

Physical Properties of Octenyl Succinic Anhydride Modified Rice, Wheat, and Potato Starches

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The physical properties of octenyl succinic anhydride (OSA) starches prepared from rice, wheat, and potato starches were studied. Rice and wheat OSA starches had significantly higher peak viscosity (PV), hot paste viscosity (HPV), and cool paste viscosity (CPV), but potato OSA starch had only significantly higher CPV, relative to the native starch. The gel hardness was higher with lower degree of substitution (DS) but lower with higher DS OSA compared to native starch. The swelling volumes (SV) of rice and wheat OSA starches were significantly higher compared to native starch, but the SV of potato OSA starch was slightly lower at high DS. The gelatinization temperature (GT) of rice OSA starches was sharply lower at low DS; for wheat OSA starch it was slightly lower even at high DS, but potato OSA starches had higher GT than the native starch. The enthalpy of all the OSA starches decreased gradually with increased DS. This study showed that the magnitude of changes in physical properties of OSA-modified starches depends not only on their DS but also on the botanical origin of the native starches.

KEYWORDS: Starch; octenyl succinate; physical properties; thermal analysis; pasting

INTRODUCTION

Chemically modified starches are generally made by treating starch with agents that introduce chemical substituents via reaction with hydroxyl groups in the starch molecule. Such starches have physicochemical properties that differ significantly from the parent starch, thus widening their usefulness in many applications in food manufacturing and other industrial processes.

The modification of starch with octenyl succinic anhydride (OSA) was patented by Caldwell and Wurzburg in 1953 (1). The starch derivative is prepared by a standard esterification reaction in which cyclic dicarboxylic acid anhydride and starch are suspended in water and mixed under alkaline conditions. OSA-modified starch was reported to be an effective emulsifier due to the addition of dual functional hydrophilic and hydrophobic groups. Starch octenyl succinate derivatives are used in a variety of oil-in-water emulsions, in some water-in-oil systems, and in pharmaceutical and industrial areas, especially in food production, due to its good filming properties and excellent emulsion-stabilizing properties (2, 3).

Studies have been reported on preparative conditions (4), distribution of OSA groups (5), and properties of OSA starches (6, 7). A uniform distribution of OSA groups over the cross section of modified waxy maize starch granules was observed

(5). Amylopectin partial debranching showed heterogeneity in OSA substitution at the branch level (5). It was found that even a low level of substitution caused a considerable decrease in the extent of degradation of OSA starches by α -amylase, amyloglucosidase, and pullulanase, and the net extent of degradation decreased with increasing degree of substitution (DS). The great resistance to degradation shows that the presence of substituents in the starch chains restricts the activity of the enzymes (6). Emulsifying activity of OSA starch against different oil phases does not necessarily increase with increasing DS. The activity was largely independent of the concentration of the concentration of the substrates when the modification was conducted in an aqueous medium, but did show an increase in activity with concentration in an organic medium (7). There are few papers available on variation in physical properties of OSA starch except the original paper indicating that alkenyl succinates of waxy maize starch have higher viscosity in aqueous suspension, lower gelatinization temperature (GT), and less tendency to retrograde than unmodified starch (8). Understanding the relationship between the physical properties of OSA starch and DS may direct their applications in industry.

The physical properties of chemically modified starch are greatly influenced by electronic properties of the introduced group and the DS. Hydrophilic substituents (such as acetyl, hydroxypropyl, and phosphate groups) usually cause reduced gelatinization temperature and increased pasting viscosity (9–12), but the magnitude of the changes depends partially on the biological source of its parent starch (10–12). Hydrophobic substituents (such as benzyl, allyl, and methyl) often result in

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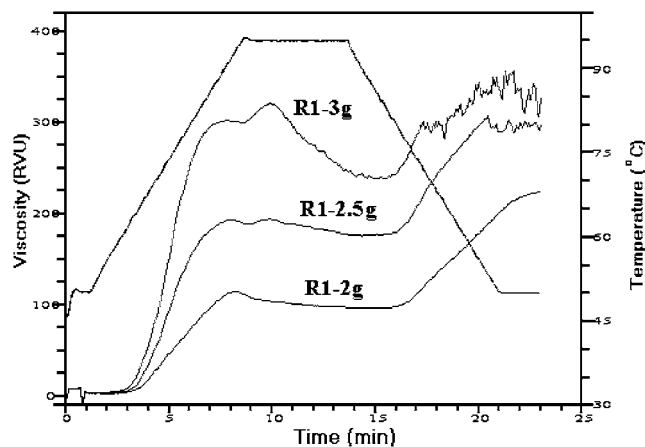


Figure 1. RVA profiles of rice OSA starch (R1, DS = 0.0180) at different levels in 25 mL of distilled water.

more complicated changes (13). The pasting viscosity of benzyl corn starch decreased as DS increased; however, the onset temperature decreased as DS increased up to 0.1, but it increased with DS > 0.1 (13). OSA modification introduces both hydrophilic and hydrophobic groups to starch, and how the dual groups affect starch physical properties of starch with different plant origin and different DS is little studied. In the present study, OSA starches were prepared with normal amylose content rice, wheat, and potato starches, and their physical properties were investigated.

MATERIALS AND METHODS

Materials. Materials were wheat starch (30% amylose) and potato starch (23% amylose) (Sigma Chemical Co., St. Louis, MO), rice starch (19% amylose) (Bangkok Starch Industrial Co., Bangkok, Thailand) (amylose content determined by a standard iodine-binding method), and 2-octen-1-yl succinic anhydride (Aldrich Chemical Co., St. Louis, MO). Octenyl succinylated starches were synthesized following a typical preparation method (1). Sodium carbonate (2.5 g) was dissolved in 75 mL of water. Starch (50 g, dry weight) was suspended in the solution with agitation, different amounts of 2-octen-1-yl succinic anhydride (from 1 to 6 mL) were added, and agitation was continued for 14 h at room temperature with the pH maintained between 8 and 9 with dilute NaOH or HCl solution. Then pH was adjusted to 6.5 with dilute HCl; samples were centrifuged for 3 min at 2500 rpm, washed three times with distilled water and once with 95% ethanol, and oven-dried at 40 °C.

The DS of octenyl succinylated starches was determined using a titrimetric method (14) with some modification. A standard KOH solution was added to a suspension of octenyl succinylated starch and placed for 12 h on a shaker. Excess alkali was titrated with standard HCl solution and retitrated 2 h later to account for any further alkali that may leach from the starch samples. Five modified rice starch samples with DS of 0.0180 (termed R1 hereafter), 0.0221 (R2), 0.0331 (R3), 0.0414 (R4), and 0.0452 (R5), four modified wheat starch samples with DS of 0.0225 (W1), 0.0289 (W2), 0.0347 (W3), and 0.0431 (W4), and five modified potato starch samples with DS of 0.0171 (P1), 0.0194 (P2), 0.0242 (P3), 0.0328 (P4), and 0.0397 (P5) were thus prepared. The unmodified rice (R0), wheat (W0), and potato (P0) starches were used as controls.

Pasting Viscosity. The pasting properties were determined using a Rapid Visco analyzer model 3-D (RVA) (Newport Scientific, Warriewood, Australia). The RVA was run using ThermoLine for Windows software (version 1.2). First, the standard 2 programmed heating and cooling cycle profile was used to determine the optimal amount of modified starch that should be used in 25 mL of distilled water (pH 6.5). When 3 g of R1 starch was used, the viscosity curve was not smooth, especially at the cooling stage (Figure 1). When 2.5 g of R1 starch was used, the curve became smoother than that of 3.0 g but was

still jagged at the later stages of testing. When 2.0 g starch was used, the viscosity profile was quite smooth; however, at the end of the test the viscosity was still increasing, indicating the testing time could be prolonged. Due to the partial hydrophobic property of OSA starch, it was difficult to disperse in water, so the sample was stirred for 1 min to ensure complete dispersion. In addition, we prolonged the programmed high-speed rotation period of the paddle at the beginning of the test to 2 min at 960 rpm instead of the usual 10 s, after which a constant rotation of 160 rpm was continued as usual. The samples were held at 50 °C for 1.5 min, heated to 95 °C in 7.5 min, held at 95 °C for 5 min, cooled to 50 °C in 7.5 min, and held at 50 °C for 3.5 min. The peak (PV), hot (holding) paste (HPV), and cool paste (final) (CPV) viscosities and their derived parameters of breakdown (BD = PV - HPV) and setback (SB = CPV - HPV) were recorded. The viscosity parameters were measured in arbitrary rapid visco units (RVU).

Texture Profiles. The resulting starch gels from Rapid Visco analyzer experiments were kept in the canister, sealed with Parafilm, and held at 4 °C for 24 h. Texture profile analysis was carried out on a TA-XT2i texture analyzer (Texture Technologies Corp., Scarsdale, NY; Stable Micro Systems, Godalming, Surrey, U.K.) equipped with Texture Expert software (version 5.16). A standard two-cycle program was used to compress the gels for a distance of 10 mm at 4 mm/s using a 5 mm cylindrical probe with a flat end. Hardness (the maximum force, g) was derived from the instrument software.

Swelling Volume. The starch swelling volume test was based on that of ref 15. Because of the high viscosity of modified starch, less than the standard amount of starch, that is, 0.35 g (db), was used in the test. The starch was mixed with 12.5 mL of distilled water (pH 6.5) in 125 × 16 mm Pyrex culture tubes, equilibrated at 25 °C for 5 min, heated to 92.5 °C, and then held at that temperature for 30 min. The samples were cooled in an ice water bath for 1 min, equilibrated at 25 °C for 5 min, and then centrifuged at 1000g for 15 min. The swelling volume was calculated by converting the height of the resultant gels to a volume basis, and the results were expressed as milliliters per gram of dry starch.

Gelatinization Properties. The gelatinization properties were analyzed using a DSC 2920 thermal analyzer (TA Instruments, Newcastle, DE) equipped with DSC standard and dual sample cells. Modified starch (1.8 mg db) was weighed into an aluminum pan, and 12 μ L of distilled water (pH 6.5) was added and mixed with a needle. The pan was hermetically sealed and then heated at a rate of 10 °C/min from 30 to 110 °C. A sealed pan with 12 μ L of distilled water was used as a reference. Onset (T_o , °C), peak (T_p , °C), and conclusion (T_c , °C) temperatures and enthalpy (ΔH_g , J/g) of gelatinization were calculated automatically by the Universal Analysis program, version 1.9D (TA Instruments).

Statistical Analysis. All measurements were made in duplicate. Analysis of variance (ANOVA) was performed with the SAS program version 6.04 (SAS Institute Inc., Cary, NC). Least significant differences (LSD) for comparison of means were computed at $P < 0.05$.

RESULTS AND DISCUSSION

Pasting Viscosity. Generally, 2 g of unmodified rice starch was not suitable for RVA viscosity testing because the PV, HPV, and CPV were quite low (Figure 2). Consequently, the estimates of BD and SB could not be considered to reflect the true properties of the native starch. However, the viscosities of OSA rice starches (2 g) were significantly higher than for the native starch. The PV but not the HPV and CPV was increased with increase of DS. The modified starches with larger DS, such as R4 and R5, showed lower HPV and CPV than R2 and R3 starches, which indicated that continued increase of DS could not further increase its pasting viscosity. Because the hydrophobic alkenyl groups were incorporated into a normally hydrophilic native starch granule, the modified starch attains surface active properties that lead to starch granule aggregation and hence difficult dispersion in water. It appeared that the higher the DS, the more the granules aggregated and floated on the

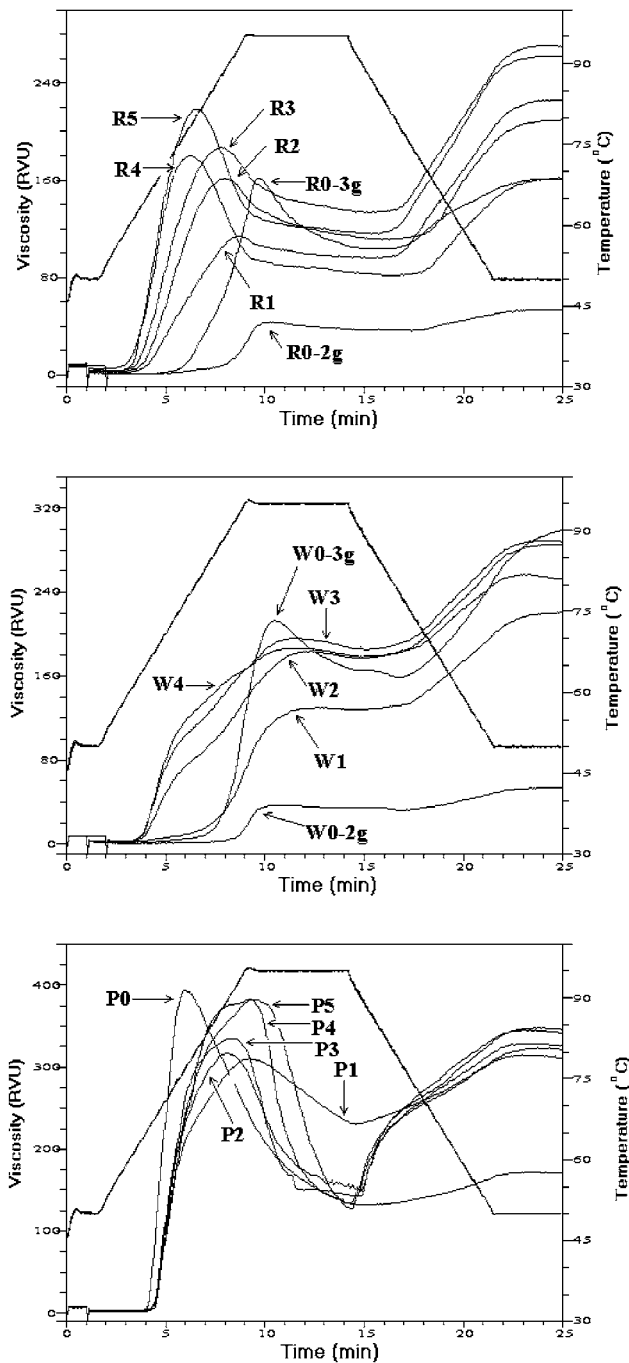


Figure 2. RVA profiles for OSA-modified rice, wheat, and potato starches.

surface. These aggregated granules might be broken down quickly at high temperature, causing the viscosity at 95 °C to decrease quickly, resulting in a lower HPV. For comparison, we also tested the viscosity of 3 g of unmodified starch in 25 mL of distilled water. The PV and HPV of R3 and R4 (2 g) were larger than those of R0 at 3 g, whereas the CPV of all the modified starches was higher than or similar to that of R0 (3 g). This would allow applications in some food systems (where permitted by prevailing food regulations) especially at high temperature; that is, OSA starch could be used as a thickener, with lower levels of OSA starch replacing unmodified starch. Low BD (7 RVU) of native starch (2 g) was observed, although the overall viscosity was low. R1 and R2 starches had lower BD than native starch in (3 g concentration) (57 RVU), showing that they were more resistant to high-temperature thinning (Figure 2).

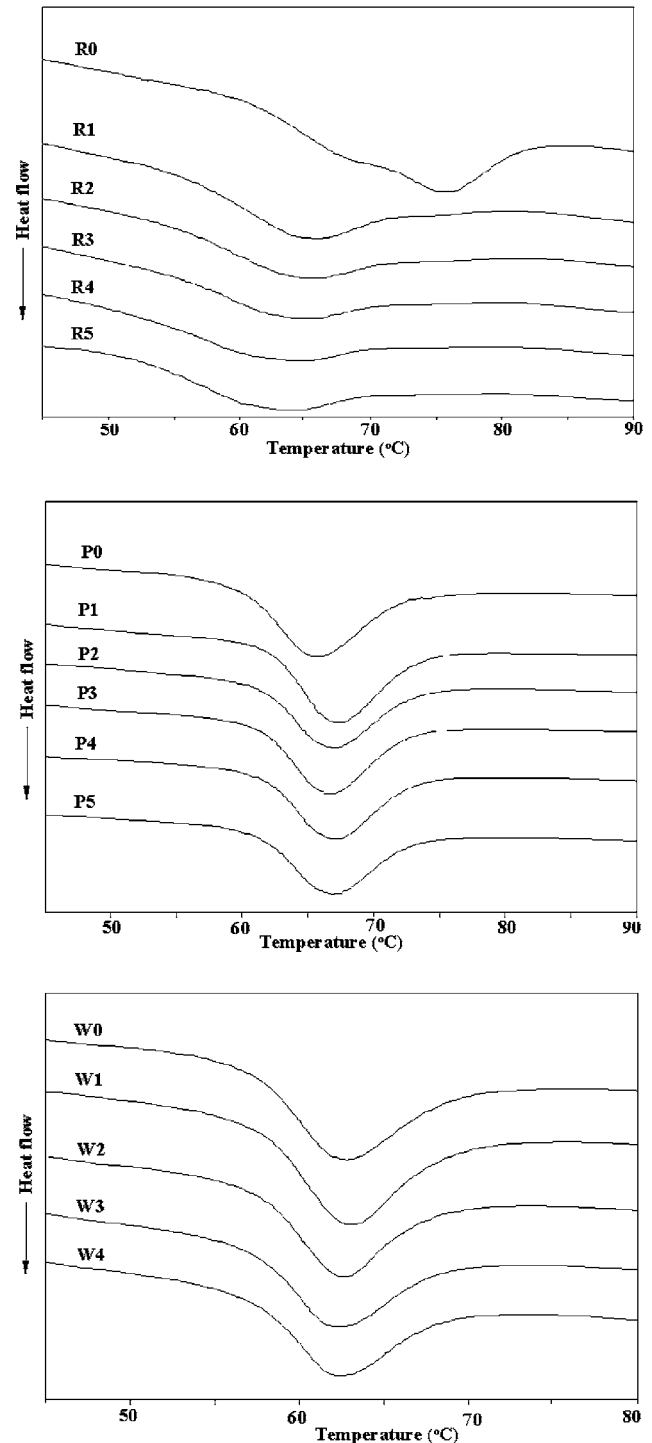


Figure 3. DSC thermal properties of OSA-modified rice, wheat, and potato starches.

Similar to rice starch, all paste viscosity parameters of the OSA-modified wheat starch were significantly higher than for unmodified starch (2 g) (Table 1). The PV, HPV, and CPV of W1, W2, and W3 generally increased with increase of DS, whereas W4 values were lower than that of W3 (Table 1). Only W1 had a plateau at high temperature (like R1, R2, and R3 starches), whereas W2, W3, and W4 gelatinized at a relatively lower temperature (Figure 2). The PV and CPV of unmodified wheat starch (3 g) were higher than for the modified starches (2 g). Unlike the case for rice OSA starch, the BD of W2 was higher than those of W3 and W4, but BD of all wheat OSA starch was lower than that of unmodified starch (3 g).

Table 1. Summary of the Physical Properties of OSA-Modified Rice (R0–R5), Wheat (W0–W4), and Potato (P0–P5) Starches^a

| | PV | HPV | VPC | BD | SB | hardness | SV | T_o | T_p | T_c | dH |
|--------|----------|----------|---------|---------|---------|----------|---------|---------|---------|---------|--------|
| rice | | | | | | | | | | | |
| R0-3g | 162.1 c | 105.4 c | 161.6 c | 57.1 b | 56.2 e | 20.9 a | | | | | |
| R0 | 43.4 e | 36.3 f | 53.5 d | 7.1 e | 17.2 f | 10.4 d | 20.4 b | 61.0 a | 75.2 a | 82.2 a | 11.4 a |
| R1 | 114.4 d | 96.5 d | 224.9 b | 17.9 d | 128.4 b | 20.5 a | 38.3 a | 55.5 b | 64.9 b | 73.9 b | 8.5 b |
| R2 | 161.1 c | 116.3 b | 263.7 a | 44.8 c | 147.4 a | 19.1 b | 38.4 a | 54.3 bc | 64.3 b | 73.0 c | 7.6 c |
| R3 | 185.7 b | 133.5 a | 269.0 a | 52.2 bc | 135.6 b | 15.9 c | 38.4 a | 53.0 cd | 63.2 c | 70.8 d | 6.7 d |
| R4 | 193.2 b | 86.8 e | 174.5 c | 106.4 a | 87.7 d | 7.3 e | 38.4 a | 50.8 d | 62.7 cd | 70.6 de | 6.7 d |
| R5 | 218.1 a | 111.1 bc | 209.5 b | 107.0 a | 98.4 c | 7.4 e | 38.4 a | 52.5 cd | 62.3 d | 69.9 e | 6.4 d |
| wheat | | | | | | | | | | | |
| W0-3g | 217.3 a | 162.1 c | 306.2 a | 55.3 a | 144.1 a | 103.5 a | | | | | |
| W0 | 34.8 e | 30.5 e | 50.8 e | 4.4 d | 20.4 f | 37.5 bc | 15.1 c | 57.4 b | 62.8 ab | 70.4 ab | 10.8 a |
| W1 | 129.3 d | 107.9 d | 218.4 d | 21.5 b | 110.6 c | 46.4 b | 29.6 b | 58.0 a | 63.3 a | 70.8 a | 11.2 a |
| W2 | 182.5 c | 162.2 c | 284.9 b | 20.4 b | 122.8 b | 34.1 cd | 38.2 a | 57.5 ab | 62.4 bc | 69.5 bc | 9.3 b |
| W3 | 196.2 b | 184.7 a | 288.9 b | 11.5 c | 104.2 d | 27.0 de | 38.1 a | 57.1 b | 62.1 c | 69.1 c | 8.3 b |
| W4 | 185.5 c | 175.6 b | 248.4 c | 9.9 c | 72.8 e | 18.7 e | 37.7 a | 57.1 b | 62.1 c | 69.2 c | 8.7 b |
| potato | | | | | | | | | | | |
| P0 | 395.4 a | 132.2 d | 171.5 d | 263.3 a | 39.3 e | 35.4 b | 37.7 ab | 60.0 d | 65.7 c | 73.5 b | 17.2 a |
| P1 | 309.3 d | 228.9 a | 309.5 c | 80.4 e | 80.6 d | 49.0 a | 38.3 a | 62.1 a | 67.2 a | 74.2 ab | 16.6 a |
| P2 | 320.0 d | 148.8 b | 325.8 b | 171.3 d | 177.0 c | 47.5 a | 37.6 ab | 61.5 bc | 66.9 ab | 74.1 ab | 15.2 b |
| P3 | 336.0 c | 140.4 c | 342.1 a | 195.7 c | 201.8 b | 47.3 a | 37.4 b | 61.4 bc | 66.7 b | 73.8 ab | 15.3 b |
| P4 | 378.9 b | 132.0 d | 344.3 a | 246.9 b | 212.3 a | 27.6 c | 35.0 c | 61.8 ab | 67.1 ab | 74.3 ab | 15.0 b |
| P5 | 387.7 ab | 125.1 e | 323.9 b | 262.6 a | 198.8 b | 16.8 d | 34.4 c | 61.4 c | 66.9 ab | 74.5 a | 14.3 c |

^a The number following the prefix indicates different degrees of substitution (DS). Rice and wheat native starches were tested for RVA viscosity and gel texture both in 2 g and in 3 g systems. Numbers in the same column followed by a letter in common were not significantly different at $P < 0.05$.

As expected for a typical high-swelling root or tuber starch, unmodified potato starch (2 g) had higher PV and BD than rice and wheat starch (3 g) (Table 1). However, the OSA modification did not increase PV and increased HPV only at the P1 level. All modified potato starches had higher CPV and SB than the unmodified starch, which was similar to the case with rice and wheat starches. Potato starch is relatively high in phosphate groups, which may have been affected during OSA starch preparation in alkaline conditions, resulting in its different pasting behavior from those of rice and wheat OSA starches.

Gel Texture. The hardness of R1, R2, and R3 OSA starch gels was significantly higher than for native starch (2 g), but R1 was as hard as unmodified starch (3 g). With increase of DS, hardness decreased. R4 and R5 were much softer than the native starch, indicating that R4 and R5 had low tendency to retrograde. SB is often used as one of the parameters to evaluate the retrogradation profile of native starch. However, SB values of R4 and R5 were higher than that of native starch (for both 2 and 3 g), indicating that SB was not a suitable parameter to evaluate retrogradation properties of these modified starches. The hardnesses of W1 and W2 starches were similar to that of native wheat starch (2 g), but W3 and W4 were significantly softer than native starch (2 g). For potato starch, P1, P2, and P3 were harder than P0, but P4 and P5 were much softer.

Swelling Volume. Modification of starch with OSA greatly increased swelling volume (Table 1). Unmodified rice starch had an SV of 20 mL/g, but all of the OSA-modified starch increased to 38 mL/g (the maximum measurable in this system). The SV of native wheat starch was 15 mL/g, W1 doubled it to 30 mL/g, whereas W2, W3, and W4 reached the maximum (38 mL/g). However, OSA potato starch tended not to have increased SV, the starch gels for P0, P1, P2, and P3 were near maximal, but the SV of P4 and P5 was less. For native starch, the swelling was often positively correlated to PV, but the present study showed that the swelling of OSA starch correlated to PV within only a limited DS range. The native potato starch (with a large granule and containing phosphate groups) swelled well, but further OSA modification led to lower SV.

Gelatinization Properties. OSA rice starch had lower gelatinization temperatures than the native starch; T_o , T_p , and

T_c were all much lower even at low DS (0.018 for R1) (Table 1; Figure 3). In OSA wheat starch, T_o values were similar among all treatments except W1; only T_p and T_c of W3 and W4 were a little lower than others (Table 1; Figure 3). For OSA potato starch, T_o and T_p were higher than for the native starch (Table 1; Figure 3). The thermal temperatures of the starches were also indicated by the pasting temperature from the RVA profile, that is, the point at which the viscosity began to increase (Figure 2). The effect can be explained as a weakening of internal hydrogen bonding by the hydrophobic alkenyl groups, helping starch swelling at relatively low temperatures and hence gradually decreasing the enthalpy of all the OSA starches with increased DS.

OSA-modified starch had useful physical properties compared to the native starch. The modification of starch physical properties was dependent on not only the DS but also the plant origin of the starches. Rice and wheat OSA starch had increased pasting viscosity (especially CPV) and swelling volume and had poor tendency to retrograde at higher DS, whereas the thermal temperatures and enthalpy decreased with the increase of DS. It seemed that the DS values of R3 and W3 were optimal, and higher DS did not improve their physical properties. OSA modification of potato starch significantly increased only CPV as compared with the native starch, so this starch likely has limited applications. These results illustrate the importance of examining the interaction of biological variation (within and among species) and the effect of chemical modification in determining starch properties.

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