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Synthesis and Characterization of Carboxy Methyl Cellulose-Based Hydrogel Cross-linked with Citric Acid

Alia Badra Pitaloka*, Alda Sadilillah Rukmana, Tia Yufika Nur'afiani

Jurusan Teknik Kimia, Fakultas Teknik, Universitas Sultan Ageng Tirtayasa
Jalan Jendral Sudirman Km.3, Cilegon-Banten, Indonesia

*Corresponding Author Email: *aliabp@untirta.ac.id*

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ABSTRACT

Hydrogel is a three-dimensional hydrophilic polymer network which is capable of absorbing large amounts of water, urine, blood, and other biological fluids. The applications of hydrogel are present in various fields such as pharmaceuticals, agriculture, food, and medical fields. Hydrogel is used as a wound dressing, in a drug release system, in diapers, in and menstrual products. The purpose of this research is to produce carboxymethyl cellulose (NaCMC) hydrogels using citric acid as the crosslinking agent, and to determine the optimum conditions to produce hydrogels with a high absorption capacity of liquids using various concentrations of citric acid. The first step of this research is to mix NaCMC and citric acid by stirring it with an agitator at room temperature until the mixture becomes homogeneous. Then, the mixture is casted in a petri dish and dried for 24 hours at 30°C. Then, the crosslinking reaction was carried out at 80°C for a certain time. After that, the gels are put out of the petri dish and tested to determine their values of water absorption capacity (swelling) and gel fractions. Lastly, the hydrogels are characterized using FTIR and SEM. The results showed that the NaCMC hydrogel with anhydrous citric acid with 10%-wt is the best with 3779.16% swelling ratio and gel fraction of 60%.

Keywords: *hydrogel, NaCMC, citric acid, swelling ratio, gel fraction*

1. INTRODUCTION

Hydrogel is a three-dimensional hydrophilic polymer network which is capable of absorbing large amounts of water, urine, blood, and other biological fluids. Hydrogel has an absorption capacity up to fifteen times of its dry weight, is able to expand, insoluble in water, while is able to maintain its original shape (Kiatkamjornwong, 2007), which make it an interesting water-storing material. When hydrogel absorbs water to its equilibrium state, its shape becomes similar to water as almost all of its part is composed of water. Those unique properties make hydrogel useful for many applications and demanded in high quantities yearly worldwide. Hydrogels are also used as a water-storage medium in agriculture, to absorb dye and metal ions, and to absorb bacteria and fungi in wound dressing (Erizal, 2012). In the last few years, research about hydrogel has been focused on cellulose derivatives base materials (Zohuriaan & Kabiri, 2008).

Hydrogel is widely used for diapers and feminine hygiene products and is starting to be developed using environmentally friendly materials. Absorbent polymer is a polymer which is able to absorb water in a relatively high quantity per its mass. A hydrogel which has an absorption capacity of 1,000-100,000% of its weight is called Superabsorbent polymer (SAP). Research about hydrogel materials is increasing nowadays, especially those sourced from economically valuable carbohydrate polymers. Hydrogels from carbohydrate polymers are biodegradable, non-toxic, biocompatible, renewable, and the materials are cheaper to obtain (Anah & Lik, 2015). Polysaccharide polymers such as sodium carboxymethyl cellulose (NaCMC) could be used as a material to synthesize hydrogel. NaCMC which is non-toxic, renewable, and biodegradable is a derivative of cellulose which is produced by carboxymethylation of cellulose with monochloroacetic acid (Zheng *et al*., 2015). Cellulose is an organic, linear-chain polymer which is widely available in nature.

Hydrogels are synthesized by either chemical, radiation, or physical crosslinking processes (Varaprasad *et al.*, 2017). Cross-linking in hydrogel synthesis is critical to produce a hydrogel with high fluid absorption capacity. Most chemicals used for the linking agent are toxic, while chemicals unreactive in the synthesis will be eliminated after the crosslinking process. The use of toxic chemicals in hydrogel production has to be avoided. Therefore, research about synthesis of hydrogel using a non-toxic linking agent needs to be done. In this research, NaMC will be crosslinked using citric acid as a linking agent. Citric acid is used due to its carboxylate functional group which can form a link with cellulose chain. Other than that, citric acid is a crosslinking agent with a good performance, which can overcome the toxicity and cost problems in producing hydrogels. Citric acid is also widely available in nature and can be produced on a commercial scale.

In a previous research, Demitri *et al.* (2008) have synthesized NaCMC-based hydrogel with citric acid as the crosslinking agent. In their research, a NaCMC of 2%-wt was used, and the highest swelling ratio occurs in hydrogel with 10% citric acid concentration, pre-drying for 24 hours in the temperature of 30°C, and crosslinking reaction temperature of 80°C (Demitri *et al.*, 2008). This research is aimed to study the effect of crosslinking agents with different concentrations, the types of crosslinking agents, and the reaction time on absorption capacity (swelling) of hydrogel.

2. METHODS

2.1 Materials

Materials used in this research are NaCMC (Anqiu Eagle), monohydrate citric acid (Merck), anhydrous citric acid (Weifang Ensign Industry Co. ltd), and distilled water.

2.2 Synthesis of Hydrogel

Hydrogel was synthesized by mixing NaCMC 2%-w in 100 ml distilled water, then added with citric acid in different concentration (5%, 10% and 15% w/w NaCMC). The mixture was homogenized with an agitator at room temperature. The final solution was poured into a petri dish for a *pre-drying* treatment in 30°C for 24 hours. Afterwards, the crosslinking kept at 80°C with time variations of 4, 5, 6, and 7 hours.

2.3 Characterization of Hydrogel

Hydrogel was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM), swelling ratio and gel fraction test. FTIR data was obtained from Cary 630 FTIR Agilent Technologies with the absorbance at the wavenumbers of 4000-650 cm^{-1}. SEM analysis was done to observe hydrogel morphology which affects hydrogel's capacity to absorb liquid.

The swelling ratio was tested by weighing the hydrogels before and after immersed in distilled water for 24 hours at room temperature using analytical scale. The swelling ratio was determined using the following equation:

$$Swelling\ Ratio(\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

W_s is the hydrogel's weight after absorbing liquid and W_d is hydrogel's dry weight (Slaughter *et al.*, 2009).

The determination of the gel fraction of a hydrogel was measured by inserting a hydrogel inside a tea bag then weighing it on a scale (W_a). The hydrogel then immersed in distilled water for 24 hour, and dried in the oven at 60°C for 24 hours until its weight became constant (W_b). Gel fraction was determined using the following equation (Ediningsih, 2018):

$$Gel\ Fraction(\%) = \frac{W_b}{W_a} \times 100 \qquad (2)$$

3. RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared (FITR)

An ester group contains one C=O bond and two C-O bonds. The peak of carbonyl stretching (C=O) is strong and commonly occurs at 1800 -1600 cm^{-1}. The C-O peak stretching commonly occurs at 1300 – 1000 cm^{-1} (Smith, 2018). The analyzed samples are NaCMC-anhydrous citric acid (NaCMC-CAA) 10% hydrogel and NaCMC-monohydrate citric acid (NaCMC-CAM) 15% hydrogel.

The FTIR spectra of NaCMC-CAA 10% is shown in Figure 1. The peak at 1218.84 cm^{-1} corresponds to the presence of C-O group. At 1690,35 cm^{-1}, there is another peak which indicates the presence of carbonyl group (C=O). The presence of carbonyl group signifies that crosslinking had occurred.

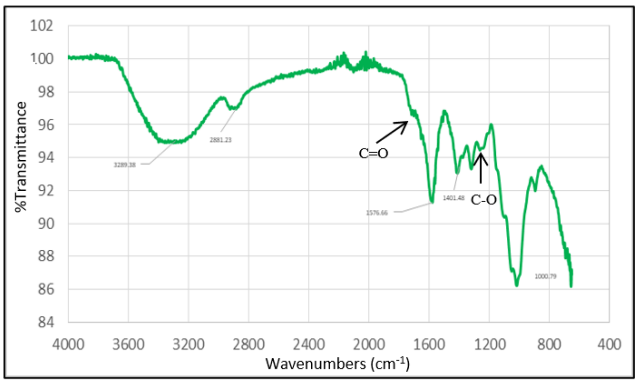

Fig. 1. FTIR Spectrum of NaCMC-Anhydrous Citric Acid 10% Hydrogel

Figure 2. shows a peak at 1207,66 cm^{-1} which indicates presence of C-O group and at the peak of 1694,08 cm^{-1} which shows the presence of C=O group that indicates crosslinking is present in hydrogel. Figure 3. shows that new peaks appear at 1690.35 cm^{-1} and 1694.08 cm^{-1} on NaCMC-citric acid hydrogel samples compared with NaCMC. It shows that the hydroxyl group

(-OH) from pure NaCMC has been replaced with carbonyl group, which indicates that crosslinking has occurred (Demitri *et al.*, 2008). It could be concluded that a crosslinking has occured between NaCMC polymer chains with cyclic anhydride of citric acid.

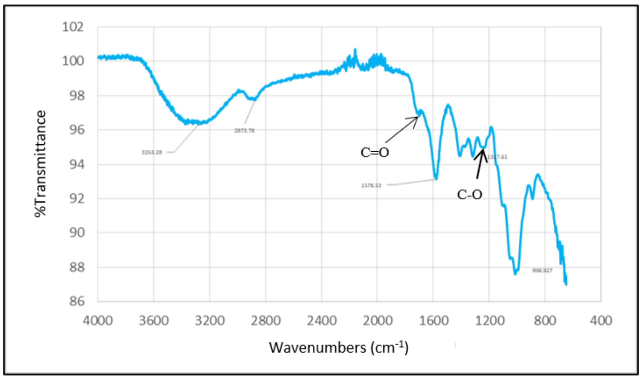

Fig. 2. FITR Spectrum of NaCMC-Monohydrate Citric Acid 15% Hydrogel

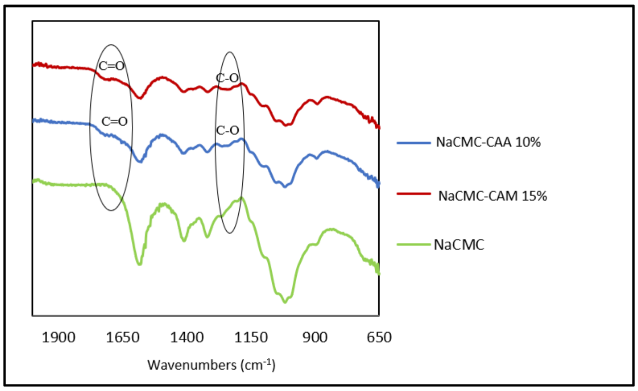

Fig. 3. FTIR Spectrum of NaCMC and NaCMC-Citric Acid Hydrogel

3.2 Determination of The Optimum Cross-Linking Reaction Time

It could be inferred from Figure 4. that the value of swelling ratio of citric acid cross-linked NaCMC hydrogel is decreasing as the crosslinking reaction time increases. The highest swelling ratio value is achieved in the crosslinking reaction time of 4 hours, which is 3323.53%. The decrease of swelling ratio may occur due to the hydrophilicity decreases throughout the amount of hydrophilic group during the crosslinking process (Zohuriaan & Kabiri, 2008). These hydrophilic groups make hydrogels able to absorb water; when the groups decrease, so does a hydrogel's capacity to absorb water (Tanaka, 2011). Longer crosslinking reaction time decreases the electrostatic repulsion which reduces NaCMC-citric acid hydrogel swelling ability. Prolonging the reaction time will increase the amount of ester bond between citric acid and NaCMC, which further lowers the swelling ability (Rimdusit *et al.*, 2012).

3.3 Effect of Concentration and Type of Cross-Linking Agents on Swelling Ratio

The addition of citric acid as a crosslinking agent will increase the swelling ratio, yet at one point, the swelling ratio will eventually decrease. The elevation concentration of crosslinking agents will increase the hydrogel density, causing it to be rigid and reduce its absorption capacity along with its swelling ratio.

In Figure 5., the highest swelling ratio occurs in the 10% citric acid, both anhydrous and monohydrate. The research by Demitri *et al.* in 2008 also concludes that hydrogel crosslinked with citric acid shows the highest swelling at 10% concentration (Demitri *et al.*, 2008). In the use of anhydrous citric acid of 5%, 10% and 15% concentration; the swelling ratio values are 666.67%; 3779.167%, 3313.75%, respectively. Meanwhile for monohydrate citric acid concentration of 5%, 10%, and 15%; the swelling ratio values are 0%, 13037.5%, and 1206.67% respectively.

In the lowest crosslinking agent concentration of 5%, only a few hydrophilic groups were found. The resulting hydrogel will be dissolved when immersed in water; hence its absorption capacity could not be measured. This happens because of an inadequate amount of crosslinking agents that the agents cannot be sufficiently linked with NaCMC chains. The dissolved hydrogel indicates the lack or absence of gel fraction. According to research by Saputra et al. in 2015, the increase in crosslinking agent concentration will lower the absorption capacity of the resulting hydrogel. Excess crosslinking agents will cause the resulting hydrogel's structure to be more rigid. The polymer network will only function as a barrier against water diffusion; thus, only a few amounts of water could get into the network (Saputra *et al.*, 2015). These happened in the addition of a crosslinking agent with 15% concentration.

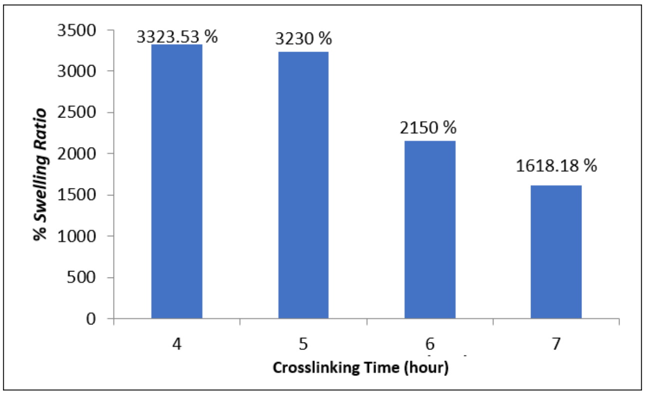

Fig. 4. Effect of Crosslinking Reaction Time on Swelling Ratio of NaCMC-Anhydrous Citric Acid 10% Hydrogel

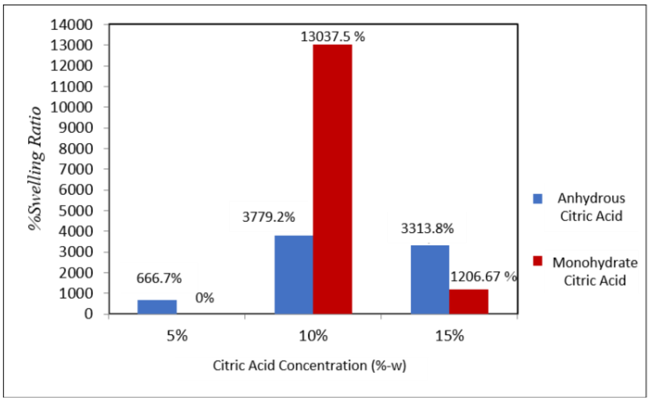

Fig. 5. Effect of Citric Acid Concentration Towards Swelling Ratio

In anhydrous and monohydrate citric acid, the highest swelling ratio values are 3779.71% and 13037.5% respectively. The resulting hydrogel mixture using monohydrate citric acid as an agent is less viscous than the one that used anhydrous citric acid. If we were to compare NaCMC-CAA and NaCMC-CAM hydrogels, NaCMC-CAM hydrogels have the highest swelling ratio. However, when NaCMC-CAM hydrogel swells, said hydrogel is difficult to separate from the water fraction because of breakage or is too liquid to handle due to the low amount of formed gel fraction.

3.4 Effect of Concentration and Type of Cross-Linking Agents Towards Gel Fraction

Gel fraction increases alongside citric acid concentration. High amount of crosslinking agents in a system will cause more rigidity of the hydrogel structure and lower its capability to absorb water (Hashem *et al.*, 2013). Therefore, excessive addition of crosslinking agents is disadvantageous in hydrogel synthesis (Bukhari *et al.*, 2015).

Based on Figure 6., variations of monohydrate citric acid of 5% and 10% do not have a gel fraction as it is soluble in water and obtained gel fraction for monohydrate citric acid of 15% is 62.22%. Meanwhile, for anhydrous citric acid of 5%, 10%, and 15% are 3.33%, 60%, and 45 %, respectively. Higher citric acid concentration will ensure a higher amount of gel fraction as gel formation is faster, thus the number of linked polymer chains will increase at the time of gel formation (Saputra *et al.*, 2015).

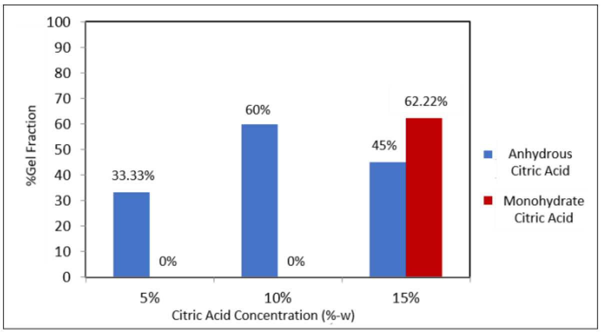

Fig. 6. Effect of Citric Acid Concentration on Gel Fraction

At monohydrate citric acid concentrations of 5% and 10%, the resulting hydrogels are soluble in water because the gel fraction did not form, which indicates that there was no crosslinking occurred in said polymer. Meanwhile at anhydrous citric acid concentration of 15%, there was a decrease in gel fraction value due to the high oxygen content in the NaCMC-anhydrous citric acid mixture. The oxygen would form bubbles which lowered the gel fraction of the hydrogel (Aziz *et al.*, 2005). Low value in gel fraction indicates that all the double bonds in the crosslinking agent structure (citric acid) did not completely react and later formed a structure with a lower amount of crosslinking (Saputra *et al.*, 2015), which occurred in anhydrous citric acid concentration of 5%. This cross-linked sample, even if not dissolved during the gel fraction test, showed lower gel integrity. This happened because the polymer has been absorbing water exceeding its hydrogel structure's capacity to hold (Devine & Higginbotham, 2005). The comparison of the swelling ratio and gel fraction could be seen in Table 1.

Tabel 1. The Comparison Between Swelling Ratio and Gel Fraction Values.

Variable	NaCMC-Anhydrous Citric Acid			NaCMC-Monohydrate Citric Acid		
	5%	10%	15%	5%	10%	15%
Swelling Ratio	666.7%	3779.2%	3313.8%	0%	13037.5%	1206.7%
Gel Fraction	33.33%	60%	45%	0%	0%	62.22%

Table 1 shows that the use of anhydrous citric acid 10%-w is better for carboxymethyl cellulose-based synthesis compared with monohydrate citric acid. For instance, NaCMC-anhydrous citric acid 10% hydrogel has swelling ratio and gel fraction values of 3779.16% and 60%, respectively. These high values indicate the abundance of formed crosslinks, making the produced hydrogel insoluble in water and maintaining its shape when absorbing water.

3.5 Morphology of Hydrogel

Each produced hydrogel has a known water absorption capacity which is determined using the swelling ratio test. A hydrogel's capability to absorb water is significantly tied to the pattern of networks that form pores on the surface of said hydrogel. Therefore, analysis using a scanning electron microscope (SEM) is needed to determine the network pattern or pores formed on a hydrogel surface. Analysis using SEM is also capable of giving information on the heterogeneity or homogeneity of a hydrogel surface.

Figure 7 shows the morphology of NaCMC- anhydrous citric acid hydrogel and without any addition of citric acid. The produced hydrogels have a smooth surface. In 5000x magnification, no porous structure could be clearly observed. Pores in SEM images are shown as an empty black space. The pores act as a water permeation region to ease water diffusion (Tang *et al.*, 2013). At NaCMC-CAA 5% hydrogel, the surface has fewer but larger, unevenly distributed pores. Larger pores on hydrogel allow more water to be absorbed. However, with anhydrous citric acid concentration of 5%, only few crosslinking processes occurred that the hydrogel will be dissolved once immersed in water as explained before. Figure 7.b shows hydrogel with citric acid of 10% has more amount of pores that are evenly spread. The high amount of pores in a hydrogel signifies that a crosslinking process has taken place, which is indicated by the presence of ester bond between NaCMC and citric acid. Figure 7.c shows a less-even distribution of pores in NaCMC-CAA 15% hydrogel. A heterogeneous surface in a hydrogel causes it to have differing absorption capacities. Corresponding with the previous explanation, compared to NaCMC-CAA 10% hydrogel, the NaCMC-CAA 15% hydrogel has lower swelling ratio and gel fraction values. The resulting hydrogel has smaller pores because the use of a crosslinking agent increases the number of crosslinked polymers (Indri *et al.*, 2019). Other than indicating higher water absorption capacity, smaller pores facilitate better water retention (Saputra *et al.*, 2015). The sample without addition of citric acid in Figure 7.d has few pores and a heterogeneous surface. This heterogeneous surface is caused by the more viscous solution (Rahman, 2019), in which addition of crosslinking agent will reduce its viscosity (Maitra & Vivek, 2014).

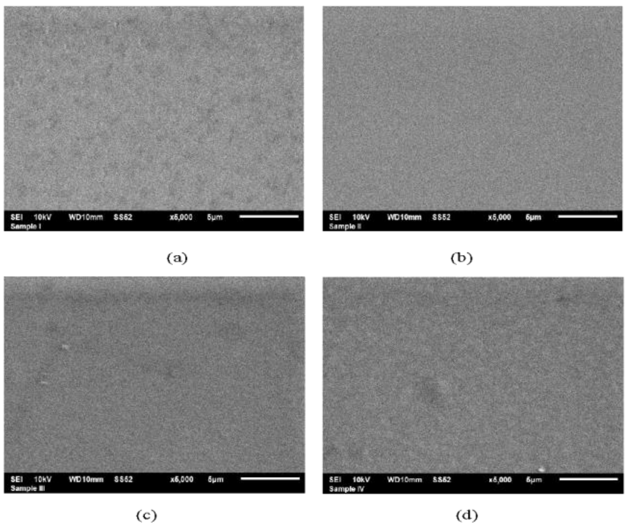

Fig. 7. Morphology of NaCMC hydrogels at 5000x magnification (a) with anhydrous citric acid 5%, (b) 10%, (c) 15%, (d) without citric acid.

4. CONCLUSION

Carboxymethyl cellulose (NaCMC) hydrogel crosslinked with citric acid has satisfactory absorption capacity and could be categorized as superabsorbent polymer (SAP). Hydrogel which is linked with anhydrous citric acid (NaCMC-CAA) has better *swelling ratio* and gel fraction values compared to one linked with monohydrate citric acid (NaCMC-CAM). The optimum condition for hydrogel NaCMC-citric acid is with anhydrous citric acid concentration of 10% and crosslinking reaction time of 4 hours, which resulted in swelling ratio and gel fraction values of 3779.16% and 60% respectively. The gel fraction value will increase as citric acid concentration increases, yet the swelling ratio will decrease.

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