Quality Assurance and Safety of Crops & Foods, 2015; 7 (4): 431-440

Wageningen Academic Publishers

Effect of potassium phosphate on the thermal, pasting, and flowing properties of chickpea and potato starches

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Received: 19 December 2013 / Accepted: 18 April 2014

RESEARCH ARTICLE

Abstract

The effect of potassium phosphate on potato and chickpea (CP) starches pasting, rheological, and textural properties were investigated using differential scanning calorimetry, rapid visco-analyser (RVA), viscometer, and texture analyser. Starch parameters were determined in 0.5, 1.0, and 1.5 M potassium phosphate at pH=5, 7, and 9, while distilled water was used as a control. Significant drop in the peak viscosity of potato starch was recorded in the presence of potassium phosphate at pH=5, but increased at pH=9 at the same salt concentration. CP starch exhibited significant increase in peak viscosity at higher pH and mixed behaviour in 1.5 M. The setback of potato starch increased significantly at pH=9 and 1.5 M salt concentration, while CP starch exhibited higher setback when cooked in 0.5, 1.0, and 1.5 M at higher pH. The peak gelatinisation temperature was higher in salt compared to the control, but CP starch showed gradual decrease at higher pH. The shear rate/shear stress data was fitted into power law model, where the flow behaviour index (n) was $n<1$ suggesting pseudoplasticity, whereas the consistency coefficient decreased at higher temperature indicating lower viscosity. The effect of salt concentration on CP starch was more pronounced compared to potato starch. The data was also fitted into Arrhenius equation to establish the effect of temperature on the activation energy (Ea), where CP starch exhibited higher Ea compared to potato starch. Higher gel hardness was noticed for both starch samples cooked in potassium phosphate compared to the control.

Keywords: starch, potato, chickpea, kinetics, rapid visco-analyser, differential scanning calorimetry

1. Introduction

Usually, starch co-exists with other ingredients in many food formulations. One such common ingredient is salt, where the effects of salt on the flowing properties of starch have been reported by other researchers. Salts were found to effect starch retrogradation (Chang and Liu, 1991; Katsuta, 1998), granule swelling (Zhu *et al.*, 2009), and rheological properties (Ahmad and Williams, 1999; Katsuta, 1998).The gelatinisation temperatures of starches with A-, B-, or C-type starches increased and then decreased as the NaCl concentration increased. However, due to the difference in structure between X-ray diffraction patterns, salt effect on starches varied (Lii and Lee, 1993). Differential scanning calorimetry (DSC) of rice starch revealed that the addition of salts significantly increased starch gelatinisation temperatures, whereas gelatinisation enthalpy was slightly affected. Structure formation of gelatinised rice starch was significantly enhanced by salt addition as shown by dynamic rheology (Samutsri and Suphantharika, 2012). Zhou *et al.* (2011) reported higher starch peak viscosity, trough, final viscosities, and the pasting temperatures of Baizhi starches at higher NaCl concentration (0 to 3.0%). However, the peak viscosities of Baizhi starches had increased at 0.2% Na_2CO_3 concentration and decreased at higher concentrations. The pasting temperature, trough, and final viscosities have decreased at higher Na_2CO_3 concentration. The peak viscosities increased in the presence of 0.1% NaOH, but decreased at 0.2% concentration. Sodium chloride was reported to increase the gelatinisation temperature of Sago starch at lower salt concentration, but higher salt concentration decreased it (Maaurf *et al.*, 2001). The pasting viscosity and the change in enthalpy (ΔH) of waxy or common corn starches were decreased at higher sodium chloride after X-rays treatment (Baik *et al.*, 2010; Bello-Perze and Paredes-Lopez, 1995; Chungcharoen and Lund, 1987).

Depending on their nature and concentration, salts can cause either a rise or depression of the gelatinisation temperature as determined by DSC. Salts listed on the upper end of the Hofmeister lyotropic series, such as HPO_4 (anionic compound), Na_2SO_4, sodium and potassium acetates, increase the gelatinisation temperature and therefore are denoted as gelatinisation inhibitors (Villwock and BeMiller, 2005). Widespread variation was observed in the pasting and swelling properties of cassava starch in the presence of cations, anions, acids (acetic acid) and oxidising agents (sodium metabisulphite). At lower concentrations (1%), acids enhanced the peak viscosity. As an oxidising agent, sodium metabisulphite increased the peak viscosity, whereas sodium sulphite and sodium thiosulphate brought about increase in the ΔH, peak and onset temperatures of cassava starch. However, sodium chloride was reported to reduce granule swelling unlike sodium sulphite (Jyothi *et al.*, 2005). Acetic acid improved cassava gel clarity (Sajeev*et al.*, 2003). Protective effect of monovalent salts on wheat starch was demonstrated by DSC at 0.1 M salts concentration. Nonetheless, chlorides and nitrates effects were different at higher salts concentration. A very similar inclination was also observed from the viscosity of gelatinised starch (Zhu *et al.*, 2009).

The objectives of this work were to highlight how potassium phosphate at different concentrations and pH can affect the rheological, thermal and pasting properties of starches from different sources, having different structure, and composition (i.e. tuber: potato and legume: chickpea).

2. Materials and methods

Materials

Chickpea (CP) (*Cicer arietinum* var. *surutato*) starch was isolated from grains obtained from a local supermarket. Potato starch was donated by Winlab Laboratory Chemicals (Leicestershire, UK).

Starches isolation

Slurry was prepared by blending CP whole meal in distilled water (50/50; w/w) in heavy duty blender for 5 min. The slurry was passed through 200 mesh sieve, where the filtrate was centrifuged at 2,000×*g* for 15 min. After centrifugation, the layer on top of the precipitate was removed and the white material at the bottom of the bottle (the pellet) was re-suspended in distilled water and centrifuged using the same mentioned above conditions. This procedure was repeated five times after which a pure white starch was then air-dried using acetone, ground in a coffee grinder, and stored in air-tight glass bottles at 4 °C for further analysis.

Study plan

Both starches were suspended in 0.5, 1 and 1.5 M potassium phosphate (KH_2PO_4) solutions having pH of 5, 7 or 9, while distilled water was used as a control for all runs. The suspensions were cooked using rapid visco-analyser.

Rapid visco-analyser measurements

Pasting properties of both starches were determined using a rapid visco-analyser (RVA) (Newport Scientific, Warriewood, Australia). CP starch (3 g at 14% moisture basis) or potato starch (1.5 g at 14% moisture basis) were directly weighed into aluminium RVA canisters and the total weight was brought to 28 g by adding distilled water or 0.5 M, 1 M or 1.5 M KH_2PO_4 solutions at pH 5, 7 or 9. The obtained slurry was held at 50 °C for 30 seconds, heated to 95 °C in 4.67 minutes (at 10.23 °C/min) and held at 95 °C for 4 minutes, cooled to 50 °C in 2 minutes (at 22.5 °C/min), and held at 50 °C for 2 minutes. The rotating paddle started at 960 rpm for the first 10 seconds and reduced to 160 rpm for the rest of the experiment.

Differential scanning calorimetry

The thermal properties of the starches were determined using DSC analysis (Setaram instruments Micro DSC III Evo; Setaram Instruments, Caluire, France). Sample (240 mg) was placed in a standard Hastelloy cell (Setaram Instruments) and 400 μl distilled water or 0.5, 1 or 1.5 M potassium phosphate solutions at 5, 7 or 9 pH were added, while the reference cell contained same mass as the sample of distilled water. Sealed sample was equilibrated for 1 hour and scanned from 20 to 110 °C at a heating rate of 2 °C/min. Gelatinisation parameters, ΔH (J/g), onset, and peak temperatures were determined using Calisto Processing software for DSC (Setaram Instruments). In addition, the same parameters were calculated for the amylose lipid complex observed in the same scan at higher temperature than starch gelatinisation.

Rheological measurements

Starch samples, 1.5 g in a total of 28 g, were cooked in RVA canisters using the same protocol described in 'Rapid visco-analyser measurements', where the produced gel was designated for the determination of the viscosity and steady shear measurements using Brookfield viscometer (DV-III; Brookfield Engineering Laboratories, Inc., Middleboro, MA, USA). A LV3 spindle (Brookfield Engineering, Inc., Middleborn, MA, USA) 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. Brookfield apparent viscosity and shear stress were recorded at 25 different rpm's starting upward from 2 to 26 rpm in increment of 2 rpm and downward from 26 to 2 rpm in decrement of 2 rpm. The shear rate was ramped up and downward between 0.66 s^{-1} (2 rpm) and 8.58 s^{-1} (26 rpm). Data was recorded at 50, 30 and 20 °C for apparent viscosity (mPa.s) and shear stress (N/m^2) in three replicates for each freshly prepared sample.

Since nonstandard spindle (not standardised by the manufacturer) was used to determine the viscosity, constants of the spindle used (SMC and SRC) were calculated as follows:

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

Where SMC = Spindle multiplier constant, which was used to calculate cP values; RI = full scale viscosity range of the rheometer; and TK = DV-III torque constant given by the manufacturer = 1.

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

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

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

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

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

Where N = spindle speed in rpm.

Temperature dependency (Arrhenius equation)

The temperature dependency was assessed by fitting the Arrhenius equation model to the experimental data using consistence index (K) as a marker of the viscous character of the starch gel.

Gel texture

Gel texture parameters were determined on RVA-prepared gels as described in 'Rapid visco-analyser measurements'. The gels (35 mm in height) were transferred into 25 ml beakers having internal diameters of 30 mm and stored overnight at room temperature. Gels were compressed using Brookfield CT3 Texture Analyzer (Brookfield Engineering Laboratories, Inc.) in two penetration cycles at a speed of 0.5 mm/sec to a distance of 10 mm using 12.7 mm wide and 35 mm high cylindrical probe. Gel hardness, springiness, cohesiveness and adhesiveness were recorded. The gumminess was calculated as a product of hardness and cohesiveness while chewiness as a product of gumminess and springiness.

Statistical analysis

All the measurements were done in triplicate. One-way analysis of variance technique was used to study the effect of KH_2PO_4 of a particular molarity (0.5, 1 or 1.5) at different pH (5, 7 or 9) on CP and potato starches. Duncan's multiple range test at $P \leq 0.05$ was used to compare means using PASW® Statistics 18 software (SPSS Inc., Hong Kong, China P.R.).

3. Results and discussion

The peak viscosity (PV) of potato starch as determined by RVA indicated a significant drop at all three salt concentrations, but 0.5 M showed the lowest value (Table 1 and Figure 1). It is also apparent that there was a gradual increase in PV at higher pH but not higher than distilled water. Higher PV was noted for higher salt concentration for potato starch. Unlike potato starch, CP starch exhibited significant increase in PV at higher salt concentration, where higher molarity further increased PV (Table 1).The PV of potato starch exhibited the largest drop by 63% at 0.5 M potassium phosphate (pH 5), while PV of CP has increased by 84% at the same salt concentration (pH=9). The drop in PV of potato starch could be attributed to the action of potassium phosphate, which is anionic salt and behaves as gelatinisation inhibitor, as suggested by Villwock and BeMiller (2005), i.e. the inhibition causes limited granule swelling thus delays gelatinisation. Conversely, CP starch increase in PV could be caused by the interaction of the potassium phosphate (anion) with the starch and facilitates for better swelling. Anionic salts, such as dihydrogen phosphate, are known to induce starch gelatinisation by rupturing hydrogen bonding between starch fractions within the granule, but this property could depend on starch type. The final viscosity (FV) of potato starch was dropped as well, but at 0.5 and 1.0 M, the FV showed no significant difference at different pH values (Table 1). Significantly ($P \leq 0.05$) higher FV of potato starch was recorded for the 1.5 M salt concentration and pH=9, which could be attributed to rupture of hydrogen bonding between starch fractions resulting in gelatinisation induction. Higher setback was recorded for potato starch at higher pH and molar concentration. Samples cooked at 1.5 M exhibited two times more setback than those cooked in 0.5 M. The higher setback indicates higher amylose retrogradation. The higher retrogradation could be attributed to the interaction of salts with the water molecules allowing amylose molecules to come together. The setback of CP starch followed the same pattern as potato starch but at higher setback magnitude,

Table 1. Rapid visco-analyser properties of potato and chickpea starches.[1,2]

			Distilled water	pH 5	pH 7	pH 9
Potato starch	0.5 M	PV (cP)	2,034.50±20.51a	763.00±2.83d	832.00±0.00c	950.50±16.26b
		Final viscosity	1,521.00±42.43a	1,027.50±20.51b	935.00±79.20b	993.00±49.50b
		Setback	349.00±8.49a	334.50±7.78ab	294.50±24.75b	313.00±24.04ab
		PT	67.98±0.39d	74.35±0.42a	72.08±0.95b	70.20±0.00c
	1 M	PV	2,034.50±20.51a	848.50±2.12d	1,004.50±12.02c	1,161.50±31.82b
		Final viscosity	1,521.00±42.43a	1,031.50±6.36b	1,128.50±31.82b	1,148.50±68.59b
		setback	349.00±8.49b	260.50±3.54c	348.50±2.12b	407.50±24.75a
		PT	67.98±0.39d	78.95±0.42a	75.70±0.42b	72.13±0.11c
	1.5 M	PV	2,034.50±20.51a	741.00±42.43d	1,021.50±9.19c	1,247.00±10.26b
		Final viscosity	1,521.00±42.43b	1,049.00±57.98d	1,246.00±35.36c	1,831.33±38.40a
		Setback	349.00±8.49c	508.50±20.51b	336.00±14.14c	805.33±53.16a
		PT	67.98±0.39c	91.78±1.31a	79.85±0.00b	78.62±0.03b
Chickpea starch	0.5 M	PV	2,828.00±91.92d	3,969.00±87.68c	4,165.50±3.54b	5,186.00±5.66a
		Final viscosity	4,066.50±194.45c	5,815.00±154.15b	5,779.00±4.24b	6,538.50±10.61a
		Setback	2,471.50±106.77c	3,007.50±197.28b	3,301.00±2.83b	3,578.00±131.52a
		PT	69.20±0.49d	78.55±0.00a	76.7±0.00b	74.73±0.04c
	1 M	PV	2,828.00±91.92d	4,088.50±24.75c	4,480.50±127.99b	5,570.00±9.90a
		Final viscosity	4,066.50±194.45b	6,274.50±210.01a	6,120.50±232.64a	6,634.50±137.89a
		Setback	2,471.50±106.77c	3,474.00±258.80b	3,814.50±178.90b	4,502.50±24.75a
		PT	69.20±0.49d	81.83±0.04a	79.20±0.00b	74.68±0.04c
	1.5 M	PV	2,828.00±91.92d	3,271.50±70.00c	3,820.50±77.07b	6,474.50±159.10a
		Final viscosity	4,066.50±194.45d	5,000.50±77.07c	7,076.50±142.13b	10,904.00±301.23a
		Setback	2,471.50±106.77c	2,810.50±45.96c	5,337.50±183.14b	8,976.00±231.93a
		PT	69.20±0.49d	88.70±0.49a	84.15±0.49b	81.75±0.14c

[1] M = potassium phosphate molarity; PV = peak viscosity; cP = centipoise; PT = pasting temperature (°C).

[2] Means within the same row followed by the same letter are not significantly different.

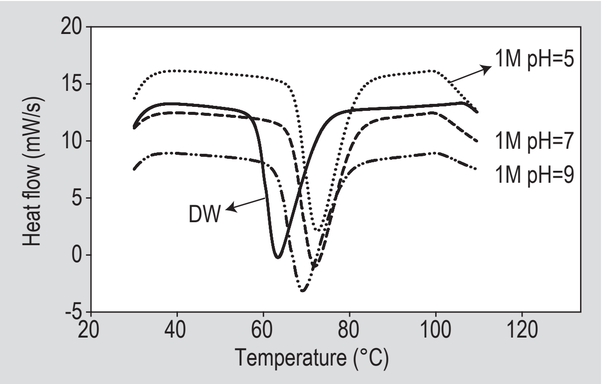

Figure 1. Differential scanning calorimetry thermograms of potato starch cooked in distilled water (DW) and 1 M potassium phosphate at pH=5, 7, or 9.

where 8,976 cP was recorded for CP starch versus 805 cP for potato starch (Table 1). The difference in setback could also be due to initial amylose content of the native starch, which was reported as 40-45% amylose content for CP versus 16-18% for potato starch(Alamri *et al.*, 2013). Bear in mind that only 1.5 g/28 g potato starch was used for the RVA data because the viscosity of potato starch when used at 3.0/28 g was excessively high for rheological testing. Nonetheless, we could extrapolate by theoretically calculating the setback for the 28 g potato starch using the value obtained for the 1.5 g. For instance, the setback for the 1.5 g potato starch in distilled water was 349 cP which would be 651.5 cP for the 2.8 g. Therefore, the recalculation of the setback put the setback of potato starch much lower than CP starch. The pasting temperature (PT) significantly increased at higher pH and higher salt concentrations. Accordingly, the PT of both starches in water was < 0.5 M < 1.0 M < 1.5 M, but PT of pH=5 > pH=7 > pH=9 > water. In addition, the PT of CP starch was higher than potato starch when compared at the same molarity and pH (Table 1). The PT pattern was similar to that recorded for the peak temperature obtained from DSC analysis.

The gelatinisation ΔH of potato starch in water was significantly lower ($P \leq 0.05$) as compared to samples in potassium phosphate as shown by DSC data, whereas higher molarity for the same pH reduced the ΔH (Table 2 and Figure 2). Within the same pH, potato starch exhibited lower ΔH at higher molarity indicating instable granules

Table 2. Differential scanning colorimeter properties of potato and chickpea starches.[1,2]

			Distilled water	pH 5	pH 7	pH 9
Potato starch	0.5 M	ΔH	16.71±0.09b[3]	18.22±0.55a	18.50±0.43a	18.17±0.45a
		PT	63.35±0.07d	67.82±0.01a	66.14±0.07b	65.13±0.06c
		OT	58.69±0.05d	62.52±0.15a	60.94±0.01b	60.07±0.07c
	1 M	ΔH	16.71±0.09c	18.07±0.07b	18.25±0.09a	17.99±0.05b
		PT	63.35±0.07d	71.43±0.04a	69.47±0.00b	66.43±0.05c
		OT	58.69±0.05d	65.89±0.09a	63.90±0.02b	61.00±0.26c
	1.5 M	ΔH	16.71±0.09ab	17.35±0.82a	16.64±0.03ab	15.86±0.17b
		PT	63.35±0.07d	74.99±0.02a	71.99±0.02b	71.60±0.01c
		OT	58.69±0.05d	69.26±0.02a	66.39±0.03b	65.64±0.25c
Chickpea starch	0.5 M	ΔH	11.49±0.35c	13.86±0.16a	13.8±0.08a	13.0±0.00b
		PT	62.87±0.14d	69.0±0.03a	67.6±0.13b	66.0±0.01c
		OT	56.10±0.57c	59.7±0.21a	58.9±0.01ab	58.2±0.10b
	1 M	ΔH	11.49±0.35c	13.5±0.33ab	13.7±0.11a	12.9±0.15b
		PT	62.87±0.14d	70.7±0.13a	67.8±0.04b	66.9±0.01c
		OT	56.10±0.57d	61.8±0.07a	59.9±0.10b	58.9±0.13c
	1.5 M	ΔH	11.49±0.35b	12.6±0.34a	12.9±0.10a	12.4±0.13a
		PT	62.87±0.14d	85.5±0.29a	81.1±0.30b	73.0±0.33c
		OT	56.10±0.57d	65.6±0.01a	62.9±0.23c	64.0±0.02b

[1] M = potassium phosphate molarity; ΔH = change in enthalpy (J/g); PT = peak temperature (°C); OT = onset temperature (°C).

[2] Means within the same row followed by the same letter are not significantly different.

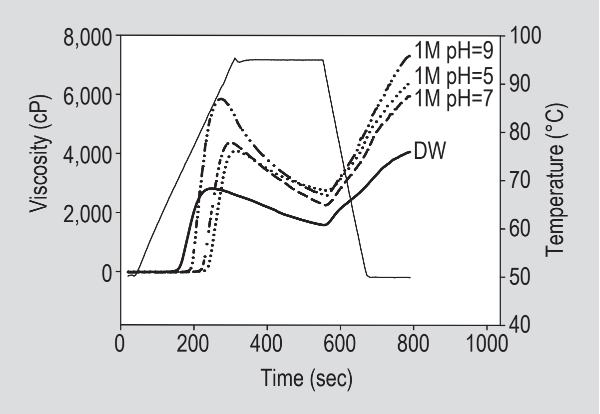

Figure 2. Rapid viso-analyser profile of chickpea starch cooked in distilled water (DW) and 1 M potassium phosphate at pH=5, 7, or 9.

due to extended swelling at higher salt concentration. However, the values of ΔH within the same molarity were significantly lower at higher pH. The instability of starches at higher salt concentrations, as indicated by lower ΔH, was reported by other researchers (Zhu*et al.*, 2009). Some researchers stated that anionic salts have more influence on starch granules swelling thus direct effect on the thermal properties of the starch as shown by the data presented here (Ahmad and Williams 1999). Therefore, at 0.5 M starch was more stable compared to higher molarity. The peak temperature of potato starch was lower at higher pH for the three salt concentrations, while at the same pH and different molarity, values were increasing with salt. Other salts, such as NaCl, were reported to slightly increase peak temperature at lower concentration (Ahmad and Williams, 1999; Chinachoti *et al.*, 1991; Jane, 1993; Lii and Lee, 1993; Maaurf *et al.*, 2000; Wootton and Bamunuarachchi, 1980), but at higher salt concentrations the peak temperature decreased. Some starches are more resistant to change caused by salts such as wheat and corn starches where the ΔH of these starches decreased at 1 M NaCl or higher, while the ΔH of rice starch decreased at 0.3 M NaCl. This indicates structural differences between these starches as demonstrated by their X-ray diffraction pattern (Baik *et al.*, 2010; Bello-Perze and Paredes-Lopez, 1995). Conversely, other studies showed that the ΔH of corn starch increased as the concentration of NaCl or $CaCl_2$ increased for up to 6 M NaCl and 4 M $CaCl_2$ (Jane, 1993). The instability of starch granules in presence of anions is due to the ability of anions to break hydrogen bonding between the granules. The effectiveness of $CaCl_2$ was due to the release of two Cl^- ions versus one Cl^- released from NaCl. The ΔH of CP starch was significantly ($P \leq 0.05$) higher in 0.5 M potassium phosphate, but it was reduced at higher pH (Table 2). As we observed for potato starch, higher salt concentration had no significant effect on the ΔH of CP starch. The peak temperature of CP starch was significantly higher at 0.5 M potassium phosphate but decreased at 1.0 and 1.5 M (Table 2).

Following RVA cooking, starch gels were tested for apparent viscosity at 50 °C (Brookfield) to obtain shear rate versus shear stress data. The shear rate (rpm) was set to rise from 20 to 200 rpm at a rate of 15 rpm increment (ramping up) which was followed by a decrease (ramping down) from 200 to 20 rpm at the same rate. The rpm were converted to shear rate and the power law model ($T = K \acute{y}^{n}$) was fitted to the experimental data, where T is shear stress (Pa·s), K is the consistency coefficient (Pa·s), $\acute{y}^{n}$ is shear rate (s^{-1}) converted from rpm, and n is flow behaviour index (dimensionless). The K and n values were obtained by taking the natural log of the shear stress and shear rate plot. The n value can be obtained from the slope of the line as determined by linear regression of the shear rate against shear stress, whereas the intercept of the regression line is considered as k (graphs are not shown) (Table 3 and 4). The n value of both starches cooked in the different conditions was $n<1$ (Table 3 and 4), which signifies that starch gels were pseudoplastic material irrespective of the molarity, pH, and the type of starch, which is supported by previous reports (Razavi *et al.*, 2007). Gels with $n=1$ are considered to follow Newtonian flow. The high R^2 recorded in Table 3 and 4 indicates that the power law can be implemented for linking the flow behaviour of the gels within the range of viscosities of the starches cooked under the specified conditions. It has been reported that pseudoplasticity of macromolecules solutions, such as starch gels, is due to disentanglement of long chain molecules which results in a decrease in intermolecular resistance to flow under specified shear conditions (Nurul *et al.*, 1999). The flow behaviour index (n) of potato starch decreased at higher temperature for all specified salt molar concentration, but at higher pH and same molarity, potato starch gels became less pseudoplastic (higher n). Whereas, at higher salt molarity and same pH, potato starch gels turned into a more pseudoplastic material (low n), which can be attributed to salt ability to limit disentanglement of starch fractions by restricting water mobility. Conversely, CP starch became less pseudoplastic at higher temperature and 0.5 or 1.5 M (Table 4) indicating pseudoplasticity of CP starch is directly influenced by salt concentration. CP starch was more pseudoplastic at 1.0 M followed by 1.5 and 0.5 M. This could mean increase in starch fractions disentanglement. The consistency coefficient (K) value was greatly influenced by the high solutes content in the liquid phase of the system, which could mean that a large portion of the phosphate was located in the liquid phase. The K value of potato starch dropped at higher temperature and appeared not to be influenced by salt concentration at pH 5, but it was greater at pH 7 and 9 at higher salt concentration. The drop in K value at higher temperature indicates lower viscosity which is consistent with general behaviour of biomaterials. The effect of salt concentration and higher temperature was more pronounced for CP starch, where K value dropped at higher temperature within a given salt molarity, but across salt molarity the K values were at 1.0 M > 1.5 M > 0.5 M (Table 4).

Table 3. n and K values for potato starch.[1]

		Temp. (°C)	Distilled water			pH 5			pH 7			pH 9		
			n	K	R^2	n	K	R^2	n	K	R^2	n	K	R^2
0.5 M	Ramping up	30	0.666	2.874	0.998	0.471	2.918	0.996	0.457	2.820	0.997	0.487	2.763	0.998
		40	0.581	2.922	0.998	0.436	2.837	0.995	0.447	2.756	0.998	0.468	2.750	0.996
		50	0.552	2.905	0.993	0.439	2.638	0.996	0.464	2.457	0.995	0.476	2.515	0.996
	Ramping down	30	0.604	3.074	0.996	0.509	2.771	0.999	0.523	2.550	0.999	0.531	2.583	0.999
		40	0.568	2.952	0.998	0.472	2.682	0.991	0.524	2.432	0.999	0.535	2.475	0.999
		50	0.545	2.953	0.996	0.480	2.487	0.999	0.507	2.294	0.999	0.520	2.346	0.999
1 M	Ramping up	30	0.666	2.874	0.998	0.418	2.963	0.996	0.446	3.067	0.997	0.488	2.971	0.998
		40	0.581	2.922	0.998	0.395	2.897	0.996	0.424	2.991	0.994	0.458	2.934	0.996
		50	0.552	2.905	0.993	0.390	2.773	0.994	0.413	2.858	0.993	0.473	2.701	0.995
	Ramping down	30	0.604	3.074	0.996	0.195	1.236	0.997	0.509	2.806	0.998	0.534	2.780	0.999
		40	0.568	2.952	0.998	0.188	1.197	0.999	0.480	2.778	0.998	0.533	2.627	0.999
		50	0.545	2.953	0.996	0.181	1.167	0.999	0.469	2.650	0.999	0.516	2.534	0.999
1.5 M	Ramping up	30	0.666	2.874	0.998	0.330	2.974	0.995	0.410	3.319	0.994	0.416	3.981	0.996
		40	0.581	2.922	0.998	0.314	2.937	0.993	0.353	3.353	0.994	0.365	4.004	0.996
		50	0.552	2.905	0.993	0.305	2.928	0.989	0.341	3.299	0.986	0.438	3.467	0.996
	Ramping down	30	0.604	3.074	0.996	0.341	2.961	0.999	0.465	3.089	0.996	0.497	3.642	0.998
		40	0.568	2.952	0.998	0.342	2.852	0.999	0.412	3.110	0.993	0.489	3.481	0.998
		50	0.545	2.953	0.996	0.347	2.790	0.999	0.407	3.052	0.998	0.475	3.329	0.999

[1] M = potassium phosphate molarity; n = flow behaviour index (dimensionless); K = consistency index (Pa).

Table 4. n and K values for chickpea starch.[1]

		Temp. (°C)	Distilled water			pH 5			pH 7			pH 9		
			n	K	R^2	n	K	R^2	n	K	R^2	n	K	R^2
0.5 M	Ramping up	30	0.186	2.664	0.996	0.308	2.515	0.997	0.186	3.175	0.979	0.277	3.127	0.995
		40	0.163	2.580	0.960	0.377	1.832	0.997	0.207	2.851	0.991	0.249	3.035	0.988
		50	0.261	1.793	0.999	0.521	0.778	0.999	0.261	2.434	0.995	0.310	2.614	0.996
	Ramping down	30	0.281	2.451	0.951	0.479	1.789	0.999	0.324	2.597	0.995	0.346	2.847	0.999
		40	0.292	2.190	0.990	0.624	0.809	0.997	0.360	2.212	0.998	0.366	2.561	0.999
		50	0.430	1.423	0.993	0.721	0.671	0.979	0.380	1.934	0.999	0.375	2.352	0.999
1 M	Ramping up	30	0.186	2.664	0.996	0.070	4.661	0.988	0.082	4.670	0.993	0.112	4.673	0.978
		40	0.163	2.580	0.960	0.053	4.657	0.989	0.094	4.590	0.992	0.099	4.651	0.986
		50	0.261	1.793	0.999	0.044	4.606	0.966	0.064	4.581	0.978	0.100	4.570	0.982
	Ramping down	30	0.281	2.451	0.951	0.094	4.538	0.976	0.110	4.548	0.988	0.134	4.582	0.987
		40	0.292	2.190	0.990	0.083	4.524	0.987	0.115	4.494	0.982	0.128	4.536	0.989
		50	0.430	1.423	0.993	0.072	4.486	0.983	0.087	4.476	0.979	0.116	4.510	0.991
1.5 M	Ramping up	30	0.186	2.664	0.996	0.132	3.168	0.725	0.331	2.904	0.977	0.323	3.493	0.991
		40	0.163	2.580	0.960	0.148	3.033	0.679	0.268	2.921	0.996	0.255	3.512	0.993
		50	0.261	1.793	0.999	0.156	2.278	0.856	0.121	3.093	0.995	0.226	3.397	0.990
	Ramping down	30	0.281	2.451	0.951	0.170	3.042	0.837	0.380	2.747	0.994	0.392	3.208	0.997
		40	0.292	2.190	0.990	0.377	2.111	0.944	0.392	2.387	0.998	0.391	2.951	0.997
		50	0.430	1.423	0.993	0.445	1.076	0.981	0.362	2.067	0.664	0.427	2.557	0.998

[1] M = potassium phosphate molarity; n = flow behaviour index (dimensionless); K = consistency index (Pa).

The temperature dependence of the viscosity of potato and CP starches at the specified pH and salt concentration was determined by fitting the data to Arrhenius model, where the reciprocal of temperature (30, 40 and 50 °C) was plotted against the log of consistency coefficient (K) obtained from the power law model. The high coefficient of determination (R^2) listed in Table 5 is suggestive of good correlation between apparent viscosity and the specified temperatures and obeys Arrhenius model. The apparent viscosity (μ_0) of potato starch at the specified temperature appeared to descend at high pH within all three salts concentrations, but displayed diverse values across potassium phosphate concentration (Table 5). The activation energy (Ea) showed increase at 1.0 M salt as a function of pH, but 0.5 and 1.5 M displayed mixed values where pH 7 and 1.5 M seems to change the behaviour of the starch by giving different Ea values. Overall, the Ea during ramping down was more consistent and displayed lower Ea at higher pH which is expected because starch is less stable at higher pH and can gelatinise easier. In the case of CP starch, the recorded Ea was lower at higher pH for 0.5 and 1.5 M, whereas 1.0 M potassium phosphate has shown higher Ea at higher pH (Table 5) indicating a more stable starch. The different behaviour of these starches in 1.0 M potassium phosphate was observed as well in the RVA PV and setback values (Table 1), which is a call for further investigation of the phenomenon.

The control potato starch gel (in distilled water) exhibited the lowest hardness, whereas at all salt concentrations, samples showed significant ($P \leq 0.05$) increase in hardness (Table 6). Gel hardness was higher at higher pH where starch cooked in 1.5 M potassium phosphate and pH 9 was the hardest of all. This indicates stronger amylose network within the gel. This data was partially in agreement with the setback data in Table 1which is also dependent on amylose network formation. As we make such a comparison, one should bear in mind that setback was determined at 50 °C while gel hardness was determined at room temperature which allows molecular proximity and facilitates network formation. The gel hardness of CP starch was much higher than potato starch due to higher total solids and amylose content of CP. The hardness of CP starch followed similar pattern as potato starch except for pH 5 where high salt concentration reduced gel hardness (Table 6). The cohesiveness of potato starch gel was significantly higher than the control, but only 1.0 M and 1.5 M showed significant decrease in cohesiveness. Once again, 1.0 M exhibited different effect on gel cohesiveness compared to the other molarities. The CP starch cohesiveness dropped at higher pH and increased in higher molar concentration. In general, the mechanical properties of starch gels is dependent on a number of factors, such as the movement characteristics of the amylose network, the volume fraction and the flexibility of the amylose and amylopectin fractions, as well as the interactions between the dispersed and

Table 5. Effect of KH_2PO_4 on the Arrhenius equation parameters of potato starch and chickpea starch.[1]

			Ramping up			Ramping down		
			Ea (J/mol/K)	μ_o (Pa·s^n)	R^2	Ea (J/mol/K)	μ_o (Pa·s^n)	R^2
Potato starch	Distilled water		675.80	0.2658	0.96	1,651.03	0.6305	0.76
	0.5 M	pH 5	4,082.46	0.5813	0.93	4,379.43	0.4908	0.94
		pH 7	5,564.73	0.3145	0.86	4,298.25	0.4641	0.99
		pH 9	3,711.16	0.6229	0.77	3,909.65	0.5484	0.99
	1.0 M	pH 5	2,686.29	0.9766	0.96	2,339.29	0.4879	0.99
		pH 7	2,861.76	0.9885	0.96	2,310.41	0.8861	0.86
		pH 9	3,844.75	0.6535	0.83	3,777.31	0.6189	0.99
	1.5 M	pH 5	5,557.87	0.4494	0.71	3,655.14	0.8539	0.99
		pH 7	658.56	0.2336	0.97	767.97	0.2413	0.98
		pH 9	5,827.80	0.0288	0.92	3,655.14	0.8538	0.99
Chickpea starch	Distilled water		15,960.16	0.004	0.81	21,976.97	0.004	0.86
	0.5 M	pH 5	47,487.68	0.000	0.92	40,148.18	0.000	0.90
		pH 7	10,787.79	0.0443	0.98	12,000.29	0.0221	0.99
		pH 9	7,236.50	0.1804	0.86	7,777.47	0.1296	0.99
	1.0 M	pH 5	478.39	0.2589	0.78	466.43	0.2649	0.92
		pH 7	789.25	0.2936	0.84	652.48	0.2853	0.93
		pH 9	900.95	0.3053	0.89	646.07	0.2822	0.98
	1.5 M	pH 5	13,308.85	0.0168	0.84	42,136.10	0.000	0.96
		pH 7	2,542.26	0.1266	0.81	11,566.28	0.0279	0.99
		pH 9	1,116.71	0.4431	0.69	9,199.20	0.0841	0.97

[1] M = potassium phosphate molarity; μ_o (Pa·s^n) = is the apparent viscosity at a reference temperature; Ea = activation energy (J/mol/K) parameters were obtained by fitting experimental data to the Arrhenius equation ($\ln \mu_a = \ln \mu_o + Ea/RT$); the Ea data were based on three different heating rates: 30, 40, and 50 °C.

continuous phases in the gel (Biliaderis, 1998). Generally, textural parameters presented in Table 6 for potato starch were increased by higher pH and molarity, whereas CP starch exhibited no significant difference.

4. Conclusions

Chickpea and potato starches exhibited pseudoplastic behaviour ($n<1$) and the shear stress and shear rate obeyed the power law. Both starches showed different interaction with potassium phosphate in terms of peak viscosity, setback, and gel texture. The Arrhenius model can be used to point out the association between temperature and the viscous property of the two starches. Starches behaved in a different way in 1.0 M potassium phosphate. The RVA pasting temperature and the DSC peak temperature decreased at higher pH. Generally, the activation energy of potato starch increased at higher salt concentration with much lower value during ramping down, while CP starch exhibited lower activation energy at higher pH and molarity. Gel hardness of both starches increased at higher pH, but CP starch gels were much harder than potato starch.

Table 6. Texture profile analysis of potato and chickpea starches.[1,2]

			Distilled water	pH 5	pH 7	pH 9
Potato starch	0.5 M	Hardness (g)	11.00±1.41c	27.50±2.12a	20.50±2.12b	20.00±1.41b
		Cohesiveness	0.75±0.01a	0.62±0.04b	0.64±0.03b	0.64±0.02b
		Springiness (mm)	8.50±0.28a	10.10±0.00b	9.95±0.07b	10.05±0.21b
		Adhesiveness (mJ)	0.15±0.07b	0.25±0.07ab	0.25±0.07ab	0.45±0.07a
		Chewiness	69.86±11.94c	172.21±25.07a	130.54±8.66b	127.64±2.07b
	1 M	Hardness (g)	11.00±1.41c	39.00±1.41b	50.00±2.83a	40.00±1.41b
		Cohesiveness	0.75±0.01a	0.48±0.01c	0.47±0.02c	0.52±0.01b
		Springiness (mm)	8.50±0.28b	10.10±0.14a	10.05±0.07a	10.00±0.14a
		Adhesiveness (mJ)	0.15±0.07c	0.25±0.07bc	0.40±0.00ab	0.60±0.14a
		Chewiness	69.86±11.94c	187.10±12.19b	233.66±0.92a	206.00±13.03ab
	1.5 M	Hardness (g)	11.00±1.41d	45.50±0.71c	59.00±1.41b	75.00±4.24a
		Cohesiveness	0.75±0.01a	0.54±0.04b	0.44±0.00c	0.45±0.01c
		Springiness (mm)	8.50±0.28b	8.35±0.21b	9.95±0.07a	10.00±0.14a
		Adhesiveness (mJ)	0.15±0.07b	0.20±0.14b	0.65±0.07a	0.55±0.07a
		Chewiness	69.86±11.94c	203.26±21.76b	258.30±8.03b	337.50±196.67a
Chickpea starch	0.5 M	Hardness (g)	33.00±1.41c	52.00±2.83b	39.00±2.83c	83.50±7.78a
		Cohesiveness	0.40±0.04a	0.39±0.02a	0.38±0.00a	0.35±0.01a
		Springiness (mm)	9.50±0.28ab	9.15±0.07b	9.55±0.07ab	9.70±0.14a
		Adhesiveness (mJ)	0.15±0.07b	0.10±0.00b	0.20±0.00b	0.35±0.07a
		Chewiness	123.83±2.10b	183.18±21.47b	141.53±11.31b	279.43±35.83a
	1 M	Hardness (g)	33.00±1.41c	52.50±3.54b	46.00±1.41b	91.00±5.66a
		Cohesiveness	0.40±0.04a	0.37±0.06a	0.40±0.06a	0.33±0.01a
		Springiness (mm)	9.50±0.28a	9.50±0.00a	9.55±0.21a	9.75±0.21a
		Adhesiveness (mJ)	0.15±0.07b	0.20±0.00b	0.10±0.00b	0.55±0.21a
		Chewiness	123.83±2.10c	182.04±19.48b	175.72±15.55b	292.79±24.37a
	1.5 M	Hardness (g)	33.00±1.41c	35.50±2.12c	54.00±4.24b	88.00±5.66a
		Cohesiveness	0.40±0.04b	0.73±0.11a	0.43±0.00b	0.39±0.01b
		Springiness (mm)	9.50±0.28a	9.50±0.14a	8.60±0.14b	9.50±0.14a
		Adhesiveness (mJ)	0.15±0.07a	0.10±0.00a	0.15±0.07a	0.25±0.07a
		Chewiness	123.83±2.10d	246.19±19.80b	199.69±12.41c	326.04±4.29a

[1] M = potassium phosphate molarity.

[2] Means within the same row followed by the same letter are not significantly different.

Acknowledgements

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project (no. RGP-VPP-114i).

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