The Synthesis of Superabsorbent Polymer From Carboxymethyl Selulose, Aluminum Sulfate and Oxidized Bread Fruit Starch

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Abstract. Superabsorbent polymers (CMC-Al-BSM) were synthesized from aqueous solutions of sodium carboxymethyl cellulose (CMC), aluminum sulfateoctadecahydrate (Al) and oxidized bread fruit starch (BSM). BSM is obtained by oxidizing the starch (BS) with 2\% hydrogen peroxide solution. CMC-Al-BSM was prepared by mixing 100 mL of 2\% Na-CMC solution and 50 mL of 2\% BSM solution, stirring with a magnetic stirrer for 60 minutes at 80\°C and then adding 0.01 g of aluminum sulphate and stirring for 30 minutes. The mixture formed is poured onto Teflon and dried at 70 \°C until the film is formed and then the film formed is made as a powder. The same experiment was carried out with variations in the weight of aluminum sulfate 0.03 and 0.06 g. BS and BSM are characterized by measuring the carboxyl group content, recording the FTIR spectrum and morphological analysis with SEM. CMC-Al-BSM is characterized by measuring WAC by tea bag method, surface morphology with SEM and Tg with DSC. Based on the calculation, the carboxyl group content of BSM that obtained is 0.09 \% and SEM Photograph shows that the BSM particle size is smaller than the BS particle size. The optimum water absorption capacity of SAP is obtained at CMC-Al3-BSM which reaches 8330\% (in 1.0 g dry weight of CMC-Al3-BSM can absorb 83.3 g of water). SEM photograph also shows that the surface morphology of CMC-Al3-BSM is more homogeneous and smooth than other SAP compositions and from DSC analysis it can be concluded that CMC-Al3-BSM is a miscible mixture

1. Introduction

Polymer superabsorbent (SAP) is a material that has been widely studied in modern polymer technology because of its unique nature and ability to absorb and retain large amounts of water [1]. The ability of SAP to absorb and retain water causes SAP to be widely used in various fields of application such as health supplies, medical materials, [2], sewage treatment and agriculture [3,4]. SAP is a crosslinked macro molecule that is insoluble in water and it has hydrophilic groups such as carboxylates, hydroxyl and amines that are located along the polymer chain and serves to draw diffused water into the interior of the molecule so that the water molecule is dissolved through the formation of hydrogen bonds [5]. The absorption of water by SAP causes a decrease in entropy so that SAP can to swell [6]. Polyacrylate, a synthetic polymer, is the main base material used to make SAP. Polyacrylates are non-renewable materials that depend on the petrochemical industry.
Preparation of biopolymer-based SAP derived from agricultural products such as corn starch, cassava starch, sago starch and cellulose have been done [7,8]. Compared to synthesized SAP, SAP based on biopolymers have advantages because of their strong hydrophilicity, renewable, biodegradable and non-toxic [9]. In this study, CMC-Al-BSM based on carboxymethyl cellulose (CMC), modified breadfruit starch (BSM) and aluminum sulfate octahydrate (Al) as crosslinking agent will be synthesized. Characterization of CMC-Al-BSM is done by measuring water absorption capacity, evaluating surface morphology with SEM and determining Tg with DSC. Breadfruit is obtained from breadfruit plants (Artocarpus altilis), and it has a starch content of 19.09%, [10] and this plant is widely found in Indonesia, especially in the Province of North Sumatra.

2. Materials and Methods

2.1 Materials
Breadfruit starch was isolated from ripe breadfruit. Sodium carboxymethyl cellulose, hydrogen peroxide and aluminum sulfate octadecahydrate are purchased from Merck, Germany. The other chemicals were of analytical grade and used as received without further purification.

2.2 Isolation of starch from breadfruit
Breadfruit starch production is done by peeling the skin of the ripe breadfruit, cutting it into small pieces and soaking it in water to remove the sap. Then the breadfruit that has been cut is crushed using a blender and filtered using a cloth filter. The starch in the filtrate is allowed to settle and the water in toplayer is removed. Then the starch is dried at 45 °C and then ground and sieved using a 100 mesh filter.

2.3 Modifikasi Pati Sukun
A total 20 grams of starch were suspended in 80 mL aquadest at 35 °C and added 15 mL of 2% hydrogen peroxide solution and the pH was adjusted = 5. After 50 minutes, the starch was filtered in a Buchner funnel, washed with 150 mL of distilled water, filtered and dried at a temperature 42 °C [11]. The modified starch obtained was then characterized by recording the FT-IR spectrum, counting the number of carboxyl groups and calculating the particle size with SEM.

2.4 Preparation of Superabsorbent Polymers
As much as 2 grams of Na-CMC was dissolved with 100 mL aquadest, heated on a hot plate at a temperature of 70 °C for 60 minutes. Then 0.2 g BSM was gelatinized in 10 mL aquadest at 70 °C while stirring using a magnetic stirrer for 45 minutes. The gelatinized BSM was then added to the Na-CMC solution while stirring for 60 minutes. Then add 0.01 g Al and stir again for 30 minutes. The solution formed is poured onto the Teflon, dried at a temperature of 70°C until the film is formed and the film is ground into a powder. The CMC-Al-BSM formed was evaluated by calculating the water absorption and surface morphology. The same experiment was carried out at variations of 0.03 and 0.06 g Al.

2.5 Characterization

2.5.1 Determination of Carboxyl Content. The carboxyl content of BSM was determined according to the procedure [9, 10].

The carboxyl content was calculated with formula:

\[-\text{COOH} (%) = \left( \frac{V_1}{m_1} - \frac{V_0}{m_0} \right) \times C \times 0.045 \times 100\]
m₁ and m₀ are the masses of the BSM and BS, and C is the concentration of NaOH (mol/L), respectively. V₁ and V₀ are the volumes of the consumed standard NaOH solution (mL) for the titration of samples and blank [12]

2.5.2 Water Absorption Capacity (WAC). The WAC from CMC-Al-BSM is determined by putting the sample in a tea bag, then soaking it in water for 24 hours and then weighing it. WAC are calculated by using the equation.

\[
\text{WAC} \text{ (%) } = \frac{W₁ - W₂}{W₁}
\]

w₁: Weight of sample after soaking
w₂: Weight of dry sample

2.5.3 Scanning Electron Microscopy (SEM). The morphology of the surface of BS, BSM and CMC-Al-BSM film was discovered by using scanning electron microscope (Bruker) with magnification 2500 dan 10000 times under 10.00 kV of voltage.

3. Results and Discussion

3.1 FTIR spectra of BS and BSM
FT-IR spectra of BS and BSM can be seen at figure 1. The absorption peak at 3387 cm⁻¹ is stretching group (O-H) and the absorption peak at 2924 cm⁻¹ indicates the presence of C-H (-CH₂) bond. The absorption peak at wave number 1157 cm⁻¹ represents the absorption peak of C-O alcohol and the absorption peak at 1018 cm⁻¹ indicates the glycosidic C-O function group [13].

![Figure 1. Spectra FTIR of BS (a) and BSM (b)](image)

This spectrum shows that the spectrum in figure 1 is a spectrum of carbohydrate compounds (starch). When we compare the FTIR BS spectrum and the BSM FTIR spectrum, it appears that the two spectra are almost the same and there is no difference at the absorption peak. The only significant difference was the absorption intensity in the OH group, where the intensity at BSM was lower than BS. This indicates that the number of OH groups in BSM is less than the number of OH groups in BS. Based on the calculation of the carboxyl group content in BSM is 0.09%. This number is so small that no carboxylic group is detected in the spectrum.
3.2 SEM Photograph BS and BSM

Furthermore, when compared to the SEM photograph between BS BSM starches there were significant differences in particle size. BSM particle size becomes smaller when compared with BS particle size after oxidation process with 2% hydrogen peroxide. Based on FTIR spectra and SEM Photograph BS and BSM it can be assumed that BS oxidation by only slightly oxidizing OH groups in C6 atoms into carboxylic groups, but the most likely to occur is hydrolysis and termination of 1-4 glycoside bonds from starch.

3.3 Water Content Capacity of CMC-Al-BSM

WAC data of CMC-Al-BSM was shown in table 1.

| Sample     | Na-CMC 2 % (mL) | Al\(_2\)(SO\(_4\))_3\ 18 H\(_2\)O (g) | BS 2 % mL | BSM 2 % mL | WAC (%) |
|------------|-----------------|-------------------------------------|------------|-------------|---------|
| CMC-Al1-BSM| 100             | 0.01                                | 0          | 50          | 6430    |
| CMC-Al3-BSM| 100             | 0.03                                | 0          | 50          | 8330    |
| CMC-Al6-BSM| 100             | 0.06                                | 0          | 50          | 7760    |
| CMC-Al3-BS | 100             | 0.03                                | 50         | 0           | 2444    |

Determination of WAC is done by entering 0.1 g CMC-Al-BSM into a tea bag weighing 0.8 g and then soaking it in 100 mL DM water. Based on table 1 it can be seen that the optimum WAC value is found in CMC-Al3-BSM which is 8330%. If the weight of Al is lower than 0.03 g, the number of WAC decreases. This is due to the small number of Al\(^3\) + ions reacting with Na-CMC so that the amount of CMC-Al-BSM formed is also small, meaning that the number of cross-bonds formed is also small. If the weight of Al is greater than 0.03 g, there is also a decrease in WAC. The more the amount of Al, the more the amount of Al\(^3\) + ions that react to form cross bonds with CMC and BS. This increased degree of cross-linking results in a decreased degree of swelling and the number of free hydroxyl groups decreases, thereby reducing the affinity of water diffusing into the CMC-Al-BSM molecule [14].
Figure 3 is SEM photographs of CMC-Al1-BSM, CMC-Al3-BSM, and CMC-Al6-BSM. When compared to the three SEM photographs, it can be seen that CMC-Al3-BSM has a more homogeneous and smoother surface morphology. This shows that the mixture of CMC, Al and BSM is a miscible mixture. [15,16]

![Figure 3. SEM photographs of A (CMC-Al1-BSM), B (CMC-Al3-BSM), C (CMC-Al6-BSM)](image)

Curves show that the glass transition value (Tg) of CMC-Al3-BSM is at 99.85 °C, BS at 105.72 °C, and Na-CMC at 98.23 °C. The aim of investigation with DSC is to determine whether CMC-Al3-BSM is a miscible polymer mixture. The presence of one value of Tg value indicates that the polymer mixture is miscible. The curve shows that the Tg value of CMC-Al3-BSM is between the number of Tg BS and Na-CMC and this shows that the mixture of CMC, Al and BS is miscible or Al-CMC-BSM is a miscible mixture [15].

![Figure 4. DSC Curves of Na-CMC (1), BSM (2) and CMC-Al3-BSM](image)
4. Conclusion
A super absorbent polymer material from CMC, aluminum octahydrate and BSM called CMC-Al-BSM has been successfully synthesized. The modification of BS to BSM is very influential in increasing the CMC-Al-BSM power to water, from 24.4 g water / g CMC-Al-BSM to 83.3 g water / g CMC-Al-BSM. Super absorbent Al-CMC-BSM is a miscible mixture.

5. References
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