

Functional Properties of Dual Modified White Corn Starch

Rijanti Rahaju Maulani, Asep Hidayat, Ujang Dinar Husyari

Abstract: Dual-modified of white corn starch using hydroxypropylation and cross-linking methods were carried out to overcome the lack of native white corn starches properties in food processing application. Modifications can improve or add specific functional properties which not found in native starch. The objective of the research was to study functional properties of dual-modified two varieties of white corn starch, namely Anoman and Pulut. Modifications of white corn starch used two treatment factors, namely hydroxypropylation reaction at two levels of propylene oxide concentration (8% and 10%) followed by crosslinking reactions on two combinations of STMP phosphate compounds and STPP (ratio 1%:4% and 2%:5%). The results showed that the dual modification can improve the functional properties of white corn starch Anoman dan Pulut variety compared with its native. The dual modified white corn starches of Anoman variety significantly different with Anoman variety on the characteristic of pasting properties, water absorption capacity, swelling volume, clarity of paste, and freeze thaw stability.

Index Terms: Keywords: Dual Modified Starch, White Corn, Functional Properties, Hydroxypropylation, Cross-linking.

I. INTRODUCTION

Local white corn (Anoman and Pulut Uri 1 varieties) contain a high polyphenol compound [1], high starch, attractive white color, and higher productivity than the yellow one [2]. However, the utilization of corn starches in native form has less desirable physicochemical properties. Consequently, there was need to modify of flour properties to increase the utilization. To improve the starch properties, native starches can be modified by the chemically method through a hydroxypropylation 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 (-OCH₂CH₂CH₃) 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 [3].

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 [4]. Cross-linking can also modify the properties of granule swelling, improve the texture and the rheological properties of the paste [5], and is useful for improving the film formation properties of the paste [6]. Chemical modification of the native white corn 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 crosslink methods will produce a starch that can swell, but the starch granules remain intact [7]. In addition, starch with dual modifications will have stability in acid, heat, and mechanical degradation, and may delay retrogradation during storage [8] and increase the swelling power [3]. Utilization of white corn 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 [8]. The purpose of this research was to study the functional properties of dual-modified two varieties of white corn starch, namely Anoman and Pulut.

II. LITERATURE REVIEW

The hydroxypropylation reaction of the starch is a substitution of the hydroxyl group on anhydroglucose unit of chains [7], through etherification reaction of native starch with propylene oxide in alkaline conditions [9]. Naturally, the hydroxypropyl group is hydrophilic. When the hydroxyl group enters the starch granule, the internal bonding structure can be weakened, maintain the stability of the granule, and prevent the separation of water from the paste through syneresis. Hydroxypropylation can protect and improve the appearance and texture of food product after storage, cooling, and freezing [10]. The entry of a hydroxypropyl group randomly into the hydroxyl group of the starch chain is to protect the disruption of hydrogen bonds that encourage retrogradation-slowing the restructuring of starch polymers [10].

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This application requires an optimum level and a balance between hydroxypropyl substitution and cross-link.

Cross-linked starch is formed through chemical bonds that act as bridges between molecules in starch granules. Cross-linked starch can maintain viscosity and show lower viscosity changes [4]. Cross-linked starch can modify the properties of pasta in terms of developing granules, improving the texture, and rheological properties of paste [5], and it is useful for improving the film formation properties of paste [6]. Cross-linking can improve the resistance of starch to heat conditions for a long time, stability in acidic conditions, and more resistant to mechanical friction [10]. Cross-linking can occur by giving treatment to starch granules with multifunctional reagents which will form ether or ester bonds with hydroxyl groups in starch [4]. The legally chemical reagents that can be used to modify food starch are monosodium phosphate (SOP) (maximum 0.4%), sodium tri meta phosphate (STMP) (maximum 0.4%), sodium tri poly phosphate (STPP) (maximum 0.4%), epichlorohydrin (maximum 5 ppm), phosphoryl chloride (POCl₃) (maximum 2.5%), mixture of adipate and acetic anhydride (maximum 0.12%), and mixture of succinic anhydride and vinyl acetate (maximum 2.5%) [11].

The combination of starch substitution reactions through hydroxypropylation and cross linking has been carried out on corn starch, tapioca, wheat, waxy corn, waxy barley, rice, and sago [9], with the aim of increasing stability in acid, heat, and mechanical degradation, as well as to delay retrogradation during storage. The dual modification of ydroxypropylation and cross linking was carried out on starch which is widely used for making salad dressings, canned foods, frozen foods, and puddings [12]. Stability of molecular structure makes the starch more resistant to stirring and acid hydrolysis or breakdown of starch molecules [8].

III. METHODOLOGY/MATERIALS

A. Materials

The starch used in this study was obtained from two varieties of white corn starch, namely Anoman and Pulut. Starch was extracted by a wet extraction method. The main chemicals for the modification of the starch were STMP (sodium tri-metaphosphate), STPP (sodium tri-poly phosphate), and propylene oxide. All chemicals were purchased from the Sigma-Aldrich Chemical Company.

B. Preparation of Dual Modified Starch

The hydroxypropylation and cross-link method was conducted according to the method described by previous study [8]. White corn 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.

C. Pasting Properties

The pasting properties of white corn starch were determined by using a Rapid Visco Analyser (RVA) Tec Master type RVA-S4, according to the previous procedure [13]. The observed parameters were maximum temperature of gelatinization, peak viscosity, holding strength, final viscosity, breakdown, and setback (retrogradation).

D. Swelling Volume

The swelling volume of the starches were determined as described by previous study [3]. 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 95oC 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 120oC. The swelling volume were calculated based on equations 1:

$$\text{Swelling volume (\%)} = \frac{\text{Weight of sediment paste (g)}}{\text{Weight of starch sample (g)} \times (100 - \% \text{Solubility})} \times 100 \quad (1)$$

E. Water Absorption Capacity (WAC)

Starch (2.5 g dry weight basis db) was mixed with 20 mL distilled water in a pre-weighted centrifuge tube and then stirred for 2 min on vortex mixer and allowed it to stand for 30 min at 25°C, centrifuged at 3000g for 10 min at 25 °C and the supernatant was decanted. Gain in weight was expressed as water absorption capacity [14].

F. Paste Clarity

Starch solution 1% (1 g / 100 g) was heated in a water bath for 30 minutes while stirring, then cooled to room temperature for one hour. Paste clarity was measured using a spectrophotometer with percent transmittance (% T) at 650 nm and water was used as blank [15].

G. 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 -18oC 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% [3].

H. 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 $\alpha = 0.05$.

IV. RESULTS AND FINDINGS

A. Pasting Properties

The patterns of pasting properties of the dual modified two varieties of white corn starch are shown in Fig. 1 and the value of pasting properties are shown in table I. Pasting properties of Anoman variety starch showed in that the final viscosity value almost the same with the peak viscosity value, but Pulut variety showed that the final viscosity lower than peak viscosity (a type A pattern) [16]. Type A pattern of pasting properties has a fairly high development ability as indicated by higher peak viscosity compared to final viscosity. Compare with the pasting properties of native white corn starch (A0 and P0), the final viscosity all of dual modified white corn starches were highest.

The stability of starch paste during processing at both high and low temperatures is indicated by the value of the breakdown and setback viscosity. White corn starch of Pulut variety has higher peak viscosity value (>5000cP) than white corn starch from Anoman variety (4000-5000cP). The breakdown viscosity of white corn starch of Pulut variety that is quite sharp with the value of breakdown viscosity higher than Pulut variety. Dual modified white corn starch of Anoman variety have the setback value higher than Pulut variety, indicating a higher trend of retrogradation.

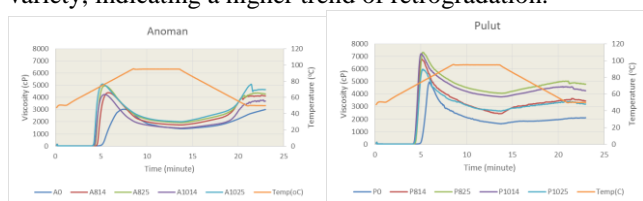


Fig. 1. The pattern of pasting properties of Anoman and Pulut varieties of white corn starches

Fig. 1 showed that in each variety of white corn starch, the breakdown viscosity of the modified starch pastes was quite sharp at 95°C, meaning the starch’s resistance to heat treatment was relatively low. When the temperature increased, the paste viscosity of modified Pulut white corn starch increased sharply. Modified Pulut white corn starch with 8% propylene oxide and STMP 2%: 5% STPP ratio (P825) showed the highest viscosity (7328 cP), while the lowest viscosity was the modified starch with 10% propylene oxide and STMP 2%: 5% STPP ratio (P1025). However, dual modification of white corn starch can accelerated the gelatinization time and reduced the pasting temperature. The

higher level of hydroxypropyl substitution was indicated by the low temperature of gelatinization [7], because hydroxypropylation will increase water accessibility so that it can reduce the pasting temperature [9]. Until the high level concentration of propylene oxide and STMP:STPP ratio, the pasting temperature of modified white corn starch decreases.

Table I: Pasting properties of Anoman and Pulut varieties of white corn starches

Treatments	Peak (cP)	Trough (cP)	Breakdown (cP)	Final Viscosity (cP)	Setback (cP)	Peak Time (minute)	Pasting Temperature (°C)
A0	3033	1431	1602	3005	1574	7.53	73.75
A814	4396	1741	2655	4137	2396	5.80	70.45
A825	4963	1936	3027	4287	2351	5.40	69.25
A1014	4244	1482	2762	3701	2219	5.40	68.80
A1025	5109	2011	3098	4648	2637	5.20	68.00
P0	4967	1634	3333	2113	479	5.93	73.25
P814	6794	2433	4361	3454	1021	5.13	69.20
P825	7329	4070	3259	4794	724	5.20	69.65
P1014	7227	3784	3443	4271	487	5.07	68.85
P1025	5987	2648	3339	3202	554	5.20	69.20

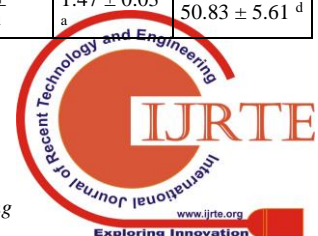
Notes: A = Anoman variety; P = Pulut variety

B. Swelling Volume

The swelling volume of modified Anoman white corn starch increased with increasing concentration levels of propylene oxide but its value decreased with increasing STPP: STMP ratio. There were significant difference ($p \leq 0.05$) among the dual-modified treatments of Anoman and Pulut white corn starches. The value of swelling volume of native Anoman white corn starch is $19.00 \pm 1.41\%$, but it’s dual-modified starch have the value of swelling volume on the rate of $28.00 \pm 1.98 - 33.00 \pm 2.33\%$. Whereas for modified Pulut white corn starch, the swelling volume decreased compared to its native starch (Table II). The value of swelling volume of native Pulut white corn starch is $87.50 \pm 3.54\%$, higher than the dual-modified starch that have the value of swelling volume on the rate of $35.50 \pm 0.71 - 52.50 \pm 3.54\%$. Hydroxypropylation increased the swelling factor of all the starches compared with their corresponding native starches, whereas cross-linking decreased the swelling factor. The existence of cross-linked groups caused the starch granules to become more rigid, which will inhibit the swelling excess [7]. The presence of hydroxypropyl groups in the starch granules increased the swelling volume.

Table II: Swelling volume, Water Absorption Capacity, Paste Clarity, and Syneresis of dual modified white corn starches

Treatments	Swelling volume (%)	WAC (%)	Paste Clarity (%T)	Syneresis (%)
A0	19.00 ± 1.41^a	208.45 ± 3.42^{abcd}	1.47 ± 0.03^a	50.83 ± 5.61^d



A814	30.50 ± 0.71 ^{bc}	206.43 ± 21.60 ^{abc}	6.08 ± 0.47 ^{cd}	33.83 ± 12.59 ^c
A825	30.00 ± 2.12 ^{bc}	191.66 ± 12.56 ^a	6.61 ± 0.14 ^{de}	22.23 ± 9.48 ^{bc}
A1014	33.00 ± 2.33 ^{bc}	198.19 ± 4.21 ^{ab}	7.75 ± 2.12 ^f	17.20 ± 7.92 ^{ab}
A1025	28.00 ± 1.98 ^b	199.11 ± 4.42 ^{ab}	6.12 ± 0.18 ^{cd}	18.67 ± 8.67 ^{abc}
P0	87.50 ± 3.54 ^f	234.61 ± 6.07 ^e	3.27 ± 0.20 ^b	6.07 ± 3.87 ^{ab}
P814	52.50 ± 3.54 ^e	218.59 ± 4.49 ^{bcde}	8.08 ± 0.41 ^f	5.34 ± 0.00 ^a
P825	35.50 ± 0.71 ^{cd}	228.28 ± 1.61 ^{de}	5.01 ± 0.28 ^c	4.29 ± 1.29 ^a
P1014	38.00 ± 2.69 ^d	225.44 ± 0.04 ^{cde}	5.69 ± 0.29 ^{cd}	3.69 ± 0.13 ^a
P1025	50.00 ± 3.54 ^e	225.36 ± 4.86 ^{cde}	7.41 ± 0.16 ^{ef}	3.50 ± 0.03 ^a

Notes: A = Anoman variety; P = Pulut variety Figures followed by the same letter are not significant according to Duncan's multiple range test ($p \leq 0.05$)

In general, the increased swelling power and solubility of hydroxypropylated starches are due to the incorporation of a hydroxypropyl group that is capable of disrupting inter- and intramolecular hydrogen bonds in the starch chains, thereby weakening the granular structure of starch and increasing the accessibility of the starch granules to water [3]. Hydroxypropyl groups in the neighboring starch chains prevent interchain association and they facilitate water molecules to penetrate into the granules and thereby increase swelling. But cross-linking reinforces the structure of starch granules and limits water absorption, thereby restricting the mobility of starch chains in the amorphous region [17]. As expected, cross-linking of hydroxypropylated starches also decreased their swelling.

C. Water Absorption Capacity (WAC)

Water absorption capacity is a function of water holding ability of the starch. It is an important processing parameter that has implication for viscosity [18]. Water absorption capacity represents the ability of a substance to associate with water under a limited water condition [19]. There were significant difference ($p \leq 0.05$) among the value of WAC from dual modified treatments. Water absorption capacity of Anoman and Pulut white corn starch were 191.66±12.56% - 208.45±3.42% and 218.59±4.49% - 234.61±6.07%, respectively. The value of WAC of both Anoman and Pulut native starch higher than the value of it's dual-modified starches. The engagement of hydroxyl groups to form hydrogen and covalent bonds between starch chains lowers WAC. The loose association of amylose and amylopectin molecules in the native starch granules has been observed to be responsible for high WBC [19].

D. Paste Clarity

The clarity of starch reflected how light is transmitted through the paste [20]. Compared with the native Anoman and Pulut white corn starch, the paste clarity of dual-modified starch increased significantly (Table II). Paste clarity is the result of rupture of swollen starch granules, and cross-linking improved the integrity of swollen granules, reducing paste clarity. Table II showed that there are a tendency to decrease the value of paste clarity with the increasing concentration of STMP:STPP ratio. Previous study stated that the clarity of

sago starch paste significantly decreased after being given a cross-link and hydroxypropylation modification treatment [21]. The decrease in paste clarity was due to the tendency of retrogradation. The hydroxypropyl group prevents the occurrence of retrogradation, a more attractive and clearer paste appearance [9].

E. Freeze Thaw Stability

The stability of starch pastes can be demonstrated by the value of syneresis: the amount of water that is separated from the granules after a freeze-thaw cycle. Syneresis is a process in which a gel contracts on standing and exudes liquid [22]. Although syneresis is a physical characteristic of most gels, it can be used to assess the freeze-thaw stability of starch by measuring the water exuded from a gel on standing or after freezing and thawing [23]. A higher value of syneresis shows a lower degree of stability. A low syneresis value on freezing and thawing is indicative of slow retrogradation of starch gels due to strong interactions between dispersed amylose/amylopectin and water molecules [24]. The syneresis value of the modified white corn starch of Anoman variety have significantly lower value than the native (Table II). There are a tendency to decrease the value of syneresis with the increasing concentration of STMP:STPP ratio. The syneresis of native Pulut white corn starch is low and the value was not significant with it's dual-modified starches. Lower values of syneresis can be used as an indicator that the starch was relatively stable at low temperatures. This low value of syneresis was consistent with the low setback viscosity shown in Fig. 1.

V. CONCLUSION

From the results obtained in this study, it can be concluded that dual modified white corn starches of Anoman variety significantly different with Anoman variety. The pasting properties of Anoman variety white corn starch have the final viscosity value almost the same with the peak viscosity value, but Pulut variety showed that the final viscosity lower than peak viscosity (a type A pattern) and low setback viscosity. Increasing concentration level of propylene oxide and STPP: STMP ratio on the dual modification reaction of white corn starch can accelerated the gelatinization time and reduced the pasting temperature. The swelling volume of modified Anoman white corn starch increased with increasing concentration levels of propylene oxide, but its value decreased with increasing STPP: STMP ratio. Whereas for modified Pulut white corn starch, the swelling volume decreased compared to its native starch. The value of water absorption capacity of both Anoman and Pulut native starch higher than the value of it's dual-modified starches.

Compared with the native Anoman and Pulut white corn starch, the paste clarity of dual-modified starch increased significantly, there are a tendency to decrease the value of paste clarity with the increasing concentration of STMP:STPP ratio. The syneresis value of the modified white



corn starch of Anoman variety have significantly lower value than the native. There are a tendency to decrease the value of syneresis with the increasing concentration of STMP:STPP ratio. The syneresis of native Pulut white corn starch is low and the value was not significant with it's dual-modified starches. Lower values of syneresis can be used as an indicator that the starch was relatively stable at low temperatures.

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