Article

Carboxymethylation of Cassava Peel: Effect Sodium Monochloroacetate and Temperature

Sperisa Distantina*, Inayati, Fahmi Achmad Saputra, and M. Fitra Arifianto
Chemical Engineering Department,
Universitas Sebelas Maret,
Jl. Ir. Sutami No. 36 A Surakarta, Indonesia.
Corresponding author: sperisa_distantina@staff.uns.ac.id
distantina@staff.uns.ac.id

Abstract. Cassava peel contains cellulose that can be chemically modified to be more useful product. In this work, carboxymethylcellulose (CMC) from cassava peel powder was prepared by alkalization using sodium hydroxyde and then followed by carboxymethylation using sodium monochloroacetate. The aims of this work were to investigate the effect of sodium monochloroacetate-powder ratio (0.59, 1.47, 2.95, 4.42) and carboxymethylation temperature (45^{O}C and 70^{O}C) on the degree of substitution (DS) and reaction efficiency (RE). The result of FTIR spectra indicated that carboxylmethyl groups successfully attached on the cellulose backbone to form CMC structure. The higher of sodium monochloroacetate-powder ratio and higher carboxymethylation temperature enhanced its DS but reduced the RE.

Keywords: cassava peel; carboxymethylation, carboxymethyl-cellulose; degree of substitution

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I. Introduction

Cassava (*Manihot esculenta Crantz*) is the third food-based in Indonesia after rice field and corn. The production of cassava in Indonesia was more than 24 million ton in 2012 (5^{th} ranked in the world). Sixteen percent of the total weight of cassava is cassava peel. It shows that the waste of cassava peel reaches almost 3.84 million ton each year.

The cassava peel is polysaccharide containing cellulose and starch. Due to the presence of hydroxyl groups in repeated unit of the polysaccharides chain, the cassava peel may be chemically modified in order to get a new material with better functional properties. Carboxymethylcellulose (CMC) is a green polymer with great important in pharmacy, medicine, cosmetics, and food industries. CMC is generally made from raw material wood pulp. By using alternative raw materials from unused cassava peel, it will indirectly affect the reduction of tree-cutting action by the producer of CMC.

CMC can be made from the cellulose into form of Na-CMC in a way alkalization with NaOH and then carboxymethylation with sodium monochloroacetate (Na-MCA). The quality of the CMC can be seen from the number of carboxyl groups attached to the cellulose. The number of carboxyl groups attached to the powder, is known as degree of substitution (DS). The ratio of reagent Na-MCA as carboxymethylation reagent and powder material is one of parameters that affects the value of DS [1].

The aims of this research were to determine the effect of carboxymethylation parameters, namely the ratio of sodium monochloroacetic-cassava peel powder and temperature of carboxymethylation on the degree of substitution and reaction efficiency. The changes of chemical structures during CMC preparation were confirmed by FTIR measurement.

II. Materials and Methods

A. Materials

Polysaccharide material that used in this research was cassava peel obtained from local market. Cassava peel was crushed, dried, and sieved into 50 mesh screen. The undersize product was collected as cassava peel powder and kept in dry until further processing was done. Another chemical materials used, namely $ClCH_2COONa$ (Na-MCA), NaOH, C_2H_5OH, HCl, and other chemicals were purchased and used without further purification.

B. CMC Preparation

The CMC preparation was based on the previous researcher method [2]. Preparation of CMC was done with 2 processes separately and respectively. The first process was alkalization. Five grams of cassava peel powder, 10 ml ethanol 80%, and 28 mmol NaOH were mixed and stirred with magnetic stirrer at $25^{O}C$ in three neck rounded flask for 5 minutes. The second process was carboxymethylation. In this step, the Na-MCA was added into the mixture produced by previous alkalization. The molar ratio of of sodium monochloroacetate-cassava peel powder, called as reagent-powder molar ratio (RPMR), was varied for 0.59. 1.47, 2.95, and 4.42. The mixture was then heated up to $45^{O}C$ for 60 minutes and continuously stirred using magnetic stirrer. To study the effect of carboxymethylation temperature, the carboxymethylation was carried out at $45^{O}C$ and $75^{O}C$.

C. CMC Purification

CMC product was purified by immersing it in ethanol 80%, and then the CMC was filtered and dried at temperature $100^{O}C$ until a constant weight was attained.

D. FTIR Analysis

Molecular groups were identified using FTIR spectrometer (Shimadzu IR Prestige-21). Prior to the FTIR test, samples were powdered and was formed into pellet using KBr powder. Transmission was measured at the wave number range of 4500-500 cm^{-1}.

E. Determination of DS

The DS value was determined by back titration method [3]. Firstly, CMC must be changed into H-CMC. Five grams of CMC was dissolved in 100 ml HCl 1.8 M by continuously stirred for 30 minutes. The dispersion

was then filtered. In order to remove the excess acid, the precipitate was washed using ethanol, until the conducivity of the filtrate was about 25 ɥs/cm. Then, the precipitate dried at 50^{O}C for 2 hours.
After H-CMC was formed, the H-CMC was converted into soluble sodium salt. The value of DS was determined using back titration method. The 0.5 grams H-CMC was dissolved in 20 mL of 0.2 M NaOH and added aquadest so that the volume of the solution became 100 mL. The 25 mL of the solution was poured into an erlenmeyer flask and diluted by addition of distilled water. The excess of NaOH was back-titrated using standard 0.05 M HCl, and phenolphtalein was used as the indicator. The titration was repeated for three times and the average value of the HCl volume was used for the calculations data. A blank was also titrated. The number of COOH was determined using equation (1).

$$ncooh = (vb - v) \times MHCl \times 4 \qquad (1)$$

Where vb and v (in mL) is the volume of HCl for titration of the blank and the sample, respectively. MHCl (in mol/L) is the HCl concentration and 4 is the ration of the total volume (100 mL) and the volume taken for titration (25 mL).

The DS was calculated using equation (2).

$$DS = \frac{162 \times ncooh}{mds - (58 \times ncooh)} \qquad (2)$$

Where 162 g/mol is the molar mass of an anhydroglucose unit (AGU); ncooh (in mol) is the amount of COOH calculated from the obtained value of equivalent volume; 58 g/mol is the net increase in the mass of an AGU for each carboxymethyl group substituted. The mds (in gram) is the mass of dry sample calculated from known sample mass ms (in gram) and the water content (wwater). The mds is calculated using equation (3).

$$mds = \left(1 - \frac{w\ water}{100}\right) \times ms \qquad (3)$$

The reaction efficiency (%RE) was calculated by method proposed by [2] and using equation (4).

$$\%RE = \frac{DS \times 100}{RSMR} \qquad (4)$$

III. Results and Discussion

The quality of CMC can be shown by the amount of carboxyl groups attaching in polysaccharide. In this research, the presence of attached carboxyl group was confirmed by FTIR spectra and the degree of substitution value.

Sodium monochloroacetate reacted with cassava peel powder in the presence of sodium hydroxide to form carboxymethylcellulose. The process involved two main reactions as depicted in equation (5), (6), and (7).

$$\text{Cel-OH} + \text{NaOH} \xrightarrow{\text{Alkalization}} \text{Cel-ONa} + H_2O \qquad (5)$$

$$\text{Cel-ONa} + \text{Cl} - CH_2COONa \xrightarrow{\text{Carboxymethylation}} \text{Cel-O}CH_2COONa + NaCl \qquad (6)$$

Overall, the reaction can be written as follows:

$$\text{Cel-OH} + \text{Cl}-CH_2COONa \xrightarrow{NaOH} \text{Cel-O}CH_2COONa + H_2O + NaCl \qquad (7)$$

The hydrolysis reaction leads the removal of sodium monochloroacetate during side reactions with formation of sodium glycolate [2].

F. FTIR Spectra

The native starch and CMC samples were analysed by FTIR, which could be depicted in the two spectra in Fig. 2. Native starch was cassava peel powder sample that used as raw material for preparing CMC. CMC sample was prepared by carboxymethylation with 45^{O}C and RPMR for 4.42. The x-axis represents the wavelength (cm^{-1}) and y-axis respresents 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 1100, 1300, 1600, 3400 cm^{-1}, respectively.

Fig. 1 shows the spectra of carboxymethyl cellulose from cassava peel. The presence of a new and strong absorption band of 1609 cm^{-1} was reffered to the COO- group. The arrow (↑) from the figure shows that there was COO- group attached in the cellulose. It is an evidence that hydroxyl group of cellulose was succesfully replaced with carboxyl group when carboxymethylation reaction occured. In CMC prepared from palm kernel cake, the carboxyl groups and its salts wave numbers were 1604 cm^{-1} and 1421 cm^{-1} [4]. In CMC prepared from cellulose, the carboxyl groups and its salts wave numbers were 1563 cm^{-1} and 1419 cm^{-1} [5].

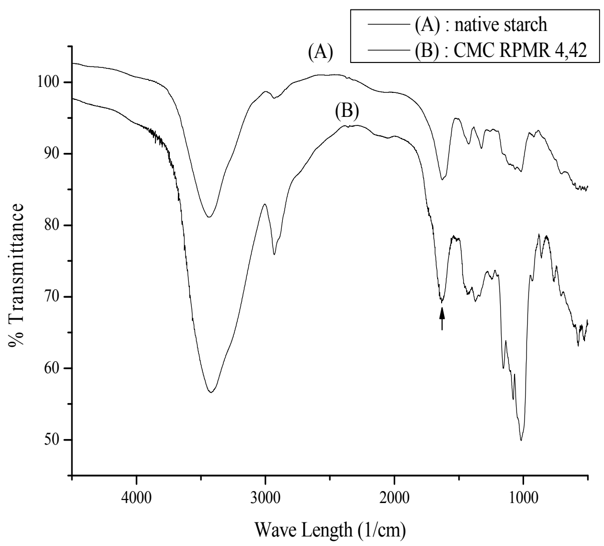

Figure. 1. Ftir Spectra of Cassava Peel Powder (A) and Prepared CMC (B)

G. The Effect of Reagent-Powder Molar Ratio (RPMR) on the Degree of Substitution

Fig. 2 shows the relationship between DS with RPMR and % RE with RPMR at carboxymethylation temperature for 45^{O}C. The effect of RPMR was investigated at RPMR 0.59, 1.47, 2.95, and 4.42. From Fig. 2, it can be seen that there was a trend that with the more of RPMR, the DS was higher. The higher of RPMR indicated the higher content of carboxyl in the reactant mixture. Thus the more substitution of functional group occured.

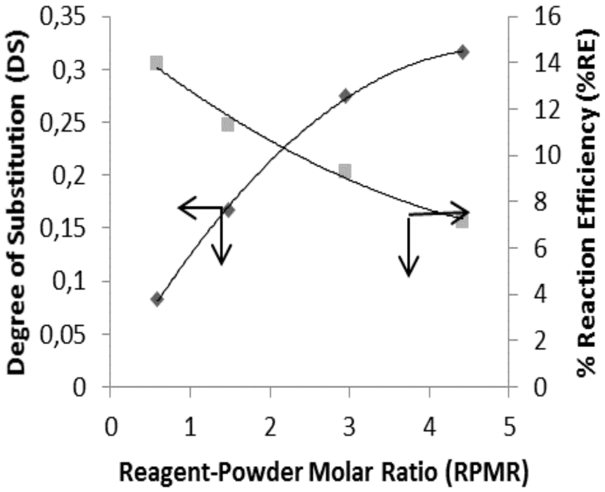

Figure 2. Effect of Reagent-Powder Ratio on DS and RE

However, the more RPMR, the reaction efficiency was lower. The higher of RPMR expressed the increasing amount of Na-MCA. In the alkaline reaction medium, these Na-MCA tend to produce sodium glycolate [2]. In this experiment data range, the optimum RPMR was 2.1 where the DS was 0.22 and RE was 10.45% (Fig. 2).

H. The Effect of Temperature on the Degree of Substitution

Table 1 shows the value of DS of sample with different carboxymethylation temperature. The effect of temperature on degree of substitution was investigated by varying the temperature from 45^{O}C to 70^{O}C. Table 1 shows when the carboxymethylation temperature was increased, the DS was higher. It was known that enhancement of the reaction temperature will increase reaction rate as shown by Arhenius equation. Higher temperature increased the rate of reaction, so that the more number of carboxylmethyl groups attaching in CMC as described by the higher value of DS.

Table 1. Effect of Temperature on Degree of Sustitution

Temperature (^{o}C)	RPMR	DS
45	2.95	0.2744
	4.42	0.3164
70	2.95	0.6267
	4.42	0.7588

IV. Conclusion

Based on FTIR spectra and DS of sample, CMC can be prepared from cassava peel powder. The increasing of sodium monochloroacetic-powder ratio and carboxymethylation temperature enhanced the DS but decreased the RE.

V. Acknowledgment

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