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CHARACTERIZATION OF THE FUNCTIONAL PROPERTIES OF HYDROXYPROPYLATED AND CROSS-LINKED ARROWROOT STARCH IN VARIOUS ACIDIC pH MEDIUMS

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ABSTRACT

Chemical modification of the native arrowroot starch by hydroxypropylation and cross link methods is done to improve or add certain functionality. This method is gaining popular interest from food industry practitioners to enable the stability of starch during acidic food processing. This research studied the changes in the functional properties of modified arrowroot starch in various acidic pH mediums. Being modified by hydroxypropylation and cross-linked methods changes the starch's functional properties in mediums with a variety of pH conditions. The patterns of pasting properties of dual-modified arrowroot starch are similar to each other at different pH mediums, in which the final viscosity value was lower than the peak viscosity value (a type A pattern). The solubility of the modified arrowroot starch increased in a pH of 3.5. Increasing the starch solubility caused the swelling power of starch granules to decrease, and thus lessened the sedimentation volume. Modifying arrowroot starch by using propylene oxide 8% tends to maintain the structure of the granule upon swelling in mediums with any pH conditions. The syneresis value of modified arrowroot starch using 10% propylene oxide and a STMP 1% : STPP 4% ratio showed the lowest value in various pH mediums. The most stable modified starches were those with propylene oxide 8% and a ratio of STMP 1% : STPP 4%.

Keywords: Acidic food; Cross-link, Hydroxypropylation; Modified arrowroot starch

1. INTRODUCTION

Tubers of arrowroot plants (*Marantha arundinacea*) have been developed into an alternative source of carbohydrate foods in the forms of flour and starch, for direct consumption or as raw material for food and non-food industries. As raw material, starch should able to tolerate a broad range of processing techniques to fulfil the demands of modern and highly dynamic food industries, to create diverse products. This requires overcoming the disadvantages of the native starch, such as susceptibility to shear and acidic conditions, less stability, instability of viscosity, and low solubility. Based on these facts, the researchers were encouraged to made modifications to the native starch, which is an important functional ingredient in the food industry. These modifications will change the starch's composition and physicochemical properties (Das et al., 2010), thus improving several of its functional properties: solubility in cold water, gelatinization properties, gel formation, film formation, stability of the acidic conditions, reduced retrogradation, and syneresis.

The native starches can be chemically modified by the hydroxypropylation method through a

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reaction between the starches with a propylene oxide compound, by etherification under alkaline conditions. Etherification with a low degree of substitution causes the hydroxypropyl groups (-$OCH_2CH_2CH_3$) to take the place of the hydroxyl groups. The hydroxypropylation method is commonly used in the food industry, because it can improve the durability, freeze-thaw stability, stability of storage at low temperatures, clarity, and texture of paste; it can also reduce the temperature of gelatinization and increase the swelling power of starches (Perera et al., 1997; Hoover et al., 1998; Liu et al., 1999; Pal et al., 2002; Miyazaki et al., 2006; Lee & Yoo, 2011).

The cross-linking method is a treatment in which a small number of compounds that can react with more than one hydroxyl group are added to the starch polymer. The cross-link reaction involves the replacement of hydrogen bonds between the starch chains with the phosphate group from a combination of STMP and STPP reagents, forming a cross-link bridge through covalent bonds that are stronger and more permanent. Cross-linked starch can maintain a higher viscosity and shows low changes in viscosity (Wurzburg, 1989). Cross-linking can also modify the properties of granule swelling, improve the texture and the rheological properties of the paste (Kim & Lee, 1996), and is useful for improving the film formation properties of the paste (Rutenberg & Solarek, 1984).

Chemical modification of the native arrowroot starch by hydroxypropylation and cross-link methods was done to improve or add certain functional properties that have widespread application when used in the food industry. The combination of hydroxypropylation and cross-link methods will produce a starch that can swell, but the starch granules remain intact (Miyazaki et al., 2006). In addition, starch with dual modifications will have stability in acid, heat, and mechanical degradation, and may delay retrogradation during storage (Singh et al., 2007; Maulani et al., 2013) and increase the swelling power (Lee & Yoo, 2011). Gunaratne and Corke (2007) stated that the dual-modification of starch derived from the root and tuber showed some changes in the functional properties of the starch, which improved the stability of stirring at high temperatures and the resistance to enzymatic hydrolysis.

Utilization of arrowroot starch as raw material for the food industry needs further study, particularly of changes in the functional properties in various acidic pH values, as well as in types of food that are relatively acidic. In this way, it has a chance to be developed as a raw material that has improved properties compared with native starch (Maulani et al., 2013). The purpose of this research was to study the changes in the functional properties of modified arrowroot starch in various acidic pH mediums.

2. MATERIALS AND METHODS

2.1. Materials

The starch used in this study was obtained from arrowroot tubers (harvest age of 10 months). Starch was extracted by a wet extraction method, a common procedure in starch extraction derived from tubers (Grace, 1977). Based on our preliminary study, the characteristics of native arrowroot were as follows: moisture content 12.60%, ash 0.62%, lipid 0.88%, protein 1.44%, and amylose 29.41%. The main chemicals for the modification of the starch were STMP (sodium tri-meta phosphate), STPP (sodium tri-poly phosphate), and propylene oxide. All chemicals were purchased from the Sigma-Aldrich Chemical Company.

2.2. Preparation of Dual Modified Starch

The hydroxypropylation and cross-link method was conducted according to the method described by Maulani et al. (2013). Arrowroot starch (100 g, dry basis) was dissolved in a 10% sodium sulfate solution to obtain a suspension with a concentration of 40%. While stirring, the pH was increased to 10.5 by adding NaOH 5%. Propylene oxide was added with concentrations

of 8% and 10% by the weight of starch used, respectively. The suspension was stirred for 30 min at room temperature. The suspension was then placed on a shaking incubator for 24 h (40°C; 200 rpm). Mixtures of STMP and STPP were added at a ratio of 1% : 4% and 2% : 5% by the weight of starch used, respectively. Each suspension was stirred for 30 min at room temperature, and the pH was lowered to 5.5 by adding HCl 1M. The suspension was placed back on the shaking incubator for 24 h (40°C; 200 rpm). The next step was separation of the starch from the precipitated solvent by centrifugation, at 2500 rpm for 15 min, after which the precipitate was washed with distilled water five times. The precipitated starch was dried at a temperature of 50°C for 12 h (moisture content 10-12%) and then crushed and sieved with a 100 mesh size.

2.3. Pasting Properties

The pasting properties were determined by using a Rapid Visco Analyser (RVA) Tec Master type RVA-S4, according to the procedure of Deetae et al. (2008). The observed parameters were maximum temperature of gelatinization, peak viscosity, holding strength, final viscosity, breakdown, and setback (retrogradation).

2.4. Solubility and Swelling Power

The solubility and swelling power of the starches were determined as described by Lee and Yoo (2011). The starch dispersion (0.5g/100g) was prepared by mixing starch with distilled water and moderately stirring it for 1 h at room temperature, then heating it to 95°C in a water bath for 30 min. The hot starch paste was cooled to room temperature in an iced water bath, and centrifuged at 2300 × g for 30 min. The supernatant was decanted and the swelling power was determined as the ratio of the weight of the sediment to the weight of the dry starch. An aliquot of the supernatant was evaporated for 4 h in a vacuum oven at 120°C. The solubility was determined as the ratio of the weight of the dried supernatant to the weight of the dry starch. The solubility and swelling power were calculated based on Equations 1 and 2, respectively:

$$\text{Solubility (\%)} = \frac{\text{Weight of dried supernatant (g)}}{\text{Weight of starch sample in dry basis (g)}} \times 100 \quad (1)$$

$$\text{Swelling power (\%)} = \frac{\text{Weight of sediment paste (g)}}{\text{Weight of starch sample (g)} \times (100 - \text{\%Solubility})} \times 100 \quad (2)$$

2.5. Volume of Sedimentation

The volume of sedimentation was determined according to the procedure of Tessler (1978). A starch solution of 1% (1g /100g) was heated in a water bath for 15 minutes while stirring. Distilled water was added again to reach a 100g weight of solution. The mixture was stirred and then inserted into a cylinder (100 ml). The cylinder was covered with aluminum foil and stored for 24 hours at room temperature. Sedimentation was measured as the volume of the sediment containing swelled granules.

2.6. Freeze-thaw Stability

The freeze-thaw stability value for the starch suspension (5g in 100g of distilled water) was determined by heating it to 95°C with stirring for 30 minutes. A paste was formed, cooled to room temperature, and then weighed (15g) and put into centrifuge tubes. The sample in each tube was placed in a -18°C freezer for 24 hours. Next, the frozen paste was thawed at 30°C in a water bath for 1.5 hours, then centrifuged (3500 rpm; 15 min). The liquid was decanted and the residue weighed. The percentage of syneresis was calculated based on the ratio between the weight of the liquid decantation and the total weight of the sample multiplied by 100% (Deetae et al., 2008; Lee & Yoo, 2011).

2.7. Statistical and Data Analysis

Means and standard deviations were obtained using Microsoft Excel software. The significance of difference was determined by using analysis of variance (ANOVA). Comparison of means was performed by using Duncan's multiple-range test at $\alpha = 0.05$.

3. RESULTS AND DISCUSSION

3.1. Pasting Properties

The patterns of pasting properties of the dual-modified arrowroot starch are similar to each other at different pH mediums (Figure 1), in that the final viscosity value was lower compared to the peak viscosity value (a type A pattern). Maulani et al. (2013a) reported that the gelatinization profile of native arrowroot starch is type A, marked by a high peak viscosity value and a breakdown viscosity that is quite sharp. Modified starches with a high concentration of phosphate salts showed higher viscosity values at each pH medium. The existence of hydroxypropyl and cross-linked groups in the starch granules provided stable structure to the pastes, even in conditions of low acidity, making them more resistant to the acid hydrolysis process.

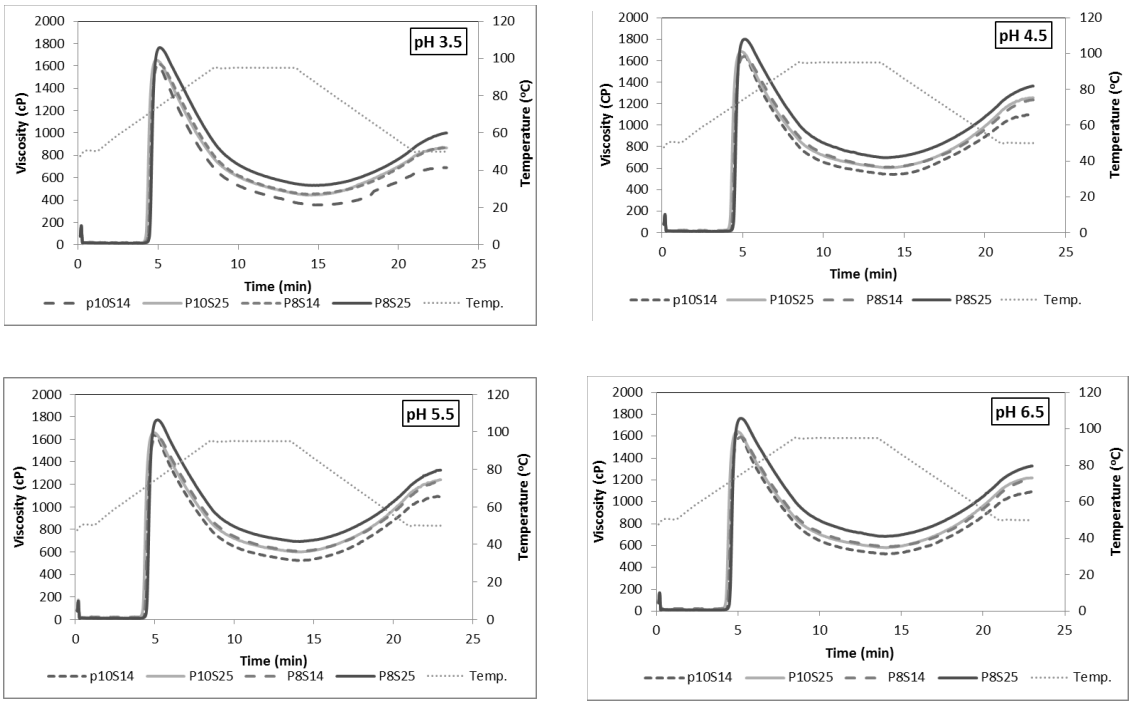

Figure 1 Pasting properties of dual-modified arrowroot starch at various pH mediums: (a) 3.5; (b) 4.5; (c) 5.5; (d) 6.5 (P8 = propylene oxide 8%; p10 = propylene oxide 10%; S14 = ratio STMP 1% : 4% STPP; S25 = ratio STMP 2% : 5% STPP)

Figure 1 showed that in each medium with different pH values, the breakdown viscosity of the modified starch pastes was quite high at 95°C, meaning the starch's resistance to heat treatment was relatively low. When the temperature increased, the viscosity of modified arrowroot starch paste increased slightly in a medium with 3.5 pH compared with higher-pH mediums (low setback viscosity), indicating a lower trend of retrogradation. According to Wattanachant et al. (2002), acid treatment will reduce the paste viscosity and consistency of the modified starch.

In each medium with different pH values, modified starch with 8% propylene oxide and a STMP 2%: 5% STPP ratio showed the highest viscosity, while the lowest viscosity was the modified starch with 10% propylene oxide and a STMP 1%: 4% STPP ratio. This shows that the process of dual-modification of arrowroot starch provides a more stable structure for the paste even in a state of low acidity, making it more resistant to the acid hydrolysis process.

3.2. Solubility, Swelling Power, and Sedimentation Volume

The solubility of modified arrowroot starch was increased in the 3.5 pH medium (Figure 2). Increasing the starch solubility caused the swelling power of starch granules to decrease (Figure 3), so that the sedimentation volume was low (Figure 4).

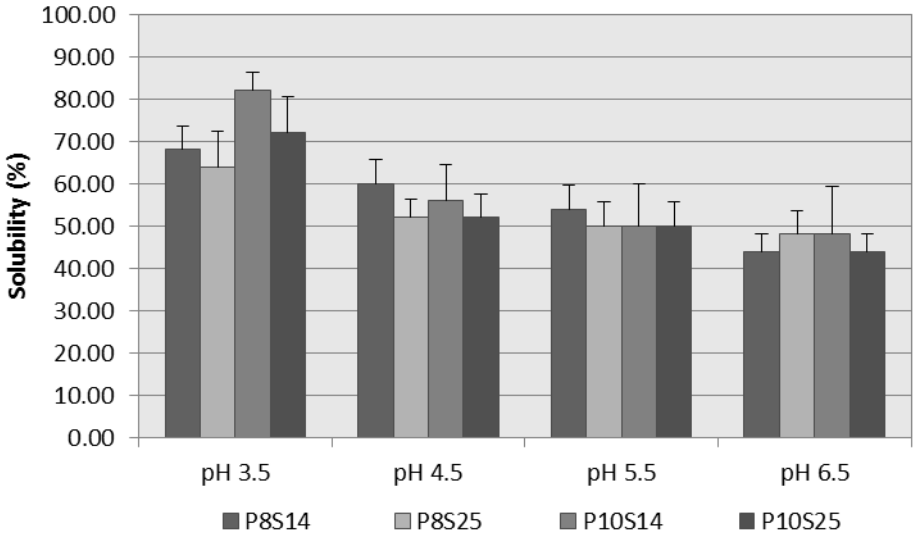

Figure 2 Solubility of dual-modified arrowroot starch at various pH mediums (P8 = propylene oxide 8%; p10 = propylene oxide 10%; S14 = ratio STMP 1% : 4% STPP; S25 = ratio STMP 2% : 5% STPP)

At higher pH mediums, the values of solubility, swelling power, and sedimentation volume of the modified arrowroot starch were quite stable. The existence of cross-linked groups caused the starch granules to become more rigid, which will inhibit the swelling excess (Miyazaki et al., 2006). The presence of hydroxypropyl groups in the starch granules increased the swelling power. In general, the increased swelling power and solubility of hydroxyproylated starches are due to the incorporation of a hydroxypropyl group that is capable of disrupting inter- and intra-molecular hydrogen bonds in the starch chains, thereby weakening the granular structure of starch and increasing the accessibility of the starch granules to water (Lawal, 2009; Lee & Yoo 2011). Dual-modified arrowroot starch through hydroxypropylation and cross-linked reactions produced starch which has good resistance to swelling in low pH mediums (pH 4.5 and 5.5).

The sedimentation volume of modified arrowroot starch stable at pH> 3.5 was in the range of the average value of 35% (Figure 4). Sedimentation volume indicates changes in the starch molecular association during the process of modification, which also depends on the type of modification (Yadav et al., 2006). Dual modification with hydroxypropylation and the cross-link method might influence the sedimentation volume of arrowroot starch. The cross-link groups in the starch granule structure have the ability to trap more water, so that the volume of sediment can be higher than at acidic pH values (3.5). In conditions of low acidity, arrowroot starch modified with propylene oxide 8% and a STMP2% : STPP5% ratio has a higher volume of sediment than other treatments.

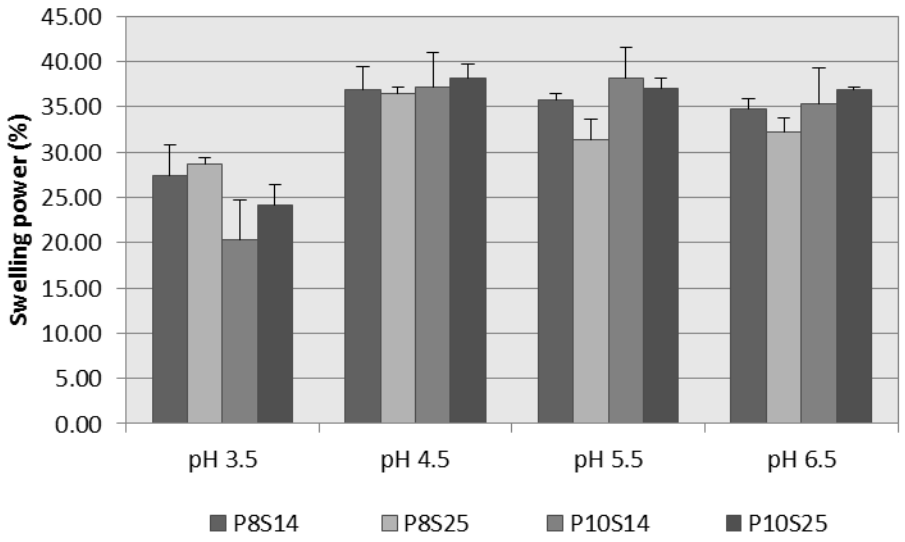

Figure 3 Swelling power of dual-modified arrowroot starch at various pH mediums (P8 = propylene oxide 8%; p10 = propylene oxide 10%; S14 = ratio STMP 1% : 4% STPP; S25 = ratio STMP 2% : 5% STPP)

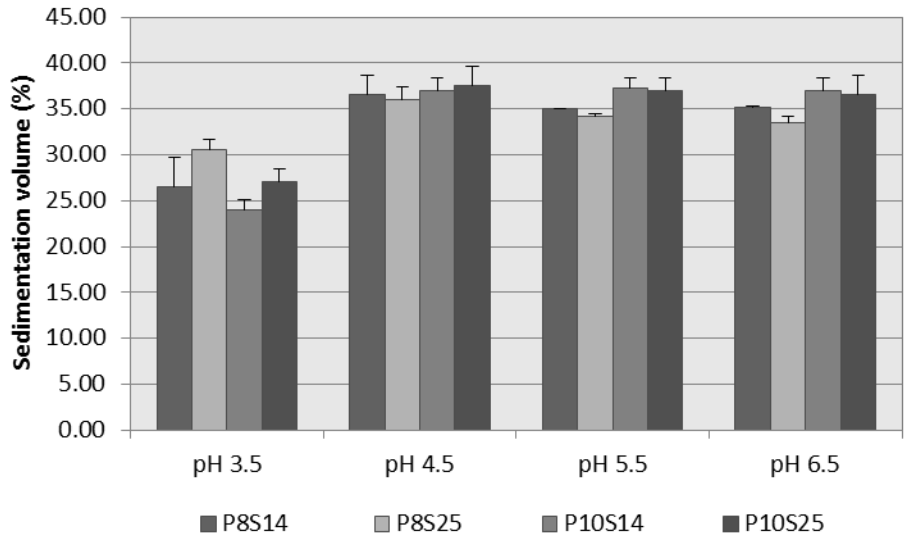

Figure 4 Sedimentation volume of dual-modified arrowroot starch at various pH mediums (P8 = propylene oxide 8%; p10 = propylene oxide 10%; S14 = ratio STMP 1% : 4% STPP; S25 = ratio STMP 2% : 5% STPP)

3.3. Change of Granular Form at Swelling

Changes of granular form of the modified arrowroot starch at swelling are shown in Figure 5. The behavior of the starch granule during heating is that water penetrates into the more accessible amorphous region of the starch granule, resulting in hydration and limited swelling (Liu et al., 1999). Modifying arrowroot starch by using propylene oxide 8% tends to maintain the structure of the granule upon swelling in any pH medium conditions. The existence of cross-linked groups on the starch granules improves the granules' ability to trap more water without breaking, so that the pasting viscosity can be maintained.

3.4. Percentage of Syneresis

The stability of starch pastes in an acidic medium can be demonstrated by the value of syneresis: the amount of water that is separated from the granules after a freeze-thaw cycle. A higher value of syneresis shows a lower degree of stability.

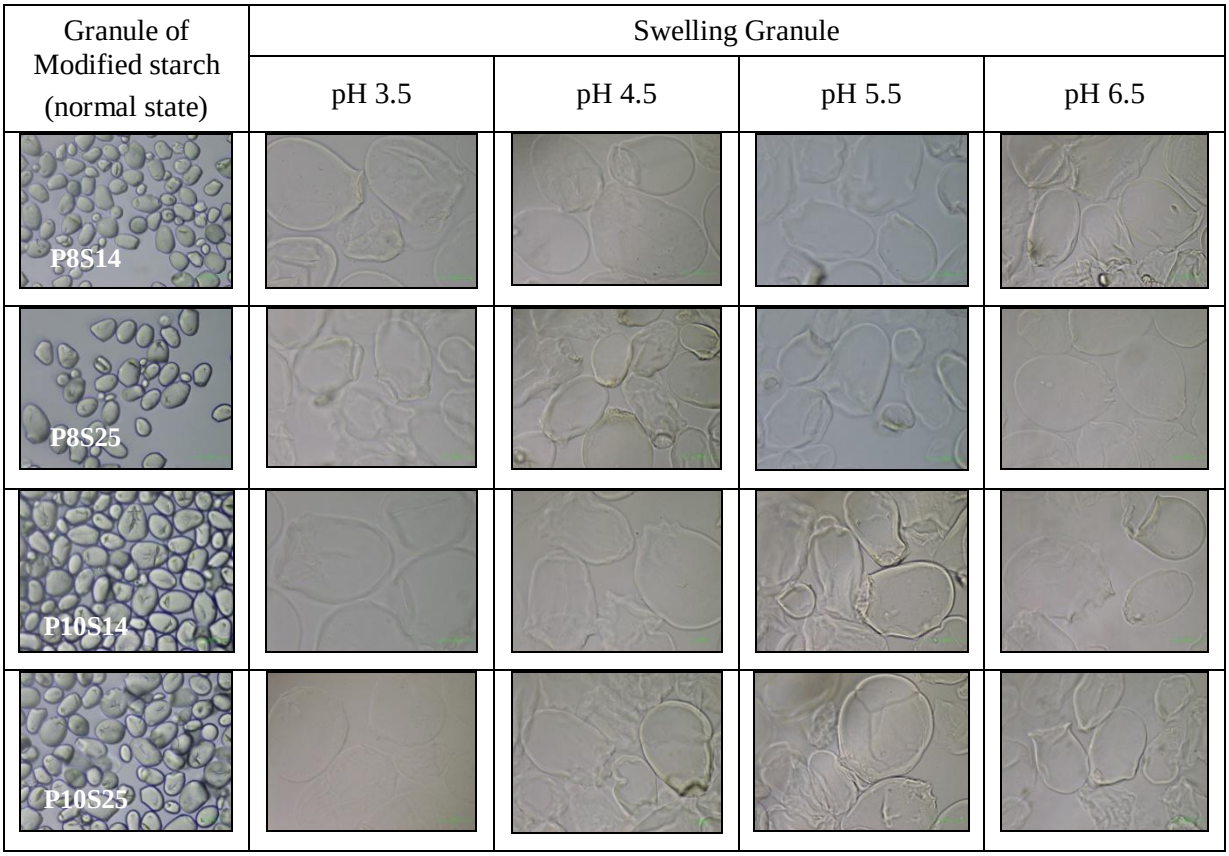

Figure 5 Changes of granular form of dual-modified arrowroot starch in various pH mediums at swelling, using a light microscope (Magn. 40x). (P8 = propylene oxide 8%; p10 = propylene oxide 10%; S14 = ratio STMP 1% : 4% STPP; S25 = ratio STMP 2% : 5% STPP)

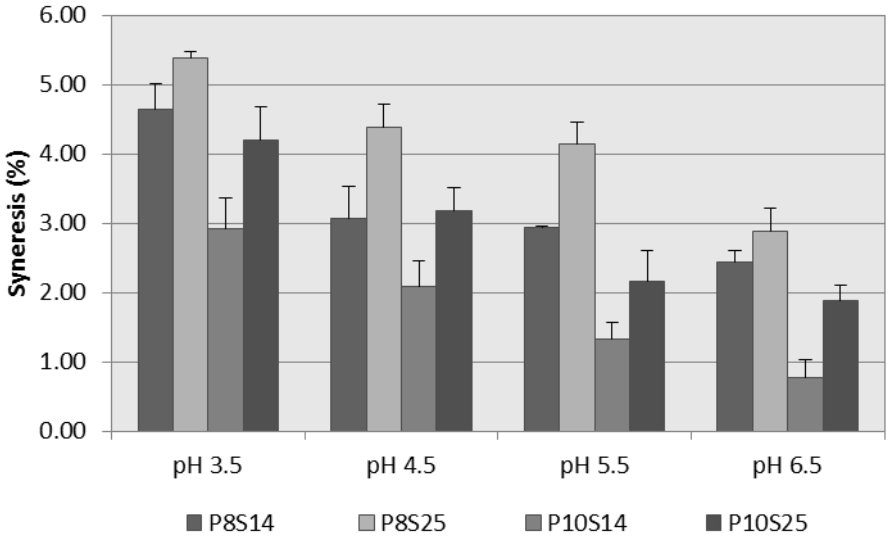

Figure 6 Percentage of syneresis of dual-modified arrowroot starch at various pH mediums (P8 = propylene oxide 8%; p10 = propylene oxide 10%; S14 = ratio STMP 1% : 4% STPP; S25 = ratio STMP 2% : 5% STPP)

The syneresis value of the modified arrowroot starch using 10% propylene oxide and a STMP1% : STPP 4% ratio showed the lowest value in various pH mediums. Hydroxypropyl

groups on the granules will retain water in the granules from the process of water separation, because they are hydrophilic (Hung & Morita, 2005). Hydroxypropylation introduces mono-functional hydroxypropyl groups to the hydroxyl group of the starch molecule, thus preventing dissolved linear starch molecules from associating closely, by reducing the attractive forces between hydroxyl groups on adjacent chains during cooling or freezing (Wattanachant et al., 2002).

Syneresis values of modified arrowroot starch are in the range of < 6% and decreased with increasing pH value mediums. The lowest value of syneresis was indicated in arrowroot starch that was modified using propylene oxide 10% with a STMP 1% : STPP 4% ratio of phosphate salts. The presence of phosphate bridges in the starch granules can provide freeze-thaw stability (Deetae et al., 2008). Lower values of syneresis can be used as an indicator that the starch was relatively stable at low temperatures (Damat et al., 2007). This low value of syneresis was consistent with the low setback viscosity shown in Figure 1.

4. CONCLUSION

Modifying arrowroot starch by hydroxypropylation and cross-linked methods changes its functional properties in mediums with a variety of pH conditions. All the modified starches tested had a relatively stable treatment in each medium, except at pH values of 3.5. Increasing starch solubility decreased the swelling power of starch granules, and thus lessened the sedimentation volume. Modified arrowroot starch by using propylene oxide 8% tended to maintain its granule structure upon swelling in any medium pH conditions. The syneresis value of modified arrowroot starch using 10% propylene oxide and a STMP1% : STPP 4% ratio showed the lowest value in various pH mediums. The modified arrowroot starch which has the most stable properties in various medium pH conditions was that with propylene oxide 8% and a ratio of STMP1% : STPP 4%.

5. ACKNOWLEDGEMENT

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6. REFERENCES

Damat, H., Marsono, Y., Nurcahyanto, M., 2007. The Effectiveness of the Synthesis Reaction Time of Butyrate Arrowroot Starch. *Agritek*, Volume 15(5), pp. 988–1279 [in Bahasa]

Das, A.B., Singh, G., Singh, S., Riar, C.S., 2010. Effect of Acetylation and Dual Modification on Physico-chemical, Rheological and Morphological Characteristics of Sweet Potato (Ipomoea batatas) Starch. *Carbohydrate Polymers*, Volume 80, pp. 725–732

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. *Carbohydrate Polymers*, Volume 73, pp. 351–358

Gunaratne, A., Corke, H., 2007. Functional Properties of Hydroxypropylated, Cross-linked, and Hydroxypropylated Cross-linked Ttuber and Root Starches. *Cereal Chemistry*, Volume 84(1), pp. 30–37

Grace, H.R., 1977. *Cassava Processing*. FAO Plant Production and Protection Series, Roma

Hoover, R., Hannouz, D., Sosulski, F.W., 1988. Effect of Hydroxypropylation on Thermal Properties, Starch Digestibility and Freeze-thaw Stability of Field Pea (Pisum sativum cv. Trapper) Starch. *Starch/Starke*, Volume 40, pp. 383–387

Hung, P.V., Morita, N., 2005. Physicochemical Properties of Hydroxy-propylated and Cross-linked Starches from A-type and B-type Wheat Starch Granules. *Carbohydrate Polymers*, Volume 59, pp. 239–246

Kim, H.S., Lee, Y.E., 1996. Physicochemical Properties of Crosslinked Potato Starch. *Korean Journal of Food Science and Technology*, Volume 28, pp. 573–579

Lawal, O.S., 2009. Starch Hydroxyalkylation: Physicochemical Properties and Enzymatic Digestibility of Native and Hydroxypropylated Finger Millet (Eleusine coracana) Starch. *Food Hydrocolloid*, Volume 23, pp. 415–425

Lee, H.L., Yoo, B., 2011. Effect of Hydroxypropylation on Physical and Rheological Properties of Sweet Potato Starch. *LWT Food Science and Technology*, Volume 44, pp. 765–770

Liu, H., Ramsden, L., Corke, H., 1999. Physical Properties and Enzymatic Digestibility of Hydroxypropylated ae, wx, and Normal Maize Starch. *Carbohydrate Polymers*, Volume 40, pp. 175–182

Maulani, R.R., Fardiaz, D., Kusnandar, F., Sunarti, T.C., 2013. Characterization of Chemical and Physical Properties of Hydroxypropylated and Cross-linked Arrowroot (Marantha arundinacea) Starch. *Journal of Engineering and Technology Science*, Volume 45B(3), pp. 207–221

Maulani, R.R., Fardiaz, D., Kusnandar, F., Sunarti, T.C., 2013a. Functional Properties of Hydroxypropylated and Crosslinked Arrowroot Starch. *Jurnal Teknologi dan Industri Pangan*, Volume XXIV(1), pp. 60–67 [in Bahasa]

Miyazaki, M., Hung, P.V., Maeda, T., Morita, N., 2006. Recent Advances in Application of Modified Starches for Breadmaking. *Trend of Food Science and Technology*, Volume 17, pp. 591–599

Pal, J., Singhal, P.S., Kulkarni, P.R., 2002. Physicochemical Properties of Hydroxypropyl Derivative from Corn and Amaranth Starch. *Carbohydrate Polymers*, Volume 48, pp. 49–53

Perera, C., Hoover, R., Martin, A.M., 1997. The Effect of Hydroxypropylation on the Structure and Physicochemical Properties of Native, Defatted and Heat-moisture Treated Potato Starches. *Food Res. International*, Volume 30, pp. 235–247

Rutenberg, M.W., Solarek, D., 1984. *Starch Derivatives: Production and Uses*. *In*: Whistler, R.L., BeMiler, J.N., Paschall, E.F., (Eds.), Starch Chemistry and Technology, 2nd Edition. Academic Press: Orlando, FL, pp. 311–388

Singh, J., Kaur, L., McCarthy, O.J., 2007. Factors Influencing the Physicochemical, Morphological, Thermal and Rheological Properties of Some Chemically Modified Starches for Food Applications-A Review. *Food Hydrocoloid*, Volume 21, pp. 1–22

Tessler M.M., 1978. *Process for Preparing Cross-linked Starches*. US Patent 4098997

Wattanachant, S., Muhammad, S.K.S., Hashim, D.M., Rahman, R.A., 2002. Characterization of Hydroxypropylated Cross-linked Sago Starch as Compared to Commercial Modified Starches. *Songklanakarin Journal of Science and Technology*, Volume 24, pp. 439-450

Wurzburg, O.B., 1989. *Modified Starches: Properties and Uses. 4th printing*. CRC Press, Boca Raton, FL

Yadav, A.R., Guha, M., Tharanathan, R.N., Ramteke, R.S., 2006. Changes in Characteristics of Sweet Potato Flour Prepared by Different Drying Techniques. *LWT – Food Science and Technology*, Volume 39, pp. 20–26