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Synthesis of Sodium Carboxymethyl Cellulose-Based Hydrogel from Durian (*Durio zibethinus*) Rind Using Aluminium Sulphate as Crosslinking Agent

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ABSTRACT

Chemical cross-linked hydrogel possesses a more stable polymeric network, but nowadays, chemical crosslinking agents that are frequently used have been reported to have a toxic effect on humans. This present study was aimed at synthesizing a user-friendly hydrogel from a natural polymer, durian (*Durio zibethinus*) rind using aluminium sulphate as a crosslinking agent. Crude cellulose was isolated from durian rind and used to synthesize sodium carboxymethyl cellulose (NaCMC), which was subjected to infrared spectrophotometric analysis. This product was used to produce hydrogel using polyvinyl alcohol (PVA)-CMC-glycerol with aluminium sulphate as a crosslinking agent. The NaCMC-based hydrogel films were characterized by determining the swelling ratio, gel fraction, and Fourier Transform Infrared (FTIR) spectroscopic analysis. The percentage yield of cellulose from durian rind was 20 %, while the synthesized NaCMC was 145 %. The synthesized hydrogel was thin transparent film and flexible. The characteristics of the swelling ratio, gel fraction, and FTIR indicated that a crosslink was formed. The lower the concentration of glycerol, the higher the swelling degree and gel fraction of hydrogel. The findings from this research demonstrated that hydrogel film could be synthesized from durian rind NaCMC using aluminium sulphate as a crosslinking agent.

Keywords: Aluminium sulphate, Durian rind, Hydrogel, Natural polymer.

Introduction

Durian (*Durio zibethinus*) is regarded as the king of fruit, and is one of the plants that is first harvested in Indonesia. In 2018, about 1.142 ton of durian was produced in Borneo and Sumatera Islands. Only one-third of durian was consumed, while the seeds and rinds were considered as wastes.[1] Cellulose is the principal constituent of plant materials,[2] including durian, and several researchers have isolated cellulose from durian rinds. Cellulose is a natural polymer that is insoluble in water because of its hydrogen bonds.[3] Conversion of raw cellulose into sodium carboxymethyl cellulose is formed by the carboxymethylation process which increases its solubility in water, thereby leading to the formation of a gel.[4] Hydrogels are the three-dimensional network of a water-soluble polymer chain that crosslinks with a chemical or physical crosslinking agent.[5] The water-swollen capability material can absorb enormous water and maintaining its physical dimensional structure.[6] The use of hydrogel has increased significantly nowadays in every field, such as biomedical applications ranging from drug delivery to tissue engineering, wound dressing, bioimaging, wearable sensors,[7] agricultural,[8] and hygienic products.[9] There are two methods of achieving the three-dimensional network structure of a hydrogel: physical and chemical crosslinks. A chemical crosslink has a permanent function, while a physical crosslink is temporary.[10] Many chemical crosslinking agents that are frequently used in the development of hydrogel are poly (methyl methacrylate) (PMMA), poly (butyl acrylate) (PBA),[11] glutaraldehyde,[12] and epichlorohydrins.[8]

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Also the chemical cross-linker can give a more physically stable hydrogel, but the major disadvantage of a chemical crosslinking agent is its toxic effect on humans. Therefore, this study was conducted to synthesize non-toxic cellulose-based hydrogels from durian (*Durio zibethinus*) rind waste using aluminium sulphate as a chemical crosslinking agent.

Materials and Methods

Chemicals and reagents

All solvents and reagents used for this study were of analytical grade and products of Merck. They included sodium chloride, ethanol, methanol, glacial acetic acid, isopropyl alcohol, methanol, aluminium sulphate, polyvinyl alcohol (PVA), glycerol, sodium monochloro acetate, and distilled water.

Sample collection and isolation of crude cellulose

Durian rind wastes were collected from a durian fruit seller in Medan city, Indonesia and rinsed with water to remove dirt and unused parts. They were then cut into small pieces and dried. The dried samples were ground into powder. Cellulose was prepared by alkaline delignification and bleaching process. The alkaline delignification was performed using 200 g sample which was mixed with 2 M sodium hydroxide solution by stirring at 80°C for 4 hours. At the end of alkaline delignification, the black slurry obtained was filtered and the residue was washed using distilled water until the pH became 7. The neutral residue was dried in an oven at 50°C to constant weight for 24 hours. The durian rind cellulose obtained was bleached with 30% H_2O_2 at 50 °C for 1 hour. Furthermore, the bleached cellulose was rewashed using water until pH became 7, and then dried in an oven at 50°C to constant weight.[13] The cellulose was ground into powder using a blender.

Synthesis of carboxymethyl cellulose

Five grams of cellulose were immersed in isopropanol: ethanol (1:1) solvent and stirred for 5 minutes. After that, 10% NaOH was added and stirred continually at room temperature for one hour. The

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etherification process was followed by the addition of 4 g of mono chloroacetic acid into the system and continually stirred for 3 hours at 55 °C. Then, the slurry was filtered, and the solid was suspended in methanol and left overnight after which it was neutralized with acetic acid. The solid obtained as carboxymethyl cellulose (CMC) was dried at 50°C until constant weight. The yield was calculated based on the amount of cellulose used as in the equation below.

$$\text{Yield of CMC (\%)} = \frac{weight\ of\ cmc\ (g)}{weight\ of\ cellulose\ (g)}\ x\ 100 \qquad ^{14}$$

Infrared spectrophotometric analysis of sodium carboxymethyl cellulose
Sodium carboxymethyl cellulose (NaCMC) functional group was measured using the KBR method. The sample was mixed with KBR and ground until it became homogenous. Then, the infrared spectra were recorded using Shimadzu FTIR between 400-4000 cm^{-1}.[15]

Preparation of carboxymethyl cellulose-based hydrogel
The NaCMC-based hydrogel films were prepared using aluminium sulphate as a crosslinking agent. CMC (2%) aqueous solution containing NaCMC, PVA, and aluminium sulphate was prepared using a magnetic stirrer at 70°C. The solutions were poured into Petri dishes (9 cm diameter) and dried in a hot air oven at 50°C for 24 hours. Table 1 shows the formula of the hydrogel.

Determination of swelling ratio of hydrogel films
The swelling ratio of the hydrogel films was determined according to the method of Ghorpade *et al*. (2016) previously reported[13] with certain modifications. Hydrogel films (0.2 g) were immersed in distilled water at 25°C. The swollen samples were removed from the medium, and the excess medium was blotted using tissue paper, and the swollen hydrogel was weighed. Then, the swelling ratio was measured using the following formula:

$$\text{Swelling ratio (g/g)} = \frac{Ws - Wo}{Wo}\ x\ 100\% \qquad ^{13}$$

Where, Ws is the weight of the swollen films, and Wo is the weight of the dry films. The hydrogel films were again immersed in the medium, and absorbency was determined for one hour. After 24 hours, the swelling ratio was analyzed in the same way.

Estimation of gel fraction of hydrogel films
At room temperature, the hydrogel obtained was placed in distilled water for 24 hours for the removal of the soluble parts. The insoluble gel obtained was dried in the oven at 50°C for 24 hours until it reached a constant dry weight. The gel fraction was determined from the weight ratio between the insoluble dry gel weight and the polymer's initial weight.

$$\text{Gel Fraction} = \frac{Wc}{Wo}\ x\ 100\% \qquad ^{16}$$

Where, Wc is the weight of the insoluble dry films, and Wo is the weight of the dry films.

Fourier Transform Infrared (FTIR) spectroscopic analysis of hydrogel films
Using the FTIR spectrophotometer (Shimadzu, Japan), the infrared spectra of the hydrogel films were obtained. The samples to be analyzed were transferred to the compartment and the spectra were obtained for the range of 400-4000 cm-^{1}.

Results and Discussion

Percentage yield of cellulose and sodium carboxymethyl cellulose
Alkaline delignification treatment of durian rind using 2 M solutions of NaOH was performed to extract cellulose from durian rind. The weight of the dried samples was 46 g, and the percentage yield of cellulose from durian rind was 20%. Durian rind consists of hemicellulose, cellulose, and lignin. Hemicellulose and lignin were removed with the alkaline delignification step. A total weight of 20 g of cellulose was immersed in ethanol-isopropanol with 10% NaOH solution and stirred at room temperature for one hour. This was followed by the addition of 4 g sodium mono chloroacetate into the system and stirred continually for 3 hours at 55°C. The yield of NaCMC from durian rind cellulose was 145%. According to Rachtanapun (2012),[4] the process of NaCMC synthesis yielded two substances.[4] The reaction between cellulose hydroxyl and sodium monochloro acetate formed NaCMC as the main product and conversion of sodium monochloro acetate to sodium glycolate as a by-product.[4]

Spectroscopic analysis of sodium carboxymethyl cellulose
The results obtained from the spectroscopic analysis of NaCMC produced from durian rind and commercial celluloses are presented in Figures 1 and 2. As shown in Fig. 1, a strong absorption peak at a wavenumber of 1600.92 cm^{-1} indicated carboxyl groups, while the peak at a wavenumber of 1415. 75 cm^{-1} indicated methyl groups. It was revealed that cellulose had been substituted with a carboxyl group into NaCMC from the stretching vibrations of 3412.72 cm^{-1} which indicated the hydroxyl groups. The peak at a wavenumber of 2924.09 cm^{-1} showed C-H aliphatic configuration, while the peaks at wavenumbers of 1600-1640 cm^{-1} and 1400-1450 cm^{-1} indicated carboxyl groups as their salts.[17] The similarity of spectra between Figures 1 and 2 revealed that NaCMC could be synthesized from rind.

Formation of carboxymethyl cellulose cross-linked with aluminium sulphate hydrogel
NaCMC from durian cellulose was synthesized into hydrogel using aluminium sulphate as a crosslinking agent. Polyvinyl alcohol and glycerol were used as the basis for the hydrogel to improve its characteristics. The hydrogel film was formed due to the crosslinking function between Al^{3+} and carboxyl groups of CMC.[15] The hydrogel obtained from this research is a thin transparent film and flexible. Meanwhile, the higher concentration of glycerol used for the production of hydrogel is easier to break. Glycerol is a hygroscopic compound that has many hydroxyl groups in its structure. It can quickly form intermolecular hydrogen with the air. The absorption of water from the environment caused the structure of the formed films to turn into soft materials which are easy to break.

Characterization of synthesized hydrogel films
The characterization of synthesized hydrogel films includes swelling ratio, gel fraction, and FTIR spectra of hydrogel films. The results of swelling ratio and gel fraction are highlighted in Table 2, while the infrared spectrum of the synthesized hydrogel is presented in Figure 5. As shown in Figures 3 and 4, the higher the concentration of glycerol used, the lower the swelling ratio and gel fraction. This observation was due to the inability of all the hydroxyl groups of the glycerol to form a gel. The swelling ratio and gel fraction indicated the crosslink density of a hydrogel. The higher the glycerol concentration on CMC-based hydrogel, the lower the swelling degree and gel fraction of hydrogel films. As shown in the data, the hydrogel films immersed in an aqueous medium increased its swelling degree. According to Ghorpade (2017),[13] the hydrogel has its equilibrium point, thereby making the materials not able to absorb any more water.[13]

Table 1: Formula of synthesized sodium carboxymethyl cellulose-based hydrogel

Parameter	Batch Code					
	H0	**H1**	**H2**	**H3**	**H4**	**H5**
CMC: PVA	3:1	3:1	3:1	3:1	3:1	3:1
Glycerol (%)	-	5	10	15	20	25
Aluminium sulphate (%)	0.8	0.8	0.8	0.8	0.8	0.8

CMC: Carboxymethyl cellulose (sodium salt), 2%; PVA: Polyvinyl alcohol, 0.5%

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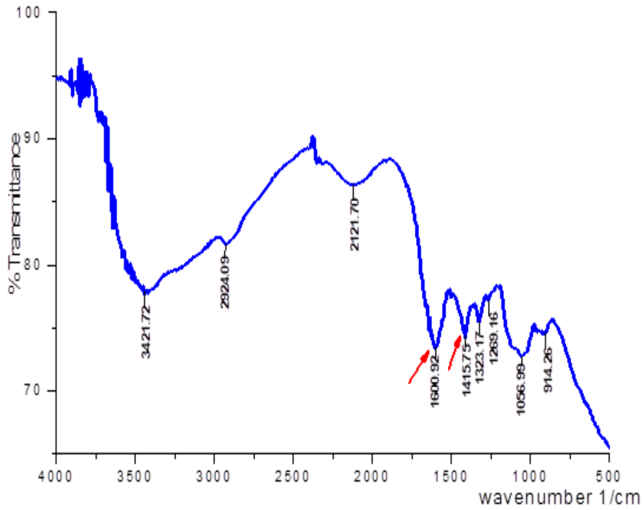

Figure 1: FTIR spectra of NaCMC produced from durian rind cellulose

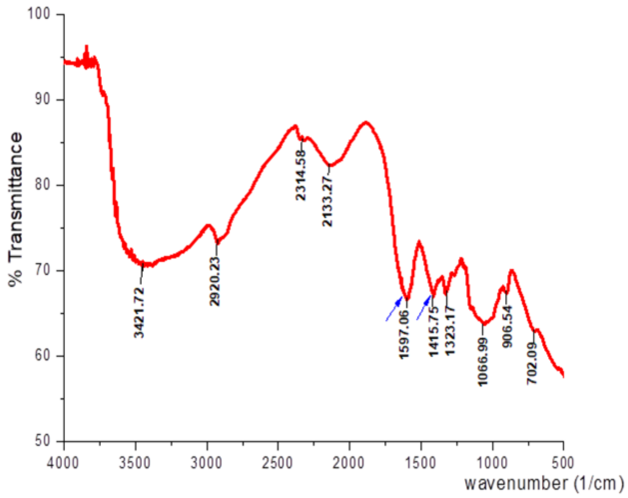

Figure 2: FTIR spectra of commercial NaCMC

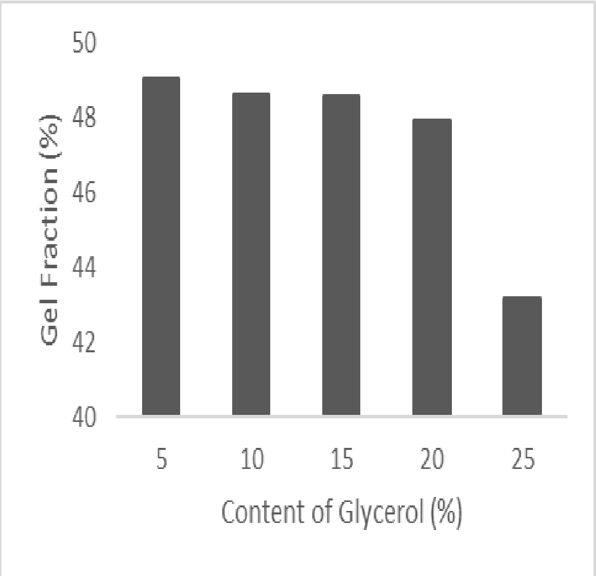

Figure 3: Gel fraction of hydrogel films

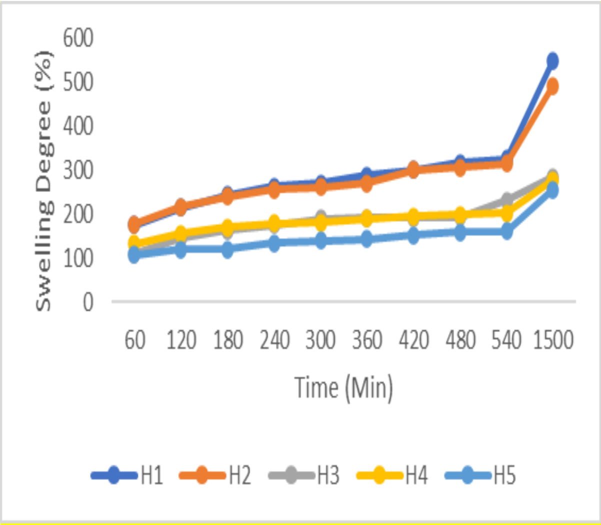

Figure 4: Swelling degree of hydrogel films

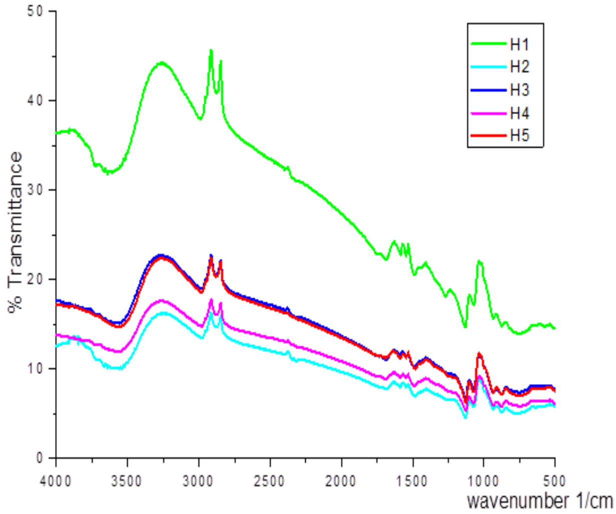

Figure 5: FTIR spectra of carboxymethyl cellulose-based hydrogel with variation in concentration of glycerol (H1-H5)

Table 2: Swelling ratio and gel fraction of hydrogel

Batch Code	Parameters	
	Swelling Degree (%)	Gel Fraction (%)
H1	551	49
H2	492	48
H3	285	48
H4	277	47
H5	257	43

FTIR spectroscopy was used to indicate the interactions among NaCMC, PVA, glycerol, and aluminium sulphate to form a film. The differences between NaCMC spectra and NaCMC-based hydrogel can be observed below 1200 cm^{-1}, which shows Al and the carboxyl group of NaCMC. The presence of Al^{3+} destroyed the intermolecular bond of NaCMC. This increased the strength of the carboxyl group of NaCMC.[15]

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Conclusion

The findings obtained from this study reveal that hydrogel films can be synthesized from durian rind NaCMC using aluminium sulphate as a crosslinking agent. The characterization of hydrogel films showed that the lower the glycerol concentration, the better the hydrogel films formed.

Conflict of Interest

The authors declare no conflicting interest.

Authors' Declaration

The authors hereby declare that the work presented in this article is original and that any liability for claims relating to the content of this article will be borne by them.

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