Modification of carboxymethyl cellulose from water hyacinth (*Eichornia crassipes*) using the succinic acid crosslinking method

R D A Putri*, C A Bintang, D B Pangestu, P A Handayani

Chemical Engineering Department, Universitas Negeri Semarang, Semarang 50229, Indonesia

*Corresponding author email: dewi.artanti@mail.unnes.ac.id

Abstract. CMC (Carboxymethyl Cellulose) is an additional ingredient that is often used in the food and beverage industry. This causes the need for CMC is quite high in Indonesia. Data from the Badan Pusat Statistik shows that Indonesia still imported 4435.26 tons of CMC in 2018. In fact, cellulose as a raw material for making CMC can be easily found in nature. One of the plants which is known to have high cellulose content is water hyacinth, which can reach 66.87%. Besides having high cellulose content, water hyacinth is also often regarded as a weed that grows very fast, so it must be utilized so as not to damage the environment. In CMC synthesis isopropyl alcohol is used as a solvent in the ratio of 1:2, 1:4 and 1:6. The CMC yield can also be improved by crosslinking using succinic acid. The variation of succinic acid ratio is 1:1, 2:1 and 3:1 and the yield of CMC reaches 198%, 140.66% and 122.66%, respectively. FTIR test shows CMC without crosslinking has a group that is identical to CMC Cap Koepoe-Koepoe. While in crosslinking CMC new groups are formed which occur due to the addition of succinic acid. Organoleptic test results show results similar to CMC Cap Koepoe-Koepeoe. Meanwhile the pH test at CMC variable 2:1 and 3:1 has pH number 6, fulfilling FI/JECFA/SNI standard.

1. Introduction

Carboxymethyl Cellulose (CMC) is an additional raw material that is widely used in the food and beverage industry, this is because CMC has a function as a thickener, emulsion stabilizer and binding agent [1]. CMC is also widely used in various industries such as detergents, paints, ceramics, textiles, and paper. CMC is made from materials containing cellulose and converted to carboxymethyl. Because cellulose is the main ingredient of CMC synthesis, therefore with the high demand for CMC products, it is directly proportional to the demand for cellulose raw materials. The material most widely used in the manufacturing industry of CMC is wood with relatively high cellulose content and is easily available. But in its development the making of CMC by utilizing wood resulted in an unbalanced ecosystem impact. Besides wood, CMC can also be made from raw materials of rice straw [1], fruit skin waste such as durian [2], and corncobs [3]. The yield produced is between 50% -70%[1-3] but due to the limited availability of raw materials, these materials have not been able to be used as a solution to answer the relatively high market needs. Another material with high cellulose content that

has the potential to replace wood in the manufacturing of CMC is water hyacinth with cellulose content of 66.87% [4]. So far, water hyacinth is only considered as a weed that can damage aquatic ecosystems. Water hyacinth is a type of plant that has a high growth rate that can cause siltation in water. The high population of water hyacinth in an area of water can also cause difficulty in entering sunlight through the water and reduced oxygen content in water [5]. A CMC research was made from water hyacinth which uses variations in the concentration of NaOH, NaOCl, and alcohol as well as the modification of the addition of epichlorohydrin as a crosslinker and yields a better yield of more than 100% [6]. However, the process there is a shortage of the price of epichlorohydrin very expensive. Other studies mention the results of cellulose synthesis in water hyacinth using succinic acid crosslinking method with variations of isopropyl alcohol, isobutyl alcohol and isopropyl alcohol-isobutyl alcohol mixture obtained CMC yields were 113.3%, 131.57% and 120.06% [7]. The crosslinking method using succinic acid is an economical method because the price of succinic acid is relatively cheaper.

2. Materials and methods

2.1. Material

The materials to be used in this research are water hyacinth, technical sodium hydroxide (NaOH), technical sodium hypochlorite (NaOCl), aquades, isopropyl alcohol, sodium monochloroacetic acid ($NaCH_2COOCl$), methanol, ethanol, acetic acid (CH_3COOH), and succinic acid. Water hyacinth samples to be used in the study were obtained from Lake Rawa Pening, Semarang Regency, Central Java, Indonesia. The area is an area with abundant water hyacinth habitat.

2.2. Methods

2.2.1. Preparation of water hyacinth raw materials. Water hyacinth obtained from Lake Rawa Pening is separated from the roots and the impurities are then washed with clean water. The water hyacinth is cut into small pieces and dried in the sun for 5-7 days and then crushed to form a coarse powder. The coarse powder is dried again in an oven at 95°C for 12 hours. Sieving was carried out using a 60 mesh sieve, resulting in a finer size powder.

2.2.2. Isolation of α-cellulose from water hyacinth. The isolation process is divided into three stages, namely pre-hydrolysis, delignification, and bleaching. The water hyacinth powder is pre-hydrolyzed first by boiling it in hot water and then filtered. The insoluble part is added with 25% NaOH at a ratio of 1:40 and heated to boiling for 1 hour, then separated again by filtering. The residue obtained was washed using distilled water to pH 6-7, then the bleaching process was carried out by adding sodium hypochlorite (NaOCl) solution to soak the residue and left for 4 hours at room temperature. The residue is filtered and washed with distilled water until the chlorine odor disappears and is dried in an oven at 50°C until a constant weight is obtained. Dry residues obtained were followed by analysis of α-cellulose characterization.

2.2.3. Synthesis of CMC from α-cellulose Water Hyacinth. Water hyacinth cellulose is suspended in an isopropyl alcohol solvent in the ratio of 2: 1, 4: 1, and 6: 1 at room temperature. Each suspension was added 40% NaOH followed by stirring for 90 minutes. The mixture was added with 5 grams of sodium monochloroacetate ($NaCH_2COOCl$) slowly for 30 minutes and allowed to stand at 55°C for 3.5 hours. 70% methanol is added to the mixture and then neutralized with 90% acetic acid (CH_3COOH). CMC is obtained by filtering the residue 6 times with ethanol and washing again with pure methanol. The CMC obtained was dried using an oven at 60°C.

2.2.4. CMC Crosslinking with Succinic Acid. CMC crosslinking of water hyacinth cellulose with succinic acid with a comparison between succinic acid with CMC 1: 1, 2: 1, and 3: 1. Then dissolve it with 20 ml of distilled water. Insoluble crosslinking products are washed with ethanol and distilled water and then dried. Obtained crosslinking CMC products.

2.2.5. Data analysis technique. CMC characterization test from water hyacinth cellulose which was carried out covering the identification of functional groups using FTIR, organoleptic test, solubility test, foam test, solution pH test, and determination of degree of substitution (DS) based on SNI 06-3736-1995, The Joint FAO/WHO Expert Committee on Food Addictives (JECFA), and Pharmacopoeia Indonesia [8].

3. Results and Discussion

3.1. Isolation of α-cellulose from water hyacinth

The size of the water hyacinth sample used will be very influential in the isolation process of α-cellulose. The greater the surface area of the sample, the lignin and hemicellulose separation reaction will be more optimal. This study uses water hyacinth powder with a particle size of 60 mesh. The water hyacinth powder is carried out pre-hydrolysis stage with the aim to accelerate the process of separating the hemicellulose contained in it [6]. The addition of NaOH to the reaction is aimed at the delignification process. Delignification is the process of separating or removing lignin from cellulose fibers [9]. NaOH solution is chosen on the grounds that NaOH can dissolve other forms of cellulose such as β-cellulose, γ-cellulose, hemicellulose, and holocellulose so that the remaining is α-cellulose [10]. The results of the delignification process are obtained such as β-cellulose, γ-cellulose, hemicellulose, and holocellulose so that the remaining is α-cellulose residue with a dark white color. The dark white or brownish color of cellulose is caused by lignin compounds which are still left, so that the bleaching process is needed to get cellulose with a brighter color [1]. In the bleaching process sodium sodium hypochlorite solution is used because the sodium hypochlorite is an oxidizing compound that functions to oxidize lignin structure. The use of oxidizing compounds will break the Cα-Cβ bond in the lignin molecule [11]. Cellulose is obtained with a yield of 50.8%.

3.2. Synthesis of CMC from α-cellulose

The process of making CMC is influenced by the process of alkylation and carboxymethylation [12]. Both of these stages can take place in the form of solids or in another medium in the form of water or organic solvents. This research used isopropyl alcohol solvent. Isopropyl alcohol acts as a medium to homogenize the carboxymethylation reaction, also serves to increase the degree of substitution, disperses cellulose, increases the rate of reaction kinetics, and heat exchange media [13]. Isopropyl alcohol also acts as an inert solvent that facilitates NaOH to penetrate [10]. Alkalization process in water media will produce a less homogeneous CMC, so that the value of the degree of substitution of the CMC produced is low [14]. Alkalization is carried out using a solution of NaOH which aims to activate the -OH groups in the cellulose molecule and develop cellulose so as to facilitate the diffusion of reagents for the carboxymethylation process. In the process of alkalization of cellulose with NaOH produces white cellulose alkali [10]. The synthesis process is continued with carboxymethylation using sodium monochloroacetate which will produce carboxymethyl cellulose compounds through a substitution reaction with a byproduct in the form of glycolic acid. The addition of methanol to the reaction aims to separate CMC products from side products. Acetic acid is used to neutralize the product because the process runs in an alkaline atmosphere. The increase in temperature on the addition of acetic acid is due to the exothermic running reaction. Washing using pure ethanol and methanol aims to eliminate glycolic acid [10].

Table 1. CMC synthesis result

No	Variable of Isopropil Alkohol : Celullose	CMC (g)	Yield
1	Variable 2 : 1	1.95 g	39%
2	Variable 4 : 1	2.43 g	48.%
3	Variable 6 : 1	1.38 g	27.6%

From these data it can be concluded that the CMC with the highest yield is found in the 4:1 variable of 48.6%. In the 2:1 variable the solvent ratio used is still not optimum so the alkylation reaction that

occurs is not optimal. While the 6:1 variable has the least amount of yield, which is as much as 27.6%, this is because the addition of the amount of isopropyl alcohol solvent is too excessive so that it inhibits NaOH in the process of cellulose development, where the process is very influential on the carboxymethylation process [15].

3.3. Crosslinking with Succinic Acid

The crosslinking reaction between CMC and succinic acid produces an ester compound formed between the hydroxyl group owned by CMC polymers with two carboxylic groups on succinic acid [7].

Table 2. *Crosslinking* of CMC result

No	Variable of CMC : Sccinic acid	CMC (g)	Yield
1	Variabel 1 : 1	2.97 g	198%
2	Variabel 2 : 1	2.11 g	140.66%
3	Variabel 3 : 1	1.84 g	122.66%

Based on the results of the CMC crosslinking reaction with succinic acid, all CMCs produced have a yield above 100%. This shows that CMC has crosslinked with succinic acid so that there is an increase in mass in the CMC product. The addition of succinic acid in crosslinking is directly proportional to the increase in yield of CMC products produced. Research conducted by [7] using succinic acid as a crosslinker with a comparison of CMC to succinic acid 2: 1 only produced CMC products with a yield of 113.3% [7].

3.4. CMC Characterization

Based on the CMC characteristic test, the color and odor test results obtained from each sample meet the requirements. The taste test results showed the Crosslinking CMC 2: 1 and 3: 1 samples were slightly acidic, while the Crosslinking CMC 1: 1 sample was acidic. This is because the result of the addition of succinic acid which is acidic. The more succinic acid is added, the more acidic CMC is produced. The solubility test results in water and ethanol show that each CMC sample tested meets the requirements. In the pH test the CMC samples of the Koepoe-koepoe and CMC cap without crosslinking show the pH indicating the sample meets the requirements. In CMC crosslinking 2: 1 and 3: 1 samples obtained CMC with a pH of 6, this is due to the addition of succinic acid which has a pH below 7. The results obtained still meet the pH qualification requirements which is between 6.0 to 8.0. As for the 1: 1 CMC crosslinking sample the pH obtained indicates a value of 4. The value does not meet the pH qualification standard. In the foam formation test (foam test) each sample does not indicate the formation of foam.

3.5. FTIR Test

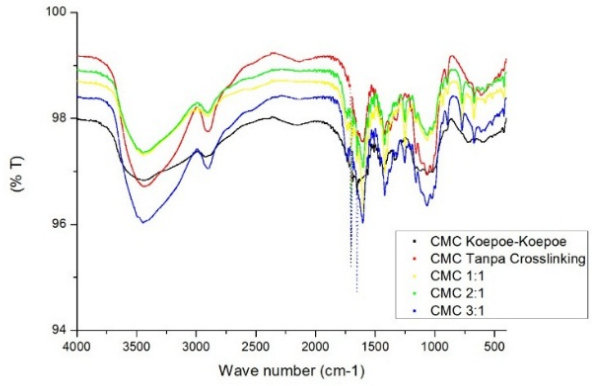

Figure 1. FTIR test

The results of the CMC Cap Koepoe-koepoe FTIR analysis showed that there was a peak with strong intensity at 3433.42 cm^{-1} wave number indicating a hydroxyl group (–OH) stretching. The -OH group in the range of wave numbers also shows the existence of intramolecular hydrogen bonds. While the CH group is at a wavelength of 2924.25 cm^{-1}. Carboxylate groups (COO-) can also be seen at wavelengths of 1700.75 cm^{-1}. Whereas the Carboxymethyl Ether group (CH-O-CH_2) is seen at wavelengths of 1061.32 cm^{-1} [16]. Other CH groups are also formed and can be seen at wavelengths of 591.46 cm^{-1} [17]. This result is also seen in CMC without crosslinking which shows that CMC in this study is close to CMC on the market, evidenced by the peak% T at almost the same wavelength. The %T difference shows the difference in the concentration of the group in the study sample.

Whereas the CMC that has passed the crosslinking process shows that many new groups have formed due to the addition of succinic acid compounds in the crosslinking process. As in the wavelength of 1600.76 cm^{-1}, there was a sharp decrease in% T and was not experienced in the Koepoe-Koepoe and CMC without crosslinking. This is due to the formation of new ester compounds as a result of the crosslinking process [7]. In addition, the% T in the -OH group is also increased when compared to CMC without crosslinking, in which the -OH group changes with other groups such as CH2 at 1419.58 cm^{-1} and other -OH bonds at 1248.97 cm^{-1} [18].

3.6. Analysis of Degree of Substitution

The degree of substitution is carried out to determine the number of hydroxyl groups, namely Sodium Monochloroacetate (NaMCA) as a marker of CMC formation. In this case, the esterification process occurs between the alkali cellulose and sodium monochloroacetate. Determination of the price of the degree of substitution (DS) generated based on infrared spectrum analysis.

Table 3. Degree of Subsitition calculation

No	Sample	%T OH	%T Ester	Abs OH	Abs Ester
1.	CMC Cap Koepoe-Koepoe	96.83	95.21	1.986	1.978
2.	CMC without *Crosslinking*	96.71	96.63	1.985	1.985
3.	CMC 1:1	97.31	96.04	1.988	1.982
4.	CMC 2:1	97.35	96.26	1.988	1.983
5.	CMC 3:1	96.03	95.53	1.982	1.980

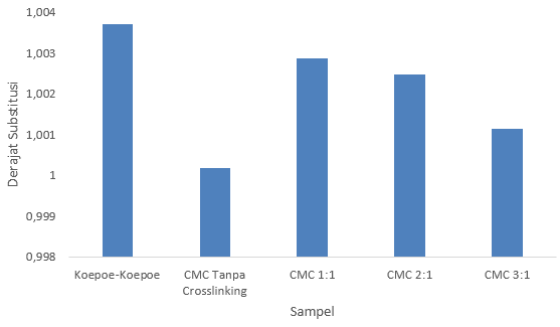

Figure 2. Degree of Substition Chart

From figure 2 it can be seen that the degree of substitution increases with increasing concentration of succinic acid used, but it is still very stable in the range of 1.0001 – 1.003. Based on the data obtained, it can be seen that the figures obtained based on the infrared spectrum are still within the numbers required in determining the degree of substitution, from 0 - 3.00, and are still in the DS CMC standard for food, which is 0.2 - 1.5 (Anonymous, 2011).

The value of the degree of substitution produced is related to the role of the reagent and the amount of succinic acid added in the CMC synthesis process. The effect of the reagent used can be seen from the polarity value of the solvent used. The effect of the amount of succinic acid influences the number of the -OH group which is replaced by the ester group.

4. Conclusion

Based on the results of research adding the isopropyl alcohol solvent in the CMC synthesis process has an effect on the final yield of yield, because isopropyl alcohol is an inert solvent that functions as a supporting medium for NaOH to penetrate cellulose. The less the amount of solvent is added, the reaction will not run optimally. Meanwhile, if the amount of excess added solvents this will actually be an inhibitor of NaOH to develop cellulose. This can be seen in the ratio of 1: 6 with the largest amount of solvents but the least amount of yield is obtained. The optimum variable which shows the ratio between cellulose and isopropyl alcohol is 1: 6 with a yield of 48.6%

The addition of succinic acid crosslinkers has been shown to significantly increase the amount of yield with the quality tested shows that the results are not much different from the standard CMC on the market. However, for a 1: 1 comparison variable, a product with a pH below 6.0 does not meet the pH standard of a CMC product that is between 6.0 to 8.0, so there is a need for further processes so that the CMC has characteristics that are in accordance with the standard.

The best CMC, which is a 2: 1 comparison variable, has a high yield and is still within the standard characteristics required by FI/JECFA/SNI.

References

[1] Muzakkar M Z, Tamrin N R and Ratna 2017 *Pros. Semin. Nas. FKPT-TPI* 20–21
[2] Kurniyati Z 2015 Pemanfaatan Kulit Durian Untuk Sinstesis CMC (Carboxymethylcellulose), dengan Rasio Natrium Kloroasetat dan Selulosa. (Skripsi. Universitas Negeri Semarang)
[3] Elarini D, Radiati L E, and Purwadi 2014 Effect Of Carboxymethyl Cellulose (CMC) On Organoleptic, Color, pH, Viscosity, And Turbidity Of Honey Drink 1–10
[4] Musfiroh I and Budiman A N H I 2013 *Res. J. Pharm. Bio. Chem. Sci.* **4(4)** 1092-1099
[5] Pitaloka A B, Hidayah N A, Saputra A H, dan Nasikin M 2015 *J. Integr. Proses* **5** 108–114
[6] Indriyati W, Musfiroh I, Kusmawanti R, dan Hasanah A N 2016 *IJPST* **3**
[7] Agustriono F R 2017 *Farmaka* **15** 26–32
[8] Dirjen POM 1995 *Farmakope Indonesia*. (Departemen Kesehatan Republik Indonesia)
[9] Putera R D H 2012 Ekstraksi Serat Selulosa Dari Tanaman Eceng Gondok (*Eichornia crassipes*) dengan Variasi Pelarut (Skripsi. Universitas Indonesia)
[10] Rahmania F J and Husni P 2017 *J. Farm. dan Kesehat* **7** 141–150
[11] Jayanudin 2009 *J. Rekayasa Proses* **3** 10–14
[12] Sari N K 2009 *J. Tek. Kim.* **4** 265–273
[13] Aprilia L 2009 Preparasi Produk Nata De Pina dan Aplikasi Pengikatannya Terhadap Logam Kobalt (II) (Skripsi. Institut Pertanian Bogor, 2009)
[14] Zuraida I 2016 Sintesis Natrium Karboksimetil Selulosa Dari Mikrokristalin Selulosa Kayu Sengon (Paraserianthes Falcataria (L.) Nielsen) dengan Pelarut Campuran Isopropanol-Etanol. (Skripsi. Universitas Negeri Semarang)
[15] Kentjana Y 1996 *Karboksimetilasi bahan bukan kayu.(Carboxymethylation from Non Wood Material)*.
[16] Pushpamalar V, Langford S J, Ahmad M, and Lim Y Y 2006 *Carbohydr. Polym.* **64** 312–318
[17] Dachriyanus 2004 *Analisis Struktur Senyawa Organik Secara Spektroskopi*. (Lembaga Pengembangan Teknologi Informasi dan Komunikasi (LPTIK)
[18] Hashem M, Sharaf S, El-hady M M A, and Hebeish A 2013 *Carbohydr. Polym.* **95** 421–427