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Optimization of Synthesis Conditions for Carboxymethyl Cellulose from Pineapple Leaf Waste using Microwave-Assisted Heating and Its Application as a Food Thickener

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Pineapple leaf waste, with its high cellulose content, can serve as alternative starting material for the production of carboxymethyl cellulose (CMC). In this study, synthesis conditions of CMC from pineapple leaves *via* the use of microwave heating were optimized. Box-Behnken design and response surface methodology were applied to schedule the experiments and to optimize the synthesis condition, respectively. Preparation of CMC was investigated by varying three factors, namely, sodium hydroxide (NaOH) concentration, monochloroacetic acid (MCA) dose, and etherification time. The process of carboxymethylation was optimized to produce CMC with high degree of substitution (DS). Optimal condition for CMC synthesis was noted to be 50% (w/v) NaOH solution, 8 g of MCA/g cellulose, and etherification time of 16 min; such optimal condition resulted in the maximum DS of 0.78. Synthesized CMC was utilized as a thickener for liquid foods (water, orange juice, milk, and mushroom cream soup) where 2% (w/v) as-synthesized CMC increased the viscosity of the foods and changed their characteristics from thin to nectar-like liquids.

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INTRODUCTION

Pineapple is an important agricultural produce that has widely been cultivated in Thailand and other countries in Southeast Asia. In 2019, pineapple production in Thailand was estimated to be 1.82 million metric tons (Office of Agricultural Economics 2020), accounting for 6% of the global pineapple production (Shahbandeh 2021). After the produce has been harvested, tremendous amounts of pineapple leaves, which account for

as much as 70% of the total mass of pineapple plant, is discarded as agricultural waste, causing various problems to farmers and the environment (Kengkhetkit and Amornsakchai 2012; Phan *et al.* 2021). Finding a means to utilize such a residue is clearly of interest, as it would reduce the volume of waste accumulation, minimizing the environmental impact and adding value to the waste. Since pineapple leaves contain higher than 80 wt% cellulose (dry mass), the leaves could potentially be used as a starting raw material for the production of renewable and biodegradable materials (Cherian *et al*. 2010). Numerous works have indeed reported the use of cellulose from pineapple leaves in various applications, *e.g*., as reinforcement fiber in thermoplastics (Chollakup *et al*. 2011; Kengkhetkit and Amornsakchai 2012; Balakrishnan *et al*. 2018), cellulose nanocrystals for food packaging (Santos *et al*. 2013; Sasikala and Umapathy 2018), cellulose nanofibers (Mahardika *et al*. 2018), and adsorbents for heavy metals removal (Tangtubtim and Saikrasun 2019). In some application areas such as food, pharmaceutical and medical, however, cellulose must be modified into cellulose derivatives, *e.g.*, carboxymethyl cellulose, methyl cellulose, ethyl cellulose, hydroxypropyl cellulose, and cyano-ethyl cellulose, prior to its use.

Among cellulose derivatives, sodium carboxymethyl cellulose (CMC) is one of the most important. CMC is generally prepared from natural cellulose, which is modified with the creation of ether linkages to carboxylic acid groups. CMC has broad applications in the food, pharmaceutical, cosmetic, paint, textile, paper, and consumer product industries (Abe *et al*. 2018). The global market size of CMC was valued at $1,735.2 million in 2018 and is forecasted to reach approximately $2,370.6 million by 2026, with a compound annual growth rate of 4.1% (Chouhan *et al.* 2019). In the food industry, CMC is widely used as a stabilizer, thickener, and moisture binder for improving the stability and texture of various foods and beverages (Yu *et al*. 2019). Since CMC is tasteless and odorless and can form a clear solution without any cloudiness or opacity, it is also widely used to prevent separation due to sedimentation of suspended particles and to promote desirable textural attributes and mouth feel. Increasing application of CMC in a wide variety of food and beverage products, *e.g.*, milk, ice cream, bakery products, candies, chewing gums, margarine, and peanut butter, as a thickening agent and/or stabilizer has naturally increased the demand for CMC (Bayarri *et al.* 2009; Arancibia e*t al.* 2016; Chouhan *et al.* 2019). While CMC is typically produced from cotton and wood pulp cellulose (Chouhan *et al.* 2019), several studies attempted to prepare CMC from other lignocellulosic materials such as banana pseudo stem (Adinugraha *et al*. 2005), sago waste (Pushpamalar *et al*. 2006), cotton stalk (Zhang *et al*, 2011), rice straw (Panchan and Niamnuy 2015), brewer's spent grain (Santos *et al*. 2015), corn stalk (Shui *et al*. 2017), seaweed cellulose (Lakshmi *et al*. 2017), sugarcane bagasse (Asl *et al.* 2017), and asparagus stalk end (Klunklin *et al.* 2021).

Despite the aforementioned increasing demand, synthesis of CMC by use of conventional methods requires lengthy reaction time to achieve adequate yield and degree of substitution (DS). Microwave heating, which is known for its rapid heating capability, is therefore of interest. Microwave-assisted synthesis methods have indeed been reported to provide a number of advantages over the conventional synthesis means (Kappe 2004); such advantages include shortened reaction time and increased product yield and purity (Santos *et al*. 2015; Panchan *et al*. 2018). Nevertheless, there is so far no information on microwave-assisted synthesis of CMC from pineapple leaf waste.

The objectives of this work were to synthesize CMC from pineapple leaf waste using microwave-assisted heating and to investigate the effects of various key parameters, *i.e*., sodium hydroxide (NaOH) concentration, monochloroacetic acid (MCA) dose, and

etherification time, on the DS of prepared CMC. Optimization of the synthesis condition was conducted to maximize the DS. The work also highlighted the significance of the rheological properties and potential of the as-synthesized CMC as a food thickener.

EXPERIMENTAL

Materials

Pineapple leaves (Smooth Cayenne variety) were collected from a local field in Prachuap Khiri Khan Province, Thailand. Sodium hydroxide and sodium chlorite were purchased from Ajax Finechem (Auckland, New Zealand). Monochloroacetic acid was obtained from Sigma-Aldrich (St. Louis, MO, USA). Glacial acetic acid was purchased from Merck KGaA (Darmstadt, Germany). Ethanol was purchased from RCI Labscan (Bangkok, Thailand). All solutions were prepared in deionized water (DI water). Commercial CMC with DS of 0.83 was domestically purchased from Krungthepchemi (Bangkok, Thailand).

Isolation of Cellulose from Pineapple Leaves

Pineapple leaves were washed to remove minerals; the leaves were then dried and ground into powder prior to the isolation of cellulose as per the methods of Mandal *et al.* (2015) with some modification. The ground pineapple leaves were bleached with 0.7% (w/v) sodium chlorite ($NaClO_2$) at 70 °C for 5 h. The bleaching mixture was cooled to 10 °C to avoid free-gaseous chlorine. Precipitated bleached pineapple leaves were washed with tap water until they were free of chlorine odor.

For the alkali treatment step, the bleached pineapple leaves were soaked in 5% (w/v) NaOH solution for 24 h at room temperature and then heated at 90 °C with gentle stirring for 2 h. Precipitated cellulose was filtered and washed with tap water until neutrality had been reached. The product was dried at 60 °C overnight and kept in a vacuum container. The degree of α-cellulose contained in the isolated cellulose product was determined according to the TAPPI T203 om-88 (1992) standard.

Synthesis of CMC from Isolated Cellulose

The synthesis methods of CMC were those of Mandal *et al.* (2015) and Panchan *et al.* (2018) with appropriate modification. The first synthesis step was alkalization in which 4.0 g of isolated cellulose was added into a three-neck round bottom flask, which was subsequently placed in a modified domestic microwave oven (LG, MS2343DAR, Seoul, Korea) equipped with a condenser and glass agitator. Two hundred mL of ethanol was added along with 50 mL of either 10, 30 or 50 g/100 mL aqueous NaOH solution. The mixture was agitated at 450 rpm for 30 min at room temperature to complete the alkalization reaction. Etherification reaction was then conducted by adding 1, 4.5, or 8 g of MCA/g cellulose, with an etherification period of 2, 16, or 30 min at input microwave power of 320 W. After the reaction, the content was suspended in 80% (v/v) ethanol, neutralized with glacial acetic acid, filtered, and thrice washed with 70% (v/v) ethanol. The obtained CMC cake was dried at 60 °C for 6 h and kept in a vacuum container until further analysis and use.

A total of 17 experiments were scheduled using the Box-Behnken design. Response surface methodology (RSM) was employed to analyze the experimental data to determine the optimal synthesis condition using Design Expert®9.0 (Stat-Ease Inc., Minneapolis, MN, USA). DS and purity of the prepared CMC were determined using ASTM D1439-94 standard method (ASTM 1994).

Characterization of As-Synthesized CMC

Functional groups of cellulose and CMC samples were identified using Fourier transform infrared (FTIR) spectroscopy. Prior to the analysis, a sample was dried overnight at 60 °C. Pellets were made of 0.2 mg of the sample ground with 2.0 mg of KBr; the mixture was compressed to form a transparent disk. FTIR spectra were recorded using an FTIR spectrometer (Bruker, Tensor 27, Karlsruhe, Germany) within the wavenumber range of 400 to 4000 cm^{-1}.

XRD patterns of isolated cellulose, alkali-cellulose and as-synthesized CMC samples were determined using an X-ray diffractometer (Bruker, D8 Advance, Karlsruhe, Germany) equipped with CuKα radiation in the 2θ range of 10 to 50° with a scan rate of 5° min^{-1} at room temperature. Crystallinity index (CrI) of a sample was calculated as per Eq. 1:

$$CrI = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \qquad (1)$$

where I_{200} is the maximum diffraction intensity at (200) lattice peak and I_{am} is the minimum diffraction intensity between (110) and (200) lattice peaks (Wei *et al*. 2019).

Morphologies of untreated leaves as well as those of cellulose and as-synthesized CMC were investigated using a scanning electron microscope (JEOL, JSM7001F, Tokyo, Japan). A dried sample was coated with an ultrathin layer of gold in a sputter coater prior to the scanning electron microscopy.

Determination of Solubility and Viscoelastic Properties

The methods for determining the solubility of CMC were those of Ambjörnsson *et al*. (2013) with some modification. Different masses of as-synthesized CMC powder were dissolved in 100 mL of DI water and stirred at 1200 rpm for 2 h. Each solution was filtered with gentle suction through a sintered glass crucible porosity no. 3 to separate the gel part and undissolved residuals. The insoluble part was dried at 105 °C until reaching a constant mass. The solubility was calculated as per Eq. 2,

$$Solubility\ (\%) = \frac{W_f}{W_i} \times 100 \qquad (2)$$

where W_i is the initial mass of the dried as-synthesized CMC sample and W_f is the mass of the remaining dried undissolved part after extraction with water.

Viscoelastic properties of CMC suspension were determined by dissolving CMC in DI water at a concentration of 2% (w/v). A rheometer (TA instrument, ARES-G2, New Castle, DE, USA) equipped with 40-mm sandblasted parallel plates was used; the gap between the plates was fixed at 1.0 mm. Each sample was measured by applying a strain sweep with frequency sweep in the linear viscoelastic region. The strain sweep test was conducted at a frequency of 1 Hz over the range of 0.1 to 500%. Storage modulus (G') and loss modulus (G'') were measured as a function of the angular frequency ($\omega = 0.1$ to 100 rad s^{-1}) at 30% strain. Flow behavior of the suspension under steady-state relationship

between the shear stress and shear rate is expressed by fitting the results to the Power-law model shown in Eq. 3,

$$\sigma = K\dot{\gamma}^n \qquad (3)$$

where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient (Pa·s^n), and n is the flow behavior index (dimensionless).

The effect of CMC on the behavior of liquid food samples was evaluated by measuring their viscosity change after adding 2% (w/v) CMC. The CMC solution was slowly poured into four different liquid food samples: drinking water, UHT whole milk (Thai-Denmark, Saraburi, Thailand), orange juice (Tipco, Bangkok, Thailand), and mushroom cream soup (Roza, Samut Prakan, Thailand). Each content was continuously stirred at 400 rpm for 5 min. All the food samples were measured for their viscosity using a viscometer (Brookfield Engineering, RV DVII, Middleboro, MA, USA) equipped with spindle 27 at a shear rate of 51 s^{-1} and speed of 55 rpm.

RESULTS AND DISCUSSION

Optimization of CMC Synthesis Condition

The isolation of cellulose was undertaken to observe lignocellulosic composition in pineapple leaves. The isolated cellulose from pineapple leaves were composed of α-cellulose, hemicelluloses, lignin and non-cellulosic substances, accounting for 84.18, 6.75, 1.93, and 7.18 wt%, respectively.

Box-Behnken experimental design-based predictions of the DS of CMC with different combinations of the three independent variables are summarized in Table 1. According to multiple regression analysis, second order polynomial equation was obtained as shown in Eq. 4,

$$Y = 1.38 + (1.58 \times 10^{-2})X_1 + (4.89 \times 10^{-2})X_2 + (2.89 \times 10^{-2})X_3 - (1.28 \times 10^{-3})X_2X_3$$
$$- (8.20 \times 10^{-5})X_1{}^2 - (5.28 \times 10^{-3})X_2{}^2 - (5.91 \times 10^{-3})X_3{}^2 \qquad (4)$$

where Y, X_1, X_2, and X_3 denote the DS, NaOH concentration (g/100 mL), MCA dose (g/g cellulose) and etherification time (min), respectively.

The results revealed the significance of the regression model; p-values lower than 0.05 implied that the X_1, X_2, X_3, X_2X_3, $X_1{}^2$, $X_2{}^2$ and $X_3{}^2$ terms of the model were significant independent variables of the DS with $R^2 = 0.993$. The results also indicated that the model was significant at 95% confidence level. This quadratic regression model predicted the maximum DS as 0.80. Such a DS value was obtained when the etherification reaction was carried out using 50 g/100 mL of NaOH, 8 g of MCA/g cellulose, and etherification time of 16 min at input microwave power of 320 W. To verify the predicted result, five duplicated experiments were conducted at the optimal synthesis condition; the average DS was noted to be 0.78.

Results on the comparison of the yield of α-cellulose, purity of CMC as well as DS of the as-synthesized CMC with those of CMC synthesized by various other raw materials and methods are given in Table 2. The as-synthesized CMC possessed similar levels of α-cellulose yield as well as purity of CMC and DS when compared with CMC prepared from selected other lignocellulosic wastes. Purity of the as-synthesized CMC was 93.32%; such a value meets the requirement of the GB/T1904-2005 standard (Zhang *et al.* 2011).

**Table 1.** Variance Analysis of Regression Equation

Source	Sum of Square	Df[*]	Mean Square	*F*-value	*p*-value
Model	0.5773	9	0.0641	87.47	< 0.0001
X_1	0.4540	1	0.4540	618.97	< 0.0001
X_2	0.0057	1	0.0057	7.79	0.0269
X_3	0.0133	1	0.0133	18.18	0.0037
X_1X_2	0.0029	1	0.0029	3.89	0.0892
X_1X_3	0.0006	1	0.0006	0.8010	0.4005
X_2X_3	0.0156	1	0.0156	21.30	0.0024
X_1^2	0.0045	1	0.0045	6.12	0.0426
X_2^2	0.0176	1	0.0176	24.02	0.0018
X_3^2	0.0564	1	0.0564	76.91	< 0.0001

Table 2. Comparison of CMC Derived from Various Raw Materials and Methods

Raw material	Method	Yield of α-cellulose (%)	Purity of CMC	DS	Reference
Pineapple leaves	Microwave heating	86.18	93.32	0.78	**This work**
Banana pseudo stem	Conventional heating	n/a	98.63	0.75	Adinugraha *et al.* 2005
Cotton stalk	Microwave heating	87.52	92.00	0.77	Zhang *et al.* 2011
Cotton linter waste	Ultrasound/ microwave synthesis	98.11	98.33	0.74	Hivechi *et al.* 2015
Rice stubble waste	Conventional heating	90.05	90.18	0.64	Rodsamran and Sothornvit 2020

The influence of each independent variable on the DS of the as-synthesized CMC is described using response surface plots shown in Fig. 1(a–c). DS is a major factor indicating water solubility and viscoelastic properties of CMC (Panchan and Niamnuy 2015). Therefore, it was chosen as the dependent variable to denote the CMC quality in this work. Since NaOH concentration plays an important role in the swelling of the cellulose structure and affects the reactivity of the hydroxyl group on the cellulose chain (Zhang *et al.* 2011), the isolated cellulose was treated, in the first step, with NaOH at concentrations ranging from 10 to 50 g/100 mL; alkalization reaction was therefore performed. The product of this reaction is typically called alkali-cellulose (Na-cellulose), which is highly reactive towards MCA added in the following step (Ambjörnsson *et al.* 2013). Note that MCA is an etherifying agent that substitutes the hydroxyl group of cellulose with its carboxyl group (Tasaso 2015). NaOH reacts with MCA to form substantial amount of sodium glycolate and sodium chloride by-product. Therefore, when the NaOH concentration and MCA dose increased, DS also increased (see Eq. 4). Excess amount of MCA would nevertheless lead to the formation of sodium glycolate by-product from the side reaction and hence the decreased formation of CMC with lower DS value (Jia *et al.* 2016). Extended etherification time, on the other hand, enhances the diffusion of MCA to the cellulose structure. Contact time between MCA and the activated hydroxyl group of the cellulose would also increase, leading to an increase in the DS value. However, when the etherification time was longer than 16 min under the microwave heating at 320 W, DS was noted to decrease (Figs. 1b and 1c). This is probably due to the fact that the

structure of cellulose or the completely formed CMC were destroyed when the reaction was conducted under extended microwave heating (Zhang *et al*. 2011; Panchan *et al*. 2018).
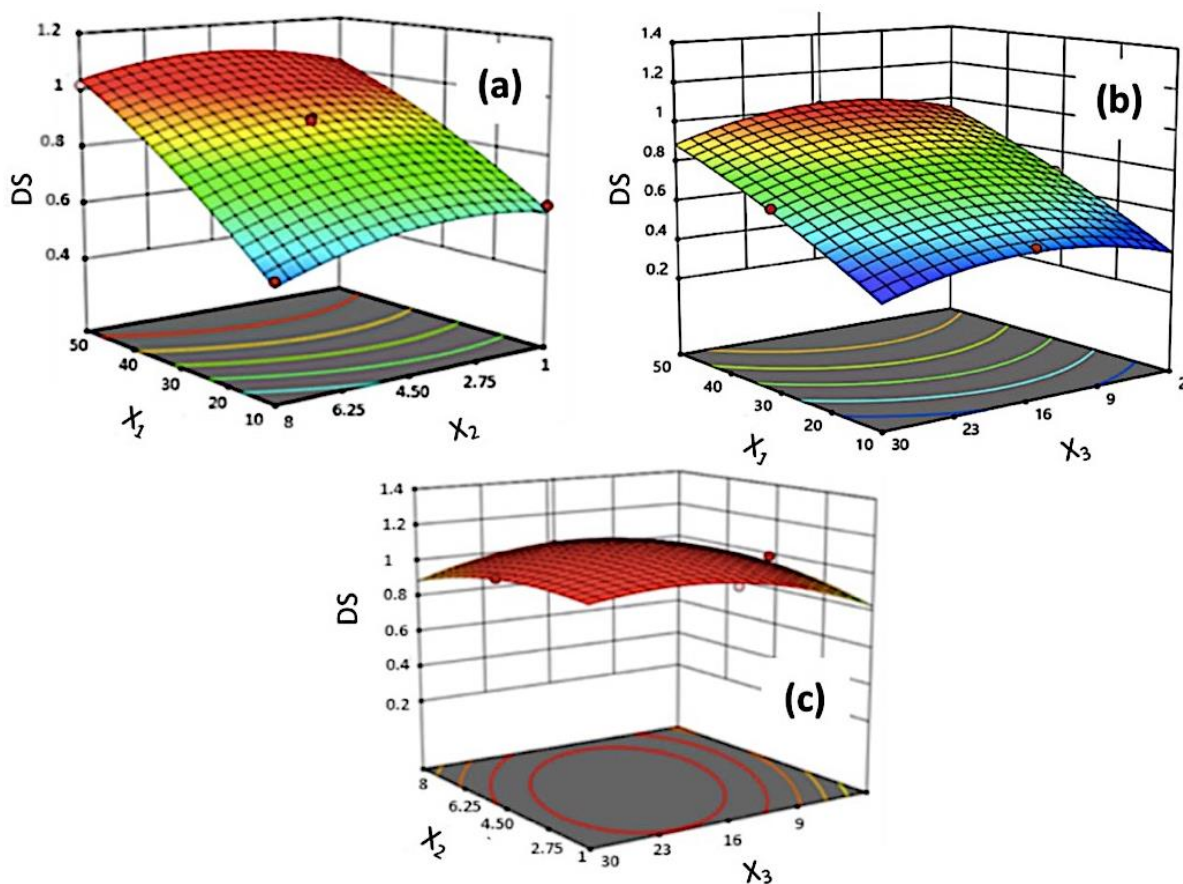

Fig. 1. 3-dimensional response surface plots for analysis of combined effect of independent variables on DS. (a) NaOH concentration (X_1) and MCA dose (X_2), (b) NaOH concentration (X_1) and time (X_3) and (c) MCA dose (X_2) and time (X_3)

Characterization of As-Synthesized CMC

XRD patterns of isolated cellulose, alkali-cellulose, and as-synthesized CMC from pineapple leaves shown in Fig. 2 signify the differences in microstructures of these samples. Diffractogram of the isolated cellulose displayed main peaks at $2\theta = 14.8°$, $16.4°$, $22.5°$, and $34.7°$, which are, respectively, the positions of (101), ($10\bar{1}$), (200), and (040) crystallographic planes typically assigned to cellulose I (Santos *et al*. 2015; Carrillo-Varela *et al*. 2018). After alkalization, the diffractogram peaks shifted to $2\theta = 12.1°$, $20.2°$, $22.0°$ and $37.1°$, which correspond to the positions of (101), ($10\bar{1}$), (200), and (040) crystallographic planes, which are typical of the cellulose II polymorph (Mansikkamäki *et al*. 2005; Oudiani *et al*. 2011). Such shifts indicated that the crystalline form of cellulose changed during the alkalization reaction (Su *et al*. 2019). When focusing on the as-synthesized CMC, it is clear that the characteristic peaks of cellulose had almost disappeared. This indicated the transformation into an amorphous phase due to the cleavage of hydrogen bonds upon being treated with NaOH (Panchan and Niamnuy 2015).

Crystallinity index (CrI) values of isolated cellulose, alkali-cellulose, and as-synthesized CMC were noted to be 93.98%, 69.16%, and 49.85%. Crystallinity of the samples decreased after alkalization and etherification due to the transformation and destruction of the crystalline cellulose (Wei *et al.* 2019). XRD patterns of the as-synthesized CMC and commercial CMC were noted to be almost similar. Crystallinity indices of the as-synthesized CMC and commercial CMC were 49.85% and 52.03%, respectively. CrI of the as-synthesized CMC was different from those of CMC prepared from other raw materials, namely, banana pseudo stem and cotton linter waste, which had the crystallinity indices of 7.37 and 38, respectively (Adinugraha *et al.* 2005; Hivechi *et al.* 2015). Such observations are due to the fact that CrI does not depend only on DS, but also on the distribution of substituents within the anhydroglucose unit (AGU), molecular weight and polysaccharide chain structure, among other factors. These parameters are related to the type of raw materials, ratio of reactants and synthesis method (Mondal *et al.* 2015; Cai *et al.* 2018; Rahman *et al.* 2021).
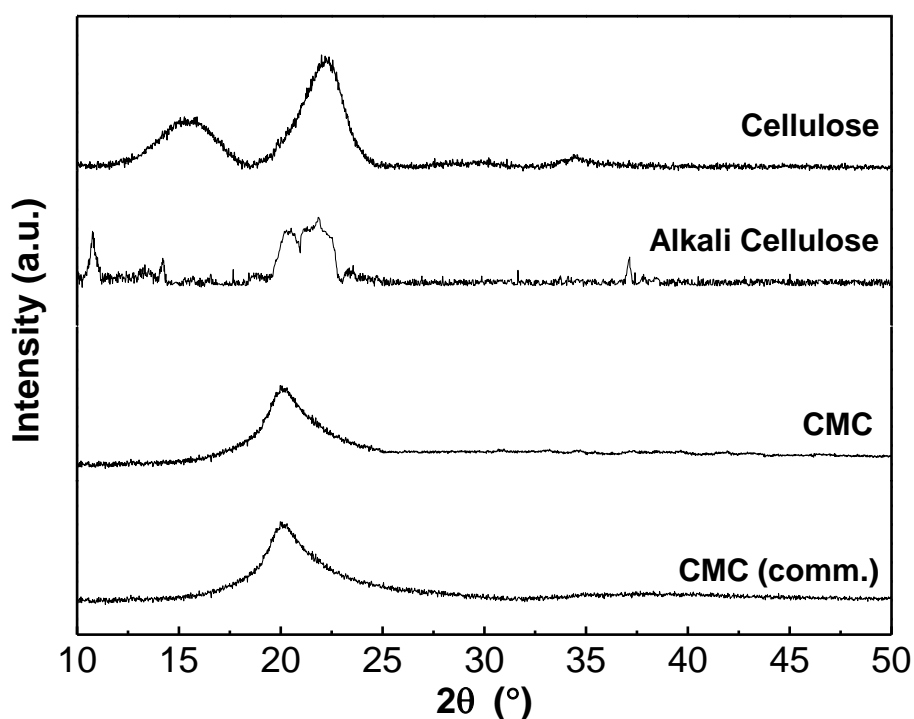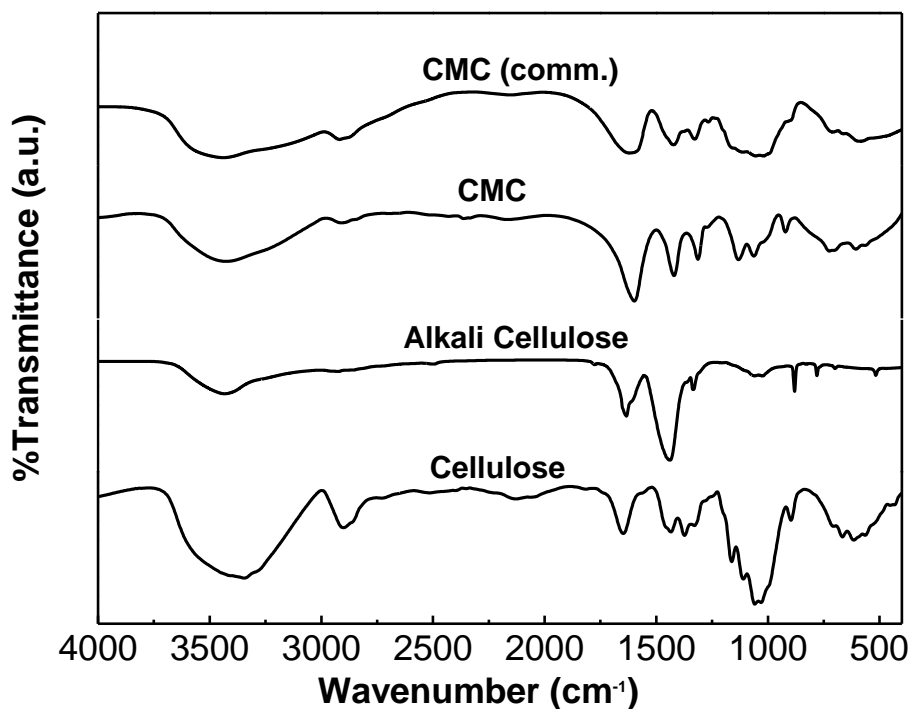

Fig. 2. XRD patterns of cellulose, alkali-cellulose, as-synthesized CMC and commercial CMC

FTIR spectra of cellulose, alkali-cellulose, and as-synthesized CMC are shown in Fig. 3. The peak appearing between 3700 to 3000 cm^{-1} is correlated with the hydroxyl group presented in cellulose, alkali-cellulose and CMC. The peaks appearing at 1060, 1112 and 1162 cm^{-1} correspond to the –O– stretching vibrations of the hydroxyl group of cellulose, stretching vibrations of ether bonds in the cellulose molecule, and stretching vibration of the ether bond (C-O-C) on the cellulose skeleton, respectively. The stronger peaks at 1430 and 1600 cm^{-1} are related to the asymmetric and symmetric vibrations of COO^{-} (carboxylate group), indicating the presence of the carboxymethylated anion in the cellulose structure. The peak at 1340 cm^{-1} represents the C-H bending, which could help confirm the formation of Na-cellulose and Na-CMC during the alkalization and etherification steps (Santos *et al.* 2015; Wei *et al.* 2019; Chagas *et al.* 2020). The intensity

of the peak at 900 cm^{-1} increased after the alkalization step. This result indicated the transformation of the crystalline structure of cellulose-I to II.

Similar spectra belonging to the as-synthesized CMC and commercial CMC could be observed. The as-synthesized cellulose also exhibited similar spectra to CMC prepared from other lignocellulosic biomasses (Adinugraha *et al*. 2005; Zhang *et al*. 2011; Hivechi *et al*. 2015; Rodsamran and Sothornvit 2020).

Fig. 3. FTIR spectra of cellulose, alkali-cellulose, as-synthesized CMC and commercial CMC

Morphological changes of the pineapple leaf fibers during different treatment stages were observed via scanning electron microscopy (Fig. 4). Untreated pineapple leaves exhibited rigid and highly ordered fibers, with diameters of around 35 μm. On the other hand, treated fibers possessed cellulose fiber bundles, with individual fibers having average diameters of around 6 μm (Fig. 4b); these changes are due to progressive removal of non-cellulosic layers. Figure 4(c) illustrates the regular and relatively smooth surface of the as-synthesized CMC, with approximate diameters of 29 μm. Such morphological characteristics are attributed to the bulky carboxymethyl group introduced into the surface of the cellulose fiber during the carboxymethylation reaction step (Santos *et al*. 2015).

Solubility and viscosity of the as-synthesized CMC were determined using water at 30 °C. The results are summarized in Table 3. The solubility decreased and viscosity increased when the CMC concentration increased.
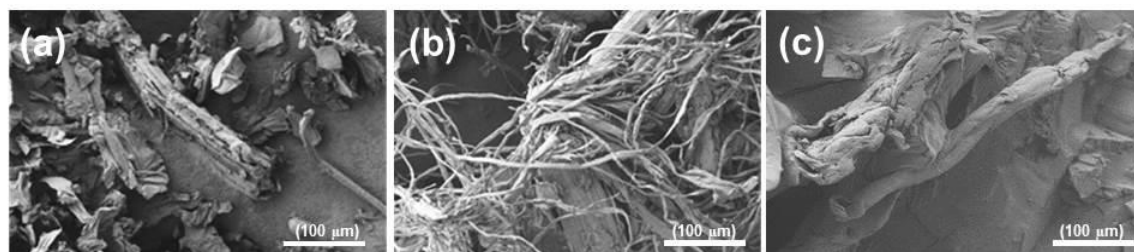
Fig. 4. Scanning electron microscopic images of (a) untreated dried pineapple leaf powder, (b) cellulose and (c) as-synthesized CMC.

Table 3. Solubility and Viscosity of as-synthesized CMC in Water at 30 °C

| Concentration of CMC (%)	Solubility (g/100 mL)	Viscosity (cP)
0	n/a	0.89
0.3	92.67	18.33
1	90.80	66.80
2	89.00	111.00

Flow Behavior of As-Synthesized CMC

Commercial food thickener (Resource, Nestle, Linda-a-Velha, Portugal) consisting of maltodextrin and xanthan gum was used as the reference thickener. Apparent viscosities of the as-synthesized CMC and commercial thickener solutions at 2 wt% concentration are shown in Fig. 5. The apparent viscosities of the as-synthesized CMC were very close to those of the commercial thickener. The two samples also exhibited similar behaviors, in that the viscosity decreased with the increased shear rate, indicating that both samples exhibited the shear-thinning behavior. These observations agree with those of Yang and Zhu (2007) and Arancibia *et al*. (2013). The observed changes can be interpreted as the result of the disruption of molecular entanglements of polymer coils upon increasing the shear rate (Chang *et al*. 2017).
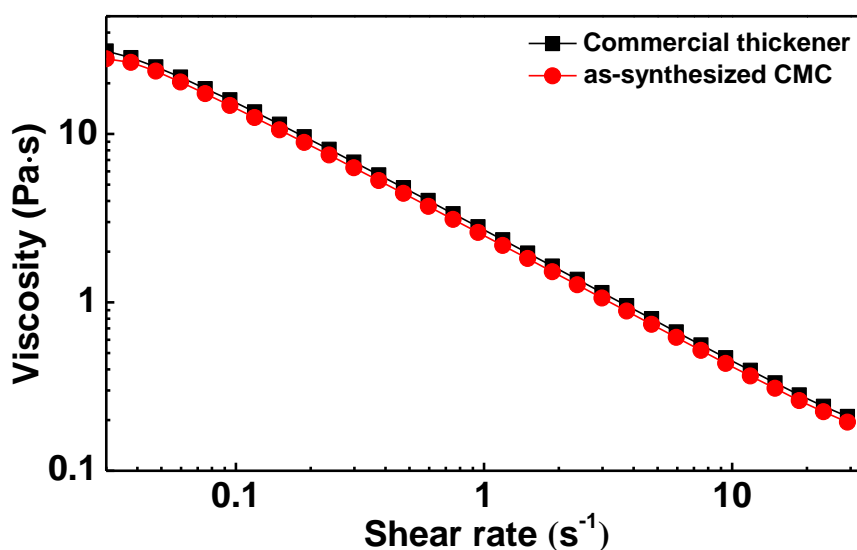
Fig. 5. Apparent viscosity changes of as-synthesized CMC and commercial thickener at 25 °C and shear rates of 0.03 to 30 s^{-1}

Figure 6 shows the plots between the shear stress (σ) and shear rate ($\dot{\gamma}$) of both the as-synthesized CMC and commercial thickener. The experimental data were well fitted to the Power-law model ($R^2 = 0.9914\text{-}0.9924$); the rheological constants are listed in Table 4. The values of the flow behavior index (n) of both the as-synthesized CMC and commercial thickener samples were less than 1, indicating the shear-thinning behavior of both samples. Such a behavior is also typical of a food thickener (Seo and Yoo 2013; Yoon and Yoo 2017). The consistency index (K) reflects the viscosity of CMC solution; K value of the as-synthesized CMC was smaller than that of the commercial CMC. This implied that the commercial thickener would lead to a slower movement of thickened water through oropharynx during swallowing when compared with the as-synthesized CMC (Pedersen *et al.* 2016, Jeong *et al.* 2019).
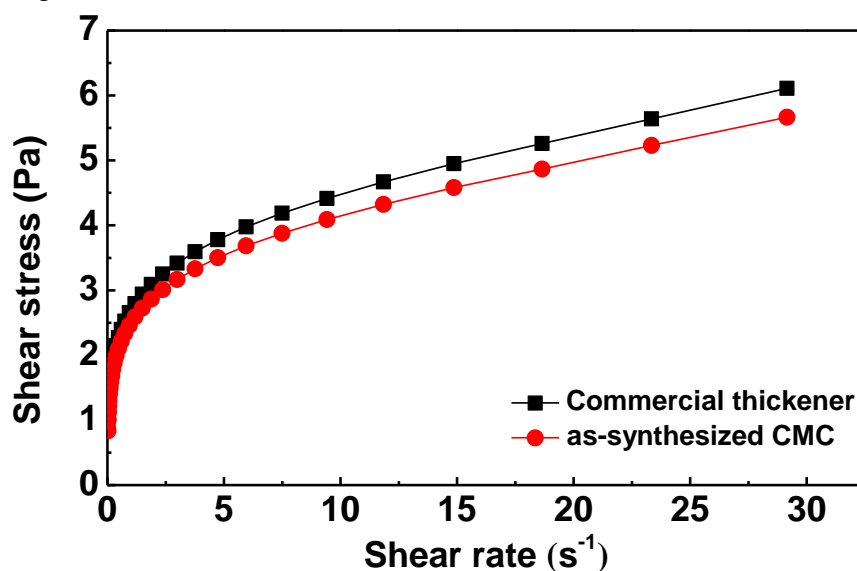
**Fig. 6.** Flow behaviors of as-synthesized CMC and commercial thickener at 25 °C and shear rates of 0.03 to 30 s^{-1}

Table 4. Power-law Model Constants of As-synthesized CMC and Commercial Thickener

Sample	Power-law model constant		
	K (Pa s^n)	n	R^2
CMC	2.4265	0.2469	0.9914
Commercial thickener	2.6190	0.2470	0.9924

Viscoelastic Properties of As-Synthesized CMC

G' reflects the elastic property, while G'' represents the viscous behavior of a material (Inglett *et al.* 2013). G' is of particular important as it is a parameter that reflects bolus formation for safe and easy swallowing (Jo *et al.* 2018). Figure 7 shows the viscoelastic behavior of water thickened by the as-synthesized CMC; the behavior of the water thickened by the commercial thickener is also illustrated. The dynamic profiles revealed the elastic over the viscous behavior. An increase in the angular frequency led to an increase in both the G' and G'' values; similar trends were reported by Kim *et al.* (2014). G' was higher than G'' over the entire frequency range for both thickeners, indicating their gel-like behavior (Barba *et al.* 2002; Moret-Tatay *et al.* 2015). Such a behavior has been interpreted as an entangled network among macromolecules (Lee and Yoo 2019).

Nevertheless, the as-synthesized CMC exhibited a larger slope of the G' curve than the commercial thickener, indicating the weaker structured system of the former (Sharma *et al.* 2017).
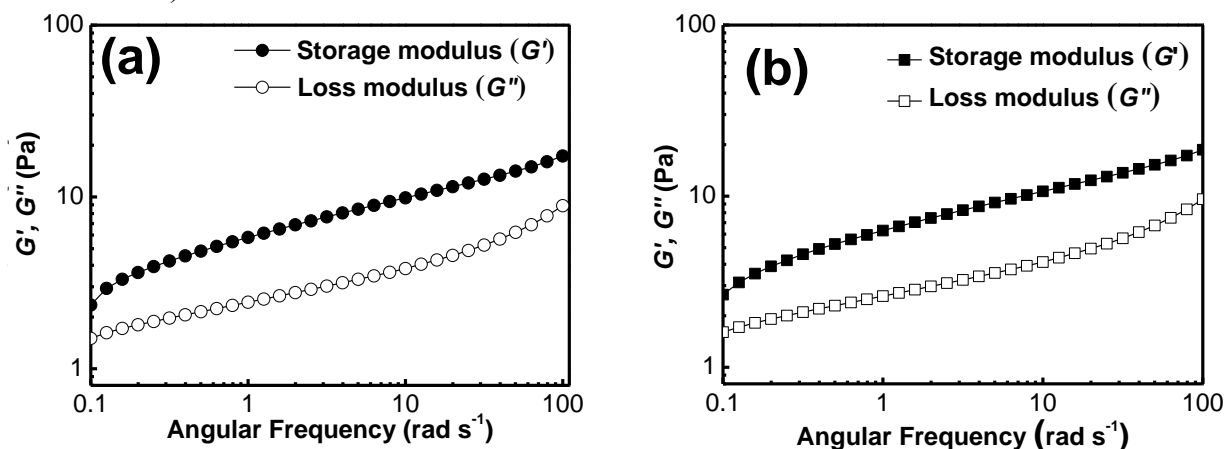
Fig. 7. Plots of storage modulus (filled symbols) and loss modulus (open symbols) versus angular frequency of (a) as-synthesized CMC from pineapple leaves and (b) commercial thickener

Experiments were conducted to evaluate the use of the as-synthesized CMC as a thickener for the selected liquid foods. The results (Table 5) illustrated that the viscosity increased by about 125, 76, and 70 folds when water, milk, and orange juice were thickened by the as-synthesized CMC. The commercial thickener increased the viscosities of the food samples by 2.15-, 2.45-, and 2.06-fold higher than the as-synthesized CMC. Such results are due to the fact that the commercial thickener contains xanthan gum, which is known for its ability to increase the viscosity of a solution even when used at a lower concentration (Desplanques *et al.* 2012). The above changes in the viscosity indicated that the behaviors of these foods had changed from thin liquids into nectar-thick consistency. In the case of mushroom cream soup, the viscosity increased only by about 1.6 folds; its behavior remained unchanged.

Based on the above-mentioned results, the as-synthesized CMC can be regarded as a potential thickener for water, milk, and orange juice because it could change the behaviors of these liquid foods into the desirable nectar-like consistency when being used at the same concentration as the commercial thickener. It is important to note that although the commercial thickener could more favorably increase the viscosity of the food samples than the as-synthesized CMC, xanthan gum in the commercial thickener can result in lower postprandial blood glucose when consumed at a larger dose (Fabek *et al.* 2014). This issue deserves careful consideration, especially in the case of elderly consumers or patients who possess swallowing and/or malnutrition issues.

Table 5. Viscosities and Behaviors of Liquid Foods Thickened by As-synthesized CMC and Commercial thickener

Sample	Viscosity (cP)			Behavior		
	Unthickened sample	Sample thickened with 2% (w/v) as-synthesized CMC	Sample thickened with 2% (w/v) commercial Thickener	Unthickened sample	Sample thickened with 2% (w/v) as-synthesized CMC	Sample thickened with 2% (w/v) commercial Thickener
Water	0.89 ± 0.01^c	111.33 ± 6.03^b	239.67 ± 17.02^a	Thin liquid	Nectar	Nectar
Milk	2.73 ± 0.02^c	207.00 ± 6.00^b	465.67 ± 23.94^a	Thin liquid	Nectar	Honey
Orange juice	3.64 ± 0.02^c	253.67 ± 8.33^b	521.67 ± 18.99^a	Thin liquid	Nectar	Honey
Mushroom cream soup	559.67 ± 6.11^c	881.67 ± 6.36^b	1226.33 ± 5.13^a	Honey	Honey	Honey

Values with different superscript letters in the same row are significantly different ($p < 0.05$).

CONCLUSIONS

1. Carboxymethyl cellulose from pineapple leaf waste was successfully synthesized by using the optimal condition of 50 g/100 mL NaOH, 8.0 g MCA/g cellulose, and an etherification time of 16 min under microwave heating at 320 W. At such a condition, the maximum degree of substitution of 0.78 was achieved.

2. As-synthesized CMC and commercial thickener exhibited similar shear-thinning behavior that is well described by the Power-law model. Such a behavior indicates its suitability as a food thickener.

3. As-synthesized CMC from pineapple leaves was characterized for its solubility and viscoelastic properties. 2% (w/v) CMC solution was noted as a non-Newtonian fluid exhibiting gel-like behavior in much the same way as the commercial thickener at the same suitable concentration. These results also reflect the suitable viscoelastic properties of the as-synthesized CMC as a food thickener.

4. As-synthesized CMC could adequately increase the viscosity of the test liquid foods, leading to the change of their behaviors from thin-liquid into nectar-like consistency. Therefore, it can be concluded that the as-synthesized CMC from pineapple leaves can serve as a potential alternative food thickener with comparable properties and behavior to the commercial food thickener.

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