

Preparation and Properties of Phosphorylated Sago Starches

Febby J. Polnaya^{1,*}, Haryadi¹, Djagal W. Marseno¹ and Muhammad Nur Cahyanto¹

¹ Post Graduate School of Food Science, Gadjah Mada University,
Jl. Flora Bulaksumur, Yogyakarta 55281, Indonesia

* Faculty of Agriculture, Pattimura University, Jl. Ir. M. Putuhena, Kampus Poka, Ambon 97233, Indonesia

Abstract The effects of the phosphorylation of native sago starch (NSS) on the physicochemical properties of phosphorylated sago starch (PSS) were investigated. PSS1 was prepared by reacting NSS with sodium tripolyphosphate, and PSS2, with phosphorus oxychloride in aqueous alkaline conditions (pH 8, 9, 10, and 11). The PSS was characterized for its phosphorus, ash, protein, fat, and amylose contents, swelling power and solubility, water-holding capacity, and paste clarity. The phosphorylation condition resulted in a decrease in the fat and protein content and an increase in the ash and amylose content. The phosphorus content of PSS1 prepared at pH 9 was higher than that prepared at other pH values, and that of PSS2 prepared at pH 11 was higher than that prepared at other pH values. The swelling power and water-holding capacity of PSS were higher than those of NSS, while the solubility was lower than that of NSS. The paste clarity of PSS1 was higher than that of NSS, and that of PSS2 was lower.

Key words: phosphorylated sago starch, alkalinity, swelling power, solubility, paste clarity, water-holding capacity

リン酸化サゴデンプンの調整と性質

Febby J. Polnaya^{1,*}, Haryadi¹, Djagal W. Marseno¹ and Muhammad Nur Cahyanto¹

¹ Gadjah Mada University, Indonesia and * Pattimura University, Indonesia

要約 リン酸化したサゴデンプン (PSS) の物理化学的性質をリン酸化していないサゴヤシデンプン (NSS) と比較した。PSS1はNSSにトリポリリン酸ナトリウムと、PSS2はアルカリ条件下 (pH8, 9, 10, 11) でオキシ塩化リンと反応させて調整した。PSSの特徴はリン酸・灰分・タンパク質・脂質・アミロース含量、膨潤度、溶解度、水分保持力、透光度から評価した。リン酸化により、脂質やタンパク質含量が低下し、灰分やアミロース含量が増加した。pH9で調整されたPSS1のリン酸含量は他のpH条件で調整された場合より高く、pH11で調整されたPSS2のリン酸含量は他のpH条件で調整された場合より高かった。PSSの膨潤度と水分保持力はNSSよりも高く、溶解度はその逆であった。PSS1の透光度はNSSよりも高く、PSS2のそれはNSSよりも低かった。

キーワード: リン酸化サゴデンプン、アルカリ度、膨潤力、溶解度、透光度、水分保持力

Introduction

Starch is perhaps the most important polymeric carbohydrate in terms of its functionality imparted to products in diverse industries. Nowadays, the new-

product development areas in those industries are searching for starches with improved functionality, such as solubility, viscosity, syneresis tendency, and low retrogradation. The utilization of native starch has

some disadvantages because the conditions of the process (e.g., temperature, pH, pressure, and shear stress) limit its use in industrial applications. These shortcomings may be overcome by starch modification using chemical, physical, and enzymatic methods (Fleche 1990). A chemically modified starch is obtained when native starch is treated with a specific reagent to change some of its properties.

Native starch generally contains small amounts (< 0.1%) of phosphorus (P). In root and tuber starches, P is covalently linked to the starch (Hizukuri et al. 1970; Hodge et al. 1948). Phosphorylated starches, which are prepared by chemical methods, have been reported to give clear pastes of high consistency, with good freeze-thaw stability and emulsifying properties (Kerr and Cleveland 1962, Lloyd 1970).

Phosphorylated starches may be grouped into two classes, i.e., monostarch phosphate (MSP) and distarch phosphate (DSP, cross-linked starch) (Lim and Seib 1993a). In DSP, a very low level of substitution can drastically alter the paste and gel properties of starch, making it very different from MSP (Yoneya et al. 2003).

The reaction of wheat starch or corn starch with sodium tripolyphosphate (STPP) at below pH 9 results in MSP, while the reaction at pH > 10 results in DSP (Lim and Seib 1993a). Probably, the reactions at pH 9-10 result in PSS containing both monostarch ester and distarch ester. For this reason, the modified sago starch in this study is named PSS1.

DSP can also be prepared by reacting starch with phosphorus oxychloride (POCl₃) at pH > 10 (Haryadi and Kuswanto 1996, Wattanachant et al. 2002, Yoneya et al. 2003). However, in this study, the result is named PSS2, since monostarch ester is possibly also formed.

The objective of this study was to investigate the effect of the reaction of sago starch with STPP or POCl₃ at pH 8, 9, 10, and 11 on the properties of PSS.

Materials and Methods

Materials

The native sago starch (NSS) was donated by PT. Tiga Pilar, Indonesia. The starch was stored in a high-density polyethylene bag before analysis and phosphorylation with STPP or POCl₃. POCl₃, amylose, NaOH, HCl, and Na₂SO₄ were purchased from Merck, while STPP was obtained from local market and was food grade. All chemicals for analyses were analytical-grade.

Proximate analysis

Standard AOAC methods (Association of Official Analytical Chemists 1984) were used for the measurement of moisture, ash, protein, and fat content. The moisture content (% w/w) was assayed by loss in weight on drying at 105 °C for 5 hr in a hot air oven (Mettler, Germany). The ash (% w/w) was determined by incineration of a known sample weight in a muffle furnace (Lenton Furnaces, UK). Starch was burnt in a furnace overnight (12 hr) at 550 °C and cooled down in desiccators. The protein content (%) was estimated from the nitrogen content by the Kjeldahl method multiplied by 6.25. Fats were Soxhlet-extracted with petroleum ether (40-60 °C).

Determination of amylose

Amylose in the starch samples was determined according to the colorimetric procedure of the Association of Official Analytical Chemists (1984). Starch (0.1 g, dry basis) was accurately weighed and dissolved by heating in 1 ml 95% ethanol and 9 ml 1 N NaOH for 10 min in a water bath at 100 °C to reach gelatinization. After the solution had dissolved, it was diluted to 100 ml in a volumetric flask with distilled water. An aliquot (5 ml) of this solution was diluted to 100 ml using distilled water. 1 N acetic acid (1 ml) and 0.2% iodine (2 ml) were added and mixed, and the absorbance of this solution was read at 620 nm using a UV-Vis 1601 Spectrophotometer (Shimadzu, Japan). Standard amylose at different concentrations of solutions was prepared. The amylose content in the starch samples was determined using the prepared standard amylose graph.

Preparation of phosphorylated starch

Phosphorylation with STPP

In this study, the phosphorylation with STPP was affected at pH 8, 9, 10, and 11, since earlier studies had reported that the reaction of starch with STPP at pH < 9 resulted in MSP while that at pH > 10 resulted in DSP (Lim and Seib 1993a).

Starch was phosphorylated according to method of Lim and Seib (1993a). Sodium sulfate was used in all reactions. The entire slurry was dried to less than 15% moisture content before reaction at high temperature.

Fifteen grams of STPP was dissolved in 300 ml of water containing 15 g of sodium sulfate. The pH of the solution was adjusted to 8, 9, 10, and 11 by adding 10% aqueous HCl or NaOH. Starch (300 g) was dispersed in the solution. The pH of the dispersion was then readjusted with 5% aqueous HCl or NaOH, and the total weight was brought to 667 g by adding water. The starch solids in the flowable dispersion amounted to 45%. The slurry was stirred for 1 hr at room temperature and dried to 10-15% moisture at 40 °C in a forced-air oven. To affect phosphorylation, the dried starch cake in the dish was heated for 2 hr at 130 °C in a forced-convection oven. After being cooled to room temperature, the reaction mixture was dispersed in distilled water (350 ml), and the pH of the dispersion was recorded. The starch was recovered by centrifugation (3,500 rpm, 10 min) and redispersed in 600 ml of distilled water. The dispersion was adjusted to pH 6.5 with aqueous 5% HCl or 5% NaOH solution. The starch was washed with water (600 ml × 4) and dried overnight at 40 °C in a cabinet drier.

Phosphorylation with POCl₃

The cross-linking with POCl₃ is usually conducted at pH > 10. In this study, the phosphorylation was affected at pH 8, 9, 10, and 11 to compare the efficacy.

PSS2 was synthesized on the basis of the method of Felton and Schopmeyer (1943). Sago starch (50 g, dry basis) was slurried in water (70 ml) containing sodium sulfate (7.5 g), and the pH was adjusted to 8, 9, 10, and 11 by adding 1.0 M NaOH. Then, POCl₃ (4% starch basis) was added drop-wise to the starch slurry

over a period of 20 min, and the pH of the reaction mixture was kept constant by periodically adding 1.0 M NaOH. The starch dispersion was stirred for 1 hr at room temperature and then adjusted to pH 6.5 with 1.0 M HCl. The starch was recovered by centrifugation (3,500 rpm, 10 min), washed with water (100 ml × 4), and dried overnight at 40 °C in a cabinet drier.

Phosphorus content

The phosphorus content of PSS samples was determined according to the method given by Smith and Caruso (1964). For the phosphorus analysis, a 10 g sample was weighed into a dish, and 10 ml of a zinc acetate solution (10%, w/v) was added. The solution was evaporated to dryness in a steam bath and a hot plate, followed by burning into ash in a muffle furnace at 550 °C for 2 hr. After cooling, the dish was wetted with three ml of nitric acid solution (29%, w/v), evaporated to dryness in a steam bath and a hot plate, and then placed into a muffle furnace at 550 °C for 30 min. After cooling, the dish was washed with 10 ml of a nitric acid solution (29%, w/v) and 15 ml water. This solution was heated to boiling and held at that temperature for 10 min. After cooling, it was filtered. The filtrate was diluted to obtain an aliquot containing less than 2.5 mg of phosphorus. Then, 10 ml of nitric acid (29%, w/v), 10 ml of ammonium vanadate (0.25%, w/v), and 10 ml of ammonium molybdate (5%, w/v) were added to the aliquot. After mixing and allowing the mixture to stand for 10 min, absorbance was measured at 460 nm with a UV-Vis 1601 Spectrophotometer. The phosphorus contents of the samples were determined from a calibration curve prepared from samples containing a known amount of phosphorus.

Swelling power and solubility

The swelling power and solubility of modified sago starch were determined by the method of Adebowale et al. (2002). A starch sample (1.0 g) was accurately weighed and quantitatively transferred into a clean dried test tube and reweighed (W_1). The starch was then dispersed in 50 cm³ of distilled water. The resultant slurry was heated at 95 °C for 30 min in a water bath.

The mixture was cooled to 30 °C and centrifuged (3,500 rpm, 15 min). Aliquots (5 ml) of the supernatant were dried to a constant weight at 105 °C. The residue obtained after drying the supernatant represented the amount of starch solubilized in water. Solubility was calculated as g per 100 g of starch on a dry-weight basis. The residue obtained was weighed (W_2).

Swelling of starch (g g^{-1}) = ($W_2 - W_1$) / weight of starch

Water-holding capacity

The water-holding capacity (WHC) was determined by the method of Ju and Mittal (1995). A suspension of 1% starch in 10 ml distilled water was agitated intermittently for 1 hr and centrifuged at 3,500 rpm for 15 min at 25 °C. The free water was decanted, and the wet starch was weighed. The WHC was calculated using the following equation:

WHC ($\text{g H}_2\text{O g}^{-1}$ starch) = (Mass of wet starch – Mass of dry starch) / Mass of dry starch

Paste clarity

The transmittance of a starch paste was measured using the method described by Craig et al. (1989). A starch suspension (2% w/v) in a screw cap tube was placed in boiling water for 30 min and thoroughly shaken every 5 min. The suspension was cooled to room temperature and stored at 4 °C for 72 hr; every 24 hr, the percentage of transmittance at 650 nm was determined against a water blank using a UV-Vis 1601 Spectrophotometer.

Statistical analysis

Analysis of variance at the 95% confidence level was performed using the Statistical Analysis System (SAS) 9.0 software (SAS, Inc.) followed with Tukey's test at $p < 0.05$ to distinguish the differences among treatments.

Results and Discussion

The composition of NSS used in this study is shown in Table 1, which agrees fairly closely with that reported by Muhammad et al. (2000), Polnaya et al. (2008), and Wattanachant et al. (2002).

Phosphorus content of phosphorylated sago starch

The NSS used in this work contained 0.0085% P. A similar result was obtained by Muhammad et al. (2000). The reaction of semi-dry sago starch with 15 g STPP in the presence of 5% sodium sulfate at pH 8, 9, 10, and 11 (130 °C for 2 hr) gave PSS1 containing 0.08, 0.15, 0.12, and 0.10% P, respectively. These results are different from those of Lim and Seib (1993a) at pH 8 to 9, who reported that in STPP phosphorylation of wheat and corn starches, the P level in the modified starches decreased gradually with increasing pH from 6 to 11; but similar trend with those of Muhammad et al. (2000), that in STPP phosphorylation of sago starch at pH 8 to 9; these researchers reported that, in the STPP phosphorylation of wheat and corn starches, the P level in the modified starches gradually decreased with increasing pH from 6 to 11. On the other hand, they show a similar trend as that in the studies of Muhammad et al. (2000), who showed that STPP phosphorylation of sago starch at pH 8 and 9 resulted in an increased P level in the modified starches from 0.134 to 0.224% but a decreased P level at pH higher than 9. These phenomena included a high pH, which possibly resulted in degradation of the substituted anhydroglucose unit, resulting in the lower P level.

In the cross-linking reaction with POCl_3 under alkaline conditions, the hydrophilic phosphorus group

Table 1. Composition of native sago starch employed in this study

Property	This study	Muhammad et al. (2000)	Polnaya et al. (2008)	Wattanachant et al. (2002)
Moisture (% w/w)	12.95 ± 0.11	12.4 ± 0.04	12.54	12.54
Ash (% w/w)	0.27 ± 0.04	0.02 ± 0.01	0.18	0.21
Amylose content (%)	33.12 ± 0.62	25 ± 0.2	27.64	33.23 ^a
Phosphorous content (%)	0.0085 ± 0.001	0.009 ± 0.02	-	-

^a Sugiyono et al. (2008)

reacted immediately with the OH of the starch, producing a PSS2. Cross-linking of banana starch with POCl₃ was reported to have occurred only on the surface of the starch granule (Carmona-Garcia et al. 2009).

The reaction of sago starch with 4% POCl₃ at pH 8, 9, 10, and 11 gave PSS2 containing 0.02, 0.28, 0.29, and 0.35% P, respectively. POCl₃ phosphorylation at pH 8 to 11 increased the total P level in the products by more than 100% (Fig. 1). These phenomena were reasonable, since earlier studies reported that substitution occurred mainly at OH groups attached to C6 of the unhydroglucose unit (Lim and Seib 1993b).

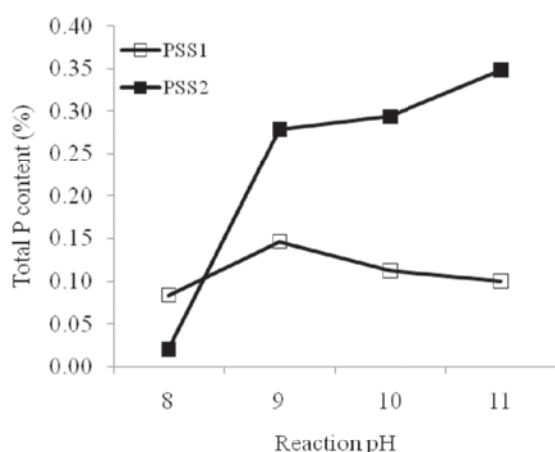


Fig. 1. Effect of initial pH on the total phosphorus content of phosphorylated sago starch prepared using 5% STPP (PSS1) and 4% POCl₃ (PSS2).

On the other hand, reactivity of OH groups attached at C6 is dependent on the alkalinity of the reaction mixture (Wotton and Haryadi 1992).

The attachment of P in starch as a result of modification using POCl₃ was higher than that by using STPP at pH 9 to 11. It is conceivable that POCl₃ gave more P substitution because it had more reactivity than STPP and therefore more phosphorus groups were substituted on the starch chain (Carmona-Garcia et al. 2009).

The total P content of PSS was within the limit (0.4%) specified for food starch by the Joint FAO/WHO Expert Committee (2001). The phosphorus content is not an indicator of the cross-linking degree because some of the substituted starch is in the form of monostarch phosphate. These findings need to be confirmed.

Chemical composition

The procedure of chemical modification applied in the experiment changed the chemical composition of the investigated starches (Table 2).

The ash content of PSS ranged between 0.25 and 1.34%. The ash level increased in the PSS in the order: POCl₃ > STPP. This pattern is likely due to the introduction of some phosphate groups in the

Table 2. Chemical composition of native sago starch and phosphorylated sago starch prepared using 5% STPP and 4% POCl₃.

Reagent (% sb*)	pH reaction condition	Ash (%)	Protein (%)	Fat (%)	Amylose (%)
Native starch					
0	-	0.27±0.04 ef	0.75±0.02 a	0.42±0.04 ab	33.1±0.88 c
STPP					
5	8	0.34±0.02 de	0.73±0.03 a	0.37±0.02 abc	34.1±0.73 bc
	9	0.38±0.03 d	0.68±0.03 ab	0.29±0.09 bcd	37.6±1.12 a
	10	0.23±0.02 f	0.63±0.02 bc	0.30±0.03 bcd	34.9±0.52 bc
	11	0.25±0.01 f	0.69±0.01 ab	0.27±0.01 cd	35.9±0.49 ab
POCl ₃					
4	8	0.47±0.05 def	0.56±0.01 c	0.20±0.04 d	35.3±0.99 abc
	9	0.82±0.03 c	0.67±0.06 ab	0.23±0.04 d	36.5±0.76 ab
	10	0.91±0.01 b	0.68±0.03 ab	0.31±0.07 bcd	20.6±0.64 d
	11	1.34±0.03 a	0.72±0.02 a	0.48±0.03 a	14.5±0.93 e

Means with the same letters in the same column are not significantly different at $p < 0.05$ level by Tukey's test.

*sb: starch basis

amylopectin molecule during the modification process. The higher ash content was detected in the sample modified with POCl_3 . This might be due to the fact that the sub-products of the reaction contained Na and P retained in the modified starch, thus increasing the ash amount.

The protein content of PSS ranged between 0.63 and 0.73% and was lower than that of NSS (0.75%). The protein content of NSS, as reported by Sugiyono et al. (2008) and Wattanachant et al. (2002), was 0.1-1.0%. The fat content of PSS ranged between 0.2 and 0.5% and, in general, was lower than that of NSS (0.42%). The modification of the NSS by phosphorylation further reduced the percentage of protein and fat. This was probably due to the partial solubilization of the protein or fat during the preparation of the modified starches. The reagent type used in the modification played an important role in the proximate composition.

The amylose content was different in NSS and PSS (Table 2). The highest amylose content of starch modified using STPP at pH 9 was 37.6%. All PSS contained a much higher amylose content than NSS, except PSS2 prepared at pH 10 and 11 (20.6 and 14.5%). The higher amylose content of the phosphorylated samples might be due to the partial loss of the amylopectin fraction during the process.

Swelling Power and Solubility

The swelling power of NSS was 12.76% (Table 3), which was similar to that reported earlier (Pimpa et al. 2007). The swelling power of NSS increased after phosphorylation with both modification reagents, except that of the starches reacted with POCl_3 at pH 10 and 11 (9.30 and 4.27%). Sago starch phosphorylated with POCl_3 caused a reduction in the swelling power of starch when the phosphorus content of PSS2 was more than 0.28% P. The reagent type used in the modification influenced the swelling power of resultant starches (Table 3), indicating differences in the molecular organization within the granules. The swelling power of PSS1 increased with increasing pH of the reaction mixture, but the inverse tendency was observed in the case of that of PSS2. For PSS1, which was expected to mainly comprise MSP, the incorporation of hydrophylic phosphate groups increased the hydration capacity, in accordance with the report of Blennow et al. (2005). Craig et al. (1989) hypothesized that the phosphate groups facilitated water penetration and absorption on the starch granules, thus resulting in higher swelling in starch.

In the case of PSS2, which was expected to comprise mainly DSP, the low swelling power was likely because of the stabilization of the granule after phosphorylation. The cross-linking reaction

Table 3. Swelling power, solubility, and water-holding capacity of native sago starch and phosphorylated sago starch prepared using 5% STPP and 4% POCl_3 .

Reagent (%, sb*)	pH reaction condition	Swelling power (g g ⁻¹)	Solubility (%)	Water Holding Capacity (g H ₂ O g ⁻¹)
Native starch				
0	-	12.76 ± 0.23 d	53.69 ± 2.11 a	0.67 ± 0.04 e
STPP				
5	8	18.74 ± 1.38 c	47.22 ± 0.96 b	0.70 ± 0.02 de
	9	21.64 ± 0.74 b	48.21 ± 1.40 b	0.75 ± 0.01 cd
	10	21.00 ± 0.19 b	47.58 ± 1.00 b	0.73 ± 0.01 de
	11	23.78 ± 1.32 a	46.12 ± 0.32 b	0.71 ± 0.01 de
POCl_3				
4	8	24.07 ± 0.65 a	19.18 ± 1.77 c	0.74 ± 0.02 cd
	9	14.81 ± 0.09 d	15.00 ± 0.78 d	0.80 ± 0.02 c
	10	9.30 ± 0.23 e	6.94 ± 0.67 e	0.89 ± 0.02 b
	11	4.27 ± 0.32 f	2.15 ± 0.78 f	1.13 ± 0.04 a

Means superscripted with the same letters in the same column are not significantly different at $p < 0.05$ level by Tukey's test.

*sb: starch basis

strengthened the bonding between the starch chains, causing an increase in the resistance of the granules to swelling with an increasing degree of cross-linking. This phenomenon was in line with phenomena reported earlier (Singh et al. 2007, Carmona-Garcia et al. 2009, Mirmoghtadaie et al. 2009, O'Brien et al. 2009).

The solubility of NSS was 53.69%, and it was higher than that of PSS1 or PSS2 (Table 3). The solubility of PSS1 and PSS2 decreased with pH. This was probably due to the stabilization of the starch granule by phosphorylation. Carmona-Garcia et al. (2009) also showed a similar result for cross-linked banana starch.

Water-holding capacity

The WHC of NSS and PSS is presented in Table 3. From the results, it was observed that NSS held lower water ($0.67 \text{ g H}_2\text{O g}^{-1}$) than PSS1 ($0.70\text{--}0.75 \text{ g H}_2\text{O g}^{-1}$) and PSS2 ($0.74\text{--}1.13 \text{ g H}_2\text{O g}^{-1}$). The variation in WHC of these starches might be due to the difference in the degree of engagement of the hydroxyl group to form hydrogen and covalent bonds between starch chains, which is different from that with water (Hoover and Sosulski 1986). In addition, the incorporation of hydrophilic phosphorus groups on the starch molecules might increase in WHC, as reported by Lim and Seib (1993a). Furthermore, differences in the degree of availability of water-binding sites among the starches may play a role in the variation of the water-binding capacity (Wotton and Bamunuarachchi 1978).

Paste clarity

The paste clarity is directly related to the circumstances of the dispersal suspension of starch and the tendency of the starch to retrograde. Unmodified sago starch produced a translucent paste (transmittance 77.20%). In general, PSS1, which was assumed to comprise MSP, had higher clarity

(79.93–86.23%), while PSS2, which was similar to DSP, had lower paste clarity (3.63–63.03%) than that observed for NSS. Waliszewski et al. (2003) showed that starch phosphate had improvement in paste clarity but cross-linked starch produced lower paste clarity than native starch. According to Lim and Seib (1993a), the repulsion between adjacent starch molecules caused by the negatively charged phosphate group apparently reduced interchain associations and gave increased levels of hydrated molecules and, therefore, an increased level of paste clarity. With an increase in the pH reaction, the paste clarity of the resulting PSS decreased. The observed pattern was similar to that described by Muhammad et al. (2000). The lower paste clarity of PSS2 was most likely due to a restriction of granular swelling rather than to retrogradation. In this study, NSS and PSS have shown a tendency to decrease in clarity during storage for up to 72 hr at 4°C (Fig. 2). If starch paste were allowed to become cold, it would eventually become opaque because retrogradation would be enhanced at low temperatures.

Conclusions

The reagents used in the phosphorylation of NSS reduced the fat and protein contents but increased the ash and amylose contents. The phosphorus content of PSS1 prepared at pH 9 was higher than that of PSS1 prepared at pH 8, 10, and 11, while that of PSS2

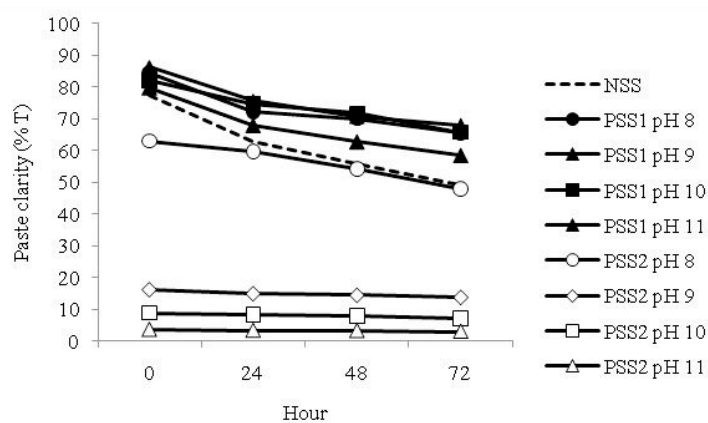


Fig. 2. The paste clarity of phosphorylated sago starch prepared using 5% STPP (PSS1) and 4% POCl_3 (PSS2), and native sago starch (NSS).

prepared at pH 11 was higher than that of PSS2 prepared at below pH 11. The swelling power and WHC of PSS was higher, while the solubility was lower than that of NSS. The paste clarity of PSS1 was higher than that of NSS, whereas that of PSS2 was lower. The paste clarity of all samples decreased with increasing time when kept at 4 °C.

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