

Preparation of Acetylated Waxy, Normal, and High-Amylose Maize Starches with Intermediate Degrees of Substitution in Aqueous Solution and Their Properties

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ABSTRACT: Acetylated waxy, normal, and high-amylose maize starches with intermediate degrees of substitution (DS) were prepared in aqueous solution with 20% (w/w) sodium hydroxide as a catalyst. The level of DS was in the order high-amylose maize starch > waxy maize starch > normal maize starch. Settling volume indicated that during the early reaction, normal maize starch swelled to a lesser extent compared with waxy and high-amylose maize starches. The settling volume of all three starches increased initially but decreased after long reaction time. Aggregation of granules was observed as DS increased. The A-type X-ray diffraction pattern of acetylated normal and waxy maize starches weakened as DS increased, whereas the diffraction peaks disappeared in acetylated high-amylose starch when DS was 0.95. Low DS promoted the swelling of the starches in water, but at high DS, the starches became more hydrophobic and the peak viscosity of acetylated starches decreased.

KEYWORDS: maize starch, acetylation, degree of substitution

INTRODUCTION

Starch, the storage polysaccharide of higher plants, is an important natural, renewable, and biodegradable material; however, native starches have limited industrial uses. Chemical modification is often used to alter the physicochemical properties of starches and to extend their applications.¹

Acetylation is one of the esterifications of starch.^{2,3} Starches with low, intermediate, or high degrees of substitution (DS) may be produced. Acetylated starches with a low DS (0.01–0.2) may function as film-forming, binding, adhesion, thickening, stabilizing, and texturing agents^{4–6} and are used widely in a large variety of foods including baked goods, canned pie fillings, sauces, retorted soups, frozen foods, baby foods, salad dressings, and snack foods.^{1–3,7} Acetylated starches with intermediate DS (0.2–1.5) and high DS (1.5–3) have been of research interest for their solubility in acetone and chloroform and for their thermoplasticity.^{5,8} As biodegradable carbohydrate polymers, acetylated starches with intermediate or high DS also have many potential uses such as hot melt adhesives, coatings, cigarette filters, biodegradable packaging materials, tablet binders, and other pharmaceutical applications.^{9–14}

Techniques used in preparing the starch esters have generally involved aqueous reactions^{15–17} for low-DS starch esters and nonaqueous systems such as anhydrous pyridine¹⁸ for high-DS starch esters. Chi et al.¹⁹ also prepared the intermediate- and high-DS starch acetate using methanesulfonic acid as a catalyst. Yellow ginger starch acetates with different DS values were prepared by reacting native starch with glacial acetic acid/acetic anhydride using sulfuric acid as a catalyst.²⁰ Using acetic acid anhydride both as a reactant and as a solvent, Volkert et al.²¹ applied three activators, acetic acid, aqueous sodium hydroxide, and potassium carbonate, to make starch acetates with high DS. A microwave-assisted method was developed to prepare starch acetates with high DS in 2 min using iodine as a catalyst.²²

Starch was also acetylated with vinyl acetate²³ and acetic anhydride²⁴ in imidazolium ionic liquids.

In an aqueous suspension, acetylated starch with a DS of 0.5 can be made by reacting the starch with acetic anhydride at pH 7–11,²⁵ but to reach a DS of 0.5, researchers must repeatedly increase reagent concentrations by filtering the starch from the reaction mixture, resuspend it in 1.25–1.5 parts of water per part of starch, and continue the acetylation. Acetylation of high-amylose (70%) maize starch to a DS of 0.57–2.23 was performed by reacting starch with acetic anhydride using 50% aqueous NaOH as a catalyst.⁸ Starch granules were destroyed during the reaction. The high cost, difficult recovery, and volatility of the solvent have limited commercial development of starch acetate products with intermediate and high DS. A method of preparing starch esters with an intermediate DS using a one-step aqueous process with organic acid anhydride in the presence of sodium hydroxide and recovery of the product by filtration was disclosed,²⁶ but structural changes of acetylated maize starch with intermediate DS in aqueous solution are not well documented. Maize starches with different amylose contents and crystallite types are available. Normal maize and waxy maize starches give an A-type X-ray diffraction pattern, whereas high-amylose maize starch gives a B-type pattern. Whether these starches with different amylose contents behave differently when used to make an intermediate-DS starch acetate is unclear.

The objectives of this study were to (1) systematically study the properties of acetylated starch with intermediate DS prepared using a one-step aqueous process with organic acid anhydride in the presence of a high concentration of sodium

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Table 1. Degree of Substitution of Native and Acetylated Starches^a

starch resource	acetylation time					
	40 min	80 min	120 min	160 min	200 min	240 min
waxy	0.30 ± 0.01ab	0.75 ± 0.01b	0.81 ± 0.02b	0.87 ± 0.03b	0.94 ± 0.01b	1.08 ± 0.02b
normal	0.27 ± 0.02b	0.50 ± 0.03c	0.67 ± 0.01c	0.69 ± 0.01c	0.70 ± 0.01c	0.71 ± 0.01c
high-amylose	0.33 ± 0.01a	0.87 ± 0.02a	0.95 ± 0.02a	1.12 ± 0.02a	1.21 ± 0.02a	1.29 ± 0.03a

^aData represent the mean ± standard deviation. Values in the same column with different letter are significantly different ($p < 0.05$).

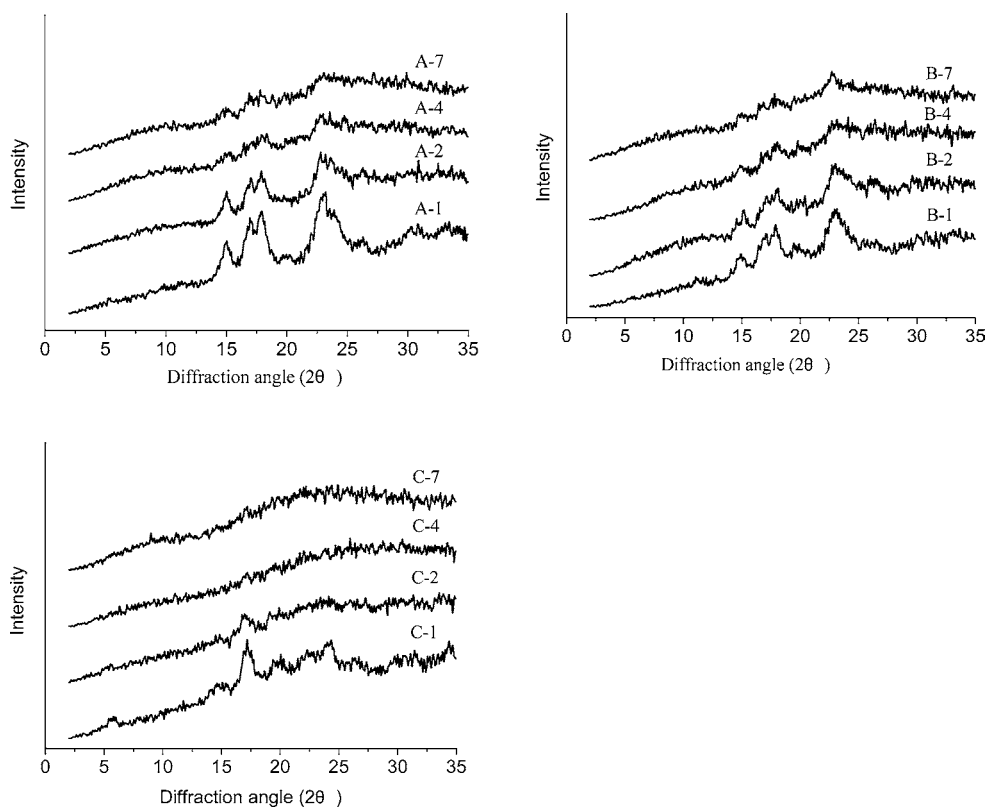


Figure 1. X-ray diffraction patterns of native and acetylated maize starches (A) waxy; (B) normal; (C) high-amylose; (1) native; (2, 4, 7) acetylated for 40, 120, and 240 min, respectively.

hydroxide and (2) compare morphological properties, crystallinity, gelatinization parameters, and pasting properties of acetylated waxy, normal, and high-amylose maize starches.

MATERIALS AND METHODS

Materials. Waxy maize (Amioca), normal maize (Melojel), and high-amylose maize (HYLON VII) starches were obtained from National Starch LLC (Bridgewater, NJ, USA). All other chemicals and solvents were of analytical grade.

Acetylation of Starch. Native starch (200 g, dry basis) was slurried in distilled water (500 mL) with an overhead mechanical stirrer, and the pH was adjusted to 8.0 and controlled at pH 8.0 during the reaction by the dropwise addition of 20% (w/w) NaOH. The temperature was lowered to 10–15 °C by an ice–water bath. When the proper temperature was reached, acetic anhydride, 33.3, 66.7, 100.0, 133.3, 166.7, and 200.0% (v/w), based on the dry weight of starch, was added dropwise and reacted for 40, 80, 120, 160, 200, and 240 min, respectively. Each sample (50 mL) was taken and adjusted to the same concentration (24.8%) with distilled water and pH 6.5 after determination of the moisture content of the samples, and their viscosity was determined by a Brookfield viscometer (model DV-II +Pro, Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA) with a no. S61 spindle to monitor the changes of starches during the reaction. The starch was adjusted to pH 6.5 with 0.5 mol/L HCl

and filtered, and the residual material was washed twice with distilled water. The final product was oven-dried at 40 °C overnight.

After each sample was analyzed by the viscometer, it was poured into a 100 mL measuring cylinder; the settling volume, which included the volume of hydrated starch granules and water between starch granules, was recorded after the sample was held at 25 °C for 24 h.

Determination of DS. The DS of acetylated starch was determined by proton nuclear magnetic resonance (¹H NMR).²⁷ Starch esters (0.015 g) were mixed with 1 mL of D₂O and freeze-dried, and then the procedure was repeated once. The D₂O-exchanged starches were stirred for >4 h and dissolved in 1 mL of deuterated dimethyl sulfoxide (DMSO-*d*₆). The solution was centrifuged at 10000g for 5 min, and the supernatant was analyzed by NMR. The ¹H NMR spectra were acquired at 37 °C using a Varian 400 NMR system (Varian Inc., Palo Alto, CA, USA). Sixteen scans were acquired for each sample with relaxation times of 1.0 s.

Microscopic Observations. Native starches and starch slurries taken from the acetylation reaction were diluted to 1% (w/w) and observed under an optical microscope (Olympus BX51, Tokyo, Japan).

The morphology of the starch granules was observed by scanning electron microscopy. Oven-dried starch samples were mounted on circular aluminum stubs with double-sided tape, coated with 20 nm of gold, and examined and photographed in a scanning electron microscope (LEO 1530VP, Oberkochen, Germany) at an accelerating potential of 20 kV.

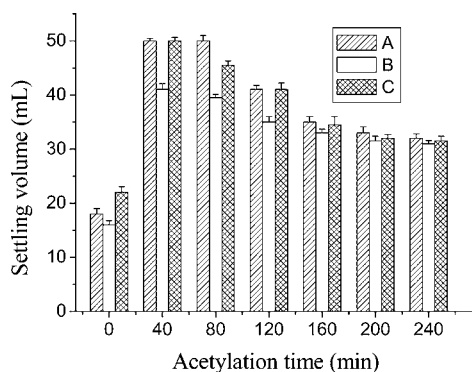


Figure 2. Settling volume of native and acetylated maize starches: (A) waxy; (B) normal; (C) high-amylose.

X-ray Diffraction. X-ray diffraction was conducted with an RU200R X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu K α radiation at 35 kV and 20 mA, a θ -compensating slit, and a diffracted beam monochromator. All samples were adjusted to about 20% moisture content before analysis. The diffractograms were recorded between 2° and 35° (2 θ).

Differential Scanning Calorimetry (DSC). Gelatinization properties were measured by a Perkin-Elmer DSC-8000 differential scanning calorimeter equipped with a thermal analysis data station (Norwalk, CT, USA). Water (7.0 μ L) was added with a microsyringe to starch (3.0 mg dry basis) in the DSC pans, which were then sealed, reweighed, and kept overnight at room temperature. Each pan was heated from 20 to 150 °C at 10 °C/min. The thermogram was recorded with an empty pan as a reference.

Pasting Properties. The starch-pasting curve was obtained with a Rapid Visco Analyzer (RVA-4, Newport Scientific Pty. Ltd., Warriewood, NSW, Australia). A starch sample of 3 g (corrected to 14% moisture content) was weighed directly in the aluminum RVA sample canister, and 25 mL of distilled water was added. For high-amylose starches, an aqueous suspension of 15% (w/w) was analyzed. The starch suspension was stirred with a paddle speed of 160 rpm/min and heated from 35 to 95 °C at 15 °C/min, held at 95 °C for 3 min, cooled to 50 °C at 10 °C/min, and held at 50 °C for 2 min.

Statistical Analysis. All tests were replicated three times, and mean values and standard deviations were reported. Analyses of variance (ANOVA) were performed, and the mean separations were determined by Tukey's HSD test ($p < 0.05$) using SigmaStat version 2.0 (Jandel Scientific/SPSS Science, Chicago, IL, USA).

RESULTS AND DISCUSSION

DS of Acetylated Starches. DS increased with reaction time but was different among the three starches (Table 1). Acetylated high-amylose maize starches showed the highest DS at the same reaction conditions. The source of starch has been reported to affect the extent of modification. Barley starch acetylated with acetic anhydride or vinyl acetate had a higher DS than corn starch.¹⁶ Corn starch showed lower acetyl content and DS than potato starches under similar experimental conditions.¹⁷ Among native starches, normal and waxy maize

showed the typical A-type X-ray diffraction pattern, whereas high-amylose maize showed the B-type X-ray pattern (Figure 1). Moreover, native high-amylose maize starch had a lower degree of crystallinity than waxy and normal maize starches^{28–30} and, interestingly, the highest settling volume (Figure 2), indicating the higher swelling of its granules at 25 °C. As a result, high-amylose maize starch granules had more amorphous regions available for reaction when acetylation started. Continued reaction and substitution further reduced crystallinity (Figure 1) and allowed more reaction.

Both waxy maize and normal maize starches showed an A-type X-ray diffraction pattern (Figure 1), but waxy maize starch had a higher DS of acetylation than normal maize starch at the same reaction conditions (Table 1). Settling volume and viscosity revealed interesting results and explained the differences between waxy maize and normal maize starches. Starch granules swelled during acetylation and led to the change in settling volume (Figure 2) and viscosity of the acetylated starch slurry (Table 2). Waxy maize starch, with essentially no amylose, swelled more than normal maize starch during the early stage of acetylation, had more sites for reaction, and therefore resulted in products with higher DS. Singh et al.³¹ also reported that the lower the amylose content of potato starch, the greater the DS.

It is interesting to note that settling volume reached the largest value after 40 min of acetylation and decreased after that (Figure 2). Consistent with the settling volume, the viscosity of acetylated starches at 25 °C was also greatest after 40 min of acetylation (Table 2). We believe that the initial acetylation promoted the swelling of starch granules, but as the DS increased, more acetyl groups were substituted and starch molecules became more hydrophobic. As a result, settling volume decreased and the viscosity of the starches at 25 °C decreased (Table 2). Furthermore, the increase in hydrophobicity also affected the viscosity of cooked starch as discussed under Pasting Properties.

Changes in Morphology. The photographs of light microscopy of native and acetylated starches are shown in Figure 3. The starch granules were swollen and lost their individuality and smoothness after 40 min of reaction time. This phenomenon was also observed in the scanning electron micrographs (Figure 4). After 40 min, some starch granules lost birefringence. More starch granules lost birefringence with increasing reaction time; however, some starch granules in the three starches remained birefringent at the end of the reaction. The acetylation resulted in aggregation, or cluster formation, of granules in the three starches. As the DS of the starch acetates increased, granules developed blisters or small protuberances on their surfaces. Singh et al.¹⁷ reported similar observations in potato starch. The aggregation of starch granules after acetylation could be attributed to the introduction of acetyl groups on the starch molecules.^{17,31,32} We suspected that the rough appearance of their surfaces was due to the surface gelatinization as

Table 2. Viscosity of Native and Acetylated Starches (cP)^a

starch resource	acetylation time						
	0 min	40 min	80 min	120 min	160 min	200 min	240 min
waxy	6.7 ± 0.5b	578.0 ± 21.7a	203.3 ± 10.1a	158.3 ± 8.9a	21.7 ± 1.3a	20.5 ± 1.1aa	19.9 ± 1.5a
normal	6.8 ± 0.7b	46.6 ± 6.7c	37.9 ± 1.2c	30.0 ± 2.1c	21.9 ± 2.2a	20.9 ± 2.3a	20.1 ± 2.1a
high-amylose	8.3 ± 0.3a	287.3 ± 12.5b	151.7 ± 7.8b	46.7 ± 3.2b	20.0 ± 1.8a	20.1 ± 1.2a	19.7 ± 1.8a

^aData represent the mean ± standard deviation. Values in the same column with different letter are significantly different ($p < 0.05$).

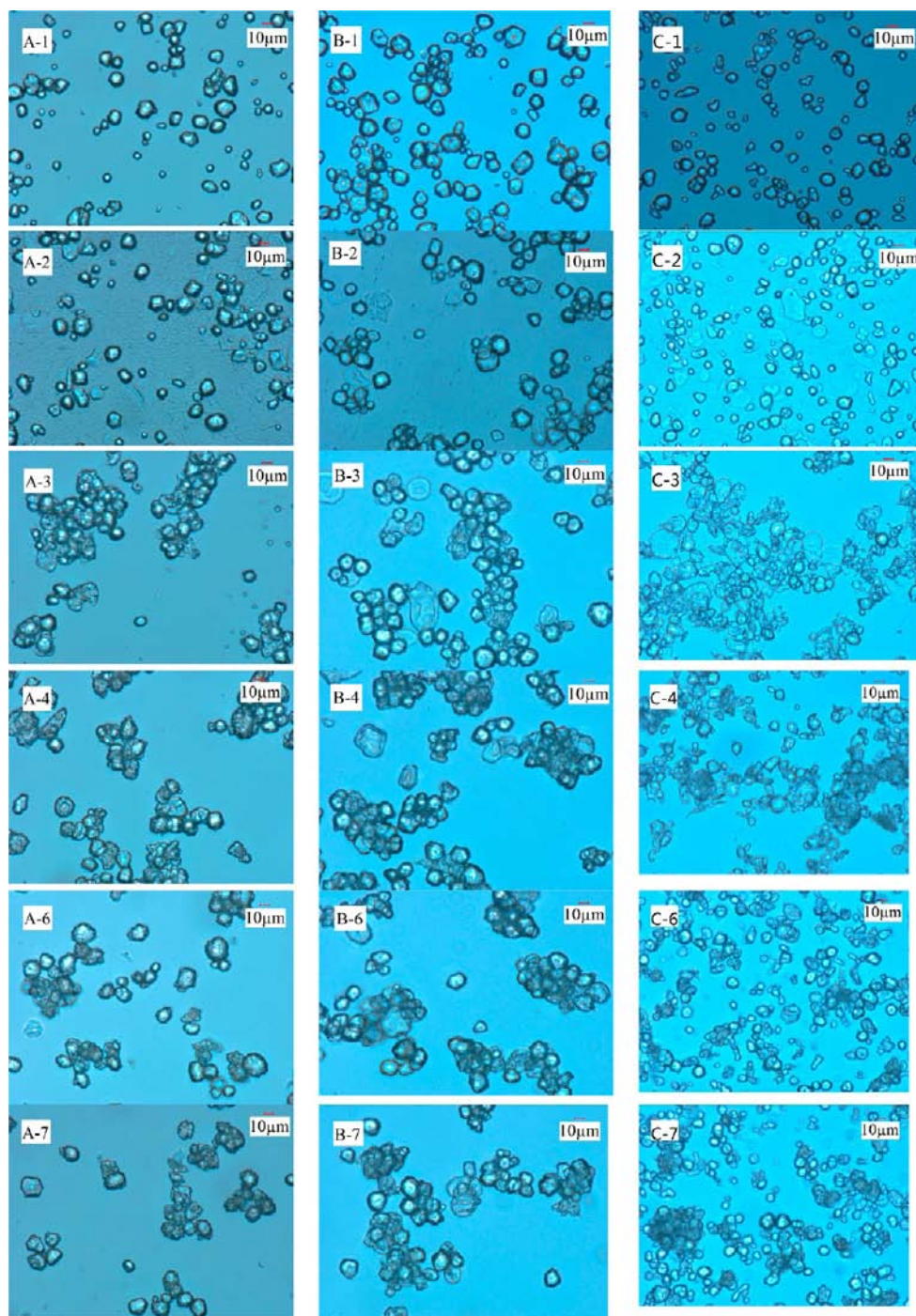


Figure 3. Photographs of light microscope of native and acetylated maize starches: (A) waxy; (B) normal; (C) high-amylose; (1) native; (2, 3, 4, 6, 7) acetylated for 40, 80, 120, 200, and 240 min, respectively.

a result of adding 20% (w/w) NaOH while keeping the pH at 8.0 during acetic anhydride addition.

Changes in X-ray Diffraction. The X-ray diffraction patterns and intensities of the major diffraction peaks of native and acetylated starches are presented in Figure 1. For normal and waxy maize starches, acetylated starch remained an A-type X-ray pattern and had weak diffusion peaks at 15° , 17° , 18° , and 23° (2θ) as DS increased. For acetylated high-amylose starch, the B-type diffraction peaks at 5.6° and 17° (2θ) and small peaks at around 2θ values of 20° , 22° , and 25° disappeared after acetylation. The diffraction peaks disappeared in acetylated high-amylose starch when the DS was 0.95. Intra- and intermolecular

hydrogen bonds were responsible for the highly ordered crystalline structure.⁸ Acetylation reduced the formation of intermolecular hydrogen bonds and thereby resulted in the destruction of the ordered crystalline structure. Destruction or even loss of the ordered crystalline structure increased with increasing DS.

Thermal Properties. Gelatinization temperatures of acetylated starches were shifted to lower temperatures compared with untreated samples and significantly decreased with increasing DS (Table 3). In general, native and acetylated high-amylose maize starches had a broader range of gelatinization compared with waxy and normal maize starches. The starch

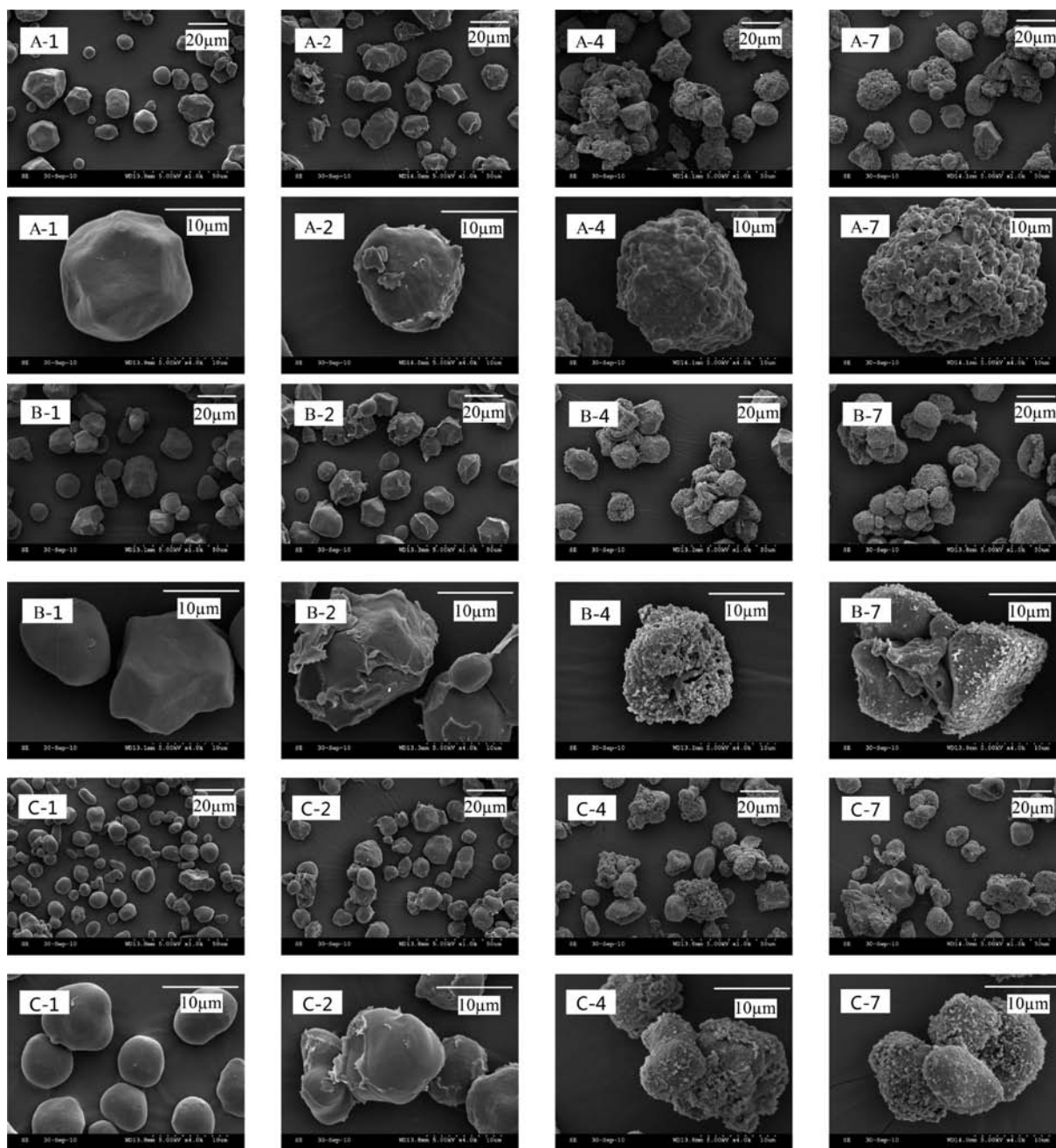


Figure 4. Photographs of SEM of native and acetylated maize starches: (A) waxy; (B) normal; (C) high-amylose; (1) native; (2, 4, 7) acetylated for 40, 120, and 240 min, respectively.

gelatinization is controlled, in part, by the amylopectin molecular structure and the granule structure.³³ The decrease in gelatinization transition temperature is in agreement with the early rupture of the amylopectin double helices and the melting of the crystalline lamellae in starches induced by the acetylation reaction. Singh et al.³¹ also reported a significant decrease in the gelatinization temperature of potato starch after acetylation. Wotton and Bamunuarachchi³⁴ suggested that introduction of acetyl groups into polymer chains resulted in destabilization of granular structure, thus causing a decrease in gelatinization temperature.

ΔH primarily reflects the loss of double-helical order rather than loss of crystalline register within the granule.^{33,35,36} The decrease in ΔH values of starch acetates suggested that some of the double helices present in crystalline and noncrystalline

regions of the granule were disrupted during the acetylation reaction. The lower ΔH suggests a lower percentage of organized arrangements or a lower stability of the crystals.³⁷ The higher the DS of the starch, the larger the decrease in ΔH values (Table 3). After 240 min of acetylation, ΔH values of the three starches decreased 55–60%. Decreases in temperature and enthalpy of gelatinization were also noted when banana starch was esterified with octenylsuccinic anhydride.³⁸

Pasting Properties. The RVA viscographs of native and acetylated starches are shown in Figure 5. The decrease in initial pasting temperature was observed as a result of acetylation of the three maize starches. For waxy and normal maize starches, the peak viscosity increased initially but decreased after prolonged acetylation. A drop in viscosity of acetylated waxy starch was found after acetylation for 80 min, and the

Table 3. DSC Characteristics of Native and Acetylated Starches^a

starch and acetylation time (min)	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
waxy maize				
0 min (native)	70.8 ± 0.6a	79.5 ± 0.8a	88.4 ± 1.1a	12.3 ± 0.5a
40 min	65.8 ± 0.4b	72.7 ± 0.9b	82.9 ± 0.7b	10.8 ± 0.4ab
80 min	64.7 ± 0.3bc	68.9 ± 0.5c	75.8 ± 0.6c	9.4 ± 0.2bc
120 min	63.2 ± 0.5cd	66.3 ± 0.3cd	73.7 ± 0.5cd	7.9 ± 0.3cd
160 min	62.5 ± 0.1de	65.9 ± 0.1cd	70.6 ± 0.6de	6.2 ± 0.4de
200 min	59.3 ± 0.4e	65.2 ± 0.4d	67.8 ± 0.5e	5.5 ± 0.2e
240 min	57.8 ± 0.2e	64.5 ± 0.5d	66.5 ± 0.3e	5.4 ± 0.3e
normal maize				
0 min (native)	68.9 ± 1.0a	76.9 ± 0.7a	82.6 ± 0.3a	10.5 ± 0.3a
40 min	65.7 ± 0.6b	71.4 ± 0.4b	77.3 ± 0.9b	8.8 ± 0.6ab
80 min	63.1 ± 0.3c	68.2 ± 0.4c	73.8 ± 0.5c	7.3 ± 0.2bc
120 min	61.5 ± 0.4cd	67.8 ± 0.3b	70.8 ± 0.5cd	6.3 ± 0.2cd
160 min	58.7 ± 0.2de	65.5 ± 0.2c	67.5 ± 0.4de	4.7 ± 0.4d
200 min	57.9 ± 0.1e	64.8 ± 0.4d	66.8 ± 0.3de	4.5 ± 0.3d
240 min	57.3 ± 0.3e	63.5 ± 0.3d	66.1 ± 0.2e	4.6 ± 0.2d
high-amylose				
0 min (native)	74.8 ± 0.7a	85.6 ± 1.3a	110.3 ± 2.1a	11.6 ± 0.5a
40 min	72.3 ± 0.4ab	77.6 ± 1.5b	98.6 ± 1.2b	9.3 ± 0.3b
80 min	70.2 ± 0.6b	73.8 ± 0.8bc	86.8 ± 1.5c	8.1 ± 0.3bc
120 min	66.5 ± 0.6c	73.0 ± 0.3cd	83.1 ± 1.0cd	7.1 ± 0.4cd
160 min	63.1 ± 0.7cd	70.7 ± 0.3cde	78.8 ± 0.5d	6.1 ± 0.3d
200 min	58.7 ± 0.3d	68.9 ± 0.6de	75.1 ± 1.1d	5.5 ± 0.4d
240 min	56.8 ± 0.5d	65.9 ± 0.6e	73.1 ± 1.4d	4.8 ± 0.7d

^aData represent the mean ± standard deviation. Values in the same column with different letter are significantly different ($p < 0.05$).

decrease in viscosity of acetylated normal starch occurred after acetylation for 120 min. High-amylose maize starch behaved differently (Figure 5). For products reacted for a longer time, peak viscosity decreased significantly. High-amylose starches became like the highly swelling-restricted starches after acetylation for 200 min.

Three possible mechanisms have been proposed to explain the effects of acetylation on the interactions between the starch chains: (1) by simple steric hindrance preventing close association of chains to allow formation of hydrogen bonds, (2) by altering the hydrophilicity of the starch and thus affecting bonding with water molecules, or (3) by participation of the acetyl groups in improved hydrogen bonding with other starch chains.³⁹ In the acetylated starch with low DS, the presence of acetyl groups introduced steric hindrance, reduced interactions between starch chains, and increased ease of hydration of the starch granules. As a result, the initial pasting temperature was decreased and starch paste maintained high viscosity when waxy and high-amylose maize starches were acetylated for 40 min or normal maize starch was acetylated for <120 min. When DS increased, more acetyl groups replaced the hydroxyl groups, and that increased the hydrophobicity of the starch and decreased the hydrogen bonding in starch molecules and the hydration of the starch granules. Starch swelled initially during acetylation as observed by the settling volume (Figure 2) and viscosity (Table 2). The settling volume and viscosity reached maximums when the starches were acetylated for 40 min (Figure 2 and Table 2), but started decreasing after 80 min of acetylation as more acetyl groups were introduced and starch chains became more hydrophobic. Due to the increase in hydrophobicity, hot pasting viscosity also decreased (Figure 5).

The level of DS of acetylated starches was in the order high-amylose maize starch > waxy maize starch > normal maize starch and did not have a linear correlation with amylose content.

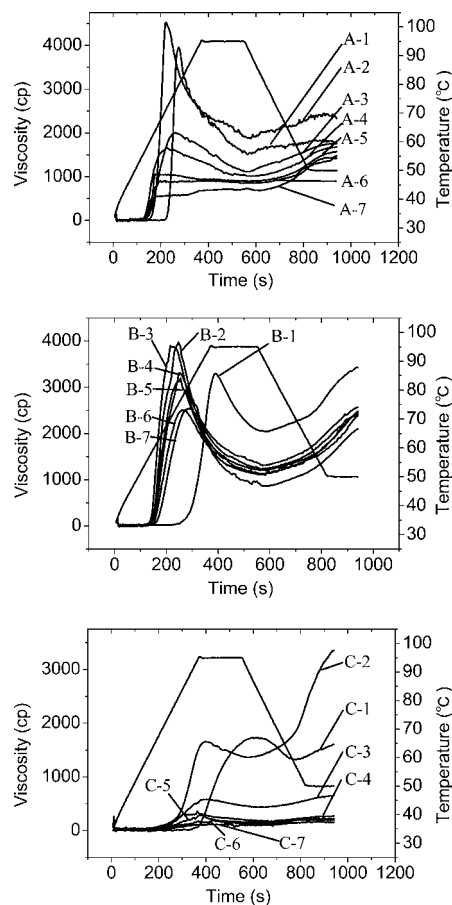


Figure 5. RVA pasting profiles of native and acetylated maize starches: (A) waxy; (B) normal; (C) high-amylose; (1) native; (2, 3, 4, 5, 6, 7) acetylated for 40, 80, 120, 160, 200, and 240 min, respectively.

Two factors, the proportion of the amorphous region and the degree of swelling during the acetylation, contributed to the level of DS. Settling volume indicated that normal maize starch swelled less during the early reaction compared with waxy and high-amylose maize starches. Hot paste viscosity suggested that low DS promoted the swelling of the starches in water and resulted in hot peak viscosity at lower temperatures. However, the starches became more hydrophobic after 80 min of acetylation for waxy and high-amylose starches and after 120 min of acetylation for normal starch, with corresponding DS values of 0.75, 0.67, and 0.87 for waxy, normal, and high-amylose maize starches, respectively, and their paste viscosity was significantly decreased. Future research is needed to understand the effect of distribution of acetyl groups in starch molecules on the functional properties of starches.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS USED

DS, degree of substitution; DSC, differential scanning calorimetry; RVA, Rapid Visco Analyzer; SEM, scanning electron microscope.

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