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Effect of okra gum on the pasting, thermal, and viscous properties of rice and sorghum starches

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ABSTRACT

The effect of okra gum (OE) on the physical properties of rice and sorghum starches was investigated using rapid visco-analyzer (RVA), Brookfield viscometer, differential scanning Calorimetry (DSC), and light microscopy. Starch was replaced with 5, 10, 15% OE weight basis (g/100 g). In the presence of OE, the peak and final viscosity as well as the setback of both starches were reduced. However, the difference between the theoretical and the measured setback was more than just can be attributed to the omitted starch. The DSC data of the blends showed higher peak temperature compared to the control, indicating slower starch gelatinization in the presence of OE. Brookfield profiles demonstrated increase in shear stress at higher shear rate confirming pseudoplasticity of the system ($n < 1$). Over all, it can be assumed that OE has influenced the properties of the starches, particularly, by decreasing viscosity, setback, and pseudoplasticity of the starch gels.

1. Introduction

Starch is one of the most abundant polysaccharide that provides a low cost source of energy for humans. Starch granule-shape and degree of crystallinity varies depending on its source. Amylose and amylopectin contents are the major determinants of the physico-chemical properties of starch (Boudries et al., 2009). Amylopectin has a much higher molecule weight as compared to amylose and it is branched at α-1–6-D-glucose unit. Amylose is linear molecule of α-1–4-D-glucose, in the most part, which is known to form a helix with different ligands, such as iodine and fatty acids. This characteristic is important because amylose–lipids complex influences its flow properties and its interaction with other components in food systems.

Functionality of a particular starch paste is determined by its water binding capacity, gelatinization temperature, paste clarity, solubility, swelling power, paste viscosity, retrogradation behavior and gel properties (Adebowale & Lawal, 2002). Starch has diverse applications as thickening, gelling, bulking and stabilizing agent in food, in addition to applications in pharmaceutical, paper and textile industries (Slattery, Kavakli, & Okita, 2000). During processing/cooking of food, starch gelatinization occurs due to heat and shear action. Upon cooling, starch paste undergoes retrogradation process which results in increase in paste viscosity (Whistler & BeMiller, 1999). Native starches often suffer low stability and loose viscosity against stress and prolonged mixing (Temsiripong, Pongsawatmanit, Ikeda, & Nishinari, 2005). Syneresis is the separation of water from starch gel and it occurs during freeze-thaw of starch-containing frozen foods. This phenomenon is more obvious throughout repeated freeze thaw cycles during supply chain operations (Lee, Baek, Cha, Park, & Lim, 2002). Plant-derived non-starch polysaccharides (gums) such as locust bean, guar gum and xanthan gum are excellent stabilizing and thickening agents, and are used in many food systems. They help to modify or control textural and rheological properties and improve food stability (Chaisawang & Suphantharika, 2005; Hallagan, La Du, Pariza, Putnam, & Borzelleca, 1997; Nagano, Tamaki, & Funami, 2008). Several researchers reported that hydrocolloids such as flaxseed gum, guar gum, xanthan gum, gellan, carrageenan have significant effects on starch-pastes viscosity (Achayuthakan & Suphantharika, 2008; Nagano et al., 2008; Rodríguez-Hernández, Durand, Garnier, Tecante, Doublier, 2006; Rosell, Yokoyama, & Shoemaker, 2011; Sae-kang & Suphantharika, 2006; Tischer, Noseda, Freitas, Sierakowski, & Duarte, 2006; Wang et al., 2008). The viscosity of potato starch is reduced by negatively charged hydrocolloids (carrageenans, CMC, xanthan gum), but increased by neutral hydrocolloids (guar gum) (Shi & BeMiller, 2002). Natural gums or mucilage are sometime preferred due to their low cost, availability and low toxicity (Baveja, Ranga Rao, & Arora, 1988). *Abelmoschus esculentus* (L) Moench commonly known as okra is rich in water extractable polysaccharides that can give high viscosity at very low concentrations (Onunkwo & Mba, 1996). Characterization of okra polysaccharide revealed

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that hot water or buffer extracted fractions were rich in galactose, rhamnose and galacturonic acid (Sengkhamparn et al., 2010; Whistler & Conrad, 1954). Due to their thickening properties, okra gum polysaccharides are being used as fat substitute in chocolate bar cookies (Romanchik-Cerpovicz, Tilmon, & Baldree, 2002), egg white substitute (Costantino & Romanchick-Cerpoviez, 2004), and in frozen dairy products (Romanchik-Cerpovicz, Costantino, & Laura, 2006). Starch is a major component of most plant-based and some muscle-based processed food. The objectives of this work were to determine the effect of okra gums (polysaccharides) on the functional and rheological properties of sorghum and rice starches.

2. Materials and methods

2.1. Materials

Okra was purchased from a local supermarket. Okra pods were cut, seeds were removed before extraction. Sorghum starch was isolated from white type sorghum flour obtained from local market and Rice starch was supplied by Winlab Laboratory Chemicals, Leicestershire, UK.

2.2. Methods

2.2.1. Starches isolation

Slurry was prepared by mixing white sorghum flour and distilled water (50/50) in heavy-duty blender for 3 min. The slurry was filtered through 200-mesh sieve. The filtrate was then centrifuged at 2000 × *g* for 15 min. After centrifugation, dark waxy layer on top was removed and the white material at the bottom of the bottle (the pellet) was reconstituted with distilled water and centrifuged at the same conditions mentioned above. This process was repeated 5 times after which a white pure starch fraction was obtained. The starch isolated was then air-dried using acetone and ground in coffee grinder. The starch powder was then transferred to airtight glass bottles and stored in cold room for further use.

2.2.2. Okra gum extraction

Seedless okra (100 g) was blended in 500 ml 0.05 M NaOH for 5 min in heavy-duty blender. After centrifugation at 2000 × *g*, the supernatant was collected and the extraction was repeated on precipitate. Supernatants were combined, pH was adjusted to 7, freeze-dried, ground and stored at 4 °C in airtight glass bottles for further use. This material will be called okra gum extract (OE) throughout this paper.

2.2.3. Preparation of okra starch blends

Okra extract/starch blends were prepared by replacing 5, 10 and 15% of each starch with okra gum powder (OE). Two types of blending procedures were adopted. The first type was mixing starch and okra gum powders in dry forms and labeled as dry mixed (DM). In the second type, slurry (60% moisture content) of starch and OE was prepared in a tube, vortexed, freeze-dried, ground, and labeled as freeze dry mixed (FD). The reason for using freeze-drying was to prevent starch gelatinization that may take place if heating method was used to dry the starch after mixing. Additionally, mixing starch, gum, and water before gelatinization was one of the points this work intended to discuss. The plain rice and sorghum starches were used as controls in all analyses.

2.2.4. Rapid visco analyzer measurements (RVA)

Pasting properties of the blends were determined using a rapid visco analyzer (Newport Scientific, Sydney, Australia). Starch control or starch/okra blends (3 g at 14% moisture basis) were directly weighed into aluminum RVA canisters and distilled water was added to reach a total weight of 28 g. The obtained slurry was held at 50 °C for 30 s, heated to 95 °C in 4.40 min (at 10.23 °C/min) and held at 95 °C for 4 min. It was then cooled to 50 °C in 2 min (at 22.5 °C/min) and held at 50 °C for 2 min. The rotating speed of paddle was 960 rpm for the first 10 s and then reduced and kept at 160 rpm throughout the remainder of the experiment. All measurements were done in triplicate and the Thermocline window software was used to process the data.

2.2.5. Rheological measurements

Starch/okra gels obtained from RVA experiment were used to determine the viscosity and steady shear measurements using a rheometer (Brookfield DV-III, Engineering Laboratories, Inc., USA). LV3 spindle with 0.7 cm diameter was used. The internal radius of the cylinder used for measurements was 1.15 cm. The calculated values of shear rate constant (SRC) and spindle multiplier constant (SMC) were 0.33 and 128, respectively. Apparent viscosity was recorded at 25 different RPMs starting upward from 20 to 200 RPM with an increment of 15 RPM and then coming downward from 200 to 20 RPM with a decline of 15 RPM. The shear rate was ramped up and downward between 6.6 (20 rpm) and 66.6 s^{-1} (200 rpm). Data was recorded for apparent viscosity (mPa s) and shear stress (N m^2) for each freshly prepared sample.

Since nonstandard spindle was used to determine the viscosity, constants of the spindle used (SMC and SRC) were calculated as follows:

$$\mathrm{SMC} = \frac{\mathrm{RI} \times \mathrm{RPM}}{\mathrm{TK}} \times 10,000 \quad (1)$$

where SMC is the spindle multiplier constant, which was used to calculate cP values; RI is the full scale viscosity range; TK is the DV-III torque constant given by the manufacturer = 1.

$$RI = \frac{100n}{Y} \quad (2)$$

where n = viscosity in cP of the Newtonian fluid and Y = torque % reading at the selected RPM (100 rpm).

$$\mathrm{SRC} = \frac{2WRb^2Rc^2}{X^2[Rbc^2 - Rcb^2]} \quad (3)$$

where SRC is the shear rate constant (1/s), which was used to calculate shear rate and shear stress; *Rc* is the radius of container (cm); *Rb* is the radius of spindle (cm); *X* is the radius at which the shear rate is to be calculated (normally is the same as *Rb* in cm); *W* is the angular velocity of spindle (Rad/s).

$$W = \frac{2\pi}{60} \times N \quad (4)$$

where *N* is the spindle speed in RPM.

2.2.6. Syneresis studies on starch gels

Gels obtained from RVA canisters were shifted to graduated centrifuge tubes and stored in a freezer at −20 °C. After 4 days of storage, gels were placed in water bath at 50 °C for 30 min and centrifuged at 3000 × *g* for 15 min. The water was separated from the gel via centrifugation. The water separated from gels was recorded and the gels were restored in freezer for another 4 days and water separation after 8 days was recorded using same procedure. Percent syneresis recorded for the two freeze-thaw cycles was reported on 4th day, 4 days after that, and total after 8 days was recorded.

2.2.7. Differential scanning calorimetry (DSC)

DSC analysis was conducted using Setaram instruments Micro DSC III Evo. Sample (240 mg) was placed in Standard Hastelloy cell and 400 μl distilled water were added, while the reference cell contained suitable amount of distilled water. Sealed sample

was equilibrated for 1 h and then scanned from 20 to 110 °C at a heating rate of 2 °C/min. Gelatinization parameters, (ΔH J/g), onset temperature, and peak temperature were determined using DSC Calisto Processing software. In addition, the same parameters were calculated for the amylose lipid complex observed in the same scan. This endothermic transition profile following starch gelatinization peak represents amylose–lipids complex melting.

2.2.8. Statistical analysis

All measurements were done in duplicate. One-way analysis of variance technique was used to study the effect of okra levels on rice and sorghum starches and two types of mixing procedures. Duncan's Multiple Range (DMR) test at $p \leq 0.05$ was used to compare means using PASW® Statistics 18 software.

3. Results and discussion

3.1. Rapid visco-analyzer (RVA) measurements

Sorghum starch (100%) exhibited higher peak viscosity (PV) compared to rice starch (Table 1). There was no effect of freeze-drying or dry mixing on either of the pure starches pasting-properties. In the presence of 5% OE, the PV of rice starch increased, while sorghum starch exhibited lower PV. Prior to Section 3, it is imperative to mention that starch/water/OE mixture is considered a biphasic system, where OE is located in the continuous phase and its concentration increases as starch granules swell by absorbing water following heating (Achayuthakan & Suphantharika, 2008). The swelling of the starch granules and the increase in OE concentration in the continuous phase caused viscosity increase. The rise in viscosity will discontinue when granules reach adequate internal pressure followed by drop in PV due to granules rupture. The process of granule rupture and drop in PV is called break down. Gonera and Cornillon (2002) reported a different mechanism in regards to PV increase at higher xanthan gum compared to guar gum. This can be accredited to xanthan gum capacity to completely cover starch granules and alleviate granules association and restrict swelling as shown by the confocal microscope and scanning electron microscope. The limited granules swelling resulted in lower peak viscosity. Possibly the increase in PV of rice starch blended with 5% OE is due to adequate granules swelling and OE ability to promote granule association which resulted in higher OE concentration located in the continuous phase. Rice starch blends with higher OE (10 and 15%) content exhibited lower PV (Table 1). This can be interpreted by the limited granules swelling and reducing granules association theory caused by OE coating of starch granules. It appears that the 10 and 15% OE provided enough material to cover starch granules contrasting with the 5% due to smaller granule size of rice starch. Obviously, this was not tested directly on rice or sorghum starches, but for sorghum starch the granules size averages around 15 μm, similar to corn starch, while rice starch is 6 μm (Huber & Bemiller, 1997). The granule size as well as amylose content could play important role on the starch pasting properties as was observed in the difference between rice and sorghum data showed in Table 1. Certainly, the small granule size of rice starch covers a larger surface area which will require additional OE for covering. Unlike rice starch, the decline in sorghum starch PV as a function of OE content at all levels corresponds to the limited granules swelling theory forced by OE. As mentioned above, larger sorghum starch granule size required less OE compared to rice starch. Therefore, PV decreased as a function of OE content. There was no difference in PV of dry mixed (DM) or freeze-dried (FD) (Table 1). Although the final viscosity (FV) of the 100% starch was higher than PV, the final viscosity (FV) of either DM or FD blends was lower at higher OE content. The RVA data (Table 1) was statistically analyzed to show the effect of OE level on the pasting properties of both starches. The peak viscosity data showed different behaviors of FD rice starch compared to sorghum starch, where it exhibited no significant difference between 0 and 15% OE, but lower values at 5 and 10% OE. Sorghum starch showed significantly lower peak viscosity at lower OE levels (Table 1), but no significant difference between 10 and 15% OE. The DM samples showed no significant difference for both starch at all OE levels. This can be attributed to the effect of mixing starch + gum + water before gelatinization, where the granules were covered with the gum, unlike dry mixing. The final viscosity data showed similar trend indicating direct effect of premixing starch and gum prior gelatinization, where higher OE significantly reduced the final viscosity of both starches at all OE levels, except for rice starch blend with 10 and 15% (Table 1). The setback values in contrast were significantly lower at all levels of OE for the FD and DM rice starch samples. Sorghum starch setback data exhibited significant drop at only at 10 and 15% OE of the FD sample and 5 and 10% for the MD blends. Therefore, the effect of premixing of starch and gum can be considered a significantly important factor that affects the pasting behavior of starch mentioned above and other parameters to be discussed later.

The replacement of starch with OE had a direct positive effect on starch retrogradation as shown by the lower setback of the blends. Setback was calculated as final viscosity minus trough, while trough is peak viscosity minus break down viscosity. The setback data in Table 1 was further analyzed so as to determine the effect of OE on starch retrogradation and to establish whether the drop in setback is due to lower starch content or to some sort of OE activity. In Table 2, the setback data was presented as theoretical or actual (measured) values. For instance, the theoretical value for the 5% OE blends was calculated based on subtracting 5% of the measured setback value of pure starch and consider that what should be the measured value for the blends. This value was compared with the actual RVA-measured value of the blends. The difference between the theoretical and the RVA-measured was designated as the reduction in setback due to OE action (Table 2). Higher OE caused more setback reduction, but the drop in setback was not linear. So as to show the linearity of the drop in calculated setback shown in Table 2, rice and sorghum control starches were tested by RVA using the same methods used for collecting the data in Table 2. This time, the amount of starch added was 5, 10, and 15% less, i.e., normally we add 2.8 g of starch for the control, but this time we have added 2.66 g for the 5% sample and the final weight of the sample with water was kept as 28 g as before (less solids). The data was analyzed and the regression comparison between the calculated and measured setback showed R^2 values as follows; for sorghum starch 0.99 and 0.95 for calculated versus measured setback, respectively, while rice starch exhibited 0.99 and 0.98 for calculated and measured, respectively.

Arocas, Sanz, and Fiszman (2009) reported reduction in setback viscosity in the presence of xanthan gum, which implies reduction in amylose retrogradation, consequently, improvement in freeze-thaw stability of starch gels. As reported by previous researchers, positive correlations were observed between setback and final viscosity, but swelling power, amylose content, and peak viscosity exhibited negative correlation (Singh, Kaur, Sandhu, & Singh Guraya, 2004). Xanthan gum was shown to reduce granules swelling thus reducing peak viscosity. The FD sorghum blends showed higher setback than DM, especially at 5% OE, where OE has a negative effect (Table 2). Lower setback was observed for DM versus FD blends of both starches, which is in line with other pasting properties presented addressed above.

Table 1
Peak and final viscosities of rice and sorghum starches as a function of okra extract content.

Okra %	Peak viscosity (cP)		Final viscosity (cP)		Set back (cP)	
	FD	DM	FD	DM	FD	DM
Rice						
0	1586 ± 103ab	1586 ± 103a	2136 ± 65a	2136 ± 65a	1174 ± 14a	1174 ± 14a
5	1645 ± 78a	1630 ± 226a	1644 ± 16b	1606 ± 201b	833 ± 16b	740 ± 29b
10	1430 ± 14c	1536 ± 152a	1334 ± 10c	1348 ± 161b	651 ± 7c	578 ± 27c
15	1563 ± 62ab	1494 ± 132a	1276 ± 23c	1200 ± 177b	535 ± 16d	461 ± 17d
Sorghum						
0	2564 ± 114a	2564 ± 114a	3092 ± 59a	3092 ± 59a	1684 ± 52a	1684 ± 52a
5	2290 ± 26b	2350 ± 183a	2869 ± 38b	2568 ± 166ab	1604 ± 89a	1408 ± 62b
10	1983 ± 43c	2007 ± 346a	2455 ± 38c	2075 ± 364b	1260 ± 33b	874 ± 1512c
15	1976 ± 18c	2054 ± 167a	2120 ± 21d	1971 ± 156b	939 ± 16c	769 ± 16c

Means ± standard deviation carrying same letters within columns are statistically non significant.

Table 2
Calculated, RVA-measured starches setback, and the % reduction due to okra extract.

% Okra	Calculated setback value due to starch replacement	Measured[a] setback value due to less starch	RVA-measured values	Difference[b] due to okra	% Reduction[c] in setback due to okra
Rice starch setback					
Freeze-dried (FD)					
0	1174	1174	–	–	–
5	1115	1025	834	281	25
10	1057	954	652	405	38
15	998	804	536	462	46
Dry mixed (DM)					
5	1115	1025	740	375	34
10	1057	954	579	478	45
15	998	804	462	536	54
Sorghum starch setback					
Freeze-dried (FD)					
0	1685	1685	–	–	–
5	1601	1579	1605	−4	−0.25
10	1517	1449	1260	257	17
15	1432	1182	940	492	34
Dry mixed (DM)					
5	1601	1579	1409	192	12
10	1517	1449	874	643	42
15	1432	1182	769	663	46

[a] Starch dilution effect measured experimentally (cP).
[b] Difference = calculated value − measured value.
[c] Difference/calculated value × 100.

3.2. Freeze-thaw stability

After the first freeze-thaw cycle, rice gel turned into a runny texture and gave no syneresis because it was impossible to separate the water. The behavior of FD sorghum starch was different compared to DM in the presence of OE. The FD and the DM of 100% sorghum starch showed same syneresis values 7.79% ± 0.8, but at 5% OE the FD sample exhibited, overall, 27.3 ± 1.6% syneresis, while DM samples showed significantly lower value 3.82 ± 1.1% ($p < 0.5$). At 10% OE, FD and DM showed 11.7 ± 2.1% and 12.2 ± 0.1% syneresis, respectively, while the 15% OE blends exhibited 12.2 ± 0.2% and 11.6 ± 0.4% correspondingly. The syneresis data was expected to show lower values than the pure starch, but it was higher as confirmed by the data (Charoenrein, Tatirat, Rengsutthi, & Thongngan, 2011). This data could mean that OE interacted with amylose or controlled water mobility thus reduced setback, but that was at 50 °C. Therefore, OE was not effective in preventing amylose retrogradation at freezing temperatures, causing syneresis of the blends to be higher than the control. It is apparent that there was no correlation between setback and syneresis action of OE. In the first 4 days, the presence of 5% OE caused increase in syneresis of the FD sample as compared to the control as well as significantly higher syneresis as compared to the DM. The DM sample showed a significant drop in syneresis relative to the control. The syneresis of the FD continue to drop after the first 4 days as a function of higher OE, indicting concentration dependency, but the DM stayed closer to the control at higher OE (10 and 15%). The difference in syneresis of the same starch, FD or DM, at the same content of OE can be attributed to the mixing before freeze-drying, where the granules are covered with the gum before gelatinization. This observation was made as in the effect of premixing and freeze-drying on the pasting properties of starch (set back) as mentioned above. This effect could be attributed to the distribution of the gum on the starch granules before gelatinization and throughout the starch gel after gelatinization. The second 4 days of storage reflected similar effect of the 5% OE on syneresis as in the first 4 days but, at higher OE, the FD and DM exhibited similar behavior, where the difference in syneresis-drop at 10% OE was similar. Generally, FD samples showed higher syneresis values on the second cycle of storage time, but the total syneresis was much higher for the 5% while the 10 and 15% exhibited similar total syneresis. After the second cycle, the gel is disrupted and lost its ability to hold the water, thus exhibited higher syneresis.

3.3. Differential scanning calorimetry (DSC)

The DSC analysis was done only on the FD starch + OE samples because DM blends showed no noticeable change in the starch

Table 3
Effect of okra extract on the DSC profile of rice and corn starch freeze-dried blends.

Sorghum						
Okra %	1st 4 days		2nd 4 days		Total	
	FD	DM	FD	DM	FD	DM
0	4.17 ± 1.52b	4.17 ± 1.52a	3.61 ± 0.69d	3.61 ± 0.69b	7.79 ± 0.83c	7.79 ± 0.83b
5	10.56 ± 1.64a	2.24 ± 0.11a	16.71 ± 0.02a	1.58 ± 1.00b	27.27 ± 1.62a	3.82 ± 1.10c
10	4.19 ± 0.26b	4.19 ± 0.58a	7.54 ± 2.35c	7.95 ± 0.08a	11.73 ± 2.08b	12.14 ± 0.50a
15	0.32 ± 0.15c	3.44 ± 0.55a	11.84 ± 0.30b	8.16 ± 1.19a	12.16 ± 0.15b	11.60 ± 0.64a

Means ± standard deviation carrying same letters in column are statistically non significant with each other.

thermal properties. The unnoticed changes could be attributed to the dry mixing process where the gum was located around the starch granules; unlike FD samples where the gum covered the granules thus had more influence of the gelatinization properties of the starch. This effect was mentioned in RVA pasting properties of Section 3. Two distinct endothermic transitions were observed on the DSC profile (Fig. 1). The first peak was sorghum starch gelatinization curve at 70.64 °C and the second peak was attributed to amylose–lipids complex at 101.06 °C, whereas for rice starch these two values were 65.53 °C and 100.50 °C (Table 3). The area under the curves which represents the ΔH was 10.90 and 10.71 (J/g) for sorghum and rice starch, respectively. To eliminate the possibility of starch dilution by OE to be the cause of the difference between the ΔH of starch gelatinization and amylose–lipids complex melting, the theoretical drop due to starch replacement was compared to measured values. Regarding the effect of starch dilution on the enthalpy of the amylose–lipid complex melting, the expected theoretical drop on enthalpy due to starch replacement for both starch gelatinization and amylose–lipids complex was calculated and compared with the measured values. The theoretical drop of rice starch enthalpy of gelatinization was 10.18, 9.38, and 7.74 (J/g) for the 5, 10 and 15% OE, while the measured values were 10.71, 10.42, and 9.1 (J/g) respectively. Sorghum starch exhibited 10.36, 9.39, and 8.16 (J/g) for the 5, 10, and 15% OE, whereas the measured was 10.90, 10.43, and 9.60 (J/g), correspondingly. Therefore, starch structure was used to compare the two starches rather than starch dilution. Concerning the amylose–lipids complex of rice starch, the theoretical values were 1.05, 1.17, and 0.38, while the measured values were 1.30, 0.45, and 0.37 (J/g), for the 5, 10, and 15% OE, respectively. Amylose–lipids complex for sorghum starch showed 0.66, 0.48, and 0.42 (J/g) for the measured values and 0.86, 0.59, and 0.41 (J/g) for the theoretical value. It can be concluded that starch structure and not starch dilution by OE is the cause of difference between amylose–lipids complex enthalpy values. The measured enthalpy of amylose–lipids complex of the two control starches, rice and sorghum, were found to be significantly different ($p \geq 0.05$).

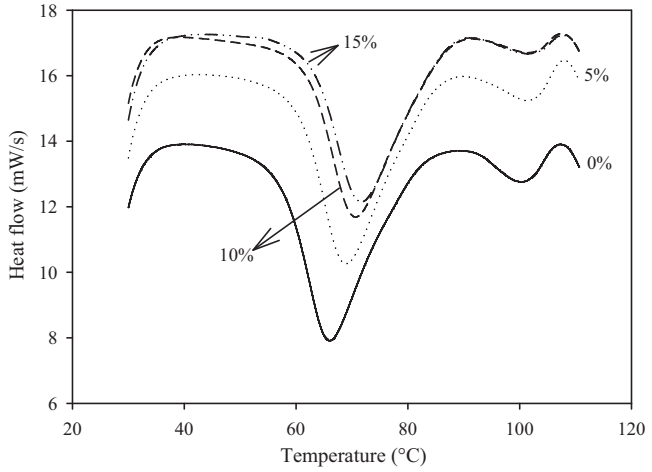


Fig. 1. DSC profile of rice starch blends at 0, 5, 10, and 15% okra extract. Samples were scanned from 20 to 120 °C at a heating rate of 2 °C/min at 60% moisture content.

This data showed that sorghum starch has more crystalline structure and more compact granules compared to rice starch as indicated by the higher peak gelatinization temperature (Table 3). Furthermore, given that starch gelatinization is moisture-dependent process, samples were prepared at 60% moisture content, which allows sufficient amount of water for starch gelatinization. This allows for factual difference between the two starches to be observed. A clear increase in peak temperature as a function of OE content was observed (Table 3). This behavior can be related to OE ability to limit water absorption as was noticed in the RVA peak viscosity discussed above. Despite the delay in water absorption, the ΔH value was decreased as a function of higher OE. The drop in ΔH in the presence of OE could be due to synergetic effect of the gum on starch gelatinization mechanism, i.e., faster gelatinization rate and not only the initial steps. The behavior of rice starch was different compared to sorghum because of the difference in granule shape and size, which can be related to OE mixed effect on the rice starch peak viscosity, where 5% OE increased peak viscosity and higher OE caused it to drop (Table 1). Singh et al. (2004) reported negative correlation between ΔH and setback and final viscosity of Indian rice cultivars as well as positive correlation with peak viscosity. The amylose lipids complex data dropped at higher OE which could indicate OE–amylose physical-interaction that prevented the formation of amylose–lipids inclusion.

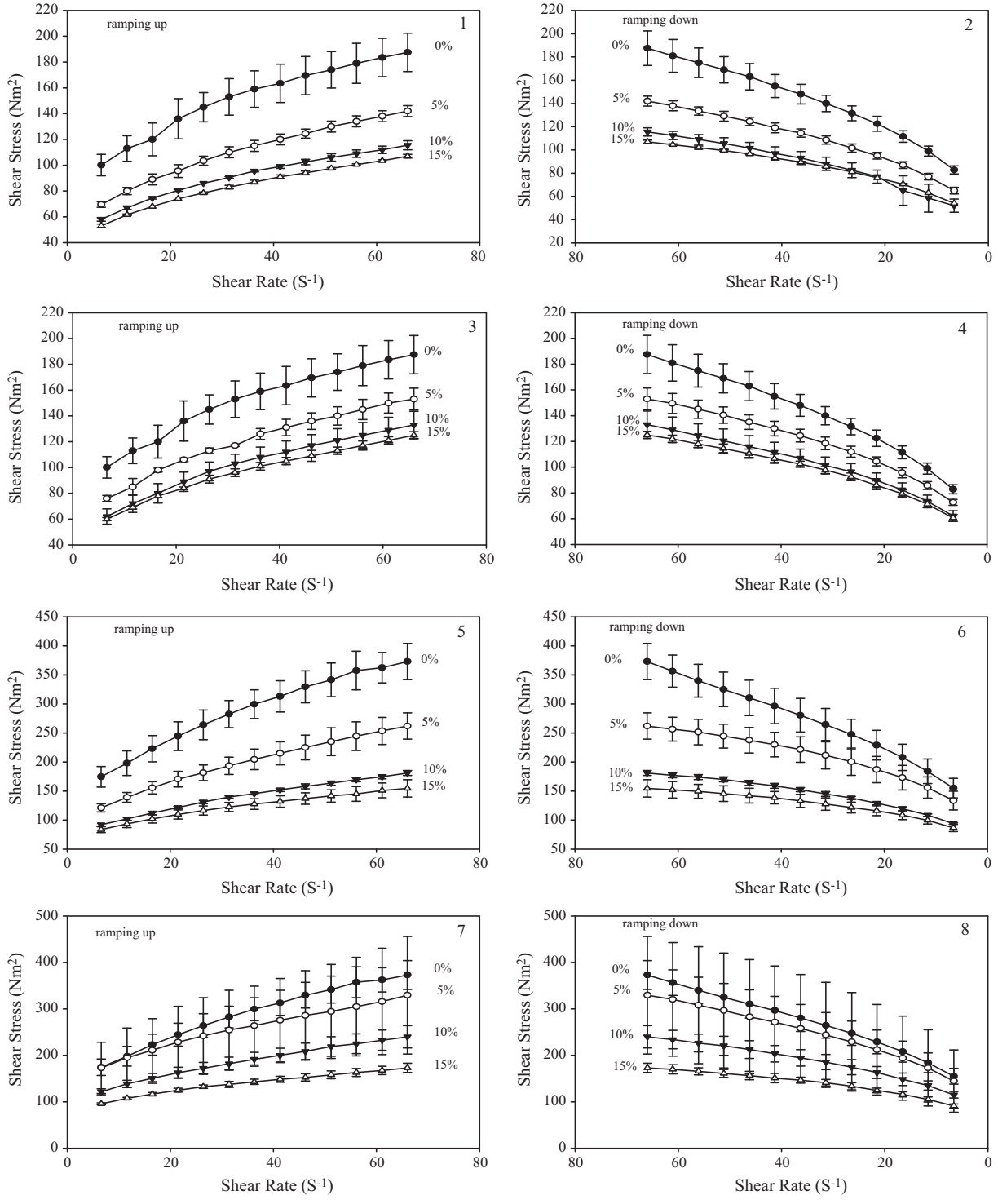
3.4. Rheological measurements

The rheological properties of starch gels prepared in RVA were measured by Brookfield rotational viscometer at 50 °C. Given that, non-standard Brookfield spindle (LV 3) was used, two constants needed to be calculated so as to complete the testing, the spindle multiplier constant (SMC) and the shear rate constant (SRC). Eqs. (1)–(4) were used to obtain the constants using the % torque for the selected RPM (100) and the cP value for mineral oil standard, which was found to be 1190 cP. The full-scale viscosity range (RI) of Eq. (2) (12.796 cP) was used to calculate SMC of Eq. (1), which turned out to be 127.95 for 100 RPM. The spindle speed for calculating SRC was 100 RPM, but the dimensions of spindle and container were physically measured as shown in Eqs. (3) and (4).

Apparent viscosity measurements were carried out at 50 °C using rotational viscometer (Brookfield) to obtain shear rate versus shear stress data. The shear rate (RPM) was programmed to increase from 20 to 200 RPM with 15 RPM increment followed immediately by a reduction from 200 to 20 RPM with the same rate. The RPM were converted to shear rate and the power law model (Eq. (5)) was fitted to the experimental data for both ramping up and down.

$$T = K\gamma^n \quad (5)$$

where T is shear stress (Pa s), γ is shear rate (s^{-1}) converted from RPM, K is the consistency coefficient (Pa s), and n is flow



1. Rice /okra blends dry mixed (ramp up)
2. Rice /okra blends dry mixed (ramp down)
3. Rice /okra blends freeze dried (ramp up)
4. Rice /okra blends freeze dried (ramp down)
5. Sorghum/ okra blends dry mixed (ramp up)
6. Sorghum/ okra blends dry mixed (ramp down)
7. Sorghum/ okra blends freeze dried (ramp up)
8. Sorghum/ okra blends freeze dried (ramp down)

Fig. 2. Shear stress ($N\,m^2$) versus shear rate (mPa s) of rice and sorghum starch gels. Apparent viscosity was determined by starting upward from 20 to 200 RPM with an increment of 15 RPM and downward from 200 to 20 RPM with a decline of 15 RPM. The shear rate was ramped up and downward between 6.6 (20 rpm) and 66.6 s^{-1} (200 rpm).

behavior index (dimensionless). Shear stresses versus shear rate curves are presented in Fig. 2. Natural log of the curves and linear regression were used to determine K and n values of Eq. (5). The linear regression results for ramping up and down measurements are presented as K and n values and shown in Table 4.

The flow behavior index, n, signifies sample deviation from Newtonian flow, which is $n = 1$. As can be seen, the parameter

Table 4
Onset, peak temperatures, and ΔH of starch gelatinization and amylose–lipids complex.

	Rice starch + okra gum				Sorghum starch + okra gum			
	0%	5%	10%	15%	0%	5%	10%	15%
ΔH, J/g	10.71 ± 0.16a	10.42 ± 0.13ab	10.27 ± 0.08b	9.1 ± 0.19c	10.9 ± 0.00a	10.43 ± 0.07b	9.60 ± 0.03c	9.22 ± 0.04d
P T, °C[a]	65.53 ± 0.75c	68.81 ± 0.16b	70.67 ± 0.01a	71.70 ± 0.01a	70.64 ± 0.06d	74.25 ± 0.04c	75.73 ± 0.13b	76.74 ± 0.08a
O T, °C[b]	57.27 ± 0.18d	60.31 ± 0.06c	62.07 ± 0.23b	62.92 ± 0.03a	65.46 ± 0.04d	69.51 ± 0.09c	71.23 ± 0.05b	72.09 ± 0.08a
ALC[c]	1.11 ± 0.01a	1.30 ± 0.31a	0.45 ± 0.04b	0.37 ± 0.11b	0.90 ± 0.04a	0.66 ± 0.19ab	0.48 ± 0.01b	0.42 ± 0.08b
ALC[d]	100.5 ± 0.06b	101.31 ± 0.56a	101.92 ± 0.08a	101.49 ± 0.08a	101.06 ± 0.22b	94.5 ± 0.30c	101.70 ± 0.08a	101.56 ± 0.16ab
ALC[e]	93.39 ± 0.04c	94.38 ± 1.14bc	95.95 ± 0.54ab	97.02 ± 0.69a	94.52 ± 1.44c	105.21 ± 0.34a	96.74 ± 0.20b	96.5 ± 0.28bc

Values with same letter in rows are not significantly different.
[a] Peak T°C.
[b] Onset T°C.
[c] Amylose lipid complex ΔH (J/g).
[d] Amylose lipid complex peak T°C.
[e] Amylose lipid complex onset T°C.

n for all samples was $n < 1$ (Table 4) signifying that OE blends were pseudoplastic material irrespective of the blends composition, which is in agreement with the work of previous researchers (Mandala & Bayas, 2004). The high coefficients of determination (R^2) obtained confirm the power law model to be adequately appropriate for relating the flow properties of OE-starch blends within the studied viscosity range. It is reported that pseudoplasticity of macromolecules solutions is due to disentanglement of long chain molecules which causes reduction in intermolecular resistance to flow under shear conditions (Nurul, Azemi, & Manan, 1999). However, when sugar is added to macromolecules solutions it suppresses disentanglement due to water molecules immobilization; therefore it reduces pseudoplasticity (Chang, Lim, & Yoo, 2004). Based on the mechanism of the effect of sugar on the flow properties of macromolecules and the increase in K value caused by sugar, it can be concluded that the effect of OE on water molecules was not evident because of the drop in K. Wang et al. (2009) reported that addition of sugar moderately increased K value, but it was significantly increased by a combination of sugar and xanthan gum. The drop in K indicates disentanglement of long chain starch molecules causing low resistance to shear, i.e., shear thinning (Table 4). This behavior was evident in the drop of n (flow behavior index) which is the reason for starch pseudoplastic nature ($n < 1$). The viscosity for both starches was FD > DM and ramping up > ramping down, while sorghum > rice starch.

Flow curves of shear stress versus shear rate shown in Fig. 3 were determined at 50 °C. The control exhibited higher slope, which could be interpreted as larger change in shear stress at higher shear rate values. Additionally, the curves showed no sign for counter-clockwise shape at the beginning, which represents hysteresis loop (antithixotropic behavior) in ramping up or down. Achayuthakan and Suphantharika (2008) reported the presence of hysteresis loop, of waxy corn starch blended with guar gum at low shear rates and thixotropic behavior of the same sample at higher shear rates. The waxy corn starch systems are dominated with amylopectin molecules responsible for the thickening and shear induced structure formation (Dintzis, Berhow, Bagley, Wu, & Felker, 1996). The differences between the behavior of OE-starch blends and reports in the literature were, previous researchers tested waxy starch at 25 °C, while this work tested common starches (contains amylose) at 50 °C, which could explain the presence of hysteresis loop due to shear thickening exerted by amylopectin reported by Dintzis et al. (1996). The overall shape of all OE-starch blends flow curves showed narrow hysteresis loops indicating small changes in the structure of the tested gels at the applied shear range at 50 °C except for FD rice starch blends in the ramping up curve (Fig. 3). The 15% blends samples were the least influenced by shear rate increase (low slope) and the 5% showed most drops in shear stress as indicated by the highest slope. The FD sorghum starch showed gradual decrease in shear stress as a function of OE concentration at shear rate increase (Fig. 3), while the DM exhibited higher drop in slope between the control and the 5% OE and smaller drop between the 10 and 15% OE. The shear stress slope of rice starch showed little drop between 10 and 15% OE. The narrow difference in shear stress change between samples indicates stability despite the drop in shear stress of the control. By and large, the slope of ramping down of the control starch and the blends was higher compared to ramping up, which implies negative effect of shear rate on shear stress (Tables 5 and 6).

Light microscope image displays a representative sample of uncooked or cooked sorghum starch. It is clear how FD sample exhibited homogeneous image as compared to DM where clusters with bigger size were present. As mentioned above, these differences between gels were also observed while discussing rheological, pasting, or thermal properties of the FD and DM of both starches. Unlike OE, guar gum is reported to prevent corn-starch amylose leaching in a 5% (w/w) starch slurry cooked at 95 °C for 30 min in the presence of 0.5% guar gum (Nagano et al., 2008). Limited initial granule swelling directly influences the beginning and ending of starch gelatinization thus the final gel image (Fig. 3). The

Table 5
The K = consistency index (Pa) and the n = flow behavior index (dimensionless) of rice and sorghum starches pastes.

DM				FD			
%	K	n	R^2	%	K	n	R^2
Rice							
Ramping Up							
0	4.04	0.28	0.99	0	4.04	0.28	0.99
5	3.61	0.32	0.99	5	3.70	0.32	0.99
10	3.46	0.30	0.99	10	3.46	0.34	0.99
15	3.37	0.31	0.99	15	3.46	0.32	0.99
Ramping down							
0	3.72	0.36	0.99	0	3.72	0.36	0.99
5	3.50	0.34	0.99	5	3.65	0.33	0.99
10	3.20	0.37	0.99	10	3.48	0.33	0.99
15	3.41	0.30	0.99	15	3.49	0.32	0.99
Sorghum							
Ramping up							
0	4.46	0.35	0.99	0	4.46	0.35	0.99
5	4.10	0.34	0.99	5	4.59	0.28	0.99
10	3.89	0.31	0.99	10	4.19	0.30	0.99
15	3.88	0.27	0.99	15	4.05	0.26	0.99
Ramping down							
0	4.28	0.38	0.99	0	4.28	0.38	0.99
5	4.32	0.30	0.99	5	4.26	0.36	0.99
10	3.97	0.29	0.99	10	4.11	0.33	0.99
15	3.97	0.26	0.99	15	3.96	0.28	0.99

K, consistency index (Pa); n, flow behavior index (dimensionless).

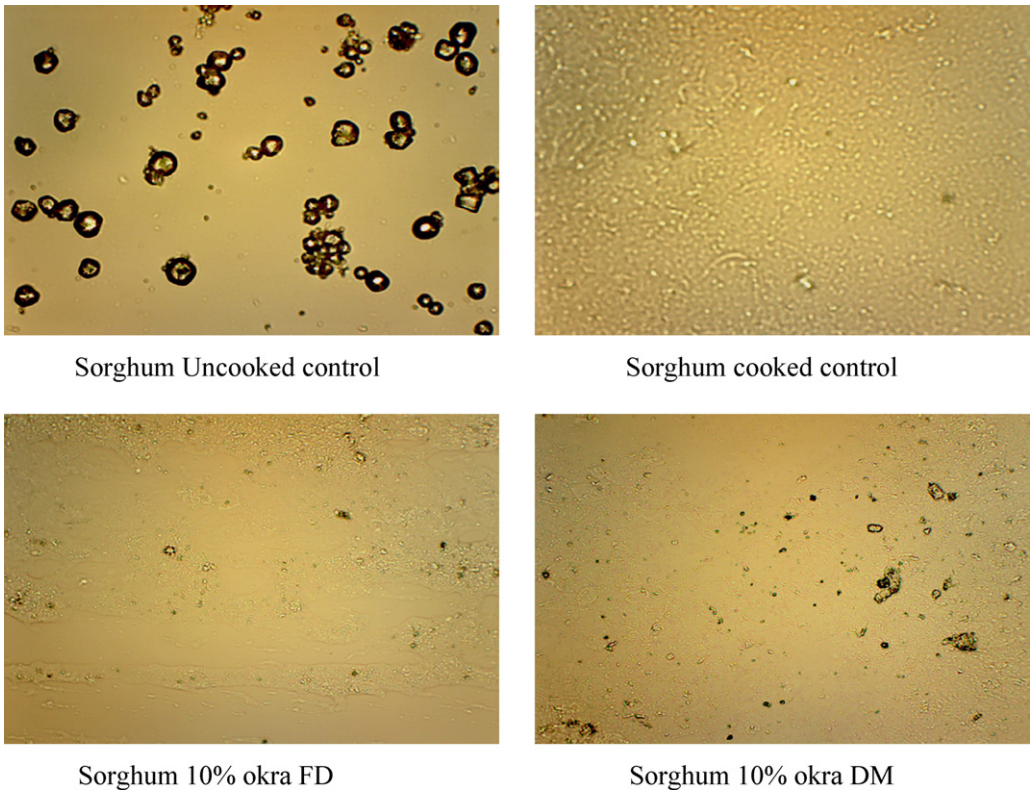


Fig. 3. Light microscope of uncooked and cooked sorghum starch control and with okra extract.

Table 6
Linear regression slopes of the shear stress as a function of shear rate for rice and sorghum starch blends.

% Okra	Freeze-dried		Dry-mixed	
	Linear regression	R^2	Linear regression	R^2
Rice starch				
0 ramping up	$Y = 1.43x + 100.7$	0.96	$Y = 1.43x + 100.7$	0.96
0 ramping down	$Y = -1.68x + 82.7$	0.98	$Y = -1.68x + 82.7$	0.96
5 ramping up	$Y = 1.26x + 75.4$	0.97	$Y = 1.18x + 68.9$	0.98
5 ramping down	$Y = -1.29x + 73.6$	0.97	$Y = -1.29x + 73.6$	0.97
10 ramping up	$Y = 1.15x + 61.9$	0.97	$Y = 0.92x + 58.7$	0.97
10 ramping down	$Y = -1.12x + 62.8$	0.97	$Y = -1.12x + 62.8$	0.97
15 ramping up	$Y = 1.04x + 59.8$	0.98	$Y = 0.86x + 53.3$	0.97
15 ramping down	$Y = -1.03x + 61.7$	0.97	$Y = -1.03x + 61.7$	0.97
Sorghum starch				
0 ramping up	$Y = 3.33x + 168.3$	0.98	$Y = 3.33x + 168.3$	0.98
0 ramping down	$Y = -3.47x + 147.8$	0.99	$Y = -3.49x + 147.8$	0.99
5 ramping up	$Y = 2.47x + 169.8$	0.99	$Y = 2.3x + 116.3$	0.99
5 ramping down	$Y = -2.99x + 142.5$	0.98	$Y = -2.05x + 137.9$	0.96
10 ramping up	$Y = 1.93x + 117.8$	0.99	$Y = 1.46x + 88.5$	0.98
10 ramping down	$Y = -2.02x + 115.2$	0.97	$Y = -1.41x + 95.8$	0.98
15 ramping up	$Y = 1.22x + 95.6$	0.98	$Y = 1.15x + 82.7$	0.98
15 ramping down	$Y = -1.31x + 93.5$	0.96	$Y = -1.08x + 89.5$	0.95

effect on the gel image can be interpreted as follows; fully swollen granules at the initial moments of gelatinization allows amylose to leach out and better distribute in the gel, which has direct effect on its overall image, because amylose mobility and distribution is the most important factor that determines gel texture and image. Delayed granules swelling, on the other hand, can cause unequal distribution of amylose causing direct effect on the final image.

4. Conclusion

This work made clear that the thermal, pasting, and rheological properties of rice and sorghum starches were primarily affected by alkaline okra-gum extract, the extent of which depended on its concentration. The peak, final, setback viscosities of sorghum starch were depressed at higher OE concentration except rice starch peak viscosity. The freeze-dried and the dry mixed blends showed different pasting properties, which indicate the importance of mixing okra gum and starch before running the pasting properties testing. The starches showed higher syneresis, lower gelatinization peak temperature, and lower amylose lipids complex ΔH in the presence of OE. The drop in the setback of FD rice starch was 25–46% due to OE (not to lower starch content) and 34–54% for the DM. FD sorghum starch exhibited decrease in setback between 17 and 34% due to OE, while DM showed values from 12 to 46%. Slightly lower K and n values calculated from the power law model indicates lower viscosity at higher OE and reaffirms the systems pseudoplasticity ($n < 1$).

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