

SYNTHESIS AND CHARACTERIZATION OF HYDROGEL FROM CELLULOSE DERIVATIVES OF WATER HYACINTH (*Eichhornia crassipes*) THROUGH CHEMICAL CROSS-LINKING METHOD BY USING CITRIC ACID

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Abstract

Hydrogels are defined as a three-dimensional polymer structures that can be formed from natural or synthetic polymers and are able to retain large amounts of water. Hydrogels can be made in two ways, i.e. physical cross-linking and chemical cross-linking. The stable structure and effective swelling of the hydrogel can be obtained through the chemical cross-linking process. In this study, hydrogel was made by natural polymer that is non-toxic. Hydrogels were synthesized by using cellulose or its derivatives (Carboxymethyl Cellulose (*CMC*)) through chemical crosslinking process with citric acid as crosslinking agent. Cellulose is derived from water hyacinth plant, as one of the potential sources of cellulosic fibres in producing of *CMC*. Various conditions of preparation, such as citric acid concentration and variations in the value of the degree of substitution of Na*CMC*, were observed through the hydrogel characterization results. Variations of variables in this research consist of the concentration of citric acid of 5, 10, and 15% and the ratio of composition isobutyl-isopropyl alcohol solvent in order to get the value of degree of substitution of *CMC*. Based on the results, the hydrogel with the highest swelling ratio is when the composition of isobutyl-isopropyl alcohol is 2:8 and the concentration of citric acid is 10%.

Keywords: Carboxymethyl Cellulose (*CMC*), Water hyacinth, Chemical cross-linking, Hydrogels, Citric acid.

Nomenclature

W_g	weight of the gel after immersion in water
W_t	weight of the swollen hydrogel
W_o	weight of dried sample

Abbreviation

CMC	Carboxymethyl Cellulose
DS	Degree of Substitution
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscope
SR	Swelling Ratio

1. Introduction

The term of hydrogel describe a three-dimensional network structure obtained from the synthetic polymer and / or natural polymer that can absorb and retain large amounts of water [1].

The amount of water that can be retained by the nets on the hydrogel network depends on the network structure of the polymer itself and was influenced by environmental conditions such as pH, temperature and ionic strength of the aqueous solution which contact with the polymer.

Currently, the hydrogel technology is continuously developing [2]. Most hydrogels on the market derived from synthetic polymers. As known that hydrogels derived from synthetic polymers have properties that are not biodegradable, biocompatible, and have toxic effects that are higher than natural polymers [3]. This is because, natural polymer-based hydrogels have similarities with natural living tissue that can absorb high water content and are also biocompatible and biodegradable [4].

Hydrogels have wide applications in many fields, for example in food, biomaterials, agriculture, water purification, and others. Recently, scientists have devote energy to develop hydrogels for other applications such as biodegradable materials for drug delivery [5, 6], tissue engineering [7, 8], sensors [9, 10], contact lenses [11], and others. One example of the application of superabsorbent hydrogel material is a sanitary napkin or baby diapers. In this application the resulting product is expected to have a high absorption and possess comfort during use. This makes the interest in the development of biocompatible and biodegradable superabsorbent hydrogel that can be obtained from natural polymers.

Cellulose is one of the natural polymer and renewable resource whose numbers are very abundant in the earth and will be the main source of chemical energy in the future [12]. Cellulose that is used in this study were derived from non-wood plants, one of which is by using water hyacinth (*Eichhornia crassipes*). Water hyacinth has the potential to be used as raw material for producing CMC because it contains high number of cellulose up to 72.63% [13].

The presence of CMC in cellulose-based hydrogels provides the electrostatic charge which is embedded in a network that has a dual effect on the ability of the

hydrogel swelling [14]. Polyelectrolyte properties of *CMC* makes it ideal for producing hydrogel.

Based on cross-linking method, hydrogels can be divided into two, chemical gels and physical gels. Physical gel formed by molecular self-assembly through hydrogen bonding or ionic reaction, whereas chemical gels formed by a covalent bond [15].

The stable structure and effective swelling of cellulose-based hydrogels can be obtained through the chemical cross-linking method [16]. Some difunctional molecules employed as a cross-linker to the cellulose or derivatives that play a role in the formation of covalent bonds with different polymer molecules in a three-dimensional network of hydrophilic. Citric acid can be one excellent candidate to be used as agent in the process of cross-linking because it has carboxylic groups that will form a network with the chains of cellulose or its derivatives. With the non-toxic property, citric acid will support the hydrogels synthesized that is biodegradable and environmentally friendly.

This study aims to get hydrogel and to observe the characteristics of the hydrogel from water hyacinth cellulose derivatives using citric acid as crosslinker through the chemical cross-linking as well as to obtain the optimum conditions in the synthesis of cellulose based-hydrogels.

2. Materials and Method

2.1. Materials

The water hyacinth was obtained from Tangerang- Indonesia. In the process of isolating water hyacinth cellulose using several materials, such as, NaClO_2 , NaOH , distilled water and CH_3COOH . The main reagents that needed in synthesis of *CMC* are Sodium monochloroacetic (NaMCA) and NaOH for alkalization and carboxymethylation process. CH_3COOH and 96% ethanol are used for neutralization and purification process. The synthesis of hydrogel use *CMC* and citric acid as a crosslinking agent.

2.2. Isolation of water Hyacinth Cellulose

Preparation begins with the separation of water hyacinth stems from roots and leaves, then to be dried to remove the water content. The dried water hyacinth was cut into small pieces and converted into powder form, then sieved to obtain powder with size of 60 mesh. The water hyacinth powder was heated using a Soxhlet apparatus and solvent of toluene and ethanol with volume ratio of 2:1 for dewaxing. The lignin content was removed by using 1 wt% solution of NaClO_2 placed in waterbath at 80 °C for 3 hours. After that, the bleached cellulose was treated using a solution of 17.5% NaOH to remove the hemicelluloses content and stand for 3 hours at room temperature. Washing is conducted by using distilled water and CH_3COOH for neutralizing the cellulose. Drying process was carried out in an oven at 60 °C for 2-3 hours.

2.3. Synthesis of Carboxymethyl Cellulose (CMC)

The alkalization process was conducted by mixing 10 grams of cellulose with composition of the reaction medium isobutyl-isopropyl alcohol at 2:8 in 3 neck flask with stirrer on for 10 minutes, then added 40 ml of 5% NaOH solution. The alkalization process was lasted for 1 hour at room temperature. After that, the synthesis process was followed by carboxymethylation process by adding NaMCA as much as 11 grams for 3.5 hours at 55 °C.

The variations in this study are the composition of the mixture of reaction medium isobutyl-isopropyl alcohol at 5:5 and 8:2. The CMC was neutralized by CH₃COOH and purified by rinse using 96% ethanol for four times to remove undesirable by products. The obtained cellulose derivative was dried at 60 °C in oven for 1-2 hours.

2.4. Synthesis of Hydrogel

Synthesis process begins by mixing 3%-w CMC in 100 ml of distilled water. After a homogenous mixture is obtained and translucent, add the citric acid as much as 5%, 10% and 15% of the weight of the polymer (CMC) that were used. This process lasted for 1 hour at room temperature. This final solution was used to make 10-mm thick sample. All samples were firstly pre-dried for 24 hours at 30°C under vacuum conditions [17]. and then kept with the process of esterification at a temperature of 80 °C for 13 hours. The obtained hydrogel was washed by soaking in 96% ethanol for 14 hours.

To obtain the swelling ratio, weigh each sample before and after soaked in distilled water for 1 hour at room temperature. After that, the excess of distilled water on the surface of the hydrogel is removed with filter paper (blotting) and the weight of hydrogel after immersion weighed [18]. Measurement of swelling ratio can be determined by Eq. (1):

$$\text{Swelling Ratio (SR)} = \frac{W_t - W_o}{W_o} \times 100\% \quad (1)$$

Equation (2) is used to determine the gel fraction. The dry polymer was soaked in water for 14 hours and water was replaced 2 times to remove components such as crosslinking agent that does not react. Then the gel was dried and weighed.

$$\% \text{ Gel Fraction} = \frac{W_g}{W_o} \times 100\% \quad (2)$$

3. Result and Discussion

3.1. Isolation of water Hyacinth Cellulose

In bleaching process (lignin removal) happened the degradation of lignin structure of water hyacinth. Cellulose which had been obtained was then characterized to determine the amount of α -cellulose content. Results of the test for water hyacinth cellulose content of α -cellulose is in the amount of 96.76%

3.2. Synthesis of carboxymethyl cellulose (CMC)

FTIR analysis is intended to prove the occurrence of carboxymethylation reactions in water hyacinth cellulose. Based on Fig. 1, the absorption peaks appear at 1400 cm^{-1} which showed the presence of -CH_2 groups and regions of 1600 cm^{-1} indicate the presence of carboxyl group (COO^-) [19]. It can be concluded that the water hyacinth from cellulosic materials have undergone carboxymethylation reaction into *CMC*.

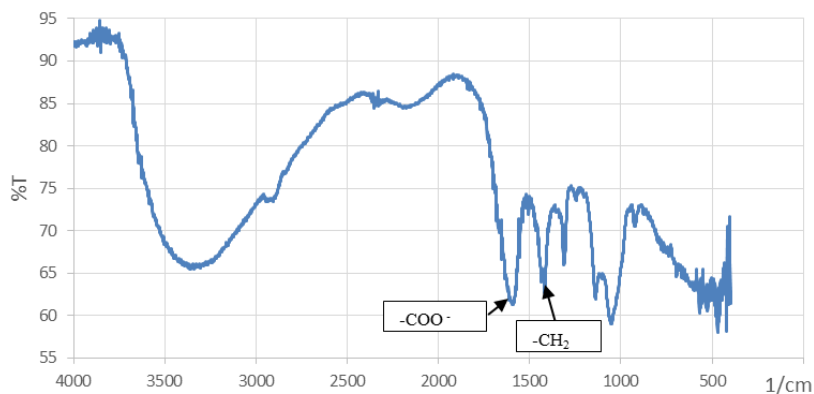


Fig. 1. *FT-IR* Spectra of *CMC* BP28.

3.3. Synthesis of cellulose based-hydrogel

The evidence of occurrence of crosslinking between *CMC* and citric acid was made by testing the functional group by using *FT-IR*. This was conducted to see where the peak of carboxyl group (COO^-) of esters appears and where OH groups that plays a role in the binding of water. Figure 2 shows the spectra of sample HG28-15% and the peak appears at a wavelength of 1757 cm^{-1} . This indicates that there has been an ester bond formation between citric acid anhydride with a hydroxyl group and cellulose derivatives [20]. Peak on the wave in the range of 1757 cm^{-1} indicate the presence of a group carboxyl group (COO^-) of the hydrogel. Thus, it can be concluded that the chemical process of crossing between *CMC* and citric acid has been successfully carried out. In addition, the peak appears at 3527 cm^{-1} spectra are according to the strain-OH. This can be explained by the hydrophilic nature of the polymer hydrogel network structure.

3.4. Effect of crosslinker concentration to the gel fraction

Gel fraction indicates the degree of crosslinking formed in the hydrogel. Crosslinker agent is needed in the formation of the polymer network hydrogels because this structure determines the water absorption (swelling) in the hydrogel. Increasing the concentration of crosslinking agent in the system will increase the degree of crosslinking and produce a strong gel. The high degree of crosslinking

will make the structure become rigid and reduces the ability of the hydrogel to absorb water [21].

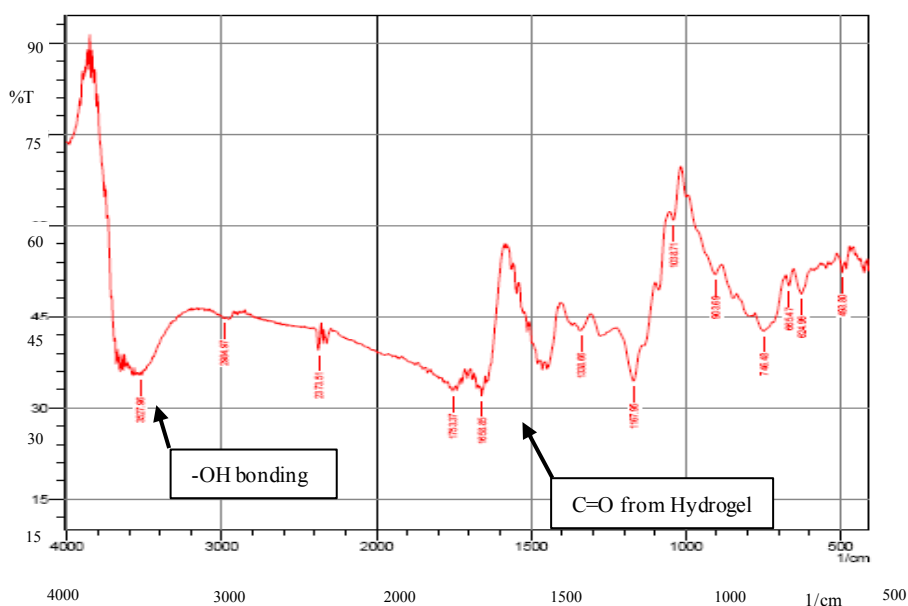


Fig. 2. FTIR Spectra of HG28-15%.

Based on Fig. 3, it can be concluded that the more crosslinking agents used can make gel fraction will be higher [22]. The gel fraction is obtained ranged from 39-58%. This indicates the presence of unreacted components. At a low concentration of citric acid (5%) gel formation occurs more slowly that makes little amount of gel formed. At this condition, with the immersion in water will cause the hydrogel dissolves back indicating that the gel fraction formed a low or none at all. This situation occurred in all the sample of HG82-5.

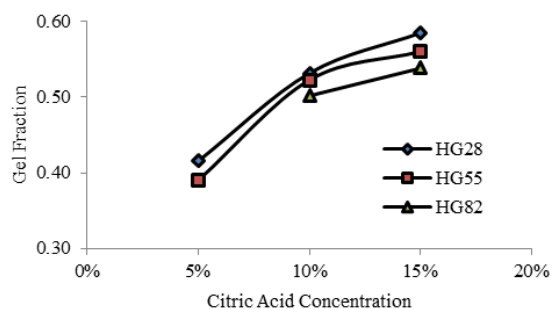


Fig. 3. Relation Between Citric Acid Concentration and Gel Fraction.

On the other hand, when the higher concentration of citric acid is used, gel formation occurs more rapidly. This is due to the increasing amount of citric acid will result in the number of polymer chains that are bound to increase in the

formation of crosslinked gel [22]. When percent which indicates a low gel formation, all double bonds exist in the structure of crosslinking agent does not react perfectly, so that the network structure is less likely to form crosslinked [4].

3.4.1. Effect of crosslinker concentration to the swelling ratio

Figure 4 shows that the maximum swelling that can be achieved is when the concentration of citric acid at 10% on any type of hydrogel. The increase in density of crosslinking will decrease the rate of water absorption due to the polymer network will act only as a barrier to water diffusion [21]. Therefore, a small amount of water molecules can diffuse into the strong crosslinked network. This is what might happen under conditions of citric acid concentration of 15%.

However, when the concentration of citric acid is higher, 15% will make the network structure of the hydrogel more solid/rigid that resulted the water hardly enter into the hydrogel network, therefore the value of its swelling ratio decreases. At a low concentration of citric acid (5%) did not happen enough chemical crosslinking between *CMC* molecules and citric acid. This makes the hydrogel at a concentration of 5% citric acid did not have good water absorption ability. While the high concentration of citric acid (15%) has excess crosslinking which limits the mobility of the polymer molecules [23].

Swelling optimum ratio that can be achieved on each type of *CMC* are as follows:

- In HG28 obtained maximum swelling ratio is equal to 759%.
- In HG55 obtained maximum swelling ratio is equal to 747%.
- In HG82 obtained maximum swelling ratio is equal to 1419%.

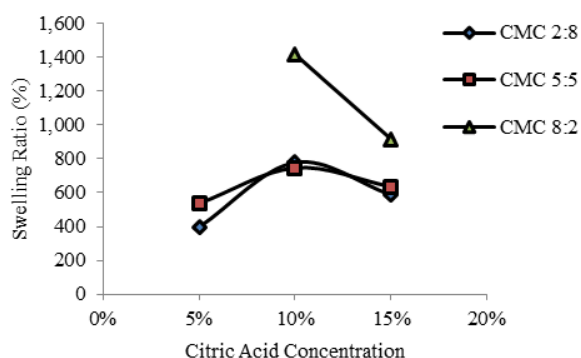


Fig. 4. Relation Between Citric Acid Concentration and Swelling Ratio.

3.4.2. Effect of *DS* value to the swelling ratio

DS is an important factor affecting the swelling properties of the hydrogel, because the polymer chains become more soluble in water when the polymer chain is replaced with a more ionized carboxyl group. Dependence of swelling the hydrogel swelling on the *DS* value of the polymer reflects better solubility of the polymer chains that have been substituted [24].

Increase number of carboxylic group will make the number of hydrogen bonds increase and bond-H also formed increasingly and difficult to solve [25]. These conditions allow for an increase in water retention in the hydrogel network. Carboxylate groups have two main effects on the absorption of water, when fully protonated (COOH) they form multiple hydrogen bonds that can reduce the absorption of water from the hydrogel. However, when ionized (COO⁻), they produce electrostatic repulsion to open gel network and increase absorption ability of the gel [25].

In Fig. 5, known that the ability of the hydrogel to absorb water increased with increasing *DS* value at *CMC*. This is because the substituted *CMC* has more –COO⁻ in its chain. Substituted polymer chains also increases the repulsion of intra-and inter-chain electrostatic, the higher value of *DS* will provide hydrogels with higher swelling capability [24]. The carboxyl group was acted in opening the electrostatic repulsion hydrogel network which allows water to enter [25]. With the limited number of this group, it will cause a decreased ability to absorb water in the hydrogel.

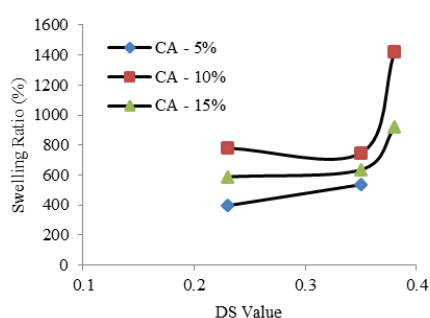


Fig. 5. Relation between *DS* Value and Swelling Ratio.

CMC which has a higher *DS* value has fewer OH groups. OH group was instrumental in the formation of the hydrogel network. where the OH group binds to the cyclic anhydride groups of citric acid. Thus the gel fraction formed also the less. This condition is shown in Fig. 6.

In Fig. 6 shows that the higher the value of *DS* the lower gel fraction formed. With increasingly the value of *DS* will make the swelling ratio increasing as shown by Fig. 5.

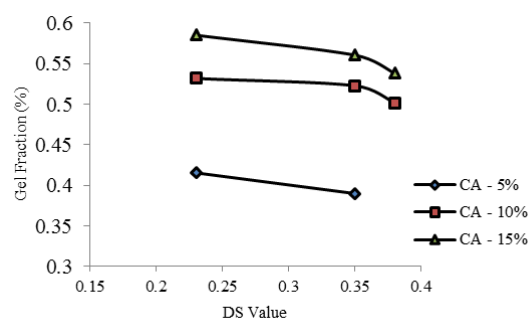


Fig. 6. Relation Between *DS* Value and Gel Fraction.

3.4.3. Morphology of hydrogel

Through the swelling ratio testing, shows that each of hydrogels have the ability to absorb water. The ability to absorb water is associated with a formed pattern of hydrogel network which results in pore formation. The pattern of the hydrogel network is also determined by the amount of crosslinking agent used. Therefore, from some hydrogels that have been made, microscopic observation using *SEM* was conducted in order to see the formed patterns of hydrogel network.

Figure 7 shows the surface of hydrogel respectively with the same basic ingredients but with different concentrations of citric acid. At a concentration of 5% citric acid, Fig. 7(a) it can be seen that the resulting hydrogel surface much smoother when compared with hydrogel with citric acid concentration of 10% and 15%. This indicates that the connective crosslinking that forms the pore is little. Connectivity of the pores play an important role in the process of rapid water uptake of hydrogel [21]. Interconnected pore structure facilitates the diffusion of water molecules to enter and exit into and through the pore. The pore structure is directly related to the ester bond that is formed in the hydrogel [21].

In Fig. 7(c), the hydrogel with 15% citric acid concentration, showed a more dense structure. This condition made possible by the much more presence of the ester bond. This event is also reinforced by the gel fraction values higher than the concentration of citric acid hydrogel with 5 and 10. In addition, the sample HG28-15% have small pores which dominates the hydrogel surface that causes the amount of water that diffuse into the hydrogel network is not much.

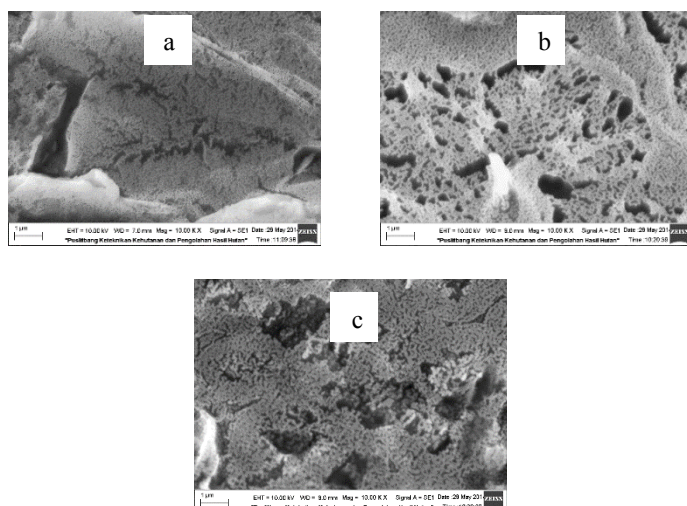


Fig. 7. Surface of the Hydrogel with 5000 Times of Magnification
(a) Sample HG 28-5% (b) Sample HG28-10% (c) Sample HG28-15%.

Seen that the hydrogel surface that has many pores present in the sample HG28-10%, Fig. 7(b). The number of small pores and large seen as much on the surface of the hydrogel sample HG28-10%. This small pores is expected not only can absorb water, but also can hold water so it is not easily separated. Besides,

large pores also has the ability to absorb more water [26] and make the transfer of water molecules easier between the hydrogel network and the liquid phase in the outer [18]. This is supported by the results of tests on the swelling ratio of the hydrogel, respectively. Samples HG28-10 is the highest ability to absorb water.

4. Conclusion

The conclusions of this research are as follow:

- Hydrogels is successfully obtained from water hyacinth cellulose derivatives using *CMC* and a variation of the concentration of citric acid and the temperature of the esterification process at 80 °C for 13 hours. It is known through *FT-IR* spectra of sample HG28-15% found the group comes from the bond carboxyl (COO-) which indicate there has been a process of cross-linking between polymer chains bind *CMC* and citric acid and OH groups that play a role in the absorption of water.
- Gel fraction increases with increasing the concentration of citric acid. However, the hydrogel's ability to absorb water is reduced.
- Higher value of the *DS*, will lead to the increasing swelling ratio of the hydrogel. The optimum conditions to obtain hydrogels of water hyacinth cellulose derivatives, is when the ratio of the reaction medium isobutyl alcohol-isopropyl is 2:8, and the concentration of citric acid is 10%.

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