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Cross-linking starch at various moisture contents by phosphate substitution in an extruder

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Abstract

Starch was extruded with sodium trimetaphosphate and sodium hydroxide in a single-screw extruder with barrel and die temperature of 130 °C at three screw speeds of 40, 90, and 140 rpm and three moisture contents of 40, 55, and 70%. Time required for phosphorylation of starch in an extruder was found to be less than 2 min, and cross-linking of starch by phosphorus, which was incorporated into starch, was confirmed by paste viscosity of extruded starch. Cross-linking starch with 2.5% sodium trimetaphosphate did not significantly affect water absorption index, but reduced water solubility index so replacement of the process including mixing of starch with synthetic polymer in the extruder with another process including cross-linking of starch and then mixing with synthetic polymer can result in composite with lower solubility of starch. On the other hand, increasing moisture content of starch reduced both water absorption and solubility index of extrudates.

Keywords: Carbohydrate; Modification; Residence time; Specific mechanical energy; Water solubility; Absorption index

1. Introduction

Starch is present in food products mainly as a thickener, but there is also interest in the incorporation of starch into plastic products. Starch can be mixed with synthetic polymers in the extruder and the product is shaped in the die. Native starch does not absorb much water, but gelatinized starch does and therefore has undesirable effect on starch containing plastic products. Since modification of starch is important to incorporate it into plastic products without undesirable effect, modification of starch in the extruder perhaps when mixed with a synthetic polymer in the extruder is a potentially interesting way of incorporating it into plastic products.

Rutledge, Islam, and James (1974) found that cross-linking parboiled rice with sodium trimetaphosphate in a batch system improved canning stability and decreased both solid loss and water uptake of rice. Salay and Ciacco (1990), Kim, Do, Shih, Champagne, and Daigle (1999) and Singh, Kaur, Singh, and Sekhon (1999) studied extrusion of starch with phosphate salts at low moisture content which results in increases in solubility of starch (Gomez & Aguilera, 1984), but the effect of moisture content was not reported. The interaction of starch with phosphorus being cross-linking or phosphorylation was not characterized and reaction time was also not reported in the studies cited above. The objective of this study was to determine residence time of starch, that was cross-linked in an extruder, and to determine the effect of moisture content on water absorption and solubility index of starch cross-linked at high moisture contents between 40 and 70% and three extruder screw speeds.

2. Materials and methods

2.1. Sample preparation and extrusion processing

Commercial raw corn starch was granulated by spraying water on to it while tumbling it in a rotating drum, and then

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dried at 40 °C to moisture content of 5–10%, which was determined by an oven drying method (Chinnaswamy & Hanna, 1988). The volume of 0.2 M sodium hydroxide required to bring the pH of a 50% starch solution to pH 10 was determined. Sodium hydroxide described above, 7.5 g sodium trimetaphosphate, and 300 g starch were mixed together. Then, water was added to adjust the moisture content to levels of 40, 55, and 70% (as weight on a dry basis) in a Hobart blender for 5 min.

A C.W. Brabender (Model No. 2802, C.W. Brabender Instruments Inc., South Hackensack, NJ) laboratory single-screw extruder with compression ratio of 3:1, the barrel diameter of 1.90 cm and the screw length-to-diameter ratio of 20:1 was used. Barrel temperatures of the compression and die sections were set to 130 °C and screw speeds were adjusted from medium to highest capacity of extruder as 40, 90, and 140 rpm. Mean residence times were determined according to the method of Seker, Sadikoglu, and Hanna (2004) for each screw speed and moisture content of feed.

Temperature, screw speed and torque were controlled and recorded by a computer interface and controller unit (PL 2000 Controller, C.W. Brabender, New Hackensack, NJ) using a program loader software version 1.95. Flow rate (m, kg/h) was calculated as:

$$m = M_s[(1 - M_e)/(1 - M_f)]60 \quad (1)$$

where M_s is mass of sample collected for min (kg), M_e is moisture content of the extrudate, M_f is moisture content of the feed.

Specific mechanical energy (SME, Wh/kg) was determined by following equation

$$\mathrm{SME} = (T2\pi N)/(m60) \quad (2)$$

where T is torque (N m), N is screw rotation (rpm) and m (kg/h) is flow rate.

2.2. Phosphorylation and selected properties of starch

Soluble phosphates were removed by washing twice with ethanol and water mixture and then drying. Phosphorus content was determined by the method of Smith and Caruso (1964). Paste viscosity of starches extruded with and without STMP and NaOH at screw speed of 40 rpm with 55% moisture content was measured using a Rapid Visco Analyzer (Newport Scientific Pty. Ltd., Warriewood, Australia). A dry extrudate of 3 g was mixed with 25 g water, inserted into a tower/holder of Rapid Visco Analyzer (RVA), and then analyzed according to the following procedure; equilibrated for 5 min at 25 °C, heated to maximum temperature of 95 °C over 5 min, held at this temperature for 10 min, cooled to 25 °C over 10 min, and held at 25 °C for 8 min. Water absorption and solubility index (WAI and WSI) was determined according to the method of Anderson, Conway, Pfeifer, and Griffin (1969).

2.3. Experimental design

Experiments were arranged as randomized complete block design and were repeated on different days as the blocking factor. Treatments, which were designed as factorial of moisture contents and screw speeds, were accepted statistically effective as p is smaller than 0.05 and software of SAS (version 6.0 statistical package, SAS Institute, Cary, NC) was used for statistical analysis. Each measurement was the average of three replicate.

3. Results and discussion

3.1. Phosphorylation

Percentage of phosphorus in starches extruded with NaOH and STMP at screw speeds between 40 and 140 rpm with moisture content between 40 and 70% was shown in Fig. 1, and it was similar to percentage of phosphorus in starch modified with NaOH and STMP in batch system as 0.3% phosphorus (Lim & Seib, 1993). Varying moisture content and screw speed did not result in change in phosphorus content that can be characterized as trend, and percentage change in phosphorus content was not significant under the studied conditions. Our result showed that phosphorus was bound to starch during extrusion in less than 2 min that is lower than the process time in a batch system (Lim & Seib, 1993), that requires drying of starch dispersion and holding at high temperature for 2 h. Graf De, Broekroelofs, Janssen, and Beenackers (1995) stated that granular starch reacts about 400 times slower compared to gelatinized starch, and Burros, Young, and Carroad (1987) reported that starch granules was disrupted physically by shear force during extrusion that results in effective transfer of water into the interior of starch. This would be expected

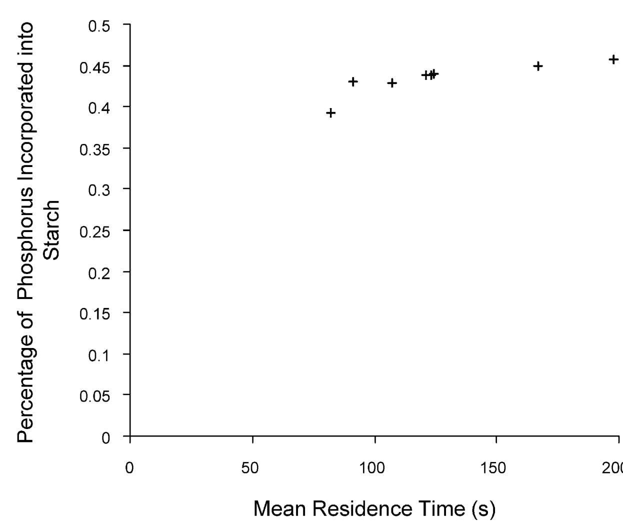

Fig. 1. Percentage of phosphorus incorporated into starches extruded at screw speed between 40 and 140 rpm and moisture content between 40 and 70%.

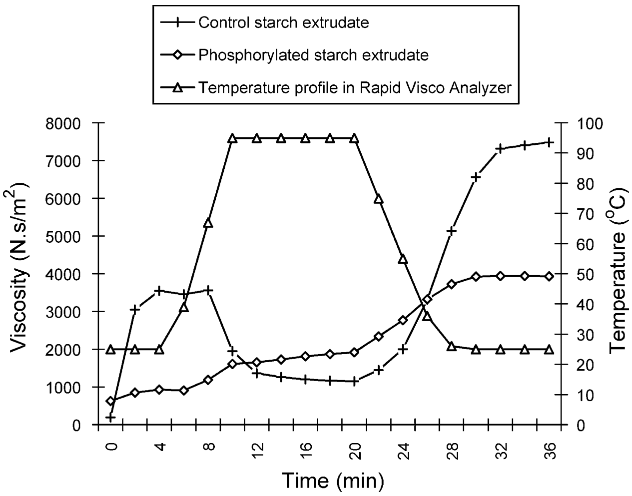

Fig. 2. Paste viscosity of control and phosphorylated starches extruded at screw speed of 40 rpm with moisture content of 55%.

to reduce the reaction time of starch in extrusion reaction compared to batch systems.

3.2. Pasting properties

The pasting properties of starch are analyzed not only for functionality of starch but also for the determination of starch modification. Paste viscosity of starch extruded with STMP and NaOH was compared with the paste viscosity of starch extruded without STMP and NaOH in Fig. 2 which suggests that the starch was cross-linked with NaOH and STMP. Initial and setback viscosity of starch extruded with NaOH and STMP was lower than initial and setback viscosity of starch extruded with NaOH and STMP, but the paste viscosity of starch extruded with NaOH and STMP was reduced during mixing in RVA in a less extent than the paste viscosity of starch extruded without NaOH and STMP was, because extensive cross-linking of starch reduces swelling and viscosity development but increase resistance to shear (Kasemsuvan & Jane 1994; Lim & Seib, 1993).

3.3. Specific mechanical energy

Increasing moisture content from 40 to 70% reduced SME input into extrudates ($p<0.001$) as shown in Table 1. Because water acts as a plasticizing agent, it reduces viscosity and mechanical energy dissipated in the extruder (Ilo, Tomschik, Berghofer, & Mundigler, 1996). Although increasing moisture content reduced SME dissipation into feed, there was exception in the case of increasing moisture content from 40 to 55% at 40 rpm in which flow rate decreased more compared to increase in moisture content at the other screw speeds and increase in flow rate resulted reduction in SME according to Eq. (2). Increasing screw speed slightly raised SME ($p<0.015$), which is proportional to torque and screw speed. Akdogan, Thomas, and Oliveira (1997) and Jin, Hsieh, and Huff (1994) reported that the negative effect of torque on SME was less than the positive effect of screw speed on SME so that increasing screw speed raised SME. Slight increase in SME with increases in screw speed was observed in our study because moisture content of feed was higher in our study.

3.4. Water solubility index

Structural characterization of starch extrudates indicates that process variables like screw speed and moisture content affect macromolecular degradation of starch reflected as change in functional properties of starch like water solubility. Screw speed did not affect water solubility index (WSI), but moisture content of feed did ($p<0.0008$) as shown in Fig. 3. SME is positively related to WSI (Della Valle, Kozlowski, Colonna, & Tayep, 1989). Although effect of screw speed on WSI was not observed because of slight change in SME with change in screw speed, there was exception in the case of increasing screw speed from 40 to 90 rpm at 40% moisture content due to more change in SME with increase in screw speed from 40 to 90 rpm at 40% moisture content. On the other hand, increasing the moisture content of the feed from 40 to 70% reduced WSI of the extrudate because SME was significantly lowered with increase in moisture content. Gomez and Aguilera (1984) and Tang and Ding (1994) found that WSI decreased when feed moisture increased at low moisture content intervals, and Govindasamy, Campanella, and Oates (1996) found the same trend at moisture contents between 35 and 50%.

WSI of starch extruded without STMP and NaOH as control sample was higher than the starch cross-linked with STMP and NaOH at the same conditions ($p<0.015$). Rutledge, Islam, and James (1972) reported that effect of cross-linking starch was lower leaching of starchy solid material and solid loss, and increase in resistance to rupture in rice. The reduction of WSI of starch with cross-linking

Table 1
Specific mechanical energy (SME, Wh/kg) and water absorption index (WAI) of extrudates at varying moisture content (%) and screw speed (rpm)

Screw speed (rpm)	Moisture content (%)					
	40%		55%		70%	
	SME	WAI	SME	WAI	SME	WAI
40rpm	50.1	6.73	56.7	6.01	24.5	6.01
90rpm	68.7	6.74	57.3	6.30	31.5	5.50
140rpm	77.3	6.72	70.5	6.39	34.7	5.70

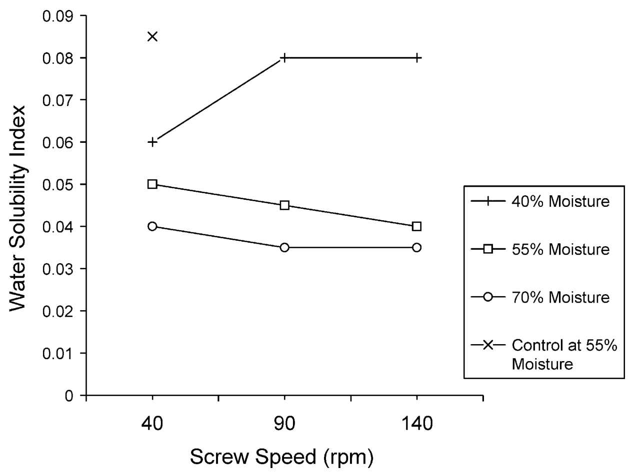

Fig. 3. Water solubility index of extrudates at varying screw speed and moisture content.

could have been a result of increased resistance of cross-linked starch against degradation, lower leaching of starchy solid material, and binding of soluble starch or combination of those factors.

3.5. Water absorption index

Water absorption index (WAI) of the control starch extrudate was not significantly different than the starch, which was cross-linked with STMP and NaOH. On the other hand there was a decrease in WAI when moisture content was increased from 40 to 70% as shown in Table 1 ($p<0.0006$). Gomez and Aguilera (1984) reported that increasing moisture content of starch from 14 to 33% reduced the water solubility index (WSI) from 60 to 7.6% and increased WAI from 4.78 to 7.57%. Undamaged long polymer chains were regarded as a reason for high values of WAI. Water solubility index was reduced from 0.08 to 0.04 when moisture content was increased from 40 to 70%, but water absorption index was also reduced in our study. In addition to the effect of undamaged long polymer chains on WSI and WAI of starch there may be another factor affecting water absorption of starch at higher moisture content intervals.

4. Conclusion

Extrusion of starch with sodium trimetaphosphate and sodium hydroxide resulted in phosphorus incorporation and cross-linking, which was conducted in less than 2 min. Cross-linking of starch in the extruder significantly reduced water solubility index so replacement of process including mixing of starch with synthetic polymer in the extruder with another process including cross-linking of starch and then mixing with synthetic polymer can result in composite with lower solubility of starch. Since, increasing moisture content decreased water solubility and absorption index, starch with lower solubility index can be obtained by cross-linking it at the higher moisture content.

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