SYNTHESIS AND PROPERTIES OF CARBOXYMETHYL CELLULOSE FROM AGRICULTURAL WASTE – SUGARCANE LEAVES

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Sugarcane leaves are an abundant agricultural waste with the potential for use as a source of cellulose. Cellulose from sugarcane leaves was converted to carboxymethyl cellulose (CMC) by carboxymethylation using sodium hydroxide and monochloroacetic acid in isopropyl alcohol. The yield of CMC was 212.16%. A degree of substitution (DS) equivalent to 0.79 was obtained during the conversion, indicating that the product was water-soluble. Fourier transform infrared (FT-IR) spectroscopy confirmed the presence of major peaks expected for carboxymethyl substitution, compared to commercial CMC. Thermal properties were studied using simultaneous thermal analysis (STA). Melting temperature (T_m) and degradation temperature (T_d) of the sample were 116.6 °C and 270.4 °C, respectively, while the residual mass of 36.49% at 800 °C indicated the presence of a non-volatile component fraction. CMC morphology showed a non-circular form with small particles. Results indicated the potential of sugarcane leaves for production of commercial grade CMC.

Keywords: carboxymethyl cellulose (CMC), sugarcane leaves, agricultural waste, biopolymer

INTRODUCTION

Sugarcane is an important agricultural crop in Thailand and critical to the economy. After harvesting, large amounts of agricultural waste remain as sugarcane leaves. Farmers burn these leaves, causing major air pollution, with serious toxicological effects on human health and the environment. Traditional petroleum-based synthetic polymers cause environmental pressure through their high carbon footprint, but they can be replaced by biopolymers synthesized directly from agricultural wastes.[1] Sugarcane leaves contain high-value cellulose that can be converted to useful new biomaterials. Cellulose consists of a linear chain of glucose units and is the most common organic compound on earth, found in the cell walls of all plants. Cellulose is insoluble in water; however, some cellulose derivatives, such as carboxymethyl cellulose (CMC), can be easily water-solubilized.[2]

CMC is an anionic linear polysaccharide that is nontoxic, renewable, abundant, biocompatible and biodegradable.[3] It exists as a copolymer of two units: ß-D-glucose and ß-D-glucopyranose 2-O-(carboxymethyl)-monosodium salt that are connected via b-1,4-glycosidic bonds. The substitution of a carboxymethyl group for the hydroxyl groups is predominant at the C-2 glucose position.[4] The CMC production process is simple and low cost,[2] and CMC has become widely used in various industries, including foods,[5,6] pharmaceutics[7], adhesives[8] and agriculture.[9] CMC is prepared by the activation of cellulose with aqueous sodium hydroxide (NaOH) in a slurry of an organic solvent, which reacts with the cellulose and monochloroacetic acid as an etherifying agent.[4]

Many researchers have studied the production of CMC from agricultural wastes as cellulose sources, including oil palm fibers, dried duckweed, coconut fibers, sugarcane bagasse, spent tea leaves and palm kernel cake,[10] young Palmyra palm fruit husk[11] and wheat straw.[12] However, the synthesis and properties of CMC from sugarcane leaves have not been previously reported. Therefore, the

objective of this study has been to propose an alternative method to produce CMC from sugarcane leaves, and investigate CMC characteristics, including yield, degree of substitution, structural groups, thermal properties and morphology.

EXPERIMENTAL
Materials
Sugarcane leaves were collected as agricultural waste in Khon Kaen, Thailand. All chemicals used in the preparation and analysis were AR grade or equivalent. Sodium hydroxide and ethanol were purchased from RCI Labscan Co., Ltd. (Bangkok, Thailand). Hydrogen peroxide (30-32%), isopropanol, methanol, nitric acid, hydrochloric acid (HCl) and potassium dichromate ($K_2Cr_2O_7$) were purchased from QReC[TM] and obtained from CLS Supply and Service Part., Ltd. (Khon Kaen, Thailand). Monochloroacetic acid was acquired from TCI (Tokyo, Japan), sulfuric acid (H_2SO_4) was purchased from Merck (Darmstadt, Germany) and ferrous ammonium sulfate and ferroin indicator were purchased from Loba Chemie (Mumbai, India).

Extraction of cellulose
The sugarcane leaves were rinsed with water until clean and then dried in an oven at 60 °C for 48 h. The dried sugarcane leaves were cut into small pieces and boiled in 1 g/20 mL NaOH (w/w of dried sugarcane leaves) at 100 °C for 3 h. The leaves were rinsed with distilled water and dried overnight in an oven at 50 °C to obtain cellulose fibers. The fibers were separated using a food processor (Sharp, Japan) and bleached with hydrogen peroxide for 24 h. After bleaching, the cellulose fibers were washed with tap water and dried in an oven at 60 °C overnight. The fibers were then powdered using a food processor. The cellulose powder was stored until use in a polyethylene bag.

Synthesis of carboxymethyl cellulose (CMC) from sugarcane leaves cellulose
The preparation of CMC followed the method described by Rachtanapun et al.[2] About 15.0 g of cellulose powder, 50 mL of 30% NaOH solution and 450 mL of isopropanol were mixed in a beaker for 30 min at room temperature. Then, etherification was initiated by adding 18 g of monochloroacetic acid. The mixture was then stirred for 1.5 h and left to stand in a beaker covered with aluminum foil at 55 °C in an oven for 3 h. After heating, the mixture was separated into two layers. The liquid phase was removed and the solid phase was suspended in 100 mL of 70% v/v methanol, neutralized with glacial acetic acid and then filtered using a Buchner funnel. The final product was washed five times by suspension in 300 mL of 70% v/v ethanol to remove undesirable by-products, and then washed with absolute methanol and filtered again. The filtration residue was dried at 55 °C in an oven overnight to obtain CMC. The CMC was ground to powder in a food processor and stored in a desiccator for further experimental use.

α-Cellulose and hemicelluloses (β- and γ-cellulose)
The α-cellulose and hemicelluloses (β- and γ-cellulose) were analyzed using TAPPI 203 om-99. The cellulose pulp was weighed at 1.5±0.1 g in a 250 mL beaker and to it 75.0 mL of 17.5% NaOH solution was added. The cellulose pulp was stirred for 30 min and then 100.0 mL of distilled water was added. The beaker containing the cellulose pulp was left to stand for 30 min and then filtered using a Buchner funnel. The first 10 mL of the filtrate was discarded and then 100 mL of the filtrate was collected in a flask for determination of α-, β- and γ-cellulose.

α-Cellulose determination
About 25.0 mL of the filtrate was pipetted into a 250 mL Erlenmeyer flask, followed by 10.0 mL of 0.5 N $K_2Cr_2O_7$ solution. Then, 50 mL of concentrated H_2SO_4 was added cautiously to the solution and shaken. The mixture was maintained hot for 15 min and then 50 mL of water was added to cool it to room temperature. Then, 2 to 4 drops of ferroin indicator were added and titrated with 0.1 N ferrous ammonium sulfate solution to purple color. A blank titration was also conducted by substituting the pulp filtrate with 12.5 mL of 17.5% NaOH and 12.5 mL of water.

Hemicellulose (β- and γ-cellulose) determination
An aliquot of 50.0 mL of the pulp filtrate was pipetted into a 100 mL graduated cylinder with a ground glass stopper, followed by 50.0 mL of 3 N H_2SO_4. The cylinder was heated in a hot water bath at 70-90 °C for a few minutes to coagulate the β-cellulose. The precipitate was then allowed to settle for several hours before decanting or filtering if necessary to obtain a clear solution. After that, 50.0 mL of the clear solution and 10.0 mL of 0.5N $K_2Cr_2O_7$ were pipetted into a 250 mL flask and then 90 mL of concentrated H_2SO_4 was added cautiously. Then, the titration was conducted similarly to the α-cellulose determination. A blank titration was performed using 12.5 mL of 17.5% NaOH, 12.5 mL of water and 25 mL of 3 N H_2SO_4.

The %α-, %γ- and %β-cellulose were calculated using Equations (1), (2) and (3), respectively:

$$\alpha\text{-cellulose (\%)} = 100 - \frac{6.85\,(V_2 - V_1)\times N \times 20}{A \times W} \qquad (1)$$

where V_1 = titration of the pulp filtrate (mL), V_2 = blank titration (mL), N = exact normality of the ferrous ammonium sulfate solution, A = volume of the pulp filtrate used in the titration (mL) and W = weight of pulp specimen (g);

$$\gamma\text{-cellulose (\%)} = \frac{6.85\,(V_4 - V_3)\times N \times 20}{25 \times W} \qquad (2)$$

where V_3 = titration of the solution after precipitation of β-cellulose (mL) and V_4 = blank titration (mL);

β-cellulose (%) = 100 - (α-cellulose % +
γ-cellulose %) $\qquad (3)$

Yield of CMC (%)

The yield of CMC was expressed as percentage and calculated based on the amount of cellulose using Equation (4):[4]

$$\text{Yield of CMC (\%)} = \frac{\text{Weight of CMC (g)}}{\text{Weight of cellulose (g)}} \times 100 \qquad (4)$$

All analyses were performed in triplicate.

Degree of substitution (DS)

The DS of CMC was determined by the ASTM D1439 method. About 4 g of dried CMC powder was stirred in 75 mL of 95% ethanol. Then, 5 mL of nitric acid was added and the solution was boiled on a hot plate for 1-2 min. The solution was then swirled in an orbital shaker for 10-15 min and allowed to cool before dividing into two phases (liquid and solid) and filtering. The solid phase was washed with 80% aqueous ethanol to remove the nitric acid. The final product was washed with methanol, dried at 105 °C for 3 h and kept in a desiccator.

For titration, 1-2 mg of dried CMC powder was suspended in 100 mL of distilled water in a 500 mL Erlenmeyer flask. Then, 25 mL of 0.3-0.5 N NaOH was added and the solution was heated until boiling for 10-15 min. After cooling, the solution was titrated with 0.3-0.5 N HCl using phenolphthalein as an indicator (dark pink to colorless). All titrations were performed in triplicate.

The DS was calculated using Equations (5) and (6):

$$DS = \left[\frac{0.162 \times A}{1 - (0.0.058 \times A)}\right] \qquad (5)$$

$$A = \frac{BC - DE}{F} \qquad (6)$$

where A = milli-equivalent of consumed acid per gram of specimen, B = volume of sodium hydroxide added (mL), C = concentration of sodium hydroxide added (N), D = volume of consumed hydrochloric acid (mL), E = concentration of hydrochloric acid used (N) and F = weight of CMC used (g).

Fourier transform infrared (FT-IR) spectroscopy

The major structural groups of cellulose and CMC were investigated using a PerkinElmer FT-IR (model Spectrum 2), operating in attenuated total reflection (ATR) mode. The FT-IR spectra were recorded in the transmission mode (wavenumbers 4000-400 cm^{-1}).

Simultaneous thermal analysis (STA)

Thermal properties, such as the melting temperature (T_m) and degradation temperature (T_d), of CMC were determined using STA (Netzsch, model STA 449F3). The CMC was weighed in a pan and heated from 30 °C to 800 °C with a heating rate of 10 °C/min in nitrogen atmosphere.

CMC morphology

Scanning electron microscopy (SEM) (Zeiss, model Auriga) was conducted to analyze the morphology of CMC with gold coating. All images were taken at an accelerating voltage of 15 kV.

RESULTS AND DISCUSSION
Physical appearance of cellulose and CMC from sugarcane leaves

The physical appearance of cellulose and CMC is described in Table 1 and shown in Figure 1 (a-b).
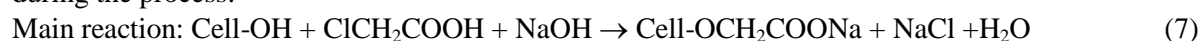
α-Cellulose and hemicelluloses (β- and γ-cellulose)

The α-cellulose and hemicellulose (β- and γ-cellulose) contents of sugarcane leaves used as raw material for CMC production were 71.07±1.48%, 18.28±0.96% and 10.65±0.96, respectively. The α-

cellulose content of the sample was higher than that of hemicelluloses. High α-cellulose content is required for the production of good quality cellulose derivatives. Lower α-cellulose content implies the presence of an excessive amount of low molar mass oligosaccharides, which may affect the yield and quality of cellulose derivatives.[13]

Yield of CMC (%)

The yield of CMC was 212.16%. This value was more than 100% because the molecular weight of the methoxy group was higher than that of the hydroxyl group.[21] These results were similar to those of earlier reports for CMC obtained from durian rind as 167% by Rachtanapun *et al.*[4] The yield of CMC was high due to swelling of the cellulose in alkaline medium during the mercerization stage of the carboxymethylation reaction.[14]

During the process, NaOH solution was used to activate the reaction. The treatment with a high concentration of NaOH increases the swelling of the cellulose granules and produces more cellulose-O-Na, resulting in more opportunities for carboxymethylation to occur with the hydroxyl group (O-H) in the cellulose molecules. The equation below shows the possible chemical reaction that occurred during the process:[13]

Main reaction: Cell-OH + ClCH$_2$COOH + NaOH → Cell-OCH$_2$COONa + NaCl +H$_2$O   (7)
Side reaction: NaOH + ClCH$_2$COOH → HOCH$_2$COONa + NaCl   (8)

Degree of substitution (DS)

The DS plays a major role in the water solubility of CMC. The normal DS range for commercially available CMC is 0.5-1.5.[15] The hydro-affinity of CMC increased with increasing DS. Polymers with the DS below 0.4 are swellable, but insoluble, whereas those with the DS above 0.4 are fully soluble.[16] In this study, the DS value of the synthesized CMC was 0.79. This was fully soluble in water and suitable for use in various industrial and biological applications.

The use of isopropanol as a solvent in the carboxymethylation reaction provides miscibility and accessibility of the etherifying reagent to the reaction center of the cellulose chain rather than glycolate formation. The efficiency of the carboxymethylation reaction is higher when using a high polarity solvent, such as isopropanol.[20] In this study, a reaction time of over 3 h was sufficient for diffusion and absorption of the reactants.

Table 1
Physical appearance of cellulose and CMC

Material	Physical appearance
Cellulose	fluffy, lightweight and white pulp
CMC	hard and light yellow flakes
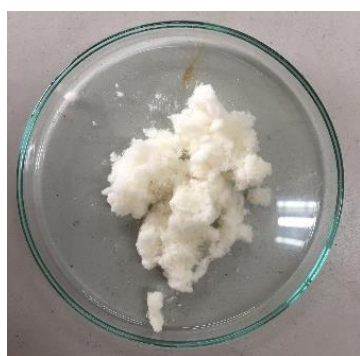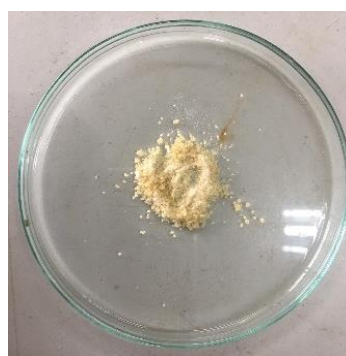
Figure 1: Bleached cellulose (a) and CMC (b) from sugarcane leaves

Table 2

Comparison of DS of CMC from sugarcane leaves and from other sources

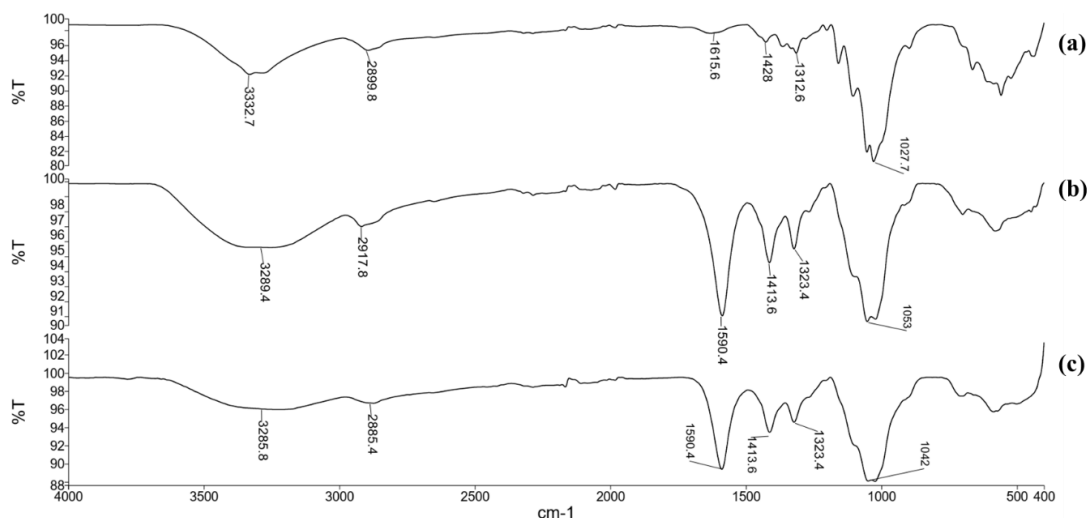| Source of CMC	DS	Reference
Durian rind	0.56-0.87	4
Pod husk of cacao	0.75	17
Seaweed	0.51	16
Musa paradisiaca and *Tithonia diversifolia*	0.17-0.33	15
Sugarcane leaves	0.79	This research

Figure 2: FT-IR spectra of cellulose (a), CMC from sugarcane leaves (b) and commercial CMC (c)

Table 3

FT-IR band frequencies of cellulose, CMC from sugarcane leaves and commercial CMC

Wavenumber (cm^{-1})			Assignment
Cellulose	CMC from sugarcane leaves	Commercial CMC	
3332	3289	3285	OH hydroxyl group
2899	2917	2885	-CH stretching CH_2 and CH_3 groups
1615	1590	1590	-C=O carbonyl group
1428	1413	1413	-CH_2 scissoring
1312	1323	1323	-OH bending vibration
1027	1053	1042	CH-O-CH_2 stretching

    A comparison between the DS value of CMC obtained from sugarcane leaves and other sources is presented in Table 2. The differences in the DS values listed in Table 2 were attributed to the diverse experimental conditions and chemicals used.

Fourier transform infrared (FT-IR) spectroscopy

    The FT-IR spectra of cellulose, CMC and commercial CMC are shown in Figure 2 (a-c), with spectral data analysis of synthesized and commercial CMC presented in Table 3.

    The FT-IR spectra of cellulose and CMC were similar in terms of the main IR peaks, such as hydroxyl groups (OH), hydrocarbon groups (CH_2), carbonyl groups (C=O) and ether groups (-O-), indicating that cellulose and CMC had similar functional groups. In the CMC sample, the spectrum showed strong absorption bands of the carbonyl group at 1590 cm^{-1} (-COO$^-$) and 1413 cm^{-1} (CH_2 scissoring). This proved that the hydroxyl group on cellulose had been substituted with a carboxyl group during the carboxylation reaction. Similar observations were previously reported.[10,15,17,18] Compared with commercial CMC, it can be noted that the spectral patterns of CMC from sugarcane leaves and commercial CMC were almost similar. The wavenumbers were slightly different, suggesting that the cellulose from sugarcane leaves was successfully modified into CMC.

Simultaneous thermal analysis (STA)

STA provides an important insight into the thermal behavior of materials. The STA thermogram of CMC is shown in Figure 3. The melting temperature (T_m) and the degradation temperature (T_d) of the synthesized CMC were 116.6 °C and 270.4 °C, respectively. The thermal decomposition process of CMC was divided into two major reaction steps. The first thermal decomposition started at below 100-120 °C, due to vaporization of moisture absorbed by CMC, with a weight loss of 20.60%. High weight loss was attributed to the porous configuration and polarity. The main thermal decomposition was then observed in the range of 270-322 °C, with a weight loss of 39.54%, indicating decarboxylation of the carboxylic groups in CMC and loss of CO_2.[19] After the final thermal degradation at 800 °C, the residual weight was 36.49%, indicating that CMC contained a non-volatile component fraction. The residual mass was high, similar to the results reported in another study.[19] Thermal properties are affected by structural features, such as the nature of crystallinity, molecular weight and orientation.[16]

A comparison of STA data for CMC from sugarcane leaves and commercial CMC (Fig. 4) is presented in Table 4. As may be remarked, the STA data of CMC from sugarcane leaves and those of commercial CMC were almost the same, except for T_m. The lower T_m of commercial CMC was caused by its nanosized particles, which show wider superficial area and degrade easier than bulk CMC from sugarcane leaves.[19]
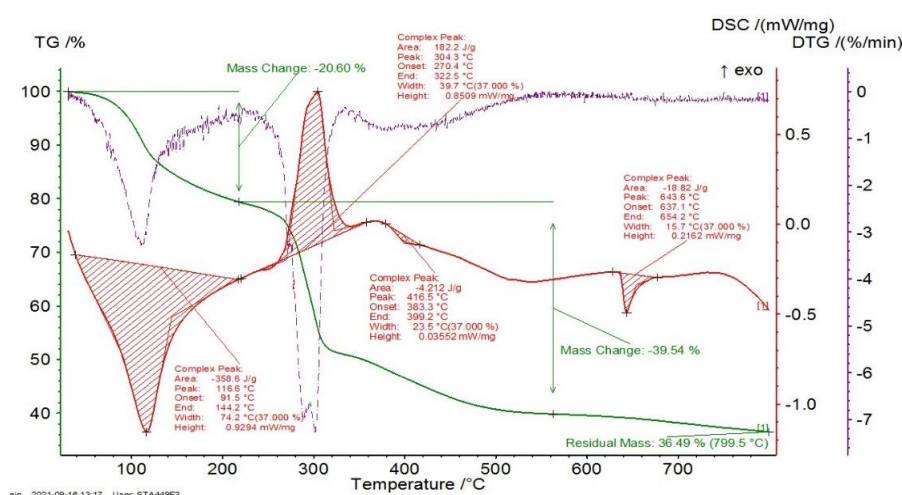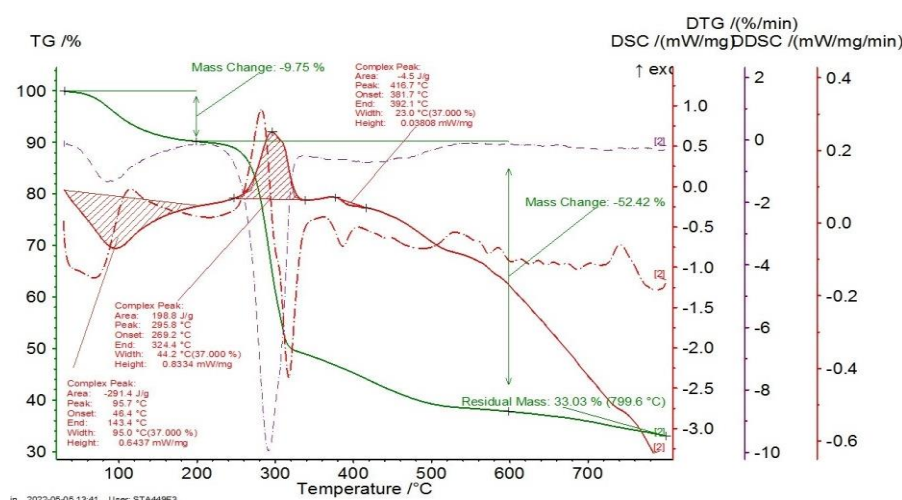

Figure 3: STA thermogram of CMC from sugarcane leaves

Figure 4: STA thermogram of commercial CMC

Table 4

STA data of CMC from sugarcane leaves and commercial CMC

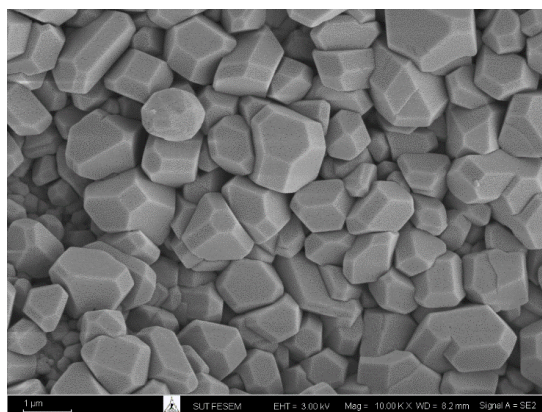| STA data	CMC from sugarcane leaves	Commercial CMC
T_m (°C)	116.6	95.7
T_d (°C)	270.4	269.2
Residual mass (%)	36.49	33.03

Figure 5: SEM image of CMC

CMC morphology

CMC morphology was investigated using a scanning electron microscope (SEM). The SEM image is shown in Figure 5. As may be observed in Figure 5, CMC is presented as non-circular small particles with an average diameter of 1±0.5 µm. The CMC particles were square because they were ground into powder in a food processor. The compatibility of particles with the matrix polymer depends on their size and shape, smaller particles and non-circular forms being more compatible than larger, circular ones.

CONCLUSION

CMC was successfully obtained from sugarcane leaves. The properties of CMC matched well with those of commercial CMC. A high yield of CMC (212.16%) was achieved. The DS was 0.79, indicating that the synthesized CMC was water-soluble. The FT-IR spectra of CMC confirmed the change of cellulose to CMC by the presence of the carboxyl COO group at 1590 cm^{-1} and the -CH group at 1413 cm^{-1}. STA revealed that the T_m and T_d of the synthesized CMC were 116.6 °C and 270.4 °C, respectively. The residual mass of 36.49% at 800 °C indicated the presence of a non-volatile component fraction. The SEM image of CMC showed small particles with a non-circular form. The CMC developed in this study showed potential as a new biopolymer that could add value to agricultural waste.

REFERENCES

[1] I. G. de Moura, A. V. de Sá, A. S. L. M. Abreu and A. V. A. Machado, in "Food Packaging", edited by A. M. Grumezescu, Academic Press, 2017, p. 223-263, https://doi.org/10.1016/B978-0-12-804302-8.00007-8

[2] P. Rachtanapun and N. Rattanapanone, *J. Appl. Polym. Sci.*, **122**, 3218 (2011), https://doi.org/10.1002/app.34316

[3] T. O. Abe, L. Lajide, B. J. Owolabi and A. O. Adebayo, *Bioresources.*, **13**, 6077 (2018), https://bioresources.cnr.ncsu.edu/resources/synthesis-and-application-of-carboxymethyl-cellulose-from-gliricidia-sepium-and-cola-gigantea/

[4] P. Rachtanapun, S. Luangkamin, K. Tanprasert and R. Suriyatem, *LWT-Food Sci. Technol.*, **48**, 52 (2012), https://doi.org/10.1016/j.lwt.2012.02.029

[5] Y. He, H. Li, X. Fei and L. Peng, *Carbohyd. Polym.*, **252**, 117156 (2021), https://doi.org/10.1016/j.carbpol.2020.117156

[6] H. Gupta, H. Kumar, M. Kumar, A. K. Gehlaut, A. Gaur *et al.*, *Environ. Eng. Res.*, **25**, 506 (2020), https://doi.org/10.4491/eer.2019.191

[7] Q. Meng, S. Zhong, S. He, Y. Gao and X. Cui, *J. Ind. Eng. Chem.*, **105**, 251 (2022), https://doi.org/10.1016/j.jiec.2021.09.021

[8] J. T. Aladejana, Z. Wu, K. G. Yves, X. Hou and Y. Xie, *Int. J. Adhes. Adhes.*, **113**, 103051 (2022), https://doi.org/10.1016/j.ijadhadh.2021.103051

[9] Y. Wang, M. Sun, D. Qiao, J. Li, Y. Wang *et al.*, *Carbohyd. Polym.*, **272**, 118483 (2021), https://doi.org/10.1016/j.carbpol.2021.118483

[10] C. M. Y. Huang, P. X. Chia, C. S. S. Lim, J. Q. Nai, D. Y. Ding *et al.*, *Cellulose Chem. Technol.*, **51**, 665 (2017), https://www.cellulosechemtechnol.ro/pdf/CCT7-8(2017)/p.665-672.pdf

[11] N. Jinaphan, J. Sangsuwan, S. Sutthasupa and S. Kamthai, *Food Hydrocoll.*, **124**, 107277 (2022), https://doi.org/10.1016/j.foodhyd.2021.107277

[12] W. Wang, S. Yang, Z. Yang and A. Zhang, *J. Environ. Chem. Eng.*, **9**, 106454 (2021), https://doi.org/10.1016/j.jece.2021.106454

[13] M. S. Yeasmin, M. A. Jalil, M. Moinuddin, N. Akter, N. U. Ahmed *et al.*, *J. Chem. Bio. Phys. Sci.*, **8**, 44460 (2018), http://dx.doi.org/10.24214/jcbps.B.8.2.44460

[14] C. M. Obele, C. M. Ewulonu and J. O. Ogbuagu, *Lignocellulose*, **6**, 109 (2017), http://lignocellulose.sbu.ac.ir/Issue%2062.2017/Ligno_192_Obele_CMC%20from%20Cassava%20Stem_109-118.pdf

[15] F. M. Alabi, L. Lajide, O. O. Ajayi, A. O. Adebayo, S. Emmanuel *et al.*, *Afr. J. Pure Appl. Chem.*, **14**, 9 (2020), http://dx.doi.org/10.5897/AJPAC2019.0821

[16] D. S. Lakshmi, N. Trivedi and C. R. K. Reddy, *Carbohyd. Polym.*, **157**, 1604 (2017), https://doi.org/10.1016/j.carbpol.2016.11.042

[17] K. Gutawa, A. T. Will and G. R. Nikita, *Adv. J. Food Sci. Technol.*, **5**, 9 (2017), https://doi.org/10.5897/AJFS12.020

[18] S. Ramli, S. M. Ja'afar, M. A. A. Sisak, N. Zainuddin and I. A. Rahman, *Malaysian J. Anal. Sci.*, **19**, 275 (2015)

[19] M. El-Sakhawy, H. S. Tohamy, A. Salama and S. Kamel, *Cellulose Chem. Technol.*, **53**, 65 (2019), http://dx.doi.org/10.35812/CelluloseChemTechnol.2019.53.65

[20] A. Bono, P. H. Ying, F. Y. Yan, C. L. Muei, R. Sarbatly *et al.*, *Adv. Nat. Appl. Sci.*, **3**, 5 (2009)

[21] S. B. Suhaimi, I. Patthrare, S. Mooktida and W. Tongdeesoontorn, *Curr. Appl. Sci. Technol.*, **17**, 232 (2017), https://li01.tci-thaijo.org/index.php/cast/article/view/128539/96676