



Effects of salts on physicochemical, microstructural and thermal properties of potato starch



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ABSTRACT

The objective of this study was to determine the effects of salts on the physicochemical, microstructural and thermal properties of potato starch. The salting-out ions were able to decrease the solubility, swelling power, transparency and particle size of potato starch significantly ($p < 0.05$), while the salting-in ions increased these properties significantly ($p < 0.05$). The microstructure of potato starch granules, observed by a light microscopy at 50 °C and 70 °C, was consistent with the above results. Differential scanning calorimetry (DSC) analysis demonstrated an increase in gelatinization temperature and enthalpy with the addition of salting-out ions, whereas there was a reverse trend for the addition of salting-in ions. The effects of anions on these properties of potato starch follow the order of $\text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{F}^-$, while effects of the cations follow the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, matching to the order of the Hofmeister series.

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1. Introduction

Potato starch has unique characteristics, such as a high phosphorus content, high viscosity, high swelling power, high paste clarity, low tendency to retrograde, as well as large granule size (Noda et al., 2006; Sandhu & Kaur, 2010; Singh, Singh, & Saxena, 2002). The exceptional high quality of potato starch is partly attributed to its large granular size, distribution, mineral content, amylose/amylopectin ratio and high content of starch phosphate esters (Kaur, Singh, Ezekiel, & Guraya, 2007; Singh, Chawla, & Singh, 2004). Moreover, phosphate monoesters in potato starch are negatively charged groups, so the ionic repulsion generated by these groups weakens the association between the molecules and increases the granule water-binding capacity and swelling power. Therefore, the presence of salts can affect such repulsion

in the starch, resulting in some changes of the physicochemical properties of potato starch.

The effects of salts on starch gelatinization have been studied by many researchers, using a wide range of techniques, such as, light microscopy (Jane, 1993; Koch & Jane, 2000), differential scanning calorimetry (DSC) (Ahmad & Williams, 1999; Chungcharoen & Lund, 1987; Evans & Haisman, 1982; Jane, 1993; Wootton & Bamunuarachchi, 1980), rheological measurements (Ahmad & Williams, 1999), scanning electron microscopy (Koch & Jane, 2000), dielectric measurement (Bircan & Barringer, 1998), light transmission (Sandstedt, Kempf, & Abbott, 1960) and NMR spectroscopy (Chinachoti, Kim-Shin, Mari, & Leah, 1991). However, considerable controversy could be found about the influence of the salt on the physicochemical properties of the starch in literature. Depending on their varieties and concentrations, salts can either elevate or depress the gelatinization temperature and enthalpy, resulting in either increasing or decreasing the rate and degree of gelatinization and retrogradation (Chiotelli & Le Meste, 2002; Sandstedt et al., 1960). Various explanations have been proposed. Evans and Haisman (1982) postulated that the effect of solutes on the gelatinization temperature was a logarithmic function of the water activity of the system and volume fraction of water in the granules. Oosten (1982) thought that starch could act as a weak

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acid based ion exchanger and cations tend to protect and stabilize the granule structure, while anions were gelatinizing agents, rupturing hydrogen bonds. Jane (1993) proposed that the mechanism of starch gelatinization in salt solutions was due to the structure-making and structure-breaking effects on water and to electrostatic interactions between salts and the hydroxyl groups on starch. The structure-breaking and structure-making effects of ions were named the Hofmeister series, which describe the effects of ions on the colloid (Hofmeister, 1888; Kunz, Henle, & Ninham, 2004). The species to the left of chloridion (Cl^-) are referred to as kosmotropes, while those to its right are called chaotropes. These terms were originally referred to the ability of an ion to alter the hydrogen bonding network of water (Collins & Washabaugh, 1985). The kosmotropes, 'water structure makers', are strongly hydrated to stabilize and salt-out effects on proteins and macromolecules. On the other hand, chaotropes (water structure breakers) are known to destabilize folded proteins to salt-in behaviour. The effects of ions or salts on a colloidal starch–water system might be related to the Hofmeister phenomena. There is no systematic study on the effects of different salts on the physicochemical properties of potato starch, which is widely used as a functional ingredient in foods. The objective of this study was to determine the effects of salts on the physicochemical, microstructural, and thermal properties of potato starch. It will provide the information for preparation of starch-based products with a variety of salts.

2. Materials and methods

2.1. Materials

Potato starch (Xue Guan Starch Company, Guyuan, Ningxia Province, China) was used after drying in the oven at 105 °C for 3 h. Salts were analytical grade reagents, including sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), potassium sulphate (K_2SO_4), potassium chloride (KCl), potassium nitrate (KNO_3), potassium thiocyanate (KSCN) and lithium chloride (LiCl) (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China).

2.2. Swelling power and solubility

Swelling power and solubility of starch were determined by the method of Leach, McCowen, and Schoch (1959). Salts in the required concentration were prepared (0.1 mol/l) and starch was added on 2% (w/v). The suspension of starch was heated at 90 °C for 30 min, followed by rapid cooling in ice water to room temperature. The suspension was then centrifuged at 3500g for 20 min. Supernatant was decanted carefully and the residue weighed for swelling power determination. The ratio between the residue and initial dry matter was calculated (g/g of starch on dry weight basis) as the swelling power. The supernatant was dried to a constant weight at 110 °C. The residue obtained after drying the supernatant represented the solubility of starch (g/g of starch on dry weight basis) (Leach et al., 1959).

2.3. Particle size distributions in salt solutions

Salts solutions were prepared (0.1 mol/l) and starch was added based on 6% (w/v) starch suspension. The suspension of starch was heated at 50 °C and 70 °C for 10 min, followed by rapid cooling in ice water to room temperature for the further test. Particle size of the potato starch samples was determined with a laser diffraction particle size analyzer (Malvern Mastersizer 2000, Malvern Instruments Ltd., Malvern, UK). The D [4, 3] (De Brouckere diameter) was measured (Han, Zeng, Zhang, & Yu, 2009).

2.4. Microstructure of potato starch granules in salt solutions

Starch suspension (6%, w/v) with salts was prepared at 50 °C and 70 °C, as described above. The cooled samples were placed onto microscope slides and stained with 0.02 N iodine solution (mixture of I:KI = 1:2), covered with the glass, and observed using a light microscopy (Shanghai Leica Microsystems Ltd., Shanghai, China) at 100-times magnification (Sae-kang & Suphantharika, 2006).

2.5. Thermal properties of starch with different salts

The DSC measurement was performed using a micro-DSC (204-F1, Netzsch, Germany). Salt solution was prepared (0.1 mol/l) and starch was added based on 6% (w/v) starch suspension. The suspension was shaken vigorously before being weighed into the DSC cell. An aliquot of the sample (10 mg) was transferred to the DSC measurement cell, sealed, and its weight recorded. An empty aluminium pan was used as reference. The cells were heated from 40 °C to 95 °C at a rate of 5 °C/min. The parameters included the temperature at which the gelatinization process began (T_o), the peak temperature (T_p), the conclusion temperature (T_c), and the gelatinization enthalpy (ΔH) (Ahmad & Williams, 1999).

2.6. Transparency

Light transmittance (%) of the starch pastes was measured using the method described by Craig, Maningat, and Seib (1989). A 2% (w/v) aqueous suspension of starch with different salts, respectively, was heated in a boiling water bath for 30 min with constant stirring. The dispersion was cooled to 25 °C. Samples were stored for 5 days at 4 °C and transmittance (%) was measured every 24 h at 640 nm against a water blank, with a UV/VIS spectrophotometer (Tianjin Precision Instrument Co., Tianjin, China) (Craig et al., 1989).

2.7. Statistical analysis

All experiments were replicated three times. Results 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 for Windows, SPSS Inc, Chicago, IL, US). Differences among the mean values of various treatments were analyzed using Duncan's multiple range test ($p < 0.05$).

3. Results and discussion

3.1. Swelling power and Solubility

The swelling power of starch indicates the ability of water absorption of starch granules during starch swelling. Fig. 1 presents the swelling power and solubility of potato starch with different salts. The addition of salts significantly ($p < 0.05$) changed the swelling power (Fig. 1a) and solubility (Fig. 1b) of the potato starch. For the anions, the swelling power and solubility decreased in the order of $\text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- \approx \text{Control} > \text{SO}_4^{2-} > \text{F}^-$. For cations, the order was $\text{Li}^+ > \text{Na}^+ > \text{Control} > \text{K}^+$ (Fig. 1). Both were consistent with the Hofmeister series.

The ions in this experiment all belong to the Hofmeister series. The descending order of the Hofmeister series of ions is related to an increasing polarity and intensity of charge on the surface of the ion (Khairy, Morsi, & Sterling, 1963). For monatomic ions, such as I^- , Br^- , Cl^- , F^- , Li^+ , Na^+ , K^+ , the larger the diameter, the greater polarization, as well as the greater influence on the water and

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