Synthesis of Cross-linked Breadfruit Starch (*Artocarpus communis*) using Epichlorohydrin

Cut Fatimah Zuhra[1,2*], Mimpin Ginting[1] and Desi Sonya Siregar[1],
[1]*Departement of Chemistry, Faculty Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan, North Sumatera , Indonesia*
[2] *Pusat Unggulan Iptek Kitosan dan Material Maju*

Keywords: Breadfruit Starch, Epichlorohydrin, Cross-linked Starch, Degree of Substitution.

Abstract: Synthesis of cross-linked starch has been successfully carried out by crosslinking reaction between breadfruit starch (*Artocarpus communis*) and epichlorohydrin with variation of epichlorohydrin 1%; 2%; and 3 %. The result of cross-linked starch was characterized by FT-IR spectrophotometer and the degree of Substitution (DS). The formation of cross-linked starch was confirmed by FT-IR spectra data with the appearance of stretching vibrational of C-O-C at 1018.41-1242.16 cm^{-1}. The value of DS for variations of epichlorohydrin 1%; 2%; 3% are 0.0552; 0.0701; 0.0613, respectively. The cross-linked starch with variation 2% of epichlorohydrin has the highest DS and then it was characterized using SEM and determined the swelling degree. The results of the swelling degree test with a variation of absorption time of 6 hours, 24 hours, 36 hours, 72 hours were 0.9925%, 1.4611%, 1.8054%, 2.0049%, 3.0124%, respectively.

1 INTRODUCTION

Starch is one of important source of food ingredients. Starch can be found in grains, tubers and fruit from plant which has shape like granules (Sauyana, 2014). The application of starch as a raw material for industry is very broad, including in the food, textile, cosmetics and paper industries. The need of starch tends to increase both for domestic consumption and exports. Considering the need of starch is quite large, many reseacher were interested to find the alternative source of starch from other crops other than the source of starch as well as we know such as cassava, potatoes and corn (Hartati and Prana, 2003).

Breadfruit is one source of starch and intensively cultivated in Indonesia. Breadfruit has high carbohydrates contain so that breadfruit is a promising source of starch. The isolation starch from breadfruit produced 18.5g/100g which have 98.86% of purity with amylose and amylopectin content of 27.68% and 72.32%, respectively (Rincón and Padilla, 2004).

Natural starches such as tapioca, corn starch, sago have problems if used as raw material for food and non-food industries. If we cooked starch takes a long time (until it needs high energy), also the pasta that is formed hard and not clear. Besides that it is too sticky. These constraints cause natural starch to have limited use in the industry. Even though the source and production of starch in our country is very abundant, which consists of cassava starch, sago starch, rice starch, and many other sources of starch that have not been produced commercially. The development of technology in the field of starch processing, starch can be modified according to the properties that we needed (Zuhra, et al, 2018).

Modified starch is starch that hydroxyl group has been altered through a reaction or by modifying its original structure. Pati is given certain treatment with the aim of producing better properties to improve the previous properties so that they can be used in accordance with industrial needs (Wijayatiningrum, 2009).

Crosslinking method is one of method to modify starch. The principle of this method is the way to replace the OH group of starch and replaced it with other functional group such as an ether, ester, or phosphate group (Stevens, 1989). The advantages of using crosslinking method can produce starch with lower swelling capacity, furthermore its impact to strengthen starch granules and make the starch more resistant to acidic and hot media so that it does not

Zuhra, C., Ginting, M. and Siregar, D.
Synthesis of Cross-linked Breadfruit Starch (Artocarpus communis) using Epichlorohydrin.
DOI: 10.5220/0008878902180222
In *Proceedings of the 1st International Conference on Chemical Science and Technology Innovation (ICOCSTI 2019)*, pages 218-222
ISBN: 978-989-758-415-2

break easily during heating process. In addition, crosslinking methods can improve texture and viscosity of starch. However, this method has disadvantages such as decreasing of the solubility, precipitation, volume and stability of starch (Raina et al., 2006).

The crosslinking of carboxymethyl starch from rice was made by reaction between rice starch and epichlorohydrin at concentrations (0.1-15% w/w). The crosslinking reaction of carboxymethylation directly using methanol as a solvent, the degree of carboxymethylation substitution was between 0.24-0.26 w/w with lower the content of amylose. The resultof SEM showed a small changes on the surface of the granule. Absorption of water volume and swelling capacity of crosslinked starch increased significantly as a result of modification (Kittipongpatana and Kittipongpatana, 2013).

Original (unmodified) rice starch has rarely use in industrial processes so modification of starch is needed to reach the standard of food products. Rice starch is cross-linked with epichlorohydrin with various different concentrations (0.5%, 0.7%, 0.9% w / w, based on dry weight). Hydrolyzed rice starch by α-amylase and hydrolyzed rice cross-linked starch showed that the degree of amylase hydrolysis is lower than hydrolyzed rice starch (Xiao et al., 2012).

The crosslinking agent used in this study were epichlorohydrin. Epichlorohydrin is the best of crosslinking agent if we compared to other monomers such as $POCl_3$ and Sodium Trimetaphospate (STMP) because its has small molecular weight (Rodríguez and Nunez, 2008). The crosslinking bond that formed between carbohydrate and epichlorohydrin generaly were ether which bridges or connects of two hydroxyl groups or more glucose units from starch molecules (Wurzburg, 2010).

Based on the background, the researcher is interested to synthesis cross-linked starch by crosslinking reaction betweeen starch that isolated from breadfruit and various concentration of epichlorohydrin.

2 MATERIALS AND METHODS

2.1 Materials and Equipment

Breadfruit starch is isolated from ripe breadfruit. Chemical used, which is sodium carboxymethyl cellulose and aluminum sulfate octadecahydrate are purchased from Merck & Co.

2.1.1 Material

The materials used in this study are: Starch Breadfruit, Epichlorohydrin, NaOH, HCl, NaCl, Aquadest, Phenolphtalein Indicator.

2.1.2 Equipment

The tools used in this study were: FT-IR Shimadzu Spectrophotometer, Scanning Electron Microscope Hitachi, Blender, Desiccator, Analytical Balance, Oven Blower, Burette, Beaker Glass, Pumpkin Measure, Measuring Cup, Hotplate Stirer, Universal Indicator, Funnel, Desiccator , Magnetic stirrer, Statif and clamp.

2.2 Methods

2.2.1 Isolation of Starch from Breadfruit

Breadfruit was peeled, cut into small piece, and then washed using water to remove the gum and other impurities. The resulted breadfruit was added with enough water and then mashed using a blender. Furthermore, the result was then pricipitated after filtered using gauze. The precipitation was washed frequently until the washed water waste was transparent. The obtained starch was dried in the oven at 45^0C for 24 hours. This step aims to prevent starch becoming charred and gelatinized. Crude starch was then milled and sieved with a size of 115 mesh (Merdikasari et al., 2009). Finally, the starch was analyzed using FT-IR and SEM.

2.2.2 Synthesis of the Cross-linked Starch

Synthesis of cross-linked starch was carried out based on the (Xiao et al., 2012) method with a slight modification, namely crosslinking of starch with epichlorohydrin. 30 gram of breadfruit were mixed with 45 ml aquadest until a suspension was formed and then 3 grams of NaCl, 1% epichlorohydrin was added successively and stirred. The mixture was made into pH = 10 by dripping 1 M NaOH while stirring and then stirred for 3 hours at 30ºC. Subsequently, the starch pulp obtained was neutralized to pH 6.0-6.5 with 1 M HCl and washed thoroughly. The starch was dried at 45^0C for 24 hours. Crude crosslinked starch was milled and sifted. The same procedure was carried out for variation 2% and 3% Epichlorohydrin. Finally, the cross-linked starch were analyzed using FT-IR and SEM, and also determined the degree of substitution (DS) and the degree of swelling capacity.

2.3 Characterization

2.3.1 Determination the Degree of Substitution (DS)

The Degree of Substitution (DS) of cross-linked starch was determined by titration method. Weighed as much as 0.1 grams of starch, dissolved in 5 mL NaOH 0.5 N and stirred for 30 minutes. Then 3 drops of phenolphthalein indicator were added and titrated with 0.5 N HCl until it reached the equivalent point.

2.3.2 Determination of Swelling Capacity

The degree of swelling capacity determined by (Zuhra, et al, 2018) method, the starch were weighed at 2-3 grams, then placed on a dry cup whose weight was known, then stored in a desiccator which had been saturated with K2SO4 or KCl solution and observed weight gain. Samples were weighed over a period of 6, 12, 24 48, 72 hours.

2.3.3 Fourier Transform Infra Red (FT-IR) Spectroscopy

The Fourier transform infrared (FTIR) spectra were recorded with Shimadzu-IR Pretige 21 Spectrometer were recorded in the transmittance mode in region 400-4000 cm^{-1} at 16 cm^{-1} resolution. Samples were mixed with KBr powder and examined using IR spectrometers.

2.3.4 Scanning Electron Microscope (SEM)

The morphology of the surface of samples were discovered by using Scanning electron microscope (SEM) Hitachi and operated at 20 kV. Sample were recorded at magnification between 1000 to 10000 times their original sizes.

3 RESULT AND DISCUSSION

3.1 Isolation of Breadfruit Starch

The result of isolation of breadfruit starch (*Artocarpus communis*) from 10 kg of breadfruit was obtained as much as 680 g (6.8%) mass of starch. The data of FTIR spectrum of fruitbread starch displayed in Figure 3.1. the characteristic vibrations that confirm of breadfruit starch appeared at the wave number area 3387cm^{-1}; 2931 cm^{-1}; 1643 cm^{-1}; 1157 cm^{-1}. The broad and intense peak at 3387 cm^{-1} attributed to O-H stretching vibration and the peak at 2931 cm^{-1} corresponded to C-H stretching and also the peak at 1157 cm^{-1} indicated as C-O-C functional group.

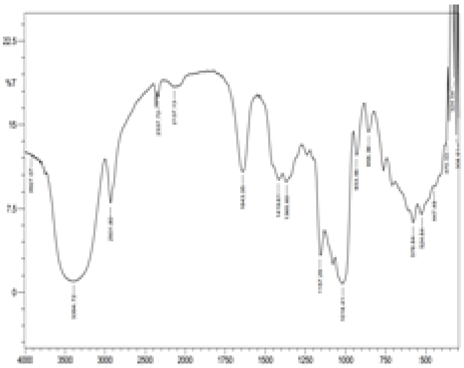

Figure 1: FTIR Spectrum of Breadfruit Fruit Starch.

3.2 Synthesis of Cross-Linked Starch

The cross-linked starch was obtained by crosslinking reaction between starch and epichlorohydrin with addition of NaOH as catalysts. The data of FTIR spectrum of cross-linked starch displayed in Figure 3.2. The formation of cross-linked starch with variation 1%,2%,3% of epichlorohydrin was showed by FT-IR spectra data with appearance of the range wave number at 3000-3500 cm^{-1}, 1630-1650 cm^{-1}, 1010-1160 cm^{-1}.

The increasing variation weight of epichlorohydrin reduced the intensity of vibration peak at 3387 cm^{-1} and the appearance of a vibration peak in the area at 1018 -1242 cm^{-1} corresponded to C-O-C functional group. The peak at 1018 cm^{-1} showed intramolecular hydrogen bonds, it was confirmed with breadfruit starch peak at 1018 - 1242 cm^{-1} more intense than cross-linked starch. This implied that hydrogen bonds have been severed (Xiao et al., 2012).

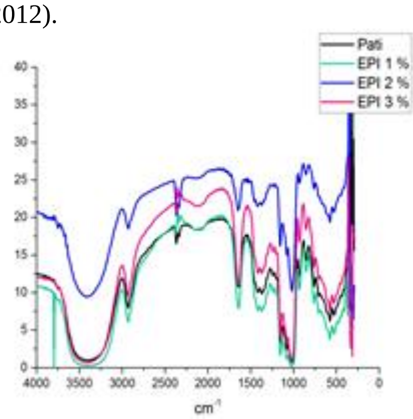

Figure 2: FTIR spectrum of cross-linked starch with various concentration of epichlorohydrin (1%, 2%, 3%).

3.3 Degree of Substitution

In this study, the DS was obtained with ranged from 0.0552 - 0.0701 that can be seen in Table 3.1. The cross-linked starch with addition 2% of epichlorohydrin was the highest DS. In process of the preparation of cross-linked starch influenced by the number of crosslinking agents used and the length of reaction time. In this study, the more epichlorohydrin used, so that the more clusters can replace the OH group. This is caused by the lenght of contact time between epichlorohydrin and breadfruit starch. The longer of contact time can weaken the hydrogen bonds in starch. But the addition of 3% epichlorohydrin, did not show improvement of the DS but a decline of the DS if it was compared with the value of the DS of cross-linked starch with addition 2% of epichlorohydrin (Zuhra, et al, 2018).

Tabel 1: The value of DS of cross-linked starch with various concentration of epichlorohydrin.

Concentration	% DS	DS
Epiklorohidrin 1%	0,33	0,0552
Epiklorohidrin 2 %	0,415	0,0701
Epiklorohidrin 3%	0,365	0,0613

3.4 The Morphology Analysis

SEM analysis was performed to investigate the surface morphology of the breadfruit starch and the cross-linked starch with magnification 2500 times that can be seen in Figure 3.3 and 3.4. In this research, the SEM test only observed for the cross-linked starch with addition 2% of epichlorohydrin that has the higest value of DS. The shape of breadfruit starch and cross-linked starch are both in the form of granules but they have a little difference which is the surface granule of breadfruit starch the surface of the granule is more finer and the distance between the granules is more tenuous while in the surface granule of cross-linked starch is more coarse and the distance is more tightly. This showed that the addition of epichlorohydrin affects the shape of starch granules (Zuhra et al., 2004).

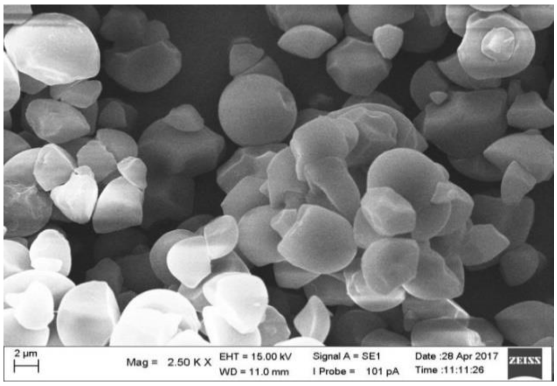

Figure 3: The surface morphology of breadfruit starch with magnification 2000x.

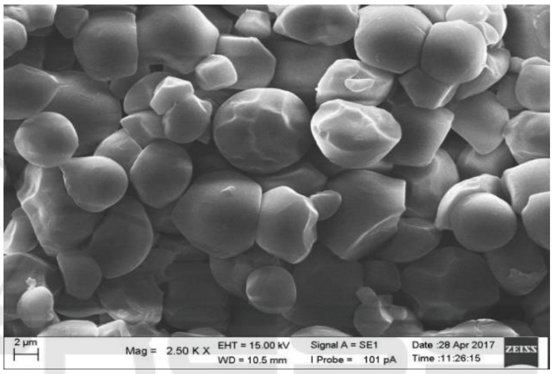

Figure 4: The surface morphology of cross-linked starch with magnification 2000x.

3.5 Degree of Swelling Capacity

In this study, the determination degree of swelling capacity was performed to breadfruit starch and the cross-linked starch with addition 2% of epichlorohydrin that has the highest value of DS. Its can be seen in Table 3.2. The results showed that the percentage of swelling capacity increased along with the rising absorption time. Furthermore, the swelling capacity decreased if it compared to breadfruit starch, This is caused by crosslinking that are formed between amylose molecules in starch granules, and then causing swelling to be limited. This is also influenced by the presence of cavities in the starch that is formed by crosslinking reaction, so that water molecules will be trapped to the cavity.

Table 2: Swelling capacity of breadfruit starch and cross-linked starch.

Time (hour)	W absorption (%)	
	Breadfruit starch	Cross-linked starch
6	1.4842	0,9925
12	2.3358	1.4611
24	3.0032	1.8054
48	4.4974	2.0049
72	6.5195	3.0124

4 CONCLUSIONS

Synthesis of cross-linked starch has been successfully carried out by crosslinking reaction between breadfruit starch (*Artocarpus communis*) and epichlorohydrin that were confirmed based on FTIR spectrum. The FT-IR spectrum of cross-linked starch showed C-O-C group that appears at wave numbers 1018.41-1242.16 cm^{-1}. The cross-linked starch with addition 2% of epichlorohydrin were the optimum condition that resulting the highest degree of substitution at 0.0701%. The measurement of degree of substitution from epichlorohydrin 1%; 2%; 3% were 0.0552%; 0.0701%; 0.0613%, respectively. The SEM analysis of cross-linked starch is more coarse and the distance between granules is more tightly. Swelling capacity at absorption time of 6, 12, 24, 48, and 72 hours are 0.9925%; 1.4611%; 1.8054%; 2.0049%; 3.0124%, respectively.

ACKNOWLEDGEMENTS

Author would like to thank to Universitas Sumatera Urara has facilitated all equipment until this journal has been published successfully.

REFERENCES

Kittipongpatana, O.S., Kittipongpatana, N., 2013. Physicochemical, in vitro digestibility and functional properties of carboxymethyl rice starch cross-linked with epichlorohydrin. Food Chem.

Merdikasari, Nurdjanah, S., Yulian, N., Lintang, N., 2009. Amilografi Pasta Pati Sukun Termodifikasi Menggunakan Sodium Tripolifosfat. Teknol. Ind. dan Has. Pertan. 14, 173–177.

Raina, C.S., Singh, S., Bawa, A.S., Saxena, D.C., 2006. Some characteristics of acetylated, cross-linked and dual modified Indian rice starches. Eur. Food Res. Technol.

Rincón, A.M., Padilla, F.C., 2004. Physicochemical properties of Venezuelan breadfruit (Artocarpus altilis) starch. Arch. Latinoam. Nutr.

Rodríguez, M., Nunez, S., 2008. Structural and rheological characteristics of cross-linked banana starch with different cross-linking agents. mexico 3–4.

Sauyana, Y., 2014. Produksi pati asetat dengan menggunakan pati sagu nanokristalin. Dep. IlmuPertanian FTP, IPB.

Wijayatiningrum, F.N.U.R., 2009. Makalah Seminar Penelitian Modifikasi Cassava Starch Dengan Proses Oksidasi Sodium Hypoclorite Untuk Industri Kertas, Kimia, Jurusan Teknik Teknik, Fakultas Diponegoro, Universitas Sudharto.

Wurzburg, O., 2010. Modified Starches. In: Food Polysaccharides and Their Applications.

Xiao, H., Lin, Q., Liu, G.Q., 2012. Effect of cross-linking and enzymatic hydrolysis composite modification on the properties of rice starches. Molecules.

Zuhra, C.F., Ginting, M., Syufiatun, A., 2004. Modifikasi Pati Sukun Dengan Metode Ikat Silang Menggunakan Trinatrium Trimetafosfat. Chem. Nat. Acta 4, 142–146.