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Sustainable Synthesis and Characterization of Carboxymethyl Cellulose from Agricultural Byproducts: Corn Leaf and Rice Straw

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Abstract

This study explores the sustainable production of carboxymethyl cellulose (CMC) from corn (Zea mays L.) leaf (CL) and rice (Oryza sativa L.) straw (RS), two abundant agricultural byproducts. A novel carboxymethylation method was employed, using sodium hydroxide (NaOH) concentrations of 20–60 g/100 mL. Optimal conditions were determined at 40 g/100 mL NaOH, yielding degrees of substitution (DS) of 0.87 for CL and 0.89 for RS. The DS significantly enhances CMC properties, such as water solubility and viscosity, making it suitable for applications in pharmaceuticals and food industries. Fourier transform infrared spectroscopy confirmed the presence of carboxymethyl groups, while thermogravimetric analysis (TGA), X-ray diffraction, and field emission scanning electron microscopy revealed structural and morphological characteristics. Heavy metal analysis via inductively coupled plasma-mass spectrometer (ICP-MS) showed compliance with World Health Organization (WHO)/Food and Agriculture Organization (FAO) limits, except for lead. The high purity of CMC_{CL} and CMC_{RS} (99.35% and 99.36%) exceeds commercial-grade standards, emphasizing their industrial potential in sectors such as paper, textiles, and ceramics.

Keywords: Sustainable; Carboxymethyl cellulose; Agricultural byproducts; Corn leaf; Rice straw.
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1. Introduction

Approximately five billion hectares, or 36% of the world's land, are dedicated to cultivation. This highlights the economic importance of agriculture for many countries.[1] However, the rapid generation of agricultural waste, increasing annually by 5–10%, presents significant environmental challenges. The burning of such waste pollutes water, soil, and air. Globally, millions of tons of agricultural waste are produced every year. This includes 731 million tons (MT) of rice straw, 354 MT of wheat straw, 203 MT of corn straw, and 180 MT of bagasse. The Asian mainland, particularly, is the largest producer of rice straw.[2] Thailand, a predominantly agricultural country with nearly half of its land dedicated to farming, generates a significant amount of agricultural residues. These by-products include rice straw, rice husk, sugarcane leaves and tops, bagasse, corn husks and stalks, cassava roots, palm trunks and leaves, and cashew nut shells, among others.

Over the years, significant efforts have been made to repurpose agricultural residues into products such as animal feed, fertilizers, or bio-based energy sources.[3] Despite these efforts, certain agricultural wastes remain challenging to utilize through conventional methods. As a result, they are often disposed of in landfills or incinerated, causing adverse environmental impacts such as air pollution. In 2018, over 160 million tons of agricultural waste were left unutilized, even after secondary recycling attempts. CL and RS are examples of surplus biomass left in the fields after the harvesting of corn and rice, with an estimated 15 million and 28 million tons, respectively, remaining unused.[4]

The growing accumulation of agricultural waste from

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farming activities and agro-based processing presents critical environmental challenges, largely due to pollution concerns. A significant portion of this waste consists of cellulose, the most abundant natural polymer and organic compound on earth.[5-7] Produced through photosynthesis, cellulose accounts for approximately 40% of the dry weight of crops, with an estimated annual production of 200 million tons. Its content varies across plants: around 33% in general plant matter, 50% in wood, and up to 90% in cotton fibers.[6,8]

Cellulose is a high molecular weight linear polymer composed of glucose units linked by beta-acetal bonds. Its extensive hydrogen bonding results in poor solubility and resistance to melting, which limits its direct industrial applications. However, cellulose is widely used in wood construction, paper production, textiles (cotton, linen, rayon), nitrocellulose explosives, cellulose acetate films, and the food industry.[9-10] Despite its limitations, cellulose's chemical structure makes it suitable for derivatization, enabling its conversion into high-value cellulose esters and ethers through etherification. This process has become a focal point in green and sustainable chemistry, fostering the development of environmentally friendly technologies.[9,11-13]

Carboxymethyl cellulose (CMC) is an anionic, water-soluble derivative of cellulose, a linear polysaccharide composed of anhydroglucose units linked by β-1,4-glycosidic bonds. The primary structural distinction between CMC and cellulose is the substitution of some hydroxyl groups in cellulose with anionic carboxymethyl groups ($–CH_2COOH$) in CMC.[14] Due to its non-toxic, biodegradable nature, CMC is considered environmentally friendly and has been widely utilized across various industries, including paper, textiles, pharmaceuticals, food, paints, biomedical applications, construction, plastics, cosmetics, and oil exploration.[9,14]

The properties of cellulose derivatives, such as CMC, are primarily assessed based on their DS, which refers to the average number of hydroxyl groups in the cellulose molecule replaced by carboxymethyl groups. The maximum possible DS value is 3, corresponding to the full substitution of the three hydroxyl groups per anhydroglucose unit.[14-17] However, commercial CMC typically exhibits DS values ranging from 0.4 to 1.4.[15] The DS is influenced by factors such as the concentration of reagents, reaction time, solvent, and temperature during the carboxymethylation process.[15,18]

Several studies have focused on the production of CMC from various agricultural byproducts and waste materials, including corn husk,[9,19] mimosa pigra,[7] corn cob,[8,20] sugarcane straw,[13] cashew tree,[15] brewer's spent grain,[11] sugar beet pulp,[12] durian rind,[21] banana pseudo stem,[22] lantana camara,[23] sago palm,[24] bagasse,[25] palm bunch,[25,26] papaya peel,[27,28] sugarcane leaves,[29] office wastepaper,[6,13] carbon foam,[30] and domestic matchstick waste.[31] Despite extensive research on various sources, there is a notable absence of studies investigating CMC production from CL, and limited research has focused on RS.

Both CL and RS have been identified in prior studies for their high cellulose content.[32-35] The isolation of cellulose from these materials facilitates their conversion into CMC through etherification in an alkaline medium with an etherifying agent. This research aims to explore the influence of different sodium hydroxide (NaOH) concentrations on the CMC synthesis process. NaOH concentration plays a critical role in the etherification reaction, affecting the DS, yield, purity, and physicochemical properties of the resulting CMC. This study evaluates key properties of CMC derived from CL and RS, including DS, yield percentage, purity, sodium chloride content, ash content, chemical structure, and crystallinity. By addressing the limited utilization of CL and RS as feedstocks for CMC production, this research aims to advance sustainable waste valorization while providing insights into optimizing CMC synthesis for industrial and environmental applications.

2. Materials and methods

2.1 Materials

CL used in this study were sourced from cornfields located in Satuek district (15.105016°N, 103.330240°E) in Buriram, Thailand. In Thailand, CL is typically left unused after the corn harvesting process, with over 15 million tons remaining in the fields. Similarly, RS is left in the fields following the rice grain harvest, with more than 28 million tons remaining unutilized. A large portion of this straw is often burned to clear the land for the next crop cycle, contributing to air pollution. RS used in this study was collected from rice fields also located in Satuek district (15.117261°N, 103.349324°E), Buriram, Thailand. The chemicals employed in the experimental procedures, including isopropyl alcohol, methyl alcohol, acetic acid, ethyl alcohol, monochloroacetic acid, sulfuric acid, hexyl alcohol, ammonium oxalate, sodium metabisulfite, sodium hydroxide, and sodium chlorite, were obtained from Italmar, Thailand.

2.2 Preparation of sample

The locally sourced CL and RS samples were manually cut into small pieces and sun-dried to remove moisture. The dried material was then finely ground using a pin mill and sieved through a 70-mesh screen (0.210 mm) to achieve a uniform particle size distribution.[21] The resulting finely powdered CL and RS samples were stored in airtight zip-lock polybags at room temperature to minimize moisture absorption, ensuring optimal preservation for subsequent characterization and experimental analysis.

2.3 Isolation of α-cellulose

A measured quantity of powdered RS samples was treated with an 18% NaOH solution for 2 hours with intermittent stirring, maintaining a solid-to-liquid ratio of 1:100 at room temperature. After the reaction, the cellulose residue was separated through filtration and thoroughly washed with 2% acetic acid, followed by rinsing with hot distilled water. The cellulose was then stirred with n-hexane for 1 hour at room temperature and further washed with 95% ethanol. Following the initial filtration, the cellulose was heated with a 0.7% $NaClO_2$ solution, buffered to pH 4, at a solid-to-liquid ratio of 1:50, within a temperature range of 90-95 °C for 90 minutes. The resulting α-cellulose was separated by filtration and subjected to successive washing steps using ethanol and distilled water. The isolated α-cellulose was then treated with a 0.2% sodium metabisulfite solution for 15 minutes, followed by filtration and additional washing with distilled water. Finally, the α-cellulose was dried at 60 °C until it reached a constant weight.[19,36] The percentage yield of the α-cellulose products was calculated using Eq. (1).

$$\text{Yield of alpha-cellulose (\%)} = \frac{W1}{W0} \times 100\% \tag{1}$$

where W_1 is the weight of alpha-cellulose, and W_0 is the weight of powder.

2.4 Synthesis of carboxymethyl cellulose

In this study, CMC was synthesized from cellulose extracted from CL and RS using varying concentrations of sodium hydroxide (NaOH) (20%, 30%, 40%, 50%, and 60% w/v). The synthesis process began by adding 15.0 g of cellulose powder to 50 ml of NaOH solution at the specified concentrations, followed by stirring for 30 minutes. The mixture was then covered with aluminum foil and heated in an oven at 55 °C for 3.5 hours. Upon completion of the heating process, the mixture separated into two phases: a liquid phase, which was discarded, and a solid phase, which was suspended in 100 ml of 70% (v/v) methanol. The suspension was then neutralized with glacial acetic acid and filtered using a Buchner funnel. To remove any unwanted byproducts, the solid residue was washed five times by suspending it in 300 mL of 70% (v/v) ethanol for 10 minutes each time. Finally, the material was washed with 300 ml of absolute methanol and dried in an oven at 55 °C overnight.[21,29] The percentage yield of the CMC products was calculated using Eq. (2).

$$\text{Yield of CMC (\%)} = \frac{W1}{W0} \times 100\% \tag{2}$$

where W_1 is the weight of CMC, and W_0 is the weight of alpha-cellulose.

2.5 Characterization

2.5.1 Degree of substitution (DS)

The DS for the synthesized CMC was determined according to the Standard Test Methods for Sodium Carboxymethylcellulose (ASTM D1439-03). First, 5 g of CMC were added to a 200 ml solution of nitric acid-methanol (1:1 v/v) and the mixture was agitated and allowed to stand for 3 hours. Afterward, the solution was rinsed with 70% (v/v) methanol and dried in an oven until a constant weight was reached. Subsequently, 2 g of the dried sample were dissolved in 200 mL of distilled water along with 30 ml of 1 N NaOH. The resulting solution was titrated with excess NaOH, using 1 N HCl to neutralize it to the phenolphthalein endpoint. The titration was deemed complete when the solution color changed from dark pink to colorless.[37] The DS was calculated using Eqs. (3) and (4).

$$\text{Degree of substitution} = \frac{0.162A}{(1-0.0584A)} \tag{3}$$

$$A = \frac{(BC-DE)}{F} \tag{4}$$

where A is Milliequivalents of acid consumed per gram of sample, B is NaOH solution added (ml), C is Normality of the NaOH solution (N), D is HCl required for titration of the excess NaOH (mL), E is Normality of the HCl (N), F is acid carboxymethylcellulose used (g), 162 is gram molecular mass of the anhydro glucose unit of cellulose, and 584 is net increase in molecular mass of anhydro glucose unit for each carboxymethyl group substituted.

2.5.2 Purity

A total of 1.5 g of CMC was added to 100 ml of 80% (v/v) methanol. The solution was stirred and allowed to stand for 10 minutes. It was then filtered and rinsed with an additional 100 ml of 80% (v/v) methanol. To obtain pure CMC, the sample was dried at 100 °C until a constant weight was achieved.[12,13] The CMC purity percentage was calculated using Eq. (5).

$$\text{Percentage of CMC purity (\%)} = \frac{W1}{W0} \times 100\% \tag{5}$$

where W_1 is the final weight, and W_0 is the initial weight.

2.5.3 Sodium chloride content

A total of 2.0 g of CMC was added to 250 mL of a 65% (v/v) methanol solution and allowed to stand for 5 hours, resulting in the separation of two distinct phases. A 100 ml portion of the liquid phase was then neutralized with diluted HNO_3 and titrated with 0.1 N $AgNO_3$ solution until the potassium chromate (K_2CrO_4) endpoint was reached. The titration was considered complete when the color changed from red to brick orange.[12] The sodium chloride (NaCl) content in the CMC was calculated using Eq. (6).

$$\text{NaCl}\ (\%) = \frac{1.461\ \times V}{m} \tag{6}$$

where V is the amount of $AgNO_3$ (mL), and m is the weight of the dried sample (g).

2.5.4 Ash content

The ash content of CMC was determined following the Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis (ASTM D 7582-15).[38] The ash yield reflects the residual material that remains after the samples are subjected to high-temperature heating.

2.5.5 Inductively coupled plasma-mass spectrometer (ICP-MS)

The ICP-MS instrument used in this study was the NexION 350X, provided by PerkinElmer, USA. Data analysis and instrument control were carried out using Syngistix™ for ICP-MS version 1.0. Sample preparation was conducted via microwave digestion, utilizing the Titan MPS instrument from PerkinElmer, Germany. In this process, microwave energy was applied to decompose the sample matrix, converting the target elements into their atomic form. The resulting ions were then introduced into the ICP-MS system, separated based on their mass-to-charge ratio, and subsequently quantified.[39]

2.5.6 Fourier transform infrared spectroscopy (FTIR)

The functional groups of both α-cellulose and carboxymethylcellulose were identified using infrared spectroscopy with the KBr disc technique. The analysis was conducted on a Nicolet iS50 spectrophotometer from Thermo Scientific, USA, with data processed through OMNIC software. Pellets were prepared by grinding 0.2 mg of α-cellulose or carboxymethylcellulose with 2 mg of KBr. Transmission measurements were recorded across a wavenumber range of 4000–400 cm^{-1}.

2.5.7 X-ray diffractometry (XRD)

The X-ray diffraction (XRD) patterns, used to evaluate the crystallinity of cellulose and carboxymethyl cellulose (CMC), were obtained using a Bruker AXS Model D8 Advance X-ray diffractometer (Germany). The scattering angle (2θ) was scanned from 5° to 80° at a rate of 0.02° per step, with a step duration of 0.2 seconds. The powdered samples were irradiated with X-ray beams at 40 kV and 40 mA. The crystallinity index of the samples was calculated using the Segal equation, as shown in Eq. (7).[34]

$$I_c(\%) = \frac{I_{crystalline} - I_{amorphous}}{I_{crystalline}} \times 100\% \tag{7}$$

where $I_{\text{crystalline}}$ is the maximum diffraction intensity representing the crystalline phase (2θ of 22-24°), and $I_{\text{amorphous}}$ is the minimum diffraction intensity representing the amorphous phase (2θ of 18–19°).

2.5.8 Field emission scanning electron microscopy (FE-SEM)

The morphological analysis of the cellulose and CMC samples was conducted using FESEM with a JEOL JSM 7800F instrument (Japan). The samples were mounted onto carbon tape attached to a specimen stub and sputter-coated with a thin layer of gold using a QUORUM Q150R ES sputter coater (United Kingdom). Imaging was performed at an accelerating voltage of 2 kV with a magnification of 500x.

2.5.9 Thermogravimetric analysis (TGA)

The thermal stability of the samples was assessed using TGA performed on a TGA 2 instrument (Mettler Toledo, Switzerland). Approximately 3 mg of each sample was analyzed under a nitrogen atmosphere with a gas flow rate of 50 mL/min. The samples were heated from room temperature to 600 °C at a rate of 10 °C/min to evaluate their thermal degradation behavior.

3. Results and discussion

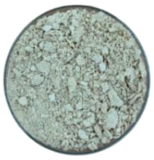
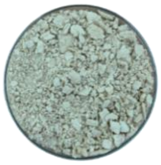
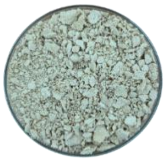
α-Cellulose refers to the fraction of cellulosic material that remains insoluble in a sodium hydroxide solution of mercerizing strength under defined conditions and time duration.[40] This α-cellulose is a white, odorless, and tasteless powder that is insoluble in water. It is widely used as a raw material in the production of various products, including propellants, paper, paperboards, textiles, electrical cable insulators, cellulose derivatives, and more.[41] The compositional data for the CL and RS samples, used as raw materials, are detailed in Table 1.

Notably, Table 1 indicates that the α-cellulose yield was 33.64 g per 100 g of dry CL biomass and 43.45 g per 100 g of dry RS biomass. These values are consistent with results from similar studies, such as those reporting α-cellulose content in corn cob at 34.45 g per 100 g of dry biomass.[8] Additionally, research by Churam *et al*.[29] reported an α-cellulose content of 41.71 g per 100 g in sugarcane leaves. The extraction process showed reasonable consistency with standard deviations of 0.32074 for CL and 0.42646 for

Table 1: The α-cellulose content of the sample.

α-Cellulose	Weight of powder (g)	Weight of α-cellulose (g)	Yield of α-cellulose (%)	Maximum weight (g)	Minimum weight (g)	Standard deviation
CL	10.00	3.3640	33.64	3.9380	2.9004	0.32074
RS	10.00	4.3651	43.65	5.7647	3.9037	0.42646

Table 2: The physical appearance of the raw materials, α-cellulose, and CMC derived from CL and RS under varying conditions is documented.

Sample		Isolation of α - cellulose	CMC synthesis with various NaOH concentrations (w/v)				
Material		α – Cellulose	20% of NaOH	30% of NaOH	40% of NaOH	50% of NaOH	60% of NaOH
CL							
RS							

RS across 41 production batches. The higher variability observed in RS can be attributed to differences in the raw material properties; RS harvested in different years exhibited variations in dryness and brittleness. These differences affected the grinding process, resulting in finer powders for older, more brittle RS samples and leading to variable material losses during cellulose extraction.

Despite this variability, the fundamental properties of the extracted cellulose remained consistent. To minimize variations in future extractions, steps will be taken to standardize the post-harvest collection period to ensure RS materials maintain similar dryness and brittleness levels, thereby reducing variability and optimizing the overall extraction process. The visual characteristics of α-cellulose and CMC derived from CL and RS are presented in Table 2.

3.1 DS and percent yield of CMC

The DS is a crucial property of CMC, as it significantly influences both its solubility and solution behavior.[42] DS values between 0.0 and 0.4 indicate that CMC is insoluble but swellable, while higher values reflect complete water solubility.[25] CMC is typically produced from cellulose through alkalization followed by carboxymethylation using monochloroacetic acid (MCA), yielding DS values in the range of 0.4-1.3.[18,21-23] In this study, the DS values for CMC derived from CL ranged from 0.47 to 0.87, while those for RS ranged from 0.44 to 0.89, which are well within the expected range (Fig. 1).

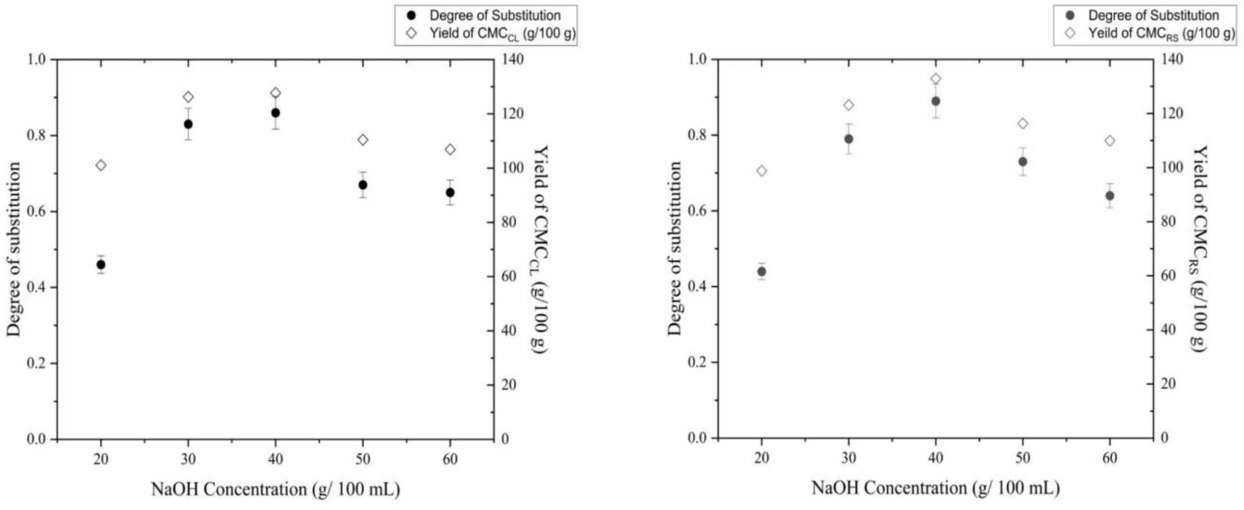
The degree of substitution (DS) increased with rising NaOH concentrations (20–40 g/100 mL), reaching a peak DS of 0.87 at 40 g/100 mL NaOH for CL and 0.89 at 40 g/100 mL NaOH for RS, followed by a significant decline in Eq. (8-10). This behavior can be explained by the carboxymethylation process, in which two competing reactions occur. The first reaction involves the interaction of cellulose hydroxyl groups with monochloroacetic acid (MCA), producing CMC_{CL} and CMC_{RS}, as shown in Eq. (9). The second reaction, driven by NaOH and MCA, leads to the formation of sodium glycolate as a byproduct, as described in Eq. (10).[5-7,43]

$$[C_6H_7O_2(OH)_3]_n + nNaOH \rightarrow [C_6H_7O_2(OH)_2ONa]_n + nH_2O \tag{8}$$

$$[C_6H_7O_2(OH)_2ONa]_n + nClCH_2COOH \rightarrow [C_6H_7O_2(OH)_2OCH_2COONa]_n + nNaCl \tag{9}$$

$$2nNaOH + nClCH_2COOH \rightarrow HOCH_2COONa + nH_2O + nNaCl \tag{10}$$

At higher NaOH concentrations, the second reaction predominates, leading to the formation of sodium glycolate and a consequent reduction in DS. Additionally, the observed decrease in DS at elevated NaOH concentrations may be attributed to the potential degradation of CMC polymer chains.[7,8] A similar trend has been observed in CMC derived from other cellulose sources, including corn cobs (DS = 0.48–1.18), sugar beet pulp (DS = 0.102–0.667), durian rind (DS = 0.56–0.87), cavendish banana pseudo stems (DS = 0.26–0.75), lantana camara (DS = 0.59–1.22), sago palm (DS = 0.328–



(a) (b)

Fig. 1: Effect of NaOH concentration on DS (●) and percent yield (◊) of (a) CMC$_{\mathrm{CL}}$ (b) CMC$_{\mathrm{RS}}$ synthesizing with various NaOH concentrations.

0.821), and sugarcane leaves (DS = 0.46–0.86).[29] Furthermore, the percentage yield of CMC$_{\mathrm{CL}}$ and CMC$_{\mathrm{RS}}$ followed a trend similar to the DS results, as shown in Fig. 1, consistent with previous studies.[21,22,29]

The DS of CMC is a critical factor in determining its properties and suitability for specific industrial applications. As DS increases, water solubility improves, affecting viscosity and dissolution kinetics. This characteristic is particularly important in applications requiring rapid dissolution, such as pharmaceutical formulations and food products, where CMC is widely used as a thickener and stabilizer. For food applications, DS typically ranges from 0.6 to 0.95. Higher DS values in CMC can enhance electrostatic repulsion between protein particles, preventing phase separation in acidified milk drinks.[29]

3.2 Purity, NaCl and ash contents analysis

The purity of CMC was evaluated following multiple washes with 80% methanol, effectively removing reaction by-products such as sodium chloride and sodium glycolate. For CMC intended for human consumption, a purification level of at least 99.5% is required. In contrast, CMC intended for industrial applications – such as paper coating, textile sizing and printing, ceramic glazing, and oil drilling muds – must meet a slightly lower purity standard of 98.0%.

The CMC content and sodium chloride percentages in the prepared CMC were carefully analyzed and compared to the established standards for commercial and pharmaceutical-grade CMC. The results are summarized in Table 3. Analysis of the data reveals that the CMC content obtained in this study ranged from 98.94% to 99.35% for CMC$_{\mathrm{CL}}$ and from 98.86% to 99.36% for CMC$_{\mathrm{RS}}$. Although slightly below the 99.5% purity benchmark required for food and pharmaceutical-grade CMC, these values comfortably exceed the 98.0% purity threshold for commercial applications. Additionally, the sodium chloride content in the prepared CMC was found to be notably low, at just 0.04%. Considering that the sodium salt content in food additives should not exceed 0.5%, either individually or in combination, the prepared CMC demonstrates suitability for various industrial applications.

The ash content of the prepared CMC is also presented in Table 3. The ash content observed in this study ranged from 11.25% to 18.33% for CMC$_{\mathrm{CL}}$ and from 11.14% to 21.94% for CMC$_{\mathrm{RS}}$. These findings align closely with those from similar studies, where standard CMC samples exhibited an ash content of 14.23%.[19] The higher ash content is indicative of a greater degree of substitution (DS) in the CMC, likely due to the increased substitution of hydroxyl groups by sodium salts of carboxymethyl groups during the etherification process.[19,29]

3.3 Heavy metals of CMC

Heavy metals are potential environmental contaminants that pose significant health risks due to their toxic effects, even at very low concentrations.[29] The levels of toxic metals in the prepared CMC$_{\mathrm{CL}}$ and CMC$_{\mathrm{RS}}$ were assessed and compared with the recommended values, as shown in Table 4. The results indicate that the concentrations of arsenic (As), cadmium (Cd), and mercury (Hg) are all below 0.04 ppm, which falls within the permissible limits established by the World Health Organization (WHO) for food additives and emulsifiers. However, the lead (Pb) concentrations in CMC$_{\mathrm{CL}}$ and CMC$_{\mathrm{RS}}$ were found to range from 1.87 to 7.04 ppm and 11.23 to 34.34

Table 3: Determination of CMC, NaCl and ash contents.

Parameters	CMC_{CL}			CMC_{RS}			Reference
	Content of CMC or purity, %	Content of NaCl, %	Content of Ash, %	Content of CMC or purity, %	Content of NaCl, %	Content of Ash, %	
CMC (20% w/v of NaOH)	99.13	0.04	15.37	99.23	0.04	12.74	This work
CMC (30% w/v of NaOH)	98.94	0.04	18.33	98.96	0.04	16.91	This work
CMC (40% w/v of NaOH)	99.35	0.04	16.44	99.36	0.04	21.94	This work
CMC (50% w/v of NaOH)	99.34	0.04	13.83	99.30	0.04	12.69	This work
CMC (60% w/v of NaOH)	99.10	0.04	11.25	99.32	0.04	11.14	This work
CMC food and pharmaceutical grade	> 99.50	< 0.5 (sodium salts)	-	> 99.50	< 0.5 (sodium salts)	-	[44]
CMC commercial grade	> 98.00	< 2.0 (sodium salts)	-	> 98.00	< 2.0 (sodium salts)	-	[44]

Table 4: Concentration of heavy metals in the synthesized CMC_{CL} and CMC_{RS}.

Heavy metal	As	Cd	Hg	Pb
Concentration in ppm (CL)	-	-	-	< 50.00
Concentration in ppm (RS)	-	-	-	< 50.00
Concentration in ppm (CMC_{CL})	< 0.04	< 0.04	< 0.04	1.87 – 7.04
Concentration in ppm (CMC_{RS})	< 0.04	< 0.04	< 0.04	11.23 – 34.34
Concentration in ppm (proposed permissible limit)[19,29]	3	1	1	1

ppm, respectively, exceeding the WHO's permissible limits for food additives and emulsifiers. Notably, the lead concentrations in the raw CL and RS materials, which are below 50 ppm, are approximately 50 times the allowable limit. This suggests that during the processes of α-cellulose isolation and carboxymethyl cellulose synthesis – particularly through alkalization and etherification reactions – the lead concentration in CMC_{CL} and CMC_{RS} decreases.

The presence of lead is attributed to its accumulation from the application of herbicides during the agricultural cultivation process in Thailand.[45]

Previous studies have reported that the use of chelating agents can effectively facilitate the removal of heavy metals from contaminated materials. For instance, Suprapti *et al.*[46] demonstrated that acetic acid, used as a chelating agent, successfully removed Pb, Cr, and Cd from green mussels. Among chelating agents, ethylenediaminetetraacetic acid (EDTA) is recognized as one of the most efficient chelating agents for heavy metals.[47,48] However, to ensure that Pb concentrations fall within the permissible limits established by the World Health Organization (WHO) for food additives and emulsifiers, the current process of washing α-cellulose with 2% acetic acid during isolation may be insufficient for effective Pb removal. It is recommended to increase the concentration of chelating agents and extend the soaking time, as both factors significantly enhance the efficiency of heavy metal removal.[46,47]

3.4 FTIR analysis

The identification of the produced α-cellulose and CMC was carried out using Fourier transform infrared (FTIR) spectroscopy. The FTIR spectra of the synthesized CMC samples and α-cellulose are shown in Figs. 2 and 3. As illustrated in these figures, the spectra display characteristic absorptions related to the cellulose backbone and the presence of carboxymethyl ether groups, notably at 1589.41–1591.75 cm^{-1} for CMC_{CL} and 1588.67–1589.74 cm^{-1} for CMC_{RS}.

The broad band in the range of 3200–3600 cm^{-1} corresponds to O-H stretching, while the band between 2800 and 3100 cm^{-1} is attributed to C-H stretching vibrations. The band near 1600 cm^{-1} represents C=O stretching, and the bands around 1420 cm^{-1} and 1320 cm^{-1} are associated with $-\text{CH}_2$

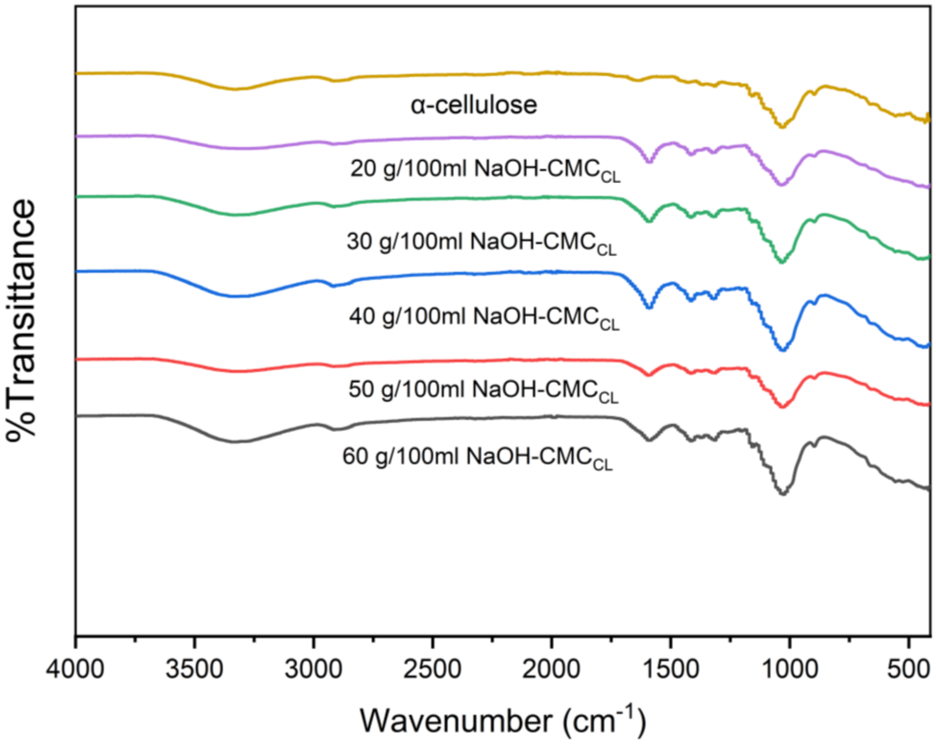


Fig. 2: FTIR spectra of α-cellulose of CL and CMC$_{CL}$ synthesized with various NaOH concentrations.

scissoring and -OH bending vibrations, respectively. The band spanning 1000–1200 cm^{-1} is linked to -O- stretching, while the band around 1030 cm^{-1} corresponds to -CH-O-CH$_2$ stretching. Additionally, a wavelength near 890 cm^{-1} indicates the 1,4-β glycosidic linkage of cellulose.[5,9,21,24,25,49]

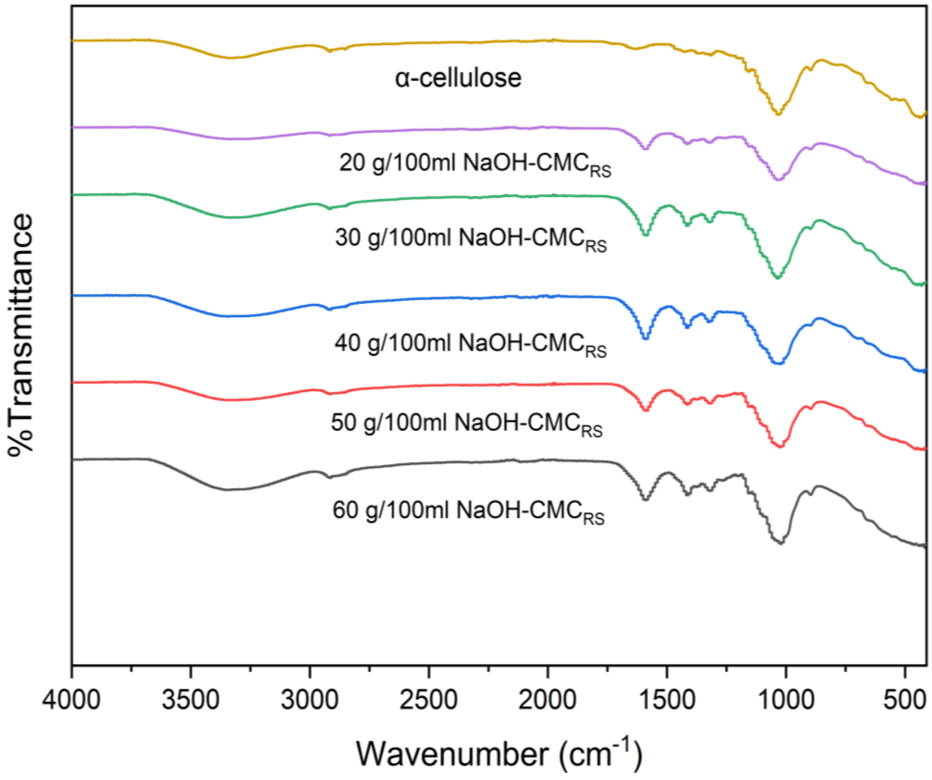


Fig. 3: FTIR spectra of α-cellulose of RS and CMC$_{RS}$ synthesized with various NaOH concentrations.

The absorbance bands in the FTIR spectra of CMC$_{CL}$ and CMC$_{RS}$ remained consistent across different NaOH concentrations but exhibited distinct variations from those of α-cellulose. Notably, the appearance of a new, strong absorption band at 1589.41–1591.75 cm^{-1} for CMC$_{CL}$ and

1588.67–1589.74 cm^{-1} for CMC$_{RS}$ clearly indicates the stretching vibrations associated with the carboxyl group (COO-). In contrast, the band at 1411.97–1414.48 cm^{-1} in the α-cellulose spectrum of CL and the band at 1412.07–1413.62 cm^{-1} in the α-cellulose spectrum of RS are attributed to the carboxyl groups in the sample salts.[5,21,22] A comprehensive dataset of FTIR spectra for α-cellulose and CMC, synthesized at varying NaOH concentrations, is presented in Table 5. These results confirm the successful carboxymethylation of cellulose molecules, consistent with previous studies.[5,7,8,21,22,24,25,29]

3.5 XRD analysis

X-ray diffraction (XRD) analysis is a crucial technique for assessing the crystallinity of polymers, with cellulose being inherently semicrystalline in nature.[19] This study presents the XRD patterns of α-cellulose and carboxymethyl cellulose (CMC) sodium salt synthesized at different sodium hydroxide (NaOH) concentrations, as shown in Figs. 4 and 5.

Table 5: FTIR spectra data of α-cellulose and CMC synthesized with various NaOH concentrations.

Material	Wave number (cm^{-1})						Assignment
	α-cellulose	CMC (20% w/v of NaOH)	CMC (30% w/v of NaOH)	CMC (40% w/v of NaOH)	CMC (50% w/v of NaOH)	CMC (60% w/v of NaOH)	
CL	3333.63	3271.23	3333.12	3331.36	3328.88	3334.06	OH stretching
	2916.05	2916.80	2917.15	2917.85	2916.88	2916.45	CH stretching CH$_2$ and CH$_3$ groups
	-	1589.52	1590.09	1590.06	1591.75	1589.41	C=O region (indicated CMC)
	-	1413.38	1413.91	1414.48	1413.07	1411.97	CH$_2$ bonding (indicated CMC)
	1315.52	1321.36	1319.01	1319.80	1317.53	1316.91	OH in plane bending
	1158.36	1149.58	1161.73	1155.66	1157.68	1156.92	C-O-C asymmetry bridge stretching
	1030.98	1034.91	1031.84	1030.36	1030.57	1027.79	C-O stretching
	897.10	896.34	898.37	900.39	896.82	896.34	β-Glycoside linkage
RS	3332.63	3318.72	3334.20	3350.55	3330.13	3342.74	OH stretching
	2916.99	2916.52	2916.83	2918.02	2916.82	2917.45	CH stretching CH$_2$ and CH$_3$ groups
	-	1589.74	1588.67	1588.97	1589.05	1588.96	C=O region (indicated CMC)
	-	1413.62	1413.33	1413.23	1412.79	1412.07	CH$_2$ bonding (indicated CMC)
	1316.22	1320.68	1320.60	1322.37	1319.55	1319.81	OH in plane bending
	1163.76	1155.66	1161.73	1155.66	1157.68	1155.66	C-O-C asymmetry bridge stretching
	1031.47	1031.04	1034.37	1023.31	1022.77	1020.24	C-O stretching
	896.74	898.37	896.34	900.39	898.37	896.59	β-Glycoside linkage

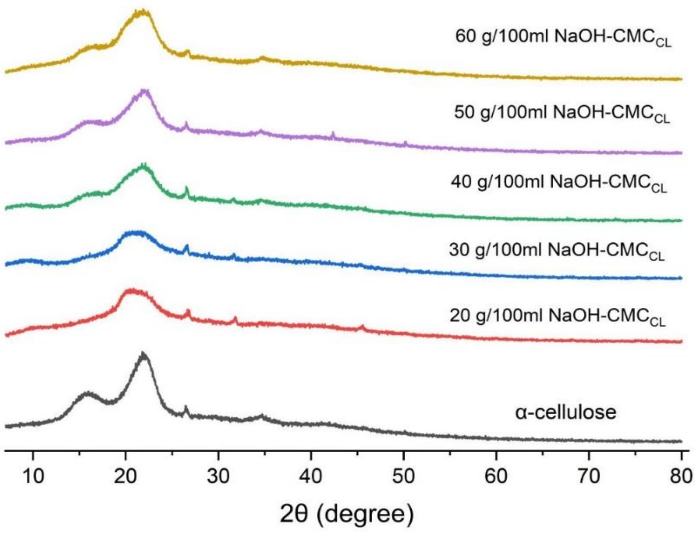


Fig. 4: XRD patterns of α-cellulose and CMC$_{CL}$ synthesized with various NaOH concentrations.

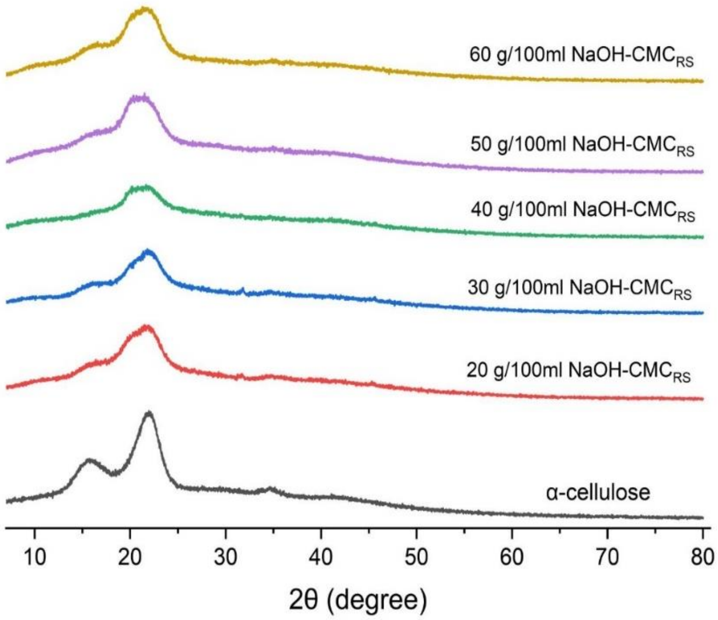


Fig. 5: XRD patterns of α-cellulose and CMC$_{RS}$ synthesized with various NaOH concentrations.

The crystallinity index (CI) values for α-cellulose and CMC are summarized in Table 6. The results indicate a decline in the CI for CMC$_{CL}$ and CMC$_{RS}$ as NaOH concentrations increase, suggesting a reduction in crystallinity. This decrease in crystallinity is likely due to the disruption of hydrogen bonds during NaOH treatment.[22,43] These findings are consistent with previous studies that reported similar effects in CMC derived from various cellulose sources, including corn husk,[5] durian rind,[21] sugarcane leaves,[29] and brewer’s spent grain,[43] all of which exhibited reduced crystallinity following alkaline processing.

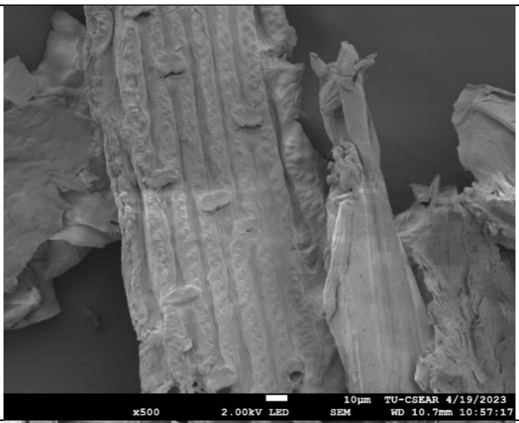
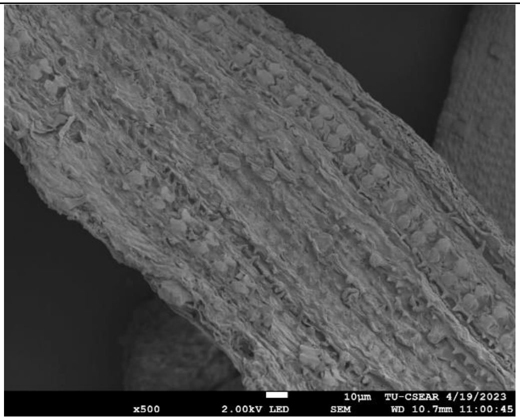
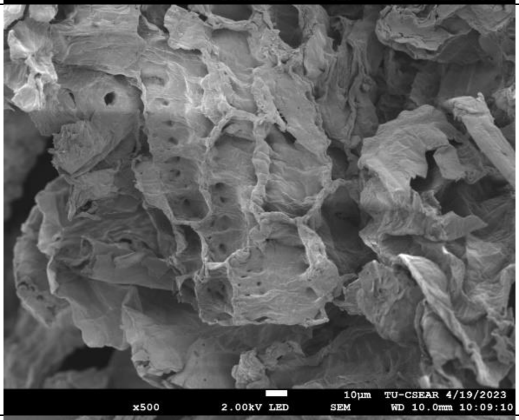
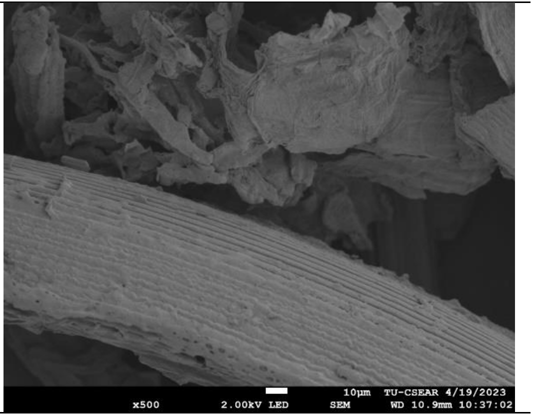
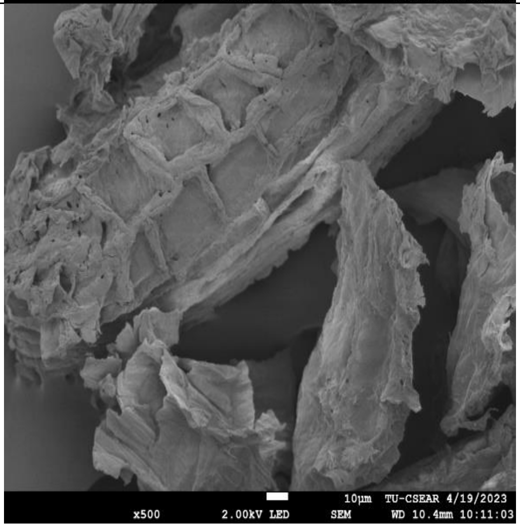
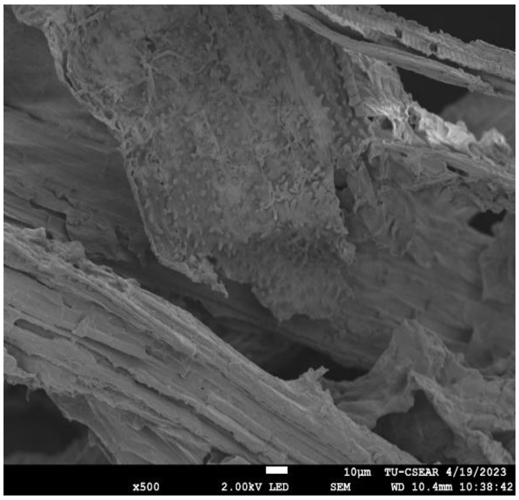
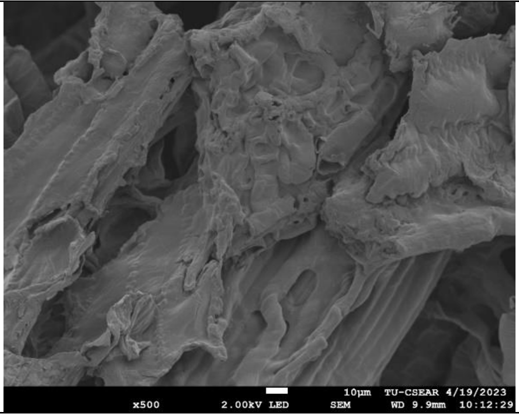
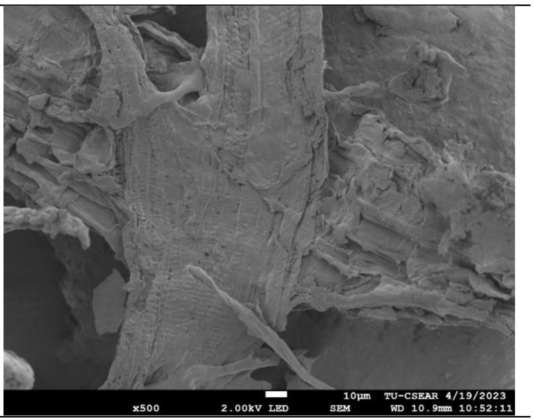
3.6 Morphology of α-cellulose and CMC analysis

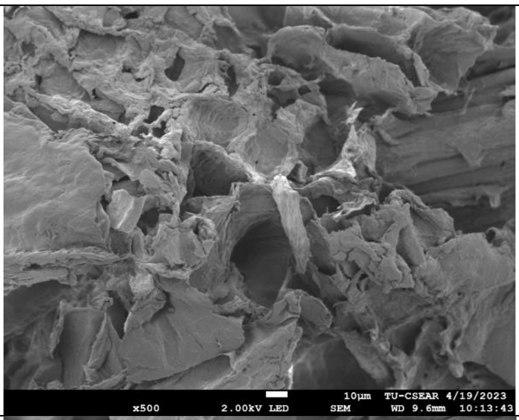
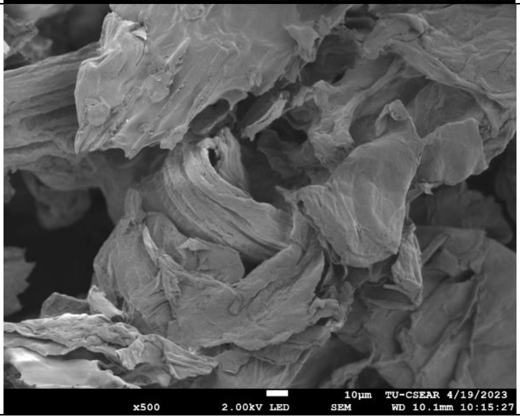
FE-SEM is a highly advanced technique used to visualize the microstructure of materials. In this study, FE-SEM was employed to examine the morphologies of α-cellulose and CMC synthesized with different concentrations of NaOH. Table 7 presents the morphological characteristics of α-cellulose and CMC at 500× magnification, synthesized using various NaOH concentrations. After alkali treatment, the surfaces of CL and RS fibers appeared rougher, with diameters ranging from 80 to 150 µm. Before cellulose extraction, the fiber surfaces were coated with substances, likely lignin and hemicellulose, which encrusted the cellulose.[25] Following extraction at different NaOH concentrations (20–60% w/v), FE-SEM images of CL and RS cellulose showed the removal of these encrusting materials from the fiber surfaces. For CMC$_{CL}$ and CMC$_{RS}$ synthesized with varying NaOH concentrations, the resulting molecules displayed a rod-like or ribbon-shaped structure, indicating the presence of some crystallinity within the material. This observed morphology is consistent with the typical structure of CMC molecules, as reported in previous studies.[19,29,31]

Table 6: The crystallinity index of α-cellulose and CMC synthesized with various NaOH concentrations estimated from XRD results.

Material	Parameters	I_{AM}	I_{002}	I_C (%)
CL	α-cellulose	1800	3441	47.69
	CMC (20% w/v of NaOH)	1300	2036	36.15
	CMC (30% w/v of NaOH)	1221	2001	38.98
	CMC (40% w/v of NaOH)	1401	2321	39.64
	CMC (50% w/v of NaOH)	1400	2264	38.16
	CMC (60% w/v of NaOH)	1693	2703	37.37
RS	α-cellulose	1860	3999	53.49
	CMC (20% w/v of NaOH)	1570	2693	41.70
	CMC (30% w/v of NaOH)	1280	2281	43.88
	CMC (40% w/v of NaOH)	1295	1974	34.40
	CMC (50% w/v of NaOH)	1788	2845	37.15
	CMC (60% w/v of NaOH)	1737	2836	38.75

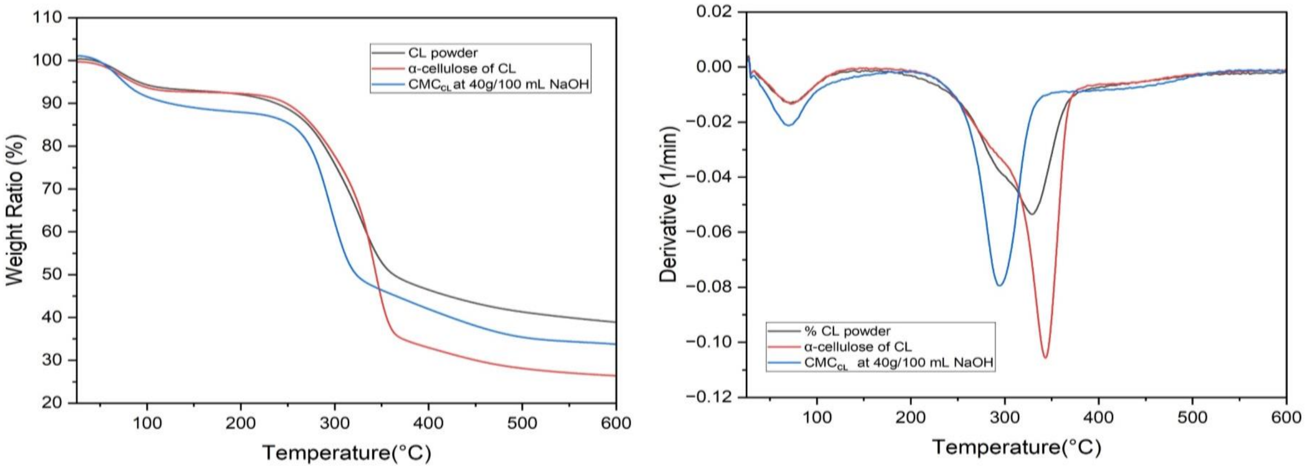
Table 7: Morphological characteristics of α-cellulose and CMC synthesized using different NaOH concentrations.

Materials	CL	RS
α-cellulose		
CMC (20% w/v of NaOH)		
CMC (30% w/v of NaOH)		
CMC (40% w/v of NaOH)		

Materials	CL	RS
CMC (50% w/v of NaOH)		
CMC (60% w/v of NaOH)		

3.7 Thermogravimetric analysis

Figs. 6 and 7 illustrate the TGA and DTG curves for raw material powders, α-cellulose, and CMC synthesized with a NaOH concentration of 40 g/100 mL. The TGA curves reveal minimal weight loss up to approximately 100 °C across all samples, indicating low moisture content. The thermal decomposition of the raw material powders begins at around 250–300 °C, demonstrating the highest thermal stability among the samples. In contrast, α-cellulose exhibits an earlier degradation onset between 220–250 °C, which can be attributed to the removal of hemicellulose and lignin during the purification process. The CMC curve shows a similar degradation onset but extends over a broader temperature range, reflecting reduced thermal stability. This reduction is likely due to the structural modifications introduced during carboxymethylation, such as decreased crystallinity and the incorporation of weaker ether bonds.



(a) (b)

Fig. 6: (a) TG and (b) DTG curves for CL powder, α-cellulose derived from CL, and CMC$_{CL}$ synthesized with 40 g/100 mL NaOH concentration.

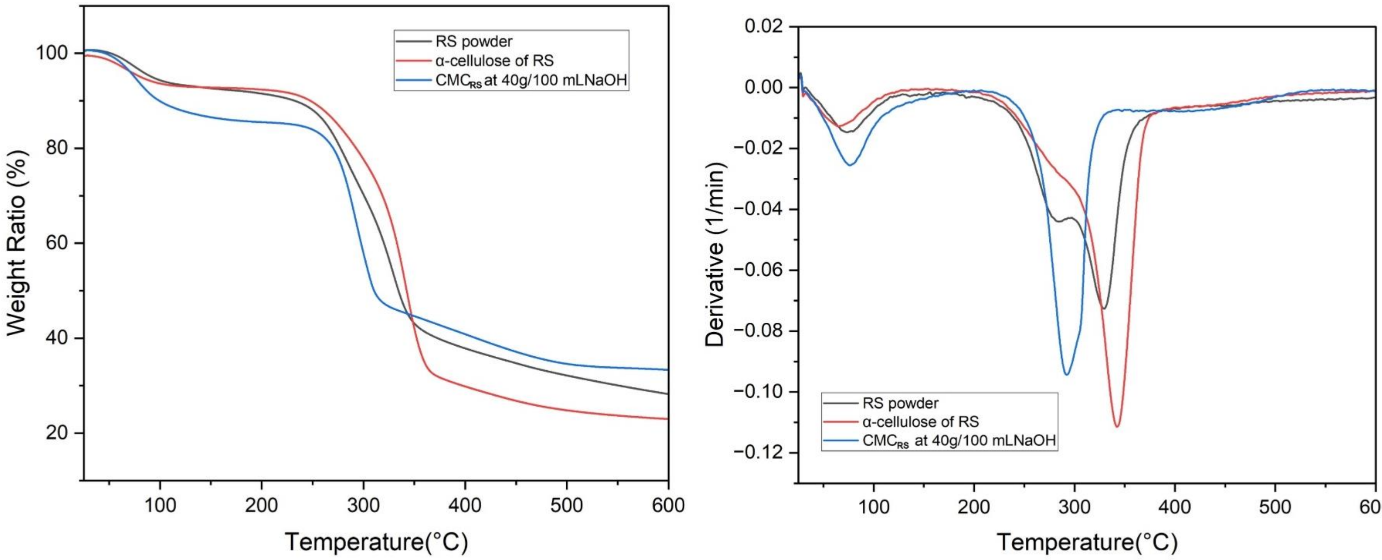


Fig. 7: (a) TG and (b) DTG curves for RS powder, α-cellulose derived from RS, and CMC_{RS} synthesized with 40 g/100 mL NaOH concentration.

In the DTG curves, the thermal decomposition peak of the raw material powders occurs at a higher temperature, centered around 300 °C, further supporting its superior thermal stability, likely due to the presence of lignin and other structurally intact components. The α-cellulose curve shows a sharper degradation peak near 280 °C, with the absence of a shoulder peak typically associated with hemicellulose, confirming its effective removal. Conversely, the CMC curve displays a broader degradation peak at a slightly lower temperature (~270 °C), indicating a reduction in thermal stability caused by the negatively charged carboxymethyl groups, which disrupt the cellulose structure.[11,46,50,51]

The residual weight at temperatures between 400 °C and 600 °C is considerably lower for α-cellulose and CMC compared to the raw powders, reflecting the absence of thermally stable lignin in the modified samples. This decrease in residue fraction at higher temperatures aligns with structural modifications in CMC, as supported by X-ray diffraction studies that reveal a less ordered arrangement compared to the parent raw materials. This analysis underscores the trade-off between enhanced functional properties and reduced thermal stability in chemically modified cellulose derivatives.

4. Conclusion

In Thailand, surplus CL and RS are often left as biomass waste in the fields following the corn and rice harvesting processes. Traditional methods for managing this waste are limited, with most of the straw and leaf being burned to prepare the land for the next crop season, contributing to air pollution. However, utilizing CL and RS as chemical feedstock for large-scale production presents a modern and sustainable solution, offering the potential to mitigate pollution. This study successfully isolated cellulose from CL and RS through chemical treatments involving alkali and sodium chlorite, effectively removing non-cellulosic components and yielding fibers with high α-cellulose content, making them suitable for CMC production. Carboxymethylation of the cellulose was achieved, producing CMC samples with degrees of substitution (DS) ranging from 0.44 to 0.89, depending on the reaction conditions. The highest DS of 0.89 was obtained for CMC_{RS} using 40 g/100 mL NaOH. Characterization techniques, including FTIR, XRD, TGA, FE-SEM, and ICP-MS, were utilized to comprehensively analyze the chemical structure, crystallinity, morphology, and purity (99.36%) of the CMC. The heavy metal content was within permissible limits, except for lead. However, increasing the concentration of chelating agents and extending the soaking time significantly improved the efficiency of lead removal. The resulting high-purity CMC is suitable for various industrial applications, including paper coating, textile sizing and printing, ceramic glazing, and oil-related uses. This research highlights a sustainable approach to agricultural waste management, potentially reducing environmental pollution while providing a pathway for diverse industrial applications of CMC.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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