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ScienceDirect
Carbohydrate Polymers 68 (2007) 447–456
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Effect of octenylsuccinylation on physicochemical and functional properties of waxy maize and amaranth starches

Rajesh Bhosale, Rekha Singhal *

Food Engineering & Technology Department, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India

Received 16 September 2006; received in revised form 7 November 2006; accepted 17 November 2006
Available online 28 December 2006

Abstract

The physicochemical properties of octenyl succinic anhydride (OSA) starches prepared from waxy maize and amaranth starches as a function of OSA concentration used for modification of starch were studied. Swelling power increased significantly with an increase in concentration of OSA and temperature for both waxy corn and amaranth starches. Brabender viscoamylograph of OSA-modified starches showed an increase in peak viscosity and a decrease in breakdown viscosity on modification. Freeze-thaw stability improved with an increase in OSA concentration used for modification, and so also the paste clarity of the starches. Differential scanning calorimetry (DSC) thermograms of OSA-modified starches showed lower onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and endothermic energy (ΔH_g) than their native counterpart. X-ray diffraction analysis did not show any significant alteration in the crystallinity of starch on treatment with OSA for both starches.

Keywords: Starch octenylsuccinate; Physical properties; Functional properties; Thermal analysis; Brabender characteristics

1. Introduction

Native starches are very often tailored by modification to develop desirable functional properties such as solubility, texture adhesion, and dispersion and heat tolerance, so as to be suitable for specific industrial applications (Rutenberg & Solarek, 1984). Efforts have been made to treat starch with dicarboxylic acid anhydride to form ester containing both hydrophilic and hydrophobic groups that have excellent emulsifying properties. Of these, starch alkenylsuccinic acid esters are most popular. Starch alkenylsuccinates are usually prepared commercially by base catalyzed reaction of alkenyl succinic anhydride with granular starch in aqueous suspension (Trubiano, 1986, 1995). Among alkenyl succinic anhydrides, octenyl succinic anhydride (*n*-OSA) has been permitted by US FDA to be used in foods at level of 3.0% treatment (degree of substitution, DS ~ 0.02). The modification of starches with *n*-OSA was patented by Cadwell and Wurzburg (1953), and reported to be an effective emulsifier in water in oil emulsion as well as some oil in water emulsion systems. Besides it is also useful in pharmaceutical and foods due to its film forming and stabilizing properties. Studies have been reported on the preparative conditions, distribution of OSA groups and properties of OSA starches. A uniform distribution of OSA starches over the cross section of modified waxy corn starch granule was observed (Shorgen, Vishwanathan, Felker, & Gross, 2000). Some recent works examine the effect of degree of substitution (DS) of OSA starches on the emulsification activity and susceptibility to enzymatic degradation (Vishwanathan, 1999a, 1999b). Starches of low DS has shown considerably decreased susceptibility to enzymes such as α-amylase, amyloglucosidase, and pullulanase, and the net extent of degradation decreasing with increasing DS. Emulsification activity of OSA starch was found to be independent of its concentration, when modification was carried out in aqueous medium (Vishwanathan, 1999b). Reports that correlate the relationship between the physical properties of OSA starches with

* Corresponding author. Tel.: +91 22 2414 5616; fax: +91 22 2414 5614.
E-mail address: rekha@udct.org (R. Singhal).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.11.011

extent of OSA treatment are scant in scientific literature. This information is useful for applications in food industry (He, Song, Ruan, & Chen, 2006).

Octenylsuccinylation imparts hydrophobic character to starch and it known to weaken the internal bonding that holds the granules together. For specific food application, degree of swelling of starch is important, which depends on the starch species and extent of modification (Buchholz et al., 1996; Rutenberg, Jarowenko, & Ross, 1961). Swelling power is generally calculated over the entire pasting temperature range at temperature interval of 10 °C. It is a measure of hydration capacity, since it is a weight measure of swollen granules. In Brabender amylograph, swelling of starch as a function of temperature is continuously recorded as change in viscosity. When pasted starch gel is employed as thickening agent in foods, the accelerated retrogradation at lower temperature may produce undesirable physical changes including gel formation and synerisis. The freeze-thaw stability of 5% starch paste is determined by the alternative freezing and thawing of starch paste. One freeze-thaw cycle is equivalent to 2–3 weeks of frozen storage (Tuschoff, 1987). Paste clarity is another important functional property of all OSA starches. A fairly transparent paste is desirable in encapsulation applications, and not in salad dressing. The effect of octenylsuccinylation on the thermal behavior of starches can be studied by differential scanning calorimetry (DSC). It is an important technique to understand the thermodynamics of the starch gelatinization.

The physical properties of chemically modified starches are greatly influenced by electronic properties of introduced groups and DS. Hydrophilic substituents such as acetyl, hydroxypropyl, and phosphate groups usually decrease the gelatinization temperature and increase the viscosity, but the magnitude of changes depends partially on the biological source of parent starches (Liu, Ramsden, & Corke, 1997, 1999). Hydrophobic substituents such as benzyl, allyl, and menthyl often result in more complicated changes (Cho & Lim, 1998). Pasting viscosity and onset temperature of benzyl corn starch is shown to decrease with an increase in DS.

Amaranthus paniculatus L. (Rajgeera) is important millet containing about 50–60% of starch. It is extensively grown in India, particularly in Maharashtra, Gujarat, and some parts of South India and used as human food. Amaranth starch has gained interest for food applications due to its waxy nature (Breene, 1991; Lee, Kim, Song, & Shin, 1999; Lehman, 1992; Perez, Bahanassey, & Breene, 1993; Singhal & Kulkarni, 1990) and small granule size of 1–3 μm in diameter. Although many studies on physicochemical properties of different starches modified with OSA are reported (Bao, Xing, Phillips, & Corke, 2003; He et al., 2006; Shih & Daigle, 2003; Song, He, Ruan, & Chen, 2006a), there are no reports on effect of octenylsuccinylation on the physicochemical properties of amaranth starch. Earlier work in our laboratory investigated the effect of different chemical modification on physicochemical properties of waxy starch from amaranth (Bhandari & Singhal, 2002; Bhattacharyya, Singhal, & Kulkarni, 1995; Pal, Singhal, & Kulkarni, 2002). In extension, this works investigates the effect of extent of OSA treatment on the physicochemical, functional, and thermal properties of waxy maize and amaranth starch.

2. Materials and methods

2.1. Materials

Waxy maize starch (C* Gel 4320) was obtained as a gift sample from Cargill Inc., USA. Amaranth starch was isolated in the laboratory by alkali steeping method (Yanez & Walker, 1986) from *A. paniculatus* L. seeds. Octenyl succinic anhydride (*n*-OSA) (99.9%) was obtained from Dixie Chemical, USA. Other chemicals and reagents used were of analytical grade, and procured from reliable sources.

2.2. Preparation of OSA starches

Amaranth and waxy maize OSA starches were prepared under optimized conditions by treating with different amount of OSA (1.0%, 1.5%, 2.0%, 2.5%, and 3.0% based on weight of starch). Degree of substitution (DS) of OSA-modified starches was determined as per method of Whistler and Paschall (1967) and reported in our earlier work (Bhosale & Singhal, 2006).

2.3. Determination of swelling power

This was determined by the method reported by Subramanian, Hoseney, and Bramel-Cox (1994) with minor modifications.

2.4. Brabender characteristics of the OSA starches

Pasting properties were studied on 5% w/v starch suspension (22.5 g in 450 ml of distilled water) of starch sample on Brabender viscoamylograph (Model PT-100). The samples were heated from 30 to 95 °C at 1.5 °C/min at a bowl speed of 75 rpm, held at 95 °C for 30 min and then cooled to 30 °C at the rate of 1.5 °C/min. The results were interpreted with respect to gelatinization temperature, peak viscosity, viscosity at 95 °C, viscosity at 95 °C after 30 min, and viscosity at 30 °C, breakdown viscosity (BV), and setback viscosity (SV).

2.5. Freeze-thaw stability

Freeze-thaw stability of the OSA starches was studied by subjecting 5% w/v starch paste to repeated cycles of freezing and thawing. The paste was weighed (exactly 20 g each) into polypropylene centrifuge tubes, and then tightly capped. The tubes containing starch paste were stored at 4 °C for 24 h before being subjected to

freeze-thaw cycles. In each cycle, the tubes were frozen at −20 °C for 18 h and then thawed at 30 °C in water bath for 2 h. After each cycle, the sample was centrifuged at 4000 rpm for 20 min and the percentage of the separated water measured of the ratio of the weight of the water separated to the weight of the paste. To increase the severity of the freeze-thaw testing of the starches the cooked starch paste were held first at 4 °C for 24 h and then subjected to eight freeze-thaw cycles. Holding at 4 °C accelerates starch retrogradation by favoring the crystallization of starch (Kite, Maywald, & Schoch, 1963).

2.6. Paste clarity

This was carried out by method of Craig, Maningat, Seib, and Hoseney (1989). Two hundred and fifty milligrams of starch sample was suspended in 20 ml of distilled water in a 40 ml test tube with plastic cap. The tubes were then placed in a boiling water bath for 30 min, shaken thoroughly at 5 min interval and then cooled to room temperature (25–30 °C) for about 10 min. The percent transmittance (% T) was determined at 650 nm against water as blank in spectrophotometer (Hellios spectrophotometer, USA).

2.7. Differential scanning calorimetry (DSC) of native and OSA-modified waxy maize and amaranth starches

The thermal analyses of native and modified OSA starches were studied using differential scanning calorimetry (DSC model: TA Instruments). Approximately 2.2 mg of sample and 12.5 μl of distilled water were weighed into sample pan and mixed by using pin. A stream of dry nitrogen was flushed through the DSC head at 60–70 ml/min throughout the study. Keeping the reference cell empty, the sample pan and reference pan were heated simultaneously at rate of 5 °C/min from 40 to 100 °C to analyse the thermal transition of starch (Biliaderis, 1990; White, Abbas, & Johnson, 1990). Each sample was analysed three times consecutively. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and enthalpy of gelatinization (ΔH_g) were recorded by Universal Analysis Programme Version 1.9D. (TA, Instruments, USA). $T_o - T_c$ was calculated as range of gelatinization.

2.8. X-ray diffractometry

The crystallinity of the powdered starch samples was analysed using X-ray diffractometer, Model X-Pert PRO, PANalytical (Spectris Technologies Pvt. Ltd., The Netherland) with following conditions: target Cu–K_∞, filter Ni, scanning speed 0.003555°2T/s, diffraction angle (°2T) 9–40°, voltage 40 kV, and current 20 mA. Type of crystalline structure and crystallanities of starch samples were determined from location and intensity of peak and area under the peak.

2.9. Statistical analysis

All determinations were done in triplicates, and the mean and standard deviations were reported. Analysis of variance was performed and results were evaluated by Turkey–Kramer Multiple Comparison Test. ($P < 0.05$) using statistical software NCSS for Windows (NCSS Statistical Software, Kaysville, UT, USA).

3. Results and discussion

3.1. Effect of OSA treatment on the DS of amaranth and waxy maize starches

Starches modified with different level of OSA were subjected to DS analysis. DS values of 1.0%, 1.5%, 2.0%, 2.5%, and 3.0% OSA treated waxy maize starches were 0.0062, 0.0089, 0.0159, 0.0183, and 0.0206, respectively. Similarly the corresponding values for amaranth starches modified with OSA were 0.0072, 0.0084, 0.0165, 0.0175, and 0.0203. Similar trend of reactivity of OSA with starches was observed with both amaranth and waxy maize starches.

3.2. Swelling power

Swelling power of native and OSA-modified waxy maize and amaranth starches were determined over the temperature range of 55–95 °C (Table 1). Swelling power of native waxy maize starch increased from 2.65% to 37.37% while that for amaranth starch increased from 2.42% to 17.19% (Table 1). The swelling power of both OSA-modified starches increased with an increase in concentration of % OSA used for modification at all the temperatures used in the study. Swelling power of native as well as OSA-modified waxy maize starches was higher than their amaranth starch counterparts. It was increased considerably between 65 and 95 °C. The increase in swelling power may be due to weakening of intermolecular hydrogen bond due to introduction of bulky OSA group (Perez et al., 1993). Similar behaviour was reported for succinylation of canavalia (Bentacur-Ancona, Garcia-Cervera, Canizares-Hernadez, & Chef-Guerrero, 2002) in addition to corn and amaranth starches (Bhandari & Singhal, 2002). This is one of the benefits of octenylsuccinylation which allows to utilize these starches in processes in which a thickening agent must form gel at lower temperatures, or simply to reduce energy consumption during cooking.

3.3. Brabender characteristics

Pasting properties of all starch samples were tested at 5% dry starch basis. Table 2 shows the Brabender characteristics of native and OSA-modified waxy maize and amaranth starches at pH 7.0, respectively. Waxy maize starch showed a slightly lower pasting temperature (69 °C) than amaranth starch (70.5 °C). Pasting temperature for both

Table 1
Effect of octenylsuccinylation on swelling power* of waxy maize and amaranth starches

% OSA treated starch	Swelling power at different temperatures [°C]				
	55	65	75	85	95
Amaranth					
Control	2.42 ± 0.01^{a}	3.97 ± 0.10^{a}	13.38 ± 0.08^{a}	14.86 ± 0.50^{a}	17.19 ± 0.60^{a}
1.0	3.52 ± 0.01^{b}	7.28 ± 0.04^{b}	26.79 ± 0.04^{b}	27.08 ± 0.03^{b}	28.26 ± 0.04^{b}
1.5	3.62 ± 0.02^{c}	9.08 ± 0.06^{c}	26.67 ± 0.03^{c}	33.73 ± 0.02^{c}	34.05 ± 0.01^{c}
2.0	3.66 ± 0.02^{d}	13.96 ± 0.1^{d}	33.73 ± 0.02^{d}	34.05 ± 0.02^{d}	34.08 ± 0.03^{c}
2.5	5.17 ± 0.01^{e}	17.02 ± 0.25^{e}	34.45 ± 0.01^{e}	34.56 ± 0.02^{e}	34.72 ± 0.02^{d}
3.0	5.19 ± 0.02^{e}	21.53 ± 0.40^{f}	34.54 ± 0.05^{e}	34.80 ± 0.00^{f}	34.82 ± 0.01^{d}
Waxy maize					
Control	2.65 ± 0.01^{a}	3.67 ± 0.04^{a}	25.94 ± 0.05^{a}	32.56 ± 0.20^{a}	37.37 ± 0.50^{a}
1.0	2.69 ± 0.02^{a}	6.92 ± 0.05^{b}	39.74 ± 0.30^{b}	50.04 ± 0.34^{b}	51.17 ± 0.05^{b}
1.5	3.00 ± 0.00^{b}	8.26 ± 0.20^{c}	41.37 ± 0.60^{c}	48.30 ± 0.25^{c}	51.58 ± 0.48^{b}
2.0	3.40 ± 0.01^{c}	13.85 ± 0.50^{d}	48.76 ± 0.05^{d}	50.37 ± 0.08^{b}	52.25 ± 0.05^{c}
2.5	3.69 ± 0.03^{d}	19.26 ± 0.09^{e}	49.25 ± 0.06^{d}	51.60 ± 0.02^{d}	52.84 ± 0.01^{c}
3.0	3.79 ± 0.01^{e}	20.48 ± 0.05^{f}	51.36 ± 0.02^{e}	52.53 ± 0.01^{e}	53.16 ± 0.05^{d}

Different letters in the same column of each starch base indicate statistical difference ($P \leqslant 0.5$).
* Results are means ± SD of three determinations.

starches decreased with an increase in concentration of OSA used for modification. Peak viscosity of amaranth starch (310 BU) was lower than that of waxy maize starch (765 BU). Peak viscosities for both OSA-modified starches increased with an increase in OSA concentration used for modification in both starches. At pH 7.0, peak viscosity for amaranth starch treated with 3% OSA increased from 310 to 965 BU, compared to an increases from 765 to 985 BU for waxy maize starch. This showed the effect of OSA on pasting characteristics of amaranth starch to be more pronounced than waxy maize starch. Viscosity after holding at 95 °C for 30 min (hot paste viscosity) and viscosity after cooling to 30 °C (cold paste viscosity) of all OSA starches were higher than parent starches. The high viscosity of starch is beneficial as a thickener, with lower levels of OSA starch replacing unmodified starch (Bao et al., 2003; Thirathumthvorn & Charoenrein, 2006). The enhancement in the viscosity of OSA starch is believed to be due to high swelling volume of OSA starch (Bao et al., 2003; Han & Bemiller, 2007; Shih & Daigle, 2003; Shorgen et al., 2000) and hydrophobic interactions (Ortega-Ojeda, Larsson, & Eliasson, 2005; Park, Chung, & Yoo, 2004; Thomas & Atwell, 1999). The bulky OSA groups on starch molecules cause a structural reorganization, as a result of steric hindrance, and this result in repulsion, thus facilitating an increase in water percolation within the granules with subsequent increase in swelling volumes (Bao et al., 2003; Lawal, 2004). The associative effect of hydrophobic chains in the OSA starches can also enhance the viscosity of OSA starches (Ortega-Ojeda et al., 2005; Park et al., 2004; Thomas & Atwell, 1999). 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).

Breakdown viscosity (BV) is difference between peak viscosity and viscosity at 95 °C after 30 min. A higher BV indicates granule disruption or the tendency of starch to succumb to shear force during heating. The BV for amaranth starch was 60 BU compared to 570 BU for waxy maize starch, showing amaranth starch to be more stable under cooking conditions than waxy maize starch. On modification with OSA, BV decreased with an increase in concentration of OSA treatment for both the starches. The BV for waxy maize starch treated with 3% OSA was zero compared to 55 BU for similarly treated amaranth starch. As discussed above, OSA starches had very high swelling power and thus high hot paste viscosity after cooking. Therefore lower breakdown viscosity of OSA starch does not necessarily indicate the higher resistance to shear force compared with their native forms. Similar results have been reported by Thirathumthvorn and Charoenrein (2006) for tapioca starch modified with OSA. Setback viscosity (SV) for native waxy maize starch was high (125 BU) as compared to amaranth starch (50 BU), showing amaranth starch to be more resistant to retrogradation compared to waxy maize starch. SV of waxy maize starch decreased to zero on treatment with OSA. For OSA amaranth starch, setback was high compared to native form, but decreased with an increased in % OSA treatment. SV normally indicates the degree of retrogradation of starch. However it not a suitable parameter to indicate retrogradation properties of OSA starch (Bao et al., 2003). A similar trend has been observed with the results of rapid visco analyser (RVA) analysis done with starches of rice, wheat, tapioca, and potato treated with OSA (Bao et al., 2003; Shih & Daigle, 2003; Thirathumthvorn & Charoenrein, 2006).

Table 2
Effect of octenylsuccinylation on brabender characteristic of waxy maize and amaranth starches at pH 7.0

% OSA treatment	Pasting temperature [°C]		Peak viscosity [BU]		Viscosity at 95 °C [BU]		Viscosity after holding at 95 °C for 30 min [BU]		Viscosity after cooling to 30 °C [BU]		Breakdown[a] viscosity [BU]		Setback[b] viscosity [BU]	
	WC	Am	WC	Am	WC	Am	WC	Am	WC	Am	WC	Am	WC	Am
0 (Control)	69.75 ± 0.25	70.50 ± 0.25	765 ± 5	310 ± 10	345 ± 10	285 ± 5	195 ± 5	250 ± 10	320 ± 10	300 ± 5	570	60	125	50
1.0	67.50 ± 0.50	69.00 ± 0.50	875 ± 10	865 ± 5	875 ± 5	870 ± 5	690 ± 5	600 ± 10	720 ± 10	765 ± 5	185	265	30	165
1.5	66.00 ± 0.50	68.00 ± 0.25	890 ± 10	870 ± 10	890 ± 10	870 ± 10	750 ± 10	725 ± 10	740 ± 5	780 ± 10	140	145	10	55
2.0	64.50 ± 0.05	67.50 ± 0.50	880 ± 5	895 ± 5	880 ± 5	895 ± 5	880 ± 5	770 ± 10	880 ± 10	790 ± 5	0	125	0	20
2.5	64.30 ± 0.05	65.00 ± 0.60	925 ± 10	930 ± 5	920 ± 5	930 ± 5	925 ± 10	810 ± 10	925 ± 10	865 ± 10	0	120	0	55
3.0	61.50 ± 0.25	63.80 ± 0.30	985 ± 5	965 ± 10	980 ± 5	970 ± 5	985 ± 5	910 ± 10	985 ± 10	960 ± 15	0	55	0	50

Where WC, waxy maize starch; Am, amaranth starch.
Results are means ± SD of three determinations.
[a] Breakdown viscosity (BV) = peak viscosity − viscosity at 95 °C after 30 min.
[b] Setback viscosity (SV) = viscosity at 95 °C after 30 min − Viscosity at 30 °C.

3.4. Freeze-thaw stability

Native and OSA-modified maize and amaranth OSA starches were subjected to alternate freeze-thaw cycles (Table 3). Native waxy maize and amaranth starches showed syneresis from first and second cycle, respectively. Amaranth starch showed 51.0% syneresis as compared to 83.5% for waxy maize starch after eight cycles of freeze-thaw, showing waxy maize starch paste to be more susceptible to syneresis compared to amaranth starch paste (Bhattacharyya et al., 1995). The differences in freeze-thaw stability among different types of starches may be due to variety of factors, such as amylose content, the length of the starch chains, degree of association between starch component, degree of polymerization of amylose and amylopectin content (Hoover, Roorke, & Martin, 1991), length of storage, rate of freezing, number of freeze-thaw cycles and the addition of other food ingredients (Dreher, Tinsley, Scheerens, & Berry, 1983). With increase in the concentration of OSA for modification of both the starches, resistance to syneresis improved as indicated by decreased synerisis. The poor freeze-thaw stability exhibited by native starches indicated extensive retrogradation during frozen storage. However increasing concentration of OSA used for modification improved the water-holding capacity of starch gel by decreasing in the extent of retrogradation (Islam & Azemi, 1997). Reduction in the extent of retrogradation of OSA-modified starches could be attributed to the steric effect imposed by bulky OSA group, which prevents the alignment of chain of starch (Islam & Azemi, 1997). Freeze-thaw cycle indicates the storage stability at low temperatures and one such cycle is equivalent to 2–3 weeks of frozen storage (Liu et al., 1997). For 3.0% OSA-modified amaranth and waxy maize starch pastes, there was no syneresis at all for first six cycles showing both the OSA-modified starches to be very stable to freeze-thaw cycles, and hence can be used as excellent emulsion stabilizer in frozen foods. Song et al. (2006a, 2006b) were reported about increase in freeze-thaw stability for the octenylsuccinylated derivative of early *indica* rice starch.

3.5. Paste clarity

Percent transmittance at 650 nm of the starch paste is a measure of paste clarity (Table 4). The higher % transmittance of native waxy maize starch as compared to the native amaranth starch can be explained by greater swelling of the former which allows more light to pass through the granules instead of being reflected. This is because starch granule dissociates and ability of granules to reflect light diminishes (Craig et al., 1989). This was also observed for OSA-modified waxy maize and amaranth starches. As the concentration of OSA used for modification increased, the paste clarity improved. The changes to the granular and molecular structure induced by octenylsuccinylation facilitated better penetration and absorption of water within starch granules which ultimately lead to more swelling of

Table 3
Effect of octenylsuccinylation on freeze-thaw stability* of waxy maize and amaranth starches

% OSA treatment	% syneresis after freeze-thaw cycles[a]							
	1	2	3	4	5	6	7	8
Waxy maize starch								
0 (Control)	2.0 ± 0.1^{a}	33.0 ± 0.8^{a}	40.0 ± 1.5^{a}	42.0 ± 1.2^{a}	49.0 ± 0.9^{a}	56.0 ± 1.8^{a}	64.0 ± 1.6^{a}	83.5 ± 2.2^{a}
1.0	NIL	6.5 ± 0.9^{b}	28.5 ± 0.6^{b}	37.5 ± 0.8^{b}	40.5 ± 1.1^{b}	53.0 ± 1.8^{a}	56.0 ± 0.9^{b}	58.0 ± 1.7^{b}
1.5	NIL	2.5 ± 0.1^{c}	28.0 ± 0.8^{b}	30.5 ± 1.2^{c}	35.5 ± 1.6^{c}	40.0 ± 1.1^{b}	42.0 ± 1.3^{c}	46.5 ± 1.1^{c}
2.0	NIL	NIL	NIL	NIL	4.0 ± 0.3^{d}	7.33 ± 1.1^{b}	10.6 ± 0.7^{d}	12.0 ± 0.8^{d}
2.5	NIL	NIL	NIL	NIL	2.0 ± 0.0^{e}	5.0 ± 0.9^{d}	8.0 ± 0.6^{e}	10.0 ± 0.9^{d}
3.0	NIL	NIL	NIL	NIL	NIL	NIL	2.0 ± 0.6^{f}	4.5 ± 0.3^{e}
Native amaranth starch								
0 (Control)	NIL	3.0 ± 0.1^{a}	11.0 ± 0.9^{a}	15.0 ± 0.9^{a}	28.5 ± 1.5^{a}	44.0 ± 1.1^{a}	48.5 ± 2.5^{a}	51.0 ± 1.2^{a}
1.0	NIL	NIL	NIL	22.0 ± 1.2^{b}	24.0 ± 1.9^{b}	28.0 ± 1.6^{b}	30.0 ± 1.8^{b}	32.0 ± 1.5^{b}
1.5	NIL	NIL	1.0 ± 0.1^{b}	1.0 ± 0.1^{c}	2.0 ± 0.2^{c}	5.0 ± 0.9^{c}	6.0 ± 0.9^{c}	8.0 ± 0.9^{c}
2.0	NIL	NIL	NIL	NIL	NIL	NIL	2.0 ± 0.2^{d}	2.0 ± 0.5^{d}
2.5	NIL	NIL	NIL	NIL	NIL	NIL	2.0 ± 0.3^{d}	2.0 ± 0.4^{d}
3.0	NIL	NIL	NIL	NIL	NIL	NIL	1.0 ± 0.1^{e}	1.0 ± 0.04^{e}

Different letters in the same column of each starch base indicate statistical difference ($P \leqslant 0.05$).
* Results are means ± SD of three determinations.

Table 4
Effect of octenylsuccinylation on the thermal properties[a] and paste clarity[a] of waxy maize and amaranth starch

% OSA treatment	ΔH_g [J/g]	Transition temperature [°C]				% T at 650 nm
		T_o	T_p	T_c	$T_o - T_c$	
Waxy maize starch						
0.0 (Control)	2.62 ± 0.10^{a}	67.19 ± 0.10^{a}	72.42 ± 0.10^{a}	82.21 ± 0.00^{a}	15.02	46.42 ± 0.08^{a}
1.0	2.58 ± 0.03^{a}	67.19 ± 0.06^{a}	72.76 ± 0.11^{b}	82.74 ± 0.14^{b}	15.55	50.84 ± 0.57^{b}
1.5	2.28 ± 0.13^{b}	66.09 ± 0.04^{b}	71.86 ± 0.03^{c}	80.10 ± 0.20^{c}	14.01	52.02 ± 0.24^{c}
2.0	2.23 ± 0.02^{b}	65.93 ± 0.00^{b}	71.42 ± 0.08^{d}	79.52 ± 0.01^{d}	13.59	53.38 ± 0.15^{d}
2.5	2.22 ± 0.0^{b}	65.41 ± 0.10^{c}	71.20 ± 0.02^{d}	78.55 ± 0.05^{e}	13.14	55.43 ± 0.06^{e}
3.0	2.06 ± 0.05^{c}	64.86 ± 0.04^{d}	70.41 ± 0.20^{e}	77.64 ± 0.07^{f}	12.78	61.09 ± 0.18^{f}
Amaranth starch						
0.0 (Control)	2.17 ± 0.02^{a}	67.72 ± 0.10^{a}	73.2 ± 0.0^{a}	82.08 ± 0.20^{a}	14.36	6.31 ± 0.07^{a}
1.0	1.85 ± 0.15^{b}	66.34 ± 0.05^{a}	72.47 ± 0.2^{b}	80.76 ± 0.05^{b}	14.42	11.60 ± 0.06^{b}
1.5	1.62 ± 0.05^{c}	65.55 ± 0.2^{b}	72.07 ± 0.0^{b}	80.27 ± 0.16^{c}	14.72	12.96 ± 0.10^{c}
2.0	1.55 ± 0.03^{c}	65.04 ± 0.15^{b}	71.91 ± 0.3^{b}	80.08 ± 0.10^{c}	15.04	13.98 ± 0.01^{d}
2.5	1.43 ± 0.11^{d}	64.78 ± 0.05^{c}	71.88 ± 0.05^{c}	79.61 ± 0.03^{d}	14.83	14.09 ± 0.05^{d}
3.0	1.31 ± 0.07^{d}	64.35 ± 0.0^{d}	69.51 ± 0.2^{d}	78.13 ± 0.19^{e}	13.78	15.94 ± 0.15^{e}

Different letters in the same column of each starch base indicate statistical difference ($P \leqslant 0.5$).
[a] Values are means ± SD of three determinations.

starch and resulted in more transmittance of light (Pal, Singhal, & Kulkarni, 2000). Bhandari and Singhal (2002) were reported about increased in paste clarity for succinylated derivative of amaranth and maize starches. Increase in paste clarity with increase in DS of OSA modified early *indica* rice starch was reported by Song et al. (2006a, 2006b). Improved paste clarity is a useful property in the manufacture of some foods like jellies, sausages, and fruit pastes, which require transparency (Jyothi et al., 2005).

3.6. Thermal analysis of OSA-modified starches

DSC results of native and modified maize OSA and amaranth OSA starches are given in Table 4. The graphical representations of DSC are shown in Figs. 1 and 2. T_o, T_p, T_e, and ΔH_g values decreased with increasing concentration of OSA used for the modification of amaranth and waxy maize starches. The gelatinization enthalpy (ΔH_g) indicates the energy required to disrupt the starch granule structure and is obtained directly as the area under the endotherm. Generally gelatinization temperatures have been related to degree of perfection of crystallites in the starch granules, and 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 to swell at lower temperature and hence gradually decreasing the enthalpy of all OSA starches (Bao et al., 2003; Rutenberg & Solarek, 1984). Also introduction of bulky OSA groups into the backbone of the biopolymer enhances structural flexibility, and contributes to the reduction of gelatinization temperature of

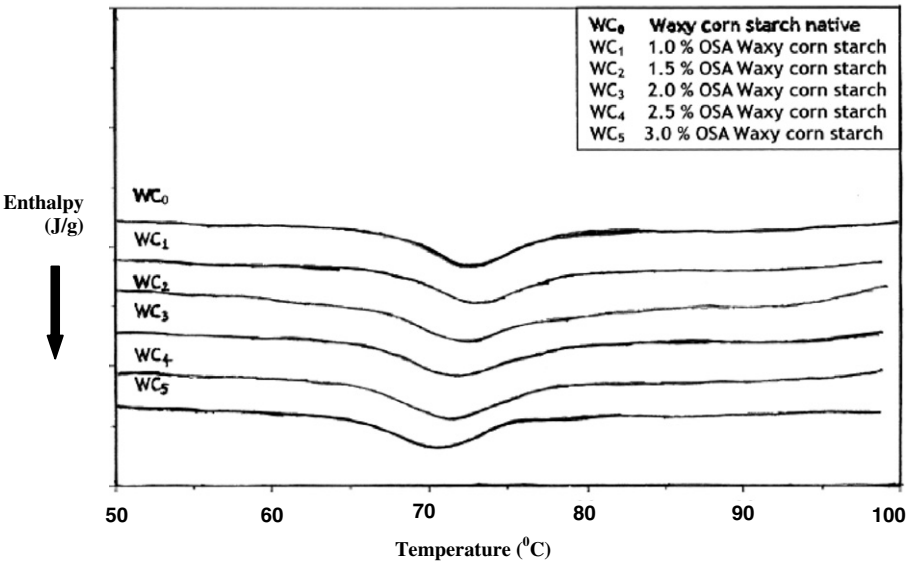

Fig. 1. Effect of octenylsuccinylation on DSC thermograms of waxy maize starch.

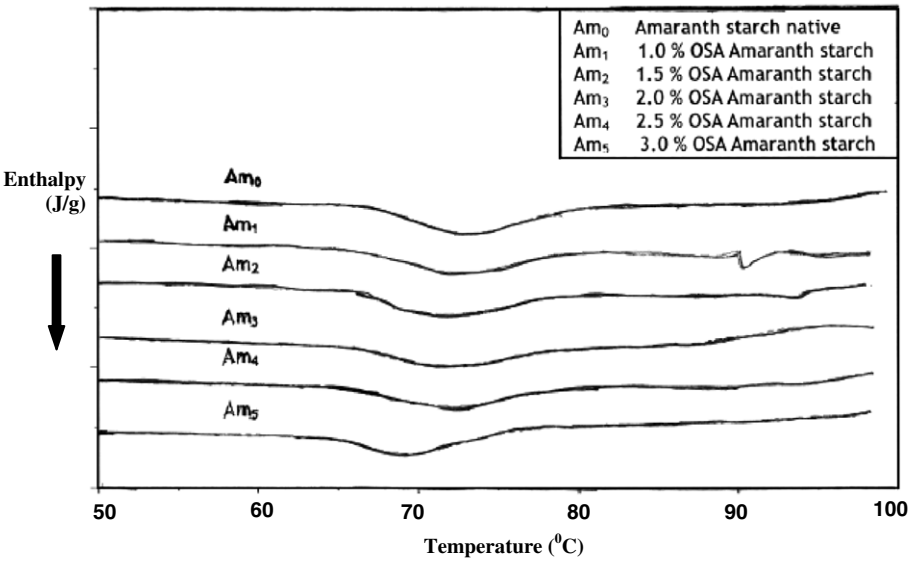

Fig. 2. Effect of octenylsuccinylation on DSC thermograms of amaranth starch.

the modified starches (Lawal, 2004; Miller, Gordon, & Davis, 1991). Additionally, the OSA effect on the gelatinization temperature of starch is dependent on the starch base and degree of substitution (Bao et al., 2003; Miller et al., 1991). At molecular level, this may be expected to involve the cleavage of existing hydrogen bonds between starch molecules and formation of new bond involving water to give less order structure with increased entropy (Paton, 1987). The effect can be explained as the weakening of hydrogen bonding by the hydrophobic octenylsuccinyl groups, helping starch swelling at relatively lower temperature. Similar trend in thermal properties of OSA starches has been reported by earlier researchers (Bao et al., 2003; Shih & Daigle, 2003).

For amaranth starch, as the concentration of OSA used for modification increased from 0 to 3.0, ΔH_g values decreased from 2.17 to 1.31 J/g, whereas for waxy maize starch it decreased from 2.62 to 2.06 J/g. T_p value of amaranth starch was higher as compared to waxy maize starch. Similar results were obtained for OSA waxy corn starch (DS = 0.015) (Miller et al., 1991), in addition to OSA wheat (DS = 0.0225) and potato starches (DS = 0.0171) (Bao et al., 2003). The variation in OSA effects on gelatinization may be related to the difference in molecular alignment of each starch origin that influences the properties of OSA-modified starch differently. T_o, T_p, and T_e values of both native waxy maize and amaranth starches were found to be comparable to the earlier reports (Baker &

Rayas-Durate, 1998; Wooton & Manatsathit, 1984; Wootton & Bamunuarachihi, 1979a, 1979b). $T_o - T_p$ indicates the range of temperature over which starch gelatinizes. For waxy maize starch, the range of gelatinization decreased with an increased in the concentration of OSA used for modification. For amaranth OSA starch, no

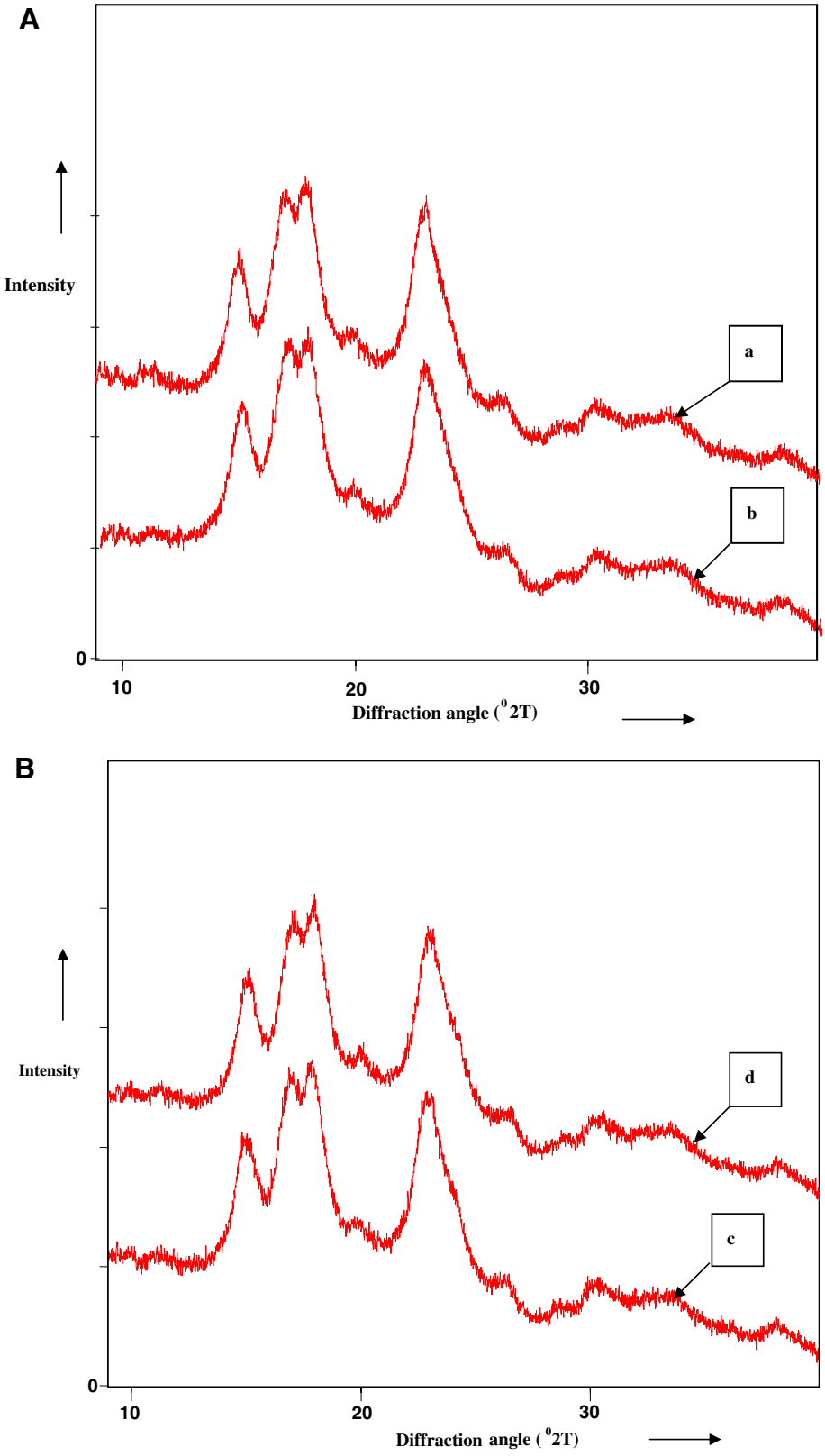

Fig. 3. X-ray diffractograms of (A) (a) waxy corn, (b) OSA waxy corn starch (3% OSA) and (B) (c) native amaranth starch, and (d) OSA amaranth starch (3% OSA).

particular trend was observed between gelatinization range and the concentration of OSA used for its modification.

3.7. X-ray diffractometry

In order to study the effect of OSA modification on the crystal structure, native and OSA starches were examined by powder X-ray diffraction analysis. Fig. 3 indicates that both native and OSA-modified amaranth and waxy maize starches possessed typical "**A**" type of crystallinity. Majority of the peaks were in the range of 14.0–24.0, indicating the modification of starch with OSA to have no significant effect on the crystallinity of both the starches under study. These results are in agreement with reports of Shorgen et al. (2000); Wang and Wang (2002) and Song et al. (2006a, 2006b) who indicated the esterification to occur primarily in the amorphous regions, and leave the crystalline pattern of starches unchanged.

4. Conclusion

Octenylsuccinylation of waxy maize and amaranth starches improved their swelling power as well as other functional properties such as paste clarity and freeze-thaw stability. The OSA-modified amaranth and waxy cornstarch showed good stability at pH 7.0. The changes in technological properties could be correlated to the concentration of OSA used for modification. The crystallinity of both the starches was not affected to any significant extent due to modification by OSA. Such OSA-modified starches could have potential industrial applications in food industry in emulsification, and as wall material for encapsulation after hydrolysis.

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