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Original Research Article

Preparation of Edible Corn Starch Phosphate with Highly Reactive Sodium Tripolyphosphate in the Absence of Catalyst

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Abstract

Purpose: *To prepare edible corn starch phosphate under optimized experimental conditions.*
Methods: *Edible corn starch phosphate was prepared via the reaction of starch with active sodium tripolyphosphate. Reaction efficiency and viscosity were used as indices to optimize experimental conditions. Freeze-thaw stability and transparency of starch phosphate and native starch were comparatively studied.*
Results: *Starch phosphate with optimal combined phosphate content (0.39 %) was obtained under optimized conditions: reaction duration, 90 min; temperature, 160 oC; pH, 5.0; and phosphate, 1.5 g. Starch phosphate with optimal viscosity (230 cp) was obtained under different conditions: reaction duration, 120 min; temperature, 140 oC; pH, 6.0; and phosphate, 1.5 g. Significant differences ($p < 0.05$) were observed in syneresis and paste transparency of starch phosphate and native starch.*
Conclusion: *Edible corn starch phosphate has been successfully prepared under optimized experimental conditions whose freeze-thaw stability and paste transparency has obvious improvement compared with native starch.*

Keywords: *Starch phosphate, Combined phosphate, Sodium tripolyphosphate, Syneresis, Paste efficiency*

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INTRODUCTION

Starch phosphate, one of the esterified starches, is produced from esterification of starch and phosphate. In food industry, starch phosphate can replace some colloids as thickener and stabilizer used in flour products, meat, soup or drink products because it has high viscosity, freeze-thaw stability and anti-aging resistance [1-3]. Usually, starch phosphate is prepared with phosphate as esterifying agent and urea as catalyst [4,5]. However, the use of harmful urea makes the target product unsuitable for human consumption.

Herein, highly reactive sodium tripolyphosphate (STP) was used as esterifying agent to react with starch to prepare edible corn starch phosphate in the absence of catalyst (urea). Through single factor tests and orthogonal experiments, we confirm the optimized reaction conditions of starch phosphate with the optimal combined phosphate content and that with the optimal paste viscosity. In the meanwhile, paste

transparency and freeze-thaw stability of the prepared starch phosphate and native starch are comparatively studied.

EXPERIMENTAL

Materials

Ordinary corn starch was purchased from Shandong Shou Guang Corn Starch Company. Sodium tripolyphosphate (STP, chemical pure), sodium hydrogen phosphate (analytical pure) and sodium dihydrogen phosphate (analytical pure) were purchased from Shanghai Chemical Reagent Company.

Main equipment

High-speed homogenate machine, Jiangsu Jintan Rong Hua Instrument Manufacture Company; Oven, Xinli Instrument Manufacture Factory; pHs - 3c Precision pH meter, Shanghai Ray Magnetic Instrument Factory; DZF - 6010 vacuum drying oven, Henan Gongyi Yingyu Yuhua Instrument Factory; 752 Ultraviolet grating spectrophotometer, Shanghai Third Analysis Instrument Factory; Micro sprayer, self-made; NDJ - 9 viscometer, Shanghai Shangtian Precision Instrument Company.

Preparation of starch phosphate

A certain quality of STP was dissolved in 10 ml of water and pH value was adjusted to a certain value. The sample was sprayed evenly on to 100 g dried starch after dissolving completely. The mixture was stirred about 30 min in a homogenate machine and the product was obtained after reaction at certain temperature for certain duration. At last the product was washed with water and filtered.

The effects of pH value, reaction temperature, reaction duration and added amount of phosphate on reaction efficiency and viscosity of starch phosphate were examined through single factor experiments. The orthogonal experiments were designed according to the results of single factor tests. The level of design factors are shown in Table 1, choosing L_9 (3^4) to arrange the experiment.

Determination of combined phosphorus content of starch phosphate

The total phosphorus content (phosphorus content of unwashed product) was measured according to GB 12092-89.

Free phosphorus refers to the phosphorus existing in the form of inorganic phosphorus, which mainly comes from the incomplete reaction of esterifying agent with starch. Assay method is as follows: 1.0 ~ 2.0 g sample was put into a 50 ml beaker and dissolved with 1 mol/L hydrochloric acid. And then it was transferred into a 250 ml volumetric flask, diluted with water to volume, shaken well and filtered for use. The filtrate (5~10 ml) was transferred into a 50 ml conical flask. Color reaction was manipulated according to GB 12092-89 and the phosphorus content was determined by measuring the light absorbance.

Combined phosphorus content is the difference between total phosphorus content and free phosphorus content.

Determination of reaction efficiency

Reaction efficiency (RE) was calculated according to Eq 1.

$$RE(\%)=(X1-Y)/(Y1-Y)\times 100 \quad (1)$$

Where X1 = combined phosphorus content of starch phosphate, Y = total phosphorus content of native starch, and Y1 = total phosphorus content of starch phosphate.

Performance test

Viscosity was measured according to GB 12098-89. Freeze-thaw stability (syneresis %) was measured according to literature [6]. Paste transparency was measured according to literature [7].

Table 1: Factors and levels during preparation of starch phosphate

Factor	Reaction duration A (min)	Reaction temperature B (^oC)	pH value C	Added amount of phosphate D (g)
1	60	120	5.0	0.5
2	90	140	5.5	1.0
3	120	160	6.0	1.5

Statistical analysis

The results are reported as mean ± SD (n = 3). Differences were determined using Duncan's new multiple range test. Single factor and other experiments for means and differences were set $p < 0.05$. All data were statistically analyzed using SPSS software (version 12.0; SPSS Inc, Chicago, IL, USA).

RESULTS

Optimized experimental conditions

The effects of added amount of phosphate, pH value, reaction temperature and reaction duration on reaction efficiency and viscosity of starch phosphate are initially determined through single factor experiment and the results are shown in Figures 1 ~ 4. The optimal conditions were as follows: phosphate < 1.5 g; pH: 5.5; temperature: < 160 ^{o}C; reaction duration: < 2 h.

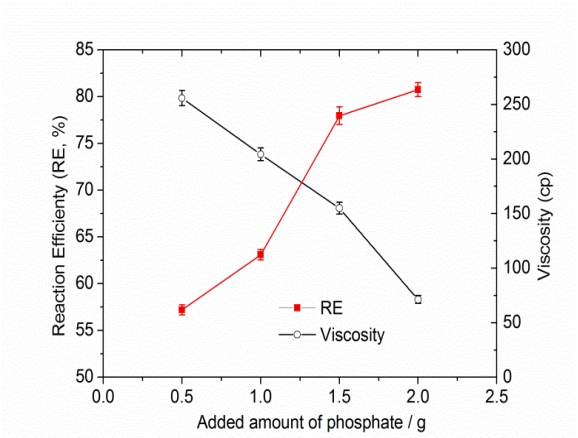

Figure 1: Effect of adde amounts of phosphate on the esterification reaction (pH: 5.5; temperature: 140 ^{o}C; reaction duration: 2 h)

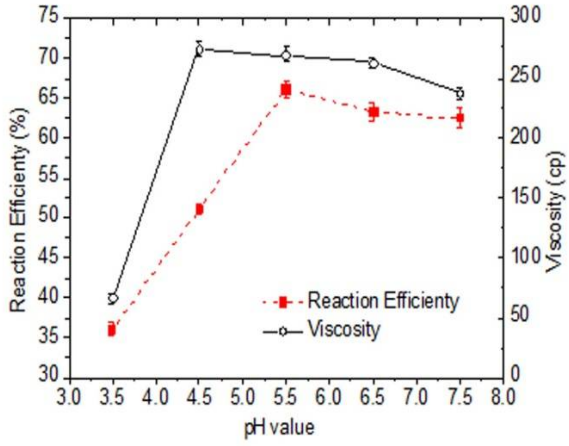

Figure 2: Effect of pH value on the esterification reaction (phosphate: 1.5 g; temperature: 140 ^{o}C; reaction duration: 2 h)

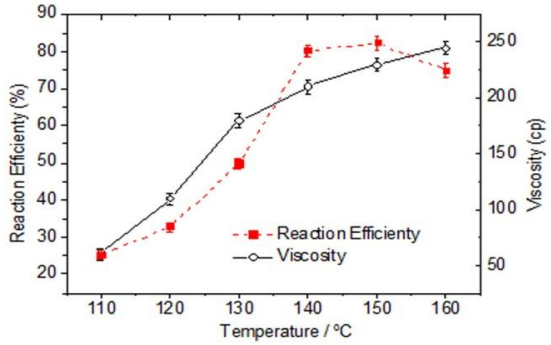

Fig 3: Effect of reaction temperature on the esterification reaction (phosphate: 1.5 g; pH: 5.5; reaction duration: 2 h)

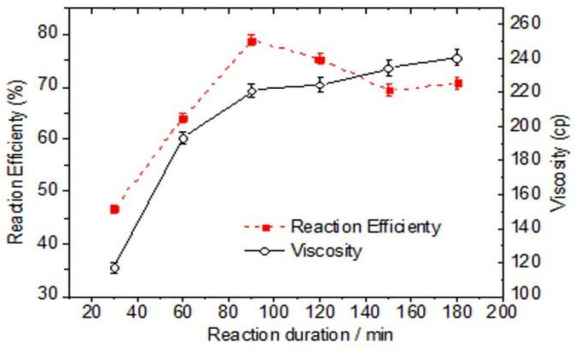

Figure 4: Effect of reaction duration on the esterification reaction (phosphate: 1.5 g; pH: 5.5; temperature: 140 ^{o}C)

The results of orthogonal design experiments are shown in Table 2. Statistically significant differences are observed in the combined phosphate content and viscosity of starch phosphate prepared under different conditions. According to the table, the reaction conditions for starch phosphate with optimal combined phosphorus content (0.39 %) are A2B3C1D3. That is, the reaction conditions are optimized as follows: reaction duration: 90min; temperature: 160 ^{o}C; pH, 5.0; phosphate, 1.5 g. The reaction conditions for starch phosphate with the best viscosity (230 cp) are A3B2C3D3. It means the optimized reaction conditions are as follows: reaction duration: 120min; temperature: 140 ^{o}C; pH, 6.0; phosphate, 1.5 g.

Performance data for phosphates and native starch

Statistically significant differences also occurred in transparency and freeze-thaw stability of starch phosphates prepared under optimal reaction conditions and native starch (Table 3). The results show that starch phosphate has high viscosity, freeze-thaw stability and paste transparency compared with native starch.

Table 2: The orthogonal experimental results of starch phosphate

Experimentno.	Combined phosphate content (%)	Viscosity (cp)
1	0.059 ± 0.002^{e}	53 ± 4.0^{g}
2	0.13 ± 0.005^{d}	110 ± 4.7^{e}
3	0.33 ± 0.007^{b}	208 ± 7.5^{b}
4	0.27 ± 0.006^{c}	195 ± 6.2^{b}
5	0.14 ± 0.006^{d}	85 ± 4.7^{f}
6	0.27 ± 0.007^{c}	160 ± 5.2^{c}
7	0.13 ± 0.004^{d}	150 ± 5.0^{cd}
8	0.39 ± 0.007^{a}	230 ± 7.8^{a}
9	0.14 ± 0.004^{d}	140 ± 4.8^{d}

Table 3: Performance results for starch phosphate and native starch

Variable	Syneresis (%)	Paste transparency (%)	Viscosity (cp)
Native corn starch	65 ± 2.5^{a}	11 ± 0.3^{c}	40 ± 3.2^{c}
Starch phosphate with the optimal combined phosphorus	46 ± 1.9^{b}	28 ± 0.5^{a}	210 ± 7.4^{b}
Starch phosphate with the best viscosity	42 ± 1.8^{b}	24 ± 0.5^{b}	255 ± 8.3^{a}

DISCUSSION

Figure 1 shows that added amount of phosphate (0.5, 1.0, 1.5, 2.0 g) has great influence on reaction efficiency. With the increase of phosphate, the reaction efficiency of starch phosphate is on the decline while the viscosity is increased. When the dosage of phosphate increases from 1.5 g to 2.0 g, the viscosity increases a little while the reaction efficiency decreases much. More importantly, when the added amount of phosphate was 2.0 g, the combined phosphorus content is more than 0.4 %, which is the maximum amount prescribed by the Food and Drug Administration (FDA). And thus, the best addition of phosphate is 1.5 g. The effects of pH value (3.5, 4.5, 5.5, 6.5 and 7.5) were shown in Figure 2. The figure indicates that when the pH value raises from 3.5 to 4.5, the reaction efficiency increased from 39 % to 71 % and the viscosity increases from 40 to 140 cp; when pH raises to 5.5, the reaction efficiency decreases little while the viscosity is as high as 240 cp; when the pH value is greater than 5.5, the reaction efficiency and viscosity tend to decrease. Accordingly, the appropriate pH is about 5.5.

The effects of reaction temperature (110, 120, 130, 140, 150 and 160 ^{o}C) were shown in Figure 3. As can be seen from Figure 3, the reaction efficiency is low under 110 ^{o}C. With the increase of reaction temperature, reaction efficiency is gradually increased. From 110 ^{o}C to 140 ^{o}C, the product viscosity is on the rise. From 140 to 150 ^{o}C, the increase of viscosity is very small and the viscosity decreases at 160 ^{o}C. In addition, when reaction temperature is higher than 160 ^{o}C, the product color will be yellow, affecting the appearance of the starch. Therefore, the appropriate temperature should not be higher than 160 ^{o}C.

Effect of reaction duration (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 hours) was determined and shown in Figure 4. As can be seen from Figure 4, reaction duration and reaction efficiency are positively correlated from 30 min to 90 min. When the reaction duration increases from 90 min to 3.0 hours, the reaction efficiency is increased slowly and the viscosity is decreased gradually. Long reaction duration will also deepen the color of starch phosphates, making unfavorable performance of the final product. For reasons given above as well as the perspective of saving energy, it is advisable to choose the reaction duration not higher than 120 min.

On the basis of single-factor experiments, an orthogonal experiment was carried out. The reaction conditions for the preparation of starch phosphate with optimal combined phosphorus content (0.39 %) are optimized. The reaction conditions for starch phosphate with the best viscosity (238 cp) are the same with the former except for the reaction temperature. The results of transparency and freeze-thaw stability show that the prepared starch phosphates have high viscosity, freeze-thaw stability and paste transparency compared with native starch. And thus, corn starch phosphate is more suitable for use as a thickener in food industry.

CONCLUSION

Starch phosphate with optimal combined phosphorus content (0.39 %) and starch phosphate with the optimal viscosity (255 cp)

have been successfully prepared under optimized reaction conditions. Compared with native starch, corn starch phosphate is more effective as a thickener in food industry because it has great improvement in viscosity, freeze-thaw stability and paste transparency.

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