The Effect of Reaction Time and pH on the Process of Sago Starch

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Abstract. The purpose of this study was to determine the optimal operating conditions in the process of making oxidized starch. Tapioca oxidizing reaction is using sodium hypochlorite compound. The fixed variable is the weight of cassava starch as much as 20 gr, 50 ml of 0.01 N sodium hypochlorite and condition of reaction is at room temperature. Variable changes are pH 6, 7, 8, 9 and reaction time 30, 60, 90, 120 minutes. Characteristics of oxidized starch were a carboxyl group, swelling power, and solubility analysis. The application of oxidized sago starch is as an adhesive in the pulping process. From the results of the study it can be seen that as the reaction time increases, carboxyl groups increase, decrease in swelling power and increase in solubility. Whereas along with the increase in pH of the solution there was an increase to pH 8 but then decreased at pH 9 and reaction time 90 minutes.

1. Introduction

Abundant sago is very unfortunate if its use is not maximized because sago flour can support various industries, both home, medium and high-tech industries. For example, sago flour can be used as the main ingredient or additional material for the paper industry. However, natural sago has several constraints if used as raw materials or additives in the industry, especially the paper industry. This is related to the characteristics of the sago itself, for example, the pasta formed is hard and not clear. Besides that, it is too sticky and cannot stand the treatment with acid. These constraints cause natural sago starch to be limited in their use in industry.

Starch oxidation is one of the types of chemical modification and is an important and widely used modification method. This is because the starch produced has low viscosity, high paste stability, good bonding and film formation properties, and higher clarity. Oxidized starch can also be applied more widely in various industries such as paper, textiles, laundry and as a surface coating material. Sodium hypochlorite is one of the many oxidizing compounds used for starch oxidation. The addition of NaOCl will produce a modified starch containing carboxyl and carbonyl groups, each of which is obtained by the oxidation of the primary hydroxyl group and secondary hydroxyl. Oxidation of these hydroxyl groups prevents the formation of hydrogen bonds which affect retrogradation and gel formation, thus affecting the texture and strength of gel properties, hence it is suitable to be applied in the paper industry.

Several studies on starch oxidation have been carried out and developed. [1] also modified starch in oxidation and suggested that the solubility of oxidized starch would cause the gel to have a high degree of purity because only a small degree of oxidation would produce quality products. [2] used hypochlorite solution to oxidize potato amylose and wheat at pH 7 and the results showed a decrease
in viscosity and a decrease in the velocity of retrogradation and also an increase in aldehyde and carbonyl groups, if the pH was increased there was the decrease of carbonyl while carboxyl increased.

In this study, researchers were interested in conducting starch modification research with oxidation techniques on sago starch, it is expected that after starch modification, starch has a gel that has a high degree of purity, and has a good level of retrogradation and dispersion ability. So that the starch oxidation products have high use values in the paper industry in general, also as adhesives and overtake the textile industry.

2. Experimental procedure

2.1. Materials
Materials used are sago, Sodium Hypochlorite (NaOCl) 0.1 N, Sulfuric Acid (H2SO4) 0.5 N, Sodium Hydroxide (NaOH) 0.1 N, Chloride Acid (HCl) 0.1 N, AgNO3 0.1 N, Indicator PP, Banana midrib, Acetic Acid (CH3COOH) and distilled Water.

2.2. Equipments
The equipment used are analytical balance, filter paper, plastic container, blender, oven, measuring cup, dropper pipette, measuring pipette, sieve (100 mesh), chemical glasses, cup glasses, heater and stirrer, thermometer, vacuum filter, watch glass, funnel, petri dish, measuring flask, pH paper, scissors, aluminum foil and a set of centrifuges.

2.3. Methods
Modification process of oxidized sago starch
Making a solution with 20 g of sago starch composition and 50 ml of sodium hypochlorite (0.1 N) with continuous stirring of 400 rpm. The pH of the solution is adjusted according to the variables specified 6, 7, 8, 9 with the addition of 0.1 N NaHCO3 solution. Stop the reaction after reaching a certain time 30, 60, 90, 120 minutes. The sample is filtered by using filter paper and rinsed by using distilled water until the pH becomes 6.5—7. Then the sample is heated in an oven at 50 °C until it is completely dry. The dried sample is pureed using a blender and sieved to obtain a homogeneous size.

Swelling power analysis [3]
An amount of 0.1 g of oxidized starch was dissolved in 10 ml of distilled water. The solution is heated in a 60 °C water bath for 30 minutes with continuous stirring. Then separate the supernatant and paste formed by centrifuge at a speed of 2500 rpm for 15 minutes. Swelling power is calculated using the calculation formula:

\[
Swelling\ Power = \frac{\text{Weight of pasta of sample dried of Weight of dried sample}}{\text{Weight of dried sample of Weight of pasta}} \times 100\%
\]  

Solubility analysis [4]
Solubility test is a test of starch solubility when dissolved by water. Tests can be done by Kainuma's method, 2007 in Amrin, 2009, which is: As much as 1 gram of oxidized starch was dissolved in 20 ml of distilled water. The solution is heated in a water bath with a temperature of 60 °C for 30 minutes with continuous stirring. Then separate the supernatant and paste formed by centrifuge at a speed of 3000 rpm for 20 minutes. Take the 10 m supernatant then dry it in a 105 °C oven. Consider the dry weight of the supernatant.

\[
\%\ Solubility = \frac{\text{Weight of dried sample of Supernatant volume}}{\text{Weight of dried sample}} \times 100\%
\]  

Analysis of carboxyl content [5]
Testing of carboxyl levels is used to determine the number of carboxyl groups that infiltrate the starch chain. A total of 3 grams of modified starch were dissolved in 25 ml of 0.1 N HCl and stirred for 30 minutes. The slurry was filtered and rinsed using distilled water until the filtrate did not contain Cl−. Cl− free precipitate is dissolved in 300 ml of distilled water and heated until gelatin is formed.
Continue heating 15 minutes. The still hot solution is dripped with PP indicator and titrated using 0.1 N. NaOH. Record the volume of the titrant.

\[
\% \text{ Carboxyl group} = \left( \frac{V_{\text{oxidized NaOH}} - V_{\text{native NaOH}}}{\text{Sample weight (gr)}} \right) \times 0.0045 \times 100\% \tag{3}
\]

3. Results and discussion

3.1. The effect of oxidation time on carboxyl groups

Carboxyl groups are affected by how much carboxyl groups are substituted into oxidized sago starch. The effect of the oxidation time shows that the percentage of the carboxyl group is increasing which can be seen in Figure 1:

Figure 1 shows that at pH 8, it has a higher carboxyl value also has increased as the oxidation time at 30 minutes so the carboxyl value is 0.325% and at oxidation time of 120 minutes, the carboxyl values become 0.620%. This is due to the longer contact time of sodium hypochlorite with sago starch so that more carboxyls infiltrate the starch chain. The existence of these carboxyl groups prevents the reduction of amylose and retrogradation.

The hydroxyl group of the starch molecule is initially oxidized to a carbonyl group and is rapidly oxidized to a carboxyl group. Therefore the number of carboxyl groups formed shows the level of starch oxidation [6]. From the observation shows that the highest amount of carboxyl levels obtained at pH 8 and in 120 minutes with the value of 0.620%. This is in accordance with [5] requirements that the maximum carboxyl content obtained from the oxidation process is no more than 1.1%.

The performance of the oxidizing agent (NaOCl) which can break the saccharide monomer bond. Based on the literature referenced, that the use of NaOCl will produce modified starches containing shorter amylose chains [7].

3.2. The effect of pH on the carboxyl groups

Carboxyl levels tend to change with various pH treatments. The effect of pH on carboxyl levels can be seen in Figure 2. Figure 2 shows that the higher the pH, the carboxyl content will increase at a certain pH level, this causes more carboxyl to infiltrate the starch chain. Along the data observation, there was an increase in pH 6 to pH 8 at 120 minutes oxidation time which was 0.49% to 0.62% due to the neutral and alkaline pH of the carboxyl groups which are more substituted into oxidized -modified sago starch. However, at pH 9 there was a decrease in the carboxyl group content becomes 0.39% which was caused by the optimum condition that had exceeded the limit which resulted in the weakening of the power of the carboxyl group to infiltrate the starch chain. This also occurs at
oxidation times of 30, 60 and 90 minutes where at pH 6 to pH 8, an increase occurs and at pH 9 there is a decrease.

Figure 2. pH of the solution upon the carboxyl groups.

The optimum condition obtained in the carboxyl content analysis is at pH 8 with an oxidation time of 120 minutes because of the highest carboxyl group at pH 8 and at 120 minutes there is the most intrusion into the starch chain and still under [5] requirements.

3.3. The effect of reaction time on swelling power
Swelling in starch is highly dependent on the strength and natural properties of the molecules in the starch granules, which also depend on the natural properties and the strength of the granular binding capacity. Various factors that determine the binding capacity are the ratio of amylose and amylopectin, the molecular weight of the fractions, the molecular weight distribution, the degree of branching, the length of the branches of the outermost amylopectin molecule that play a role in the bonding bond. The effect of oxidation time on oxidized starch swelling power can be seen in Figure 3.

Figure 3. Oxidation time to the swelling power.

Figure 3 shows that pH 8 at oxidation time of 30 minutes has a high swelling power value of 7.295 g/g and decreases as the increasing of oxidation time to 120 minutes with a swelling power value of 6.247 g/g. This is due to the increasing amount of amylose content. Starch with high amylose content will prevent swelling, so the higher the amylose, the lower the swelling value. [6] reported that an increase in the amount of amylose occurs due to the breakdown of the amylopectin branch chain in α 1-6 glycoside bonds. Automatically the number of amylopectin branch chains will decrease and
increase the number of amylose main chains as a result of cracking the amylpectin branch. Amylose in oxidized-modified starch will increase as the reaction time increases and as the carboxylic group increases. There is a negative correlation between swelling power and amylose levels, swelling power decreases with increasing amylose.

Swelling power occurs due to the non-covalent bond between starch molecules. The amount of water absorbed and swelling is limited to only 30% [8]. When starch granules are heated in water batch, starch granules begin to swell. Swelling occurs in the amorphous area of starch granules. The weak hydrogen bonds between starch molecules in the amorphous region will be cracked during heating, resulting in water hydration by starch granules. Starch granules will continue to expand, and the starch molecules are completely hydrated, the molecules begin to spread to the media outside and the first one comes out is amylose molecules that have a short chain. From the observations of the natural sago starch, the swelling power value was 6.746 g/g while the modification value of swelling power decreased as the effect of the oxidation time due to the increase of crystalline starch after modification, limiting the water absorbed to the starch and making starch more limited when swell.

3.4. The effect of pH to the swelling power

The pH conditions of the modification process affect the oxidized sago starch’s swelling power. Within the pH increase, further oxidation will occur then causes termination of the amylose and amylpectin chains. The effect of pH on the decrease in amylose and amylpectin levels is quite high, the higher the pH is, the more decrease in amylose and amylpectin. This is due to the degradation of amylose and amylpectin in a base condition to form D-glucos-accharinate and D-erituronate [9]. The effect of pH on oxidized starch swelling power can be seen in Figure 4.

![Figure 4. pH of solution on The swelling power.](image)

Figure 4 shows the value of swelling power which tends to be unstable, this shows that starch degradation is easily occurring in a neutral pH and in a base condition pH compared to when the base pH is 9 or more. Starch will degrade so that the amylose group will decrease and tend to increase pasta.

The effect of pH on starch is the addition of carboxyl groups (C-O) and carbonyl groups (C=O-O-H). Both groups are effective on the viscosity of the formed pasta. There was an increase in the pH range 6 and 8 with the depolymerization of starch occurring at pH 8, considering the amylose properties which are more easily depolymerized than amylpectin so that at the pH 8 the amylose chain depolymerizes and causes more formed pasta. But at pH 9 there was a decrease due to the more amylose degraded resulting in decreased solubility of starch due to the natural properties of the amylose which tends to dissolve in the reduced or insufficient amount of water.
3.5. The effect of oxidation time to solubility

Solubility in oxidized starch increases as the increasing of reaction time. This increase in solubility indicates that oxidized modified starch is easily soluble in water because it has small size granules and high amylose content. Amylose in starch is more soluble in water than amylopectin. The effect of oxidation time on solubility values can be seen in Figure 5.

![Figure 5. The oxidation time to solubility.](image)

Figure 5 shows that pH 8 at 30 minutes oxidation time has a solubility value of 0.098% and has increased as the increase in oxidation time to 120 minutes with a solubility value of 0.137%. This is effected by the increase in carboxyl levels. Substitution of carboxyl groups in sago starch weakens the hydrogen bonds in starch so that the water becomes more easily penetrated into starch granules. This causes the solubility of sago starch to increase. Water absorption ability in starch is caused by the presence of carboxyl groups found in starch molecules. If the amount of carboxyl groups in the starch molecule is numerous, so the ability to absorb water [10].

Natural sago starch has a solubility value of 0.039%, whereas, in sago starch which has been modified by oxidation, this increase is related to the presence of amylopectin compounds in natural starch. Amylopectin is insoluble in water. In the modification process, the longer the operating time, the more amylopectin compounds are reduced, so that the starch produced can be more soluble in water. This causes an increase in solubility.

Solubility is related to the ease of water molecules to interact with molecules in starch granules and replace hydrogen bonds between molecules so that granules will more easily absorb water and have high extent. The extent will press the granule from the inside so that the granule will terminate and the starch molecules especially amylose will come through. High solubility as the increase in oxidation time causes more amylose molecules to come out of starch granules.

3.6. The effect of pH to solubility

The increase in solubility at the beginning of the process is caused by polymerization and a decrease in the strength of the starch grain structure which affects the release of amylose. This is in accordance with [11] that the solubility of flour in water is effected by the amylose fraction which is released from the starch chain. The effect of pH on the solubility of oxidized sago starch can be seen in Figure 6.

Figure 6 can be seen that the effect of pH with solubility does not show a significant effect. At pH 6 and 7 there is an increase due to the depolymerization which has not occurred yet, while at the pH 8, the highest solubility occurs. In these circumstances, carboxyl groups begin to form so as to prevent the amylose from being degraded. Amylose has the solubility in solution. This causes increased
the solubility of starch. However, there is a decrease in pH 9 because it is not optimum and it’s a saturation process.

![Figure 6](image_url)

**Figure 6. pH of the solution to solubility.**

### 4. Conclusion

From this research we can conclude that Oxidation time in the range of 30 minutes to 120 minutes in the starch modification process, carboxyl group increases, swelling power decreases and solubility increases, while in the range of pH 6 to pH is increasing but having a decrease at pH 9, among the carboxyl groups, swelling power, and solubility. From the analysis results obtained the process conditions that produce modification of sago starch with an oxidation process is at pH 8 and reaction time 90 minutes.

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