

The microwave assisted-synthesis of carboxymethyl cellulose from nata de-coco bacterial cellulose

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Abstract. Bacterial cellulose (BC) is one of natural biopolymers which can be derivatized to make functionalized materials. Carboxymethyl cellulose (CMC) is a candidate derivative for such a direction. The aim of the present study is to investigate the usability of microwave energy to transform BC into CMC. The results showed that CMC was produced in a yellowish white powder by a short irradiation for 30 s at 650 W. The best combination of monochloroacetic acid and BC as anhydroglucose unit was found at the molar ratio of 1:5. The obtained CMC is soluble in distilled water, and aqueous NaOH solution. The highest degree of substitution, viscosity, and molecular weight of the CMC are 0.263, 15.61 Pa·s and 197,187, respectively. This study showed the usefulness of the microwave-assisted reaction to transform BC rapidly into water-soluble ionized derivative.

1. Introduction

Cellulose is the most abundant biomass material on Earth. Cellulose forms the basic skeletal structure of plant cell walls. It is mainly used in the textile and paper industries, and it is derived from vegetable products. Bacterial cellulose (BC) is a type of cellulose synthesized by some bacteria. BC has a crystalline polyform Ia unlike plant cellulose which is present mainly in Ib structure. Traditionally, BC frequently used comes from nata de-coco [1].

Nata de-coco BC is formed as a gellous sheet on the surface of an acidic sugary medium by the action of *Gluconacetobacter xylinus*. This BC is the most promising of biopolymers and used in a number of applications such as hydrogels [2], and medical materials such as wound dressing [3], and vascular prosthetic devices [4]. BC can be chemically modified to produce cellulose derivatives such as carboxymethylcellulose (CMC). It contained carboxymethyl groups attached to the polysaccharide backbone making it a polyelectrolyte. The conventional process to produce CMC is characterized by a slow reaction process [5], thus requiring the development of a technology that allows the reaction to progress at a higher rate. One of the identified technologies is to utilize microwave to enhance the productivity of the process. The microwave technology has been widely used in the chemical industry and is able to speed up the processing time [6].



The purpose of this study was to investigate the application of microwave power to obtain the CMC from nata de-coco BC by reaction with monochloroacetic acid. Characterization of the CMC produced was also made by FTIR spectroscopy, solubility test, and measurement of degree of substitution, viscosity, and molecular weight. This study presented a rapid process to transform BC into water-soluble ionic derivative.

2. Materials and Methods

2.1 Materials

BC was purchased from a local nata de-coco industry (Alfafood, Poasia, Kendari, Indonesia). Analytical grade reagents used in this paper were NaOH, ethanol, methanol, urea, monochloroacetic acid glacial acetic acid and HCl, purchased from the Emsure Merck, Jakarta.

2.2 Pretreatment of Bacterial Cellulose

Pretreatment of BC was adopted according to the method described by Suparjo and Nelson, (2011) [7]. BC obtained from local nata de-coco industry was pulverized in the size approximately 0.297 mm. Then, it was pasteurized repeatedly until the acidic smell was eliminated and dried by heating 1 h at 105 °C. The dried BC was demineralized by treatment with aqueous 1N HCl solution at the solid to liquid ratio of the mass of 1:15 (w/v). The mixture was allowed to stand for 30 min at room temperature, and filtrated to recover the treated BC. After repetition of this treatment for more than 3 times, BC was washed with distilled water until neutral pH, and dried again as described above. BC for derivatization was finally given as a yellowish white powder.

2.3 Synthesis of Carboxymethyl Cellulose

Synthesis of carboxymethyl cellulose (CMC) is based on the modified method described by Qi *et al.*, (2009) [8]. Two point six g of BC was dissolved in 100 mL of a solution containing NaOH (7 g), urea (12 g) and distilled water (81 g). A 200 mL Erlenmeyer glass flask was basically used for solubilization and further reaction. The mixture was stirred for 90 min at 100 °C using a shaker to produce a slurry of alkali-cellulose. This slurry was subsequently frozen at 0 °C and thawed using a shaker at room temperature to obtain a transparent cellulose solution.

The flask containing cellulose solution was set inside a modified microwave oven (1 kW) equipped with condenser as shown in Figure 1. Monochloroacetic acid was added to this solution slowly at room temperature. External addition of NaOH in the reaction medium is not necessary because the reactant BC is already solubilized in the aqueous NaOH/urea solution. Microwave-assisted carboxymethylation reaction took place for 30 s at 5 different power condition of 180, 300,

450, 650, and 800 W. For determination of the adequate combination of BC as anhydroglucose and monochloroacetic acid, microwave treatment was done under 5 different molar ratios of 1:1, 1:2, 1:3, 1:4 and 1:5. The reaction produced sodium glycolate as a byproduct by substitution of Cl with OH when concentration of monochloroacetic acid is low, leading to decrease in degree of substitution. After the reaction, acetic acid (90% v/v) was added to make a pH close to neutral for removal of excess amount of NaOH. The precipitated CMC was then recovered by vacuum filtration and washed 6 times with 70% aqueous ethanol, and dried for 5 h at 70 °C. The remaining sodium glycolate if present can be solubilized away by washing with methanol. Reaction condition and abbreviation of the reaction products are listed in Table 2.

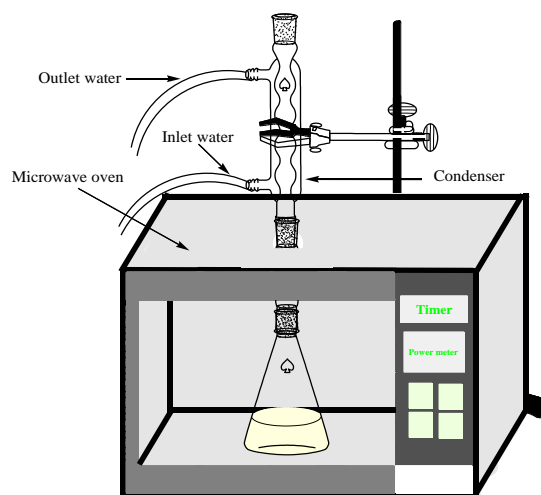


Figure 1. Schematic diagram of the modified microwave oven

2.4 Analytical Methods of Carboxymethyl Cellulose

Carboxymethyl functional group analysis was conducted by FTIR as KBr discs prepared with KBr (100-200 mg) and CMC (5 mg). The absorption spectra were measured under transmittance mode by using FTIR (Shimadzu 8400, UPI, Bandung) in the wavelength range 4000-400 cm^{-1} . The analysis of the functional groups was carried out at room temperature with a resolution of 8.0 cm^{-1} .

Solubility test was carried out using distilled water, 0.1 N HCl, and 0.1 N NaOH as the solvents. About 1 mg of CMC was loaded into an Eppendorf tube containing 1 mL of solution, and the mixture was then stirred using a vortex until the solids completely dissolved in solution.

The degree of substitution of CMC was determined by the method as described by Bono et al. (2009) [9]. A total of 2 g of CMC was dissolved in 40 mL of demineralized water. Hydrochloric acid was added into the solution to adjust the $\text{pH} < 2$. This solution was titrated with 0.1 N NaOH solution and the pH was recorded at fixed intervals using pH meter. The degree of substitution can be calculated using equation 1.

$$DS = \frac{162 \times A}{m_{CMC} - 58 \times A} \quad (1)$$

Where:

DS = degree of substitution; $A = V_{NaOH}(mL) \times C_{NaOH} (M)$; V_{NaOH} = volume of sodium hydroxide solution in mL; C_{NaOH} = concentration of sodium hydroxide solution in M; m_{CMC} = weight CMC from nata de-coco (g); 162 = molecular weight of anhydroglucose; 58 = molecular weight of carboxymethyl group

The viscosity of CMC solution was measured at 0.6, 0.7, 0.8, 0.9 and 1.0% w/v by Ostwald Viscometer at room temperature. The sample solution was supplied to the Viscometer at least 3 times. Time (t) (s) recorded were then inserted into the equation (2) to obtain the viscosity of Mark-Houwink equation the solution. The viscosity value is used to determine the molecular weight through the Mark-Houwink equation (3) [10].

$$\eta = \eta_o \frac{\rho t}{\rho_o t_o} \quad (2)$$

$$[\eta] = KM^\alpha \quad (3)$$

Where:

η = solution viscosity (Pa·s); α = coefficient of CMC, 1.00; K = coefficient, 7.92×10^{-5} ;
 t = flow time of solution(s); M = molecular weight; ρ = solution density (g/cm³);
 η_o = solvent viscosity (Pa·s); ρ_o = solvent density (g/cm³); t_o = flow time of solvent

3. Results and Discussion

3.1 Synthesis of Carboxymethyl Cellulose

The experimental results given by the microwave-assisted carboxymethylation of BC are listed in Table 1.

Table 1. Selection of the reaction condition

Product	Molar ratio (monochloroacetic acid /anhydroglucose repeating unit)	Power (W)	Mass (g)	Degree of substitution	Yield (%)
CMC1	1 : 1	650	4.14	0.142	188
CMC2	1 : 2	650	5.07	0.165	184
CMC3	1 : 3	650	5.23	0.201	189
CMC4	1 : 4	650	5.33	0.253	188
CMC5a	1 : 5	650	5.73	0.263	201
CMC5b	1 : 5	180	3.72	0.117	136
CMC5c	1 : 5	300	4.63	0.124	168
CMC5d	1 : 5	450	5.13	0.139	182
CMC5a	1 : 5	650	5.73	0.263	201
CMC5e	1 : 5	800	5.24	0.165	184

The effect of microwave irradiation in organic synthesis is a combination of thermal effects, arising from the heating rate, superheating or “hot spots” and the selective absorption of radiation by polar substances [6].

Based on the generated yield (Table 1), the amount of monochloroacetic acid tend to affect the CMC mass produced. The CMCs produced have at least three variations of mono substitution on the atom C-6, C-2 and C-3 (Figure 2).

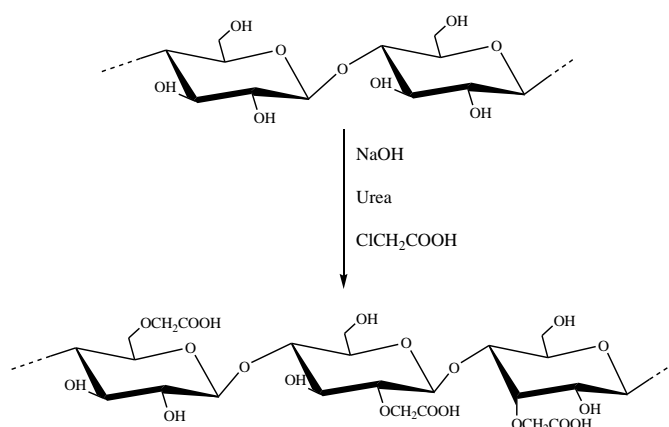


Figure 2. Reaction scheme of formation of CMC [8]

3.2 Analysis of Functional Groups

FTIR spectra of the native BC cellulose, and CMC1-CMC5 are shown in Figure 3.

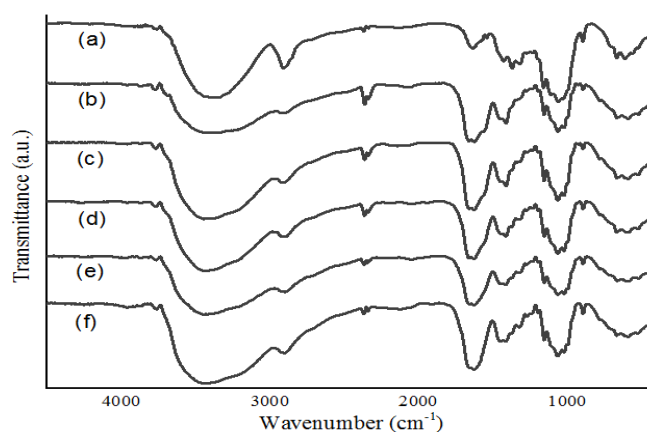


Figure 3. FTIR spectra of (a) Cellulose (b) CMC1 (c) CMC2 (d) CMC3 (e) CMC4 (f) CMC5

The results indicate the overall similarity in the spectra of CMC1-CMC5, but intensity of absorptions at about 1643 cm^{-1} due to carboxylic acid (COO^-) and 1420 cm^{-1} ($-\text{CH}_2$) strengthened in these spectra compared with the native cellulose. The differences can also be seen in the absorptions at 1054 cm^{-1} ($>\text{CH}-\text{O}-\text{CH}_2$), 2889 cm^{-1} (C-H), and 3449 cm^{-1} ($-\text{OH}$) which tend to increase. On account of solubility

all samples of CMC1-CMC5 were soluble in distilled water-and 0.1 N NaOH solution. Thereby DS can be determined by the potentiometric titration method.

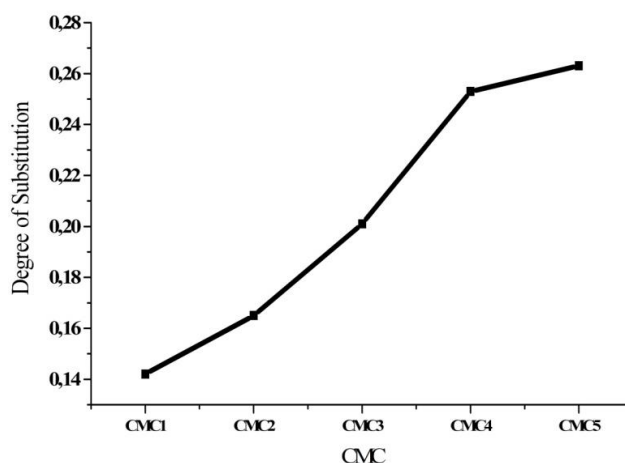


Figure 4. Effects of the amount of monochloroacetic acid on degree of substitution CMC

As shown in Figure 4, the carboxymethylation reaction progressed with increase in concentration of monochloroacetic acid, and DS attained at a value of 0.263. DS values are small, so it does not have a significant influence on the outcome of the yield. In terms of quality, the greater the degree of substitution, the better for the quality of CMC because of greater solubility in water.

The molecular weight of the products was determined by using Ostwald Viscometer. Intrinsic viscosity values of CMC1, CMC2, CMC3, CMC4, and CMC5 were 3.21, 9.57, 11.10, 12.76 and 15.61 Pa·s, respectively. The molecular weight of each CMC was calculated and the results are summarized in Figure 5.

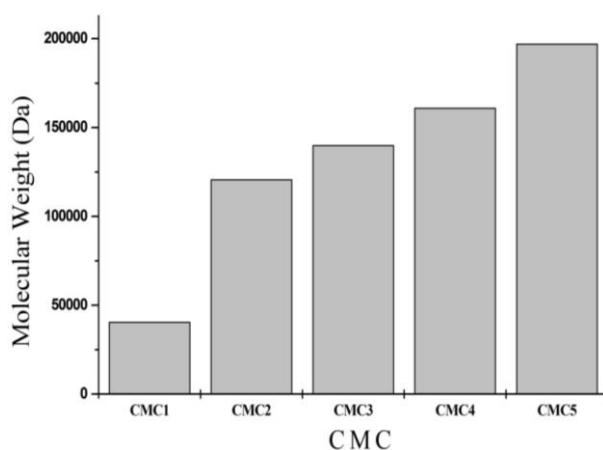


Figure 5. Molecular weight of CMC

The highest molecular weight was obtained as 197,187. The increase of molecular weight revealed that the increase of concentration of the reactants will make the molecular size higher.

4. Conclusion

CMC was synthesized from nata de-coco BC by using microwave energy. The reaction condition to achieve the DS of 0.263 (molecular weight of 197,187) was found to use 5 moles of monochloroacetic acid for 1 mole of anhydroglucose unit of cellulose. FTIR analysis of the reaction products showed the typical absorptions due to carboxymethyl group at 1620 cm^{-1} and 1423 cm^{-1} . All products can be dissolved in distilled water and 0.1 N NaOH solution. The obtained results showed that the microwave-assisted method was useful for preparation of CMC from nata de-coco.

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