

Synthesis Study of Amylum-Carboxymethyl and Amylum-Sulfonate to Increase their Solubility in Water

Khusna Widhyahrini

Tadris IPA, Fakultas Tarbiyah dan Ilmu Keguruan, Universitas Islam Negeri (UIN) Salatiga, Salatiga, Indonesia

E-mail: khusna@iainsalatiga.ac.id

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Abstract

Modified starch is synthesized to change the physical and chemical properties, one of which is solubility. Two new things were produced in the starch substitution process, namely modifications in the final stage (workup) of the reaction of each substituent, namely changes in the neutralization stage/carboxymethyl starch solids using 30% CH_3COOH and the use of methanol pro-analyst in the starch sulfonate deposition process. The results of the solubility test showed that at room temperature and a concentration of 1.5% g/L, carboxymethyl substituted starch was completely soluble in water, while starch with the same concentration was completely soluble at 30°C . The viscosity test at room temperature resulted in a flow time of 25.02 seconds for starch-carboxymethyl and 10.15 seconds for starch-sulphonate. The α -amylase test was identified by thin layer chromatography (TLC) with the presence of reducing sugar stains on the starch-carboxymethyl hydrolysis product but not on the starch-sulphonate hydrolysis product. The Dinitrosalicylate (DNS) test showed that the amount of reducing sugar of starch sulfonate was much smaller than that of starch-carboxymethyl.

Keywords: *amylum, carboxymethyl, sulfonation, solubility*

1 Introduction

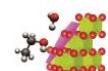
Starch is a carbohydrate in the form of a polysaccharide consisting of a large number of glucose units. Starch generally has two biopolymer components, amylose and amylopectin [1]. In the latest developments in the pharmaceutical industry, starch is used as a source of monomers or carbohydrate dimers, including for drug-binding agents, drug disintegrants, and plasma diluents [2,3]. Starch consists of amylose and amylopectin, so starch has a sticky character when dissolved in water. This behavior inhibits further utilization of starch. Therefore, the shortening of the starch glucose chain needs to be carried out, for example by a hydrolysis reaction.

Hydrolysis reactions can be carried out using several acids, bases, and enzymes. Acids that can be used for hydrolysis Examples are sulfuric acid (H_2SO_4), chlorosulfonic acid (HClSO_3), hydrochloric acid (HCl), ammonia (HNO_3), and acetic acid (CH_3COOH) [4–6]. Strong acids and strong bases are the choices for hydrolysis reactions because the products can be separated clearly. The Chlorosulfonic acid became the

sulfating agent in the reaction and showed success in the sulfonation reaction [7,8]. The product of the sulfonation reaction has a characteristic high solubility in water, in addition to having effective ion conduction properties. In the enzymatic reaction mechanism, complex carbohydrate products can be hydrolyzed to have shorter chains.

The hydrolysis reaction of starch using enzymes is a solution to produce monomers or carbohydrate dimers from starch which can then be utilized further. The hydrolysis reaction of starch using enzymes is a solution to produce monomers or carbohydrate dimers from starch which can then be further utilized in the pharmaceutical field. In the starch hydrolysis reaction using α -amylase, the glucoside bonds of amylose and amylopectin are broken to produce monosaccharides, disaccharides, and oligosaccharides. However, the hydrolysis reaction using α -amylase requires good starch solubility in the aqueous medium.

Modifications have been made to starch so that it can be dissolved in water by substitution with various functional groups including amine,



sulfonate, acetylation, and carboxymethylation. Carboxymethylation has been carried out on starch, cellulose, and also chitosan [9–11]. Modification by carboxymethylation has the effect of changing material characteristics, providing benefits both at the cellular level and in other applications such as cosmetics, bioimaging, and product packaging.

In addition to carboxymethylation, sulfonation is a modification process that can be carried out in polymer and biopolymer molecules, for example as a superabsorbent, antifungal, and also antibacterial [8,12]. Sulfonation can be carried out through several reactants for example chlorosulfonic acid and also sodium thiosulfate [7,12].

Therefore, in this study, the transformation of the hydroxyl and sulfonate groups in starch with more polar substituents was carried out [13,14]. Tests to measure the success of substitution reactions, changes in solubility, and the effectiveness of enzyme reactions using modified starch also need to be investigated in this study to solve the main problem.

2 Method

2.1 Material

Starch was obtained from cassava *Manihot esculenta* (Merck), NaOH, glacial CH_3COOH (Merck), methanol (Merck), ethanol (Merck), pyridine (Merck), chlorosulfonic acid (Merck), isopropyl alcohol (Merck).

2.2 Equipment

The tools used in this study were a reflux device, a thermometer, a beaker, a dropper, and an Infrared Spectrophotometer (FTIR).

2.3 Procedures

2.3.1 Carboxymethylation

An amount of 5 g of starch was dissolved in 150 mL of 2-propanol in a three-neck flask. Then, 15% NaOH was added to the mixture and stirred for 60 minutes at 25°C using a magnetic stirrer. 6 grams of sodium mono-chloroacetate ($\text{ClCH}_2\text{COONa}$) were added to a three-neck flask containing the suspension formed in the alkalization step, then reacted in a water bath at 55°C for 300 minutes. After 300 minutes the reaction was stopped, and the solid was filtered and washed with 80% methanol (CH_3OH) and neutralized using glacial CH_3COOH . Then, the solution was precipitated using ethanol ($\text{C}_2\text{H}_5\text{OH}$). Furthermore, the solid formed was dried at room

temperature for 60 minutes and then weighed and obtained a yield of 3.6 g (72%). Solids characterization was carried out with an FTIR spectrophotometer to determine the characteristic peaks

2.3.2 Sulfonation

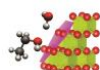
The reaction was carried out by first making a sulfating agent using pyridine as much as 14 mL was put into a three-neck flask placed in an ice bath fitted with a condenser, thermometer, and a dropper funnel containing 1 mL of chlorosulfonic acid (HSO_3Cl). Then, HSO_3Cl was slowly dripped into a flask containing pyridine to form the Pyridine- SO_3 complex, stirred using a magnetic stirrer, and the gas formed was white absorbent by using a suction flask. The reaction for the synthesis of the sulfating agent was carried out for 90 minutes and a cloudy white precipitate was obtained and a characteristic odor of pyridine. The mixture was precipitated with acetone PA twice and washed again with acetone PA with a little water.

2.3.3 Dinitrosalicylate (DNS) Test

A total of 2 grams of each starch-carboxymethyl, starch-sulphonate, and starch were dissolved in 100 mL of distilled water. An amount of 2 mL of each solution was taken and 2 mL of the enzyme was added α -amylase, then all of them were incubated at 37°C for 24 hours. After the incubation process is complete, as much as 50 μL starch-carboxymethyl, starch-sulphonate, and starch were put in a microtube and added DNS reagent then put in boiling water. After 10 minutes in boiling water, as much as 900 μL of distilled water is added to it. The resulting solution was then measured for its absorbance using a UV-Visible Spectrophotometer at a wavelength of 500 nm.

2.3.4 Viscosity Test

A viscosity test was carried out on samples of Amprotab, starch-carboxymethyl, and starch-sulphonate at a concentration of 15% (w/v) in a water solvent. Amprotab is an amylose pro tablet that was purchased commercially as a comparison control. A total of 10 mL of the sample solution was then put into the Ostwald viscometer, and the flow time was measured.



2.3.5 Thin Layer Chromatography (TLC) Test

Maltose, glucose, Amprotab, starch-carboxymethyl, and starch-sulphonate 3 each μL was spotted on the TLC plate three times. Then, elution was carried out with the eluent (butanol in ethanol) which had been made up to the mark. The plate was dried and then sprayed with a staining solution (concentrated H_2SO_4 dissolved in ethanol) and dried in an oven at 110°C until a brown stain appears.

2.3.6 Water Solubility

A solution of starch-carboxymethyl, starch-sulphonate, and starch with a concentration of 2%; 1.5%; and 1% dissolved in 25 mL distilled water at room temperature and also at 70°C and stirred for 20 minutes, and the solubility was observed by calculating the dry weight obtained after the dissolution process.

3 Result and Discussion

This research uses starch pro tablet (Amprotab) which has been modified so that later it has wider applications. Efforts have been made to modify the functional groups with hydrophilic tendencies, namely carboxymethyl and sulfonate. Modification of starch using Na-monochloroacetate ($\text{ClCH}_2\text{COO-Na}$) is a bimolecular nucleophilic substitution reaction ($\text{SN}-2$). The $-\text{CH}_2\text{COONa}$ ion is substituted for the hydroxyl group ($-\text{OH}$) found in starch. Substitution of the OH group using a carboxymethyl group can occur in all OH groups present, but it is easier to occur in the OH group attached to the C2 atom depending on the stereochemistry of the glycoside carbon. In this reaction, substitution is possible for the $-\text{OH}$ group on the C2 monomer due to the inductive effect of the glycosidic oxygen bonded between C1 and C5. The OH group is a bad leaving group, so the alcohol salt can be formed, namely an alkoxide first through a reaction with a NaOH base which is a strong base, in this case, the OH group acts as an acid. The resulting alkoxide is a strong base, so it reacts with $\text{ClCH}_2\text{COONa}$. Due to the nature of the alkoxide which is a strong base, after the substitution reaction has been carried out neutralization in this case the OH group acts as an acid. The resulting alkoxide is a strong base, so it reacts with $\text{ClCH}_2\text{COONa}$. The resulting alkoxide is a strong base, so it reacts with $\text{ClCH}_2\text{COONa}$. Due to the nature of the alkoxide which is a strong base, after the substitution reaction has been carried out neutralization [10,15].

The success of starch-carboxymethyl synthesis was analyzed using characteristic peaks indicated by the FTIR spectrum by a transmission measurement. The starch-carboxymethyl FTIR spectrum is shown in Figure 1.

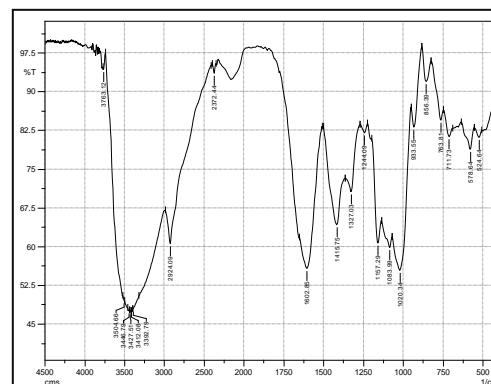
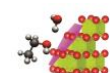


Figure 1. FTIR Spectrum of Amylum-Carboxymethyl

In the FTIR spectrum, the starch-carboxymethyl group showed a symmetric glycosidic bond ($-\text{COC}-$) at the peak of 1244 cm^{-1} and the carboxymethyl group at the peak around 1602 cm^{-1} [16,17]. The peak of 3427.51 cm^{-1} indicated the presence of a hydroxyl group ($-\text{OH}$) in the starch polysaccharide chain. At the peak of 3427.51 cm^{-1} , it shows that there is still an OH group that interacts with $-\text{CH}$ at 2924.09 cm^{-1} . The presence of a carbonyl group ($\text{C}=\text{O}$) was seen at the peaks of 1602.85 cm^{-1} and 1415.75 cm^{-1} . Further analysis was carried out on sulfonated starch by looking at the FTIR spectrum.

Starch-sulphonate synthesis was carried out using a sulfating agent. The substitution of the sulfonate group occurs at the axial $-\text{OH}$ in starch. On the side that has a chlorine group (C1), there is an electronegative $-\text{O}-$ glycosidic bond on the adjacent carbon, making each $-\text{OH}$ group more acidic. Thus, there is an OH group that is not substituted by a sulfonate group due to the electronic influence of the atoms around the OH group and the presence of steric hindrance from the branched structure of starch [18]. The organic solvent pyridine ($\text{C}_5\text{H}_5\text{N}$) was added to reduce the acidity of ClSO_3H . Sulfonation of starch is carried out by reacting a sulfating agent with Amprotab.

The resulting mixture was then washed with acetone three times, then, a mixture of acetone: distilled water at a ratio of 3:1 and precipitated with acetone PA did not form a precipitate but formed a two-phase gel that still contained pyridine [19]. Therefore, in this study, a modification of the renewal was carried out by replacing acetone as a precipitate with methanol



PA, this change in the renewal method resulted in a yellowish-white solid of 2.35 g or 78.33%. This process did not produce 100% of the product, this could be due to the possibility that starch was degraded during the reaction with sulfating agents because there was still ClSO_3H that had not reacted with pyridine so it could degrade starch. Degraded starch will dissolve during the deposition process. The starch-sulfonated FTIR spectrum is shown in Figure 2.

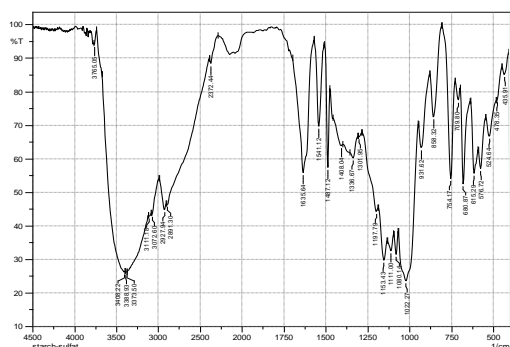


Figure 2. FTIR Spectrum of Amylum-sulfonate

Synthesis of starch-carboxymethyl and starch-sulphonate as well as cutting amylose and amylopectin into shorter [20]. In addition, starch has new characteristics with the inclusion of carboxymethyl and sulfonate groups, so it becomes attractive with the emergence of new compounds. The characteristics of the starch hydrolysis product refer to the types of amylopectin so it also affects the speed of hydrolysis [21].

3.1 Enzyme test (DNS)

Dinitrosalicylate (DNS) test was conducted to determine the mechanism of hydrolysis of modified starch. The analysis was carried out by identifying the presence of reducing sugars obtained through the hydrolysis process with enzymes α -amylase. Using glucose and maltose standards, the product obtained from the reaction with the Dinitrosalicylic reagent was then analyzed by Thin Layer Chromatography (TLC)s. From the TLC test, it is known that starch and starch-carboxymethyl which can be hydrolyzed by α -amylase, while starch-sulphonate is not hydrolyzed. This is because the starch-sulphonate formed is not a substrate of α -amylase, so it does not have an active site that can react with the enzyme.

Hydrolysis of Amprotab and soluble starch produces monomers in the form of glucose, maltose, and some stains below which may be trimers or oligomers. Hydrolysis of starch-

carboxymethyl yields glucose, maltose, and some oligomers indicated by the presence of thick stains below. The difference was seen in the intensity of the thin spots of Amprotab which was hydrolyzed using α -amylase to produce glucose, maltose, and oligomers, while in starch-carboxymethyl stains, the spots were still quite thick at positions in certain oligomers. Starch-sulphonate was not hydrolyzed by α -amylase, it was known from the TLC test that no stain was visible. One of the possible causes for the hydrolysis of starch-sulphonates is that adequate solubility of starch-sulphonates in an aqueous medium was obtained at 40°C, this temperature is not suitable for enzymatic reactions. The second possibility is that there is a change in geometry or a change in starch that has been substituted by a sulfonate which is not suitable as a substrate to undergo an enzymatic reaction mechanism.

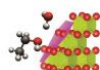
3.2 TLC Test

The TLC test was used to qualitatively determine the product of the enzymatic reaction by comparing glucose and maltose. The results of the sample TLC test are given in **Error! Reference source not found.** From the TLC test, it can be indicated that only Amprotab, soluble starch, and starch-carboxymethyl, can be hydrolyzed by α -amylase while starch-sulphonate is not hydrolyzed because there is no visible spot on the TLC plate. This is because the starch-sulphonate formed is not a substrate of α -amylase, so it does not have an active site that can react with the enzyme.



Figure 3. TLC result (Left to right: maltose, Amprotab, soluble amyllum, amyllum carboxymethyl, amyllum-sulfonate)

Hydrolysis of Amprotab and soluble starch produces monomers in the form of glucose, maltose, and some stains below which may be trimers or oligomers. Hydrolysis of starch-carboxymethyl yields glucose, maltose, and some oligomers indicated by the presence of thick stains below. The difference was seen in the intensity of the thin spots of Amprotab which was hydrolyzed using α -amylase to produce glucose, maltose, and



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that has been substituted by a sulfonate which is not suitable as a substrate to undergo an enzymatic reaction mechanism.

3.3 Viscosity Test

Viscosity tests were carried out on samples of Amprotab, starch-carboxymethyl, and starch-sulphonate at a concentration of 15% at room temperature and 30 °C. This is done based on differences in adhesion behavior and viscosity test data as shown in Table 1.

Table 1. Viscosity Measurement Result

Sample	t _{second}	average	$\eta_{\text{relatively}}$	η_{Specific}	$\eta_{\text{intrinsic}}$	Temperature
Amprotab	69.8	69.03	7.28	6.28	30.66	Room temperature
	66.54	67.18	9.20	8.20	41.00	Temperature 30°C
Amylum-carboxymethyl	24.52	25.02	2.63	1.63	8.20	Room temperature
	21.65	21.29	2.91	1.91	12.73	Temperature 30°C
Amylum-sulphonate	10.54	10.15	1.07	0.07	0.47	Room temperature
	11.23	10.52	1.44	0.44	2.93	Temperature 30°C

The sample and solvent interaction greatly affects the viscosity [22]. Based on data in Table 1, Amprotab has a high viscosity, this is due to its less polar sulfate so it cannot dissolve completely in water which has polar properties. The cohesion interaction between starch molecules and the solvent is greater than that of modified starch, either by carboxymethylation or sulfonation. This indicates that the intermolecular interactions that are adhesive between starch-carboxymethyl or starch-sulphonate with water are better than that of unmodified starch. Thus it can be concluded that the modified starch with a smaller viscosity corresponds to the solubility of starch in a water medium.

The ratio of the viscosity of Amprotab, starch-carboxymethyl, and starch-sulphonate solutions to the viscosity of the pure solvent can

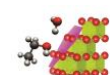
be used to determine the relative molecular mass. However, it is necessary to know the Mark-Houwink Sakurada constant which is used to determine the interaction of the polymer with the solvent.

3.4 Solubility Test

In this study, the samples used were Amprotab, starch-carboxymethyl, and starch-sulphonate with their respective concentrations; 1% g/L (w/v); 1.5% g/L; 2% g/L and proved to be soluble in water at room temperature. The dissolution process in water is carried out under certain temperature conditions so that the behavior due to modification can be seen. The results of the dissolution of Amprotab, starch-carboxymethyl, and starch-sulphonate samples are summarized in Table 2.

Table 2. Solubility Test

Sample	Concentration			Dissolving process
	2%	1.5%	1%	
Amprotab	<ul style="list-style-type: none"> Not dissolved Brownish red 	<ul style="list-style-type: none"> Not dissolved Brownish red 	<ul style="list-style-type: none"> Not dissolved brownish red 	Temperature 70°C
Amylum-carboxymethyl	<ul style="list-style-type: none"> late clear solution 	<ul style="list-style-type: none"> late clear solution 	<ul style="list-style-type: none"> late clear solution 	Room temperature
Amylum-sulphonate	<ul style="list-style-type: none"> cloudy solution soluble 0.15 gram 	<ul style="list-style-type: none"> cloudy solution soluble 0.24 gram 	<ul style="list-style-type: none"> cloudy solution soluble 0.17 gram 	Temperature 30°C

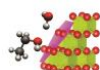


4 Conclusion

From this experiment, it can be concluded that modifying starch by using carboxymethyl and sulfonates increases the solubility of starch in water. Based on the DNS assay, hydrolyzed starch-carboxymethyl α -amylase produces more reducing groups when compared to starch-sulphonate and starch. Thus, starch-carboxymethyl can be more useful for the hydrolysis reaction of α -amylase when compared to starch-sulphonate and starch.

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