Carboxymethyl Starch Synthesis from Breadfruit Starch (Artocarpus Communis) through Esterification Reaction with Monochloro Acetate

Cut Fatimah Zuhra[1*], Mimpin Ginting[1], Arny Masyita[1] and Wilza Fithri Az-zahra[1]
[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan, Indonesia*

Keywords: Breadfruit Flesh, Carboxymethyl Starch (CMS), Monokloroacetate, Starch.

Abstract: The synthesis of carboxymethyl starch from breadfruit starch (Artocarpuscommunis) has been done through the etherification reaction with monochloroacetate. The first stage is the isolation of starch from the fruits of breadfruit fruits, where the results of FTIR analyzed obtained spectra with 3402, 2931, 1080, 1018 cm-1 waves indicating the presence of O-H, C-H stretching and C-O-C bonds, illustrating that the compound is a starch compound. The second stage is the etherification process with monochloroacetate using NaOH reagent and isopropanol as solvent. The carboxymethylation process using monochloroacetate was carried out with variations in the addition of monochloroacetate 1.5; 3; 4.5; 6; 7.5 grams and 90 times variations; 120; 150 minutes and neutralization using 2N CH_3COOH. The resultant carboxymethyl starch shows the appearance of peaks at the wavenumbers 1604 cm-1 and 1419 cm-1 in the analysis using FTIR spectroscopy showing the presence of carbonyl groups. Then the carboxymethyl starch produced was calculated by degrees of substitution and SEM analysis was performed. The highest degree of substitution was 1.8412 in weight gain of 6 grams of monochloroacetic acid with reaction time of 2 hours and obtained a rougher surface shape due to the presence of granules and a more unified appearance.

1 INTRODUCTION

Breadfruit (Artocarpus communis) has the potential as a national food security reserve because breadfruit can produce throughout the year. Besides, breadfruit contains nutrients that are not inferior to corn or tubers. This plant has long been cultivated by the people of Indonesia, but for the people of Indonesia consumption of breadfruit is generally still limited as a snack and vegetable (Pitojo, 1992). As one alternative food source, breadfruit is proven to have high nutritional content (Widowati, 2003). Breadfruit has high carbohydrate content because it is a valuable source of starch. Starch obtained from breadfruit produces 18.5 g / 100 g with a purity of 98.86% with an amylose content of 27.68% and amylopectin 72.32% (Rincom, A.M. & Fanny, 2004).

The use of starch in the industry is very broad, both in the field of food and non-food because of the ease of getting raw materials and the price is relatively cheap. However, some properties of natural starch become an obstacle if used as industrial raw materials, including the nature of starch which is easily damaged by heat and acid (Sangseethong et al., 2005). The commonly used way to overcome these weaknesses is to change the molecular structure of starch physically, chemically or combine which will improve the properties of natural starch (Liu, 2005).

Modification of starch is done by cutting the molecular structure, rearranging the molecular structure through oxidation or substitution of functional groups in starch molecules (Wurzburg, 1989). Carboxymethylation is a modification method by substituting the starch molecular function groups. This modification produces starch with low gelatinization temperature, high solubility and high shelf life (Sangseethong et al., 2005). The carboxymethylation process takes place by substituting a natural starch hydroxyl group (-OH) with a carboxymethyl group (-CH_2COO-) to produce Na-carboxymethyl starch or carboxymethyl starch (CMS) (Sangseethong et al., 2005). Utilization of Na-carboxymethyl starch, among others, as a disintegrant in the pharmaceutical industry (Shah & Augsburger, 2002) and as a sizing and printing agent in the textile industry (Ragheb et al., n.d.).

(Fachrudin, 2013) has researched Na-Carboxymethyl starch production with different

Fatimah Zuhra, C., Ginting, M., Masyita, A. and Fithri Az-zahra, W.
Carboxymethyl Starch Synthesis from Breadfruit Starch (Artocarpus Communis) through Esterification Reaction with Monochloro Acetate.
DOI: 10.5220/0010137800002775
In *Proceedings of the 1st International MIPAnet Conference on Science and Mathematics (IMC-SciMath 2019)*, pages 143-148
ISBN: 978-989-758-556-2

types of stirring at the alkalization stage, the results obtained show that the greater the concentration of NaOH and on the type of stirring carried out with homogenizer will produce higher substitution degrees. Synthesis and antibacterial of carboxymethyl starch poly-branch (vinyl imidazole) against some plant pathogens produce a degree of substitution of 0.81 and rupture of starch granules under the influence of alcohol, alkali and heat environment which replaces OH groups with carboxymethyl groups and afterwards N-vinyl imidazole is grafted to CMS in water using potassium persulfate as an initiator at 450C (El-Hamshary et al., 2014).

From the background described above, researchers are interested in examining the synthesis of carboxymethyl starch through the reaction of breadfruit starch etherification with variations in the addition of Monochloro Acetate and reaction time.

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this study include: Breadfruit, Aquadest, Isopropanol, NaOH, Monochloroacetic Acid, Acetic Acid, Acetone, HCl, Ethanol, PP indicators.

2.2 Methods

2.2.1 Isolation of Starch from Breadfruit

Breadfruit that is old or whose skin begins to turn yellow is peeled and the fruit stalk is removed. After peeling, the breadfruit is washed until it is free of dirt and sap. Then breadfruit cut into small pieces, then mashed using a blender. Breadfruit that has been mashed is filtered using gauze, the filtrate from the filter is left to form a precipitate. The precipitate obtained is washed repeatedly with water until the upper layers are clear. The starch obtained was dried in an oven at 45°C for 24 hours. The dried starch is then mashed, sieved, weighed and stored in a desiccator. Subsequently analyzed by IR spectroscopy.

2.2.2 Preparation of Carboxymethyl Starch from Pati Breadfruit

Add 5 grams of starch and 210 mL of isopropanol and 30 mL Aqudest into a three-neck flask, then the mixture is stirred with a magnetic stirrer at a speed of 400 rpm for 4 hours at a temperature of 35°C. Then 1.6 grams of NaOH has been dissolved with 25 mL aqua dest while stirred for 45 minutes and the temperature raised to 45°C. Then added 1.5 grams of Monochloro acetate which has been dissolved in 12.5 mL isopropanol and mixed with 1.5 grams of NaOH dissolved in 12.5 mL Aquadest and stirred for 2 hours. Then cooled and then the mixture was neutralized with 2 N. acetic acid. Then added acetone and filtered. The precipitate was washed with acetone-water (60:40 v/v) and pure acetone. And the end product carboxymethyl starch is dried in an oven 50°C.

The procedure was carried out with the variation in weight of Monochloro acetate 1.5; 3; 4.5; 6; 7.5 grams and reaction time of 1.2; 2; 2.5 hours. Carboxymethyl starch obtained was analyzed by FT-IR and SEM, the degree of substitution was calculated.

2.2.3 Determination of Degree of Substitution (ISO 11216-1998)

Carboxymethyl starch samples were converted to acidic form with the addition of HCl. A sample of 1.5 g was added with 45 ml of acetone, added with 3.75 ml of HCl 6M and stirred with a stirrer for 30 minutes. The filtered solution is then dispersed in 80% ethanol, filtering the solution to neutral pH. The filtration results are dispersed in absolute ethanol, then filtered and dried for 24 hours in an oven at 50°C. 0.5 g of sample was dissolved in 25 ml of 0.1 M NaOH and added with 75 ml of distilled water. Samples were then titrated using 0.1 M HCl with phenolphthalein indicator (ISO 11216-1998).

2.2.4 Functional Group Analysis with FT-IR Spectroscopy

Carboxymethyl starch was mashed with pestle and mortar and then made into pellets with KBr and spectra were measured with FT-IR spectroscopy.

2.3.5 SEM Analysis (Scanning Electron Microscopy)

The sample is placed in a cell holder with a double lid. The sample is inserted into a Scanning Electron Microscopy (SEM), then the surface image is observed and magnified as desired. Then a photoshoot is taken.

3 RESULTS AND DISCUSSION

3.1 FTIR Spectrophotometer Analysis of Breadfruit Starch

Isolated starch from 8 breadfruits with a mass of about 18 kg is 470 grams (2.61%). FT-IR spectroscopy data of breadfruit starch provide spectrum with vibrational peaks in the region of wave numbers 3402, 2931, 2121, 1381, 1080, and 1018 cm-1 (Figure 1).

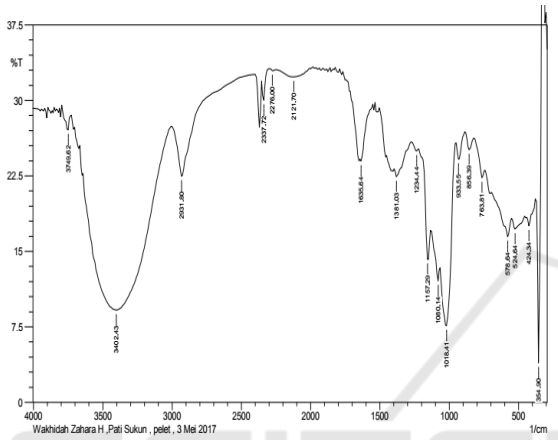

Figure 1: FTIR spectroscopy of breadfruit starch.

The spectrum shown from FT-IR data gives support that the starch obtained has an OH group with the emergence of a vibration peak at wave number 3402 cm-1, supported by the emergence of a stretching CH group at number 2931 cm-1, and the carbonyl group (C = O) at 1635 cm-1 (Figure 1) corresponding to commercial starch (Nurafrida, 2011) and COC bonds shown at numbers 1080 and 1018 cm-1 (Ochoa, 2013).

3.2 Carboxymethyl Starch

Carboxymethyl starch is produced through the process of etherification with Monochloro acetate (MCA) in an alkaline atmosphere. The first stage is alkalization with NaOH as a promoter and producing alkaline starch. Starch before entering the alkalization stage is dispersed first in an isopropanol solvent. Isopropanol functions as a reaction medium, besides that isopropanol, will also dissolve minor components such as fiber, ash, fat, and protein. The dispersed starch then undergoes a stirring process.

The alkalization stage is the opening step to activate the starch hydroxyl group (St-OH) into a negatively charged alkoxide group (St-O-). The alkalization stage creates a stress-strain on adjacent starch molecules, this will weaken the starch double helix bond area and damage the starch crystalline structure (Chen & Jane, 1994). This condition will facilitate the solvent and MCA to enter the starch granules and substitute the alkoxide group with the carboxymethyl group from the MCA (Kooijman et al., 2003).

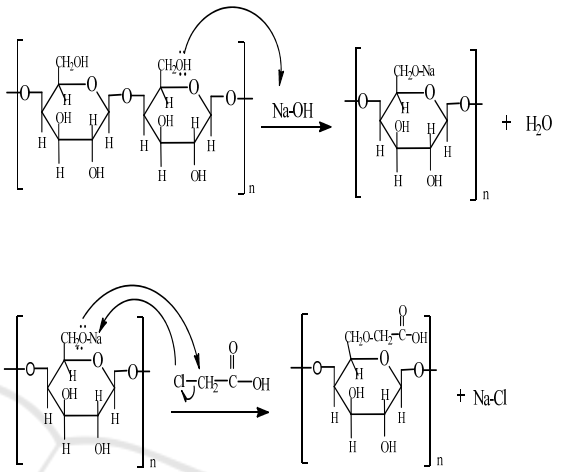

Figure 2: The reaction mechanism of an experiment making carboxymethyl starch.

The variation made in this study is the weight variation of Monokoloroetetat which is 1.5, 3, 4.5, 6, and 7.5 grams and the reaction time is 90, 120 and 150 minutes. The carboxymethyl starch obtained in the form of a carboxymethyl solid can theoretically be seen in Figure 3. The light brown color is transparent, where the carboxymethyl starch resulting from synthesis is 4,50 g respectively; 4.82 g; 4.77g; 4.95 g; 4.65 g; and 4.71 g; 4.95 g; 4.54g.

Figure 3: Synthesis of carboxymethyl starch.

3.3 FTIR Spectrophotometer Analysis of Carboxymethyl Starch

Carboxymethyl starch was analyzed using FT-IR spectroscopy. FT-IR spectrum results using 1.5 gram Monocloroacetate; monochloroacetate 3g; 4.5g monochloroacetate; 6g monochloroacetate;

Monochloroacetate 7.5g and with an etherification reaction time of 90 minutes; etherification reaction time of 120 minutes; the etherification reaction time of 150 minutes has shown vibrations in the region of wave numbers 3417, 2931, 1604, 1419, 1373, and 1026 cm^{-1}.

The formation of carboxymethyl starch was shown in the results of FT-IR analysis of monochloroacetate weight variation and reaction time. Characterized by the emergence of vibration peaks in the region of wave numbers 1601-1408 cm^{-1} which shows the COO region (El-Hamshary et al., 2014). It was also stated by (Zhang, 2012) and (Ochoa, 2013) that the emergence of the COO group was marked by the peak spectra of 1618 cm^{-1} and 1424 cm^{-1} as well as 1605 cm^{-1} and 1417 cm^{-1}. In starch carboxymethyl, there was a change in the intensity of the carbonyl group in the 1604 cm^{-1} and 1419 cm^{-1}regions. Changes in the intensity of starch carboxymethyl carbonyl groups with variations in the weight of monochloroacetate 1.5; 3; 4.5; 6; and 7.5 grams with a 120 minute etherification reaction time of 1635 cm^{-1} and 1419 cm^{-1}; 1604 cm^{-1} and 1411 cm^{-1}; 1620 cm^{-1} and 1419 cm^{-1}; 1604 cm^{-1} and 1419 cm^{-1}; 1620 cm^{-1} and 1458 cm^{-1}. From the FT-IR data, the highest intensity of the carbonyl group is at 6 grams of monochloroacetate weight. Starch weighing 6 grams of monochloroacetate was continued with time variations of 90 and 150 minutes, and the intensity of the carbonyl group was 1635 cm^{-1} and 1458 cm^{-1}; 1635 cm^{-1} and 1458 cm^{-1}. This shows the occurrence of the addition of carboxylic groups to starch carboxymethyl. From this data, the most optimum is carboxymethyl starch with 6 gram Monocloroacetate weight with 120 minutes reaction time, because the highest intensity of the carboxylate group is 11,072. Comparison of the FT-IR spectrum of monochloroacetic weight variation and reaction time variation can be seen in Figure 4 and Figure 5.

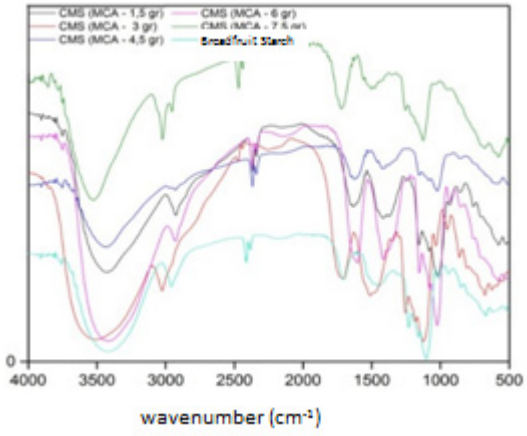

Figure 4: FTIR spectrum of carboxymethyl starch by monochloroacetate weight variation.

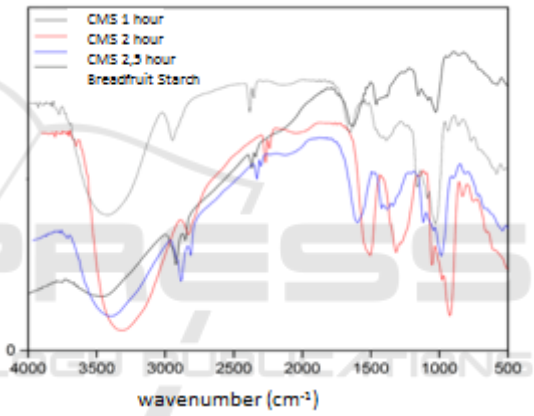

Figure 5: FTIR spectrum of carboxymethylstarch variation in reaction time.

3.4 Determination of Substitution Degree

Determination of the degree of substitution titration method based on ISO 11216-1998. In the weight variation of monocloroacetate, the highest carboxylate content was obtained, with 6 grams of monocloroacetate treatment at 1.8412 per AGU. The results of determining the degree of substitution with variations in weight Monocloroacetate and variations in the time of the etherification reaction as in Table 1 and Table 2.

Table 1: Degrees of starch carboxymethyl substitution with variation in weight Monochloroacetate.

Weight $(C_8H_{12}O_8)_n$ (g)	Degree of Substitution (by AGU)
1.5	0.1669
3	0.5823
4.5	1.1036
6	1.8412
7.5	0.8160

Table 2: Degrees of starch carboxymethyl substitution with variations in reaction time.

Esterification Time (minutes)	Degree of Substitution (by AGU)
90	0.2772
120	1.8412
150	1.4379

In this study DS results obtained ranged from 0.1669 - 1.8412. Where the highest DS of 1.8412 comes from carboxymethyl starch with 6 grams of monochloroacetate weight. In the manufacture of carboxymethyl starch when monochloroacetate is added too little so that the substituted is too little and will cause a reaction that occurs less than the maximum, whereas if the monochloroacetate added too much will react with NaOH to form Sodium glycolic acid. This is because in the starch carboxymethyl synthesis reaction using the Williamson reaction is carried out in the presence of a strong base to increase the nucleophilicity of the hydroxyl group and to help breakdown starch particles, but side reactions can also occur with sodium hydroxide, producing glycols (Lawal et al., 2007).

3.5 SEM Analysis Results

SEM testing was carried out on breadfruit starch and carboxymethyl starch with the highest degree of substitution which was in the 6 grams MCA treatment and 120 minutes reaction time as in Figure 6 and Figure 7.

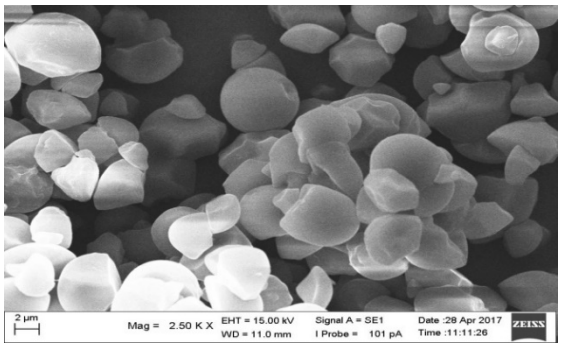

Figure 6: Surface Morphology of Breadfruit Starch (Magnification 2500x).

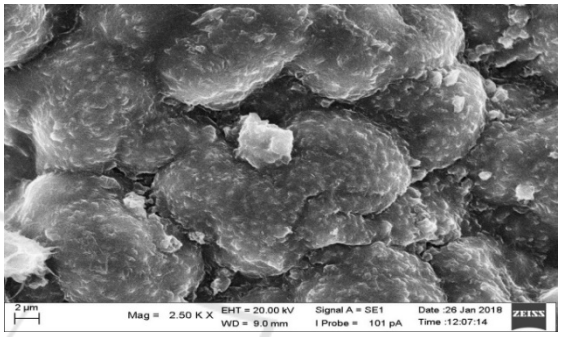

Figure 7: Morphology of Carboxymethyl Starch Surface (Magnification 2500 x).

SEM analysis is performed to see the morphology of the modified starch compounds obtained. In this study, the SEM test was only performed on carboxymethyl starch with the highest DS, carboxymethyl starch by adding 6 grams of MCA weight with a reaction time of 120 minutes, with an enlarged image of 2500 times. The surface shape of breadfruit starch at a magnification of 2500 times (figure 6) can be seen clearly that breadfruit starch consists of finely spaced granules and oval or egg granules as reported by (Ahmad et al., 1999) and the carboxymethyl starch surface shape (figure 7) showing a rougher surface shape because there are granules around it, with a smaller distance so it looks like it blends in comparison with the original breadfruit starch.

4 CONCLUSIONS

From the results of the research that has been done, the following conclusions can be drawn:

1. The carboxymethyl starch synthesis process uses 2 steps, namely the alkalization process and the carboxymethylationprocess. The optimum

conditions for the 6 grams monocloroacetate weight gain treatment with an etherification reaction time of 120 minutes showed a substituted degree of 1.8412.

2. SEM analysis results show starch surface shape is smoother, round with a large cavity. While the carboxymethyl starch surface shape is coarser, granules have granules around it, have a smaller distance so it looks like they are fused.

REFERENCES

Ahmad, F. B., Williams, P. A., Doublier, J. L., Durand, S., & Buleon, A. (1999). Physico-chemical characterisation of sago starch. *Carbohydrate Polymers*, *38*(4), 361–370.

Chen, J., & Jane, J. (1994). Preparation of granular cold-water-soluble starches by alcoholic-alkaline treatment. *Cereal Chem*, *71*, 71: 618 – 622.

El-Hamshary, M.G. Fouda, M., MeeraMohideen, El-Newehy, H. M., Al-Deyab, S. S., & Abdel-Megeed, A. . (2014). *Synthesis and Antibacterial of Carboxymethyl Starch-Grafted Poly(vinyl imidazole) Against Some Plant Pathogens*. Elsevier.

Fachrudin, R. (2013). *Produksi Pati Na-Karboksimetil dengan Perbedaan Tipe Pengadukan padaTahap Alkalisasi*. IPB Pres.

Kooijman, M., Ganzeveld, J., Manurung, R., & Heeres, H. (2003). Experimental studies on carboxymethylation of arrowroot starch in isopropanol-water media. *Starch*, *55*, 495 – 503.

Lawal, O., Lechner, M., & Kulicke, W. (2007). Single and multistep carboxymethylation of water yam (Dioscoreaalata) starch: synthesis and characterization. *Int J BiolMacromol*, 429 – 435.

Liu, Q. (2005). *Understanding starches and their role in foods.in: Food Carbohydrates: Chemistry, Physical Properties, and Applications*. Taylor & Francis.

Nurafrida. (2011). *Pembuatan Carboxymethil Strach Graft Polyacrylamide dan Karakterisasinya*.

Ochoa, N. (2013). *Modified Cassava Starches as Potential Corrosion Inhibitors for Sustainable Development*.

Pitojo, S. (1992). *Budidaya Sukun.* Kanisius.

Ragheb, A., El-Sayiad, H., & Hebeish, A. (n.d.). Preparation and characterization of carboxymethyl starch (CMS) products and their utilization in textile printing. *Starch*, *49*(Starch), 238 – 245.

Rincom, A.M., & Fanny, C. P. (2004). Physicochemical properties of Venezuelan breadfruit (Artocarpus altilis) starch. *Arch Latinoam Nutr*, *54*(4), 449–456.

Sangseethong, K., Ketship, S., & Sriroth, K. (2005). . 2005. The role of reaction parameter on the preparation and properties of carboxymethyl cassava starch. *Starch.*, *57*, 345 – 359.

Shah, U., & Augsburger, L. (2002). Multiple sources of sodium starch glycolate, NF: evaluation of functional equivalence and development of standard performance tests. *Pharm Develop Technol*, *7*, 345 – 359.

Widowati, S. (2003). *Prospek Tepung Sukun Untuk Berbagai Produk Makanan Olahan Dalam Upaya Menunjang Diversifikasi Pangan*.

Wurzburg, O. (1989). *Modified Starches: Properties and Uses*. CRC Press.

Zhang, B. (2012). *Synthesis and characterization of carboxymethyl potato starch and its application in reactive dye printing*. Elsevier Inc.