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Physicochemical and Pasting Properties of Cross Linked-Banana Flour

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Abstract. Role of milieu pH at 5, 8 and 11 has been investigated to determine the effectiveness of cross-linking by STPP (Sodium tripolyphosphate) to banana flour. Change in physicochemical and pasting properties due to the treatments have been studied. The characterization by XRD and FTIR has also been carried out to reveal the diffraction pattern and the change in the chemical functional group. The result showed that cross-linking at the pH studied did not change the diffraction pattern of banana flour. An investigation using FTIR indicated that peak absorbance at wavenumber 2300 and 928 cm^{-1} increased following the treatment with the increase of pH, suggesting the formation of diester phosphate and C-O-P linking respectively. Swelling volume and solubility were remarkably affected by crosslinking at pH 11 while freeze-thaw stability at pH 5. The effectiveness of cross-linking on changing the pasting properties was not affected by the pH but cross-linking per se decreased the breakdown viscosity compared to the native flour.

Keywords: *physicochemical properties, pasting properties, cross-linking, banana flour*

1. Introduction
Starch is a source of carbohydrate which has an important role in the human diet and also a widely used component in the food industry. Starch can be produced from several sources such as potato, sweet potato, corn, rice, wheat, breadfruit, etc. Banana is also a potential starch source, which has a high amount of starch in unripe banana (more than 60% db) [1]. Native banana starch has some shortcomings, so it could be modified to improve its properties and application in the food industry. There are some methods to modify starch i.e. physical, chemical and enzymatic modification, which gave a different effect on starch characteristics. Some studies have reported about characteristics of banana starch and flour which affected by cultivar [2], [3], [4] and modification treatments [5], [6].

Cross-linking is one chemical method to modify starch, which used chemical reagents like sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP), sodium phosphorous oxychloride, adipate, and epichlorohydrin. Some previous works have reported that different type of cross-linking agent affected the physicochemical and pasting properties of starch [7], [8]. Cross-linking of starch depends on several factors such as starch source, composition and concentration of cross-linking reagent, reaction time, the extent of substitution, temperature, and pH [9], [10], [11]. Our study focused on the effect of cross-linking at various pH treatments range of 5-11 on the physicochemical and pasting properties of banana flour.

2. Materials and Methods

2.1 Materials
Plantain "Nangka" cultivar (genotypes Musa AAB) in a green ripeness state (harvested 8 - 10 weeks after flowering) were purchased from local market (Gede Bage, Indonesia). Fruit fingers were selected for uniformity of size, color, and shape. Flour was produced immediately after the purchase of fresh samples. Chemical reagents were sodium metabisulfite, sodium hydroxide, chloride acid, sodium sulfate, barium sulfate, and sodium tripolyphosphate. All chemical reagents used in this study were analytical grade.

2.2 Preparation banana flour and cross-linked banana flour
Banana flour was prepared using method of Cahyana et.al.,[6]. First of all, banana fruit was peeled and the pulp was then cut into transverse slices approx. 2mm thick. Then the pulp slices were dipped in water for 10 minutes, drained and dried at 50 °C for 24 hours in a drying oven (Shel Lab). After that, the pulp slices were milled (Fomac miller machine FCTZ-300) and passed through 80 mesh screens.

Cross-linked flour with STPP was prepared from banana flour using method of Wu and Seib [12] with some modification. Banana flour was mixed with water (2:3) to make a mixture and 5% of Na_2SO_4 was added. pH value of mixture was adjusted to 5, 8 and 11 by using 0.5 N NaOH or 0.5 N HCl. Then mixture was heated at 40 °C for 60 minutes with constant stirred using magnetic stirrer and 0.1% STPP was then added. After finishing cross-linking reaction, the mixture was adjusted to pH 6.5 using 0.5 N NaOH or 0.5 N HCl. %. The flour was washed with water 3 times then centrifuged, dried at 40 C for 24 h and sieved using 80 mesh screens.

2.3 X-ray diffractometer (XRD) and FTIR measurements
Crystalline-type of banana flour was measured using PANalytical X'Pert PRO series PW3040/x0 that operated using Cu-K alpha radiation with a wavelength of 1.5406 nm as X-ray source at 30 mA and 40 kV. The diffraction angle (2θ) scanning was from 5.0084–49.9734° with a scanning step time of 2.95 seconds. FTIR was used to measure functional group of cross-linked banana starch. Changes in intensity were measured at a resolution 16 cm^{-1} in range of 4000-400 cm^{-1}.

2.4 Functional and pasting properties
Water absorption capacity (WAC), swelling volume and solubility, freeze-thawing stability and gel strength measurement methods refer to (Beuchat,[13] Collado and Corke,[14] Wattanachant et., al.[15] and Collado and Corke,[14] , respectively. Rapid Visco Analyzer (RVA StarchMaster 2, Warriewood, Australia) was used to analyze pasting properties of native and cross-linked banana flour. Samples and water were mixed to make starch suspension (11% moisture basis) in canister and then stirred to homogenize the mixture. The starch was equilibrated at 50 °C for 1 minute, then heated to 95 °C for 3.7 minutes, held at 95 °C for 2.5 minutes, cooled to 50 °C in 3.8 minutes and kept at 50 °C for 2 minutes.

2.5 Statistical analysis
Data were expressed as mean ± SD of triplicate determinations and were compared through one-way ANOVA using Duncan's Multiple Range test. Statistical significance was set at $P < 0.05$. Values followed by the same letter in the comparison were not significantly different ($P < 0.05$). Statistical analysis was performed using SPSS version 22.0.

3. Results and Discussion

3.1 Crystalline-Type
XRD diffractogram of native and cross-linked banana flour at various pH was presented in Figure 1. Native banana flour has a B-type crystalline pattern, which was indicated by a small peak at 5°, strong peaks at 15 and 17° and a broad peak at 22 - 24° 2θ. Previous work has reported that native banana starch shown a different type of crystalline pattern such as A-type pattern [16], B-type pattern [2], and C-type pattern [17]. Similar to native banana flour, all cross-linked banana flour have a B-type

crystalline pattern. It indicated cross-linking at all pH treatment did not alter crystalline-type of banana starch which in line with [18]. They found that cross-linking did not alter the crystalline type of kudzu root starch.

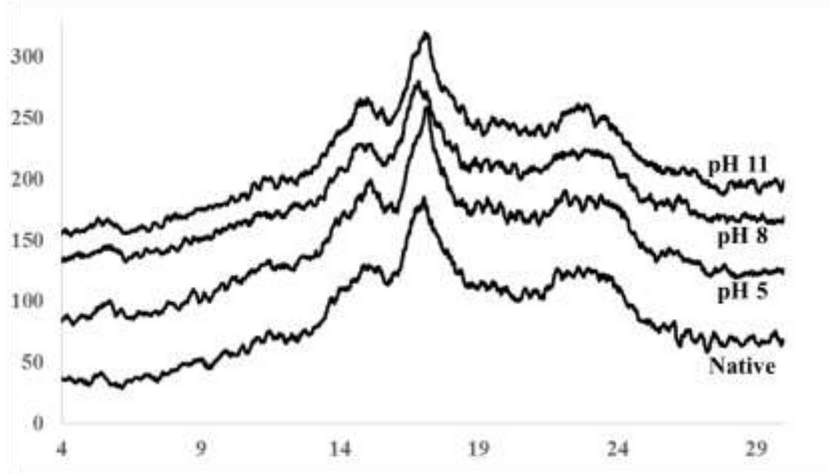

Figure 1. XRD diffractograms of native and cross-linked banana flour at various pH.

3.2 The functional groups

The FTIR (Fourier Transform Infra-Red) test was conducted to determine the functional groups formed and changed that occurred in the structure of banana flour after the cross-linking treatment. The functional groups of cross-linked banana flour were at wave number 2930, 2300, 1650, 1159 and 928 cm^{-1}.

Table 1. Effect of pH on functional group of cross-linked banana flour

Peak (cm^{-1})	Area (cm^2)			Functional group
	pH 5	pH 8	pH 11	
2930	165,346	153,520	141,475	C-H
2300	0,46	5,013	5,315	RO-PO_3-R’
1650	36,595	30,742	16,119	C=O
1159	61,110	76,682	122,807	C-O
928	48,21	102,870	127,438	C-O-P

Based on the FTIR spectrum in Table 1, it could be seen at the wave number 1650 cm^{-1}, the higher pH treatment, the lower area under the curve. Whereas at wave number 2300 cm^{-1} and 1159 cm^{-1}, there was an increase in area with increasing pH. The peak of 2300 cm^{-1} was the phosphate spectrum which indicated the formation of organic phosphate diester bonds between starch chains (RO-PO_3-R') [19]. The weak peaks around 1200 and 989 cm^{-1} characterized the existence of C-O-P bonds that organically cross-linking [20] and peaks ranged 1159-1080 cm^{-1} characterized C-O bonds. While other spectra such as carbonyl bonds appeared at 1760-1650 cm^{-1}. According to Chen et at.,[18] the absorption at 1650 cm^{-1} was a characteristic absorption band of starch because hydroxyl groups in water molecules were absorbed by starch which resulted by H_2O bending vibration.

Cross-linking decreased the quantity of C-H groups but increased the phosphate spectrum as the pH value of the solution increased. The reduced quantity of C-H bonds at wave number 2930 cm^{-1} indicated the presence of a hydrogen group substituted by a phosphate group. The infrared spectrum peak at wave number 2300 cm^{-1} increased as the pH increased. The increase in C-O groups indicated an increase in absorption of water by banana flour, which due to C-O group easily formed C-OH groups and caused the starch structure to be more amorphous. This increase in C-O group will increase swelling power, solubility, and water absorption capacity of cross-linked flour, which was in line with functional properties of cross-linked banana flour in this study. The formation peak at 1650 cm^{-1} confirmed the presence of carbonyl group (C = O). Increasing pH value caused a decrease in carbonyl group in cross-linked banana flour, which due to STPP reagent also attacked the carbonyl group in the starch granules of banana flour so that the carbonyl group decreased and the phosphate spectrum increased.

3.3 Functional Properties

Effect of pH on functional properties of cross-linked banana flour was shown in Table 2. Water absorption capacity (WAC), swelling volume (SV) and solubility (SOL) were remarkably affected by crosslinking at pH 11 while freeze-thaw stability was affected at all pH treatments. WAC, SV, and SOL of cross-linked banana flour increased with increasing pH level.

Table 2. Effect of pH on Functional properties of cross-linked banana flour

Properties	Treatments		
	pH 5	pH 8	pH 11
Water absorption capacity (g/g)	1,913 ± 0,070 [a]	1,979 ± 0,027 [a]	2,184 ± 0,038 [b]
Swelling volume (ml/g)	13,853 ± 0,316 [a]	14,048 ± 0,414 [a]	15,861 ± 0,510 [b]
Solubility (%)	9,163 ± 0,247 [a]	9,635 ± 0,206 [a]	12,112 ± 0,120 [b]
Freeze thaw stability (% syneresis)	0,616 ± 0,053 [a]	46,624 ± 0,260 [c]	33,343 ± 0,795 [b]
Gel strength (gF)	3,247 ± 0,513 [a]	3,220 ± 0,357 [a]	3,186 ± 0,700 [a]

Different letters in the compared values denote significant difference at $p < 0.05$.

Water absorption capacity (WAC) of cross-linked banana flour ranged from 1.913 – 2.184 g/g db with the highest WHC at pH 11. The modification of cross-linking in an alkaline condition disrupted the amorphous region of starch granule which due to the increase in the C-O group. Furthermore, Karim et.al. [21] suggested that the higher pH modification reduced amylose resistance to expanding and easy to absorb water. According to Hoover and Sosulki [22], modification of cross-linking interfered amorphous region of starch and did not change the crystalline pattern of starch.

The increase of WAC at pH 11 also due to intermolecular binding between phosphate and water. The higher pH, the higher amount of phosphate group which binding with water. This result was supported by the existence of FTIR spectrum data which showed an increase in absorption peak at 1649.47 cm^{-1} with increasing pH. Luo et al. [23] have reported that increasing absorption peak around 1646 cm^{-1} indicated the formation of intermolecular hydrogen bonds H_2O in the PO_4^{3-} group.

Cross-linked banana flour at pH 11 has the highest swelling volume and solubility. The increase in swelling volume could be due to stronger bonds between starch molecules by phosphate bridges formed after the cross-linking reaction so that higher the swelling of starch granules [24]. This result was supported by FTIR data, which showed an increase in the C-O group bond with increasing pH suspension. The C-O group influenced the swelling of starch granules because easier to form C-OH groups and causing the starch structure to be more amorphous.

Freeze-thaw stability expressed in percent syneresis can be interpreted as the percentage of the amount of water that is separated after the paste is treated as a storage at one cycle -15 °C. Cross-linked banana flour at pH 5 has the lowest syneresis amongst the other samples, approximately 55 and 76 times lower than cross-linked banana flour at pH 8 and 11, respectively. The lower percentage of separate water shows that the flour gel was more stable to storage at freezing temperatures. Syneresis generally occurs in starch that has undergone cooling and storage after the gelatinization process. The low% syneresis in the treatment is in line with the low setback viscosity value.

3.4 Pasting Properties

Pasting properties of cross-linked banana flour were presented in Table 3. The pasting point, peak viscosity, breakdown and setback of banana flour were not significantly different amongst cross-linked banana flour samples. It indicated cross-linking at the pH studied did not alter most of pasting properties. This resulted was in agreement with another previous work [25]. It has found that cross-linking using $POCl_3$ reagent did not alter peak viscosity of oat starch.

Pasting temperature cross-linked banana flour ranged from 72.68 to 74.02 °C, which was lower than native banana flour (75.38 °C), which due to cross-linking decreased starch structural stability by inhibiting double helical bonds such as hydrogen bonds thereby reducing the transfer of heat energy during gelatinization [26]. According to Heo, et al, [27] cross-linked starch required higher energy to swell due to its process can make starch granule more ordered. They also have found that cross-linking increased pasting temperature of native potato starch, which was not in line with this study. It could be due to different starch source and form of samples, which in this study the samples used in the flour form. Flour form contained higher non-starch components than starch from, which affected the pasting properties of starch. Peak viscosity of cross-linked banana flour (5190,50 - 5646,50 cP) higher than native banana flour (5108 cP), which was in agreement with previous works [26], [27], which due to a new strong covalent bond between starch was occurred during cross-linking treatment.

Cross-linking decreased breakdown of native banana flour. Breakdown viscosity of native and cross-linked banana flour was 2732.50 cP and 1880.17 – 2184.67 cP, respectively. The lower breakdown, the higher stability of banana flour to heating and stirring process, which in line with previous studies [24], [27]. This result indicated that cross-linking prevented loss of viscosity during heating and stirring process, due to strengthening the swollen granules to breakage under a high temperature and shear. Setback expressed the ability of starch paste to retrograde, the higher setback the higher ability of the starch paste to retrograde. Setback viscosity of native banana flour (17.60.50 cP) was in the range of cross-linked banana flour (1536.83 – 2084.83 cP). It indicated cross-linking at the pH process did not alter setback of native banana flour.

Table 3. Effect of pH on pasting properties of cross-linked banana flour

Properties	Treatments		
	pH 5	pH 8	pH 11
Pasting temperature (°C)	72,68 ± 1,60 [a]	74,02 ± 0,75 [a]	73,488 ± 1,21 [a]
Peak Viscosity (cP)	5190,50 ± 462,90 [a]	5452,33 ± 355,37 [a]	5646,50 ± 353,03 [a]
Hold viscosity (cP)	3112,50 ± 107,847 [a]	3568,17 ± 94,54 [b]	3581,50 ± 97,86 [b]
Final viscosity (cP)	4900,33 ± 163,42 [a]	5088,33 ± 288,54 [a]	5788,83 ±221,49 [b]
Breakdown (cP)	2184,67 ± 296,37 [a]	1880,17 ± 205,75 [a]	2065,00 ± 448,62 [a]
Setback (cP)	1781,17 ± 59,43 [a]	1536,83 ± 336,34 [a]	2084,83 ± 317,76 [a]

Different letters in the compared values denote significant difference at $p < 0.05$.

4. Conclusion

Cross-linking at all pH treatment did not alter crystalline-type of native banana flour, which has a B-type crystalline pattern. Peak absorbance at wavenumber 2300 and 928 cm^{-1} increased following the increase of pH treatment, suggesting the formation of diester phosphate and C-O-P linking respectively. Water absorption capacity (WAC), swelling volume (SV) and solubility (SOL) were remarkably affected by crosslinking at pH 11 while freeze-thaw stability was affected at all pH treatments. WAC, SV, and SOL of cross-linked banana flour increased with increasing pH level. The pasting point, peak viscosity, breakdown and setback of banana flour were not significantly different amongst cross-linked banana flour samples. It indicated cross-linking at the pH studied did not alter most of pasting properties. Cross-linked banana flour has a higher peak, hold and final viscosity and lower pasting temperature and breakdown than native banana flour.

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References

[1] Zhang, P.; Whistler, R. L.; BeMiller, J. N.; Hamaker, B. R., 2005 Banana starch: Production, physicochemical properties, and digestibility—a review. Carbohydr. Polym. 59 (4), 443-458.
[2] de Barros Mesquita, C.; Leonel, M.; Franco, C. M. L.; Leonel, S.; Garcia, E. L.; dos Santos, T. P. R., 2016 Characterization of banana starches obtained from cultivars grown in brazil. Int. J. Biol. Macromol. 89 (Supplement C), 632-639.
[3] Vatanasuchart, N.; Niyomwit, B.; Wongkrajang, K., 2012 Resistant starch content, in vitro starch digestibility and physico-chemical properties of flour and starch from thai bananas. Maejo Int. J. Sci. Technol. 6 (2), 259-271.

[4] Hung, P. V.; Cham, N. T. M.; Truc, P. T. T., 2013 Characterization of vietnamese banana starch and its resistant starch improvement. Int. Food Res J. 20 (1), 205-211.
[5] Cahyana, Y.; Wijaya, E.; Halimah, T. S.; Marta, H.; Suryadi, E.; Kurniati, D., 2019 The effect of different thermal modifications on slowly digestible starch and physicochemical properties of green banana flour (musa acuminata colla). Food Chem. 274, 274-280.
[6] Cahyana, Y.; Titipanillah, R.; Mardawati, E.; Sukarminah, E.; Rialita, T.; Andoyo, R.; Djali, M.; Hanidah, I.-I.; Setiasih, I. S.; Handarini, K., 2018 Non-starch contents affect the susceptibility of banana starch and flour to ozonation. J. Food Sci. Technol 55 (5), 1726-1733.
[7] Cheng, G.; Duan, X.; Jiang, Y.; Sun, J.; Yang, S.; Yang, B.; He, S.; Liang, H.; Luo, Y., 2009 Modification of hemicellulose polysaccharides during ripening of postharvest banana fruit. Food Chem. 115 (1), 43-47.
[8] Shah, N.; Mewada, R.; Mehta, T., Crosslinking of starch and its effect on viscosity behaviour. 2016; Vol. 32.
[9] Koo, S. H.; Lee, K. Y.; Lee, H. G., 2010 Effect of cross-linking on the physicochemical and physiological properties of corn starch. Food Hydrocoll. 24 (6), 619-625.
[10] Ashogbon, A. O.; Akintayo, E. T., 2013 Recent trend in the physical and chemical modification of starches from different botanical sources: A review. Starch - Stärke 66 (1-2), 41-57.
[11] Blennow, A., 2015; Phosphorylation of the starch granule. In Starch, Nakamura, Y., Ed. Springer: Japan.
[12] Woo, K. S.; Seib, P. A., 2002 Cross-linked resistant starch: Preparation and properties. Cereal Chem. 79 (6), 819-825.
[13] R. Beuchat, L., Functional and electrophoretic characteristics of succinylated peanut flour. 1977; Vol. 25.
[14] Collado, L. S.; Corke, H., 1999 Heat-moisture treatment effects on sweetpotato starches differing in amylose content. Food Chem. 65 (3), 339-346.
[15] Wattanachant, S.; Muhammad, K.; Mat Hashim, D.; Rahman, R. A., 2003 Effect of crosslinking reagents and hydroxypropylation levels on dual-modified sago starch properties. Food Chem. 80 (4), 463-471.
[16] Bello-Pérez, L. A.; Romero-Manilla, R.; Paredes-López, O., 2000 Preparation and properties of physically modified banana starch prepared by alcoholic-alkaline treatment. Starch - Stärke 52 (5), 154-159.
[17] Pelissari, F. M.; Andrade-Mahecha, M. M.; Sobral, P. J. d. A.; Menegalli, F. C., 2012 Isolation and characterization of the flour and starch of plantain bananas (musa paradisiaca). Starch - Stärke 64 (5), 382-391.
[18] Chen, B.; Dang, L.; Zhang, X.; Fang, W.; Hou, M.; Liu, T.; Wang, Z., 2017 Physicochemical properties and micro-structural characteristics in starch from kudzu root as affected by cross-linking. Food Chem. 219, 93-101.
[19] Wanrosli, W. D.; Rohaizu, R.; Ghazali, A., 2011 Synthesis and characterization of cellulose phosphate from oil palm empty fruit bunches microcrystalline cellulose. Carbohydr. Polym. 84 (1), 262-267.
[20] Passauer, L.; Bender, H.; Fischer, S., 2010 Synthesis and characterisation of starch phosphates. Carbohydr. Polym. 82 (3), 809-814.
[21] Karim, A. A.; Nadiha, M. Z.; Chen, F. K.; Phuah, Y. P.; Chui, Y. M.; Fazilah, A., 2008 Pasting and retrogradation properties of alkali-treated sago (metroxylon sagu) starch. Food Hydrocoll. 22 (6), 1044-1053.
[22] Hoover, R.; Sosulski, F., 1986 Effect of cross-linking on functional properties of legume starches. Starch - Stärke 38 (5), 149-155.
[23] Luo, F.-x.; Huang, Q.; Fu, X.; Zhang, L.-x.; Yu, S.-j., 2009 Preparation and characterisation of crosslinked waxy potato starch. Food Chem. 115 (2), 563-568.
[24] Xiao, H. X.; Lin, Q. L.; Liu, G. Q.; Yu, F. X., 2012 A comparative study of the characteristics of cross-linked, oxidized and dual-modified rice starches. Molecules 17 (9), 10946-57.
[25] Mirmoghtadaie, L.; Kadivar, M.; Shahedi, M., 2009 Effects of cross-linking and acetylation on oat starch properties. Food Chem. 116 (3), 709-713.

[26] Deetae, P.; Shobsngob, S.; Varanyanond, W.; Chinachoti, P.; Naivikul, O.; Varavinit, S., 2008 Preparation, pasting properties and freeze–thaw stability of dual modified crosslink-phosphorylated rice starch. Carbohydr. Polym. 73 (2), 351-358.

[27] Heo, H.; Lee, Y.-K.; Chang, Y. H., 2017 Rheological, pasting, and structural properties of potato starch by cross-linking. Int. J. Food Prop. 20 (sup2), 2138-2150.