1. Introduction

Potato starch is unique among other starches and has been widely used in the food industry (Yusuph, Tester, Ansell & Snape, 2003). Potato starch contains high levels of phosphorus, low gelatinization temperature as well as a high water-binding capacity (Noda et al., 2006; Wiesenborn et al., 1994; Zaidul et al., 2008). However, potato starch also has its own shortcomings, e.g. poor heat and shear stability of the swelling granules in the producing process, etc. Now a lot of researches have shown that blends of starches and hydrocolloids have been used in food processing to modify and control the stability and quality of the products (Appelqvist & Debet, 1997; Baranowska et al., 2008). Researches have indicated that the viscosity of different kinds of starch pastes was greatly enhanced by adding a small amount of hydrocolloids (Achayuthakan & Suphantharika, 2008; Lee et al., 2002; Rosell et al., 2011; Sae-kang & Suphantharika, 2006). Some studies reported the starch/hydrocolloid combinations exhibited a phase-separated microstructure, mutual exclusion of amylase and gum as a result of their increased concentration in each microdomains respectively (Biliaderis et al., 1997), thus bringing a significant increase in the viscosity of the combinations. Some other researches showed that the stable hydrogen bonds could be formed between the gum and the soluble amylase of the starch granules, leading to the large enhancement in the paste viscosity when starch heated in the gum dispersions.

However, what the differences from other starches were that the pasting viscosity of potato starch was obviously reduced by negatively charged hydrocolloids (carageenans, CMC, xanthan gum), but increased by neutral hydrocolloids (guar gum) (Shi & BeMiller, 2002). Much less work had been carried out on the effect of hydrocolloids on the pasting properties of potato starch, the electrostatic interactions effect on the pasting and the microstructures of potato starch/hydrocolloid combinations also have not been presented by these authors.

The main objective of this paper is to gain an insight into the effect of electrostatic interactions on pasting properties of potato starch (negatively charged starch)/xanthan gum (negatively charged hydrocolloid) combination. The zeta potential and micro-phase separation of the combinations were determined by the measurement of a Malvern Zetasizer, and the microstructures of potato starch granules mixed with hydrocolloids were analyzed by scanning electron microscope (SEM).
2. Materials and methods

2.1. Materials

Potato starch (moisture: 18.4%, m/m) was produced by Beidahuang Potato Industry Group (Hei Longjiang, P. R. China). And Xanthan gum (moisture: 9.5%, m/m) was provided from Danisco (China) Co., Ltd.

2.2. Preparation of modified potato starches

2.2.1. Preparation of cationic potato starch

Cationic potato starch was prepared according to the method described by Kuo and Lai (Kuo & Lai, 2007). Native potato starch (100 g, dry basis) was suspended with 150 ml water in a bottle (40% w/w dry basis), then been mixed with 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (Dow Center, 4.34 g, 5.79 g, 7.24 g for CP1, CP2, CP3, respectively) which had been adjusted to pH 11.5 with 5 mol/L NaOH. Besides the mixture was adjusted to pH 11 with 2 mol/L NaOH and reacted at 45 °C for 2 min, then maintained rotation speed of 160 r/min. The mixture was neutralized with 4.8 mol/L HCl. The cationic potato starch was washed by 63% (v/v) ethanol several times until free of chlorides in washing solution. The final cationic starch was dried at 40 °C and saved.

2.2.2. Nitrogen content

The determination of nitrogen content of starch was according to the Kjeldahl method described by AACC (2000).

2.2.3. Preparation of anionic potato starch

Mono-phosphorylation of potato starch was performed by using the dry method based on the sodium tripolyphosphate (STP) (Sinopharm Chemical Reagent Co. Ltd) (Landerito & Wang, 2005). Prior to phosphorylation, different amounts (3 g, 4 g or 5 g) of STP were dissolved in 20 mL water and the pH was adjusted to 6, then STP solution added into the 100 g starch by spraying. Spraying by starching for 30 min at an ambient temperature to achieve homogenous mixing. The starch cake was dried in an oven at 40 °C to decrease its moisture content to 20–25%. Then the mixture was kept at 130 °C with stirring for 3 h. After cooling to 25 °C, the product was washed by water several times and the supernatant was decanted. The final product was dried at 40 °C in the oven.

2.2.4. Phosphorus content

The determination of phosphorus content of anionic potato starch was according to a standard method described by ISO 3946 (1982).

2.3. RVA pasting properties

Pasting properties of 6% w/w (dry basis) combinations at different ratio (PS:XG was 1280:1, 320:1, 160:1, 80:1, 40:1, 20:1, 10:1) were determined using rapid visco-analyzer (Model RVA-4C, Newport Scientific Pty. Ltd., Warriewood, Australia). In the case of combinations, xanthan gum was firstly dispersed in distilled water with stirring, and PS was added into XG solution. Test profile was programmed according to the general pasting method (STD 2). The slurry was held at 50 °C for 1 min, heated to 95 °C within 7 min 30 s and then held at 95 °C for 5 min, then subsequently cooled to 50 °C within 7 min 30 s and held at 50 °C for 2 min, while maintaining rotation speed of 160 r/min.

Pasting properties of 6% w/w AP, CP and CP/XG or AP/XG (starch: gum was 80:1) were also determined by the same profile.

2.4. Measurement of Zeta potential

0.1% w/w (dry basis) of PS and combinations (PS:XG was 80:1) were put into centrifuge tubes and been heated in a boiling water bath for 30 min under minimum shear condition. In this work, zeta potential and conductivity were measured using a Malvern Zetasizer (Malvern Zetasizer Nano ZS, Malvern Instruments Ltd., Worcester, UK). The measurement of zeta potential was calculated based on the Henry equation as follow:

\[ \gamma = 1.5U_e \eta / \varepsilon \epsilon_0 K_a \]  

(1)

Where \( \gamma \) is zeta potential, \( U_e \) is the relative magnitude of electrophoretic mobility, \( \varepsilon \) is dielectric constant, \( \eta \) is the viscosity of the medium, and \( f (K_a) \) is Henry function (Mirhosseini et al., 2008).

2.5. Scanning electron microscopy (SEM)

6% w/w (dry basis) of PS and combinations (PS:XG was 80:1) were put into centrifuge tubes and been heated in a water bath at temperatures of 50 °C, 60 °C, 65 °C, 70 °C, 80 °C and 95 °C for 10 min under minimum shear condition respectively. For the SEM observation, the samples were freeze-dried and mounted on aluminum nails then coated with gold-palladium. The morphology of all specimens were observed by scanning electron microscope (Quanta-200, Holland) at 600× magnification.

2.6. Statistical analysis

All measurements were carried out using at least three times. Analysis of variance (ANOVA) and Tukey’s test were used to conduct the statistical analysis of the results. The statistical analyses were performed using SPSS version 12.0 for Windows program (SPSS Inc., 1998, Chicago, IL, USA). Significant differences were reported for p ≤ 0.05.

3. Results and discussion

3.1. Pasting properties of potato starch and potato starch/xanthan gum combinations

The pasting curves of PS and combinations of various mixing ratios determined were shown in Fig. 1. Pasting properties of PS were greatly affected with the addition of XG. With the addition of different proportions of XG, peaks and breakdown viscosities reduced, but the pasting temperature increased.

When the ratios of combinations were 1280/1, 640/1, 320/1, 160/1 or 80/1 (m/m) respectively, a significant decrease in peak viscosity of combinations with adding XG. The strong electrostatic repulsion, which was existed between the negatively charged phosphate group of PS and the negative charges of the side chain of XG molecule, caused XG molecule attach to the surface of starch granules rather than penetrate through PS granules (Chaisawang & Suphantharika, 2006). Under this situation, XG inhibited the expansion of starch granules and leach of amylose. The starch granule shapes were remained, making it difficult to gelatinization. When the ratio for XG up, the amount of XG which was attached to the surface of PS granules also added continually, while the inhibitory

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Fig. 1. RVA pasting profiles of 6% w/w PS and different mixing ratios of 6% w/w PS/XG combinations.
effects on the expansion of starch granules would strengthened continually (Chantaro & Pongsawatmanit, 2010). Furthermore this can also indicate a significant decrease in the breakdown of viscosity and increase in pasting temperature of combinations.

In contrast, with increasing proportion of XG, that was, when the ratios were 40/1, 20/1 or 10/1, XG played an important role in the system and the peak viscosity of the combinations was gradually raised. So a high content of XG would have a good water-soluble as to make the initial viscosity raise and the curve of combinations shift up (García-Ochoa et al., 2000). However, the strong electrostatic interactions between the PS granules and XG molecules, it was still difficult to gelatinization for starch granules, the peak viscosity of combinations was always lower than PS.

From the ratios of 80/1, 40/1, 20/1 or 10/1 pasting curves, a shoulder in the pasting peak of starch could be detected in combinations by RVA and the size of the shoulder grew with the increasing proportions of XG. However, this result had some different with the former results, which Liu and Eskin reported this shoulder could be illustrated that starch gelatinization consisted in two stages, the first stage was about starch swelling process and the second stage was the large changes in viscosity of starch. However, the first stage was not detected with the viscograph (Liu & Michael Eskin, 1998) but could be done with the oscillatory rheometer (Rosell, Yokoyama, & Shoemaker, 2011). The increase of viscosity in the first stage was for the interactions between XG, leached molecules and primarily amyloses (Shi & BeMiller, 2002). The shoulder of combinations pasting curves also could be detected by RVA that depend on the starch origin and the ratio of starch and hydrocolloid.

3.2. Analysis and regression model of RVA pasting properties

Peak viscosity, breakdown and pasting temperature all play a crucial role in the product processing of food industry. These pasting properties depended on XG concentrations in the system as showed in Fig. 2. Linear regression was conducted to relate these pasting properties with different proportions of XG to predict response/dependent variables (Y: Peak viscosity, breakdown or pasting temperature) from a set of explanatory/dependent variables (X: XG). The linear regression analysis yielded Eqs. (2) (3) (4) for pasting properties respectively:

\[
\begin{align*}
\text{Peak viscosity} &= 310 \exp(-50.97X_{\text{an}}) + 1317 \exp(0.8795X_{\text{an}}) \\
R^2 &= 0.9982 \\
\text{Breakdown} &= 2701 \exp(-63.83X_{\text{an}}) + 171.1 \exp(1.974X_{\text{an}}) \\
R^2 &= 0.9975 \\
\text{Pasting temperature} &= 6.62 \sqrt{X_{\text{an}}} + 67.53 \\
R^2 &= 0.9883
\end{align*}
\]

where \(X_{\text{an}}\) = xanthan gum concentration (0–0.6%).

It could be indicated by the corresponding correlation coefficient \(R^2\) and small value of the root mean square error (RMSE = 61.36) that a good predictability of pasting properties at different proportions of XG between the modeling dataset and testing dataset was achieved (Chantaro & Pongsawatmanit, 2010). And it was also can be drawn that there were electrostatic interactions between combinations and XG. Furthermore, these models could be used to predict and control the pasting properties of PS/XG-based products (Pongsawatmanit & Srijunthongsiri, 2008).

3.3. Pasting properties of cationic or anionic potato starch with or without xanthan gum combinations

To investigate further effect of electrostatic interactions on pasting properties of PS/XG combinations, Pasting properties of three CP with different contents of positive charges (The nitrogen contents of CP1, CP2, CP3 were 0.17, 0.24, 0.33 mg/100 g starches (dry basis), respectively.) with and without XG additions were depicted in Fig. 3, respectively.
Fig. 3. RVA pasting profiles of 6% w/w CP (CP1, CP2 and CP3) and 6% w/w CP/XG (CP1/XG, CP2/XG and CP3/XG) combinations (starch:gum was 80:1).

Fig. 4. RVA peak viscosity (a) and pasting temperature (b) of 6% w/w CP (CP1, CP2 and CP3) and 6% w/w CP/XG (CP1/XG, CP2/XG and CP3/XG) combinations (starch:gum was 80:1).

Fig. 5. RVA pasting profiles of 6% w/w AP (AP1, AP2 and AP3) and 6% w/w AP/XG (AP1/XG, AP2/XG and AP3/XG) combinations (starch:gum was 80:1).

Fig. 6. RVA peak viscosity (a) and pasting temperature (b) of 6% w/w AP (AP1, AP2 and AP3) and 6% w/w AP/XG (AP1/XG, AP2/XG and AP3/XG) combinations (starch:gum was 80:1).
increased. When the positive charges of CP increased to a certain extent, electrostatic attractions between positive charges on the surface of starch granules and negative charges on the XG molecules played a major role, XG molecules could penetrate the starch granules, which promoted the expansion of starch granules and leach of amylose. XG molecules were interaction easily with the leaking soluble amylose from CP granules, so as to increase of the concentration of mobile phase system which made the enhance of viscosities of the CP/XG combinations (Chaisawang & Suphantharika, 2005). Because of the ion bridging of the opposite charges of CP and XG made water access to starch granules easily, leading to the decrease of pasting temperature of CP/XG.

Pasting properties of three AP (The phosphorus contents of AP1, AP2, AP3 were 0.17, 0.22, 0.29 mg/100 g starch (dry basis), respectively.) with and without XG additions were also depicted in Fig. 5, respectively. Statistical analyses of peak viscosity and pasting temperature were also performed in Fig. 6. Compared with PS, peak viscosity of AP/XG was significantly reduced, moreover, the difference value of peak viscosity between AP/XG and AP was larger with increasing the content of negative charged of AP. When heated, hydrogen bond between starch molecules was weakened, irreversible granular swelling occurred leading to the enhancement of viscosity. When the content of negative charges rose in AP, the repulsive interaction between AP and XG was greatly strengthened and much higher than hydrogen bond, which intensified the strength and integrity of the structure of starch granule, resulting in an increase of pasting temperature of AP.

3.4. Zeta potential results

In general, the hydrocolloids were usually stabilized by repulsive force. Steric repulsion and electrostatic repulsion were two important repulsive forces. The electrostatic interactions between the same ionic charges of the particles would repel each other and there was dispersion stability. Zeta potential could be used as a good measure of the electrostatic repulsive force, which could give a prediction of the potential stability of the hydrocolloids system and also could

<table>
<thead>
<tr>
<th>Samples</th>
<th>Zeta potential (mV)</th>
<th>Conductivity (mS/cm)</th>
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<tbody>
<tr>
<td>PS</td>
<td>$-35.3 \pm 0.26^a$</td>
<td>$0.00743 \pm 0.0004^a$</td>
</tr>
<tr>
<td>XG</td>
<td>$-69.3 \pm 0.49^a$</td>
<td>$0.00878 \pm 0.0011^a$</td>
</tr>
<tr>
<td>PS/XG</td>
<td>$-54.6 \pm 0.40^b$</td>
<td>$0.01210 \pm 0.0022^b$</td>
</tr>
</tbody>
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Table 1: Zeta potential values of 0.1% w/w PS (a), 0.1% w/w PS/XG combinations (mixing ratio = 80/1) (c) and xanthan gum without starch as control (b) in water.
Fig. 8. Scanning electron micrographs (SEM) of potato starch with and without XG: (a)–(f) PS for 50, 60, 65, 70, 80, 95 °C respectively; (g)–(l) PS/XG combinations for 50, 60, 65, 70, 80, 95 °C respectively.
help get the stable formulation for the production (Mirhosseini, Tan, Hamid, & Yusof, 2008). Regularly, if the particles had large negative or positive zeta potential values, the system was considered to be stability and anti-cohesive. (Genovese & Lozano, 2001).

The zeta potential and conductivity of native PS with and without XG additions were summarized in Table 1. XG solutions without starch were also run under the same conditions for control. It could be observed that the zeta potential value of combinations was significant higher than PS alone, which illustrated the combinations had more electromegativity, stability and difficult to retrogradation. Two possible reasons were proposed: (a) It would enhance the electrostatic repulsive force between PS granules when added XG which had negatively charged side chains; (b) XG molecules which was added to the system reinforced the steric repulsion.

From zeta potential distribution (Fig. 7 (a) and (b)), PS and XG had only one peak, respectively, while the combinations had two peaks whose area ratio was about 2:1, but the mixing ratio for the combinations was 80:1 (Fig. 7 (c)), it would prove that the combinations to be phase-separated, with the hydrocolloid which interacted with leached amyllose and low molecular weight amyllopectins located in the continuous phase, and starch fragments located in the dispersed phase (Mandal & Bayas, 2004). These interactions between starch and hydrocolloid resulted in the more stability in the combinations than PS alone.

3.5. Morphological structures of potato starch and potato starch/xanthan gum combinations

At 50 °C, the larger PS granules were oval or shell-shaped, the smaller ones were round. Some of starch granules had been started to absorb water and swollen slightly (Fig. 8 (a)). XG molecule was a helix conformational which had some degree of flexibility, polysaccharide chains cross-linked with each other to produce a wound rod-like structure of the complex network. PS granules embedded in the network structure of XG, the size of which was much smaller than PS only (Fig. 8 (g)). At 60 °C, most of PS granules were destructed and lost their original structures, (Fig. 8 (b)). With the presence of XG, PS granules did water absorbed only so that the shapes were not destructed, these granules contacted with each other and got together, thus gelatinization phenomena did not happen (Fig. 8 (h)). At 65 °C, most of PS almost completely gelatinized (except for some smaller granules) and connected into a sheet structure (Fig. 8 (c)). In the combinations (Fig. 8 (i)), the swelling of starch granules got to the maximum, XG film attached to the surface of the starch granules. This phenomenon inhibited the destruction of starch granules and leaching of amylase, this result was in accordance with the pasting characteristics that the addition of XG may lead to a increase of pasting temperature and a significant decrease of peak viscosity as well as the breakdown of the PS.

At 70 °C, starch molecules curled randomly, the stiffness of starch was reduced by the further hydration and heating, thus the starch molecules which can not resist mechanical or thermal cutting power became so (Fig. 8 (d)) (Ratnakaye & Jackson, 2007). From Fig. 8 (j), PS interacted with XG became a certain form of network structure. At 80 °C, gelatinized starch was composed by expansion of starch granules fragments, hydrated starch blocks and dissolved starch molecules. PS had larger mesh opening and did not well-distributed (Fig. 8 (e)). Compared with PS alone, the combinations had tighter mesh opening, and well-distributed (Fig. 8 (k)). At 95 °C, the messy texture and the thin mesh wall of PS paste assuming the PS system to be relatively soft (Fig. 8 (f)). XG interspersed with the soluble amyllose and insoluble amylopectin fragment to form a thick, ordered conformational structure (Fig. 8 (l)). The electrostatic repulsion led to more rigid for combinations. These results implied that XG addition could promote a three dimensional network structure and improve the shear stability of PS pastes.

4. Conclusions

This work clarified that the pasting properties of PS were strongly affected by XG. The strong electrostatic interactions between starch and XG played an important role in the pasting properties. Electrostatic repulsions between PS or AP and anionic XG reduced the pasting peak viscosity, but increased the pasting temperatures of these combinations greatly. On the contrary, electrostatic attractions between CP and XG showed the opposite effect. The analysis and regression model performance of RVA measurement revealed a good agreement with the experimental dataset, and there was a direct correlation between pasting properties of combinations and the proportions of XG. Zeta potential results showed that the combinations had more electromegativity and stability, also a phase-separated microstructure was exhibited in the combinations. SEM micrographs revealed that XG film attached to the surface of PS granules, which inhibited the destruction of starch granules and leaching of amylase. The electrostatic repulsion leaded to more stability of the three dimensional network structures of combinations.

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References


