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Thermal and pasting properties of native and acid-treated starches derivatized by 1-octenyl succinic anhydride

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Abstract

The thermal and pasting properties of native and acid-treated starches derivatized by 1-octenyl succinic anhydride (OSA) were investigated. The pasting properties were tested using a Rapid Visco-Analyzer. The gelatinization and retrogradation properties were determined using a differential scanning calorimeter. OSA starches prepared from both native tapioca and rice starches had significantly higher peak viscosity, final viscosity, and setback than their native starches. Also, even when DP of tapioca starch was reduced by half, the peak viscosity of this OSA starch was still higher than that of native tapioca starch. The enhancement in peak viscosity was related to the high swelling volume of OSA starch, hydrophobic interactions and amylose–OSA inclusion complex. The gelatinization temperature of OSA starches decreased, whereas the gelatinization temperature range increased. The gelatinization enthalpy of OSA-modified rice-based starches was reduced, however, that of OSA-modified tapioca-based starches were not significantly different ($P > 0.05$). After storing gelatinized starches at 4 °C for 2 weeks, the enthalpy values for melting the retrograded OSA starches were less than the native starches. This effect was very apparent in tapioca-based starch. OSA starches had lower gelatinization temperature and slower retrogradation, but significantly higher peak viscosity than their native starches.

Keywords: Octenyl starch succinate; Thermal properties; Pasting properties; Retrogradation; Acid-treated starch

1. Introduction

The hydrophilicity of starch, its propensity to interact with water, can be transformed into a schizophrenic hydrophilic–hydrophobic duality by derivatizing with an agent containing a hydrophobic group such as alkenyl succinic anhydrides. Octenyl succinic anhydride (OSA) starches are attracted to, and stabilize, the oil–water interface of an emulsion. The glucose part of starch binds the water, while the lipophilic, octenyl part binds the oil. In this way complete separation of the oil and water phases is prevented (Murphy, 2000). The applications include beverage emulsions, flavors, clouding agents, salad dressings, creams, fragrances, emulsion paints, lattices, coatings and adhesives (Trubiano, 1986; Thomas & Atwell, 1999; Wurzburg, 1995) as well as biodegradable plastics (Jane, Robert, Nidolov, & Roque, 1991).

OSA starch can be prepared by treating a starch suspension with 1-OSA (Rutenberg & Solarek, 1984). The methods for preparing OSA starch were patented by Caldwell, Hills, and Wurgburg (1953). The optimum reaction conditions of starch esterified with alkenyl succinic anhydride are pH 8.5–9.0, reaction temperature 23 °C and 5% anhydride concentration (Jeon, Viswanathan, & Gross, 1999). FDA (1994) allowed the maximum level of OSA at 3% dry basis of starch for preparing modified food starch.

OSA groups are located throughout the starch granule, mainly on the granule surface (Shogren, Viswanathan, Felker, & Gross, 2000). The introduction of hydrophobic groups at low degree of substitution levels (0.01–0.1) imparts some hydrophobic properties to the starch without

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destroying the water-dispersibility. To disperse OSA starch in water, it is necessary to moisten them with a water-miscible solvent such as ethanol or to use a high-shear mixer to suspend the starch uniformly in the water in which the starch is to be heated to disperse it (Rutenberg, 1980). OSA starches have higher viscosities in aqueous suspension, lower gelatinization temperatures (Bao, Xing, Phillips, & Corke, 2003; Trubiano, 1986; Thomas & Atwell, 1999; Wurzburg, 1995) and less tendency to retrograde than unmodified starches (Bao et al., 2003; Ortega-Ojeda, Larsson, & Eliasson, 2005; Thomas & Atwell, 1999; Trubiano, 1986). The viscosity of OSA starches is generally higher than that of other substituted derivatives. This phenomenon may be caused by an associative effect of the hydrophobic chains (Ortega-Ojeda et al., 2005; Park, Chung, & Yoo, 2004; Thomas & Atwell, 1999) and the formation of amylose–OSA inclusion complexes (Ortega-Ojeda et al., 2005).The molecular weight of starch can be lowered to the desirable range by acid hydrolysis, thus producing OSA starch with reduced viscosity (Thomas & Atwell, 1999; Wurzburg, 1995). The gelatinization properties of OSA starch can be evaluated by using differential scanning calorimeter (Bao et al., 2003; Miller, Gordon, & Davis, 1991). The gelatinization temperature of OSA starches was found to be related to starch type and degree of substitution (Bao et al., 2003). The gelatinization temperature of OSA rice starches was sharply lower at low DS (Bao et al., 2003), but potato OSA starches had higher gelatinization temperature than the native starch (Bao et al., 2003; Ortega-Ojeda et al., 2005). However, the onset temperature of OSA wheat starch (DS 0.0225) and OSA waxy corn starch (DS 0.015) were not significantly different from the parent starches (Bao et al., 2003; Miller et al., 1991). The enthalpy of all the OSA starches decreased gradually with increased DS because the alkenyl groups reduced the internal hydrogen bonding; thus, helping starch swell at low temperature and hence gradually decreasing the enthalpy (Bao et al., 2003). However, the enthalpy of gelatinized OSA waxy corn starch (Miller et al., 1991), OSA wheat starch (DS 0.0225) and OSA potato starch (DS 0.0171) (Bao et al., 2003) were not significantly different from that of the native starches.

There is no report of OSA starches on retrogradation properties studied by differential scanning calorimetry. In this experiment, rice and tapioca-based starches were used to study thermal and pasting properties. Moreover, acid-treated starches derivatizing with OSA were also studied in order to investigate the effect of OSA substitution on pasting properties and thermal properties of those OSA starches compared to their native and acid-treated starches.

2. Materials and methods

2.1. Materials

Tapioca starch and rice starch were provided by Tapioca Development Co., Ltd. (Bangkok, Thailand) and Choheng Co., Ltd. (Nakorn Prathom, Thailand), respectively. The 1-octenyl succinic anhydride was from Halterman Custom Processing, UK. All chemicals were analytical grade.

2.2. Preparation of modified starches

The preparation method of acid-treated starch and starch octenyl succinate followed those in Thirathumthavorn and Charoenrein (2005) and Shogren et al. (2000), respectively. OSA-modified acid-treated starches were prepared by dispersing starch in 1 N HCl to give a concentration at 40% dry starch basis. The beaker containing starch slurry was immersed in a water bath to control the reaction at 35 °C with continuous stirring for 1–4 h. The acid hydrolysis reaction was stopped by adding 7% NaOH to obtain pH 6.5. Distilled water was added to adjust starch concentration to 30% dry starch basis while cooling the solution to 23 °C in a water bath. Then, pH was adjusted and maintained at 8.5–9.0 by addition of 2% NaOH. Octenyl succinic anhydride was slowly added and reaction was controlled for 6 hours with stirring and pH adjustment. The OSA reaction was adjusted to pH 6.5 with 1 N HCl. The slurry was washed three times with a two-fold volume of distilled water prior to centrifuging at 2000 rpm for 10 min. The starch was dried in an oven at 45 °C for 10–12 h, then ground and sieved through a 100-mesh sifter. The DS of OSA starch was determined by a titration method (FAO, 1997). The DS of OSA-modified tapioca and OSA-modified rice were 0.0137 ± 0.0006 and 0.0128 ± 0.0004, respectively.

2.3. Degree of polymerization

Degree of polymerization (DP) of starch was calculated from total carbohydrate (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) divided by reducing sugar (Hizukuri, Takeda, & Yasuda, 1981). All measurements were done in triplicate. The DP of native tapioca, 1 h acid-treated tapioca, 4 h acid-treated tapioca, native rice, 1 h acid-treated rice and 4 h acid-treated rice starch were 6212 ± 139, 3080 ± 57, 1335 ± 20, 1626 ± 48, 1197 ± 92 and 762 ± 32, respectively.

2.4. Pasting properties

Pasting properties of starches were measured with AACC Approved Method using a Rapid Visco-Analyzer. Samples were determined at 5–10% dry solid by dispersing in distilled water. All measurements were done with 2 replicates.

2.5. Gelatinization

The gelatinization properties of starch were analyzed using differential scanning calorimeter (DSC, Pyris-1, Perkin Elmer) (Charoenrein, Udomrati, & Reid, 2002).

Samples (6 mg dry basis of starch) at 70% moisture content were prepared in stainless steel pans and then hermetically sealed. They were heated at 10 °C/min from 25 to 130 °C. All measurements were done in 2 replicates.

2.6. Retrogradation

Retrogradation properties of gelatinized samples stored at 4 °C for 14 days were tested by DSC (Charoenrein et al., 2002). The samples were heated from 25 to 130 °C at 10 °C/min to determine the enthalpy changes of retrograded starch. All measurements were done with 2 replicates.

2.7. Statistical analysis

The experiments were a completely randomized design and the difference in means was determined by Duncan News Multiple Range Test. The data were analyzed using SPSS 10.0 for Windows.

3. Results and discussion

3.1. Pasting properties

Pasting properties of all starch samples were tested at 5% dry starch basis (Figs. 1 and 3) and 10% dry starch basis (Figs. 2 and 4) due to a large difference in viscosity between unmodified starches and OSA starches. The starch having low viscosity at low starch concentration was not suitable for RVA viscosity testing due to the error in evaluating the true properties of starch, i.e. breakdown and setback. However, the viscosity of OSA starch was significantly higher than for the native starch (Bao et al., 2003). The pasting viscosity of OSA tapioca and OSA rice starches could not be tested at 10% dry starch basis due to too

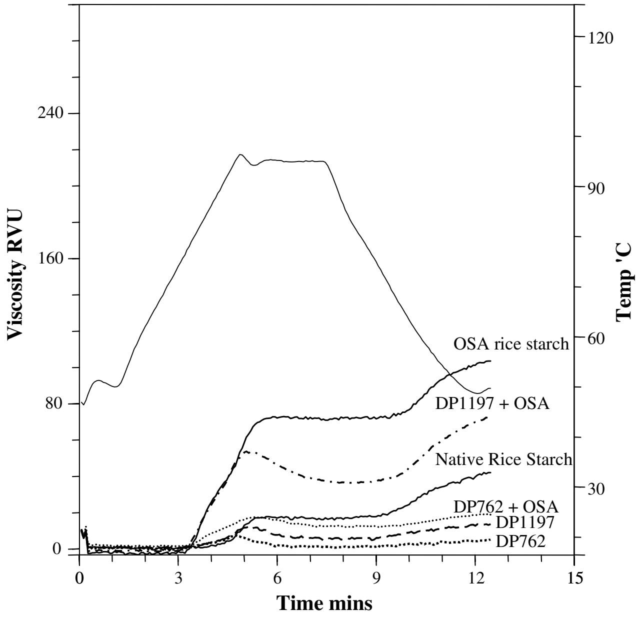

Fig. 1. Viscosity profile of modified rice starches compared with native rice starch at 5% dry starch basis measured by Rapid Visco-Analyzer. (DP1197 = acid-treated rice starch having DP1197, DP762 = acid-treated rice starch having DP762, DP1197 + OSA = OSA-modified acid-treated rice starch having DP1197, DP762 + OSA = OSA-modified acid-treated rice starch having DP762.)

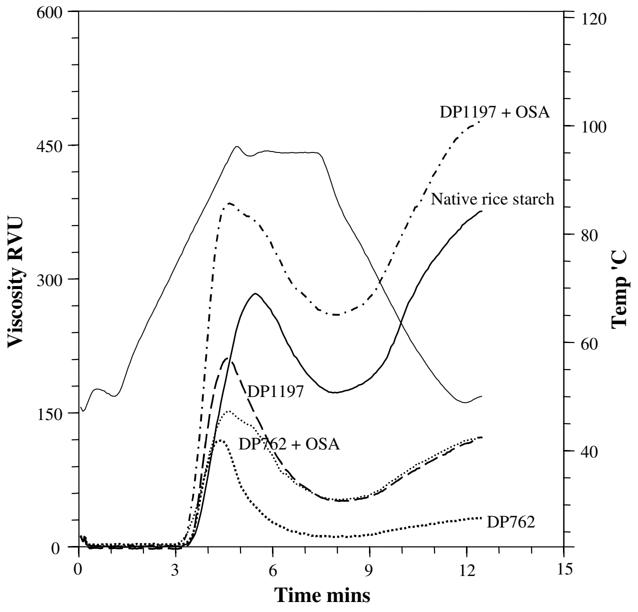

Fig. 2. Viscosity profile of modified rice starches compared with native rice starch at 10% dry starch basis measured by Rapid Visco-Analyzer. (DP1197 = acid-treated rice starch having DP1197, DP762 = acid-treated rice starch having DP762, DP1197 + OSA = OSA-modified acid-treated rice starch having DP1197, DP762 + OSA = OSA-modified acid-treated rice starch having DP762.)

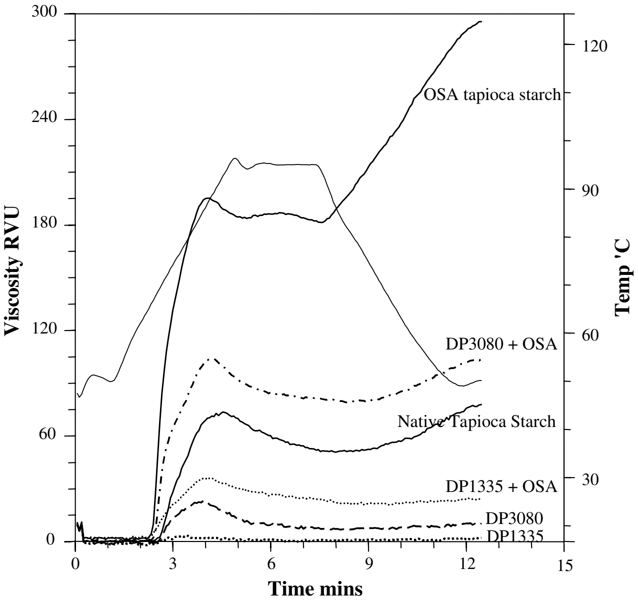

Fig. 3. Viscosity profile of modified tapioca starches compared with native tapioca starch at 5% dry starch basis measured by Rapid Visco-Analyzer. (DP3080 = acid-treated tapioca starch having DP3080, DP1335 = acid-treated tapioca starch having DP1335, DP3080 + OSA = OSA-modified acid-treated tapioca starch having DP 3080, DP1335 + OSA = OSA-modified acid-treated tapioca starch having DP1335.)

high viscosity of the sample to be tested at 10% dry starch basis.

The hot paste and cold paste viscosities of all OSA starches were higher than their parent starches. The peak viscosity tested at 5% dry starch basis of OSA rice and OSA tapioca starches was higher than that of their native starches by around four and three times, respectively. The high viscosity starch is of benefit for using as a thickener, with lower levels of OSA starch replacing unmodified starch (Bao et al., 2003). However, some applications need low viscosity starch in order to apply it at higher concentration or for less viscosity effect. Acid-hydrolysis reduces starch chain length randomly and gives less hot paste viscosity than unmodified starch. In this study, starches treated with 1 N HCl for 1 and 4 h were used to reduce starch chain length. At 10% dry starch basis, the peak viscosity of native rice starch (282 RVU) (DP of native rice starch = 1626) was reduced to 211 and 113 RVU. for acid-treated rice starch having DP1197 and 762, respectively (Fig. 2). The peak viscosity of native tapioca starch (456 RVU) (DP of native tapioca starch = 6212) was decreased to 124 and 17 RVU for acid-treated tapioca starch having DP3080 and 1335, respectively (Fig. 4). The peak viscosity of OSA-modified acid-treated rice starch tested at 10% dry starch basis was higher than that of acid-treated rice starch by approximately 1.5–2 times (Fig. 2). Similarly, the peak viscosity of OSA-modified acid-treated tapioca starch tested at 10% dry starch basis was higher than that of acid-treated tapioca starch by approximately 4–10 times. The enhancement in the viscosity of OSA starch is probably due to three possible reasons, that are the high swelling volume of OSA starch (Bao et al., 2003; Shogren et al., 2000), hydrophobic interactions (Ortega-Ojeda et al., 2005; Park et al., 2004; Thomas & Atwell, 1999) and amylose–OSA inclusion complex (Ortega-Ojeda et al., 2005). First, the high swelling volumes of OSA starch are related to the OSA bulky groups on starch molecules. They cause a structural reorganization, as a result of steric hindrance, and this results in repulsion, thus facilitating an increase in water percolation within the granules with subsequent increase in swelling volumes (Bao et al., 2003; Lawal, 2004). While the associative effect of hydrophobic chains in the OSA starches can enhance the viscosity of OSA starches (Ortega-Ojeda et al., 2005; Park et al., 2004; Thomas & Atwell, 1999) according to the formation network by hydrophobic interactions. It is also observed with other hydrophobically modified polymers like hydrophobically modified cellulose (Charpentier et al., 1997; Charpentier-Valenza, Merle, Mocanu, Picton, & Muller, 2005), hydrophobically modified pullulan (Kuroda, Fujimoto, Sunamoto, & Akiyoshi, 2002) and hydrophobically modified polyacrylamides (Xue, Hamley, Castelletto, & Olmsted, 2004). Finally, amylose can form the extended network formation of amylose–OSA complex by joining with neighbouring amylopectin (Ortega-Ojeda et al., 2005). Therefore, this solution showed a development in viscosity. Generally, amylose is known to form inclusion complexes with certain hydrophobic ligands such as iodine, alcohols, fatty acids, or surfactants (Egermayer, Karlberg, & Piculell, 2004). It has been reported for the formation of inclusion complexes with other hydrophobically modified polymers, for example, hydrophobically modified hydroxyethyl cellulose (Chronakis, Egermayer, & Piculell, 2002) and hydrophobically modified ethyl(hydroxyethyl) cellulose (Egermayer et al., 2004).

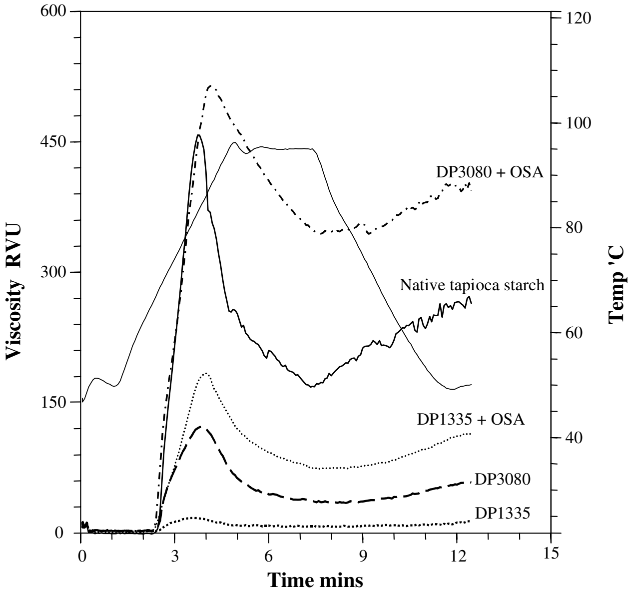

Fig. 4. Viscosity profile of modified tapioca starches compared with native tapioca starch at 10% dry starch basis measured by Rapid Visco-Analyzer. (DP3080 = acid-treated tapioca starch having DP3080, DP1335 = acid-treated tapioca starch having DP1335, DP3080 + OSA = OSA-modified acid-treated tapioca starch having DP 3080, DP1335 + OSA = OSA-modified acid-treated tapioca starch having DP1335.)

The breakdown viscosity is the difference between the peak viscosity and the minimum viscosity during heating. Higher the breakdown viscosity indicates granule disruption or the less tendency of starch to resist shear force during heating. Starch normally disrupts and viscosity is reduced during heating. The breakdown viscosities tested at 5% dry starch basis of OSA tapioca starch (8 RVU) as well as at 10% dry starch basis of OSA-modified acid-treated rice starch having DP1197 (132 RVU) and 762 (99 RVU) were lower than those of native tapioca (23 RVU) and acid-treated rice starches (160 and 105 RVU for DP1197 and 762, respectively). As discussed above, OSA starches had very high swelling volumes and, thus, the hot paste starch viscosity after cooking was still high. Therefore, the lower breakdown viscosity of OSA starch does not necessarily indicate the higher resistance to shear force compared with their native forms.

The setback viscosity of all OSA starch samples was higher than that of native and acid-treated forms of rice and tapioca starches. The setback viscosity normally indicates the degree of retrogradation of starch, mainly amylose. However, it is not a suitable parameter to indicate the retrogradation properties of OSA starch (Bao et al., 2003).

3.2. Gelatinization properties

Fig. 5 and Table 1 presented the gelatinization thermograms and parameters of native, acid-treated, OSA and OSA-modified acid-treated starches. The results showed that the onset and peak temperature for gelatinization of native and acid-treated rice starches were not significantly different ($P > 0.05$), but those of acid-treated tapioca starches increased significantly ($P < 0.01$). While the gelatinization enthalpy of acid-treated rice starch decreased with increasing hydrolysis time, however, that of acid-treated tapioca starches were not significantly different. It was suggested that the variation in acid hydrolysis on gelatinization parameters of different starch origin could be due to the molecular structure in the starch granule (Noda et al., 1998), amylopectin chain length (Jane et al., 1999; Yuan, Thompson, & Boyer, 1993) and reordering of the crystalline structure (Biliaderis, Grant, & Vose, 1981) after hydrolysis.

At the same DP and starch origin, OSA modification decreased the onset temperature significantly ($P < 0.01$). The conclusion temperature and enthalpy of OSA-modified native and acid-treated (DP762) rice starches were lower than native and acid-treated (DP762) rice starches significantly ($P < 0.01$). These results are in agreement with Bao et al. (2003). Generally, the gelatinization temperatures have been related to the degree of perfection of crystallites in the starch granules, and the gelatinization enthalpies to the degree of crystallinity (Eliasson & Gudmunsson, 1996).The lower gelatinization temperature and enthalpy were due to the weakening of hydrogen bonding by the hydrophobic alkenyl groups, helping starch swell at relatively low temperature and hence gradually decreasing the enthalpy of all the OSA starches (Bao et al., 2003; Rutenberg, 1980). Also, the introduction of bulky groups into the backbone of the bio-polymer enhances structural flexibility, and this also contributes to the reduction of gelatinization temperature of the modified starches (Lawal, 2004; Miller et al., 1991). Additionally, the OSA effect on the gelatinization temperature of starch is dependent on starch base and degree of substitution (Bao et al., 2003; Miller et al., 1991). Our results also showed that OSA modification had no statistically significant effect on the conclusion temperature and enthalpy of tapioca-based starches (Table 1). Similar results were obtained for OSA waxy corn starch (DS = 0.015) (Miller et al., 1991), wheat starch (DS 0.0225) and OSA potato starch (DS 0.0171) (Bao et al., 2003). The variation in OSA effects on gelatinization may

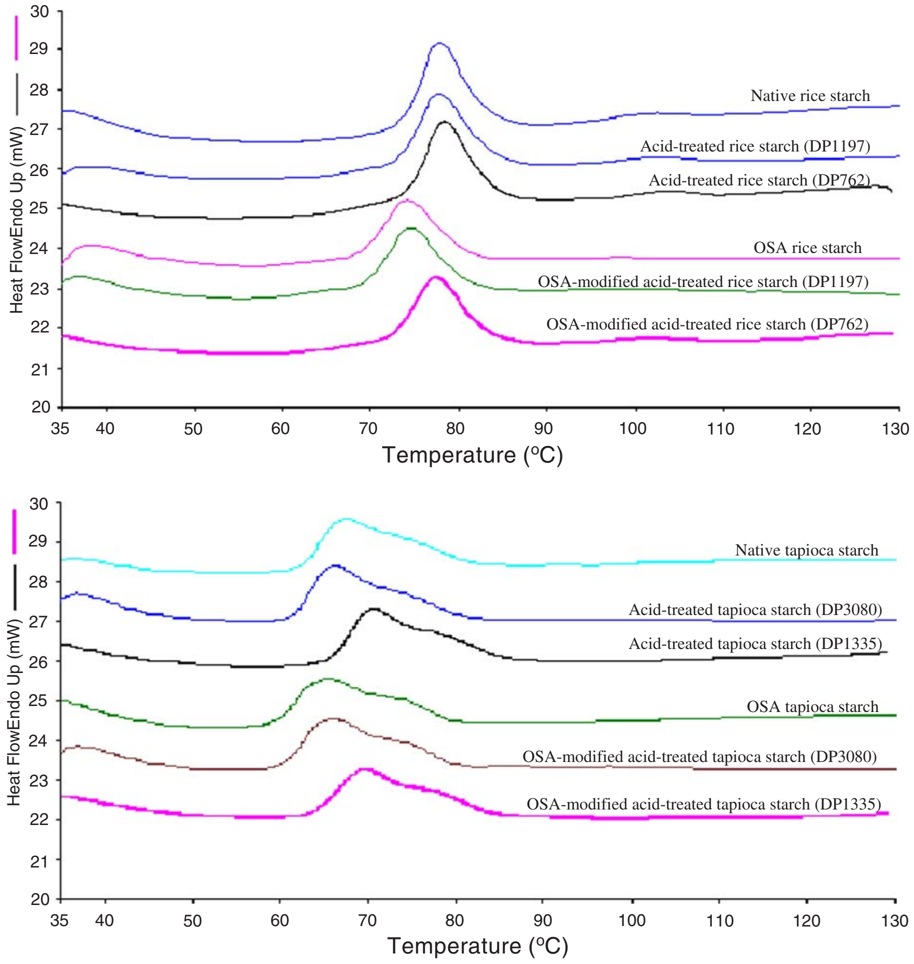

Fig. 5. Gelatinization endotherms of native, acid-treated, OSA and OSA-modified acid-treated starches.

Table 1
Gelatinization properties of native, acid-treated, OSA and OSA-modified acid-treated starches

Starch	Onset temperature (°C)	Peak temperature (°C)	Conclusion temperature (°C)	Enthalpy (J/g dry starch)
Rice starch				
Native (DP[a] 1626)	73.45 ± 0.07^{ab}	77.77 ± 0.06^{ab}	83.52 ± 0.18^{a}	15.07 ± 0.97^{a}
Acid-treated (DP1197)	72.80 ± 0.29^{bc}	77.47 ± 0.49^{ab}	83.59 ± 0.86^{a}	14.34 ± 0.08^{ab}
Acid-treated (DP762)	74.19 ± 0.08^{a}	78.38 ± 0.06^{a}	83.79 ± 0.13^{a}	12.94 ± 0.57^{bc}
OSA (DP1626)	68.68 ± 0.45^{d}	73.93 ± 0.24^{c}	80.59 ± 0.52^{b}	12.23 ± 0.85^{cd}
OSA-modified acid-treated (DP1197)	69.25 ± 0.01^{d}	74.58 ± 0.01^{c}	80.80 ± 0.16^{b}	12.90 ± 0.23^{bc}
OSA-modified acid-treated (DP762)	72.38 ± 0.64^{c}	76.93 ± 0.77^{b}	82.67 ± 0.63^{a}	11.23 ± 0.24^{d}
Tapioca starch				
Native (DP6212)	63.68 ± 0.15^{b}	68.36 ± 0.22^{b}	79.83 ± 0.84^{ns}	14.30 ± 0.22^{ns}
Acid-treated (DP3080)	61.87 ± 0.38^{c}	66.58 ± 0.36^{c}	75.79 ± 0.43	14.24 ± 0.25
Acid-treated (DP1335)	65.90 ± 0.00^{a}	70.56 ± 0.11^{a}	80.06 ± 0.44	14.50 ± 0.15
OSA (DP6212)	59.71 ± 0.00^{d}	65.56 ± 0.09^{c}	79.69 ± 0.01	13.65 ± 0.63
OSA-modified acid-treated (DP3080)	60.62 ± 0.00^{d}	66.07 ± 0.12^{c}	75.87 ± 0.13	13.90 ± 0.06
OSA-modified acid-treated (DP1335)	64.01 ± 0.04^{b}	69.56 ± 0.10^{a}	79.02 ± 0.56	13.54 ± 0.19

Different letters in the same column of each starch base indicate statistical differences ($P < 0.05$).

[a] DP, degree of polymerization of starch molecules.

be related to the difference in molecular alignment of each starch origin that influences the properties of OSA-modified starch differently.

In addition, there was an increase in the gelatinization temperature range of all OSA starches. This was because derivatization has a greater effect on the amorphous regions than on the crystalline regions and increased inhomogeneity within both the amorphous as well as crystalline regions of the starch granules (Seow & Thevamalar, 1993). These results agreed with the reports of succinylated starch and acetylated starch (Lawal, 2004).

3.3. Retrogradation properties

Retrograded amylopectin of all starch samples melted at temperature range 42–68 °C, which was lower than their gelatinization temperatures of cooked starches (Table 2). It indicates that retrograded amylopectin cannot arrange in the same order as the native starch (Fig. 6). The enthalpy values of retrogradation of starch reflect the melting of amylopectin crystallites formed by association between adjacent double helices during gel storage (Hoover & Senanayake, 1996). The retrograded rice amylopectin had higher enthalpy than did tapioca amylopectin (Table 2), indicating that rice amylopectin developed more crystallinity after storage at 4 °C for 2 weeks. This was related to the crystallinity of starch (Shi & Seib, 1992; Ward, Hoseney, & Seib, 1994) and the branch chain length of amylopectin (Jane et al., 1999; Shi & Seib, 1992; Ward et al., 1994; Yuan et al., 1993). The enthalpy of all OSA starches was less than that of their parent starches (Table 2), indicating that OSA group can prevent retrogradation of amylopectin. This was because the substituent group retards inter- and intra-hydrogen bonding between starch molecules. OSA group takes places mostly in the amylopectin branches (Shogren et al., 2000) and interrupts the linearity of the amylose and branched portions of the amylopectin, stabilizing dispersions against gelling or pasting (Wurzburg, 1995). The

Table 2
Retrogradation properties of native, acid-treated, OSA and OSA-modified acid-treated starches after storage at 4 °C for 2 weeks

Starch	Onset temperature (°C)	Peak temperature (°C)	Conclusion temperature (°C)	Enthalpy (J/g dry starch)
Rice starch				
Native (DP[a] 1626)	46.10 ± 0.07^{b}	55.21 ± 0.00^{c}	65.93 ± 0.21^{b}	5.96 ± 0.30^{a}
Acid-treated (DP1197)	41.72 ± 0.21^{d}	52.01 ± 0.47^{d}	65.34 ± 0.07^{bc}	5.46 ± 0.45^{ab}
Acid-treated (DP762)	49.08 ± 0.85^{a}	57.40 ± 0.75^{b}	66.17 ± 0.10^{b}	5.88 ± 0.09^{a}
OSA (DP1626)	43.58 ± 0.18^{c}	54.04 ± 0.51^{c}	63.98 ± 0.91^{d}	3.48 ± 0.02^{c}
OSA-modified acid-treated (DP1197)	45.46 ± 0.23^{b}	54.51 ± 0.02^{c}	63.81 ± 0.09^{cd}	3.81 ± 0.14^{c}
OSA-modified acid-treated (DP762)	49.98 ± 1.40^{a}	59.35 ± 1.13^{a}	67.86 ± 0.17^{a}	5.05 ± 0.03^{b}
Tapioca starch				
Native (DP6212)	46.78 ± 0.18^{c}	55.62 ± 0.15^{c}	62.89 ± 0.33^{b}	3.32 ± 0.59^{a}
Acid-treated (DP3080)	43.07 ± 0.74^{d}	52.46 ± 0.02^{d}	61.60 ± 0.44^{a}	2.84 ± 0.28^{ab}
Acid-treated (DP1335)	49.68 ± 1.77^{ab}	58.16 ± 1.52^{a}	64.96 ± 1.20^{a}	3.71 ± 0.49^{a}
OSA (DP6212)	49.48 ± 0.12^{ab}	57.59 ± 0.25^{ab}	62.93 ± 0.04^{ab}	0.48 ± 0.11^{c}
OSA-modified acid-treated (DP3080)	48.10 ± 0.10^{bc}	56.19 ± 0.48^{bc}	61.71 ± 0.18^{bc}	0.88 ± 0.08^{c}
OSA-modified acid-treated (DP1335)	50.35 ± 0.61^{a}	59.02 ± 0.08^{a}	64.79 ± 1.05^{a}	2.10 ± 0.71^{b}

Different letters in the same column of each starch sample indicate statistical difference ($P < 0.05$).

[a] DP, degree of polymerization of starch molecules.

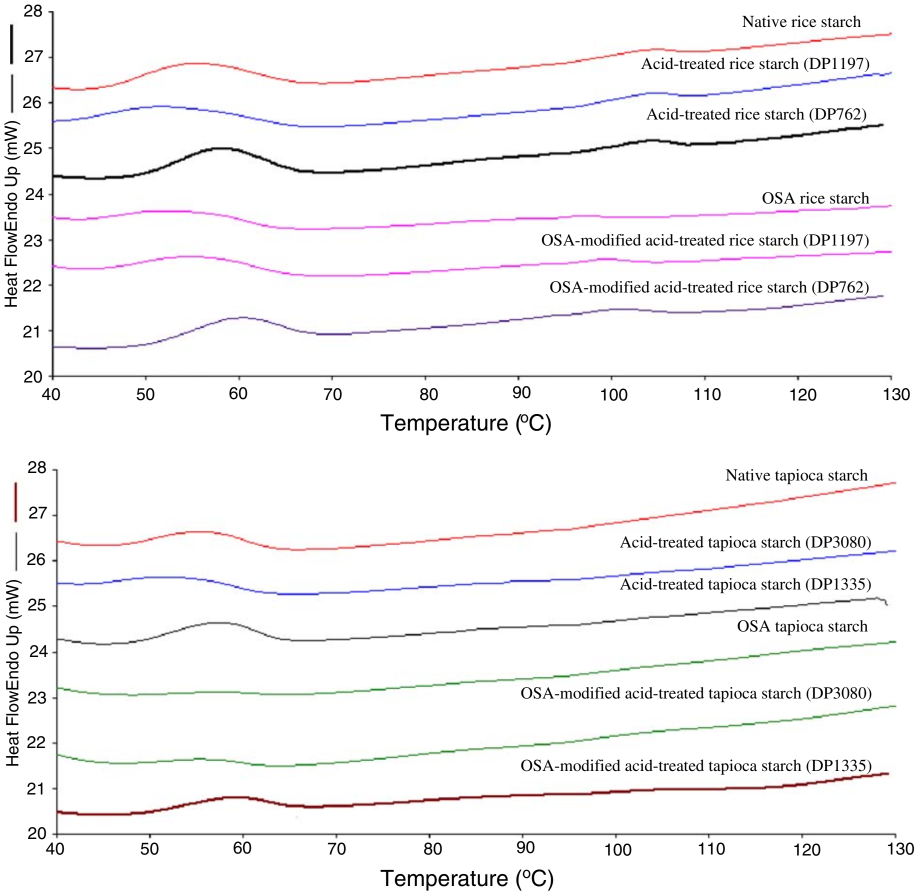

Fig. 6. Retrogradation endotherms of native, acid-treated, OSA and OSA-modified acid-treated starches.

prevention effect of OSA group on amylopectin retrogradation was more noticeable in tapioca-based starch because native tapioca starch itself had lower retrogradation than native rice starch. The melting enthalpy of retrograded amylopectin of acid-treated rice and acid-treated tapioca starches after storage at 4 °C for 14 days showed no significant difference compared with their native starches. However, acid-treated starch combined with OSA modification had a distinct effect on the melting enthalpy depending on degree of hydrolysis. The OSA-modified acid-treated rice starches having DP762 had greater enthalpy than OSA rice starch and OSA-modified acid-treated rice starch having DP1197. In accordance with OSA-modified rice-based starch, OSA-modified acid-treated tapioca starch having DP 1335 had the greatest enthalpy among the retrograded OSA-modified tapioca samples. This might be related to a molecular rearrangement after acid hydrolysis and OSA distribution in the starch granules.

4. Conclusions

The derivatization of starch by OSA markedly increased peak viscosity in both native and acid-treated forms of tapioca- and rice-based starches. The gelatinization temperature of OSA starches was significantly lower than native and acid-treated starches. The gelatinization enthalpy of OSA rice starch was significantly lower than that of native rice starch. Contrary to the gelatinization enthalpy of OSA modified and native rice-based starches, there was no significant difference in gelatinization enthalpy among all of those tapioca starch samples. The melting temperature of retrograded AP from all starch samples was in the range of 42–68 °C with less tendency to retrograde in OSA-modified starches.

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