

Cocoa Pod (*Theobroma cacao L.*) Utilization as Material for CMC

Yeni Afriani, Zanira Urfa Harahap, Era Fazira Matondang and Cut Fatimah Zuhra*

Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, Medan, Indonesia

Keywords: CMC, Alkalization, Carboxymethylation, Cocoa Pod.

Abstract: Cocoa pod contain 31.25% cellulose. It can be used for CMC (carboxymethyl cellulose) with four phases involving alkalization, carboxymethylation, neutralization and drainage were used to making of CMC. The first proses using NaOH. Media such as methanol, propanol, sodium monochloroacetate, and water. The neutralization process, acetic acid was added. And for the last step it was heating in the oven. The result showed that contents of CMC of NaCl 87-91%, viscosity 5.5 cP, pH 8, and DS value is 0.872. On the other hand, acetic acid did not give significant effect for colors of CMC.

1 INTRODUCTION

Indonesia is the third largest producer of cacao (*Theobroma cacao L.*) in the world. The large number of processing cocoa fruit in Indonesia are mostly only used the seeds and pulp to be produced while the cocoa pod husks were being a waste unused. S hile it, in the pod husks containing crude fiber composed of cellulose (31.25%), hemicellulose (48.64%) and lignin (20.11%) (Ashadi, 1988).

Cellulose is a polysaccharide which if hydrolysed will produce glucose monomers and some cellobiose. Cellulose can swell if reacted with alkali metal, salts in strong base solutions and amine compounds. The amine compound that is commonly used to develop cellulose bonds is NaOH (Irawadi, 1990). Cellulose is also insoluble in water and is very easy to absorb water. It's really support to make the pod husks as raw material for the manufacture of carboxymethyl cellulose or carboxymethyl cellulose (CMC).

CMC is derivative from cellulose used in industry food for get good texture. There are several the most important CMC function that is as thickener, stabilizer, gelling agent, as emulsifier, and in some could levelling spread antibiotics. CMC has group carboxyl, then viscosity CMC solution is affected by the pH of the solution (Winarno, 1995). CMC is capable tie water so water molecules are trapped in gel structure formed by CMC. CMC is an ingredients stabilizer that has power strong tie and play a role for improve viscosity and texture product food, like jelly, salad and produkes (Belitz and Grosch, 1987).

Rahman et al. (2016) conducted a study on the use of cellulose to CMC produced from rice straw cellulose resulting in optimum purity conditions of CMC, which were added to 4 grams of NaMCA (sodium monochloroacetic) and 5 grams of cellulose. The amount of sodium monochloroacetate used will affect it substitution of anhydrous unit glucose in cellulose. Increasing the amount of alkali used will result in an increase in the amount of monochloroacetate. This carboxymethylation process is actually an etherification process. At this stage is the process of attaching the carboxylic group to the cellulose structure. This is very important to control when making CMC (Personal, 1985).

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this study include: Cocoa pod, NaOH 30%, NaOH 2%, H₂O₂ 10%, methanol, propanol, acetate acid 90%, aquadest, Fehling A, Fehling B, Na-MCA, K₂CrO₄, AgNO₃, Nitric acid.

2.2 Preparation PVA 10%

Waste of cocoa fruit peel is broken and cleaned with water. Then dried in the sun. Mashed using a blender. Sifted using 80 mesh sieves. Furthermore, the water content is determined by weighing 2 grams of cocoa pod powder into a weighing bottle, put in the oven for

4 hours at 105°C and then put into the desiccator and weighed until the weight remains.

2.3 Isolation of Cellulose

Cocoa pod husk was weighed as much as 250 grams then mixed with NaOH 2% and then heated at 80°C for 4 hours while stirring. Then is filtered, the sediment will be washed with aquadest until pH 7 and then bleached with H₂O₂ 10% as much as 250 ml after that it was heated at 60°C for 15 minutes then left for 1 night. Ovened cellulose for 1 night at 75°C then characterized by FT-IR and tested qualitatively. Cellulose is prepared in the form of pulp. Porridge is examined in a thin film placed between flat salt plates. The test is done by clamping the mixed film on the sample site. Then the film is placed on the plate in the direction of infrared light. The result will be recorded periodic paper in the form of a 4000-200 cm⁻¹ wave number curve flow to intensity.

2.4 Antimicrobial Activity

About 10 gram cocoa pot husk put into 3 neck flask placed on waterbath then added 400mL propanol p.a, 50 ml methanol, 50 mL aquadest and stirred for 10 minutes. Then added 30% NaOH solution (22 grams of NaOH) drop by drop and the alkalization process continues for 1hour at 24°C. After completed followed carboxymethylation process by adding as much as 20 grams of sodium monochloroacetate for 3.5 hours at a temperature of 55°C.

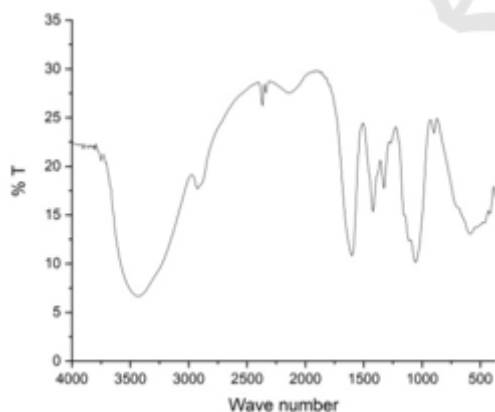


Figure 1: FTIR spectra of CMC.

After the carboxymethylation process is complete, the stirrer is turned off then the mixture is transferred to the beaker glass and the pH is measured. Next, 90% acetic acid was added until the pH was neutral and decanted. The residue obtained was added with 200

mL of methanol and stirred and then filtered using a vacuum pump. Finally wrapped in aluminum foil dried in the oven for 4 hours at 60°C. The dried CMC is then mashed with a blender and stored in a closed place. The CMC obtained will be analyzed by FT-IR. CMC is prepared in the form of pulp. Porridge is examined in a thin film placed between flat salt plates. The test is done by clamping the mixed film on the sample site. Then the film is placed on the plate in the direction of infrared light. The result will be recorded periodic paper in the form of a 4000-200 cm⁻¹ wave number curve flow to intensity.

3 RESULTS AND DISCUSSION

3.1 Characterization of Cellulose

The FT-IR spectrophotometric test results also showed positive results by comparing wave number of bagasse cellulose and commercial cellulose. Figure 1 is the result of FT-IR spectroscopic test which shown spectrum with vibration peak in area of 3448.72 cm⁻¹ for -OH group, supported by emergence of vibrational peaks at wave number 2900.94 cm⁻¹ which shows C-H stretching groups, 1064, 71 cm⁻¹ which shows the ether group, and the glycoside bond in α-cellulose structure is found at wave number 1635.64 cm⁻¹ (Epriadi, 2017).

Results infrared spectra from cellulose to show absorption on number wave 3332,66 cm⁻¹ which is a OH area on number wave 1321,54 cm⁻¹ to show area peak for CH groups, and on number wave 1040,31 cm⁻¹ which is a C-O-C group.

3.2 Characterization of CMC

The CMC samples were analyzed by FTIR, which can be depicted in the two spectra in Fig. 1. The x-axis represents the wavelength (cm⁻¹) and y-axis whos the light transmittance through the sample. The FTIR spectrum of the sample shows that the carboxyl, methyl and hydroxyl functional groups are found at wavelength of 1617.60, 1454.44 and 1195.72 cm⁻¹ (for CMC-55-10), 1613.57, 1426.01 and 1214.54 cm⁻¹ (for CMC-28-10), respectively. However, for sample CMC-82-10 only carboxyl and methyl functional groups are shown in the peak at 1654.16 and 1458.13 cm⁻¹. Consequently, for all CMC samples synthesized the IR spectra indicates the typical absorptions of the cellulose backbone as well as the presence of the carboxymethyl ether group at 1654.16, 1617.60 and 1613.57 cm⁻¹ consecutively for each sample. The additional peak at wavelength of

2357.27 cm^{-1} at sample CMC-55-10 might be due to the existence of the contamination from impurities or combination band with water. Subsequently the bands around 1458.15 – 1420.05 cm^{-1} are assigned to CH₂ scissoring. It is obvious that those in the broad absorption band of approximately above 3500 cm^{-1} is due to the stretching frequency of the hydroxyl group (-OH) (Saputra, 2014). Based on Table 1, the viscosity of CMC is 5.5 cP. The purity of CMC based on NaCl contents is 94,15%. The substitution degree during carboxymethylation was 0.872.

Table 1: Result of viscosity test.

CMC (g)	Viscosity (cP)
0.01	5.5
0.02	5.3
0.03	5.6
0.04	5.5
0.05	5.6

4 CONCLUSIONS

Based on the results of the research it can be concluded that CMC from cacao pod husk can be used. But CMC were obtained to show less result as well from facet viscosity. Expected next researcher more pay attention composition in making CMC.

ACKNOWLEDGEMENTS

The authors would like to send gratitude to Risekti dikti for the financial support towards this research in the PKM-PE Project 2019 and also for Universitas Sumatera Utara which facilitated this research.

REFERENCES

- Adinugraha M. P, Marseno, D. W., Haryadi., 2005. Synthesis and Characterization of Sodium Carboxymethyl Cellulose from Cavendish Banana Pseudo Stem (*Musa cavendishii* LAMBERT). *Carbohydrate Polymers*, 62: 164-169.
- Figueira A, Janick J., 1993. New products from *Theobroma cacao*: Seed pulp and pod gum. New York: New crops. 475- 478
- Hong, K. M., 2013. Preparation and Characterization of Carboxymethyl Cellulose from Sugarcane Bagasse. Malaysia: Universiti Tunku Abdul Rahman. 1:21-84.
- Mandal, A, Chakrabarty D. 2011. Isolation of Nanocellulose from Sugarcane

- Bagasse (SCB) and Its Characterization *Carbohydrate Polymers*. 86(1): 1292 –1299.
- McKee T, McKee J. R., 2003. *Biochemistry: The Molecular Basis of Life*. New York: McGrawHill Companies, Inc. 3: 219-220.
- Ott, Spurlin., 1995. Cellulose and Cellulose Derivative, Vol 5 Part 2. New York: Inter Science Publisher Inc. Preparation, Proximate Composition and Culinary Properties, *Journal of food research* 18: 1283-1287.
- Susanto, F. X., 1994. *Tanaman Kakao: Budidaya dan Pengolahan Hasil*. Yogyakarta: Penerbit Kanisius. 43-54