Preparation of iron-fortified potato starch and its properties

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Abstract Iron fortification was applied to commercial potato starch by immersion in different concentrations of ferrous sulfate (FeSO_4) aqueous solutions. To determine the impact of iron fortification on the properties of potato starch, all of the starches obtained through the process mentioned above were analyzed for their pasting properties, color, gelatinization properties, and resistant starch content. Results indicated that the iron content markedly increased from 16 to 890 ppm when the potato starch was treated with a FeSO_4 aqueous solution. During iron fortification, pasting properties markedly changed. Peak viscosity and breakdown decreased while peak viscosity temperature increased with iron fortification. Iron fortification caused a little reduced whiteness (slightly lower L^* -value) and enhanced yellowish color (higher b^* -value). In contrast, iron fortification had little influence on the gelatinization temperature and enthalpy. Moreover, no significant change in the resistant starch content was observed due to iron fortification.

Keywords Potato starch · Iron-fortification · Pasting properties · Gelatinization properties · Resistant starch

Introduction

Native starch has small amounts of covalently bound phosphate groups in amylopectin molecules. As compared to other starches, potato starch is known to contain a higher

amount of phosphate (Hizukuri et al. 1970; Hoover 2001; Noda et al. 2008). The phosphorus content of potato starch generally varies from 600 to 1000 ppm. Additionally, it is well-known that, in potato starch, metal cations are attached to the phosphate by ion forces (Kainuma et al. 1976; Md. Zaidul et al. 2007; Noda et al. 2005; Yamamoto et al. 1981). The accumulation of vital cations by potato starch could be useful for a daily diet supplement. It has been revealed that both phosphate and metal cations substantially impact starch pasting properties as measured by an amylograph and the Rapid Visco-Analyzer (RVA). A high degree of phosphate substitution usually enhances the viscosity of starch gels (Hoover 2001; Noda et al. 2004, 2008). A higher level of divalent cations, such as calcium and magnesium, is associated with a lower peak viscosity and breakdown, implying that divalent cation-fortified starch has good viscosity stability (Fortuna et al. 2013; Kainuma et al. 1976; Yamamoto et al. 1981). Potato starches produced in local factories in Hokkaido, the northernmost island of Japan, generally have high concentrations of potassium (500–900 ppm) and low concentrations of other metal cations (Md. Zaidul et al. 2007). In our previous works (Noda et al. 2014, 2015), factory-made potato starches have been treated with a solution containing high levels of divalent cations to improve the viscosity stability of starch gels. We have succeeded in preparing calcium- and magnesium-fortified potato starches by immersion in various concentrations of CaCl_2 and MgCl_2 aqueous solutions, respectively (Noda et al. 2014). We have also reported that calcium-fortified potato starch prepared by immersion in natural mineral water contained an extremely high level of calcium (Noda et al. 2015). Iron is an essential mineral that is necessary for red blood cell formation. Iron deficiency is one of the most widely known nutritional disorders that affects about two billion people

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worldwide (Zimmermann and Hurrell 2007). Review articles regarding iron-fortified foods (Martinez-Navarrete et al. 2002) and crops (Finkelstein et al. 2017) have been published. Dissolved iron is found as ferrous ion (divalent) and ferric ion (trivalent). Because of its low cost and high bioavailability, ferrous sulfate (FeSO_4) has been used frequently as a food additive to prevent iron deficiency in humans. Recently, Rożnowski et al. (2014) obtained potato starch with a higher content of iron (585.8 ppm) by treating the control potato starch with a FeSO_4 aqueous solution. However, they did not investigate in detail the pasting properties of the iron-fortified potato starch and the condition for the reaction of iron fortification. The aim of this study was to prepare iron-fortified potato starch by the immersion of factory-made potato starch in different concentrations of FeSO_4 aqueous solutions and to examine the effects of iron enrichment on starch properties.

Materials and methods

Materials

Native potato starch purchased from Toubu Tokachi Noukouron Starch Factory (Urahoro, Hokkaido, Japan) was used as the control in this study. Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Preparation of iron-fortified potato starch

To prepare the iron-fortified potato starch, the control potato starch (100 g) was suspended in a 0.0125–1% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution (300 ml) and held for 3 h. The supernatant was discarded, and the remaining starch pellet was washed twice with distilled water, and then dried at 20 °C. The obtained starch samples were stored at 4 °C until analysis.

Determination of starch characteristics

For all starch samples examined, the measurements of RVA, differential scanning calorimetry (DSC), color, and content of resistant starch and iron were conducted. The RVA paste viscosity at 4% starch suspension (dry-weight basis, w/w) was determined using an RVA-4 (Newport Scientific Pvt., Ltd., Warriewood, NSW, Australia) as previously reported (Noda et al. 2004). DSC thermal properties at 30% starch suspension (dry-weight basis, w/w) were determined using a DSC 6100 (Seiko Instruments, Tokyo, Japan), in accordance with the procedures of Noda et al. (2004). The color of the starch was measured using color meter NE 4000 (Nippon Denshoku Industries

Co., Ltd., Tokyo, Japan). The lightness (L^* -value), redness-greenness (a^* -value), and blueness-yellowness (b^* -value) were recorded. The resistant starch content (the ratio of resistant starch to total starch) was determined using a Megazyme Resistant Starch Assay Kit, 05/2008 (Megazyme International Ireland Ltd., Co., County Wicklow, Ireland) in accordance with AOAC method 2002.02 (McCleary and Monaghan 2002). To measure the iron content, each starch (2–4 g) was ashed in a muffle furnace for 10 h at 500 °C, and the ash was refluxed in 2.5 ml of 20% HCl. The solution's iron content was analyzed by ICP atomic emission spectroscopy (ICPE-9000, Shimadzu Co., Ltd., Kyoto, Japan) at 238.204 nm. For the representative iron-fortified potato starch and the control potato starch, the content of five minerals—phosphorus, calcium, magnesium, sodium, and potassium—was analyzed. Phosphorus content was analyzed as described previously (Noda et al. 2004), whereas the contents of calcium, magnesium, sodium, and potassium were determined according to the method reported previously (Noda et al. 2005). Measurements of RVA pasting properties, DSC thermal properties, color, and resistant starch were carried out in triplicate, whereas the estimations of minerals were performed only once.

Statistical analysis

Averages of the RVA pasting property parameters, DSC gelatinization parameters, color parameters, and resistant starch content were computed, and Tukey's range tests were conducted to measure variations in these parameters among various concentrations of the FeSO_4 aqueous solution.

Results and discussion

Preparation of iron-fortified potato starch

The iron content of the control potato starch was as low as 16 ppm; therefore, we attempted to prepare iron-fortified potato starches from the control potato starch. First, 100 g of the control potato starch was treated with different amounts of iron, using 300 ml of the FeSO_4 aqueous solution. As shown in Fig. 1, the iron content of the treated potato starches increased drastically with the increase of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration up to 0.1%. Varying $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentrations, from 0.2 to 1%, resulted in a slight increase in iron content in the treated starches (782–890 ppm). We compared the mineral composition of the representative iron-fortified potato starch treated with 0.5% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution with that of the control potato starch. As shown in Fig. 2, the iron-fortified potato starch

Fig. 1 The iron content of the potato starches treated with FeSO₄ aqueous solution

Fig. 2 The content of phosphorus, calcium, magnesium, sodium, potassium, and iron of the control and iron-fortified potato starches

had small amounts of sodium, magnesium, and calcium. Furthermore, potassium, which was the predominant cation of the control potato starch, was not detected in the iron-fortified potato starch. Potato starch is frequently used for various foods, such as instant noodles (Noda et al. 2006); therefore, it is a plausible vehicle for iron fortification. We have succeeded in preparing iron-fortified potato starch by treating factory-made potato starch with a FeSO₄ aqueous solution. The iron-fortified potato starch obtained in this study contained more than fifty times the iron (maximum 890 ppm) as the control potato starch. The molar ratio of iron to phosphorus was 0.616 for the iron-fortified potato starch. The calcium- and magnesium-fortified potato starches were reported to have similar molar ratios of calcium and magnesium to phosphorus, respectively (Kainuma et al. 1976; Noda et al. 2014; Yamamoto et al. 1981). A previous study (Rożnowski et al. 2014) recorded lower iron content (585.8 ppm) of the fortified potato starch, presumably because the phosphorus content of the fortified starch was higher in our study (798 ppm) than in the previous one (688.3 ppm). In a related study of Pietrzyk et al. (2013), treating oxidized potato starch with a 1% (w/w) FeSO₄ solution resulted in an increased content of iron (998.7 ppm). Manifestly higher iron contents (2110–3520 ppm) were reported by Szymonska et al.

(2015), who studied iron-fortified potato starches obtained by immersing in FeCl₃ and Fe(NO₃)₃ aqueous solutions. Thus, it was suggested that treating potato starch with a ferric ion-containing solution enhances the iron content more than that with a ferrous ion-containing solution.

Pasting properties

Pasting properties at 4% starch suspension in the process of heating and cooling with continuous stirring were analyzed using an RVA, and the results of potato starches treated with different concentrations of FeSO₄ aqueous solutions are presented in Fig. 3. The RVA parameters recorded were peak viscosity, breakdown, and peak viscosity temperature. There were vast differences in the peak viscosity (124–279 RVU), breakdown (46–170 RVU), and peak viscosity temperature (78.2–96.1 °C) of all potato starches examined. Parallel to the results of the iron content of treated potato starches, marked reductions in peak viscosity and breakdown, as well as manifest increases in peak viscosity temperatures, were recorded with the increase in FeSO₄·7H₂O concentrations up to 0.1%. Similar values of peak viscosity, breakdown, and peak viscosity temperature of the treated starches were obtained at concentrations of 0.2–1% FeSO₄·7H₂O. It was previously reported that

Fig. 3 RVA pasting properties of the potato starches treated with FeSO₄ aqueous solution. For each RVA parameter (peak viscosity, breakdown, or peak viscosity temperature), bars labeled with the same letter are not significantly different ($p < 0.05$)

fortifying potato starch with calcium (Kainuma et al. 1976; Yamamoto et al. 1981; Noda et al. 2014, 2015) and magnesium (Fortuna et al. 2013; Noda et al. 2014) led to remarkable decreases in peak viscosity and breakdown. Thus, previous and present investigations have confirmed that enriching potato starch with divalent cations (e.g., calcium, magnesium, or iron) results in improved viscosity stability against mechanical shearing. The formation of cross-links between phosphate esters in potato starch by divalent cations would markedly suppress paste viscosity during an RVA or amylograph test. Starch pasting properties would play a crucial role in governing food qualities. As found in our previous report (Noda et al. 2015), pound cakes made from calcium-fortified potato starch with improved pasting properties exhibited good quality in appearance. Iron-fortified potato starch appears to be promising for making food products with desirable characteristics.

Color components

Table 1 shows variations of color components (L^* -value, a^* -value, and b^* -value) of potato starches treated with different concentrations of FeSO_4 aqueous solutions. The L^* -value of all potato starches examined ranged between 92.68 and 95.86, which may be regarded as nearly perfectly white. The L^* -value decreased significantly with an increase of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration up to 0.04%. In contrast, little change in the L^* -value was seen when the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration rose from 0.04 to 1%. There was a large range of the b^* -value (1.15–9.33), while the range of the a^* -value was narrow (–0.04 to –0.75). The a^* -value was reduced significantly but slightly with the enhancement of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentrations up to 0.1%. Little difference in the a^* -value was found as the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration was raised from 0.1 to 1%. The b^* -

value increased sharply with the enhancement of the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration up to 0.1%. The b^* -value increased significantly but slightly when the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration rose from 0.1 to 1%. Hence, as compared to the control potato starch, all potato starches treated with a FeSO_4 aqueous solution had slightly reduced whiteness (slightly lower L^* -value) and enhanced yellowish color (higher b^* -value). Supporting this, Pietrzyk et al. (2013) reported that iron fortification resulted in a decreased L^* -value and elevated b^* -value in oxidized potato starch. The yellowish color is specific to ferric ion complexes, which may suggest the existence of trivalent iron in the iron-fortified potato starch. The data are meaningful, due to the fact that the color of potato starch has a strong influence on consumers' choices to purchase food products made from potato starch.

Gelatinization properties

Thermal properties of potato starches treated with different concentrations of FeSO_4 aqueous solutions were measured by DSC, and the results of DSC gelatinization parameters, onset temperature (T_o), peak temperature (T_p), and enthalpy (ΔH) for gelatinization, are presented in Table 2. The T_o , T_p , and ΔH of all potato starches examined varied from 62.6 to 63.6 °C, from 66.7 to 68.0 °C, and from 15.6 to 16.4 J/g, respectively. An increased concentration of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, up to 0.1%, resulted in slight increases in T_o and T_p . Similar values of T_o (63.2–63.6 °C) and T_p (67.6–68.0 °C) of the treated potato starches were observed with treatment at concentrations of 0.1–1% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. All treated potato starches exhibited slightly lower ΔH than did the control starch; however, the difference was insignificant. The data obtained here suggest that iron fortification of the control potato starch only slightly influenced the gelatinization parameters by DSC. Similar results were obtained by Rożnowski et al. (2014), who studied the effect of enriching potato starch with iron on starch gelatinization properties. It was reported that, in potato starch, the fortification of calcium (Noda et al. 2014) and magnesium (Fortuna et al. 2013; Noda et al. 2014) did not strongly influence gelatinization temperature and enthalpy. In common with these, the impact of the fortification of magnesium and iron on gelatinization temperature and enthalpy was not so large in oxidized potato starch (Pietrzyk et al. 2013). Hence, it appears that gelatinization properties of potato starch are not largely altered by the replacement of monovalent cations by divalent cations.

Resistant starch content

Resistant starch has been regarded as the portion of starch that is not digested by amylolytic enzymes in the small

Table 1 The color components of the potato starches treated with FeSO_4 aqueous solution

Starch profiles	L^*	a^*	b^*
Control	95.86 ± 0.36 ^a	–0.04 ± 0.06 ^a	1.15 ± 0.05 ^g
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration (%)			
0.0125	93.64 ± 0.12 ^b	–0.18 ± 0.02 ^a	4.28 ± 0.08 ^f
0.04	92.68 ± 0.03 ^c	–0.41 ± 0.04 ^b	6.46 ± 0.03 ^e
0.1	92.90 ± 0.11 ^c	–0.71 ± 0.03 ^c	7.61 ± 0.04 ^d
0.2	92.74 ± 0.02 ^c	–0.74 ± 0.04 ^c	8.07 ± 0.04 ^c
0.5	92.81 ± 0.03 ^c	–0.75 ± 0.01 ^c	8.65 ± 0.04 ^b
1.0	92.68 ± 0.04 ^c	–0.67 ± 0.04 ^c	9.33 ± 0.03 ^a

The data are averages ± SD of three determinations, and the same letter does not show significant difference among samples at $p < 0.05$

Table 2 DSC gelatinization properties and resistant starch content of the potato starches treated with FeSO₄ aqueous solution

Starch Profiles	DSC parameters			Resistant starch content (%)
	To (°C)	Tp (°C)	ΔH(J/g)	
Control	62.6 ± 0.2 ^c	66.7 ± 0.1 ^c	16.4 ± 0.2 ^a	84.8 ± 0.4 ^a
FeSO ₄ ·7H ₂ O concentration (%)				
0.0125	62.7 ± 0.2 ^{bc}	67.2 ± 0.1 ^{bc}	15.9 ± 0.1 ^a	83.9 ± 0.4 ^a
0.04	63.0 ± 0.2 ^{abc}	67.3 ± 0.1 ^b	16.1 ± 0.3 ^a	83.9 ± 0.4 ^a
0.1	63.4 ± 0.1 ^a	67.7 ± 0.2 ^{ab}	15.9 ± 0.4 ^a	84.8 ± 0.2 ^a
0.2	63.2 ± 0.2 ^{abc}	67.6 ± 0.1 ^{ab}	15.9 ± 0.4 ^a	84.9 ± 0.2 ^a
0.5	63.6 ± 0.1 ^a	68.0 ± 0.1 ^a	15.6 ± 0.3 ^a	84.6 ± 0.2 ^a
1.0	63.4 ± 0.1 ^{ab}	67.9 ± 0.2 ^a	15.9 ± 0.3 ^a	84.8 ± 0.2 ^a

The data are averages ± SD of three determinations, and the same letter does not show significant difference among samples at $p < 0.05$

intestine and enters the large intestine (Englyst et al. 1992; McCleary and Monaghan 2002; Thompson 2000). Resistant starch appears to have beneficial effects on human health, as it possesses physiological functions similar to dietary fiber. In this study, each raw starch was subjected to degradation by pancreatic α -amylase and amyloglucosidase for 16 h at 37 °C to analyze the resistant starch content. The results of resistant starch content of potato starches treated with different concentrations of FeSO₄ aqueous solutions are presented in Table 2. As raw potato starch is normally highly resistant to hydrolysis with amylase, it has a large amount of resistant starch (Englyst et al. 1992; Hoover 2001; McCleary and Monaghan 2002; Noda et al. 2008). In agreement with the above results, higher resistant starch content (83.9–84.9%) was found in all potato starch samples examined in our present study. In addition, no significant difference in resistant starch content was found among these samples. Our previous study indicated that the fortification of potato starches with calcium and magnesium resulted in no alterations in resistant starch content (Noda et al. 2014). Thus, from our previous and present studies, it is concluded that substituting divalent cations for monovalent cations in potato starch did not impact the resistant starch content. However, contradictory data, which reveal that the hydrolysis rate of raw starch by pancreatic α -amylase was markedly higher in iron-fortified potato starch than in the control potato starch, were reported by Rożnowski et al. (2014). Additionally, Fortuna et al. (2013) also reported that magnesium-fortified potato starch was more susceptible to enzymatic hydrolysis than was the control potato starch. To reach an evident conclusion concerning the contribution of the substitution of divalent cations for monovalent cations in potato starch to resistant starch content, further research is needed.

Conclusion

Commercial potato starch was immersed in FeSO₄ aqueous solutions to obtain iron-fortified potato starch. The maximum iron content of the fortified potato starch was as high as 890 ppm, whereas the iron content of the control potato starch was 16 ppm. From the RVA data of the fortified potato starches, reduced peak viscosity and breakdown and increased peak viscosity temperature, implying good paste stability, were observed due to iron fortification. Iron fortification slightly decreased starch whiteness and increased its yellowness. The thermal properties measured by DSC revealed that the gelatinization temperature and enthalpy were not largely changed by iron fortification. Resistant starch content was constant during iron fortification. These results suggest that iron-fortified potato starch is an important food material because of its value-added traits, especially improved nutrition and viscosity.

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