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Cite as: AIP Conference Proceedings 2342, 030006 (2021); https://doi.org/10.1063/5.0045339
Published Online: 22 April 2021

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The Synthesis of Carboxymethyl Polysaccharide from *Arenga pinnata* Merr. Endosperm and Sodium Chloroacetate with Microwave Irradiation

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**Abstract.** Carboxymethyl polysaccharides of *Arenga pinnata* endosperm (APE) seeds can be synthesized directly without the addition of water through the reaction between soft and hard APE polysaccharides with chloroacetate using NaOH solution under irradiation of microwaves for 5 minutes. Firstly the soft and hard APE were crushed. Next the etherification process using NaOH solution and sodium chloroacetate reagent in 96% ethanol was conducted with a ratio of sodium chloroacetate and NaOH used was 1.95: 2.6 (w/w) and in soft and hard APE seeds. The carboxymethyl polysaccharides of soft and hard APE seeds obtained have brown color and were analyzed by spectrophotometer FT-IR, X-RD and SEM. The formation of carboxymethyl polysaccharides was characterized by the appearance of absorption bands in the wavenumber area of 1729 cm⁻¹ which indicates the presence of C = O stretching vibrations from carboxymethyl. The degree of substitution obtained by the titration method is between 1.58 - 1.86. The X-RD results show that the hard and soft carboxymethyl APE seeds are amorphous and the intensity of the carboxymethyl polysaccharides of the soft APE seeds is lower than from the hard APE and the degree of substitution is lower. The surface morphology of hard APE is finer than soft APE seeds.

**INTRODUCTION**

The modification of polysaccharide can be done by physical or chemical. One of the chemically modification of polysaccharide is making carboxymethyl polysaccharide. The carboxymethyl galactomannan is widely used in various industrial applications such as food systems, paints, mineral industries, textiles and etc [1-4]. Previous researchers have carried out the manufacture of carboxymethyl polysaccharides but still using heating for a long time. In this study, microwave heating was used to reduce the reaction time. Sharma and Vikas (2017) have conducted research using a microwave on *Terminalia Catappa* [5]. Other researcher has conducted study on the synthesis of carboxymethyl polysaccharides from palm seed powder (*Arenga pinnata* Merr) through an etherification reaction with monochloroacetate using a NaOH catalyst and heated in an oven at 60°C for 10 hours with the degree of substitution is determined by the titration method [6].

The APE used are soft seeds without the extraction process being carried out first, or used directly after being pulverized, thereby shortening the process of making raw materials. Soft APE has the advantage that the solubility level of their polysaccharides is greater than medium and hard APE. Based on the description above, this present study aimed to synthesize carboxymethyl polysaccharides from soft and hard sugar APE through a reaction between soft and hard polysaccharides with sodium chloroacetate using microwave irradiation. The polysaccharides are used directly from soft and hard APE without first extracting them into powdered. The carboxymethyl polysaccharide obtained was determined by the degree of substitution by titration method, functional groups using spectrophotometer FT-IR, surface properties using Scanning Electron Microscopy (SEM) and crystallinity properties using X-Ray Diffraction (X-RD).
MATERIALS AND METHODS

Materials

The APE was collected from local market in Medan, Indonesia and directly used without any pretreatment. The chemicals were purchased from local distributor and also used without further treatment.

Determination of the Texture of Arenga pinnata Merr. Endosperm

Sampling of the measured APE was carried out by using a stratified random sampling technique. Texture measurements were carried out objectively using a penetrometer. The prepared sample was pierced at four points using a precision penetrometer which was given a pressure of 250 g on a scale of 1/10 mm for 10 seconds. Texture values can be read on the scale indicated by the manual needle, the four values are averaged. The texture value is calculated using the formula below.

\[ \text{Texture (g/mm)} = \frac{250}{\frac{X_1+X_2+X_3+X_4}{4}} \]

Preparation of Carboxymethyl Polysaccharides of APE with the Addition of NaOH Solution and Water Solvent

A total of 60 g of soft APE was cleaned and thinly sliced was poured into a blender tube that has been filled with 150 ml distilled water, then blended for 3 minutes. The refined APE was put into an Erlenmeyer glass then 2 ml of 45% NaOH is added while cooling at a temperature of 0-8 °C and stirring until homogeneous. The temperature is raised to 15-18°C and then is added with 7 ml of 75% sodium chloroacetate in water. The Erlenmeyer glass was irradiated in microwave at 10 P for 5 minutes then let stand for 24 hours. The crude product is added with 70% ethanol: water at a ratio of 80: 2, then filtered. The residue is washed repeatedly to neutral pH with 96% ethanol. 20 mL of 2M HCl in methanol 70% was added then stir for 2 hours followed by addition of 96% ethanol and filtered. The precipitate was washed with 70% ethanol up to three times. Then dissolved in distilled water and washed to neutral pH. The precipitate formed was filtered and washed with ethanol pure then dried in a desiccator until constant weight formed. The carboxymethyl crude obtained was analyzed using a FT-IR spectrophotometer. The same procedure was carried out on soft APE with variations in the addition of NaOH: chloro acetate.

Making Carboxymethyl Polysaccharides of Palm Seeds Using NaOH Powder and Without Addition of Water Solvent

A total of 60 g of soft APE are cleaned and thinned. The palm seeds that have been thinned are put into the blender jar. Then blend for 3 minutes. The refined palm seeds are put into the Erlenmeyer glass. Then 1.95 g of NaOH powder was added while cooling at 0-8 °C and stirred until homogeneous. The temperature is increased to 15-18°C, then 2.6 g of sodium chloroacetate is added. The Erlenmeyer glass was irradiated in the microwave at 10 P for 5 minutes. Then let stand for 24 hours. The left idle Na-carboxymethyl polysaccharide is added with 50 ml of 70% ethanol: water with a ratio of 80: 2, then filtered. The residue is washed repeatedly to neutral pH with 96% ethanol. 20 mL of 2M HCl in methanol 70% was added then stir for 2 hours followed by addition of 96% ethanol and filtered. The precipitate was washed with 70% ethanol and then dried in a desiccator until constant weight formed. The carboxymethyl obtained were analyzed by degree of substitution, FT-IR spectrophotometer, SEM surface morphology test, and XRD test. The same procedure was carried out on soft APE with variations in the addition of NaOH: chloro acetate.
Determination of the Degree of Substitution

A total of 0.2 g carboxymethyl polysaccharide of APE seeds was dissolved in 20 ml of 0.1 M NaOH solution and stirred for 2 hours using a magnetic stirrer. The carboxymethyl polysaccharide was then titrated using a standard solution of 0.1 M HCl with the addition of the phenolphthalein indicator as the indicator. The same treatment was carried out for carboxymethyl polysaccharide of hard palm seeds with a weight ratio of NaOH: sodium chloroacetate 1.95 g: 2.6 g and 2.6 g: 2.6 g.

RESULTS AND DISCUSSION

Determination of the texture of the seeds is using a penetrometer that is inserted at four points of the APE. The sample tests were carried out at different levels of maturity of APE, namely hard and soft. The changes in the physical and chemical properties of the palm seeds cause the texture value of hard APE to be higher than those of soft APE. The soft APE was selected as sample in the study because soft APE has a high level of solubility which due to the higher content of galactomannan (water soluble fraction).

FIGURE 1. The FT-IR spectrum of (A) carboxymethyl polysaccharide of hard APE without the addition of water, (B) hard APE with the addition of water, (C) carboxymethyl polysaccharide of soft APE without the addition of water, (D) Soft APE with the addition of water.

In the process of adding water when refining hard and soft APE followed by the addition of 45% NaOH solution, no carboxymethyl polysaccharide compounds were formed as evidenced by the absence of absorption bands at wave numbers of 1800 - 1650 cm⁻¹ which was a stretching vibration C = O (carbonyl) of the carboxymethyl. The absorption bands for carboxymethyl polysaccharides of soft and hard APE in A and C give an overview of the OH groups of the polysaccharides which are supported by the absorption bands at wave number 1640 cm⁻¹ which shows the –OH group that is bound to water or the bending vibration of the -OH group. The formation of the carbonyl group (C = O) at the wave number 1800 - 1650 cm⁻¹ or to be precise 1729 cm⁻¹, is a C = O stretching vibration of carboxymethyl.

The process of carboxymethyl polysaccharide synthesis is influenced by two main factors, namely alkalinization and carboxymethylation. The initial stage is the alkalinization process with the addition of NaOH, then added with sodium chloroacetate. The alkalinization stage uses NaOH, with the aim of activating the –OH groups in the polysaccharide molecule in the form of galactomannan and mannan, breaking the hydrogen bonds of the galactomannan molecule.

The swelling process in galactomannan occurs due to the breaking of intramolecular and intermolecular hydrogen bonds. In addition, the hydroxyl group in galactomannan is also more reactive because it is ionized by an alkaline ion, namely Na+, to form an RO- alkoxide ion. During the alkalinization stage, it is seen that galactomannan undergoes swelling and then changes color to light brown. The next process is etherification between alkaline galactomannan and sodium chloroacetate or what is called the carboxymethylation process. The following is a chemical reaction for the synthesis of carboxymethyl polysaccharides or often known as the Williamson etherification reaction. The general reaction is shown in figure 2. Nucleophilic substitution reactions are reactions in which there is a selective attack by
an electron-rich nucleophile to the positive charge of a C atom on the carbon chain that binds the leaving group so that the nucleophile will replace the leaving group.

**FIGURE 2.** The mechanism reaction of carboxymethyl polysaccharide formation.

There is a difference in the degree of substitution between soft and hard palm seeds, where for soft palm seeds the degree of substitution is higher than for hard palm seeds. This is because the soft palm seed polysaccharides contain more galactose groups, so that NaOH is easier to penetrate thus has better swelling properties, for that chloro acetate compounds are easier to substitute.

Testing of surface morphology analysis by SEM on carboxymethyl polysaccharides of soft and hard palm seeds without the addition of water in the variation of chloro acetate 2.6 g: NaOH 2.6 g.

**FIGURE 3.** The SEM morphological images of (A) carboxymethyl polysaccharide of hard APE (Magnification 5000 times) and (B) carboxymethyl polysaccharide soft palm seeds (Magnification 5000 times)

Figure 3 determines the surface morphology of the carboxymethyl polysaccharide of hard APE, where the fiber structure is smoother, expands and the fibers are still visible. This is because the hard APE contains more mannan fraction or less galactomannan. In contrast to the surface morphology of the carboxymethyl polysaccharide of soft APE (Figure 3B), where there are coarser fibers which can be seen with a hollow wavy surface. This is because there are more galactomannan groups.
FIGURE 4. The carboxymethyl diffractogram of (A) soft APE without the addition of water and (B) carboxymethyl of hard APE without the addition of water.

CONCLUSION

Carboxymethyl polysaccharides of APE have been synthesized directly without the addition of water through the reaction between soft and hard APE polysaccharides with sodium chloroacetate under alkaline conditions using NaOH and irradiated in microwave for 5 minutes and power of 10 P. The degree substitution of carboxymethyl polysaccharide of soft and hard APE obtained were ranging from 1.58 to 1.86 with the degree of substitution of soft APE is higher than that of hard APE. The crystallinity degree of carboxymethyl of hard APE was greater than that of soft palm seeds. The carboxymethyl surface morphology of hard APE is smoother than that of soft palm seeds.

ACKNOWLEDGMENTS

The authors acknowledge the Rector of Universitas Sumatera Utara and Organic Chemistry Laboratory, Faculty of Mathematics and Natural Sciences, for providing laboratory facilities.

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