

Impact of octenyl succinic anhydride on rheological properties of sorghum starch

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Abstract

The impact of pH conditions (4, 6, and 8) during modification by dry heated octenyl succinic anhydride on physicochemical, pasting and rheological properties of sorghum starch was studied. Degree of substitution and reaction efficiency values of modified starches varied from 0.013 to 0.021 and 54.6 to 88.2%, respectively, the highest values were observed for starch modified at pH 8. Amylose content of modified starches decreased as compared to native starch. Swelling power and solubility of starches were observed the highest for starch modified at pH 8 and pH 4, respectively. Peak viscosity of starches varied from 239 to 3,138 mPa s, the highest and the lowest values were observed for starches modified at pH 8 and pH 4, respectively. Modified starches showed lower pasting temperature as compared to native counterpart starch. G' and G'' values of starches during heating ranged from 811 to 1,982 Pa and 108 to 191 Pa, respectively. $\tan \delta$ values of native and modified starches were less than 1, indicating their elastic nature. G' values of modified starches during frequency sweep measurements were less than native starch. Starch pastes from native and modified starches showed shear thinning behaviour during steady shear measurements.

Keywords: sorghum, OSA, dynamic shear rheology, steady shear rheology

1. Introduction

Sorghum (*Sorghum bicolor* [(L.) Moench] family-Poaceae) is a major food crop providing energy, protein, vitamins and other nutrients to millions of people living in the warm and arid regions of the world (Meera *et al.*, 2011). Sorghum is the world's fourth major cereal crop in terms of production and fifth in acreage after wheat, rice, maize and barley (Udachan *et al.*, 2012). In many countries of Africa, Asia and Central America, sorghum is a staple food for human feeding; however, it is underutilized in countries like the United States, Australia and Brazil, and used mainly for animal feeding (Taylor *et al.*, 2006; Waniska and Rooney, 2000). Starch is the major storage carbohydrate of sorghum, accounting for 55.6-77% on kernel weight basis (Reddy *et al.*, 2006). Many scientists have characterized sorghum starch (Singh *et al.*, 2010; Udachan *et al.*, 2012), heat moisture treated (HMT) and succinylated sorghum starch (Olayinka *et al.*, 2008, 2011). Corn starch is widely used in food industries; however, availability of corn starch is decreasing day by day due to its increased demand by industries. Sorghum starch is very similar to commercially

important corn starch in many of its functional properties, whereas in terms of agronomic properties sorghum is even better than corn (Arshad *et al.*, 2018). So, sorghum starch can be good substitute for corn starch.

Native starches have limited applications due to various drawbacks such as low paste clarity, low shear stress resistance, and high retrogradation (Kaur and Bhullar, 2016). Therefore, starches are commonly modified either by physical and chemical modifications or both to improve functional properties so as to increase their applications in the food industries (Ali and Hasnain, 2014). The substitution of starch with octenyl succinic anhydride (OSA) was first patented by Caldwell and Wurzburg, 1953. Many countries permit 3% modification of starch with OSA in food products (CFR, 2001). OSA starches stabilize the oil-water interface of an emulsion. The glucose part of starch binds the water whereas the lipophilic octenyl part binds the oil. In this way complete separation of the oil and water phases is prevented (Murphy, 2000). Applications of OSA modified starch include its use in beverage emulsions, flavours, clouding agents, salad dressings, creams, fragrances, emulsion paints,

lattices, coatings and adhesives (Thomas and Atwell, 1999; Trubiano, 1986; Wurzburg, 1995). The optimum reaction conditions reported for starch esterification with alkenyl succinic anhydride were pH 8.5-9.0, reaction temperature 23 °C and 5% anhydride concentration (Jeon *et al.*, 1999). After OSA modification, starch becomes an effective emulsifier, due to the addition of bifunctional groups that are both hydrophilic and hydrophobic (Tesch *et al.*, 2002). Heacock *et al.* (2004) found that esterification of starch with OSA impaired the binding of α -amylase, thus decreasing the extent of starch digestion. Their study indicated that OSA starch has higher proportion of resistant starch, which could be potentially used as a functional fiber for the treatment of certain human diseases. Work on starch modification using OSA has been reported on corn, amaranth (Bhosale and Singhal, 2007), wheat, rice (Bao *et al.*, 2003), potato (Hui *et al.*, 2009), sorghum (Olayinka *et al.*, 2011), acha (Arueya and Oyewale, 2015) and ginkgo (Zheng *et al.*, 2017). In present study, the effect of pH conditions of dry heated OSA modification on functional and rheological properties of sorghum starch was investigated.

2. Materials and methods

Materials

Sorghum cultivar (cv.HC-136) was procured from Chaudhary Charan Singh Haryana Agricultural University, Hissar, India. The chemicals and reagents [2-Octen-1-ylsuccinic anhydride and potassium iodide (Sigma-Aldrich, St. Louis, MI, USA), iodine resublimed (Qualigens, Mumbai, India), sodium hydroxide (CDH, New Delhi, India), hydrochloric acid (Rankem, New Delhi, India), potassium hydroxide (CDH, New Delhi, India), sodium metabisulphite (CDH, New Delhi, India)] used were of analytical grade.

Starch isolation

Starch was isolated from sorghum grains by following the method described by Sandhu and Singh (2005). About 500 g of clean, sound and whole were added to 1.25 l of distilled water containing sodium metabisulphite (0.1%). The mixture was maintained at 50 °C for about 18-20 h with intermittent circulation of liquid. After 20 h, the steep water was drained off and grains were ground in laboratory grinder (Maxie Plus, New Delhi, India). About 250 g of steeped grains were ground with 250 ml of distilled water. The ground slurry was passed through 0.250, 0.150, 0.100, 0.075, 0.045 mm sieve. The starch-protein slurry was then allowed to stand for 4-5 h. The supernatant was removed by suction and the settled starch layer was re-suspended in distilled water and centrifuged in wide mouthed cup centrifuge (Remi, New Delhi, India) at 605 g for 10 min and the upper non-white layer was scrapped off. The white layer was re-suspended in distilled water and re-centrifuged 3-4

times. The starch was then collected and dried in an oven (NSW-143, New Delhi, India) at 45 °C for 12 h.

Preparation of OSA starch

The OSA sorghum starch was prepared according to the method described by Kim *et al.* (2010) and further modified by Chung *et al.* (2010). OSA (3.0 g, 3% based on starch solids) was dissolved in distilled water (120 ml). The sorghum starch (100 g, dry basis) was then dispersed into the OSA solution. The pH of the slurry was adjusted to 4.0, 6.0 or 8.0 with 1 M HCl or 1 M NaOH. The reaction was continued with stirring for 1 h at room temperature. The starch was dried at 40-50 °C in a convection oven for 24 h to moisture content less than 5%, ground and then sieved. The dried OSA starch powders were then heated in an electric oven at 130 °C for 2 h. The dry heated OSA starch samples were cooled and then dispersed in distilled water (150 ml). The pH of the dispersion was adjusted to 6.0 with 1 M HCl or 1 M NaOH. The samples were washed twice with water (450 ml) and once with ethanol (150 ml), and then air-dried.

Degree of substitution

The degree of substitution (DS) is the average number of hydroxyl groups substituted per glucose unit. It was determined by alkali saponification. Octenyl succinylation level of the modified starches was determined using the titrimetric method of Whistler and Paschall (1967).

The reaction efficiency (RE) was calculated as:

$$RE(\%) = (DS / \text{theoretical DS}) \times 100$$

The theoretical DS was calculated by assuming that all of the added anhydride reacted with the starch to form the ester derivative.

Amylose content

The amylose content of starch was determined by following the method described by Williams *et al.* (1970). Starch (0.020 g) was thoroughly mixed with 10 ml of 0.5 mol/l KOH. The dispersed sample was transferred to volumetric flask (100 ml) and diluted to the mark with distilled water. An aliquot of test starch solution (10 ml) was pipetted into volumetric flask (50 ml) and 5 ml of 0.1 mol/l HCl was added followed by the 0.5 ml of iodine reagent. The volume was diluted to 50 ml and the absorbance was measured at 625 nm in a spectrophotometer (Systronics, Ahmadabad, India). The measurement of the amylose was determined in triplicate from a standard curve developed using amylose and amylopectin blends.

Transmittance

Transmittance of native and OSA-modified sorghum starch was measured by following the method of Perera and Hoover (1999). A 1% aqueous suspension of starch was heated in a water bath at 90 °C for 1 h with constant stirring. The suspension was cooled for 1 h at 30 °C. The samples were stored for 5 days at 4 °C in a refrigerator and transmittance was determined every 24 h by measuring absorbance at 640 nm against a water blank.

Swelling power and solubility

The swelling power and solubility of starches were determined by following the method described by Leach *et al.* (1959). Starch (1 g) was added to distilled water (99 ml) and heated to 90 °C for 1 h. The heated samples were cooled rapidly in ice water bath for 1 min, equilibrated at 25 °C for 5 min and then centrifuged at 605 g for 30 min. The supernatants were drained into pre-weighed moisture dishes, evaporated to dryness in a hot air oven at 100 °C and cooled to room temperature in a desiccator prior to reweighing.

Pasting properties

The pasting properties of sorghum starch were determined using an in-built starch cell of Modular Compact Rheometer (Model-52, Anton Paar, Austria). Starch slurries (1.2 g starch in 13.8 g distilled water) were held at 50 °C for 1 min and then heated from 50 to 95 °C at a heating rate of 6 °C/min, held for 2.7 min, cooled to 50 °C at the same rate and again held at 50 °C for 2 min. Each sample was analysed in triplicate. Peak viscosity (PV), breakdown viscosity (BV), setback viscosity (SV), final viscosity (FV) and pasting temperature (PT) were obtained from the pasting graph.

Dynamic shear properties

A small amplitude oscillatory rheological measurement was made for native and modified starches with a Modular Compact Rheometer (Model-52, Anton Paar, Austria) equipped with parallel plate system (0.04 m diameter). The gap size was set at 1000 µm. The strain and frequency were set at 2% and 10 rad/s, respectively, for all determinations. The dynamic rheological properties, such as storage modulus (G'), loss modulus (G'') and loss factor ($\tan \delta$) were determined for starches. Starch suspensions of 10% (w/w) concentration were loaded onto the ram of the rheometer and covered with a thin layer of low-density silicon oil (to minimize evaporation losses). The starch samples were subjected to temperature sweep testing and were heated from 45 to 95 °C at the rate of 2 °C/min).

For frequency sweep measurement, the starch slurry (10%, w/w) was prepared and manually stirred and then heated at 85 °C in a water bath followed by stirring for 3 min. The sample was allowed to cool at room temperature and then loaded on the ram of rheometer. Frequency sweep tests from 0.1 to 100 rad/s were performed at 25 °C. G' , G'' , and $\tan \delta$ were derived at 25 °C.

Steady shear measurement

Steady shear properties were determined by following the method described by Park *et al.* (2004) as modified by Sandhu and Siroha (2017). The sample preparation method has been described in frequency sweep measurement method. The sample (10%) was sheared continuously from 1 to 500 s⁻¹. In order to describe the variation in the rheological properties of samples under steady shear, the data was fitted to Herschel-Bulkley model:

$$\sigma = \sigma_0 + K(\dot{\gamma})^n$$

where σ is the shear stress (Pa), σ_0 is the yield stress, $\dot{\gamma}$ is the shear rate (s⁻¹), K is the consistency index (Pa.sⁿ), n is the flow behaviour index (dimensionless).

Statistical analysis

The data reported in the tables were carried out in triplicate and they were subjected to one-way analysis of variance (ANOVA) using Minitab Statistical Software version 15 (Minitab, Inc., State College, USA).

3. Results and discussion

Degree of substitution and reaction efficiency (%) of octenyl succinic anhydride modified starches

DS and RE (%) values of starches are reported in Table 1. DS and RE values of OSA modified starches varied from 0.013 to 0.021 and 54.6 to 88.2%, the highest values were observed for starch modified at pH 8. DS and RE increased with increase in reaction pH. Chung *et al.* (2010) also reported similar results for dry-heated octenyl succinylated waxy corn starches. Olayinka *et al.* (2011) reported DS values of 0.016 and 0.025 for red and white sorghum starches, respectively. The pH of the aqueous slurry is important for esterification of starch. As a catalyst, NaOH starts the reaction by the formation of alcoholate ions along the starch polymer (Funke and Lindhauer, 2001). Hui *et al.* (2009) observed that DS and RE decreased strongly at pH < 7.5 or > 8. They reported that when pH values were > 8, side reactions were favoured, whereas at pH < 7.5, the hydroxyl groups of starch were not sufficiently activated for nucleophilic attack of the anhydride moieties.

Table 1. Degree of substitution (DS), reaction efficiency (RE), amylose content, swelling power and solubility of native and modified starches.¹

Sample ²	DS	RE (%)	Amylose content (%)	Swelling power (g/g)	Solubility (%)
Native starch	–	–	15.1±0.2 ^d	17.7±0.5 ^b	14.0±0.1 ^b
OSA-4	0.013 ^a	54.6±0.5 ^a	12.9±0.3 ^c	13.5±0.2 ^a	28.1±0.1 ^d
OSA-6	0.016 ^a	67.2±0.4 ^b	11.5±0.2 ^b	19.4±0.3 ^c	17.4±0.2 ^c
OSA-8	0.021 ^a	88.2±0.8 ^c	10.4±0.1 ^a	25.8±0.3 ^d	12.6±0.2 ^a

¹ Means followed by same superscript within a column do not differ significantly ($P < 0.05$). Mean (\pm standard deviation) of triplicate analysis.

² OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

Physicochemical properties

Amylose content, swelling power, and solubility of starches are reported in Table 1. Amylose content of native and modified starches varied from 10.4 to 15.1%, the highest and the lowest value were observed for native starch and the starch modified at pH 8, respectively. The decrease in amylose content with increase in the DS was observed. Segura-Campos's *et al.* (2008) observed decrease in amylose content after OSA modification of *Phaseolus lunatus* starch, which may be due to introduction of a substitute group with a long hydrophobic chain thus increasing ramification and preventing absorption of the iodine used in the determination technique. Sandhu *et al.* (2015) also observed decrease in amylose content after OSA modification of potato starches. Swelling power and solubility of starches varied from 13.5 to 25.8 g/g and 12.6 to 28.1%, the highest values were observed for starch modified at pH 8 and pH 4, respectively. Swelling power increased with increase in OSA concentration used during modification. Bhosale and Singhal (2007) reported increase in swelling power of waxy maize starch and amaranth starch after OSA modification. 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). Sandhu *et al.* (2015) reported decrease in solubility with increase in the DS for OSA modified potato starches. The light transmittance (%) of OSA modified starch pastes was higher than native starch after similar storage intervals (Figure 1). For both native and OSA modified sorghum starch pastes, light transmittance decreased progressively during storage. Bhandari and Singhal (2002) also reported increased paste clarity for the succinylated derivatives of corn and amaranth starches. The increase in light transmittance of the OSA starches might be attributed to the introduction of carboxyl group, which retained the water molecules to form hydrogen bonds in the starch granules, thereby, increasing the clarity of starch pastes.

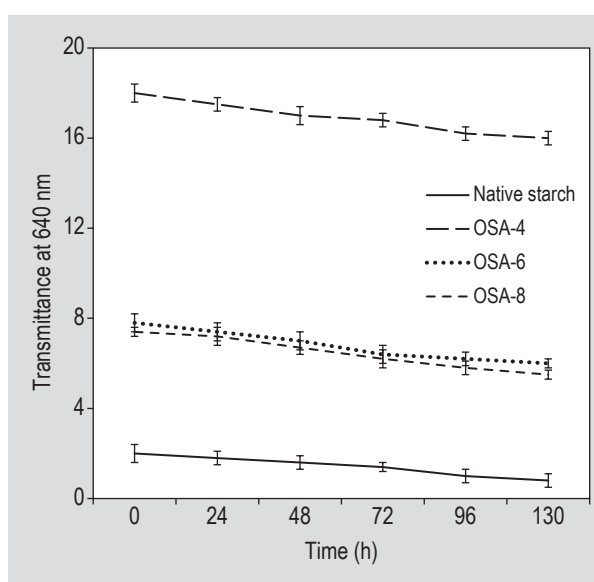


Figure 1. Light transmittance of native and octenyl succinic anhydride (OSA) modified starch at different pH levels. OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

Pasting properties

Pasting properties of native and OSA modified starches are reported in Table 2 and their curves are shown in Figure 2. PV of native and modified starches varied from 239 to 3,138 mPa s, the highest and the lowest values were observed for starch modified at pH 8 and pH 4, respectively. Except for starch modified at pH 8, the decrease in PV of OSA modified starches was observed as compared to native starch. The increase in viscosity by OSA substitution has been previously reported for starches, which may be due to the formation of amylose-OA inclusion complexes (Ortega-Ojeda *et al.*, 2005; Park *et al.*, 2004). BV, indicating paste stability of modified starches ranged from 136 to 1,177 mPa s. BV values of modified starches were higher than native starch except for modification done at pH 4. Trough viscosity (TV) and SV of native and modified starches varied from 103 to 1961 mPa s and 42 to 867 mPa s, respectively.

Table 2. Pasting properties of native and modified starches.^{1,2}

Sample	PV (mPa·s)	BV (mPa·s)	TV (mPa·s)	SV (mPa·s)	FV (mPa·s)	PT (°C)
Native starch	1,620±18 ^c	317±6 ^b	1,303±1 ^c	576±9 ^b	1,879±20 ^b	79.4±0.5 ^d
OSA-4	239±12 ^a	136±4 ^a	103±4 ^a	42±3 ^a	145±4 ^a	69.2±0.4 ^a
OSA-6	1,597±20 ^b	588±6 ^c	1,009±10 ^b	867±8 ^c	1,876±16 ^b	71.6±0.6 ^b
OSA-8	3,138±26 ^d	1,177±9 ^d	1,961±22 ^d	831±9 ^c	2,792±22 ^c	74.6±0.5 ^c

¹ Means followed by same superscript within a column do not differ significantly ($P<0.05$). Mean (\pm standard deviation) of triplicate analysis.

² BV = breakdown viscosity; FV = final viscosity; OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8; PT = pasting temperature; PV = peak viscosity; SV = setback viscosity; TV = trough viscosity.

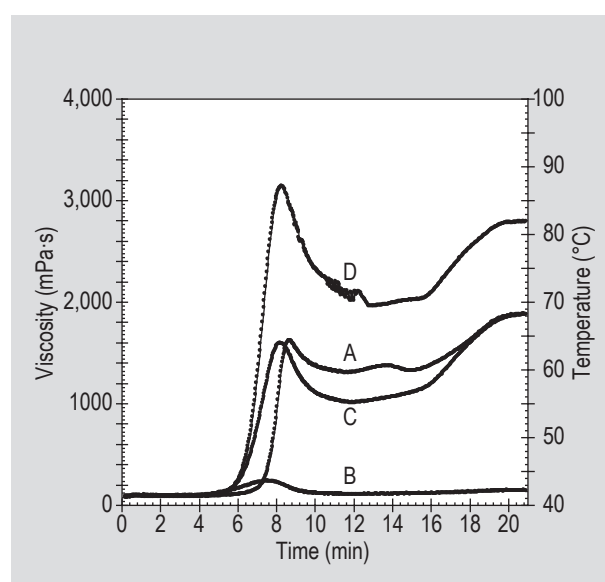


Figure 2. Pasting properties of native and octenyl succinic anhydride (OSA) modified starch at different pH levels (A: Native starch, B: OSA-4, C: OSA-6, D: OSA-8). OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

PT – the minimum temperature required to cook the starch – varied from 69.2 to 79.4 °C. After modification, PT of modified starches decreased as compared to native starch. Bhosale and Singhal (2007) reported that after OSA

modification, PV and SV of starches increased while BV and PT decreased as compared to native starch.

Dynamic shear properties

Significant ($P<0.05$) differences in the rheological properties of native and modified starch suspensions during heating were observed (Table 3). The effect of temperature on rheological properties needs to be documented as wide range of temperatures is required during processing and storage of fluid foods (Rao, 1999). G' and G'' values of all starch suspensions, increased to a maximum, and then decreased with continuous heating. The values of G' and G'' ranged from 811 Pa to 1,982 Pa and 108 Pa to 191 Pa, respectively with native starch showing the highest values for peaks of both these moduli. The increase in G' during heating may be due to starch granules swelling followed by leaching. Peak G' is the measure of stored energy in material and recovered from it per cycle whereas peak G'' is the measure of energy dissipated or lost per cycle during sinusoidal deformation (Ferry, 1980). The breakdown in G' is the difference between peak G' at TG' (temperature at which G' was maximum) and minimum G' at 90 °C. The breakdown in G' values of starches varied from 634 Pa to 1,510 Pa. TG' value of starches varied from 62.5 °C to 67.5 °C, the highest value was found for native starch. For all starches, $\tan \delta$ value was less than 1, indicating their elastic behaviour.

Table 3. Rheological properties of starches during heating.^{1,2}

Sample	G' (Pa)	G'' (Pa)	Breakdown in G' (Pa)	$\tan \delta$	TG' (°C)
Native starch	1,982±18 ^c	191±4 ^d	1,055±10 ^c	0.09 ^a	67.5±0.2 ^c
OSA-4	811±7 ^a	108±5 ^a	634±7 ^a	0.13 ^a	62.5±0.3 ^a
OSA-6	1,436±11 ^b	126±5 ^b	825±9 ^b	0.08 ^a	65.0±0.2 ^b
OSA-8	1,940±22 ^c	166±3 ^c	1,510±11 ^d	0.08 ^a	62.5±0.1 ^a

¹ Means followed by same superscript within a column do not differ significantly ($P<0.05$). Mean (\pm standard deviation) of triplicate analysis.

² OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

The changes in G' , G'' and $\tan \delta$ for native and OSA modified sorghum starch pastes during frequency sweep test are reported in Table 4 and the curves are shown in

Figure 3. G' reflects the solid-like properties and elastic contribution, while G'' demonstrates the liquid like character and viscous contribution for a visco-elastic material (Chang

Table 4. Storage modulus (G'), loss modulus (G'') and $\tan \delta$ at 6.28 rad/s for starches at 25 °C.^{1,2}

Sample	G' (Pa)	G'' (Pa)	$\tan \delta$
Native starch	1,573±12 ^d	98±1 ^b	0.06 ^a
OSA-4	222±3 ^a	52±2 ^a	0.23 ^b
OSA-6	835±7 ^b	102±2 ^c	0.12 ^a
OSA-8	1,210±9 ^c	125±1 ^d	0.10 ^a

¹ Means followed by same superscript within a column do not differ significantly ($P < 0.05$). Mean (\pm standard deviation) of triplicate analysis.

² OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

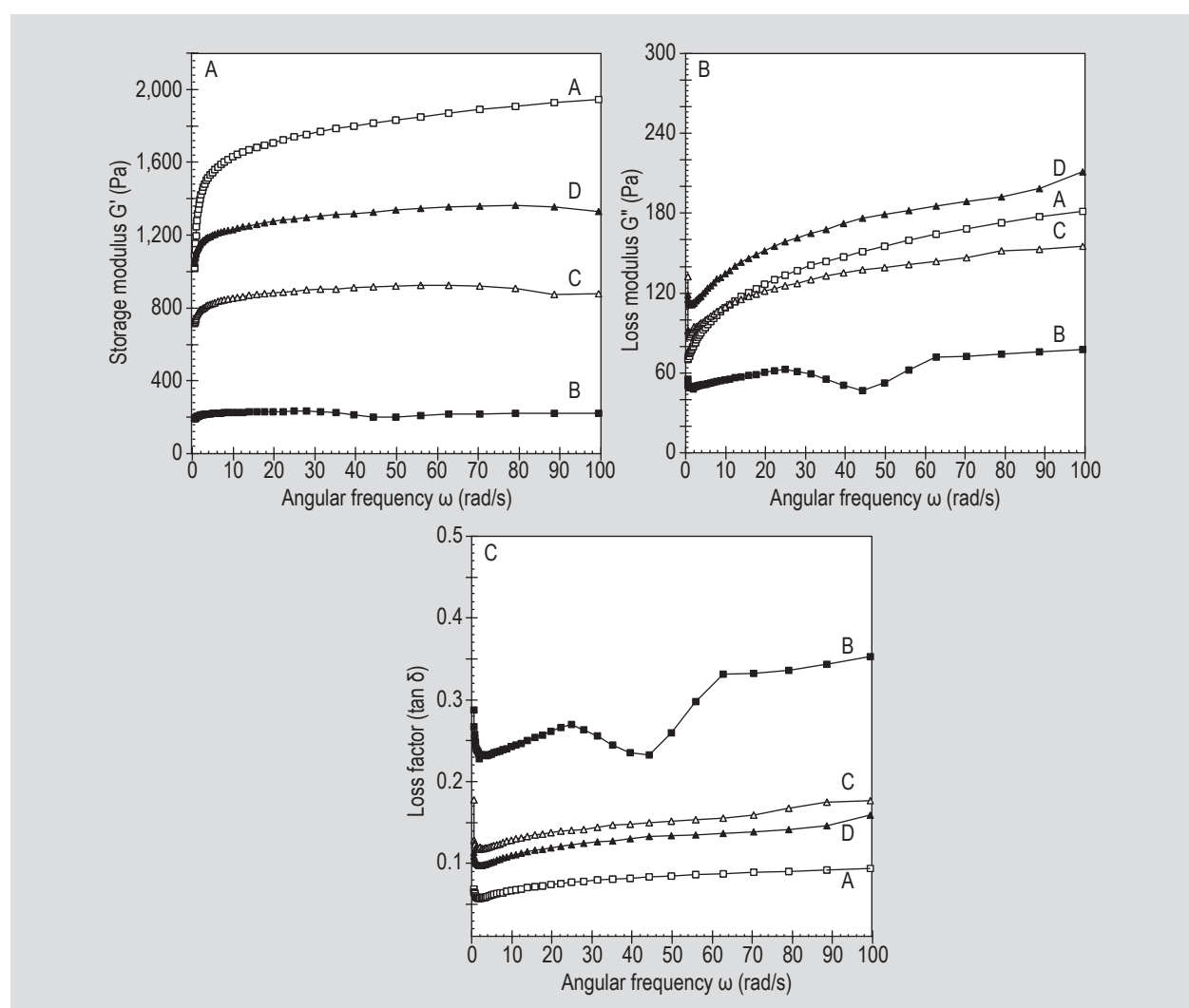


Figure 3. (A) Angular frequency dependence of G' at 25 °C for starches (B) Angular frequency dependence of G'' at 25 °C for different starches; (C) Angular frequency dependence of $\tan \delta$ at 25 °C for different starches (A: Native starch, B: OSA-4, C: OSA-6, D: OSA-8). OSA-4 = octenyl succinic anhydride (OSA) starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

and Cui, 2011). G' and G'' values of starches varied from 222 Pa to 1,573 Pa and 52 Pa to 125 Pa, respectively. G' value of OSA modified starches decreased as compared to native counterpart starch. The highest decrease was observed for starch modified at pH 4, which may be due to the lowest DS at pH 4. Lee and Yoo (2009) reported an increase in G' and G'' values at lower DS after acetylation as compared to its native sweet potato starch while reverse was observed at higher DS. The decrease in G' and G'' values after higher substitution may be due to a weaker granular integrity caused by greater water uptake in the swollen granules of starch paste. $\tan \delta$ can be used to describe the viscoelastic behavior of semisolid foods. $\tan \delta$ value of less than 1 indicates elastic behavior, whereas those above 1 reflects viscous behaviour of starch pastes (Siroha and Sandhu, 2018). $\tan \delta$ values of native and OSA modified starch pastes varied from 0.06 to 0.23, the highest value was observed for OSA starch paste at pH 4.

Steady shear properties

Figure 4 exhibits the flow behaviour of pastes of native and OSA modified starches under steady-shear conditions at 25 °C. The experimental data of flow behaviour fitted well with Herschel Bulkley model (Table 5). Correlation coefficient square (R^2) between regression equations and curves were 0.98 to 0.99, suggesting that the Herschel Bulkley model fitted well to the profile of rheological characteristics of the samples. Consistency index (K) value of native and modified starches varied from 3.86 to 19.77 Pa.s, the highest and the lowest value was observed for starch modified at pH 8 and pH 4, respectively. K values of OSA modified starches were observed higher as compared to native starch, except for starch modified at pH 4. Yield stress value of starches varied from 20.9 to 201.7 Pa, the highest value was observed for native starch. n value is typically used to characterize fluid and semi-fluid behaviour with n value of less than 1 describes a shear thinning, whereas the value of greater than 1 shows a shear thickening fluid behaviour. Flow behaviour index of native and modified starches was less than 1 with modified starches having higher value as compared to native starch. According to Morris (1989), the observed shear thinning

behaviour can be explained by the disruption of a network of entangled polysaccharide molecules during shearing. With increasing shear rate, the rate of disruption of the existing intermolecular entanglements becomes greater than the rate of reformation, consequently leading to the resultant reduction in apparent viscosity.

4. Conclusions

Modification of sorghum starch by OSA at different pH conditions caused significant changes in physicochemical and rheological properties. OSA treatment resulted in significant decrease in amylose content of starches. Swelling power of modified starches increased as compared to native starch, except for starch modified at pH 4 whereas solubility of modified starches decreased progressively with increase in pH. PV was observed the highest for starch modified at

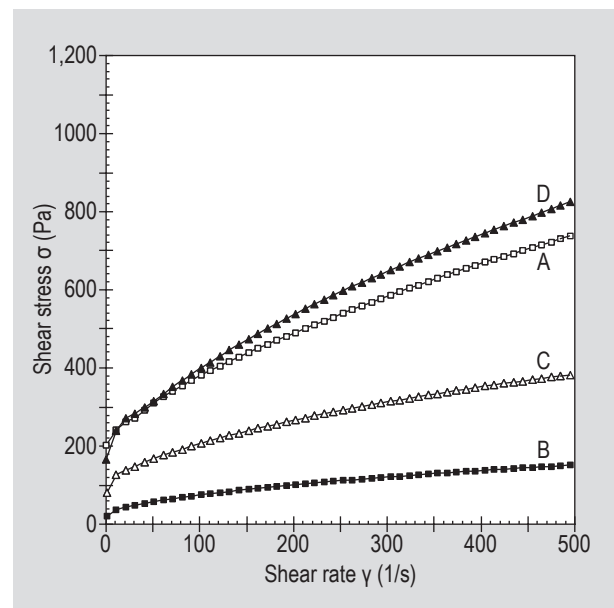


Figure 4. Steady shear profiles of native and octenyl succinic anhydride (OSA) modified starch at different pH levels (A: Native starch, B: OSA-4, C: OSA-6, D: OSA-8). OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

Table 5. Herschel-Bulkley model fitted to starch pastes during steady shear rate.^{1,2}

Sample	Yield stress (Pa)	K (Pa·s)	n	R^2
Native starch	201.7±1 ^d	6.04±0.1 ^b	0.72±0.008 ^c	0.99
OSA-4	20.9±0.4 ^a	3.86±0.2 ^a	0.57±0.009 ^b	0.99
OSA-6	80.9±0.3 ^b	13.16±0.1 ^c	0.48±0.007 ^a	0.99
OSA-8	166.2±1 ^c	19.77±0.3 ^d	0.52±0.008 ^b	0.98

¹ Means followed by same superscript within a column do not differ significantly ($P < 0.05$). Mean (\pm standard deviation) of triplicate analysis.

² OSA-4 = OSA starch modified at pH-4; OSA-6 = OSA starch modified at pH-6; OSA-8 = OSA starch modified at pH-8.

pH 8. Pasting temperature decreased after modification indicating lower temperature required for their cooking. G' values during heating and frequency sweep test decreased as compared to native counterpart starch. Rheological properties revealed that starches were more elastic than viscous. During steady shear measurement, n values were less than 1, indicating shear thinning behaviour of starch pastes. OSA modifications of sorghum starch at different pH conditions showed a range of physicochemical and rheological properties. The possible applications of OSA modified starch could be in food products where high solid content is required without excessive thickening.

References

- Ali, T.M. and Hasnain, A., 2014. Morphological, physicochemical, and pasting properties of modified white sorghum (*Sorghum bicolor*) starch. *International Journal of Food Properties* 17: 523-535.
- Arshad, H., Ali, T.M. and Hasnain, A., 2018. Native and modified Sorghum starches as wall materials in microencapsulation of nutmeg oleoresin. *International Journal of Biological Macromolecules* 114: 700-709.
- Arueya, G.L. and Oyewale, T.M., 2015. Effect of varying degrees of succinylation on the functional and morphological properties of starch from acha (*Digitaria exilis Kippis Stapf*) *Food Chemistry* 177: 258-266.
- Bao, J., Xing, J., Phillips, D.L. and Corke, H., 2003. Physical properties of octenyl succinic anhydride modified rice, wheat, and potato starches. *Journal of Agricultural and Food Chemistry* 51: 2283-2287.
- Bhandari, P.N. and Singhal, R.S., 2002. Effect of succinylation on the corn and amaranth starch pastes. *Carbohydrate Polymers* 48: 233-240.
- Bhosale, R. and Singhal, R., 2007. Effect of octenylsuccinylation on physicochemical and functional properties of waxy maize and amaranth starches. *Carbohydrate Polymers* 68: 447-456.
- Caldwell, C.G. and Wurzburg, O.B., 1953. U.S. Patent No. 2,661,349. Patent and Trademark Office, Washington, DC, USA.
- Code of Federal Regulation (CFR), 2001. Food starch modified. 21/1/172/172.892. Food additives permitted in food for human consumption. Government Printing Office, Washington, DC, USA.
- Chang, Y.H. and Cui, S.W., 2011. Steady and dynamic shear rheological properties of extrusion modified fenugreek gum solutions. *Food Science and Biotechnology* 20: 1663-1668.
- Chung, H.J., Lee, S.E., Han, J.A. and Lim, S.T., 2010. Physical properties of dry-heated octenyl succinylated waxy corn starches and its application in fat-reduced muffin. *Journal of Cereal Science* 52(3): 496-501.
- Ferry, J.D., 1980. Viscoelastic properties of polymers, 3rd edition. John Wiley and Sons, New York, NY, USA, pp. 41-42.
- Funke, U. and Lindhauer, M.G., 2001. Effect of reaction conditions and alkyl chain lengths on the properties of hydroxyalkyl starch ethers. *Starch/Stärke* 53: 547-554.
- Heacock, P.M., Hertzler, S.R. and Wolf, B., 2004. The glycemic, insulinemic, and breath hydrogen responses in humans to a food starch esterified by 1-octenyl succinic anhydride. *Nutrition Research* 24: 581-592.
- Hui, R., Qi-He, C., Ming-liang, F., Qiong, X. and Guo-qing, H., 2009. Preparation and properties of octenyl succinic anhydride modified potato starch. *Food Chemistry* 114: 81-86.
- Jeon, Y.S., Lowell, A.V. and Gross, R.A., 1999. Studies of starch esterification: reactions with alkenyl succinates in aqueous slurry systems. *Starch/Stärke* 51: 90-93.
- Kaur, M. and Bhullar, G.K., 2016. Partial characterization of tamarind (*Tamarindus indica* L.) kernel starch oxidized at different levels of sodium hypochlorite. *International Journal of Food Properties* 19: 605-617.
- Kim, H.N., Sandhu, K.S., Lee, J.H., Lim, H.S. and Lim, S.T., 2010. Characterisation of 2-octen-1-ylsuccinylated waxy rice amyloextrins prepared by dry-heating. *Food Chemistry* 119(3): 1189-1194.
- Leach, H.W., McCowen, L.D. and Schoch, T.J., 1959. Structure of the starch granule I. Swelling and solubility patterns of various starches. *Cereal Chemistry* 36: 534-544.
- Lee, H.L. and Yoo, B., 2009. Dynamic rheological and thermal properties of acetylated sweet potato starch. *Starch/Stärke* 61(7): 407-413.
- Meera, M.S., Bhashyam, M.K. and Ali, S.Z., 2011. Effect of heat treatment of sorghum grains on storage stability of flour. *LWT – Food Science and Technology* 44: 2199-2204.
- Morris, E.R., 1989. Polysaccharide solution properties: origin, rheological characterization and implications for food system. In: Millane, R.P., BeMiller, J.N. and Cahndrasekavan, R. (eds.) *Frontiers in Carbohydrate Research – 1: food applications*. Elsevier Applied Science Publishers, London/New York, UK/USA, pp. 132-163.
- Murphy, P., 2000. Starch. In: Phillips, G.O. and Williams, P.A. (eds.) *Handbook of hydrocolloids*. CRC Press, Boca Raton, FL, USA, pp. 41-65.
- Olayinka, O.O., Adebawale, K.O. and Olu-Owolabi, B.I., 2008. Effect of heat-moisture treatment on physicochemical properties of white sorghum starch. *Food Hydrocolloids* 22: 225-230.
- Olayinka, O.O., Olu-Owolabi, B.I. and Adebawale, K.O., 2011. Effect of succinylation on the physicochemical, rheological, thermal and retrogradation properties of red and white sorghum starches. *Food Hydrocolloids* 25: 515-520.
- Ortega-Ojeda, F.E., Larsson, H. and Eliasson, A.C., 2005. Gel formation in mixtures of hydrophobically modified potato and high amylopectin potato starch. *Carbohydrate Polymers* 59: 313-327.
- Park, S., Chung, M.G. and Yoo, B., 2004. Effect of octenylsuccinylation on rheological properties of corn starch pastes. *Starch/Stärke* 56: 399-406.
- Perera, C. and Hoover, R., 1999. Influence of hydroxypropylation on retrogradation properties of native, defatted and heat-moisture treated potato starches. *Food Chemistry* 64(3): 361-375.
- Perez, E., Bhanassey, Y.A. and Breene, W.M., 1993. Some chemical, physical, and functional properties of native and modified starches of *Amaranthus hypochondriacus* and *Amaranthus cruentus*. *Starch/Stärke* 45(6): 215-220.
- Rao, M.A., 1999. Flow and functional models of rheological properties of fluid foods. In: Rao, M.A. (ed.) *Rheology of fluid and semi – solid foods*. Aspen Publishers, Frederick, MD, USA, pp. 25-57.

- Reddy, V.G., Upadhyaya, H.D. and Gowda, C.L.L., 2006. Current status of sorghum genetic resources at ICRISAT: their sharing and impacts. *International Sorghum and Millets Newsletter* 47: 9-13.
- Sandhu, K.S. and Singh, N., 2005. Relationships between selected properties of starches from different corn lines. *International Journal of Food Properties* 8: 481-491.
- Sandhu, K.S. and Siroha, A.K., 2017. Relationships between physicochemical, thermal, rheological and *in vitro* digestibility properties of starches from pearl millet cultivars. *LWT – Food Science and Technology* 83: 213-224.
- Sandhu, K.S., Sharma, L. and Kaur, M., 2015. Effect of granule size on physicochemical, morphological, thermal and pasting properties of native and 2-octenyl-1-ylsuccinylated potato starch prepared by dry heating under different pH conditions. *LWT – Food Science and Technology* 61: 224-230.
- Segura-Campos, M., Chel-Guerrero, L. and Betancur-Ancona, D., 2008. Synthesis and partial characterization of octenyl succinic starch from *Phaseolus lunatus*. *Food Hydrocolloids* 22: 1467-1474.
- Singh, H., Sodhi, N.S. and Singh, N., 2010. Characterisation of starches separated from sorghum cultivars grown in India. *Food Chemistry* 119: 95-100.
- Siroha, A.K. and Sandhu, K.S., 2018. Physicochemical, rheological, morphological, and *in vitro* digestibility properties of cross-linked starch from pearl millet cultivars. *International Journal of Food Properties* 21: 1371-1385.
- Taylor, J.R.N., Schober, T.J. and Bean, S.R., 2006. Novel food and non-food uses for sorghum and millets. *Journal of Cereal Science* 44: 252-271.
- Tesch, S., Gerhards, C. and Schubert, H., 2002. Stabilization of emulsions by OSA starches. *Journal of Food Engineering* 54: 167-174.
- Thomas, D.J. and Atwell, W.A., 1999. *Starches*. American Association of Cereal Chemists, Inc., St. Paul, MN, USA.
- Trubiano, P.C., 1986. Succinate and substituted succinate derivatives of starch. In: Whistler, R.L., Bemiller, J.N. and Paschall, E.F. (eds.) *Starch: chemistry and technology*. Academic Press, Orlando, FL, USA, pp. 131-147.
- Udachan, I.S., Sahoo, A.K. and Hend, G.M., 2012. Extraction and characterization of sorghum (*Sorghum bicolor L. Moench*) starch. *International Food Research Journal* 19: 315-319.
- Waniska, R.D. and Rooney, L.W., 2000. Structure and chemistry of the sorghum caryopsis. In: Smith, W. and Frederiksen, R.A. (eds.) *Sorghum: production, agronomy, chemistry and utilization*. Wiley & Sons, New York, NY, USA, pp. 649-688.
- Whistler, R.L. and Paschall, E.F., 1967. *Starch chemistry and technology*. Academic Press, New York/London, USA/UK, pp. 369-389.
- Williams, P.C., Kuzina, F.D. and Hlynka, L., 1970. A rapid calorimetric procedure for estimating the amylose content of starches and flour. *Cereal Chemistry* 47: 411-421.
- Wurzburg, O.B., 1995. Modified starches. In: Stephen, A.M. (ed.) *Food polysaccharides and their applications* Marcel Dekker Inc., New York, NY, USA, pp. 67-97.
- Zheng, Y., Hu, L., Ding, N., Liu, P., Yao, C. and Zhang, H., 2017. Physicochemical and structural characteristics of the octenyl succinic ester of ginkgo starch. *International Journal of Biological Macromolecules* 94: 566-570.

