol (Merck), and isopropanol (Merck) and sodium monochloroacetate (Merck), were used without further purification. As a comparison, commercial carboxymethyl cellulose from Shanghai Shenguang Edible Chemicals Ltd., China, was utilized. Commercial CMC had viscocity 4000 ±5000 mPa.s with purity > 99.5%, moisture content less than 8% and degree of substitution 0.85-0.95.

Methods

Isolation of cellulose from OPEFB and rice straw

The process of producing chemical pulp was done using the sulfate (Kraft) method. Initially, OPEFB and rice straw fibers were weighed to a total of 400 g oven-dry (OD) weight. Subsequently, a cooking solution consisting of NaOH (active alkali, 19%) and Na_2S (sulfidity, 30%) was added to maintain a cooking liquor-to-fiber ratio of 5:1. The prepared mixture was then introduced into a rotary digester, rotating within a heated environment at temperatures ranging from 160-170 °C for a duration of 3.5 h. This period encompassed a 2-h interval to reach the 160-170 °C temperature range, followed by an additional 1.5 h at this temperature. Following the 3.5-hour digestion cycle, the digester was cooled for 0.5-1 h in water and filtered using a Johnson screen. This cooked pulp was designated as non-bleached OPEFB pulp.

Chlorination was then conducted using 2 wt% of chlorine (Cl_2) for 60 min at room temperature, followed by extraction with 1.5 wt% sodium hydroxide (NaOH) for 90 min at 70 °C, and hypochlorination with 2 wt% NaOCl for 240 min at 40 °C. These sequential bleaching processes resulted in a bleached OPEFB and rice straw pulp. The final products of this process were white OPEFB pulp (P-OPEFB) and rice straw pulp (P-RS).

CMC synthesis from bleached OPEFB and rice straw pulp

The synthesis of CMC from OPEFB and rice straw pulp was based on the methodologies outlined by Yimlamai et al. (2021)[22] and Dimawarnita and Panji (2018).[32] CMC production involves two distinct stages: alkalization and carboxymethylation. During the alkalization process, cellulose derived from the OPEFB and rice straw pulp (5 g) was introduced, separately, into a glass beaker. Subsequently, a mixture of 80 mL of ethanol, 20 mL of isopropanol, and 20 mL of 10% (w/v) NaOH was slowly added. The resulting solution was allowed to stand for one hour at 25 °C with continuous stirring.

The carboxymethylation process was initiated by the introduction of 3, 6, and 9 g of sodium monochloroacetate (NaMCA) dissolved in 20 mL of ethanol. This mixture was then subjected to a 3-h reaction period at a temperature of 55 °C. Subsequently, the solution was cooled and neutralized by gradual addition of 4 mL of glacial acetic acid. After this step, filtration was performed, and the resulting material was washed with 50 mL of ethanol, which was repeated four times. The obtained slurry was subsequently dried at 60 °C for 24 h, followed by conditioning in a desiccator for one hour. Ultimately, this process leads to the production of dry CMC.

The purpose of this study has been to evaluate whether the addition of NaMCA affects the properties of the generated CMC, as the carboxymethylation process takes place with the addition of NaMCA. The CMC obtained by adding different amounts of NaMCA were categorized based on the raw materials utilized, specifically oil palm empty fruit bunches (OPEFB) and rice straw (RS). Consequently, the resulting samples were labelled OPEFB3, OPEFB6, OPEFB9, RS3, RS6, and RS9.

Analytical procedures

Color measurements

The analysis was performed using the Chroma meter CR-10 Plus manufactured by Konica Minolta INC, Japan (with D65 illuminant, 10° standard observer, silicon photocells detector, size (W x H x D) 66 x 158 x 85 mm, operation temperature 0 to 40°C, relative humidity 85% or less (at 35 °C) with no condensation). The chroma meter device was calibrated using white and black color calibration standards. After completing the calibration procedure, the device was made ready for the color analysis of the samples. The samples were crushed and placed in a sample holder, completely covering the lens of the chroma meter. The color analysis included the parameters L* (representing lightness/darkness), a* (representing redness/greenness), and b* (representing yellowness/blueness).[37] The whiteness index (WI) analysis was conducted based on the outcomes of the color parameter analysis, using the WI formula presented by Udoro et al.:[38]

$$WI = \sqrt{(100 - L^*)^2 + a^{*2} + b^{*2}}$$

(1)

Moisture content

The moisture content was determined using a Moisture Balance (AND MX-50), with a detection limit of 0.01% and a maximum capacity of 51 g. Moisture content analysis was carried out by placing 0.5-1 g of sample in the moisture balance chamber until the water

content results appear on the instrument screen. Measurements were carried out with 3 repetitions.

Fourier transform infrared (FTIR) analysis

The dry samples were compressed onto zinc selenium plates. The FTIR testing method utilized the reflection principle, eliminating the need for KBr plates. Functional group analysis was conducted on bleached pulp and CMC derived from OPEFB and rice straw. The analysis was performed using a Perkin-Elmer spectrometer, covering the wavenumber range of 400-4000 cm^{-1}. Functional groups were identified at the spectral peaks based on their transmittance.

Thermal properties analysis

The thermal properties of OPEFB-derived and RS-derived CMC, rice straw and OPEFB pulp, and commercial CMC for comparison were analyzed using a Simultaneous Thermal Analyzer (Netzsch STA 449F3) with nitrogen as the purge gas. Thermogravimetric analysis (TGA) was carried out in the temperature range of 30-550 °C, at a heating rate of 10 °C/min.

Microstructure observation with scanning electron microscopy (SEM) and EDX analysis

Microstructural profiling analysis was performed following the modified methodology described by Herawati *et al.*[39] The SEM JEOL instrument was used to analyze the CMC powder. The procedural steps included preparing the sample specimens through the application of a carbon tape coating. The coating process was performed using a quorum-type Q150R-ES sputter coater. Gold was used as the coating material, with a sputter current of 20 mA and sputtering time of 60 s. After coating and securing the samples on the specimen holders, they were placed on the SEM stage for analysis. Subsequently, the samples were placed into the SEM JEOL instrument for imaging. The images were obtained using a Secondary Electron (SE) detector with a working distance (WD) of 9 mm and an accelerating voltage (EHT) of 16.00 kV, set at 0 mm.

EDX analysis was conducted using Secondary Electron-EDAX Element EDS System (100x magnification) to ascertain the extent of sodium carboxymethyl cellulose substitution following the etherification process with sodium monochloroacetate (NaMCA). The determination of the degree of substitution is determined using the formula developed by a prior study conducted by Singh and Katri.[40] The formula is as follows:

$$\text{Degree of substitution } = \frac{162 \ x \ \% \ sodium}{2300-(80 \ x \ \% \ sodium)} \quad (2)$$

Viscosity

The viscosity was measured using the RheolabQC SN82939649 instrument at the Integrated Laboratory of Bioproducts (I-Lab), National Research and Innovation Agency (BRIN) located in Cibinong. Viscosity was evaluated using 50 mL of CMC solution for each treatment, with a concentration of 0.75% (w/v), employed in constant shear condition with shear rate 1/second (1/s) for 250 seconds.

RESULTS AND DISCUSSION
Color measurement of CMC from OPEFB and rice straw

The color of CMC serves as a valuable indicator of significant physical properties that require understanding. Cellulose is commonly recognized for its white color. Hence, it is crucial to have a clear understanding of the whiteness or brightness level of CMC. In addition, when CMC is utilized as a food additive, the color brightness can impact the overall color of the food.

Figure 1 depicts that CMC obtained from oil palm empty fruit bunches (OPEFB) and rice straw (RS) exhibits white color like cellulose.

Table 1 presents the color and whiteness of the pulp and CMC derived from OPEFB and rice straw, considering different treatments.

Table 1
Color parameters (L*, a*, b*) and whiteness index (WI) of commercial CMC and CMC derived from OPEFB and rice straw with various treatments

Sample	Color parameters			WI
	L*	a*	b*	
Commercial CMC	91.910^g	0.230^a	5.280^b	90.340^g
OPEFB3	80.800^{bc}	2.220^e	11.530^g	77.495^b
OPEFB6	81.345^{cd}	2.385^f	1.175^a	81.155^e
OPEFB9	72.235^a	2.785^g	11.770^h	69.715^a
RS3	81.630^d	1.715^c	10.100^e	75.140^c
RS6	83.080^e	1.725^c	9.855^d	80.340^d
RS9	86.750^f	1.030^b	7.765^c	84.605^f
P-OPEFB	80.980^{bc}	2.080^d	10.575^f	78.140^b
P-RS	80.180^b	2.145^{de}	10.655^f	77.395^b

Note: Numbers followed by different letters in the same column are significantly different with a 95% confidence interval
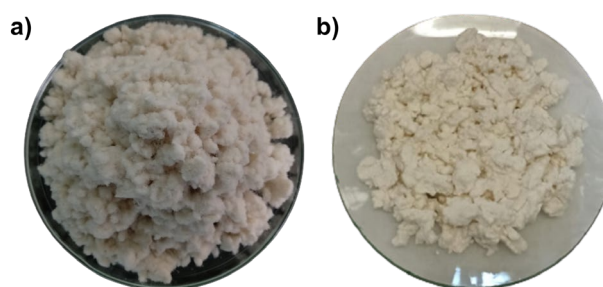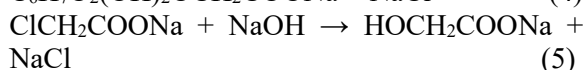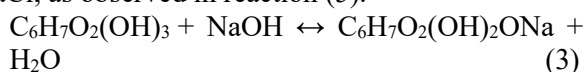
Figure 1: Appearance of CMC from a) OPEFB and b) rice straw

The color attributes are represented by indices L* (lightness), a* (redness/greenness), and b* (yellowness/blueness), whereas whiteness is measured by the whiteness index (WI). Bleached pulp from oil palm (P-OPEFB) and rice straw (P-RS) residues exhibited similar L* and WI values, resulting in a white final product. It can be observed that the pulping and bleaching processes efficiently eliminated the lignin and chromophores from the cellulose fiber bundle. Sample OPEFB9 demonstrated significantly lower WI and a darker, more yellowish color than OPEFB3 and OPEFB6. Compared to CMC-derived OPEFB, CMC derived from rice straw exhibited a brighter and whiter color. Specifically, RS9 displayed the higher brightness and WI values, surpassing RS3, RS6, and CMC-derived OPEFB. However, commercial CMC showed the highest brightness and WI values among all the samples. The lower values observed in CMC derived from OPEFB and rice straw can be attributed to the unintended formation of sodium glycolate and NaCl as a by-product during the carboxymethylation of cellulose.[41–43] As described by Konovalenko *et al*., the process of carboxymethylation of cellulose involves R-ONa, as seen in reaction (3).[44] When alkaline cellulose interacts with NaMCA or monochloroacetic acid, CMC is produced alongside NaCl and H_2O, as shown in reaction (4). During the carboxymethylation process, the primary reaction leads to the formation of CMC, NaCl, and H_2O. However, a secondary reaction also occurs, involving the hydrolysis of NaMCA, leading to the formation of sodium glycolate ($C_2H_3NaO_3$) and NaCl, as observed in reaction (5).

$$C_6H_7O_2(OH)_3 + NaOH \leftrightarrow C_6H_7O_2(OH)_2ONa + H_2O \quad (3)$$

$$C_6H_7O_2(OH)_2ONa + ClCH_2COONa \rightarrow C_6H_7O_2(OH)_2OCH_2COONa + NaCl \quad (4)$$

$$ClCH_2COONa + NaOH \rightarrow HOCH_2COONa + NaCl \quad (5)$$

Moisture content

The moisture contents of commercially available CMC and CMC derived from OPEFB and rice straw are shown in Table 2. In general, CMC derived from OPEFB had significantly higher moisture content, whereas CMC derived from rice straw had notably lower moisture content than the commercially available CMC. OPEFB3 and OPEFB6 did not comply with the moisture content regulations set by the FAO/WHO Expert Committee (2011) for CMC as a food additive, which states that the moisture content should not exceed 12%.[45] There are multiple ways in which water molecules can interact with cellulose fibers. Water molecules can form hydrogen bonds with the hydrophilic surfaces of cellulose fibers. Additionally, water may become trapped within the porous cell walls and the small pores formed by the network structure of cellulose fibers. Additionally, water molecules have the ability to hydrate swollen fiber cell walls. These walls are believed to consist of a combination of partially water-soluble polymer and insoluble polymer phase.[46] It is likely that the increased water content in the OPEFB3 and OPEFB6 samples (Table 2) is due to the greater amount of water bound to the cell walls. RS3 and RS6 exhibit a similar pattern, with a substantially higher moisture content compared to RS9. However, the water content in RS3 and RS6 is still significantly lower than that in OPEFB3 and OPEFB6.

Cellulose and CMC functional groups

The FTIR spectra of commercial CMC, OPEFB3, OPEFB6, and OPEFB9 and the maximum values of specific absorption bands are shown in Figure 2 and Table 3, respectively. The functional groups were consistently observed in CMC derived from OPEFB, exhibiting similar intensities and adjacent wavenumber values. The absorption bands observed at approximately 890

cm^{-1} and in the range of 3200-3500 cm^{-1} were found in all samples. These bands were associated with the presence of β-glycoside linkage and the stretching vibrations of the OH groups, respectively. The wavenumber peaks in the range of 2917-2920 cm^{-1} correspond to the CH stretching vibrations of the CH_2 and CH_3 groups. Three CMC samples prepared in this study showed the stretching vibrations of the C=O carboxyl group around 1590 cm^{-1} and the bonding of CH_2 at 1410 cm^{-1}, which provided evidence that the use of NaMCA in the etherification process resulted in the replacement of carboxyl groups with carboxymethyl ether groups, leading to the conversion of α-cellulose to CMC.[23,47] The absence of specific peaks in the C=O stretching of hemicelluloses (1730-1720 cm^{-1}), C=C aromatic skeletal vibrations of the benzene ring in lignin at 1505 cm^{-1}, and O-H vibrations of lignin (1320 cm^{-1}) in the synthesized CMC confirmed the removal of hemicellulose and lignin components.[48,49] FTIR spectra of commercial CMC, RS3, RS6, and RS9 and the maximum values of specific absorption bands are shown in Figure 3 and Table 4, respectively.

Table 2
Moisture content of commercial CMC and CMC derived from OPEFB and rice straw with various treatments

Sample	Moisture content (%)
Commercial CMC	9.070[d]
OPEFB3	13.490[f]
OPEFB6	13.555[f]
OPEFB9	11.370[e]
RS3	6.880[c]
RS6	6.525[bc]
RS9	3.890[a]
P-OPEFB	5.130[ab]
P-RS	7.850[cd]

Note: Numbers followed by different letters are significantly different with a 95% confidence interval
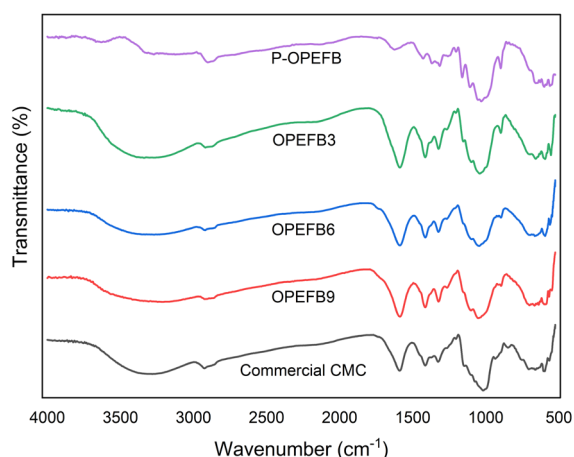

Figure 2: FTIR spectra of OPEFB pulp and CMC derived from OPEFB compared to commercial CMC

Figure 3: FTIR spectra of rice straw pulp and CMC from rice straw compared to commercial CMC

In general, CMC derived from rice straw exhibited an absorption profile similar to that of commercial CMC. The absorption bands at around 890 cm^{-1} and in the 3200-3500 cm^{-1} range were observed, as in the FTIR spectra of CMC samples derived from oil palm empty fruit bunches (Fig. 2), which was attributed t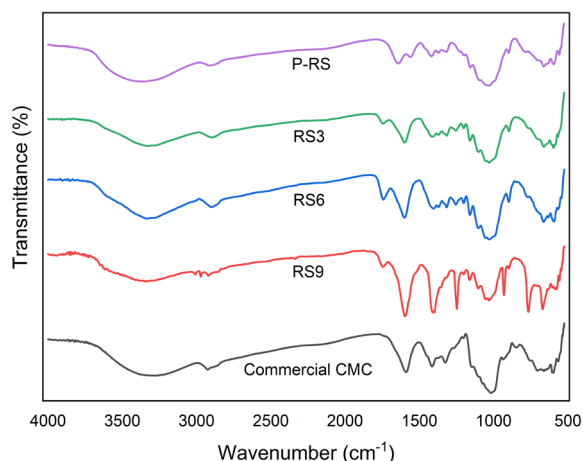o presence of β-glycoside linkage and stretching vibrations of the OH groups, respectively. The absorption bands at around 1600 cm^{-1} and 1400 cm^{-1} were observed in all the samples, which were designated as the stretching vibrations of the C=O carboxyl group and the asymmetric (C=O) and

symmetric (C-O) stretching vibrations caused by the carboxylic acid group, respectively.[50] The absorption bands at 1740 cm^{-1} and around 1250 cm^{-1} were observed in all CMC derived from rice straw. These bands were attributed to the presence of hemicelluloses,[22] suggesting that residual hemicelluloses were not completely removed during cellulose extraction or possible contamination during synthesis.

Table 3
Absorption bands in commercial and OPEFB CMC

Wavenumber (cm^{-1})				
CMC standard (Yeasmin *et al.*)[23]	Commercial CMC	OPEFB3	OPEFB6	OPEFB9
3436.26	3281.23	3338.37	3268.04	3212.97
2924.07	2925.32	2919.18	2920.16	2922.46
1620.16	1589.99	1588.39	1588.79	1587.86
1423.81	1414.52	1414.86	1414.32	1414.71
1329.32	1326.06	1322.95	1323.77	1323.17
1112.65	1017.72	1041.76	1044.65	1052.50
1066.44	847.82	897.40	897	897
898.39	662.26	658.68	664.06	
	597.05	594.59	594.48	
	565.09		561.00	
			526.85	
			525.53	

Table 4
Absorption bands in commercial and rice straw CMC

Wavenumber (cm^{-1})			
Commercial CMC	RS3	RS6	RS9
3281.23	3330.83	3332.23	3351.26
2925.32	2898.31	2902.71	2971.24
1589.99	1745.07	1742.96	2919.92
1414.52	1599.15	1600.42	1745.59
1326.06	1411.42	1406.23	1595.94
1017.72	1316.37	1316.35	1399.08
847.82	1254.34	1254.89	1247.60
662.26	1201.26	1201.76	1162.54
597.05	1159.40	1159.56	1103.16
565.09	1030.62	1030.89	1031.37
	897.46	898.13	931.22
	661.89	663.87	897.41
	597.55	592.87	766.27
	567.21		669.91

Thermal properties of CMC

The thermal decomposition behaviors of P-OPEFB, P-RS, CMC derived from OPEFB, rice straw, and commercial CMC, evaluated by TGA analysis, are compared in Figures 4 and 5. Thermal decomposition is important for determining the thermal stability of CMC. The patterns of the TGA curves of all the samples are essentially similar, although there are differences in the decomposition onset temperature (T_{onset}), maximum (T_{max}), and weight loss percentage. The thermal decomposition occurred in three steps. First, the initial weight loss (~5-20%), relative to the original weight, as the temperature was increased from 50 to 150 °C was observed, owing to the evaporation of physically bound moisture content in the cellulosic structure and loss of volatile compounds.[51,52] Second, a rapid weight loss (~40%) occurred as the temperature was increased from 150 to 350 °C, which was due to sample decomposition, dehydration, and elimination of OH groups. In the third step, a relatively small weight loss (less than 5%) was observed as the temperature was increased from 350 to 500 °C, because of the thermal degradation

of the cellulosic structure and fragmentation from pyrolytic decomposition, which formed aromatized units and decomposed carbonaceous residues.[52,53] Compared to other samples, P-OPEFB had the highest T_{onset} at 196.8 °C, which is probably due to the higher crystallinity of P-OPEFB.[54,55] Compared with commercial CMC, CMC derived from OPEFB exhibited a lower weight loss percentage (Table 5). Notably, RS-9 exhibited the highest percentage of weight loss (Table 6).

When comparing the thermal characteristics of soybean hull CMC, based on the onset temperature
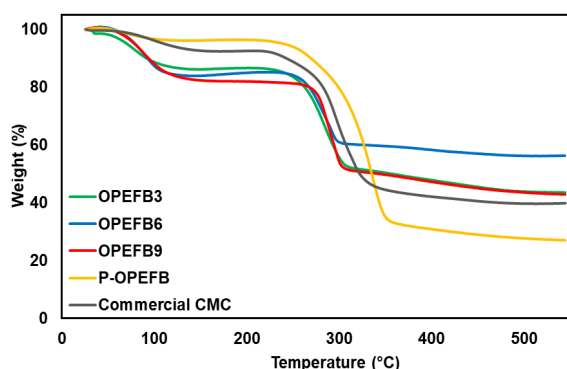
(T_{onset}) in the initial stage recorded at 49 °C,[56] with those of OPEFB CMC obtained in the present study, it can be observed that the thermal properties are fairly comparable, with T_{onset} ranging from 42 to 62 °C. Nevertheless, the onset temperature of OPEFB-derived CMC (Table 5) was lower than that of rice straw-derived CMC (Table 6).

Tables 5 and 6 indicate that changes in NaMCA have minimal impact on the maximum degradation temperature (T_{max}), but they do affect the onset temperature (T_{onset}), which indicates the initial phase of thermal degradation.

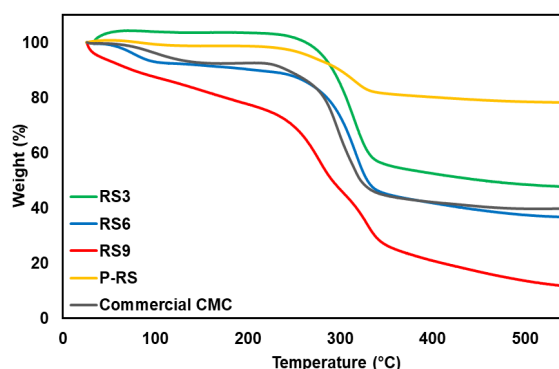Figure 4: TGA curves of OPEFB pulp and CMC from OPEFB compared to commercial CMC

Figure 5: TGA curves of rice straw pulp and CMC from rice straw compared to commercial CMC

Table 5
TGA data of OPEFB pulp and CMC from OPEFB compared to commercial CMC

Sample	Thermal decomposition T (°C)		Weight loss (%)	Residual weight (%)
	T_{onset}	T_{max}		
P-OPEFB	196.8	352.1	72.95	27.05
OPEFB3	62.6	307.4	56.44	43.56
OPEFB6	40.5	300.1	43.69	56.31
OPEFB9	41.7	305.7	57.09	42.91
Commercial CMC	26.9	332.9	60.14	39.86

Table 6
TGA data of rice straw pulp and CMC from rice straw compared to commercial CMC

Sample	Thermal decomposition T (°C)		Weight loss (%)	Residual weight (%)
	T_{onset}	T_{max}		
P-RS	52	334.9	21.79	78.21
RS3	183.4	337.3	52.30	47.70
RS6	99	337.6	63.29	36.71
RS9	67.5	347	88.29	11.71
Commercial CMC	26.9	332.9	60.14	39.86

CMC morphology and EDX analysis
SEM observations indicated that both OPEFB- and rice-straw-derived CMC exhibited a microstructure consisting of fibril strands with varying diameters (Fig. 6). At a magnification of 500x, the surface exhibited a rough texture and displayed areas of

peeling or rupture. The microstructure of the OPEFB-derived CMC in this study is consistent with that reported previously by Parid *et al.*[47] and Mohamood *et al.*,[50] who observed that CMC derived from OPEFB closely resembles the coarse fibers of OPEFB cellulose. However, the CMC

surface appeared slightly smoother and wrinkled. Sophonputtanaphoca *et al*. demonstrated the smooth surface of CMC derived from rice straw.[57]

The roughness of cellulose fibrils is typically attributed to the extraction process, which involves the use of potent chemical compounds and elevated temperatures.

The roughness of the fibril surface is typically reduced during CMC formation through the reaction of cellulose with etherification compounds. This reduction in roughness is accompanied by changes in the crystallinity of cellulose.[30,47]
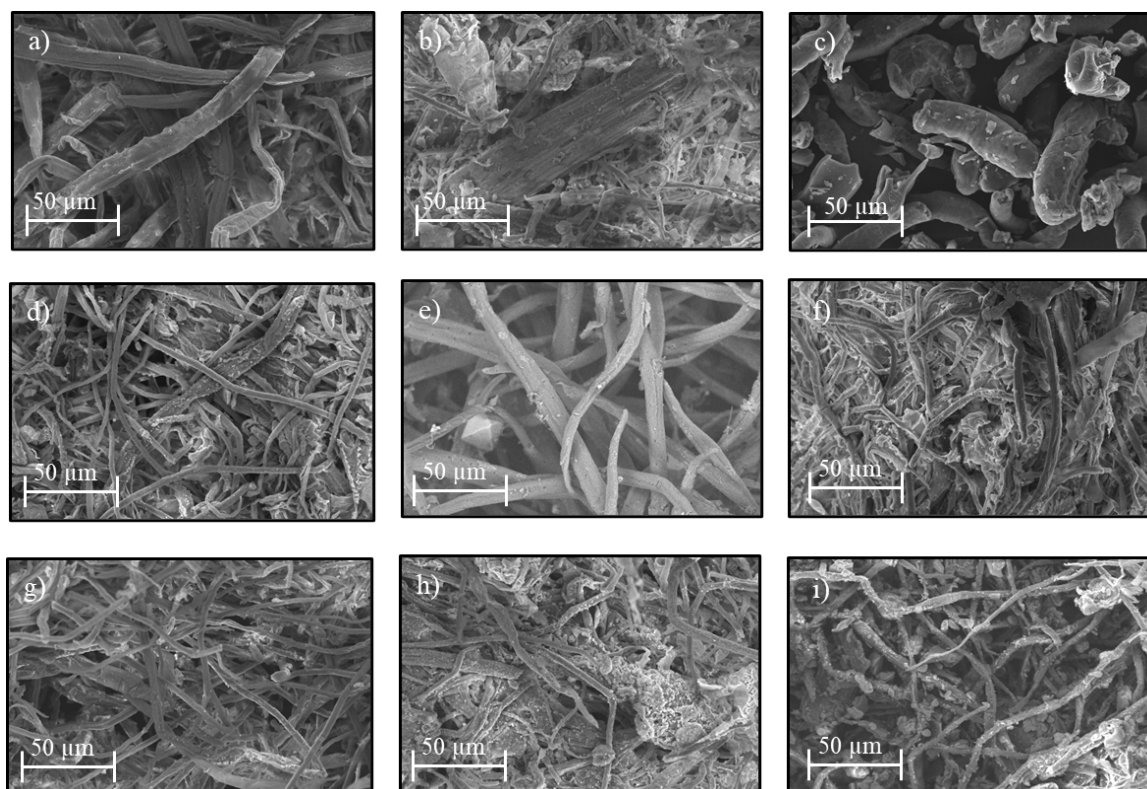

Figure 6: SEM images of a) OPEFB pulp, b) rice straw pulp, c) commercial CMC; OPEFB-derived CMC: d) OPEFB3, e) OPEFB6, f) OPEFB9; and rice straw-derived CMC: g) RS3, h) RS6, and i) RS9 at 500x magnification

Similarly, commercial CMC comprises fibril fragments. The fibrils exhibited a rough surface texture, with flaking areas. Analysis of the SEM images indicates that the etherification process of OPEFB and rice straw cellulose (pulps) into CMC does not alter the fiber shape. However, there was evidence of fiber disaggregation based on the observed changes in fiber diameter. This aligns with the findings of a study conducted by Barros and colleagues, in which they synthesized CMC from soybean hulls.[56]

The EDX results indicate that both rice straw and OPEFB-derived CMC exhibit substantial sodium content (Fig. 7) Nevertheless, the CMC samples derived from rice straw and OPEFB still exhibit a lower sodium percentage, compared to commercially available CMC. The study of the EDX spectrum also indicates that the sodium content in CMC samples derived from rice straw (RS) is higher than that in CMC samples derived from oil palm empty fruit bunches (OPEFB). The degrees of substitution (DS) of CMC were presented in Table 7. The results of assessing the degree of substitution are consistent with the findings of Singh and co-authors, who investigated the range of NaMCA concentration from 1.4 to 3.4 moles per anhydrous glucose unit (AGU).[39]
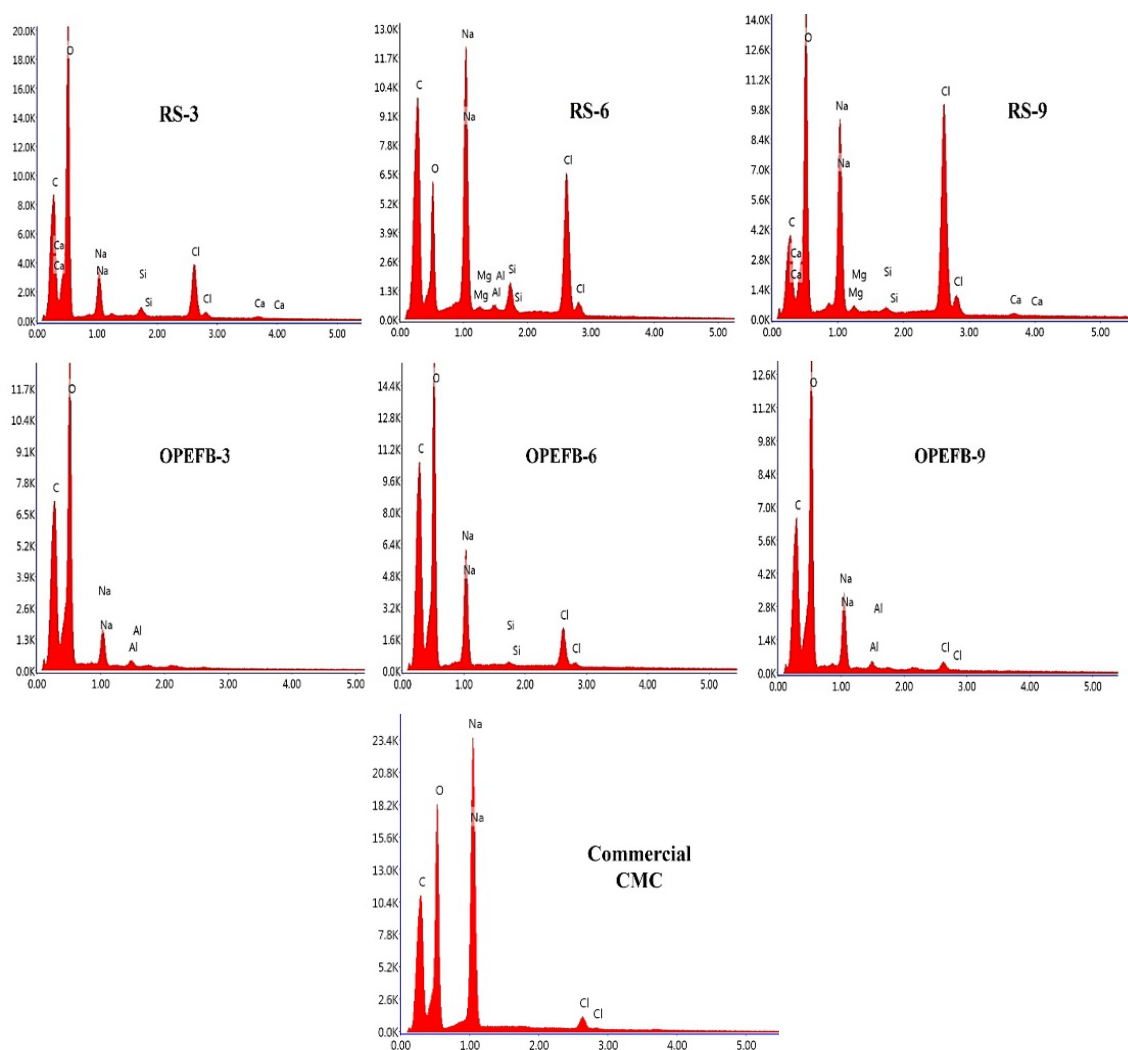
Figure 7: EDX spectra of rice straw and OPEFB-derived CMC and commercial CMC

Table 7
Estimation of degree of substitution based on EDX spectrum analysis

No.	Sample	Degree of substitution
1.	Commercial CMC	5.40
2.	OPEFB3	0.30
3.	OPEFB6	0.70
4.	OPEFB9	0.65
5.	RS3	0.34
6.	RS6	1.37
7.	RS9	1.37

One shortcoming of this EDX approach is that it is not possible to accurately estimate the exact DS values if the sample does not have purity information.[39] The higher degree of substitution (DS) can be attributed to the increased charge density of carboxymethyl cellulose (CMC).[58]

In addition, it has been demonstrated that the addition of NaMCA up to 6 g (OPEFB6 and RS6) has the tendency to increase the degree of substitution or DS (Table 7). Nevertheless, the OPEFB9 had a minor reduction in DS when using 9 g of NaMCA, while the RS9 did not experience a change in DS value compared to the sample with 6 g of NaMCA. When comparing with commercial CMC, the charge density is expected to follow the order: commercial CMC > RS-CMC > OPEFB-CMC.

Viscosity

The viscosity test was exclusively conducted on CMC samples derived from OPEFB, and compared to commercial CMC. The viscosity test findings indicate that the viscosity of the CMC solution (0.75% w/v) for OPEFB3, OPEFB6, OPEFB9, and the commercial CMC is as follows: 5.63; 4.13; 9.56 and 89.21 mPa·s. The viscosity measurement can serve as an indicator of the water retention capacity. Low water holding capacity values lead to a significant amount of water precipitation and a stronger bond between particles, resulting in an increase in viscosity.[59]

CONCLUSION

CMCs derived from OPEFB and rice straw were successfully synthesized using various concentrations of NaMCA. The characteristics of the resulting CMCs were slightly influenced by the concentration of NaMCA. When comparing color brightness, it is worth noting that CMC synthesized with 9 g of NaMCA from OPEFB exhibits the lowest level of brightness. In contrast, CMC derived from rice straw demonstrates a higher level of brightness. The SEM images suggest that the fiber shape remains unchanged during the etherification process of OPEFB and rice straw cellulose (pulps) into CMC. Different concentrations of NaMCA result in distinct thermal properties at the onset temperature, suggesting the initial thermal degradation of CMC. When a concentration of 6 g of NaMCA was used, the degree of substitution for CMC derived from OPEFB and rice straw increased. However, there was a slight decrease or no significant difference observed when the NaMCA concentration was increased to 9 g. The research findings demonstrate that, by synthesizing CMC from agricultural residues, it is possible to obtain CMC with physical and thermal properties that are comparable to those of commercial CMC. This comparable feature was attained by varying the NaMCA.

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