Synthesis and swelling characterization of nata-de-coco-and-water-hyacinth-based hydrogel

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Abstract. Hydrogel is one type of polymers that is able to absorb and retain water in huge amount in its body. A parameter of performance of hydrogel is swelling ratio. In this research, we used water hyacinth and nata de coco. Cellulose in both materials was isolated until powdered cellulose was achieved. Next, both types of cellulose were converted into carboxymethylcellulose (CMC) and then into hydrogel using citric acid as cross linker in aqueous solution. Concentration of citric acid was varied into 3 variations, 10%, 15%, 20% (w/w CMC). Each hydrogel formed was assessed in terms of performance, existence of functional group and morphology. Swelling ratio assessment was conducted per hour, which is swelling ratio at the 1st, 2nd, 3rd and 24th hour. The result of FTIR showed that cellulose, CMC and hydrogel were successfully formed. Swelling ratio assessment showed that at concentration of 10% and 15%, the hydrogel showed huge swelling ratio but very poor gel fraction and stability. At concentration of 20%, hydrogel found stable and had swelling ratio of 2291% for nata de coco and 1862% for water hyacinth. Finally, for hybrid hydrogel at concentration of 20% citric acid and ratio of mixing between nata de coco CMC and water hyacinth CMC was 50:50, hydrogel formed shows good strength and stability, but with decreasing swelling ratio which was 1171%.

Keywords: Cellulose, Carboxymethylcellulose, Hydrogel, Nata de coco, Water hyacinth

1. Introduction
Hydrogels are structures of hydrophilic polymers that are chemically or physically cross linked forming three dimensional network. They are able to absorb and retain water in their body in large amount while maintaining their structure. Hydrogel, based on their source, can be divided into 2 groups. The first group is hydrogels derived from synthetic polymer and the second is derived from natural polymer. Hydrogel that is derived from synthetic polymers is usually formed from crosslinking of poly (ethylene glycol), poly (vinyl alcohol), poly (amido-amine), poly (isopropylacrylamide), poly acrylamide and poly acrylic acid. However, the one derived from natural polymers is usually formed from crosslinking of alginate, gelatine, chitosan, hyaluronate, starch and cellulose and their derivative [1]. Hydrogels derived from natural polymers have advantage over synthetic polymers in terms of biodegradability, giving a good environment for cell annealing. In other word, it is not bio inert and it is easily degraded in the body.

Cellulose is known as an inexhaustible source of material that environmental friendly and can be derived into biocompatible products such as hydrogels. Water hyacinth has cellulose content of 72.63% [2]. While Nata de coco is a pure source of cellulose, so it needs no further purification [3]. Carboxymethyl cellulose as a derivative of cellulose has succeeded cross linked to produce hydrogel...
that good for drug delivery [4]. Hydrogel based on nata de coco for drug delivery has also synthesized by Pandey et al. [5] and have good swelling ratio. Hapsari [6] successfully used cellulose from water hyacinth to synthesize hydrogels with citric acid crosslinking.

2. Experimental Part

2.1. Materials

Bacterial cellulose was supplied by IWM shop on Tokopedia. Nata de coco was in shape of thick sheet with thickness of 1-2 cm. Cellulose content was 0.7-1% the weight. The powdered water hyacinth of 60 mesh was provided by Laboratory of Sustainable Energy, Universitas Indonesia. MCA (sodium monochloroacetic acid) was obtained from Sigma Aldrich Singapore. Ethanol and toluene that was used for wax extraction is in technical grade. The other chemical is in analytical grade and used without further purification.

2.2. Powdering of nata de coco

Nata de coco was soaked using NaOH solution of 0.1 M for 3 hours before being washed using distilled water until neutral pH was achieved. After that, it was dried using centrifugal dryer Panasonic NA-F7085 at speed of 720 rpm and ambient temperature using fan. Lastly, it was put in the oven at temperature of 70°C. The dry bacterial cellulose sheet which was achieved, was then pulverized using pulverizer at Pusat Teknologi Pengembangan Sumberdaya Mineral, BPPT, Puspiptek, Serpong. The result was nata de coco powder with the size of 60-80 mesh.

2.3. Isolation of Water Hyacinth Cellulose

Water hyacinth was processed in 3 steps to isolate the cellulose content. The steps were de-waxing, delignification and dissolution of hemicellulose. De-waxing was done by soxhlet extraction using ethanol 20% (v/v) and toluene 80% (v/v) for 24 hours with total of 16 cycles. The extraction was done twice: first was to get rid of the wax, the second to clean the water hyacinth from wax traces. Delignification or bleaching was done using sodium chlorite in acetic acid solution of 10% (w/v). Water hyacinth was soaked in the solution and heated at 80°C using water bath for 3 hours. Water hyacinth in the solution then was taken out from the water bath and incubated at room temperature overnight. Hemicellulose dissolution was done by taking out the bleached cellulose out of sodium chlorite solution and soak it in the NaOH 17.5% for 3 hours. After that, neutralization was done by washing it in acetic acid 10% until neutral pH has achieved, then the sample filtration to take the solid product.

2.4. The Making of CMC

Carboxymethylcellulose was synthesized by placing cellulose in a container with an impeller. Cellulose as much as 10 grams was reacted in a container using 200 mL isopropanol: isobutanol with ratio of 8:2 (v/v) with impeller inside the container working at 300 rpm. Next, NaOH 10% as much as 40 mL was added to the container gently using pipet. The chamber was left working for 1 hour to maximize the reaction. The second step was replacing the container into water bath with temperature of 55°C and impeller of speed of 500 rpm, 11-gram sodium chloroacetate was added to the chamber little by little. The container was left for 3.5 hour to maximize the reaction. The making of CMC from cellulose can be divided into 2 parallel reaction. The first reaction is alkalization in reaction number (1) on Fig. 1, and the second is carboxymethylation in reaction number (2) on Fig. 1.

\[ \text{[C}_6\text{H}_7\text{O}_2(\text{OH})_2\text{n]} + n\text{NaO} \rightarrow [\text{C}_6\text{H}_7\text{O}_2(\text{OH})_2\text{ONa}]_n + n\text{H}_2\text{O} \] (1)

\[ [\text{C}_6\text{H}_7\text{O}_2(\text{OH})_2\text{ONa}]_n + n\text{ClCH}_2\text{COO}\text{Na} \rightarrow [\text{C}_6\text{H}_7\text{O}_2(\text{OH})_2\text{OCH}_2\text{COO}\text{Na}] + n\text{NaCl} \] (2)

**Figure 1.** reactions in the making of CMC.
2.5. The making of Hydrogel
Hydrogel was synthesized by adding 3 gram of CMC into 100 mL of water and then stirring it with magnetic stirrer until all CMC was dissolved and a clear solution was achieved. Citric acid with variation of 10%, 15% and 20% (w/w CMC) was added to solution and stirred for 30 minutes.

![Diagram of Hydrogel Crosslinking](image)

Figure 2. Reaction of CMC crosslinking using citric acid as crosslinker.

Fig. 2 shows the phenomena of crosslinking of cellulose with cellulose with citric acid as cross linker agent. Two water molecules are produced for each crosslinking occur, but 1 monomer of CMC can experience 0-3 crosslinking in its body either to other chain or to other monomer in its own chain. Each crosslink that happens will produce 2 water molecules.

All variation was done to water-hyacinth-based CMC and nata-de-coco-based CMC. Hybrid hydrogel also was made by mixing both CMC type with ratio of 50:50 (w/w) and using citric acid with concentration of 20% (w/w CMC), the method is just the same with the previous method. Types of hydrogels made can be seen on table 1.

| Hydrogel type      | Citric acid concentration (%) |
|--------------------|-------------------------------|
|                    | 10      | 15      | 20      |
| Water hyacinth     | EG/10AS | EG/15AS | EG/20AS |
| Nata de coco       | NC/10AS | NC/15AS | NC/20AS |
| Hybrid             | -       | -       | NC50/EG50/20AS |

3. Results and Discussion
3.1. FTIR assessment of cellulose, CMC and hydrogel
FTIR analysis was done to see whether cellulose isolation, synthesis of CMC and hydrogel were successfully formed. Fig. 3 (A) shows FTIR spectra for cellulose, CMC and hydrogel. Picture a shows peak at wavenumber of 1054 cm⁻¹, 1426 cm⁻¹, 2920 cm⁻¹, 3340 cm⁻¹ which in sequence shows stretching of C-O-C alkoxy group, folding of C-H or alkane group and O-H on alcohol group. There is one alkoxy group in the ring of glucose and there is one more in the bond between glucose and glucose. OH group exist in the monomer of cellulose. This shows that cellulose had been succeed to be isolated from nata de coco and water hyacinth.
Figure 3. (A) FTIR spectra of cellulose; (B) FTIR spectra of CMC; (C) FTIR spectra of hydrogel.

The wavenumber that shows CMC was successfully synthesized is at wavenumber of 1314 cm\(^{-1}\) which is wavenumber for stretching of acyl group. It can be seen in Fig. 3 (B). The existence of peak at that wavenumber shows that -OH group on cellulose had been substituted into sodium carboxymethyl group. This acyl group has formula of RCO-ONa.

For hydrogel, chemical group that has to be present is ester group. Ester group is present because of the bond that formed between CMC and citric acid. The absorbance of ester group can be seen at wavenumber of 1712 cm\(^{-1}\). It can be seen on Fig. 3 (C), on the concentration of citric acid of 10% peak could not be seen. Instead of peak, we can only see bent of the spectra. Moreover, at concentration of 10% citric acid, 82% transmittance was shown, which means the number of crosslinking was low. On the contrary, at concentration of 20%, peak can be seen clearly.

3.2. Viscosity measurement of CMC
Viscosity assessment was done by making CMC a solution with concentration of 3% (w/v). The test was done using Cannon-Fenske viscometer by counting the time the CMC solution flow from upper
strip to lower strip. Density was measured by measuring mass of 1 mL CMC. In this research, same synthesis method was used, but CMC from nata de coco and CMC from water hyacinth show different number of viscosity. The number of viscosity is shown in the table below.

| Category | Nata de coco | Water hyacinth |
|----------|-------------|----------------|
| ρ (kg/L) | 1.19        | 1.36           |
| Viscosity(mPa.s) | 1917.99 | 875.03         |

CMC derived from nata de coco has a higher viscosity compared to CMC derived from water hyacinth. Viscosity of CMC is highly related to degree of polymerization (DP) of material. Bacterial cellulose generally has a high DP. DP of bacterial cellulose can reach to 8000 [7]. Cellulose that yielded from water hyacinth with pulping method has degree of polymerization as much as 600-1500 [8]. The degree of polymerization of both materials gives effect to number of viscosity. The higher the DP of polymer, the higher number of viscosity and vice versa.

Zhuomei and Yuhui [9] shows that the lower the number of degree of substitution (DS) of CMC will make number of viscosity of CMC increase. High DS number which is 1.02 shows low number of viscosity which is 6 mPas [10]. Value of DS that is commonly used in industry is 0.7 and for research 0.9. Lower viscosity caused by the interaction with water because of more sodium carboxymethyl group in the CMC. Relating number of DS to swelling ratio, the higher the DS, the higher the crosslinker needed and also it brings good swelling ratio. When CMC is being ionized become COO -, they will produce electrostatic repulsion that will open the network of hydrogel and the absorbance to water increased [11]. In this research, DS of water hyacinth CMC is 0.89 while DS of nata de coco CMC was not measured.

3.3. Analysis of swelling ratio

Swelling ratio is a mass ratio of water absorbed by hydrogels divided by the mass of hydrogel when it is in dry state. Value of swelling ratio shows the performance of hydrogel. Value of swelling ratio was counted for 1st, 2nd, 3rd and 24th hour. Swelling ratio was counted by measuring weight of hydrogel, soaking it in water for an hour, taking it out, eliminating water in the surface of hydrogel using tissue paper and then measuring the mass of the swollen hydrogel. Then we put it back to water and measure the mass for 2nd hour, 3rd and 24th hour soak.

![Figure 4](image-url)  
**Figure 4.** (A) swelling ratio per hour; (B) swelling ratio per concentration of crosslinker.
Fig. 4 (A) shows graph of swelling ratio of hydrogel per hour for hydrogel with 20% crosslinker. We see that at first hour absorbance of water is at a very high rate. This happen because all the pores of hydrogel is still available for water. At the second hour, hydrogel absorbing water but with rate lower than the first hour because the hydrogel is beginning to be saturated. At the third hour, hydrogel have become saturated and tend to free the water bound in it to the environment. At the third to twenty fourth hour there must be binding and unbinding of water at that hours but the trend is still rises as can be seen from the graph. Having a similar trend, there are differences in the ratio of swelling between nata de coco hydrogels and water hyacinth hydrogels. At the 24th hour, NC/20AS swelling ratio hydrogel was 2291% while for water hyacinth hydrogels produced a swelling ratio of 1862%. In the water hyacinth hydrogel, there is a smaller swelling ratio compared to nata de coco. The thing that might happen is caused by the large fibrils owned by both of them differently. Nata de coco has nano-sized fibrils while water hyacinth has larger size fibrils [7]. With the same number of crosslinkers but with smaller fibrils, it will produce better network compared to larger fibrils, where more crosslinking occurs and results in overcrowded crosslinking which reduces the ability of the hydrogel to absorb water.

In the NC50/EG50/20AS hydrogel, the swelling ratio increase continues to occur from the first, second, third and 24th hours. This shows that hybrid hydrogels have sufficient ability in water absorption, because at these hours there is no release of water as in NC/20AS and EEG/2/0AS Hybrid hydrogel bodies that are formed also have high gel fractions in the water until the 48th hour. However, the swelling ratio of this hybrid hydrogel is not as good as the water hyacinth hydrogel and nata de coco hydrogel. This high gel fraction is caused by cross linking between long chain CMCs and short chain CMCs. The low value of swelling ratio is also possible because of other interactions between two kind of CMC.

On Fig. 4 (B), the graph above shows swelling ratio to the concentration of citric acid used. At citric acid concentration of 20%, the hydrogel from nata de coco shows higher swelling ratio than hydrogel from water hyacinth. This difference shows that water hyacinth CMC will have less fibril due to its thickness compared to nata de coco CMC with the same concentration. As smaller number of fibril have to anticipate the same amount of crosslinker, this will produce a crowed network of hydrogel compared to hydrogel from nata de coco. Please note that at concentrations of 10% and 15%, the measured swelling ratio is not at the 24th hour, but in the first hour. This is caused by hydrogel dissolution in water that show small gel fraction. Meanwhile, for concentration of citric acid 20%, the data taken is data at the 24th hour where the hydrogel is still in a good and stable state, and is near the point of saturation.

3.4. Morphology Analysis

Morphological analysis is an analysis conducted to see the differences in morphology of cellulose, CMC and hydrogels based on nata de coco and water hyacinth and compare them. Fig. 5 (A) shows that CMC fiber derived from water hyacinth is clearly visible at 1000x magnification with fiber diameter of about 5-10 micrometers. CMC fiber derived from nata de coco at 5000x magnification in Fig. 5 (B) is visible in fiber but not very clear and it is even worse in magnification of 1000x. The fiber diameter is approximately 100-200 nm. The second diameter of the CMC is different because it is taken from a different cellulose source. Water hyacinth cellulose is a micro-sized cellulose while cellulose nata de coco is a nano-size cellulose. the advantage of nanofiber compared with microfiber is that it has large surface area, which directed to good absorption of molecule and attachment of functional group. However, the SEM results do not show the fibril length of CMC both nata de coco and water hyacinth.

Nata-de-coco-based hydrogels with different crosslinker concentrations which are 10% and 20% show difference in their structure. The difference is shown by the number of porous surfaces in hydrogels with a 10% crosslinker concentration on Fig. 3 (C). This is due to the rare crosslink so the hydrogel’s body is very porous. While at 20% crosslinker concentration, hydrogel that was produced shows denser structure in various places and had flower-shaped tissue where water would be absorbed in Fig. 5 (D). This is related to the high swelling ratio value in the NC/10AS hydrogel compared to NC/20AS. Poor gel fraction can also be caused by less crosslinking that the material becomes too porous.
due to poor network formation in the hydrogel. Less crosslinking on NC/10AS also confirmed by FTIR spectra which do not show peaks at wave number of 1712 cm\(^{-1}\).

**Figure 5.** (A) CMC of water hyacinth 1000x; (B) CMC of nata de coco 5000x; (C) NC/10AS 1000x; (D) NC/20AS 1000x; (E) EG/20AS 1000x; (F) NC50/EG50/20AS 5000x.

On Fig. 5 (E) water hyacinth hydrogel with 20% citric acid has two parts: smooth or non-textured parts and parts which form texture like layered and folded. In this section, the possibility of crosslink is inadequate, resulting in an imperfect body formation. The part of the body which were textured is likely to be the entrance for water into the hydrogel body. This allows good swelling of hydrogels.

Fig. 5 (F) shows an NC50/EG50/20AS hydrogel image with 5000x magnification. It shows that there are smooth parts and structured parts like on EC/20AS and NC/20AS hydrogels. The structured part formed in NC50/EG50/20AS looks stiffer compared to EC/20AS and NC/20AS hydrogels and pores cannot be seen on the structure. This shows that the hybrid hydrogel has a high number of crosslinking. This higher number of crosslinking also confirmed the higher gel fraction of NC50/EG50/20AS compared to EC/20AS and NC/20AS.

4. Conclusion

Hydrogel was synthesized using cellulose of nata de coco and water hyacinth via carboxymethyl cellulose. Hydrogel from nata de coco has better performance when the crosslinker concentration is at 20% compared to water hyacinth. The addition of crosslinker will increase the gel fraction but decrease swelling ratio. This research found that hydrogels, which were derived from water hyacinth and nata de coco based CMC with crosslinker concentration of 20%, has the best performance in term of gel fraction. Hydrogel from nata-de-coco CMC and water-hyacinth CMC hybrid has much lower swelling ratio than if stands alone.

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