Effects of salts on the freeze–thaw stability, gel strength and rheological properties of potato starch

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Abstract The objective of this study was to evaluate the effects of different salts (NaF, NaCl, NaBr, NaI, K₂SO₄, KCl, KNO₃, KSCN, LiCl) on freeze–thaw stability, gel strength and rheological properties of potato starch. Addition of the structure-making (salting-out) ions, such as F[−] and SO₄^{2−}, decreased freeze–thaw stability and increased gel strength, maximal storage modulus (G′) and maximal loss modulus (G′′) of potato starch, due to a stronger three-dimensional network by promoting the starch retrogradation and inhibiting starch gelatinization. Shear stress versus shear rate of all samples at 25 °C was well fitted to the simple power-law model with high determination coefficients ($R^2 = 0.9863\text{--}0.9990$). Flow behavior index (n), consistency index (K) and apparent viscosities increased with adding salting-out ions.

However, the structure-breaking (salting-in) ions had reverse effects on freeze–thaw stability, gel strength and rheological characteristics of potato starch. The addition of structure-breaking ions, such as Br[−], NO₃[−], I[−], SCN[−], Na⁺ and Li⁺, decreased gel strength, G′ and G′′ values and increased freeze–thaw stability. Salts could significantly influence on the retrogradation of potato starch, generally following the ion order: F[−] > SO₄^{2−} > Cl[−] > Br[−] > NO₃[−] > I[−] > SCN[−] for anions and K⁺ > Na⁺ > Li⁺ for cations, consistent with the Hofmeister series.

Keywords Potato starch · Salts · Hofmeister series · Retrogradation · Rheology

Introduction

Starch granules, when heated in excess water above their gelatinization temperature, undergo irreversible swelling and result in amylose leaching into the solution. When starch paste goes through cooling or storage, starch molecules will rearrange orderly by hydrogen bonding interaction to precipitate or be insoluble, called starch retrogradation (BeMiller and Whistler 2009). In the presence of high starch concentration, its suspension will form an elastic gel after cooling. These interactions are time and temperature dependences. Starch gel formed during retrogradation is a metastable and nonequilibrium system, so it undergoes structural changes during storage (Xie et al. 2014; Zhou et al. 2010).

During retrogradation, the amylose forms double-helical associations with 40–70 glucose units (Zhou et al. 2007), whereas the amylopectin crystallizes by association of the outermost short branches (DP = 15) (Matalanis et al. 2009). Aggregation and crystallization of amylose are

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completed within the first few hours of storage, while those of amylopectin occur at later stage (Sodhi and Singh 2003). The variation in thermal properties of starches during refrigerated storage may be attributed to the variation in amylose to amylopectin ratio, size and shape of the granules and presence/absence of lipids (Matalanis et al. 2009; Miles et al. 1985; Zhou et al. 2007). The amylose content is one of the influential factors for starch retrogradation (Fredriksson et al. 1998). A greater amount of amylose causes a greater retrogradation tendency in starch (BeMiller and Whistler 2009), but amylopectin and intermediate materials also play an important role in starch retrogradation during refrigerated storage (Yamin et al. 1999).

Effect of retrogradation on starch-based products can be either desirable or, usually, undesirable. Generally, starch retrogradation significantly contributes to staling or undesirable firming of bread and other starch-based products (Singh et al. 2006; Zhu et al. 2009). However, retrogradation is sometimes applied to modify the structural, mechanical or unsuitably organoleptic characteristics of certain starch-based products requiring low-temperature storage, such as the productions of breakfast cereals and parboiled rice, since retrogradation results in increasing hardness and reducing stickiness (Singh et al. 2006). Freezing/thawing, which accelerates retrogradation, is applied on dehydrated mashed potato to decrease the amount of soluble starch and improve the consistency of reconstituted product (Zhu et al. 2009). The production of Japanese ‘*harusame*’ noodles also involves freeze–thaw processing to reduce stickiness for a characteristic chewiness (Rockland and Stewart 1981).

Starch based/contained foods are often coexists with other ingredients in food products, such as salts. As a condiment, salts are often used in starch products. In yellow alkaline noodles (Li et al. 2015) and sauce (Krystyan et al. 2012), both starch and salt are indispensable part of the formula. The starch-salts complexes are also used in non-food field, such as starch-based films (Jiang et al. 2016). Furthermore, the addition of salts can also affect the performance of starch. Depending on their varieties and concentrations, salts can cause an elevation or depression of starch gelatinization. When discussing effects of salt on starch, there is inevitably involves Hofmeister series. Hofmeister or lyotropic series is a classification of ions in the order of their abilities to change protein solubility or other macromolecule colloid solution, such as starch solution (Leberman 1991).

Previous studies presented the effect of salts on the gelatinization characteristics of starch (Wang et al. 2017; Zhou et al. 2014). Salts or ions, following the Hofmeister series, have significant effects on the physicochemical, microstructural and thermal properties of potato starch

(Zhou et al. 2014). Generally, the salting-out ions, such as F^- and SO_4^{2-} , tend to cause decreases of swelling power, solubility, transparency of potato starch and increases of gelatinization temperature and enthalpy. The salting-in ions, such as I^- and SCN^- , have opposite effects on those properties of potato starch. Different concentrations of NaCl had different impacts on the gelatinization of starches (Li et al. 2014). NaCl inhibited the gelatinization of corn starch. Low concentration NaCl inhibited gelatinization of potato starch, but high concentration NaCl significantly promoted its gelatinization, due to its negatively charged phosphorus groups. The ionic repulsion generated by these groups weakened the association between the molecules and increased the granule water binding capacity and swelling. In this study, the objective is to evaluate the effects of different salt ions on freeze–thaw stability, gel strength and rheological properties of potato starch.

Materials and methods

Materials

Potato starch (Xue Guan Starch Company, Ning Xia, China) was used after drying in the oven (Shanghai Jing Macro Experimental Equipment Co. Ltd., Shanghai, China) at 105 °C for 3 h. Amylose and amylopectin contents were 22.16 and 74.50 %, respectively, determined by the method of Zeng et al. (2012). Salts were analytical grade, including sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), potassium sulfate (K_2SO_4), potassium chloride (KCl), potassium nitrate (KNO_3), potassium thiocyanate (KSCN) and lithium chloride (LiCl) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).

Freeze–thaw stability

The freeze–thaw stabilities of potato starch with different salts were determined by the method of Wang et al. (2013). Starch suspensions (5 %, w/v) with salts (0.1 mol/L) in distilled water were heated 30 min in a boiling water bath (HH-4, Changzhou Guohua Electric Co., Ltd., Jintan, China) with moderate mechanical agitation and then cooled. The control was starch without salt additive. Salts were dissolved in the water before adding into the starch. The paste (30 mL) was transferred to the 50 mL centrifuge tube. The tubes were placed in a freezer at $-20\text{ }^{\circ}\text{C}$ for 22 h and then placed in a $30\text{ }^{\circ}\text{C}$ water bath for 1.5 h to thaw and equilibrate. Thawed tubes were centrifuged for 15 min at $900\times g$ (Avanti J-E, Backman, California, USA). The amount of water released from the gel was measured in a graduated cylinder after 1, 2, 4, and 7 freeze–thaw cycles

and expressed as percent of water separated or syneresis (Wang et al. 2013).

Preparation of potato starch gels

Potato starch suspensions (8 %, w/v) with salts (0.1 mol/L) were obtained as described above. The gels were prepared by heating starch suspension at 95 °C for 20 min in a water bath (HH-4, Changzhou Guohua Electric Co., Ltd., Jintan, China) with manual stirring and then poured into the bottle (40 mm in diameter and 25 mm in depth). The samples were sealed to prevent moisture loss and stored at 4 °C overnight.

Gel strength

The gel texture was measured by a Texture Analyzer (Texture Technologies Corp, Scarsdale, NY, USA) using a cylindrical probe (P/0.5, 12.7 mm in diameter), which was programmed to move downwards for a compression ration of 70 % of the original height at a speed of 1 mm/s and a pre-test speed of 5 mm/s, a post-test speed of 5 mm/s as well as a trigger force of 5 g (Huang et al. 2007). Breaking force (g) and distance to rupture (mm) were obtained. The first peak force and the corresponding to distance of concave depth in curve is defined as breaking strength and distance to rupture, respectively, while the gel strength (g*mm) of starch gel is multiply breaking strength by distance to rupture (Lee and Chung 1989).

Dynamic rheological testing

A dynamic rheometer (AR2000ex Rheometer, TA Instruments Ltd., New Castle, DE, USA) was used to determine the rheological properties of potato starch with salts. The gap size was set at 1000 μ m. Starch suspensions of 8 % (w/v) with salts (0.1 mol/L) were stirred for 15 min (20 °C) at very slow speed using a magnetic stirrer and loaded on the rheometer plate (preheated to 25 °C). The sample edge was covered with a thin layer of low-density silicone oil (to minimize evaporation loss) before measurement. During the temperature sweep, strain and frequency were set at 2 % and 1 Hz, which were within its linear range. The starch samples were heated from 25 to 100 °C and cooled from 100 to 25 °C at a rate of 5 °C/min. The cooled starch gels were held at 25 °C for 20 min and then subjected to a frequency sweep with the frequency range from 0.01 to 10 Hz at 2 % strain. Storage modulus (G') and loss modulus (G'') were determined as functions of temperature and frequency (Singh et al. 2007).

Steady shear rheological analysis

The potato starch suspensions (8 %, w/w) with salts (0.1 mol/L) were heated at 95 °C in a water bath for 30 min. Then the paste was immediately transferred to the AR2000ex Rheometer (TA AR2000ex Rheometer, TA Instruments Ltd., New Castle, DE, USA) equipped with parallel plate system (40 mm in diameter) at 25 °C for the measurement of its steady shear rheological properties. The gap size was set at 1000 μ m. The exposed sample edge was covered with a thin layer of silicone oil to prevent evaporation during measurement. The flow curves were obtained by registering shear stress at shear rates from 0.1 to 300 s^{-1} (forward) in 15 min and down in 15 min from 300 to 0.1 s^{-1} (backward) at 25 °C. The power-law model (Eq. (1)) is used to describe the data of shear-induced behavior of stress.

$$\tau = K\gamma^n \quad (1)$$

where τ is the shear stress (Pa), γ is shear rate (s^{-1}), K is the consistency index ($Pa\ s^n$), and n is the flow behavior index (dimensionless).

The hysteresis loop was obtained from the area between the ascending and descending flow curves. This area was obtained by the difference between integrating the area for forward and backward measurements from γ_1 (initial shear rate) to γ_2 (final shear rate):

$$\text{Hysteresis loop area} = \int_{\gamma_1}^{\gamma_2} k \cdot \gamma^n - \int_{\gamma_1}^{\gamma_2} k' \cdot \gamma^{n'} \quad (2)$$

where k , k' and n , n' are the consistency coefficient and flow index behavior for forward and backward measurements, respectively (Razavi and Karazhiyan 2009). Software GraphPad Prism (GraphPad prism 5 for windows, GraphPad Software, Inc, San Diego California, USA) was used to calculate those values (k , n , R^2 and hysteresis loop area).

Statistical analysis

All experiments were replicated three times. Results of all measurements were reported as mean values $\pm$ standard deviation (SD). For data analysis, the analysis of variance (ANOVA) was performed using a SPSS package (SPSS 17.0, SPSS Inc, Chicago, IL, US). Differences among the mean values of various treatments were made using Duncan's multiple range tests ($p < 0.05$).

Results and discussion

Freeze–thaw stability

The “freeze–thaw” stability can be an indicator of the tendency of starch to retrograde. The amount of water

separated from the starch is directly related to the tendency of its retrogradation (Arunyanart and Charoenrein 2008). The more easily a starch retrogrades, the more water separated from the starch system, which means a worse “freeze–thaw” stability of the whole system (Muadklay and Charoenrein 2008). Figure 1 presents the freeze–thaw stability of gelatinized potato starch with different salts. Syneresis of potato starch was gradually increased as the increase of freeze/thaw cycles. The addition of salts changed freeze–thaw stability of gelatinized potato starch significantly ($p < 0.05$). For structure-making (salting-out) ions, such as F^- , SO_4^{2-} and K^+ , syneresis of potato starch was higher than that of the control. There was more water separated from the starch with those salts. Ions decreased freeze–thaw stability of potato starch. However, for structure-breaking (salting-in) ions, such as Br^- , NO_3^- , I^- , SCN^- , Na^+ and Li^+ , their syneresis values were lower than the control. There was less water separated from potato starch. Those ions increased freeze–thaw stability of potato starch. There was systematic pattern for syneresis of NaF, NaCl, NaBr, and NaI, while the order was $NaF > NaCl > NaBr > NaI$ (Fig. 1). Generally, the order of decreasing syneresis for anions was $SCN^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-} > F^-$. The order for cations was $Li^+ > Na^+ > K^+$ (Fig. 1). Both were consistent with the Hofmeister series.

When starch paste or gel was frozen, phase separation occurred with the formation of ice crystals (Yuan and Thompson 1998). During thawing, the paste or gel will continue to be composed of a starch-rich and starch-deficient aqueous phase. The extent of phase separation increases with the increase of freeze–thaw cycles, due to an increase in amylopectin retrogradation in the starch-rich phase. The water can also be easily expressed from the dense network or syneresis. This is usually viewed unfavorably as product deterioration. Generally different ions have differences in charge distribution and polarization. Ions, such as F^- , SO_4^{2-} and K^+ , have a more symmetrical

charge distribution, and thus they tended to protect the hydrogen link between starch–starch molecules and have a relatively strong tendency to retrogradation. It reduced freeze–thaw stability of starch and increased syneresis. On the other hand, ions, such as Br^- , NO_3^- , I^- , SCN^- , Na^+ and Li^+ , have a relatively large electron cloud and asymmetric structure, leading to a relatively weak tendency to retrogradation. Therefore, during freezing/thaw, potato starch pastes with such ions tend to increase freeze–thaw stability. The ability to decrease syneresis of starch was $SCN^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-} > F^-$ for anions and $Li^+ > Na^+ > K^+$ for cations (Fig. 1). It was consistent with the Hofmeister series.

Gel strength

During storage at 4 °C, the starch gel starts to retrograde and the firmness of starch gel increases, due to the rearrangement of amylose and the recrystallization of amylopectin side chains to form a three-dimensional network (Kaur et al. 2007; Zhu et al. 2009). Table 1 presents the effect of different salts on textural parameters of potato starch gels. The addition of salts significantly changed the breaking force and gel strength of gels, while there was no significant change in distance to rupture ($p > 0.05$). Breaking force and gel strength increased with the addition of structure-making (salting-out) ions, such as F^- and SO_4^{2-} . However, they decreased with the addition of structure-breaking (salting-in) ions, such as Br^- , NO_3^- , I^- , SCN^- , Na^+ and Li^+ . There was also systematic pattern for breaking force and gel strength of NaF, NaCl, NaBr, and NaI, while the order was $NaF > NaCl > NaBr > NaI$ (Table 1). Generally, the order of decreasing breaking force and gel strength for anions was $SCN^- > I^- > NO_3^- > Br^- > Cl^- > SO_4^{2-} > F^-$. The order for cations was $Li^+ > Na^+ > K^+$ (Table 1). The changes of these parameters were consistent with the ability of ions changing the tendency of starch to retrograde.

Fig. 1 Effects of different salts on the freeze–thaw stability of potato starch paste. Different letters indicated significant differences ($p < 0.05$)

Table 1 The effect of different salts on textural parameters of potato starch gel

Sample	Breaking force (g)	Distance to rupture (cm)	Gel strength (g cm)
Control	136.25 ± 4.62cd	1.38 ± 0.05a	187.77 ± 7.56cd
NaF	176.09 ± 26.13a	1.49 ± 0.07a	261.43 ± 32.90a
NaCl	130.99 ± 2.47cd	1.42 ± 0.06a	185.61 ± 11.76cd
NaBr	127.35 ± 8.06cd	1.42 ± 0.15a	181.53 ± 31.13cd
NaI	121.01 ± 2.28cd	1.41 ± 0.02a	171.14 ± 3.06cd
K ₂ SO ₄	158.82 ± 8.98ab	1.49 ± 0.04a	236.61 ± 18.84ab
KCl	138.28 ± 4.86bc	1.51 ± 0.08a	209.35 ± 13.44bc
KNO ₃	123.66 ± 8.15cd	1.43 ± 0.09a	177.11 ± 21.35cd
KSCN	112.65 ± 6.90d	1.41 ± 0.04a	158.88 ± 10.90d
LiCl	126.04 ± 2.44cd	1.47 ± 0.05a	185.19 ± 5.97cd

Different letters in the same column indicated significant differences ($p < 0.05$)

The changes in the gel strength during storage are an indication of retrogradation tendency of starch gels. The greater the textural changes during storage, the greater is the tendency of starch to retrograde (Kaur et al. 2007). Thus gel strength of starch gels further illustrated effect of salts on potato starch gels during retrogradation. Because structure-making (salting-out) ions, such as F^- and SO_4^{2-} , have smaller sizes or a lower polarization. They tend to protect the hydrogen link between starch–starch molecules and have a relatively strong tendency to retrogradation. Such structure-making ions could increase breaking force and gel strength of starch gels. However, ions, such as Br^- , NO_3^- , I^- , SCN^- , Na^+ and Li^+ , have relatively have larger diameters or less symmetric structures, so they have a relatively weak tendency to retrogradation. Therefore, during cold storage, potato starch gels with those structure-breaking ions could form a weaker three-dimensional network than the control, leading to a decrease of breaking force and gel strength or forming softer gels.

Dynamic rheological testing

Table 2 shows the rheological characteristic parameters of starch suspensions with different salts by the rheometer during the temperature sweep and Fig. 2 illustrates the continuous assessment of dynamic moduli during frequency sweep. The maximal storage modulus (G_m'), maximal loss modulus (G_m''), T_m' (the temperature corresponding to the maximal G') and T_m'' (the temperature corresponding to the maximal G'') of potato starch were increased with the addition of structure-making ions, such as F^- and SO_4^{2-} , while the addition of structure-breaking ions, such as Br^- , NO_3^- , I^- , SCN^- , Na^+ and Li^+ , caused decreases of G_m' , G_m'' , T_m' and T_m'' markedly (Table 2). The frequency dependence of G' and G'' gives valuable information of starch structure. G' and G'' increased with the addition of salting-out ions and decreased with addition

of salting-in ions during frequency sweep, comparing with the control (Fig. 2).

At early stage of heating, the amylose dissolved from the starch granules and the suspension became a sol, resulting in small increase in G' and G'' . With further heating, G' and G'' increased and reached maxima (G_m' and G_m''), which may be attributed to the formation of a network of swollen starch granules (Hagenimana et al. 2005; Julianti et al. 2015). G' and G'' of starch dispersions associated with the three-dimensional network structure of starch (Singh et al. 2008; Julianti et al. 2015). The structure-making (salting-out) ions were able to decrease the solubility, swelling power and increase the gelatinization temperature of potato starch significantly, while the structure-breaking (salting-in) ions had opposite effects (Zhou et al. 2014). When added the salting-out ions, such as F^- , SO_4^{2-} and K^+ , the gelatinization of potato starch was suppressed and there were more granular remains, which supported network structure of the potato starch paste, resulted to the increases in G' and G'' . The increase in G_m' and G_m'' may be also attributed to salting-out effects by the structure-making (salting-out) ions, which would enhance the aggregation of amylose chains and the formation of a three-dimensional network (Ahmad and Williams 1999). For the structure-breaking (salting-in) ions, the addition of those structure-breaking ions, such as Br^- , NO_3^- , I^- , SCN^- , Na^+ and Li^+ , caused the decreases of G_m' and G_m'' markedly, which might be due to promote the gelatinization and dissolution of the starch by those ions (Zhou et al. 2014).

A true gel system is frequency-independent over a large time scale range (Ferrero et al. 1994). In contrast, strong frequency dependence suggests a material structure with molecular entanglements that behaves more like a solid at higher frequency and more like a liquid at lower frequency. The G' and G'' of potato starch with structure-making ions

Table 2 Rheological characteristic parameters of potato starch suspensions with different salts during the temperature sweep

Sample	Temperature up				Temperature down	
	G_m' (Pa)	T_m' (°C)	G_m'' (Pa)	T_m'' (°C)	G_m' (Pa)	G_m'' (Pa)
Control	616.3 ± 0.10d	68.8 ± 1.25b	208.9 ± 1.51d	66.2 ± 0.44c	251.4 ± 0.56d	47.7 ± 0.46c
NaF	1023.7 ± 0.53a	73.1 ± 0.20a	262.1 ± 0.36a	68.3 ± 0.44a	396.7 ± 0.82a	58.0 ± 0.26a
K ₂ SO ₄	945.1 ± 0.26b	68.3 ± 0.35b	247.6 ± 0.75b	66.2 ± 0.30b	336.2 ± 0.26b	52.1 ± 0.44b
KCl	788.1 ± 0.44c	66.2 ± 0.30c	238.0 ± 0.36c	67.3 ± 0.53c	301.3 ± 0.44c	47.3 ± 0.36c
NaCl	463.5 ± 0.53e	64.6 ± 0.26d	152.2 ± 0.30e	64.0 ± 0.35d	202.9 ± 0.26e	38.0 ± 0.44d
LiCl	453.0 ± 0.36f	63.0 ± 0.26e	130.9 ± 0.36f	63.0 ± 0.30e	192.0 ± 0.36f	35.6 ± 0.44e
NaBr	401.8 ± 0.46g	62.4 ± 0.36e	114.1 ± 0.46g	61.3 ± 0.26f	166.5 ± 0.35g	34.8 ± 0.26f
KNO ₃	370.4 ± 0.17h	61.3 ± 0.26f	105.8 ± 0.26h	58.1 ± 0.44g	156.9 ± 0.44h	31.6 ± 0.36g
NaI	330.7 ± 0.26i	59.8 ± 0.44g	80.7 ± 0.17i	57.1 ± 0.36h	141.5 ± 0.35i	30.0 ± 0.44h
KSCN	300.8 ± 0.36j	58.1 ± 0.44g	73.4 ± 0.44j	55.5 ± 0.36i	132.9 ± 0.36j	28.5 ± 0.35i

G_m' and G_m'' were the maximal G' and maximal G'' , the T_m' (°C) and T_m'' (°C) were the corresponding temperature, respectively. Different letters in the same column indicated significant differences ($p < 0.05$)

Fig. 2 Effect of different salts on frequency dependences of G' (a) and G'' (b) of potato starch suspensions

were higher than structure-breaking ions during frequency sweep (Fig. 2), resulted from preserving the integrity of the starch granules by the addition of structure-making ions. More stable network structure of potato starch paste could be able to resist frequency increase, which exhibited the

higher value of G' and G'' . Generally, the G' and G'' during temperature and frequency sweeps increased in the order: $F^- > SO_4^{2-} > Cl^- > Br^- > NO_3^- > I^- > SCN^-$ for anions and $K^+ > Na^+ > Li^+$ for cations, consistent with the Hofmeister series.

Table 3 The rheological parameters of power-law model for ascending and descending steady flow curves (shear rate: 0.1–300 s⁻¹ and 300–0.1 s⁻¹) and thixotropic area of potato starch with salts

Sample	Thixotropic area	Ascending flow curves			Descending flow curves		
		k/Pa s ⁿ	n	R ²	k/Pa s ⁿ	n	R ²
Control	161,379	174.0 ± 1.22d	0.3039 ± 0.0004cd	0.9958	55.93 ± 0.07c	0.4582 ± 0.0121d	0.9863
NaF	158,843	186.6 ± 1.22a	0.3109 ± 0.0014a	0.9934	60.27 ± 0.16a	0.4920 ± 0.0006a	0.9881
K ₂ SO ₄	159,469	185.1 ± 0.57b	0.3081 ± 0.0012b	0.9932	58.37 ± 0.09b	0.4669 ± 0.0014b	0.9928
KCl	160,514	179.3 ± 0.70c	0.3043 ± 0.0013c	0.9986	56.10 ± 0.26c	0.4632 ± 0.0011c	0.9918
NaCl	165,374	136.2 ± 0.78e	0.3020 ± 0.0006d	0.9984	50.17 ± 0.26d	0.4579 ± 0.0009d	0.9899
LiCl	168,342	134.8 ± 0.78ef	0.2590 ± 0.0015e	0.9976	47.82 ± 0.34e	0.4331 ± 0.0007e	0.9881
NaBr	167,514	135.2 ± 0.36ef	0.2970 ± 0.0012f	0.9982	51.01 ± 0.19f	0.4478 ± 0.0009f	0.9905
KNO ₃	167,555	134.5 ± 0.56f	0.2876 ± 0.0023g	0.9985	47.42 ± 0.11g	0.4332 ± 0.0006f	0.9918
NaI	171,632	131.5 ± 0.53g	0.2656 ± 0.0013h	0.9990	43.13 ± 0.19h	0.4156 ± 0.0008g	0.9934
KSCN	173,810	129.6 ± 0.70h	0.2590 ± 0.0004h	0.9986	42.33 ± 0.11i	0.3913 ± 0.0005h	0.9936

K is the consistency index (Pa sⁿ), n is the flow behavior index (dimensionless) and R² is the correlation coefficient. Different letters in the same column indicated significant differences ($p < 0.05$)

Steady shear rheological analysis

Shear stress versus shear rate of all samples at 25 °C was well fitted to the simple power-law model (Eq. (1)) with high determination coefficients (Table 3). Pseudoplastic behavior refers to the viscosity decreases with the increase of the shear rate (shear thinning). All starch pastes exhibited a non-Newtonian pseudoplastic behavior ($n < 1$). The flow behavior index (n) values (0.2590–0.3109) showed high pseudoplasticity. The n values of potato starch with salting-out ions were higher than that of the control, indicating the pseudoplastic behavior of the mixtures was weakened by salting-out ions for the structural protective effect of those ions, while the addition of salting-in ions made them lower than the control, indicating the increase pseudoplasticity of the mixture by salting-in ions (Table 3). In the same shear rate, the consistency index (K) decreased with the addition of salting-in ions but increased with the addition of salting-out ions due to their effects on the starch three-dimensional network. Existence of a hysteresis loop indicates time-dependent fluid behavior and its area is a measure of the extent of thixotropy (Steffe 1996). Table 3 shows the hysteresis loop areas of potato starch with different salts. Potato starch with salting-in ions had a larger hysteresis area than those with salting-out ions. It may also attribute to effects of ions on the formation of starch three-dimensional network.

The salting-out ions, such as F⁻, SO₄²⁻ and K⁺, due to its small size and low polarization, tends to protect the link of hydrogen bonds between the starch–starch molecules and starch–water molecules to a certain degree (Zhou et al. 2014), thus inhibiting the gelatinization of starch granules and protecting the structure of paste network, resulting in the reduction of shear thinning and increase of consistency index. While for the salting-in ions, such as Br⁻, NO₃⁻, I⁻,

SCN⁻, Na⁺ and Li⁺, because of its larger diameter and greater polarization, tends to break the link of hydrogen bonds between the starch–starch molecules and starch–water molecules to a certain degree (Zhou et al. 2014), thus promoting the pasting of potato starch, leading to the increase of shear thinning and decrease of consistency index.

It should be pointed out that shear thinning and thixotropic behaviors have industrial and commercial significance. For example, since the viscosity of starch decreases with shear rate and shearing time during the mixing process, it will lead to less power consumption. On the other hand, pseudoplastic and thixotropic behaviors have significant impact on the ability of potato starch to spread on another material, where potato starch can break down for easy spreading, and the applied film can gain viscosity instantaneously to resist running (Abu-Jdayil 2004).

Conclusion

Salts had complex effects on freeze–thaw stability, gel strength and rheological properties of potato starch. Salting-out ions, such as F⁻ and SO₄²⁻, accelerated the retrogradation of starch, causing an increase of water amount separated from the system significantly ($p < 0.05$). Thus they increased gel strength of potato starch gels. Salting-in ions, such as NO₃⁻ and SCN⁻, inhibited the retrogradation of starch. Potato starch with all salts presented pseudoplastic behavior. The area of hysteresis loop decreased with the addition of salting-out ions but increased with the addition of salting-in ions. Under the same shear rate, the viscosity decreased with the addition of salting-in ions but increased with the addition of salting-out ions. Therefore, structurally breaking or making effects of ions on potato

starch follow on their order in the Hofmeister series. There is a potential to produce starch-based foods with desired characteristics by adding appropriate salt or ion.

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References

- Abu-Jdayil B (2004) Flow properties of sweetened sesame paste (halawa tehneh). *Eur Food Res Technol* 219:265–272
- Ahmad FB, Williams PA (1999) Effect of salts on the gelatinization and rheological properties of sago starch. *J Agric Food Chem* 47:3359–3366
- Arunyarnart T, Charoenrein S (2008) Effect of sucrose on the freeze–thaw stability of rice starch gels: correlation with microstructure and freezable water. *Carbohydr Polym* 74:514–518. doi:10.1016/j.carbpol.2008.04.002
- BeMiller JN, Whistler RL (eds) (2009) *Starch: chemistry and technology*, 3rd edn. Academic Press, New York
- Ferrero C, Martino M, Zaritzky N (1994) Corn starch–xanthan gum interaction and its effect on the stability during storage of frozen gelatinized suspension. *Starch–Stärke* 46:300–308
- Fredriksson H, Silverio J, Andersson R, Eliasson AC, Åman P (1998) The influence of amylose and amylopectin characteristics on gelatinization and retrogradation properties of different starches. *Carbohydr Polym* 35:119–134
- Hagenimana A, Pu P, Ding X (2005) Study on thermal and rheological properties of native rice starches and their corresponding mixtures. *Food Res Int* 38:257–266. doi:10.1016/j.foodres.2004.05.009
- Huang M, Kennedy J, Li B, Xu X, Xie B (2007) Characters of rice starch gel modified by gellan, carrageenan, and glucomannan: a texture profile analysis study. *Carbohydr Polym* 69:411–418
- Jiang X, Li H, Luo Y, Zhao Y, Hou L (2016) Studies of the plasticizing effect of different hydrophilic inorganic salts on starch/poly (vinyl alcohol) films. *Int J Biol Macromol* 82:223–230. doi:10.1016/j.ijbiomac.2015.11.046
- Julianti E, Rusmarilin H, Ridwansyah Yusraini E (2015) Functional and rheological properties of composite flour from sweet potato, maize, soybean and xanthan gum. *J Saudi Soc Agric Sci*. doi:10.1016/j.jssas.2015.05.005
- Kaur L, Singh J, McCarthy OJ, Singh H (2007) Physico-chemical, rheological and structural properties of fractionated potato starches. *J Food Eng* 82:383–394
- Krystyan M, Sikora M, Adamczyk G, Tomasik P (2012) Caramel sauces thickened with combinations of potato starch and xanthan gum. *J Food Eng* 112:22–28. doi:10.1016/j.jfoodeng.2012.03.035
- Leberman R (1991) The Hofmeister series and ionic strength. *Fed Eur Biochem Soc* 284:293–294
- Lee CM, Chung KH (1989) Analysis of surimi gel properties by compression and penetration tests. *J Text Stud* 20:363–377
- Li Q, Xie Q, Yu S, Gao Q (2014) Application of digital image analysis method to study the gelatinization process of starch/sodium chloride solution systems. *Food Hydrocoll* 35:392–402. doi:10.1016/j.foodhyd.2013.06.017
- Li Q, Zhang L, Ye Y, Gao Q (2015) Effect of salts on the gelatinization process of Chinese yam (*Dioscorea opposita*) starch with digital image analysis method. *Food Hydrocoll* 51:468–475. doi:10.1016/j.foodhyd.2015.05.045
- Matalanis AM, Campanella OH, Hamaker BR (2009) Storage retrogradation behavior of sorghum, maize and rice starch pastes related to amylopectin fine structure. *J Cereal Sci* 50:74–81. doi:10.1016/j.jcs.2009.02.007
- Miles MJ, Morris VJ, Orford PD, Ring SG (1985) The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydr Res* 135:271–281
- Muadklay J, Charoenrein S (2008) Effects of hydrocolloids and freezing rates on freeze–thaw stability of tapioca starch gels. *Food Hydrocoll* 22:1268–1272. doi:10.1016/j.foodhyd.2007.06.008
- Razavi S, Karazhiyan H (2009) Flow properties and thixotropy of selected hydrocolloids: experimental and modeling studies. *Food Hydrocoll* 23:908–912
- Rockland LB, Stewart GF (1981) *Water activity: influences on food quality*. Academic Press, London
- Singh J, McCarthy O, Singh H (2006) Physico-chemical and morphological characteristics of New Zealand Taewa (Maori potato) starches. *Carbohydr Polym* 64:569–581. doi:10.1016/j.carbpol.2005.11.013
- Singh McCarthy O, Singh H, Moughan PJ, Kaur L (2007) Morphological, thermal and rheological characterization of starch isolated from New Zealand Kamo Kamo (*Cucurbita pepo*) fruit—a novel source. *Carbohydr Polym* 67:233–244. doi:10.1016/j.carbpol.2006.05.021
- Singh N, Isono N, Srichuwong S, Noda T, Nishinari K (2008) Structural, thermal and viscoelastic properties of potato starches. *Food Hydrocoll* 22:979–988. doi:10.1016/j.foodhyd.2007.05.010
- Sodhi NS, Singh N (2003) Morphological, thermal and rheological properties of starches separated from rice cultivars grown in India. *Food Chem* 80:99–108
- Steffe JF (1996) *Rheological methods in food process engineering*. Freeman Press, East Lansing
- Wang L, Xie B, Xiong G, Wu W, Wang J, Qiao Y, Liao L (2013) The effect of freeze–thaw cycles on microstructure and physico-chemical properties of four starch gels. *Food Hydrocoll* 31:61–67. doi:10.1016/j.foodhyd.2012.10.004
- Wang W, Zhou H, Yang H, Zhao S, Liu Y, Liu R (2017) Effects of salts on the gelatinization and retrogradation properties of maize starch and waxy maize starch. *Food Chem* 214:319–327. doi:10.1016/j.foodchem.2016.07.040
- Xie Y, Hu X, Jin Z, Xu X, Chen H (2014) Effect of repeated retrogradation on structural characteristics and in vitro digestibility of waxy potato starch. *Food Chem* 163:219–225. doi:10.1016/j.foodchem.2014.04.102
- Yamin F, Lee M, Pollak L, White P (1999) Thermal Properties of Starch in Corn Variants Isolated After Chemical Mutagenesis of Inbred Line B73 1. *Cereal Chem* 76:175–181
- Yuan R, Thompson D (1998) Freeze–thaw stability of three waxy maize starch pastes measured by centrifugation and calorimetry. *Cereal Chem* 75:571–573
- Zeng F, Zhao X, Zhou T, Liu G (2012) Dual-wavelength colorimetric method for measuring amylose and amylopectin contents of potato starch. *Mod Food Sci Technol* 28:119–122
- Zhou Z, Robards K, Helliwell S, Blanchard C (2007) Effect of the addition of fatty acids on rice starch properties. *Food Res Int* 40:209–214. doi:10.1016/j.foodres.2006.10.006
- Zhou X, Baik B-K, Wang R, Lim S-T (2010) Retrogradation of waxy and normal corn starch gels by temperature cycling. *J Cereal Sci* 51:57–65. doi:10.1016/j.jcs.2009.09.005
- Zhou H, Wang C, Shi L, Chang T, Yang H, Cui M (2014) Effects of salts on physicochemical, microstructural and thermal properties of potato starch. *Food Chem* 156:137–143. doi:10.1016/j.foodchem.2014.02.015
- Zhu F, Cai Y-Z, Sun M, Corke H (2009) Effect of phytochemical extracts on the pasting, thermal, and gelling properties of wheat starch. *Food Chem* 112:919–923