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Physicochemical properties and textile utilization of low- and moderate-substituted carboxymethyl rice starches with various amylose content

Jutamas Tatongjai, Namfone Lumdubwong*

Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

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ABSTRACT

The effects of low and moderate levels of degree of substitution (LDS ~0.2 and MDS ~0.6) on physicochemical and textile printing properties of carboxymethyl rice starches (CMRS) containing different amylose (AM) content were investigated. With a similar level of AM, MDS CMRS displayed higher cold water solubility (CWS), yield stresses, and apparent viscosities than those of LDS CMRS. Furthermore, they were superior to LDS CMRS when used as textile print paste. AM also influenced the properties of CMRS with similar DS. When AM increased, CWS of LDS CMRS increased. However, yield stresses and apparent viscosities of CMRS decreased with increased AM. MDS waxy CMRS print paste provided the least color strength among other MDS CMRS. Nonetheless, DS was shown to have a far greater effect than AM on determination of CMRS properties.

1. Introduction

Carboxymethylation is an etherification reaction which has been commonly used for chemical modification of starch. The goal of the modification is to substitute carboxymethyl groups (CH_2COO^-), which are negatively charged, for hydroxyl groups (–OH) in starch molecules (Volkert, Loth, Lazik, & Engelhardt, 2004). As a result of the substitution reaction, many functional properties of carboxymethyl starch (CMS) such as cold water solubility, paste and film clarity, and paste and gel storage stability are significantly improved (Kittipongpattana, Chaitep, Kittipongpatana, Laenger, & Sriroth, 2007; Kwon, Cho, Park, & Ko, 1998; Sangseethong, Ketsilp, & Sriroth, 2005). This has resulted in various applications of carboxymethyl starch: in pharmaceutical excipients, textile printing pastes, adhesives, waste absorbents, paper, and medical poultices (Tijsen, Voncken, & Beenackers, 2001). To determine levels of starch modification, a degree of substitution (DS) – the average number of substituents, which in this case is the number of carboxymethyl groups per anhydroglucose unit (AGU) of the starch polymer – is used as an indication. DS values range from 0 to 3 (Jie, Wen-ren, Manurung, Ganzeveld, & Heeres, 2004; Sangseethong et al., 2005; Volkert et al., 2004).

Several previous studies have focused on factors affecting values of DS of CMS, and optimization of CMS production with specified DS (Hebeish & Khalil, 1988; Kittipongpatanaa, Sirithunvaluga, & Laenger, 2006; Kwon et al., 1998; Ragheb, El-Sayiad, & Hebeish, 1997; Sangseethong et al., 2005; Stojanovic, Jeremic, & Jovanovic, 2000; Tijsen et al., 2001; Volkert et al., 2004). However, studies of the effects of DS on the physicochemical and functional properties of CMS have been quite limited. Bhatacharyya, Singhal, and Kulkarni (1995) reported that when DS of CM corn and amaranth starches increased from 0.10 to 0.20, both peak viscosity and freeze–thaw stability of CMS paste samples decreased. Sangseethong et al. (2005) found that the viscosity of CMS samples increased when their DS increased up to 0.40. However, the study mentioned that all cassava CMS samples with 0.03–0.70 DS were completely soluble in cold water, regardless of their DS. It is interesting to further explore whether more properties of CMS besides those properties are affected by their DS level.

The amylose content (AM) of starch also influences many physicochemical and functional properties of starch products. The hardness of rice starch gels, the textural properties of cooked rice (Yu, Ma, & Sun, 2009), and the tensile strength of starch film (Lloyd & Kirst, 1963) are examples of the properties affected by the ratio of AM. It is also worthwhile to investigate whether AM plays an important role on the properties of CMS with similar DS level.

To the authors' knowledge, to date no study has been done on the physicochemical and functional properties of CMS with differ-

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* Corresponding author. Tel.: +66 25625097; fax: +66 25625092.
E-mail address: faginfl@ku.ac.th (N. Lumdubwong).

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ent DS and AM. To gain this knowledge, it is potentially beneficial to industrial end-users in order to facilitating their decision making on selection of CMS with the DS value, and possibly providing the AM criteria for starch material selection to suit their needs. Therefore, the objective of the study was to investigate the effects of two different levels of DS, low and moderate DS (DS 0.2 and 0.6), and the influence of AM content (waxy, low, and high AM) on the physicochemical and textile printing properties of carboxymethyl rice starches. To eliminate the possible effects of different botanical sources of starch on those properties of CMS, all starches in this study are from rice.

2. Materials and methods

2.1. Materials

Four varieties of Thai rice samples – waxy rice (SMJ), low-AM rice (HML 105 and CH), and high-AM rice (HT) – were obtained from the Rice Department's Bureau of Rice Research and Development (Bangkok, Thailand). The rice samples were dehulled and further used to isolate starch. Commercial sodium alginate and cotton fabric (weft × warp/m: 2760 × 2300) were purchased from a local market. A reactive dye labeled Remazol Brilliant Blue R (RBBR) was a gift from Nisher Co., Ltd. (Bangkok, Thailand). Distilled water and reagent-grade chemicals were used in the study unless otherwise noted.

2.2. General methods

All analyses were at least duplicated unless otherwise stated. Nitrogen levels in rice starches were determined by Kjeldahl's method and converted to protein content using a protein conversion factor of 5.95 (AACC method 46-13). Moisture, ash, and crude fat content were tested using AOAC and AACC methods (AACC method 44-15A and AACC method 08-01). Amylose content was assayed using the iodine binding method of Chrastil (1987). Cold water solubility was determined by the method of Chen and Jane (1994).

2.3. Scanning electron microscopy

Native and carboxymethylated starch granule morphologies were examined using a scanning electron microscope (JSM-5600 LV, JEOL Ltd., Tokyo, Japan) with an acceleration voltage of 15 kV.

2.4. Measurements of thermal and physical properties

Differential scanning calorimetry (DSC) measurements were accomplished with a Mettler-Toledo DSC 882e (Greifensee, Switzerland). The instrument was calibrated with indium. Rice starch (3 mg dry basis [db]) was weighed in an aluminum pan, and 7.5 μL distilled water was added. The pan was sealed, left overnight at room temperature, and then heated from 30 to 130 °C at 10 °C/min (Fan & Marks, 1998).

Crystalline patterns of native and CM rice samples were determined using an X-ray diffractometer, model PW 1830 (Philips, Amsterdam, The Netherlands). The diffractograms were measured at Bragg's angle (2θ) from 4 to 40 °C at 5 °C/min.

2.5. Starch isolation

Rice starch was extracted using the alkaline steeping method of Yang, Lai, and Lii (1984).

2.6. Synthesis of carboxymethyl rice starch (CMRS) with low and moderate DS

CMRS was produced using a slightly modified method of Volkert et al. (2004). Both chloroacetic acid (35 g) and 2-propanol (335.90 ml) were added into a 500 ml three-necked round-bottom flask. Then 34.85 g of aqueous NaOH (45%, w/w) was added to the solution and the mixture was stirred vigorously using a paddle stirrer. Starch (30 g db) was subsequently added. Dry NaOH (6.88 and 10.58 g) was later added, and the whole mixture was stirred (250 rpm) at 40 °C for 2 h. The molar ratios of chloroacetic acid, 2-propanol, water, and NaOH to starch were 2:1, 23.54:1, 6.75:1, and 3:1 (low-DS CMRS) or 3.5:1 (moderate-DS CMRS), respectively. The etherification reaction was terminated by the addition of glacial acetic acid, and the starch mixture was adjusted to pH 6–7. The neutralized starch mixture was centrifuged, and the sediment was washed several times with 80% ethanol until no chloride ions in the supernatant were detected with aqueous silver nitrate. CMRS was oven-dried at 60 °C for 4 h, and then ground to pass through a 100 wire mesh.

2.7. Determination of degree of substitution (DS)

The DS of CMRS was determined by the back titration method (slightly modified) of Verraest, Peters, Batelaan, and van Bekkum (1995). Starch (~0.5 g db) was dissolved in water (100 ml). The mixture was blended vigorously for 3 min using a blender, and centrifuged at 2500 × g for 15 min. The supernatant, Na-CMRS, was converted to H-CMRS by treatment with 12 ml of cation exchange resin (Amberlite IR-120) at ~3 ml/min. The column was washed with water (~400 ml, which was four times the supernatant volume). The total collected H-CMRS solution was concentrated under vacuum at 40 °C in a 500 ml round-bottom flask using a rotary evaporator at 80 rpm to a final volume of ~105–110 ml, and then dried at 60 °C for 24 h. Later, a portion of the CMRS product (~500 mg) was taken, dissolved in 100 ml of distilled water, and mixed with 2–3 drops of phenolphthalein solution, 2 ml of methanol, and 15 ml of 0.1N NaOH. The mixture was titrated with 0.1N HCl. Water (100 ml) was used as a blank. The DS was calculated using the following equations:

$$W_c = \frac{c \times M_c \times (V_b - V_s) \times 100\%}{m}$$

and

$$X_c = \frac{W_c \times M_a}{(100\% - W_c) \times M_c}$$

where W_c is the carboxymethyl group content of the soluble test sample (w/w %); c is the concentration of HCl used for titration (mol/l); M_c is the molar mass of the carboxymethyl functional group reacting with the starch (58 g/mol); M_a is the molar mass of an anhydroglucose unit (162 g/mol); V_b is the volume of dilute HCl used for the blank titration (ml); V_s is the volume of dilute HCl used for the sample titration (ml); m is the corrected weight of the CMRS sample (mg); and X_c is the degree of carboxymethyl substitution (DS) in the soluble test sample.

2.8. FTIR measurements

FTIR spectra of the samples were recorded by a FTS 175 Bio-Rad FTIR (Bio-Rad Laboratories, Hercules CA, USA) using KBr disc technique. For each sample, 256 coadded scans were taken from 4000 to 400 cm^{-1} at a resolution of 16 cm^{-1}.

Table 1
Chemical compositions and properties of native rice starches.

Variety	Amylose (%)	Cold water solubility (%)	Gelatinization				Crude fat (%)	Ash (%)	Moisture (%)	Protein (%)
			Temperature (°C)			Enthalpy				
			T_o	T_p	T_c					
SMJ	2.07^{a}	1.49^{a}	61.58^{b}	67.72^{c}	74.26^{b}	16.53^{c}	0.10^{a}	0.05^{a}	13.19^{d}	0.10^{a}
HML 105	15.16^{b}	1.15^{a}	61.58^{b}	66.60^{b}	71.77^{a}	12.94^{a}	0.11^{a}	0.11^{a}	12.99^{c}	0.11^{a}
CH	19.72^{c}	1.30^{a}	60.80^{a}	65.78^{a}	71.51^{a}	12.99^{a}	0.12^{a}	0.12^{a}	12.31^{a}	0.12^{a}
HT 60	24.84^{d}	1.14^{a}	68.65^{c}	73.53^{d}	78.38^{c}	13.58^{b}	0.15^{a}	0.11^{a}	12.48^{b}	0.15^{a}

Different superscripts on the same row are significantly different ($p < 0.05$).

2.9. *Measurements of rheological properties*

Rheological measurements of low- and moderate-DS CMRS were determined using a Physica MCR 301 rheometer (Anton Paar, Graz, Austria). Cone (CP 50-1) and plate fixtures were used. A sample (5% w/v) was mixed with water. The mixture was gently stirred with a glass rod for 1 min, and left for 15 min to fully disperse. The apparent viscosity and shear stress were measured at shear rates ranging from 0.5 to 85 s^{-1} while the system temperature was controlled at 30 °C. The values of yield stress (τ_s) of the CMRS samples were calculated using the Casson model:

$$\eta^{1/2} = \dot{\gamma}^{1/2}\tau_s^{1/2} + k\dot{\gamma}, \quad \text{or} \quad \tau^{1/2} = \tau_s^{1/2} + k\dot{\gamma}$$

where η is the apparent viscosity (Pa s), $\dot{\gamma}$ is shear rate (s^{-1}), τ_s is stress yield (Pa s), and k is a constant. The Herschel–Bulkley model ($\tau = \tau_s + m\dot{\gamma}^n$) was used to further examine the flow behavior of CMRS solutions, where m is the consistency coefficient (Pa s^n) and n is the flow behavior index (Rao, 1999).

2.10. *Preparation of print paste*

2.10.1. *Thickener paste preparation*

Two types of thickener paste were prepared using the following methods. Sodium alginate was mixed with water at a concentration of 8% (w/v) using a blender at 350 rpm for 15 min. CMRS was mixed with water (10%, w/v) and the mixture was stirred using a glass rod for 5 min.

2.10.2. *Formulation of printing paste*

Urea (12 g) was slowly added to the thickener paste (30 g), and concomitantly stirred until obtaining a homogenous mixture. Reversed salt (3 g), water (10.5 ml), and reactive dye (3 g) were added to the mixture, which was then vigorously blended using a cake blender. When the mixture was homogeneous, $NaHCO_3$ (1.5 g) was added. The mixture was vigorously blended once more, and printing paste was obtained.

2.11. *Printing technique*

The print paste was applied to the cotton fabric, using a squeegee with a screen block (20 cm × 20 cm). The fixation step was performed when the printed fabric was dried at 100 °C for 1 min in a hot-air oven, and subsequently steamed at atmospheric pressure for 8 min. The washing procedure was applied to the fabric in the following steps: cold water rinsing until the residue of the dye was completely washed out; 5 min of hot water washing (100 °C); and cold water washing. The printed fabric was air-dried and ironed on the back side.

2.12. *Analyses of printed fabrics*

Color strength of the printed fabrics was determined using the minimum reflectance method with a spectrophotometer (Color-Eye 7000, GretagMacbeth, Inc., New Windsor, NY, USA). The K/S values were calculated by the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{(2R)}$$

where K = absorption coefficient, S = scattering coefficient, and R = light reflection at a wavelength of minimum reflectance.

Bending length of printed fabrics was determined by British Standards (BS 3356:1990). Crocking fastness and washing fastness of the samples were determined by the ISO methods 105-X12 (2001) and 105-C06/C2S (1990), respectively.

Table 2
Degree of substitution (DS) of carboxymethyl rice starches (CMRS) and their physical properties.

CMRS	Determination of DS			Physical properties		
	Back titration	FTIR	Cold water solubility (%)	Rheological properties		
	DS	Peak ratio[a]		Herschel–Bulkley parameters		Yield stress (Pa)
				n value	m value	
Low-level DS						
SMJ	0.24^{a}	2.19^{a}	52.97^{a}	0.37	0.94	238.59
HML	0.16^{a}	1.94^{a}	77.56^{c}	0.37	0.93	127.54
CH	0.16^{a}	1.93^{a}	66.98^{b}	0.37	0.85	134.31
HT	0.26^{a}	2.52^{b}	80.24^{d}	0.35	0.88	115.08
Moderate-level DS						
SMJ	0.57^{b}	2.89^{c}	85.98^{e}	0.45	1.04	296.03
HML	0.53^{b}	2.90^{c}	80.63^{d}	0.38	0.91	185.09
CH	0.60^{b}	2.89^{c}	75.94^{c}	0.39	0.85	234.84
HT	0.57^{b}	3.07^{c}	81.07^{d}	0.39	0.88	163.94

[a] Peak ratio is calculated from the ratio of the height of the carbonyl peak to the pyranose ring peak at 1600 and 930 cm^{-1}.

[b] Different superscripts on the same row are significantly different ($p < 0.05$).

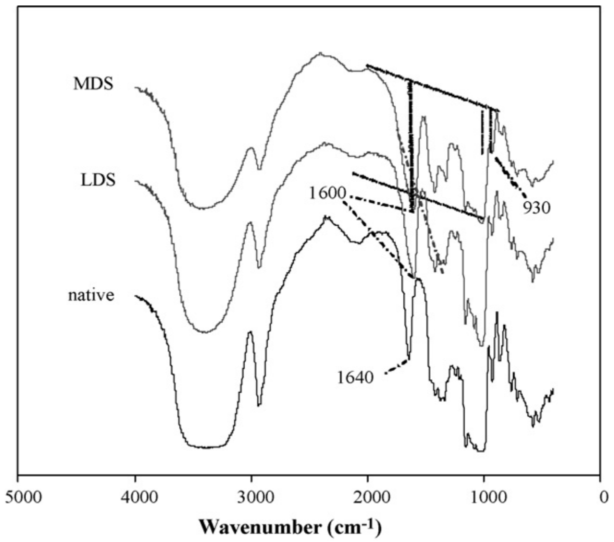

Fig. 1. FTIR spectra of: (a) native HT starch; (b) low DS of etherified HT starch; (c) high DS of etherified HT starch.

2.13. Statistical analysis

All tests were performed at least in duplicate. Statistical significance tests were performed using Duncan's multiple range test at a 95% confidence level ($p < 0.05$).

3. Results and discussion

3.1. Chemical compositions and physical properties of native rice starches

The purity of various rice starches using alkaline treatment is shown in Table 1. All Thai rice starch samples displayed low protein, fat, and ash content, and AM ranging from 2.07% to 24.84%. According to rice classification (Juliano, 1998), SMJ and HT 60 were considered to be waxy and high-AM rice, with AM ranges of 0–2% and 25–33%, respectively. HML 105 and CH were categorized as low-AM rice (10–20% AM), although AM of HML 105 was statistically significantly higher than CH. All rice starches except HT 60 had low gelatinization temperatures (midpoint temperature, $T_p < 70\,^{\circ}\mathrm{C}$). HT 60 was the only rice starch in the study with medium gelatinization temperature (70–74 °C) (Juliano, 1998).

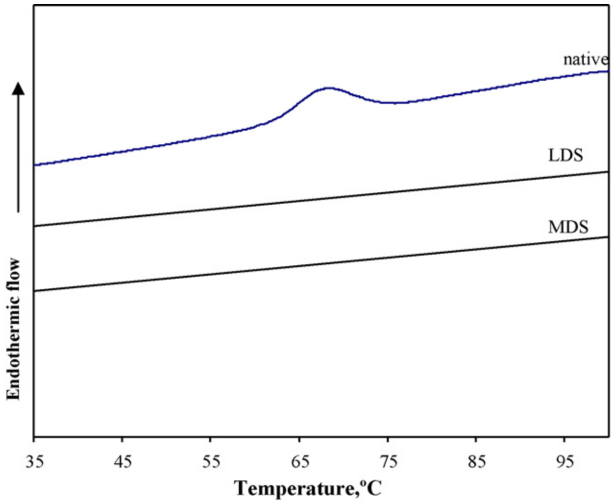

Fig. 2. An example of heating differential scanning calorimetry (DSC) curves of native and carboxymethyl (CM) HT rice starches with low DS and high DS.

3.2. Preparation of CMRS with low and moderate DS

In this study, the method of Volkert et al. (2004) was chosen in order to produce CMRS with low and moderate DS. Molar ratios of etherification agents to starch were slightly altered from the original method. Two different molar ratios of NaOH to starch (3:1 and 3.5:1) were used, while molar ratios of other reagents to starch were kept constant in the study. As a result, the DS values of CMRS with different AM determined by the back titration method were categorized into two groups, low and moderate DS (Table 2). The values of low DS ranged from 0.16 to 0.26, whereas high DS ranged from 0.53 to 0.60, resulting in average DS of 0.2 and 0.6, respectively. The DS of CMRS were also determined using flame atomic absorption spectrometry (Lawal, Lechner, Hartmann, & Kilcike, 2007), with

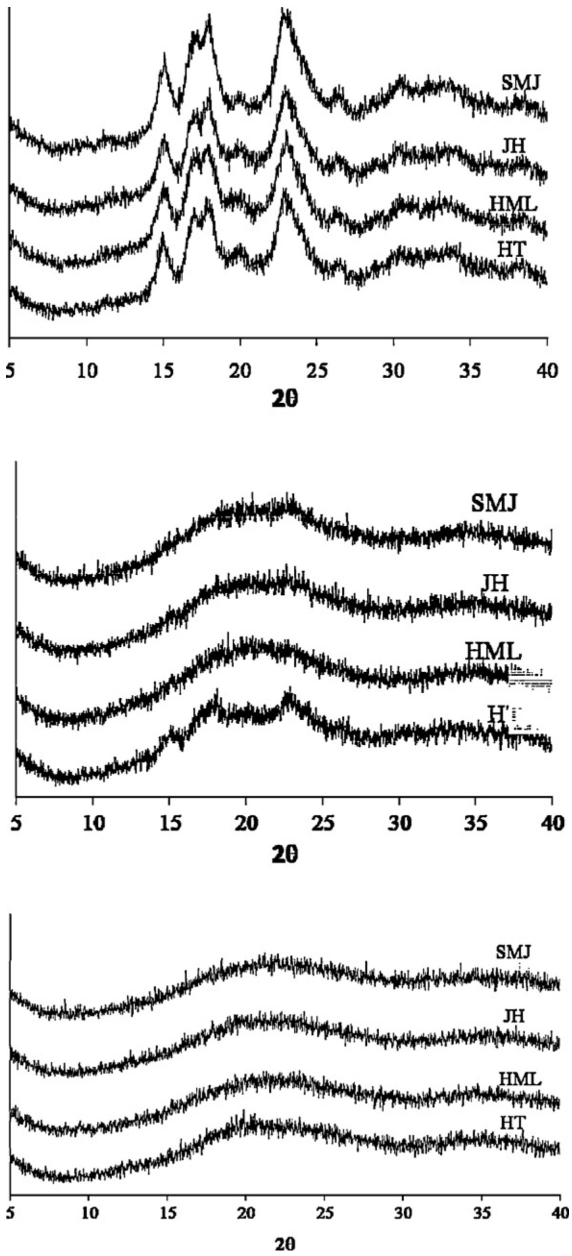

Fig. 3. X-ray diffraction of (a) native rice starches; (b) low-DS CMRS; (c) moderate-DS CMRS.

results similar to the back titration method (results not shown). Regardless of AM, all CMRS etherified under similar conditions possessed similar DS. Apparently, AM did not affect DS values of CMRS prepared under the etherification conditions used in the study.

FTIR spectra of native rice starch and CMRS are displayed in Fig. 1. The infrared absorption bands at wave numbers 930 and 1640 $\mathrm{cm^{-1}}$ were attributed to (respectively): the skeleton mode vibrations of α-1,4-glycosidic linkages (C–O–C) in native starch; and water adsorbed in the amorphous regions of starch (Kizil, Irudayaraj, & Seetharaman, 2002). In addition, the infrared absorption band at wave number 1600 $\mathrm{cm^{-1}}$, which represents the stretching of the carbonyl functional group ($\mathrm{COO^-}$), was detected in all CMRS (the etherified samples) but not in native samples. When the ratios of the peak height of $\mathrm{COO^-}$ stretching to that of the skeleton mode vibration (C–O–C) of CMRS samples were calculated, the height ratios of moderate-DS CMRS were significantly greater than those of low-DS CMRS (Table 2). Therefore, the FTIR results were in agreement with the DS values determined using the back titration method.

3.3. *Cold water solubility (CWS) of CMRS*

It was noticed that when a cold water solubility test was performed, a greater portion of low-DS (LDS) CMRS remained in the sediment after centrifugation in the form of a clear gel, as opposed to moderate-DS (MDS) CMRS which was more dissolved in the supernatant. This observation is consistent with the values of cold water solubility (CWS) of CMRS shown in Table 2. In general, MDS CMRS demonstrated an average CWS 10% higher than LDS CMRS (80% vs. 70%). At similar LDS levels, CWS of CMRS increased as AM increased: the order of CWS of CMRS was HT (high AM) > HML (low AM) > CH (low AM) > SMJ (waxy). A positive correlation between AM and CWS of LDS CMRS was reported as $r = 0.83$ ($p < 0.05$). A difference in CWS of MDS CMRS with varying AM content was also reported. However, there was no statistical correlation between AM and CWS in the MDS samples. In addition, it seems that there is an interaction of DS and AM which affects CWS of CMRS, as shown in Table 2. The difference of CWS between LDS and MDS CMRS samples tended to increase from 0.87% to 23% as AM decreased from 24.84% to 2.07%.

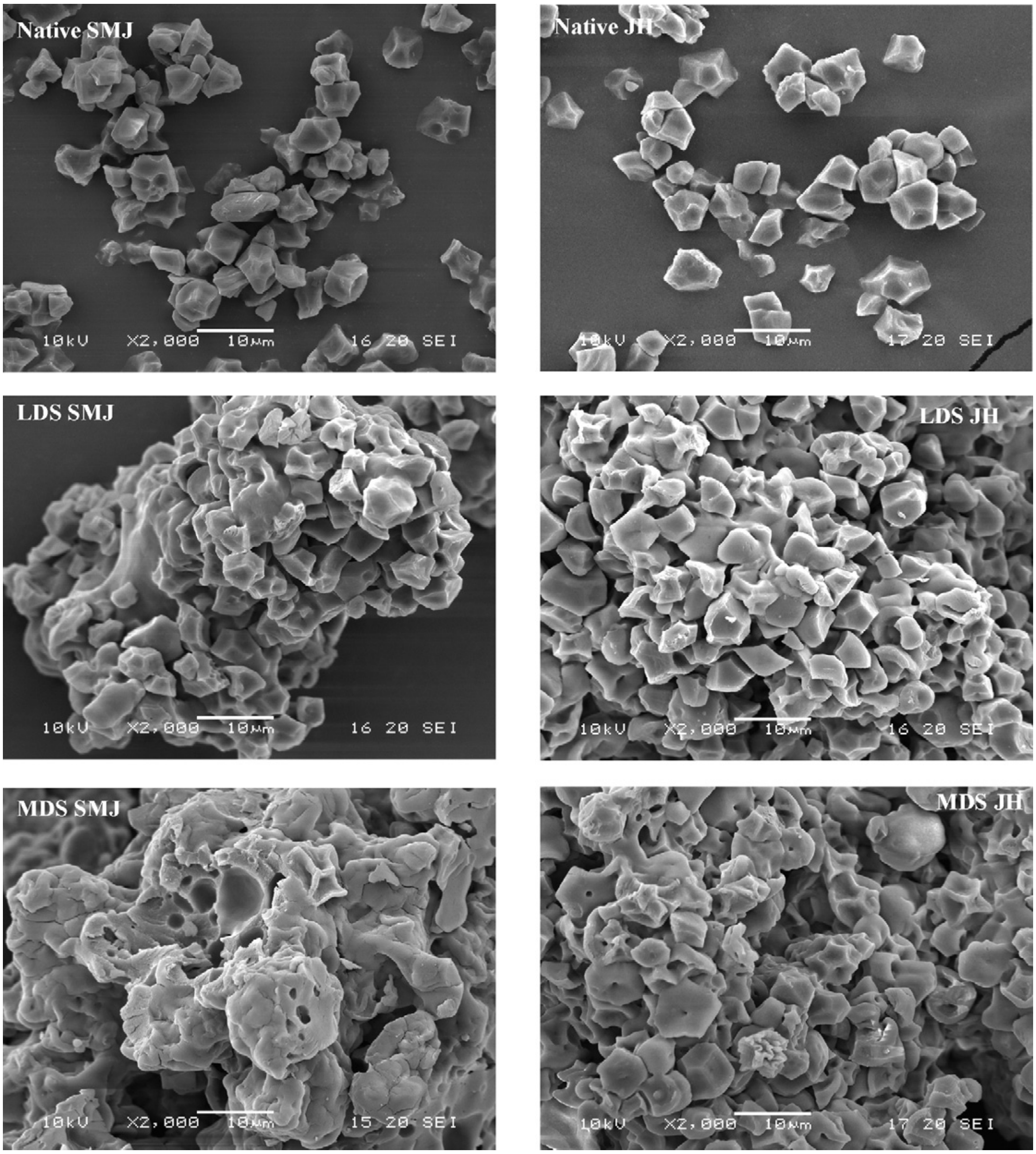

Fig. 4. Scanning electron micrographs of native, low and moderate-DS CM rice starches: (a) SMJ; (b) CH; (c) HML 105; (d) HT.

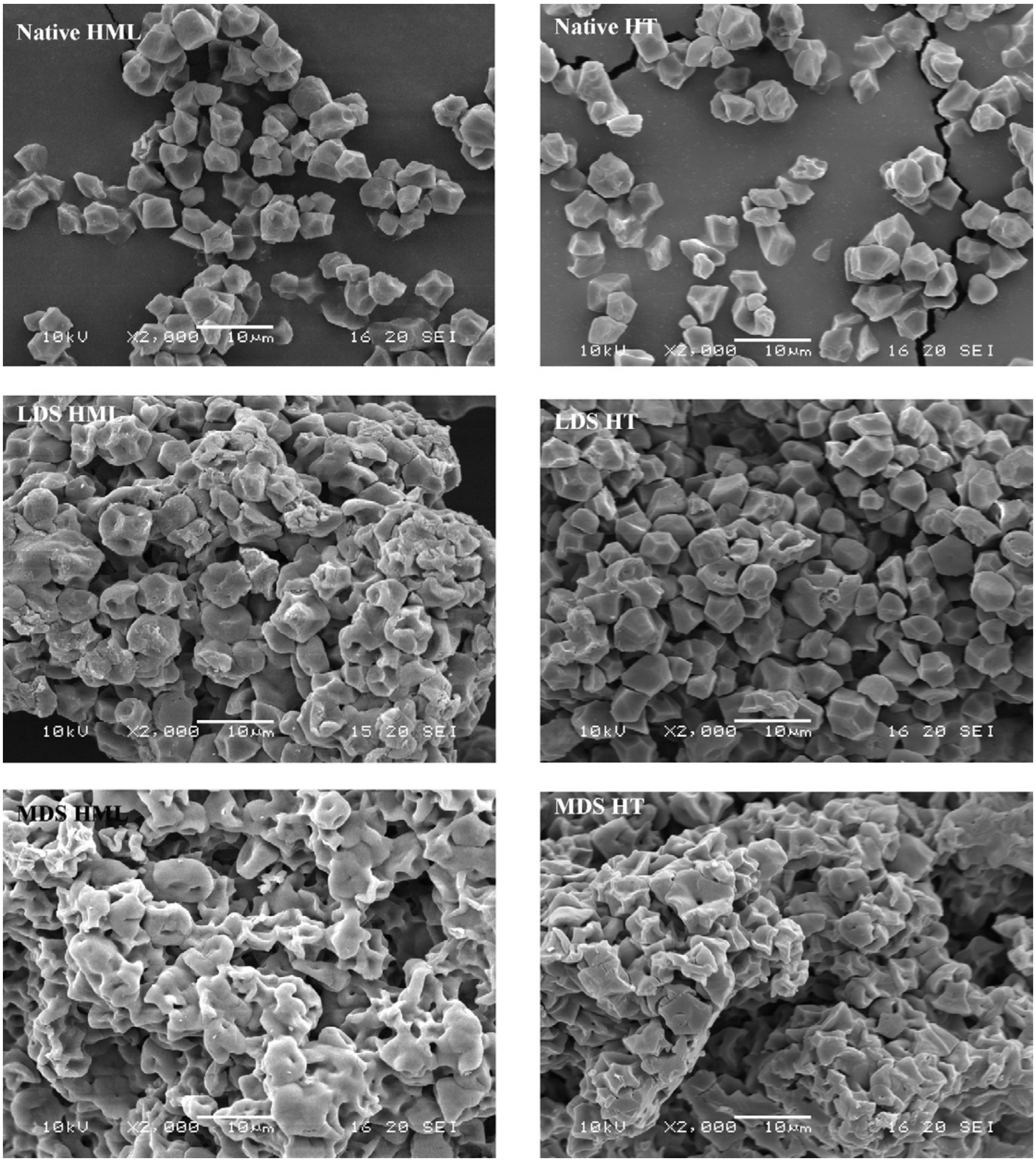

Fig. 4. (*Continued*).

3.4. Thermal properties and crystallinity of CMRS

Unlike native starch, no gelatinization endotherms were detected in any CMRS samples. The absence of endotherms in the modified starches is consistent with the increase in CWS of the modified starches. DSC thermograms of native rice and CMRS are shown in Fig. 2.

XRD of all native rice starches (Fig. 3a) displayed strong reflections at diffraction angles (2θ) of 14.8°, 16.6°, 17.7°, and 22.6°, indicating an A-type crystal pattern (Van Soest, Hulleman, de Wit, & Vliegenthart, 1996). For a low level of DS, a slight remainder of an A-type pattern was detected in high-AM CMRS (HT); an amorphous pattern was found in other LDS CMRS (Fig. 3b). For a moderate-DS level, all CMRS, regardless of AM content, displayed only an amorphous pattern, as shown in Fig. 3c. Possibly, alkaline gelatinization and the substitution of hydroxyl groups with carboxymethyl moieties were the causes of this loss of starch crystallinity. Actually, the amount of alkaline reagent used in the study for the preparation of both low- and moderate-DS CMRS was probably enough to cause granule swelling in most of the rice starches, resulting in the total destruction of their crystalline structure. However, the fact that LDS HT CMRS was the only sample that displayed a slight remainder of an A-type pattern was probably due to the effect of AM. It is known that amylopectin is responsible for the swelling property of starch, whereas amylose acts as a connector to hold the starch granules intact (Chen & Jane, 1994). Among the rice starch samples, HT (containing the highest AM) probably had the least granule swelling, especially considering the lower amount of alkaline reagent used for LDS sample preparation. In turn, less destruction of double helices and crystalline regions occurred, and thus its slight original A-type pattern remained.

3.5. CMRS morphology

Granule morphologies of native and CM rice starches are shown in Fig. 4. All native rice starches displayed polygonal-shaped granules with sizes of approximately 5–6 μm. It is clear that carboxymethylation of the rice starch altered the granule appearance.

Table 3
Analysis of samples printed with carboxymethyl rice starches, native rice starches, and alginate.

Batch name	*K*/*S*	Crocking fastness		Washing fastness		Bending length
		Dry	Wet	Change in shade	Staining	
Low DS						
SMJ	10.22^{a}	5	3/4	5	4	2.41^{c}
CH	9.95^{a}	5	3/4	5	4	2.48^{cd}
HML	10.07^{a}	5	3/4	5	4	2.85^{e}
HT	10.32^{a}	5	3/4	5	4	2.58^{d}
High DS						
SMJ	11.93^{b}	5	4/5	5	4	2.12^{a}
CH	13.45^{c}	5	4/5	5	4	2.19^{ab}
HML	14.54^{c}	5	4/5	5	4	2.25^{b}
HT	14.50^{c}	5	4/5	5	4	2.25^{b}
Alginate (8%)	13.85^{c}	5	4/5	5	4	2.20^{ab}

Different superscripts on the same row are significantly different ($p < 0.05$).

The granular shape of low-DS CM rice starches became more irregular and slightly swollen. Their surfaces were rough and wrinkled. Furthermore, some of the granules either clustered or merged together. Changes in granule appearance became more prominent as the level of carboxymethylation of the rice starches increased to DS ~0.6. Moderate-DS CM rice starch granules tended to cluster more and melt together, compared to those of LDS. Also, the noticeable granular changes of CM starches seemed to increase as AM decreased. The order of these granular changes was SMJ > HML > CH > HT (Fig. 4), which corresponds with the swelling ability of the granules related to their AM, as previously discussed.

3.6. Rheological properties of LDS and MDS CMRS

The rheological pattern of CMRS fluids at 5% w/v concentration is shown in Fig. 5. According to the values obtained from the Casson and Herschel–Bulkley models, all modified starch samples showed shear-thinning behavior with yield stresses (Table 2). In comparing MDS and LDS samples, the MDS samples possessed higher yield stresses and apparent viscosities than the LDS samples. This is possibly due to the higher amount of the substituted carboxymethyl group, which is negatively charged, in the MDS samples compared with those of the LDS samples (DS 0.6 vs. DS 0.2). The greater electrostatic repulsion among the MDS CMRS molecules, therefore, caused their higher yield stresses and apparent viscosities. Sangseethong et al. (2005) also reported an increase in apparent viscosity of CM cassava starch as DS increased from 0.4 to 0.7. At similar levels of DS, the yield stresses and apparent viscosities of CMRS declined as AM increased: SMJ > HML > CH > HT (Fig. 5). This increase in yield stresses and apparent viscosities of CMRS with lower AM content may be due to the large molecular size of amylopectin (AP) (Zhong, Yokoyama, Wang, & Shoemaker, 2006) and the high swollen granule fractions fitting the available volume of the starch–water system due to AP fractions (Svegmark & Hermansson, 1991). Further studies are needed to identify the actual factors.

3.7. Analysis of fabrics printed with reactive dyes using CMRS

Quality measurements of cotton fabrics printed with reactive dyes using either CMRS or sodium alginate, the print paste reference, as print pastes are shown in Table 3. The *K*/*S* value indicating color strength of the printed fabrics prepared from LDS CMRS were significantly lower than those of MDS CMRS and the alginate. It was found that a slightly higher concentration (~2%) of MDS CMRS than of alginate was required to obtain the equivalent printing quality of the cotton fabrics. At a similar MDS level, fabrics printed using the waxy CMRS print paste demonstrated the least color strength; whereas the samples printed using other CMRS with a higher range of AM displayed a color strength equivalent to that of alginate (Table 3). Probably both the high viscosity and solubility of the MDS waxy CMRS were the reasons for the inferior color yield. The high viscosity of the MDS waxy rice sample (Fig. 5) possibly caused a lack of penetration during the color fixation process (Kumbasar & Bide, 2000). Also, the high solubility (~84%) of the sample may have facilitated the removal of too much dye during the washing-off process and other after-treatments (Teli, Rohera, Sheikh, & Singhal, 2009a).Thus, the *K*/*S* value of the print paste from MDS waxy CMRS was rather low compared to the others.

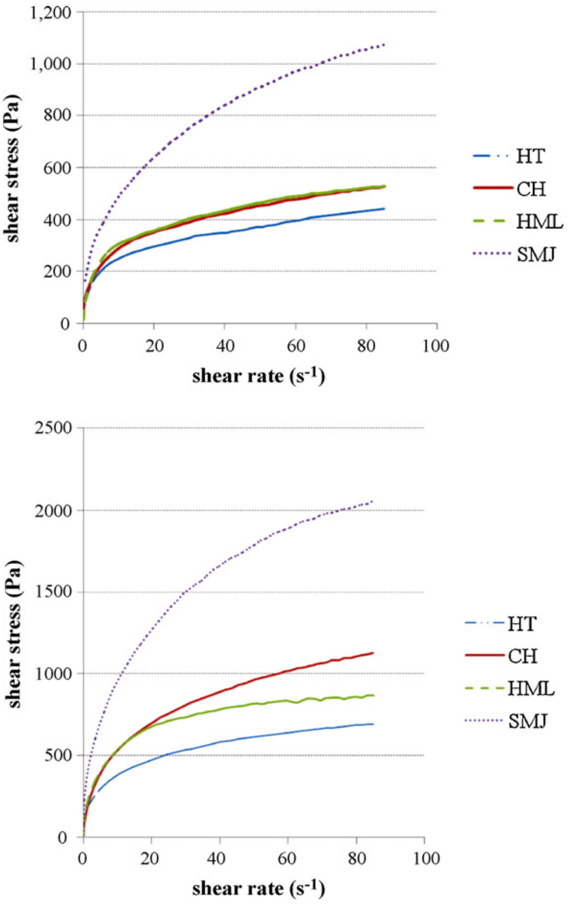

Fig. 5. Rheograms of carboxymethyl (CM) rice starches with (a) low DS; (b) moderate DS.

Ratings of washing fastness of LDS and MDS CMRS and the alginate were identical (Table 3). In contrast, the LDS CMRS printed samples had lower wet crocking fastness than the MDS CMRS and alginate printed samples. It is possible that the reactive dye interacted more with the original primary hydroxyl groups remaining in the LDS print paste, instead of interacting with the hydroxyl groups of the cotton fabrics. In this case less dye penetrated into the fabrics, binding instead with the LDS CMRS, and thus more remained on the cotton fabrics. Consequently when wet crocking was performed, the dye fixed with LDS CMRS print paste was washed out, along with some of the remaining CMRS. Bending length (Table 3), expressing stiffness of the printed fabrics, supports this explanation. A high bending length implies the presence of a high amount of undesirable starch remaining on the fabrics. As a matter of fact, printed fabrics prepared from LDS CMRS were stiffer than those prepared from MDS CMRS, indicating that a higher amount of LDS CMRS remains on the samples (Teli, Rohera, Sheikh, & Singhal, 2009b).

4. Conclusions

LDS and MDS CMRS with different AM content were produced. MDS CMRS demonstrated higher CWS, yield stresses, and apparent viscosities than LDS CMRS. Textile print pastes prepared from MDS CMRS also were superior to those from LDS samples; waxy paste provided the least color yield of the printed fabrics. At similar levels of DS, AM content also affected the properties of CMRS. CWS of LDS CMRS samples increased when AM increased. However, yield stresses and apparent viscosities of CMRS decreased with increased AM. Nonetheless, DS was found to be much more important than AM content in determining the physicochemical and functional properties of CMRS.

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