

Paste viscosity of rice starches of different amylose content and carboxymethylcellulose formed by dry heating and the physical properties of their films

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Abstract

Starch modified by combination with sodium carboxymethylcellulose (CMC) has been reported to have improved film properties. In this study, rice starches with different amylose content were heat-treated in a dry state after being impregnated with low or medium-viscosity CMC. Noticeable change was found in pasting properties of the starches after dry heat treatment with CMC. It indicated that crosslinkage occurred between the starch and CMC. The waxy starch showed significant change in viscosity throughout pasting after dry heating with CMC, suggesting that the ester bonds were mostly formed between the hydroxyl groups in amylopectin branches of rice starch and carboxylate acid groups of CMC. Particle size also increased after heat treatment with CMC. The modified starch-based films showed improvement in the tensile strength. Both water vapor and oxygen permeability reduced for the modified starch-based films. Dynamic mechanical analysis (DMA) study showed that the values of G' of modified starch-based film were higher than those of native starch-based film over the temperature range -40 to 60 °C. The heating process with CMC could be used as a modification method for starch and provide desirable properties of starch-based films.

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1. Introduction

There is considerable interest in the development of starch-based films because they fulfill an increasing need for biodegradable packaging. Starches from different botanical origins, such as potato, corn, wheat, rice, and cassava, both natural and modified, have been utilized, mainly in the manufacture of starch-based edible films (Lourdin, Della Valle, & Colonna, 1995; Ollett, Parker, & Smith, 1991; Tapia-Blácido, Sobral, & Menegalli, 2005). The edible films not only contribute to food protection and shelf-life prolongation but also protect the environment from plastic waste (Arvanitoyannis & Biliaderis, 1998; Debeaufort, Quezada-Gallo, & Volley, 1998) and

provide a potential new use for surplus farm production (Okada, 2002; Pavlath & Robertson, 1999).

Starch is a natural polymer that can readily be cast into films. The matrix of starch-based films is normally formed during the drying of a gelatinized dispersion, as hydrogen bonds form between hydroxyl groups (Lourdin et al., 1995). As these interactions are weak, the mechanical properties of starch-based films are of poor quality (Tapia-Blácido et al., 2005). Unless genetically or chemically modified, starch cannot form films with adequate mechanical properties (high percentage elongation, tensile and flexural strength) (Arvanitoyannis & Biliaderis, 1999).

Carboxymethyl-cellulose (CMC), xanthan, guar, and arabic gum, which are water-soluble heteropolysaccharides with high molecular weight are often used together with starches to provide proper texture, control moisture and water mobility, and improve overall product quality and/

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or stability (Aguirre-Cruz, Méndez-Montealvo, Solorza-Feria, & Bello-Pérez, 2005; Gurkin, 2002; Shi & BeMiller, 2002).

In addition to biodegradability, processes to produce starch-based films that use little or no toxic chemicals and produce less waste are preferred. Chiu, Schiermeyer, Thomas, & Shah, 1998 found that heating dry starch or flour at $>100\text{ }^{\circ}\text{C}$ for several hours provides functionality equivalent to chemical cross-linking. Recently, modification of starch by dry heating with ionic gums has been studied (Lim, BeMiller, & Lim, 2003; Lim, Han, Lim, & BeMiller, 2002). They reported that anionic food gums reacted with starch during dry heating, producing significant changes in pasting properties of the starch. They also found out that with proper selection of ionic gum and control of reaction conditions, a dry heating process can provide desirable starch functionality. In this study, we investigated the use of rice starch–CMC granules formed by dry heating to determine their film properties and the characteristics of amylose content on pasting and film properties.

2. Materials and methods

2.1. Materials

Waxy (CM 101), medium (M202), and long (Cocodrie) grain rice samples were grown and milled by the California Cooperative Rice Research Foundation, Biggs, CA. Low-viscosity and medium-viscosity sodium carboxymethylcellulose (CMC) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). Protease N “Amano” (activity 150,000 U/g, optimum pH 7.5) provided by Amano Pharmaceutical Co. Ltd., (Nagoya, Japan) was used to isolate the rice starches.

2.2. Isolation of rice starch

Milled rice (50 g) was soaked in 150 ml deionized water for 18 h. The rice and water were then blended in a Waring blender for 3 min. The initial pH of the solution was adjusted to 8.5 and Protease N (100 U/ml) was added. The protease hydrolysis was conducted at $50\text{ }^{\circ}\text{C}$ for 4 h with constant stirring. After the hydrolysis the slurry was centrifuged at 10,000g for 10 min. The supernatant and the surface brown layer of the starch were removed and the lower white starch layer was washed with deionized water followed by centrifugation. The washed starch was freeze dried, passed through a 200 mesh sieve and stored until analyzed.

2.3. Measurement of amylose content

Amylose content of isolated rice starches was analyzed in triplicate with an Amylose/Amylopectin assay kit based on the concanavalin A method (Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland).

2.4. Starch modification by dry heat treatment with gums

The starches were modified by dry heating with gums according to Lim et al. (2002). CMC (0.1 g) was added to distilled water (20 ml) with vigorous stirring. After the gum was completely dissolved, starch (9.9 g) was added to the gum solution and stirred for 30 min at room temperature. The whole dispersion was transferred into a glass dish and dried at $45\text{ }^{\circ}\text{C}$ in an oven to a moisture content of less than 10% (based on starch). The starch–CMC mixture was heated in an electric oven at $130\text{ }^{\circ}\text{C}$ for 4 h. The starches without gum treatment were concurrently heated as control.

2.5. Preparation of starch-based films

Three grams of native or modified starch (starch modified by dry heat treatment with 1% low-viscosity CMC as described above) was added to 50 ml distilled water with vigorous stirring. The dispersion was heated to $95\text{ }^{\circ}\text{C}$ and held for 10 min. Afterwards, the starch dispersion was mixed with CMC and glycerol solution (0.5 g CMC and 0.7 g glycerol in 50 ml distilled water) and stirred for 10 min. The dispersion was then cooled at $40\text{ }^{\circ}\text{C}$ and degassed to release all air bubbles. Films were prepared by casting. Dispersions (20 ml) were poured on each polyethylene Petri dish of 8 cm in diameter and dried at room temperature until constant weight (approximately 12 h).

2.6. Pasting properties of native and modified starches

The pasting properties of native and modified starches were determined in triplicate on a rotational rheometer (Rheolyst AR 1000, TA instrument, New Castle, DE, USA). A cone and plate geometry was used. The cone was made from a polysulfone plastic with 4° angle and 60 mm in diameter. Starch dispersions (8.8%, w/v) were prepared with degassed water. The starch was dispersed in the water with stirring for 5 min under vacuum before loading between the cone and the bottom plate. The following program was used for the pasting of the starch slurries. After loading starch dispersion between the cone and plate, it was equilibrated to $50\text{ }^{\circ}\text{C}$ for 1 min at 200 s^{-1} . The temperature was raised to $95\text{ }^{\circ}\text{C}$ at the rate of $12\text{ }^{\circ}\text{C}/\text{min}$, holding at $95\text{ }^{\circ}\text{C}$ for 2 min 30 s. The temperature was then decreased to $50\text{ }^{\circ}\text{C}$ at the same rate, and finally holding at $50\text{ }^{\circ}\text{C}$ for 1 min. The shear rate during the pasting was maintained at 200 s^{-1} .

2.7. Particle size distribution of native and modified starches

Native or modified starch samples (100 mg) were dispersed in 5 ml of water and stirred for 10 min. The dispersion was then analyzed for particle size distribution with laser diffraction in triplicate with a Microtrac S3500 (Microtrac Inc., North Largo, FL, USA).

2.8. Tensile strength and percentage elongation of starch-based films

Tensile strength and percentage elongation of native and modified starch-based films were measured on dumbbells, after their equilibration at various relative humidities according to D828-88 (ASTM, 1989), using a Mechanical Universal Testing Machine Instron 5500R-1122. Measurement conditions and calculations of tensile strength and percentage elongation were made as previously described (Arvanitoyannis and Psomiadou, 1994). The results are the average of five samples.

2.9. Oxygen permeability (PO_2) determination of starch-based films

The Oxygen permeability (PO_2) values were determined using a MOCON unit (Ox-Tran 100A, Modern Control Inc., Minneapolis, MN) according to ASTM D3985-81 Standard Method (ASTM, 1993). Film samples were masked by aluminum foil mask with effective film test area of 5 cm². Tests were performed at 25 ± 2 °C and 50% relative humidity. PO_2 was calculated by multiplying oxygen gas transmission rate (OGTR) with the thickness and dividing by partial pressure difference of oxygen across the films' surface.

2.10. Water vapor permeability (WVP) determination of starch-based films

The water vapor permeability (WVP) values were determined according to ASTM (1987) method E96 with some modifications. Films were sealed on cups containing CaCl₂. Test cups were placed in a desiccator cabinet at 25 °C and 90% relative humidity (BaCl₂ saturated solution). Periodical weightings monitored the weight changes. The WVP was calculated from the slope (C) of a linear regression of weight increase vs. time.

$$WVP = \frac{C \times X}{A \times \Delta P}$$

where X is the film thickness; A is the area of exposed film and ΔP is the differential water vapor partial pressure across the film.

2.11. Dynamic mechanical analysis (DMA) of starch-based films

Native or modified starch-based films were mounted in a dynamic mechanical analyzer (Model Q800, TA Instrument, USA) and equilibrated at 25 °C. The storage modulus (G'), loss modulus (G'') and tan delta were measured at a frequency of 1 Hz. Tests were performed at 25 °C and 50% relative humidity. The results are the average of five samples.

Dynamic mechanical behavior was determined in triplicate at 1 Hz and a heating rate of 2.5 °C /min in the temperature range from –40 to 60 °C.

3. Results and discussion

3.1. Heat treatment without CMC

Amylose content and paste viscometer data of isolated native starches before and after dry heating are presented in Table 1. It was found that for the native rice starches, the pasting onset and peak temperature correlated positively with amylose content, which was consistent with previous reports (El-Khayat, Samaan, & Brennan, 2003). The starches displayed a trend in which the pasting onset temperature, peak viscosity and final viscosity decreased after dry heating. Lim et al. (2002) reported the similar results of maize starch after heat treatment. They found out that the acidity (pH 5.1) of the commercial waxy maize starch was responsible for the viscosity decrease. But in our study, the pH of all the isolated rice starch dispersions was neutral (pH 6.7) and therefore pH was not the cause of the viscosity decrease.

3.2. Heat treatment with low-viscosity CMC

Table 2 Shows paste viscometer data of starches before and after dry heat treatment with 1% low-viscosity CMC. Heat treatment with CMC raised the peak and final viscosities of all the starches (Table 2), compared to native starches without modification (Table 1). The waxy starch (CM101) exhibited the most remarkable increase in viscosity throughout pasting after dry heating with 1% low-viscosity CMC (Fig. 1). It suggested that the starch with more amylopectin was more easily to react with CMC.

Table 1
Amylose content and paste viscometer data of starches before (B) and after (A) dry heating

Samples	Amylose content (%)	Pasting onset temperature (°C)	Peak temperature (°C)	Peak viscosity (Pa s)	Final viscosity (Pa s)
CM101 B	0.80	65.7 ± 0.1	71.7 ± 0.1	0.79 ± 0.02	0.76 ± 0.01
CM101 A		63.8 ± 0.1	72.0 ± 0.2	0.74 ± 0.01	0.70 ± 0.01
M202 B	13.4	67.7 ± 0.1	91.4 ± 0.1	0.57 ± 0.02	0.65 ± 0.03
M202 A		66.0 ± 0.1	91.5 ± 0.2	0.52 ± 0.01	0.54 ± 0.03
Cocodrie B	20.8	73.0 ± 0.2	93.5 ± 0.1	0.43 ± 0.03	0.59 ± 0.03
Cocodrie A		72.1 ± 0.2	91.7 ± 0.1	0.34 ± 0.02	0.55 ± 0.03

Table 2
Paste viscogram data of starches before (B) and after (A) dry heat treatment with 1% low-viscosity CMC

Samples	Pasting onset temperature (°C)	Peak temperature (°C)	Peak viscosity (Pa s)	Final viscosity (Pa s)
CM101–1%CMC B	65.7 ± 0.1	73.1 ± 0.2	0.78 ± 0.02	0.76 ± 0.01
CM101–1%CMC A	65.4 ± 0.1	75.8 ± 0.2	0.99 ± 0.01	0.90 ± 0.02
M202–1%CMC B	68.0 ± 0.3	95.0 ± 0.2	0.52 ± 0.03	0.61 ± 0.03
M202–1%CMC A	67.4 ± 0.2	95.0 ± 0.2	0.62 ± 0.03	0.70 ± 0.03
Cocodrie–1%CMC B	74.5 ± 0.2	95.0 ± 0.3	0.37 ± 0.04	0.64 ± 0.02
Cocodrie–1%CMC A	72.4 ± 0.2	95.4 ± 0.2	0.48 ± 0.03	0.65 ± 0.03

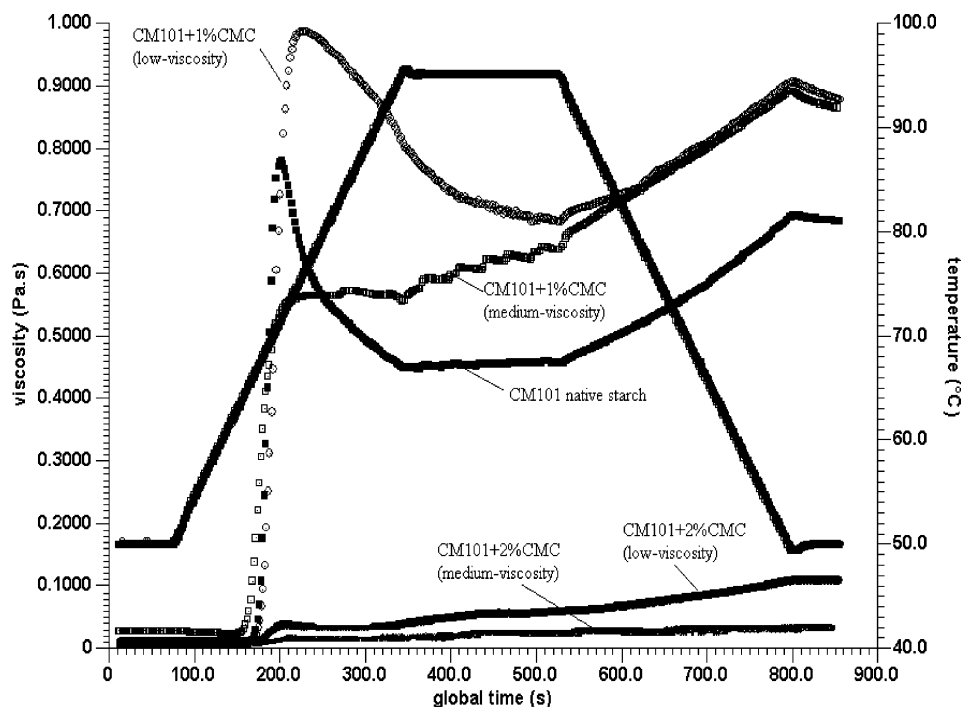


Fig. 1. Pasting curve of CM101 starches before and after dry heat treatment with CMC at different concentrations.

Paste viscogram data of starches before and after dry heat treatment with 2% low-viscosity CMC are shown in Table 3. Pasting onset and peak temperatures showed similar trend to those of starches heat-treated with 1% low-viscosity CMC. Dry heat treatment with 2% low-viscosity CMC decreased the peak and final viscosity of all the starches. The decrease of the viscosities was found negatively correlated to the amylose content of different rice starches. Waxy (CM101) starch–CMC mixture with the peak viscosity of 0.04 Pa s and final viscosity of 0.1 Pa s showed the most remarkable decrease in viscosity through-

out pasting after heat treatment with 2% low-viscosity CMC (Fig. 1). Lim et al. (2003) reported that ester bond could be formed between the starch and CMC when the starch and gum mixture were dry-heated. Since the waxy starch showed greater decrease in viscosity after heat treatment as compared to the other two starches (Tables 2 and 3), a higher number of ester crosslinks was thought to be formed between the waxy starch and CMC. This would suggest that the ester bonds were mostly formed between the hydroxyl groups in amylopectin of the starch and carboxylate acid groups of CMC.

Table 3
Paste viscogram data of starches before (B) and after (A) dry heat treatment with 2% low-viscosity CMC

Samples	Pasting onset temperature (°C)	Peak temperature (°C)	Peak viscosity (Pa s)	Final viscosity (Pa s)
CM101+2%CMC B	64.7 ± 0.2	70.8 ± 0.2	0.99 ± 0.01	0.80 ± 0.03
CM101+2%CMC A	64.1 ± 0.1	72.0 ± 0.2	0.04 ± 0.01	0.10 ± 0.02
M202+2%CMC B	67.4 ± 0.2	91.4 ± 0.1	0.60 ± 0.03	0.67 ± 0.02
M202+2%CMC A	66.7 ± 0.1	94.7 ± 0.2	0.43 ± 0.01	0.36 ± 0.01
Cocodrie+2%CMC B	73.5 ± 0.2	91.4 ± 0.3	0.39 ± 0.03	0.57 ± 0.04
Cocodrie+2%CMC A	70.0 ± 0.1	95.0 ± 0.2	0.33 ± 0.01	0.28 ± 0.02

3.3. Heat treatment with medium-viscosity CMC

Paste viscogram data of starches before and after dry heat treatment with 1% medium-viscosity CMC are presented in Table 4. Peak viscosities of all the starch decreased after dry heating, which was similar to those obtained by heat treatment with 2% low-viscosity CMC (Table 3). However, final viscosity increased after dry heating, which was similar to those obtained by heat treatment with 1% low-viscosity CMC (Table 2). No clear peak viscosity of waxy starch–CMC (1% medium-viscosity CMC) mixture was seen on the pasting curve (Fig. 1). The viscosity was maintained during the holding period at 95 °C, and the final viscosity was significantly higher than the peak viscosity. It indicated that the swelling of starch granules was restricted and shear-stabilization of the starch was provided by dry heat treatment with 1% medium-viscosity CMC. This was similar to those obtained with chemical cross-linking.

Great change in pasting properties was observed when the medium-viscosity CMC concentration increased from 1 to 2% (Table 5). No peak viscosity and very low final viscosity were found of the starches heat-treated with 2% medium-viscosity CMC. This suggested that the swelling and pasting of starch granules were completely inhibited.

3.4. Particle size distribution of starches before and after treatment

In order to address the relationship between the pasting behavior and the effect of dry heat treatment on the rice starches, particle size distribution of starches before and after treatment was measured to investigate the change in granule size and the specific combination of gum and starch during dry heating.

Dry heating without gum did not produce any remarkable change in the particle size of rice starches (Table 6).

The starch–CMC mixture before heat treatment also showed similar particle size to that of native starch. But significant change was found after the starches were dry heat-treated with CMC. The starch granule size increased dramatically and displayed bi-modal size distributions after heat treatment with low-viscosity CMC. This indicated that the starch molecules reacted with the CMC molecules. More than 50% of the rice starches with the particle size of less than 6 μm (5.62, 5.30 and 5.43 μm) did not react with CMC molecule after dry heat treatment with 1% low-viscosity CMC (Table 6). But when the concentration of CMC increased to 2%, only about 30% of the starches with the particle size of less than 6 μm (5.51, 5.48 and 5.40 μm) did not participate the reaction. CMC is multi-carboxylated so that at low concentration (1% CMC), the amount of starch molecules was more than CMC molecules. Thus, more than one starch chains could react with a gum molecule. But at higher concentration of CMC (2%), since the amylopectin of the starch has a lot of branch chains, one starch molecule could esterify to more than one CMC molecule. High crosslinkage was thusly formed between the starch and CMC molecules, which inhibited the swelling of the rice starches during pasting. It was reported that the viscosity of rice starch dispersion correlated positively with starch granule swelling during pasting (Li, Shoemaker, Ma, Kim, & Zhong, in press). From Table 3, both peak and final viscosities of the rice starches reduced when low-viscosity CMC increased to 2% concentration.

The rice starches also displayed bi-modal size distributions after heat treatment with 1% medium-viscosity CMC. But the shape of the size distributions changed from bi-modal to single peaked distribution with significant increase in particle size when the concentration increased to 2% (Table 6). This suggested that the starch molecules were highly esterified with CMC molecules. From Table 5, no pasting characters of rice starches were found after dry heat treatment with 2% medium-viscosity CMC. Since

Table 4
Paste viscogram data of starches before (B) and after (A) dry heat treatment with 1% medium-viscosity CMC

Samples	Pasting onset temperature (°C)	Peak temperature (°C)	Peak viscosity (Pa s)	Final viscosity (Pa s)
CM101+1%CMC B	64.8 ± 0.2	71.7 ± 0.2	0.92 ± 0.02	0.64 ± 0.01
CM101+1%CMC A	64.7 ± 0.2	76.1 ± 0.2	0.57 ± 0.03	0.89 ± 0.02
M202+1%CMC B	66.3 ± 0.2	91.1 ± 0.1	0.59 ± 0.04	0.51 ± 0.02
M202+1%CMC A	66.2 ± 0.1	90.7 ± 0.1	0.48 ± 0.03	0.70 ± 0.02
Cocodrie+1%CMC B	72.7 ± 0.2	91.7 ± 0.2	0.42 ± 0.04	0.46 ± 0.03
Cocodrie+1%CMC A	68.4 ± 0.2	90.7 ± 0.2	0.33 ± 0.03	0.68 ± 0.02

Table 5
Paste viscogram data of starches before (B) and after (A) dry heat treatment with 2% medium-viscosity CMC

Samples	Pasting onset temperature (°C)	Peak temperature (°C)	Peak viscosity (Pa s)	Final viscosity (Pa s)
CM101+2%CMC B	65.4 ± 0.2	71.5 ± 0.1	1.07 ± 0.03	0.89 ± 0.02
CM101+2%CMC A	64.2 ± 0.2	–	–	0.01 ± 0.01
M202+2%CMC B	65.5 ± 0.1	91.2 ± 0.2	0.68 ± 0.04	0.66 ± 0.03
M202+2%CMC A	63.9 ± 0.1	–	–	0.11 ± 0.02
Cocodrie+2%CMC B	71.4 ± 0.2	92.1 ± 0.2	0.58 ± 0.04	0.58 ± 0.02
Cocodrie+2%CMC A	67.8 ± 0.3	–	–	0.04 ± 0.02

Table 6
Particle size distribution before (B) and after (A) dry heat treatment with CMC

Samples	Particle size distribution (μm)									
	Native starch	Heat treatment without CMC	Starch+1% CMC (L) B ^a	Starch+1% CMC (L) A ^b	Starch+2% CMC (L) B	Starch+2% CMC (L) A	Starch+1% CMC (M) B ^c	Starch+1% CMC (M) A ^d	Starch+2% CMC (M) B	Starch+2% CMC (M) A
CM101	4.35	4.39	4.3	84.9 (45.1%) ^e 5.62 (54.9%)	4.31	62.5 (64.9%) 5.51 (35.1%)	4.32	65.1 (50.6%) 10.5 (49.4%)	4.3	82.7
M202	4.24	4.31	4.4	61.6 (45.8%) 5.50 (54.2%)	4.25	58.2 (65.2%) 5.48 (34.8%)	4.29	70.1 (60.7%) 6.91 (39.3%)	4.26	105.9
Cocodrie	4.39	4.45	4.4	71.6 (47.3%) 5.43 (52.7%)	4.36	63.8 (70%) 5.40(30%)	4.38	59.9 (61.2%) 6.36 (38.8%)	4.21	97.4

^a The starches were mixed with 1% low-viscosity CMC before heating.

^b The starches were heat-treated in a dry state after being impregnated with 1% low-viscosity CMC.

^c The starches were mixed with 1% medium-viscosity CMC before heating.

^d The starches were heat-treated in a dry state after being impregnated with 1% medium-viscosity CMC.

^e There were 45.1% of the granules with average particle size of 84.9 μm .

high crosslinkage and interaction between starch and CMC molecules were occurred, the swelling and pasting of starch granules were completely inhibited.

From the results above, the change in pasting properties and the increase in particle size of starch–CMC mixture depended on the reaction level of the combination between the starch and CMC. It indicated that crosslinkage occurred between the starch and CMC. The crosslinkage level depended on the amount of CMC and starch, which participated in the forming of ester linkage, as well as the viscosity of CMC.

3.5. Tensile strength and percentage elongation of starch-based films

Native and modified starches (from traditional and alternative sources) have long been used for the formation of starch-based edible films and coatings (Jansson & Thunander, 2004). The current trend is to look for alternative sources of starch with better physicochemical and functional characteristics (Romero-Bastida, Bello-Pérez, Garcia, Martino, Solorza-Feria, & Zaritzky, 2005). In our study, the rice starches dry heat-treated with 1% low-viscosity CMC were chosen for the formation of edible films to compare with those native rice starch-based films.

Tensile strength and percentage elongation of native and modified starch-based films are presented in Fig. 2. The modified starch-based films showed significant improvement in the tensile strength. Crosslinkage between the starch and CMC resulted in more compact molecule structures of starch–CMC mixture and tensile strength was thusly increased. It was found that the tensile strength correlated positively with amylose content. Zobel (1988) found that linear amylose molecules formed strong films whereas branched amylopectin-based films were weak and brittle. Although modified starch films had greater tensile strength than the native starch film, no clear improvement of percentage elongation of modified starch-based films was observed. Percentage elongation of modified M202

starch-based film was lower than that of native starch film. This was probably attributed to a case of antiplasticization by moisture which made the films more rigid rather than flexible. Antiplasticization of mechanical properties of bio-

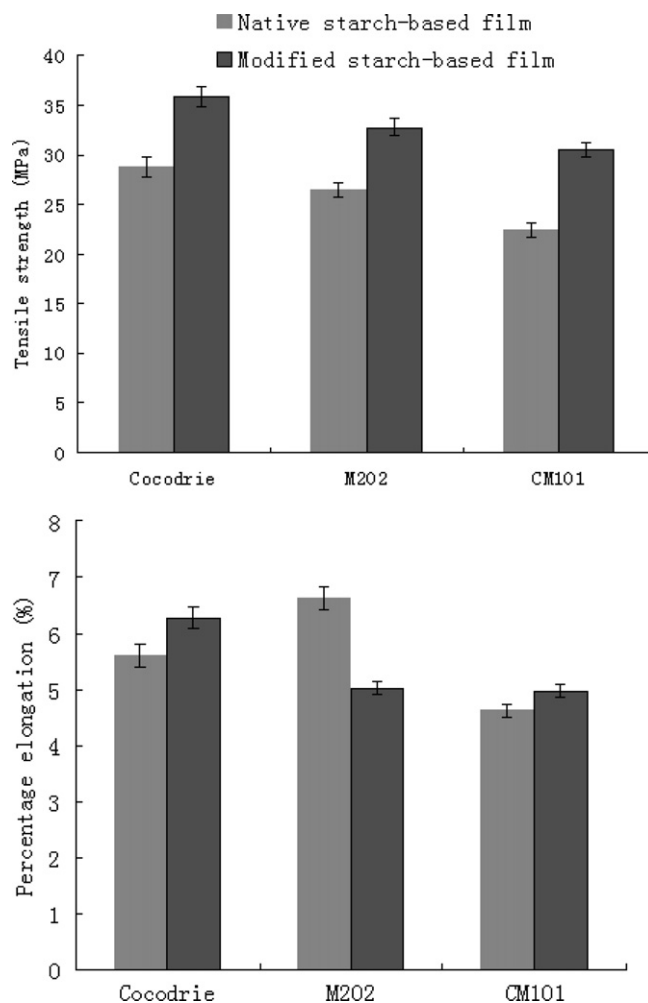


Fig. 2. Tensile strength and percentage elongation of native and modified starch-based films.

polymeric materials (including films) by water is a well-known phenomenon (Chang, Cheah, & Seow, 2000; Seow, Cheah, & Chang, 1999), though the basic mechanism behind it is still far from clear.

3.6. Water vapor and oxygen permeability of starch-based films

Water vapor permeability (WVP) and oxygen permeability (PO_2) of native and modified starch-based films are presented in Table 7. Both WVP and PO_2 decreased for the modified starch-based films. WVP of a film is believed to be dependent upon the number of “available” polar (–OH) groups that the polymer possesses (Cheng, Karim, Norziah, & Seow, 2002). The carboxylate acid groups of CMC reacted with the hydroxyl groups of the starch to form an ester bond through dry heating which would lead to the formation of a more highly structured matrix and diminish the number of available –OH groups, thereby impeding diffusion of water vapour. WVP of both native and modified rice starch-based films was found to be negatively correlated to the amylose content of different rice starches. Waxy starch consists mainly of amylopectin, which was more hydrophilic than amylose, resulting in higher WVP of waxy starch-based film. PO_2 of both native and modified rice starch-based films also negatively correlated to the amylose content of the starches. It was reported that the structure of the starch granule with high amylose content was highly strengthened and more rigid (Lii, Tsai, & Tseng, 1996). High amylose starch would form more compact and strong film, and inhibit the gas permeability.

3.7. Dynamic mechanical properties of starch-based films

Table 8 shows the storage modulus (G'), loss modulus (G'') and $\tan \delta$ of native and modified starch-based films at room temperature. The storage modulus is a measure of the energy stored and recovered in a cyclic deformation whereas the loss modulus is a measure of the energy dissipated. $\tan \delta$ is the ratio of the energy lost to the energy stored in a cyclic deformation (Ferry, 1980). After dry heat treatment with CMC, the value of G' of all modified starch-based films increased (Table 8). But $\tan \delta$ of around 0.06 was unchanged. The G' of both native and modified starch-based films was positively correlated to the amylose content of the rice starches (Table 8). It was noticed that

Table 7
Water vapor and oxygen permeability of native and modified starch-based films

Samples	Water vapor permeability (g mm/m ² h kPa)		Oxygen permeability (cm ³ mm/m ² h kPa)	
	Native	Modified	Native	Modified
Cocodrie	0.665 ± 0.014	0.584 ± 0.009	0.681 ± 0.029	0.531 ± 0.004
M202	0.674 ± 0.015	0.595 ± 0.017	1.102 ± 0.031	0.962 ± 0.005
CM101	0.764 ± 0.016	0.625 ± 0.017	1.382 ± 0.020	1.172 ± 0.006

Table 8
Storage modulus (G'), loss modulus (G'') and $\tan \delta$ of native and modified starch-based films at room temperature

Samples	G' (MPa)		G'' (MPa)		$\tan \delta$	
	Native	Modified	Native	Modified	Native	Modified
Cocodrie	2537	2659	139.7	174.4	0.06	0.06
M202	2250	2304	152.8	145.4	0.07	0.06
CM101	1936	2268	123.2	144.5	0.06	0.06

these results were similar to those of tensile strength and percentage elongation results (Fig. 2). The storage modulus and the loss modulus correlated positively to the tensile strength and percentage elongation, respectively.

The storage (G') and loss (G'') modulus of native and modified CM101 starch-based films were determined as a function of temperature (Fig. 3). DMA studies revealed that both native and modified starch films had a decreasing G' of about 2700 and 3000 MPa, respectively over the temperature range –40 to 60 °C. The decrease in the G' suggested that the material was becoming less elastic or conversely more permanently deformable. The values of G' of modified starch-based film were higher than those of native starch-based film, which indicated that the modified starch-based film were more elastic than the native starch-based film. There was also a decrease in G'' over the temperature range –40 to 60 °C. No significant

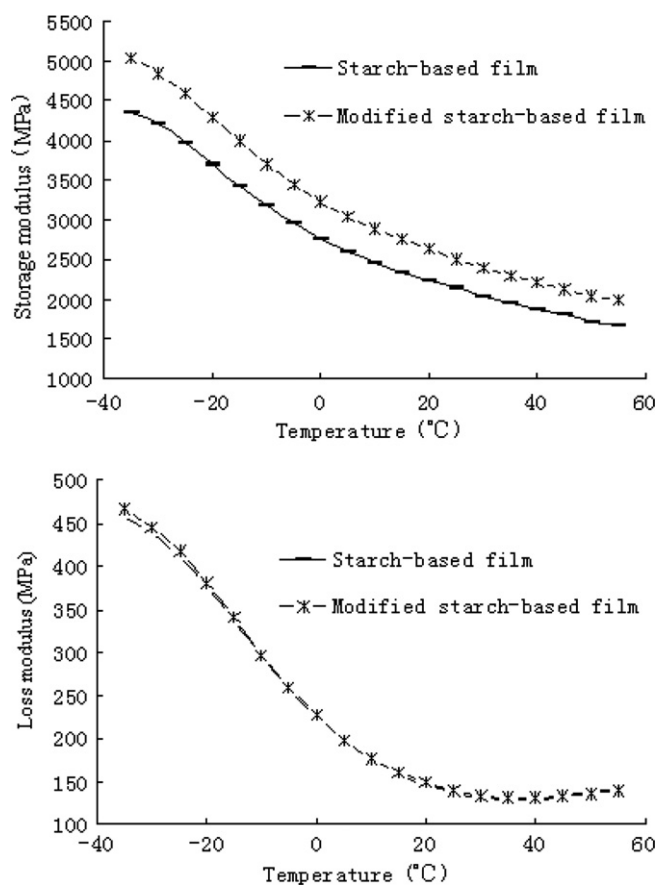


Fig. 3. Temperature dependence of the dynamic mechanical behaviors of native and modified CM101 starch-based films.

difference of G'' was observed between the native and modified starch-based film. It indicated that dry heating with CMC had more effect on the storage modulus than the loss modulus of the starch-based film.

4. Conclusion

The pasting properties of the starches after dry heat treatment with CMC changed remarkably. Dry heating with low-viscosity CMC at low concentration (1% CMC), raised the peak and final viscosities and particle size of all the starches. After heat-treated with 2% low-viscosity CMC, the waxy starch showed significant decrease in viscosity throughout pasting. It indicated that ester bonds were formed between the hydroxyl groups in amylopectin branches of the starch and carboxylate acid groups of CMC. The pasting viscosity of waxy starch–CMC (1% medium-viscosity CMC) mixture provided by dry heating was similar to those obtained with chemical cross-linking. The swelling of starch granules were completely inhibited due to high esterification when heat-treated with 2% medium-viscosity CMC carboxylates. Crosslinkage led to more compact molecule structures of starch–CMC mixture, resulting in the improvement in the tensile strength in modified starch-based film. Both water vapor and oxygen permeability decreased for the modified starch-based films, and the values of G' of modified starch-based film were higher than those of native starch-based film over the temperature range -40 to 60 °C. Dry heating process with CMC at different viscosities and concentrations can provide desirable functionality of starch and starch-based film.

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References

- Aguirre-Cruz, A., Méndez-Montealvo, G., Solorza-Feria, J., & Bello-Pérez, L. A. (2005). Effect of carboxymethyl-cellulose and xanthan gum on the thermal functional, and rheological properties of dried nixtamalised maize masa. *Carbohydrate Polymers*, *62*, 222–231.
- Arvanitoyannis, I., & Biliaderis, C. G. (1998). Physical properties of polyol-plasticized edible films made from sodium caseinate and soluble starch blends. *Food Chemistry*, *62*, 333–342.
- Arvanitoyannis, I., & Biliaderis, C. G. (1999). Physical properties of polyol-plasticized edible blends made of methyl cellulose and soluble starch. *Carbohydrate Polymers*, *38*, 47–58.
- Arvanitoyannis, I., & Psomiadou, E. (1994). Composites of anionic copolyamides (nylon6/nylon12) with short E-glass fibers: Preparation and properties. *Journal of Applied Polymer Science*, *51*, 1863–1899.
- ASTM (1987). Standard methods for water vapor transmission of materials. *Annual book of ASTM standards*, E96–80, 629–636.
- ASTM (1989). Mechanical properties; Tensile strength and elongation. *Annual book of ASTM standards*, D828–88, 730–736.
- ASTM (1993). Standard test method for oxygen gas transmission rate through plastic film and sheeting using coulometric sensor. *Annual book of ASTM standards*, D3985–81, 1656–1661.
- Chang, Y. P., Cheah, P. B., & Seow, C. C. (2000). Plasticizing–antiplasticizing effects of water on physical properties of tapioca starch films in the glassy state. *Journal of Food Science*, *65*, 445–451.
- Cheng, L. H., Karim, A. A., Norziah, M. H., & Seow, C. C. (2002). Modification of the microstructural and physical properties of konjac glucomannan-based films by alkali and sodium carboxymethylcellulose. *Food Research International*, *35*, 829–836.
- Chiu, C.-W., Schiermeyer, E., Thomas, D.J., Shah, M.B., (1998). Thermally inhibited starches and flours and process for their production. US Patent 5,725,676.
- Debeaufort, F., Quezada-Gallo, J., & Volley, A. (1998). Edible films and coatings: Tomorrow's packagings: A review. *Critical Reviews in Food Science*, *38*(4), 299–313.
- El-Khayat, G., Samaan, J., & Brennan, C. S. (2003). Evaluation of vitreous and starchy Syrian durum (*Triticum durum*) wheat grains: The effect of amylose content on starch characteristics and flour pasting properties. *Starch/Stärke*, *55*, 358–365.
- Ferry, J. D. (1980). *Viscoelastic properties of polymers* (3rd ed.). New York: John Wiley & Sons.
- Gurkin, S. (2002). Hydrocolloids-ingredients that add flexibility to tortillas processing. *Cereal Foods World*, *47*(2), 41–43.
- Jansson, A., & Thuvnander, F. (2004). Influence of thickness on the mechanical properties for starch films. *Carbohydrate Polymers*, *56*, 499–503.
- Li, Y., Shoemaker, C.F., Ma, J.G., Kim, J.M., Zhong, F. (in press). Structure–viscosity relationships for starches from different rice varieties during heating. *Food Chemistry*, doi:10.1016/j.foodchem.2007.07.039.
- Lii, C. Y., Tsai, M. L., & Tseng, K. H. (1996). Effect of amylose content on the rheological property of rice starch. *Cereal Chemistry*, *73*(4), 415–420.
- Lim, H. S., BeMiller, J. N., & Lim, S.-T. (2003). Effect of dry heating with ionic gum at controlled pH on starch paste viscosity. *Cereal Chemistry*, *80*(2), 198–202.
- Lim, S.-T., Han, J.-A., Lim, H. S., & BeMiller, J. N. (2002). Modification of starch by dry heating with ionic gums. *Cereal Chemistry*, *79*(5), 601–606.
- Lourdin, D., Della Valle, G., & Colonna, P. (1995). Influence of amylase content on starch films and foams. *Carbohydrate Polymers*, *27*, 261–270.
- Okada, M. (2002). Chemical syntheses of biodegradable polymers. *Progress in Polymer Science*, *27*, 87–133.
- Ollett, A. L., Parker, R., & Smith, A. C. (1991). Deformation and fracture behavior of wheat starch plasticized with glucose and water. *Journal of Material Science*, *26*, 1351–1356.
- Pavlat, A. E., & Robertson, G. H. (1999). Biodegradable polymers vs. recycling: What are the possibilities. *Critical Reviews in Analytical Chemistry*, *29*(3), 231–241.
- Romero-Bastida, C. A., Bello-Pérez, L. A., García, M. A., Martino, M. N., Solorza-Feria, J., & Zaritzky, N. E. (2005). Physicochemical and microstructural characterization of films prepared by thermal and cold gelatinization from non-conventional sources of starches. *Carbohydrate Polymers*, *60*, 235–244.
- Seow, C. C., Cheah, P. B., & Chang, Y. P. (1999). Antiplasticization by water in reduced-moisture food systems. *Journal of Food Science*, *64*, 576–581.
- Shi, X.-H., & BeMiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers*, *50*, 7–18.
- Tapia-Blácido, D., Sobral, P. J., & Menegalli, F. C. (2005). Development and characterization of biofilms based on Amaranth flour (*Amaranthus caudatus*). *Journal of Food Engineering*, *67*, 215–223.
- Zobel, H. F. (1988). Molecules to granules: A comprehensive starch review. *Starch/Stärke*, *40*(2), 44–45.