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Potential of Thai rice straw as a raw material for the synthesis of carboxymethylcellulose

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Abstract

Ten different Thai rice straw cultivars were used to evaluate their potential as a raw material for the synthesis of carboxymethylcellulose (CMC). The native straw samples contained 22.4-37.5% cellulose by weight of the native biomass. After cellulose extraction by alkaline peroxide pre-treatment (5% sodium hydroxide in 2.5% hydrogen peroxide), total solid recovery ranged from 38.7-49.5% of the biomass by dry weight. In these solid samples, cellulose was the main component of the materials. Cellulose content accounted for 59.8-81.2% by weight of the pre-treated biomass depending on the specific rice straw sample. Alkalisation and methylation by sodium hydroxide and sodium monochloroacetate in the presence of solvent gave CMC yields higher than 90% by weight of extracted cellulose. The characterisation of CMC revealed that Fourier-transform infrared (FT-IR) spectra of all CMC samples showed differences in terms of carboxymethyl substitution as compared to that of cellulose. X-ray diffraction analysis suggested that crystallinity of the synthesised CMC samples was reduced as compared to that of cellulose. The CMC had a degree of substitution ranging from 0.63-0.87. The highest viscosity of CMC was found in the sample of rice straw RD 6, which had a measured viscosity of 100 cP. Scanning electron microscope analysis showed that all CMC samples had a smooth surface, indicating a high level of carboxymethylation.

Introduction

Rice is one of the major crops cultivated throughout Thailand (Rice Knowledge Bank, 2017). Abundant rice straw is left in the field after harvesting the rice grain. Most of the straw is burned in the field in order to prepare the area for the next crop season and this causes air pollution (Mäki-Arvela *et al*., 2011). Utilising rice straw to make valuable products is a promising way to sustainably solve the problem. One approach to valorising rice straw is the production of cellulose derivatives since rice straw is a lignocellulosic material containing mainly cellulose, hemicelluloses and lignin. Carboxymethylcellulose (CMC) is a cellulose derivative chemically synthesised from cellulose. It is a water-soluble polymer that can be used to form films and gels (Adinugraha *et al*., 2005; Ragheb *et al*., 2012; Biswas *et al*., 2014). CMC is off-white in colour, tasteless and flavourless (Adinugraha *et al*., 2005).

The applications of CMC are widely distributed across various industries, including food (Coffey *et al*., 2006; Rachtanapun *et al*., 2012), cosmetics, pharmaceuticals (Bajpai and Giri, 2003; Agarwal *et al*., 2013), medicine (Fan *et al*., 2014; Ninan *et al*., 2014), textiles (Ragheb *et al*., 2012), food packaging (Liu *et al*., 2014), and bionanocomposites (Yadollahi *et al*., 2014). It has been estimated that 22 million tons of food-grade CMC are consumed in the US. In Western Europe, it is equal to 93 million tons and in Japan, it is equal to 17 million tons. Annually, 5% of CMC is produced worldwide, or 6.6 billion tons, and these are used in the food industry (Coffey *et al*., 2006).

Although there has been a number of studies concerning the production of CMC from agricultural wastes and industrial wastes, for example, sugar beet pulp (Toğrul and Arslan, 2003), Cavendish banana pseudo stem (Adinugraha *et al*., 2005), sago waste (Pushpamalar *et al*., 2006), orange peel (Yaşar *et al*., 2007), papaya peel (Rachtanapun *et al*., 2007),

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palm kernel cake (Bono *et al*., 2009), date palm rachis (Ramzi *et al*., 2011), bean hulls (Ibrahim *et al*., 2011), durian rind (Rachtanapun *et al*., 2012), rice hull (Biswas *et al*., 2014), wheat straw (Jahan and Rahman, 2006; Biswas *et al*., 2014), and barley straw (Biswas *et al*., 2014), there has been a limited amount of research focusing on the production of CMC from rice straw (Jahan and Rahman, 2006; Abdel-Mohdy *et al*., 2009; Ragheb *et al*., 2012). Particularly, there is no report documenting the production of CMC from different cultivars of Thai rice straw. Consequently, the concept of valorisation and utilisation of rice straw by following the ideas of the bio-based economy (FitzPatrick *et al*., 2010) is interesting. Thai rice straw can be used as a raw material to produce CMC. The present work was therefore aimed to synthesise CMC from ten cultivars of Thai rice straw in order to evaluate the potential of Thai rice straw as a raw material to produce CMC, and to characterise the obtained CMC as compared to a commercial CMC. In addition, the present work applied newly developed, single-step cellulose extraction to isolate cellulose for CMC production. The ultimate goal of the present work was to convert valueless waste into a valuable product for the development of sustainable agriculture.

Materials and methods

Rice straw

Mature aboveground biomass of ten cultivars of rice straw was collected from local farms in Nakhon Pathom, Nakhon Nayok, Pathum Thani, Sara Buri and Nongkhai provinces, Thailand. The reproductive part was removed from the straw before air drying. Air-dried straw was cut into small pieces of approximately 2.5 cm long, before it was passed through a cutting mill (Retsch, Haan, Germany) to reduce the particle size. All the cut samples were sieved to pass through a 20-mesh sieve. A total of 10 sieved samples were stored in a separate airtight jar and were kept at room temperature for further use.

Chemicals

All chemicals used in the present work were reagent grades purchased from Sigma-Aldrich (Sigma-Aldrich Co., St. Louis, MO, USA), UNIVAR (Ajax Finechem, New South Wales, Australia), LABCHEM (Ajax Finechem, New South Wales, Australia) and EMSURE (Merck Millipore, Darmstadt, Germany). Commercial carboxymethylcellulose (product no. 419303, mw ~250,000, degree of substitution 0.9) was purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO, USA).

Chemical composition of native rice straw

All analytical methods for the determination of rice straw composition were performed following the Laboratory Analytical Procedures (LAP) prepared by the National Renewable Energy Laboratory (NREL, Golden, Colorado, USA). Moisture content and ash content of the native straw were determined following the methods described by Sluiter *et al*. (2005a; 2008a), respectively. The determination of structural carbohydrates was performed with the extractives-free biomass. Extractives-free rice straw was prepared by exhaustive extraction of rice straw with distilled water for 24 h and followed by exhaustive extraction with 95% ethanol for 24 h using Soxhlet extractor (Sluiter *et al*., 2005b). Water and ethanol extractives were dried using a rotary evaporator followed by drying in a vacuum oven to obtain the amounts of extractives. The extractives-free biomass was air-dried before it was subjected to the two-step acid hydrolysis for the determination of structural carbohydrates (Sluiter *et al*., 2008b). Neutralised hydrolysate was subjected to glucose analysis by using the glucose oxidase/peroxidase method. All experiments were performed in triplicate.

Cellulose extraction

The method used for cellulose extraction was adapted from Biswas *et al*. (2013). A rice straw sample was dried in a vacuum oven at 45°C for 24 h. Approximately 0.3 g dry weight of rice straw was weighed and transferred to a 20 mL scintillation vial. Ten mL 5% (w/v) sodium hydroxide (NaOH) in 2.5% (w/v) hydrogen peroxide (H_2O_2) was added to the vial containing the sample, screw-capped and placed in a shaking incubator (25 rpm, 35°C, 24 h). The suspension was then filtered through a Gooch crucible (pore size = 10-12 µm) to separate the solid from the liquid phase. The solid phase was washed with 50 mL distilled water followed by 10 mL 0.01 mM hydrochloric acid (HCl). The solid phase was then washed with distilled water again before it was dried in a vacuum oven at 40°C for 24 h. The recovered solid was used as the cellulose extract.

Glucose analysis for determination of cellulose

Glucose analysis by glucose oxidase/peroxidase (GOPOD) assay was adapted from Sophonputtanaphoca (2012) and was employed to determine cellulose content in native rice straw samples and cellulose extracted from the straw samples. Briefly, 20 µL filtrate was placed in a 96-well microplate followed by adding 200 µL GOPOD reagent (GOPOD assay kit, Megazyme, Ireland). Glucose solutions with the concentrations of 0.1 mg/

mL to 0.8 mg/mL were used as standards. The reaction mixture was then incubated in a microplate reader at 40°C for 20 min. The absorbance of each sample was measured using a microplate reader at 510 nm. The amounts of glucose were converted into amounts of cellulose by multiplying by a correction factor of 0.9 (converting a monomeric form into a polymeric form). The experiment was done in triplicate.

Synthesis of carboxymethylcellulose (CMC)

The CMC synthesis method followed that of Biswas *et al*. (2014). Briefly, 1 g extracted cellulose sample was mixed with 20 mL isopropanol and 5 mL NaOH (6 M) and the suspension was set aside overnight for the alkalisation process. The methylation process was initiated by adding 1.08 g sodium monochloroacetate to the suspension within 30 min and the reaction mixture was incubated at 50°C for 3 h. After that, the reaction mixture was cooled down and filtered to separate the solid from the liquid phase. The obtained CMC was purified by suspending it in 70% ethanol and neutralising the suspension with glacial acetic acid. The CMC was washed three times with 70% ethanol followed by 80% methanol and 95% ethanol, respectively. The CMC was dried in a vacuum oven at 70°C overnight. The obtained product was CMC powder. The experiment was performed in triplicate. The CMC yield was calculated using Eq. 1:

$$\text{Yield of CMC} = \frac{\textit{Weight of CMC (g)}}{\textit{Weight of cellulose (g)}} \times 100 \quad \text{(Eq. 1)}$$

The CMC synthesis condition used in the present work was the same condition applied with wheat straw and barley straw by Biswas *et al*. (2014). It can be assumed that this condition was suitable for CMC synthesis from rice straw. However, the present work did not attempt to obtain the maximum yield for each straw sample by changing the synthesis condition. Thus, the same synthesis condition was applied with all straw samples.

Characterisation of CMC

Fourier-transform infrared (FTIR) analysis

The functional groups of the extracted cellulose and the ten CMC samples were determined using FTIR spectroscopy as described by Haleem *et al*. (2014). The cellulose and CMC obtained from each rice straw sample were mixed with potassium bromide (KBr) at a ratio of 2:100 (mg, w/w). Transmission mode was used at a wavelength of 400-500 cm^{-1}. The FTIR spectra of the ten CMC samples were compared with those of a commercial CMC and extracted cellulose.

X-ray diffraction (XRD) analysis

The crystallinity of CMC was determined using XRD analysis following the method described by Rachtanapun *et al*. (2012) and Haleem *et al*. (2014). CMC samples obtained from the ten rice straw samples were dried at 105°C for 3 h before the test. The scattering angle was 2θ from 1° to 80° with a scanning rate of 5°/min. The XRD patterns of the ten CMC samples were compared with those of commercial CMC and extracted cellulose.

Determination of degree of substitution (DS)

The determination of DS followed Haleem *et al*. (2014) using the titration method. Briefly, 1 g CMC sample was mixed with 95% ethanol in a 250 mL beaker and the suspension was constantly mixed. Next, 5 mL 2 M nitric acid was added, and the suspension was mixed thoroughly for 10 min at room temperature. The mixture was then heated up to boil using a hotplate stirrer for 5 min. The mixture was then stirred for 20 min. Then, it was set aside to let the solid phase settle before it was filtered using a Gooch crucible. The solid phase was washed with 100 mL 95% ethanol followed by methanol. The solid phase was transferred into a beaker and heated until all alcohol had evaporated. The obtained solid was dried in a hot air oven at 90°C for 3 h and was cooled down to room temperature.

The dried solid (0.5 g) was put into a 250 mL Erlenmeyer flask and 100 mL distilled water was added, and the mixture was mixed constantly using a magnetic stirrer. After that, 25 mL NaOH was added into the mixture and boiled for 20 min. The obtained mixture was titrated with 0.3 M HCl using phenolphthalein as indicator. The end point of the titration was observed when the colour of the mixture had changed from light pink to colourless. The DS of the CMC was calculated using Eq. 2 and Eq. 3, respectively:

$$A = \frac{(BC - DE)}{F} \quad \text{(Eq. 2)}$$

$$\text{DS} = \frac{(0.162 \times A)}{(1\text{-}0.0058 \times A)} \quad \text{(Eq. 3)}$$

where A = milli-equivalents of acid used per 1 g of sample, B = volume of NaOH used, C = concentration of NaOH, D = volume of HCl used, E = concentration of HCl, F = weight of sample (g), 162 = molecular

weight of anhydrous glucose, 58 = net molecular weight increase in anhydrous glucose due to the substitution with each carboxymethyl group

Viscosity

The determination of viscosity of CMC was adapted from Rachtanapun *et al*. (2012) by means of Rapid Visco Analyser (RVA). The CMC solution (4%, w/v) obtained from each rice straw was prepared by mixing ground CMC with distilled water. The measurement was carried out in two steps. In the first step, the solution was stirred at a speed of 960 rpm for 10 s at 45°C. Then, the stirring speed was changed to 160 rpm for 10 min at 45°C. The experiment was performed in triplicate.

Scanning electron microscope analysis

The morphology of CMC was studied using a scanning electron microscope (SEM). The sample was coated with gold and was photographed with 5,000× magnification.

Statistical analysis

Statistical analysis of the data, including means and standard deviations (SD), was performed using Excel (Microsoft; Redmond, WA, USA). The SPSS (version 11.5) statistical package (IBM; Chicago, IL, USA) was used in the statistical analysis, where a one-way ANOVA test and Duncan's test (95% confidence) were performed.

Results and discussion

Chemical composition of native rice straw

The moisture content of ten native rice straw cultivars ranged from 6-10% by dry weight of biomass. Moisture content affects the effectiveness of acid hydrolysis employed in chemical composition analysis. High moisture content (>10%) will dilute the acid concentration, resulting in a low bias in carbohydrate content due to incomplete hydrolysis of carbohydrate polymers to their constituent monomers (Hames *et al*., 2008). In addition, high moisture content will alter the alkaline concentration in the same manner when cellulose extraction is conducted in the subsequent process. The chemical composition of ten native rice straw cultivars is shown in Table 1 from which it is apparent that the cellulose content ranged from 22.4-37.5%. The amounts of cellulose in all samples, except Suphanburi 1, were comparable to the amounts in Thai rice straw reported previously (Weerasai *et al*., 2014). The total amount of water and ethanol extractives found in ten native rice straw cultivars were below 23%. Extractives are non-structural components of biomass samples that are soluble, either in water or ethanol, during exhaustive extraction. Water soluble materials (water extractives) may include inorganic material, non-structural sugars, and nitrogenous material. Ethanol-soluble material (ethanol extractives) includes chlorophyll, waxes, and other minor components (Sluiter *et al*., 2005b). A previous study by Sophonputtanaphoca *et al*. (2018) showed that water extractives obtained from the exhaustive 24 h Soxhlet extraction of rice straw RD 41 contained non-structural sugars, i.e. glucose, fructose, and non-digestible oligosaccharides. The highest ash content (14.7%) was found in Suphanburi 1, whereas Phitsanulok 2 contained the lowest (5.8%).

Total solid recovery and cellulose content after extraction

The total solid recovery of the ten native rice straw cultivars after the cellulose extraction are shown in Table 2. The recovery ranged from 38.7-49.5% by dry weight of biomass.

Table 1. Chemical composition of different rice straw cultivars.

Cultivar	% by dry weight of native biomass			
	Cellulose	Water extractives	Ethanol extractives	Ash
Suphanburi 1	22.4 ± 0.2^{a}	17.2 ± 2.0^{b}	4.7 ± 1.2^{ab}	14.7 ± 0.8^{h}
Pathum Thani 1	34.6 ± 0.7^{b}	16.1 ± 0.8^{ab}	3.9 ± 0.5^{a}	11.3 ± 0.5^{cd}
Pathum Thani 60	32.5 ± 4.6^{b}	14.7 ± 0.8^{ab}	3.7 ± 0.7^{a}	11.9 ± 1.0^{de}
Phitsanulok 2	32.0 ± 2.4^{b}	15.4 ± 1.3^{ab}	4.4 ± 1.3^{a}	5.8 ± 0.8^{a}
RD 6	32.0 ± 0.6^{b}	14.8 ± 0.5^{ab}	4.0 ± 1.1^{a}	13.4 ± 0.3^{fg}
RD 31	35.8 ± 4.4^{b}	13.8 ± 2.6^{a}	6.4 ± 1.4^{bc}	12.5 ± 1.1^{ef}
RD 35	33.4 ± 2.0^{b}	17.2 ± 0.4^{b}	4.1 ± 0.6^{a}	10.3 ± 0.3^{bc}
RD 41	35.0 ± 0.5^{b}	15.5 ± 1.9^{ab}	3.0 ± 0.7^{a}	9.7 ± 0.2^{b}
RD 49	37.5 ± 6.9^{b}	15.3 ± 1.8^{ab}	4.2 ± 1.2^{a}	14.4 ± 0.3^{gh}
Khao Dawk Mali 105	35.8 ± 5.0^{b}	16.1 ± 1.5^{ab}	6.5 ± 0.6^{c}	10.7 ± 0.0^{bc}

Data are means ± SD. Means with different letters within one column are significantly different ($p < 0.05$).

Table 2 reveals the cellulose content of the ten native rice straw cultivars after cellulose extraction using alkaline peroxide pre-treatment. The results suggest that the majority of recovered solids were cellulose as the highest cellulose content was ~80%. Alkaline peroxide (a combination of NaOH and H_2O_2) is effective in removing lignin from lignocellulosic biomass and retaining polysaccharides for subsequent processes (Karp *et al*., 2015). This cellulose extraction method proved to be an appropriate method for cellulose extraction since more than 60% of recovered solids in all samples were cellulose.

Plant cell wall composition varies between and within species, tissue types, developmental stages, and environments (Tanger *et al*., 2015). In the present work, the effect of different species, tissue types, and developmental stages were ruled out. Different rice cultivars play an important role in differences of cellulose content in native straw as reported by Tanger *et al*. (2015), who determined the influence on the cell wall composition of 20 different rice straw varieties. In addition to the original cellulose content in the straw samples, recalcitrance and heterogeneity of the biomass due to other components (hemicelluloses and lignin) and cell wall architecture (how these components are assembled together) of rice straw are key factors that influence total solid recovery and cellulose content after the pre-treatment (Tanger *et al*., 2015). These factors determine how well chemicals (in the present work, alkaline peroxide) penetrate the cell wall and solubilise hemicelluloses and lignin, leaving mainly cellulose in the total solid recovered. Therefore, different rice breeds (different genotypes) display different cellulose contents and properties in their native straws. The ability of extraction to obtain cellulose by pre-treatment varied according the reasons described above.

Yield of CMC

The yields of CMC obtained from the ten native rice straw cultivars are shown in Table 2, and were higher than 90% by dry weight of extracted cellulose. The yield of CMC obtained in the present work was lower than that of CMC synthesized from the durian rind (Rachtanapun *et al*., 2012). In that study, the yield depended on NaOH concentrations during the synthesis process and the yield increased as the DS increased. However, in the present work, the NaOH concentration was constant during the synthesis.

The yield of CMC largely depended on the feasibility of carboxymethyl substitution. In this step, 1 g cellulose extract (recovery solid) was subjected to alkalisation followed by methylation to synthesise CMC. The cellulose extract of different rice straw cultivars contained different amounts of cellulose. However, most of the CMC yields were not significantly different (Table 2). This suggests that some cultivars with low amounts of cellulose in recovery solids and high CMC yields, such as Suphanburi 1, RD 31 and Khao Dawk Mali 105, had a high feasibility of carboxymethyl substitution thus resulting in high CMC yields regardless of the amounts of cellulose. The substitution occurs more when the amorphous part of the cellulose structure is larger (Manguiat *et al*., 2001; Asl *et al*., 2017). These results also confirm that the complexity of the cell wall architecture varies depending on rice cultivars.

Table 2. Total solid recovery, cellulose content, CMC yield, degree of substitution (DS) and viscosity obtained from different rice straw cultivars.

Cultivar	Total solid recovery[1] (%)	Cellulose[2] (%)	CMC yield[2] (%)	DS	Viscosity (cP)
Suphanburi 1	38.7 ± 2.6^{a}	63.0 ± 9.2^{ab}	98.7 ± 0.6^{a}	0.77 ± 0.1^{de}	49 ± 6^{a}
Pathum Thani 1	49.5 ± 2.6^{c}	72.2 ± 2.9^{bcd}	95.5 ± 2.2^{a}	0.75 ± 0.0^{cde}	64 ± 2^{b}
Pathum Thani 60	45.5 ± 5.4^{bc}	68.9 ± 2.5^{abc}	95.5 ± 2.6^{ab}	0.72 ± 0.1^{bcd}	54 ± 2^{a}
Phitsanulok 2	42.6 ± 0.5^{ab}	69.9 ± 2.0^{abc}	94.4 ± 5.8^{ab}	0.70 ± 0.1^{abcd}	76 ± 3^{c}
RD 6	45.6 ± 1.5^{bc}	79.4 ± 4.7^{cd}	94.1 ± 4.0^{a}	0.80 ± 0.0^{ef}	100 ± 5^{d}
RD 31	39.7 ± 1.1^{ab}	59.8 ± 8.4^{a}	95.4 ± 4.6^{a}	0.68 ± 0.0^{abc}	54 ± 1^{a}
RD 35	45.9 ± 6.8^{bc}	80.8 ± 8.3^{d}	97.0 ± 1.5^{a}	0.74 ± 0.0^{cde}	66 ± 3^{b}
RD 41	46.0 ± 1.6^{bc}	81.2 ± 7.6^{d}	97.5 ± 2.6^{a}	0.64 ± 0.0^{ab}	67 ± 8^{b}
RD 49	40.8 ± 2.0^{ab}	74.0 ± 7.9^{bcd}	98.0 ± 2.0^{a}	0.87 ± 0.1^{f}	65 ± 3^{b}
Khao Dawk Mali 105	45.1 ± 3.5^{bc}	64.9 ± 3.1^{ab}	97.8 ± 2.3^{a}	0.63 ± 0.04^{a}	62 ± 2^{b}

[1]By dry weight of native biomass.

[2]By dry weight of pre-treated biomass.

Data are means ± SD. Means with different letters within one column are significantly different ($p < 0.05$).

Characterisation of CMC

Fourier-transform infrared (FTIR) analysis

Figure 1 illustrates the FTIR spectra of CMC obtained from the ten native rice straw cultivars as compared to that of a commercial CMC with a DS of 0.9 and the spectrum of cellulose extracted from Khao Dawk Mali 105. The FT-IR spectra of CMC obtained from the cellulose of rice straw are similar to the spectra reported previously by Adinugraha *et al*. (2005), Rachtanapun *et al*. (2012) and Haleem *et al*. (2014). Those studies used Cavendish banana pseudo stem cellulose, durian rind cellulose and cotton gin waste cellulose, respectively, as raw materials for the CMC synthesis. The peaks at 1618.91 and 1423.7 cm^{-1} indicated the presence of a carboxymethyl substituent. Carboxyl groups and their salts have wave numbers at about 1600-1640 cm^{-1} and 1400-1450 cm^{-1} (Adinugraha *et al*., 2005). The band at 3435.04 cm^{-1} is due to OH–stretching (Abdel-Mohdy *et al*., 2009). The band at around 1423 cm^{-1} is assigned to $–CH_2$ scissoring (Haleem *et al*., 2014). The band at 2920 cm^{-1} is due to carbon-hydrogen (C–H) stretching vibration. The strong absorption band at 1618.91 cm^{-1} confirms the presence of COO^-. The band at 1052.17 cm^{-1} is due to $–CH–O–CH_2$ stretching (Rachtanapun *et al*., 2012).

The FTIR spectra of the CMC obtained from the ten native rice straw cultivars are similar to that of commercial CMC, regardless of the rice cultivar. Slight shifts in some peaks as compared to the commercial one can be found in different CMC samples (Abdel-Mohdy *et al*., 2009; Cheng and Biswas, 2011; Haleem *et al*., 2014), regardless of the DS of the CMC (Mondal *et al*., 2015). For example, the slight shift at 3435 cm^{-1} (commercial CMC) and 3393 cm^{-1} (synthesized CMC) is in the range of the broad 3200-3600 cm^{-1} band that is due to OH-stretching (Cheng and Biswas, 2011). The band at around 1600 cm^{-1} is due to C=O stretching (1618 cm^{-1} = commercial CMC, 1587 cm^{-1} = synthesised CMC) (Rachtanapun *et al*., 2012). The DS values of synthesised CMC from rice straw were 0.6-0.8 and the DS of commercial CMC was 0.9. The differences in the DS values of CMC did not affect the FTIR spectra as reported by Mondal *et al*. (2015). The FTIR spectra for the synthesised CMC from corn husk (DS = 2.41) and standard CMC (DS = 0.8) were almost similar (Mondal *et al*., 2015). The differences between the spectra of all CMC and cellulose were observed at 1618.91 and 1423.7 cm^{-1} due to the presence of the carboxymethyl substituent that was only found in CMC. This finding agrees with Adinugraha *et al*. (2005).

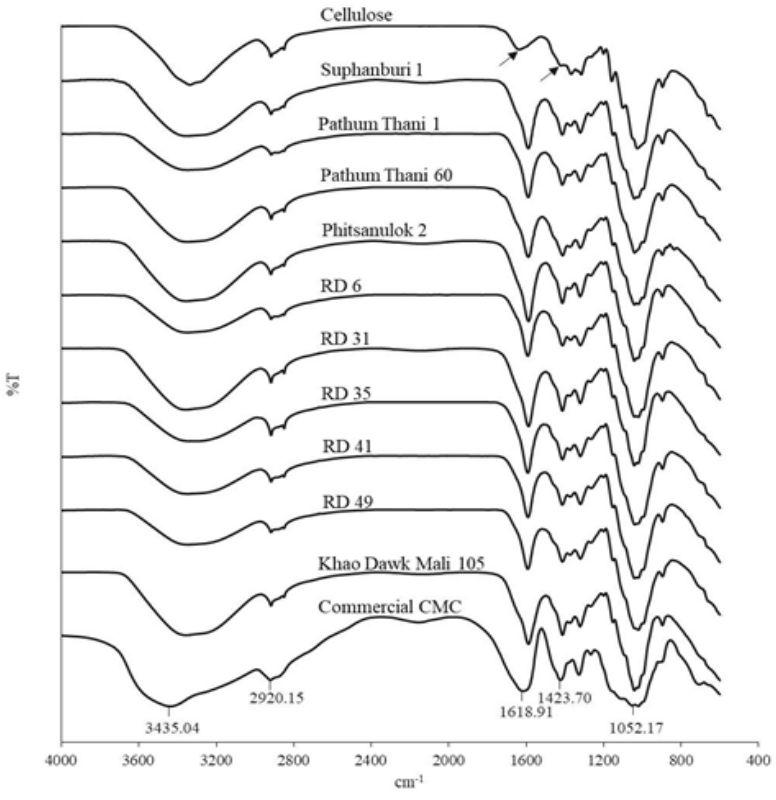

Figure 1. Comparison of FTIR spectra of CMC obtained from the 10 samples of rice straw, a commercial CMC with a DS of 0.9, and cellulose of Khao Dawk Mali 105. Arrows indicate the differences in the spectrum bands between cellulose and CMC.

X-ray diffraction (XRD) analysis

X-ray scattering techniques revealed information about the crystallographic structure of CMC and cellulose. X-ray diffractograms of CMC obtained from the ten native rice straw cultivars were higher as compared to those of commercial CMC, as observed in the height of the peaks (Figure 2). This indicates that all the synthesised CMC had higher crystallinity than that of the commercial CMC. In contrast, all CMC obtained from the ten native rice straw cultivars had lower crystallinity as compared to that of cellulose extracted from Khao Dawk Mali 105. The crystallinity of cellulose was associated with inter- and intra-molecular hydrogen bonds of cellulose (Adinugraha *et al*., 2005). It is obvious that alkalisation during the CMC synthesis reduced the crystallinity of the material.

Determination of degree of substitution (DS)

The degree of substitution (DS) is the average number of hydroxyl groups in the cellulose structure which have been substituted by carboxymethyl or sodium carboxymethyl groups at carbon 2, 3 and 6 (Asl *et al*., 2017). In general, the alkalisation of cellulose with sodium monochloroacetate gave a DS of carboxymethylcellulose in the range of 0.4-1.3. CMC is completely soluble at a DS of above 0.4 and its water solubility increases as the DS increases (Waring and Parsons, 2001). The DS values of CMC obtained from the ten native rice straw cultivars are shown in Table 2. The DS varied from 0.63-0.87. The maximum DS found in the present work was comparable to the DS of CMC obtained from the cotton gin waste studied by Haleem *et al*. (2014), when the same amount of NaOH was used during alkalisation. The concentration of NaOH affects DS values. A study reported by Asl *et al*. (2017) revealed that the maximum DS of 0.78 was obtained when CMC was synthesised from sugarcane bagasse by using 30% (w/v) NaOH during the carboxymethylation procedure. A study by Asl *et al*. (2017) also showed that NaOH concentrations above 30% yielded the CMC with a decrease in DS values since the undesired side reaction yielding sodium glycolate dominated the CMC production. Abdel-Mohdy *et al*. (2009) revealed that different CMC preparations (e.g. different solvents or NaOH concentrations) resulted in different DS of the CMC synthesised from rice straw.

The differences in the DS values of all CMC

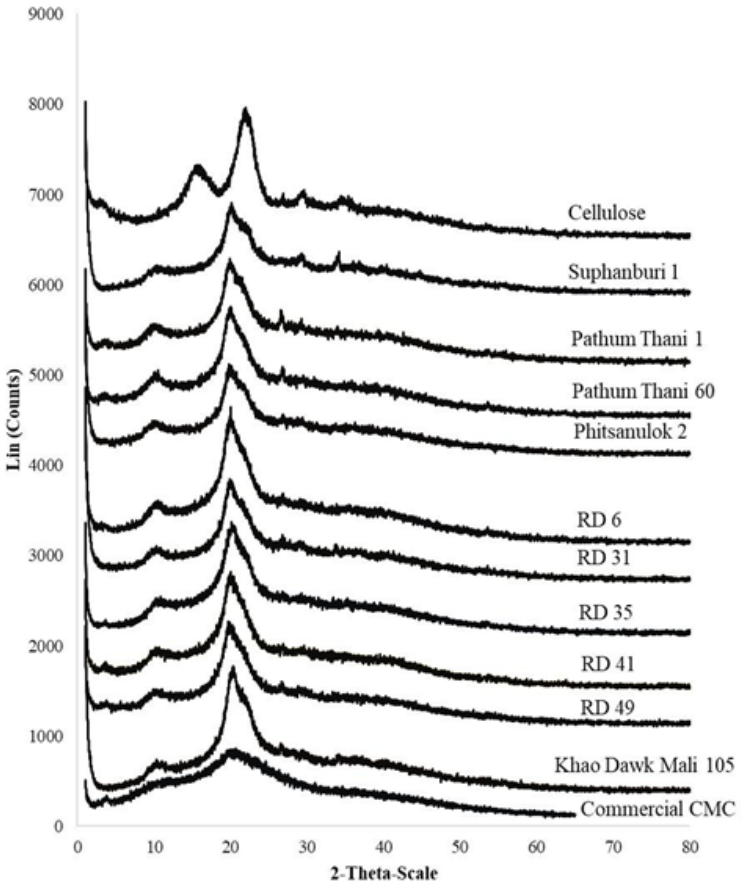

Figure 2. Comparison of X-ray diffractograms of CMC obtained from the 10 samples of rice straw, a commercial CMC with a DS of 0.9, and cellulose of Khao Dawk Mali 105.

obtained from rice straw may have been a result of the source of cellulose (different rice cultivars) (Asl *et al*., 2017) since the NaOH concentration was fixed in the present work. Different rice cultivars influenced the feasibility of carboxymethyl substitution due to the variation in the complexity of the cell wall architecture, as described earlier. Therefore, the DS of the individual CMC varied due to that reason. The crystallinity and regularity of cellulose structure based on its origin affect the DS value. The feasibility of substitution occurs more often in the amorphous part of the cellulose structure (Manguiat *et al*., 2001; Asl *et al*., 2017). In terms of crystallinity levels, all synthesised CMC from rice straw had higher crystallinity than that of the commercial CMC (Figure 2). This implies that the CMC from rice straw contained the less amorphous part of their cellulose structure. Thus, carboxymethyl substitution was less feasible as compared to the commercial CMC. Consequently, their DS values were lower than that of the commercial CMC.

Viscosity

The moisture content of all CMC samples ranged from 10-12%. In the preparation of 4% (w/v) solution for viscosity determination, the moisture content of each sample was considered. Therefore, the weight of each sample was based on its dry weight. The determination of the viscosity of a solution reveals its resistance to gradual deformation by shear stress caused by intermolecular cohesive forces. CMC concentration, temperature and DS are the forces that affect the viscosity of a CMC solution (Asl *et al*., 2017). The maximum viscosity (100 cP), as shown in Table 2, was found in the CMC obtained from rice straw RD 6. As the DS of CMC increases, the viscosity increases (Ragheb *et al*., 2012; Asl *et al*., 2017). This can be explained by the fact that increasing DS provides a greater number of hydrophilic groups in polymer structures, resulting in increasing viscosity (constant temperature). Likewise, fewer hydrophilic groups are present in the polymer structure as DS decreases (Asl *et al*., 2017). These facts are true for the maximum viscosity reported here. However, the relationships between DS and viscosity, led to some disagreement with the explanation above. Some CMC obtained from some rice straw cultivars had lower viscosity, even though their DS was higher (e.g. Suphanburi 1). This also applied to the viscosity and the DS of the commercial CMC determined in the present work (viscosity = 66 cP, DS = 0.9). It is also noted that the viscosity of a solution is a function of the molecular weight of the polymer (Coffey *et al*., 2006). However, a limitation of the present work was that it did not encompass molecular weight determination.

It is expected that the synthesised CMC, especially CMC obtained from rice straw RD 6 (the highest viscosity), may be useful as a thickening agent in food and personal care products since CMC is approved for use as food additives. The chemicals and the CMC synthesis condition were the same as those used by Biswas *et al*. (2014), whose condition was applied to wheat straw and barley straw. As recommended by that study, the synthesised CMC may be used as a thickener in food. Thus, all synthesised CMC from the ten native rice straw cultivars may be used as thickeners with varying degrees of viscosity, depending on product properties.

Scanning electron microscope (SEM) analysis

SEM analysis revealed the morphological structure of the CMC obtained from the ten native rice straw cultivars (Figure 3) which show comparable morphological structures. The external surfaces of the CMC samples show that the cellulose fibres were intensely carboxymethylated because of the smooth structure (Haleem *et al*., 2014).

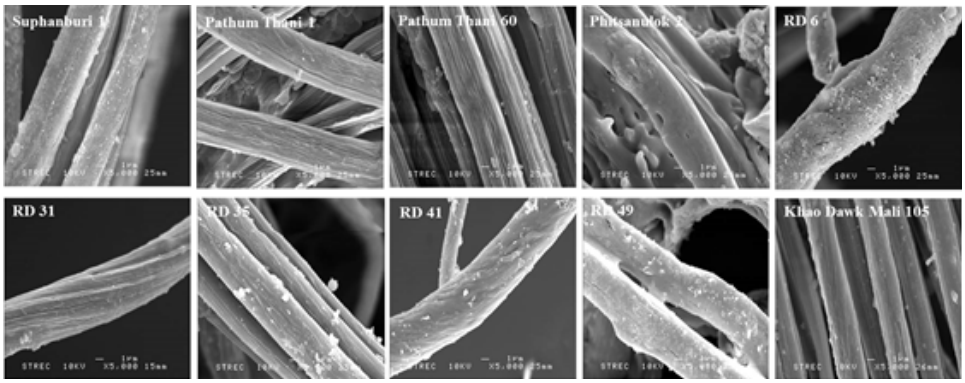

Figure 3. Morphological structures of CMC obtained from the 10 samples of rice straw analysed by SEM with 5,000× magnification.

Conclusion

A total of ten native rice straw cultivars were used as raw materials for cellulose production and CMC synthesis. Different rice cultivars (genotype) influence cellulose content, complexity of cell wall architecture, CMC yield, ability of cellulose extraction, total solid recovery, crystallinity of cellulose and CMC, DS of CMC, and viscosity. The cellulose extraction was accomplished by alkaline peroxide pre-treatment and the highest cellulose content obtained after the extraction was approximately 80% by dry weight of biomass (for rice cultivars: RD 6, RD 35, and RD 41). After the alkalisation and methylation processes, the CMC of the ten native rice straw cultivars were successfully synthesised. Less complexity in the cell wall architecture enhances the cellulose content in the recovery solid and the CMC yield. Considering the highest cellulose content, total solid recovery, and CMC yield obtained from those three rice cultivars (RD 6, RD 35, and RD 41), 1 kg (dry weight) of the native straw will yield ~340 g CMC. The characterisation by FTIR, XRD, and DS analyses confirmed the identity of CMC. Crystallinity levels and source of cellulose play a major role in the differences in the DS of all the synthesised CMC. High crystallinity results in a low DS value due to the lower feasibility of substitution. The viscosity of all CMC varied, depending partly on their DS values. Viscosity increases as the DS of CMC increases. The highest viscosity was found in CMC obtained from rice straw RD 6, which makes it suitable for application in high viscosity products. SEM analysis revealed that all CMC samples were intensely carboxymethylated. Further study on solubility, degree of polymerisation and molecular weight and its relationship with the viscosity should be carried out in order to attain a complete profile of the properties of CMC from Thai rice straw.

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