Synthesis and Characterization of Superabsorbent Polymer based on Carboxymethyl Cellulose, Breadfruit Starch and Aluminum Sulfate

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Abstract: Superabsorbent polymer is a polymeric material that able to absorb a large amount of water. The purpose of this study is to synthesize and measure water absorption capacity and study the crosslinking process of superabsorbent-aluminum-breadfruit starch (Al-CMC-BS). The preparation of Al-CMC-BS was done in two steps. The first step was reacting CMC with aluminum sulfate so that the aluminum-carboxymethyl cellulose (Al-CMC) film was produced and then mashed into powder. Al-CMC powder was dissolved in water and reacted with BS solution to obtain Al-CMC-BS. Furthermore, Al-CMC-BS produced was determined their water absorption capacity, morphology with SEM, functional group with FTIR and transition glass temperature with DSC. The results showed that the absorption capacity of water from Al-CMC-BS reached 2,444.44 %. SEM analysis shows the formation of a more homogeneous Al-CMC-BS mixture than before mixing. The FTIR spectrum shows the formation of crosslink between Al-CMC and BS. DSC analysis shows that there is one Tg value of Al-CMC-BS that is on 95.85˚C, which is in between Tg of BS on 118.72˚C and Tg of CMC on 94.23˚C. This shows that the mixture of Al, CMC and BS is miscible mixture

1 INTRODUCTION

Polymer superabsorbent (SAP) is the most interesting study in modern polymer technology because of its ability to absorb water up to 550 g of water per gram of dry SAP polymer (Klinpituksa and Kosaiyakanon, 2017). This ability to absorb high water causes SAP to be widely used in various fields of application such as concrete additives (Mechtcherine, 2016) health supplies, medical materials (Sadeghi and Soleimani, 2013), sewage treatment and agriculture(Salavati et al., 2018; Tao et al., 2018). Essentially SAP is a three-dimensional crosslinked network polymer that has hydrophilic characteristics and is not soluble in water. The hydrophilic nature is caused by the presence of ionic function groups such as carboxylic and hydroxyl groups found along the polymer chain so that it pushes to draw diffuse water into the network (Raju et al., 2003). The molecular structure of SAP is a three-dimensional cross link network that experience swelling and insoluble by solvating water molecules through the formation of hydrogen bonds. Water absorption also causes a decrease in SAP entropy, making it able to experience swelling daninsoluble (Abdel-raouf, 2019).

Polyacrylate, a synthetic polymer, is the main base material used in the industry to make SAP. Polyacrylate is modified into network molecules using organic crosslinking agents and initiators so that crosslinked SAP is formed. Polyacrylate is made from an acrylic acid polymerization reaction. Acrylic acid is a byproduct in the process of making ethylene and fuel oil. Therefore, polyacrylate is a non-renewable material that relies on the petrochemical industry. In addition, the absorption of water is still relatively lower compared to SAP based on natural materials (Chatterjee, 2002).

Lately, it was developed preparation of biopolymer-based SAPs derived from agricultural products such as corn starch, cassava starch, sago starch and cellulose and its derivatives (Chandra Sutradhar et al., 2015), (Weerawarna, 2009). Compared to petroleum-based polymers, biopolymers have advantages due to high hydrophilicity, renewable, biodegradable and non-toxic (Weerawarna, 2009), (Nnadi and Brave, 2011).

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In this study, Al-CMC-BS was synthesized from carboxymethyl cellulose (CMC), breadfruit starch (BS) isolated from breadfruit and aluminum sulfate octadecahydrate as crosslinking agents. Breadfruit is obtained from breadfruit plants where breadfruit has a starch content of 19.09 % (Masita, 2017). Breadfruit plants grow a lot in Indonesia, especially North Sumatra Province.

The purpose of this study was to synthesize and characterize superabsorbent polymer based on CMC and breadfruit starch. The resulting Al-CMC-BS was characterized by measuring water absorption capacity, FTIR spectrum, morphology with SEM, glass transition temperature (Tg) with DSC.

2 MATERIALS AND METHODS

2.1 Materials

Breadfruit starch is isolated from ripe breadfruit. Chemical used, which is sodium carboxymethyl cellulose and aluminum sulfate octadecahydrate are purchased from Merck & Co.

2.2 Methods

2.2.1 Isolation of Starch from Breadfruit

Ripe breadfruit is washed with water, peeled, cut into smaller sizes and then ground. Furthermore, breadfruit that has been finely filtered to separate the pulp. Filtrate is left for 24 hours and separated by decantation. The precipitate (BS) is dried at 70˚C.

2.2.2 Preparation of the Croos-Linked Al-CMC

About 2.8 g of sodium carboxymethyl cellulose was dissolved with 100 mL of distilled water, heated on a hot plate for 1 hour at 70˚C, then added 0.02 g octadecahydrate cross-linker and stirring continued for 30 minutes again. The formed solution pour over the Teflon pan and dry it at 80˚C. The film formed is then finely ground and the water absorption capacity (WAC) is determined.

2.2.3 Preparation of Cross-Linked Al-CMC-BS

Breadfruit starch as much as 0.5 g was dissolved with aquadest at 80˚C while stirring for 45 minutes until gelatin was formed, then added 0.5 g Al-CMC powder while stirring with a magnetic stirrer at 70˚C for 30 minutes. The mixture formed is then poured on a mold pan, then dried for 12 hours at 105˚C. Solids formed are used for examination of WAC, SEM, FTIR and DSC.

2.3 Characterization

2.3.1 Water Absorption Capacity (WAC)

The WAC of the sample is determined by inserting the sample into a tea bag, then soaking it in distilled water for 24 hours and then weighing it down. The WAC price is calculated using equation:

$$\text{WAC (\%)} = \frac{W1 - W2}{W1} \quad (1)$$

W1: Weight of sample after soaking
W2: Weight of dry sample

2.3.2 Fourier Transform Infra-Red (FT-IR) Spectroscopy

The tool used to record IR spectrum was the Shimadzu-IR Prestige 21 Spectrometer with scanning region 400-4000 cm^{-1} at 16 cm^{-1} resolution. Samples were mixed with KBr powder and examined using IR spectrometer.

2.3.3 Scanning Slectron Microscope (SEM)

The morphology of the surface of the Al-CMC-BS film was discovered by using electron microscope (Bruker) with a magnification of 500 times under 10.00 kV of voltage

2.3.4 Differential Scanning Calorimetry (DSC)

To measure Tg, differential scanning calorimetry (DSC), type METTLER TOLEDO (Switzerland), model DSC1, temperature range: 25-3000^{0}C, Heating rate:10 K/ min, N_2 gas 50 mL/min.

3 RESULT AND DISCUSSION

3.1 Isolation of Breadfruit Starch

In this study the starch used was breadfruit starch, of which 600 g of breadfruit produced 60 g of starch.

The FT-IR spectrum of breadfruit starch is shown in Fig.1. The absorption peak at 3387 cm^{-1} showed a stretching group (O-H). The absorption peak of 2924 cm^{-1} indicates the presence of a C-H ($-CH_2$) group. Almost the same OH and CH ($-CH_2$) absorption peaks from breadfruit starch were also obtained by Nurhaeni et.al at wave number 3377.37 cm^{-1} at 2927.27 cm^{-1} The absorption peak at wave number 1157 cm^{-1} was absorption peak of C-O alcohol and absorption peak at 1018 cm^{-1} was the C-O glycosidic functional group (Nurhaeni et al., 2018). This spectrum shows that the spectrum in Fig. 1 is a spectrum of carbohydrate compounds (starch).

3.2 The Cross-Linked Al-CMC

Water absorption capacity from the Cross-Linked Al-CMC can be seen in Table 1.

Table 1: WAC Values from The Cross-Linked Al-CMC.

Na – CMC (g)	$Al_2(SO_4)_3$ 18 H_2O (g)	Al-CMC (%)
2.8	0.0	772.22
2.8	0.2	1911.11
2.8	0.6	1500.01
2.8	0.8	1322.22

The test was carried out by immersing 0.1 g of Al-CMC in a tea bag which weighed 0.8 g and then immersed in 20 mL distilled water. Based on table 1, it can be seen that the WAG value of Na-CMC is the lowest that is equal to 772.22%.When the the concentration of the cross-linker is low , it leads to low degree of cross linking, and it is hard for network structure to form, so the water absorbency is low. However, when cross-linker is higher than 2%, there are much more cross-linking points and the pores become smaller in the network, which causes the decrease of the water absorbency (Braihi, 2015). The optimum absorption capacity of Al-CMC is in the ratio of 2.8: 0.2 or (98: 2) % of 1911.11 % /0.1 g Al-CMC (191.11 g water / g Al-CMC-BS)

3.3 The Cross-Linked Al-CMC-BS

The WAC values from the cross-linked Al-CMC-BS on various compositions can be seen in table 2. The cross-linked Al-CMC-BS is made by mixing the cross-linked Al-CMC that has the optimum WAC price, which is the ratio of Na- CMC against aluminum sulfate octadecahydrate 2.8: 0.2 (see table 1) with breadfruit starch. From table 2 it can be seen that the addition of breadfruit starch gives a very significant increase in WAC and the optimum WAC value is in the composition 2.8: 0.2: 0.5. that is equal to 244.444% / g Al-CMC-BS. Breadfruit starch serves to increase the number of hydrophilic groups and form a network structure that is larger than the Al-CMC network structure so that the absorption of water increases (Braihi, 2015).

Table 2: Values of WAC from the Cross-Linked Al-CMC-BS

Na – CMC (g)	$Al_2(SO_4)_3$ 18 H_2O (g)	BS (g)	Al-CMC-BS (%)
2.8	0.2	0.0	772.22
2.8	0.2	0.5	2444.44
2.8	0.2	1.0	2360.00
2.8	0.2	1.5	2356.66

The broad peak at 3300-3450 cm^{-1} is presented by O-H stretching and peak that appears at 2900-3000 cm^{-1}. is saturated aliphatic C-H group of CMC The peak around 1060 cm^{-1} is due to C-O-C stretching and peak at 1604.77 cm-1 is assigned to stretching vibration of the carbonyl group from COO-.

The small peaks detected at 894.97 cm-1 were confirmed to β 1-4 glycoside bonds. The existence of the carbonyl group and its salt that assigned to carboxymethyl group was observed at 1600-1640 cm^{-1} and 1400-1450 cm^{-1} (Siregar et al., 2019).This proves that this spectrum is a spectrum of Na-CMC. At Al-CMC-BS there is a change in the ether (CH2 O CH2) group at wave number 1327.03 cm-1 after addition of starch. This is due to the presence of a strong absorption band on carbonil groups of 1635.64 cm-1 where the absorption band has a strong influence on the strain of strong carbonil bonds so that a large dipole moment is needed. Wave number 1118.71 cm-1 with the C-O-C group is a weak asymmetric strecthing bond at wave number 848.64 cm-1. At wave number 2924.09 cm-1 with the C-H group with the stretching group CH2, the wave number 1373.32 cm-1 is a wave number which indicates a bending of the -OH vibration.

Figure 3 is a DSC thermogram from samples. Investigation with DSC aims to determine whether Al-CMC-BS is a miscible polymer mixture. The presence of one Tg price indicates that the polymer mixture is miscible and if two Tg prices indicate the polymer mixture is immiscible. Curve shows that there is one glass transition value (Tg) on Al-CMC-BS that is at 95.85˚C, which is between Tg from BS at 118.72˚C and Tg from CMC at 94.23˚C. This shows that the mixture of CMC and BS is miscible or Al-CMC-BS is a miscible mixture (Braihi, 2015).

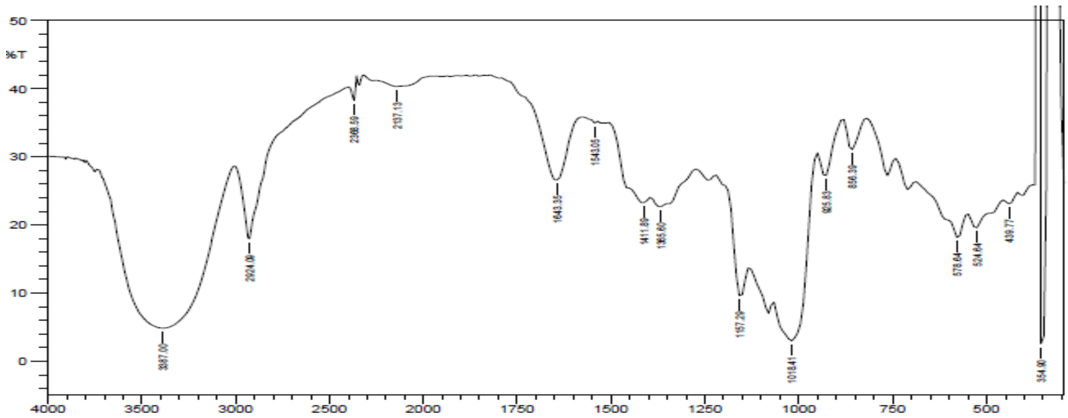


Figure 1: FTIR Spectrum of Breadfruit Fruit Starch.

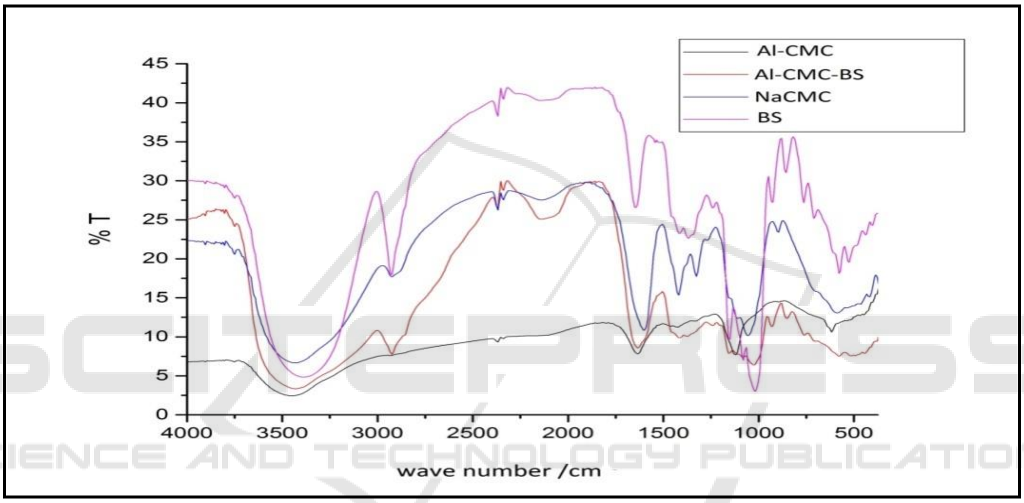


Figure 2: Increasing FT-IR Spectrum BS, Na-CMC, Al-CMC and Al-CMC-BS

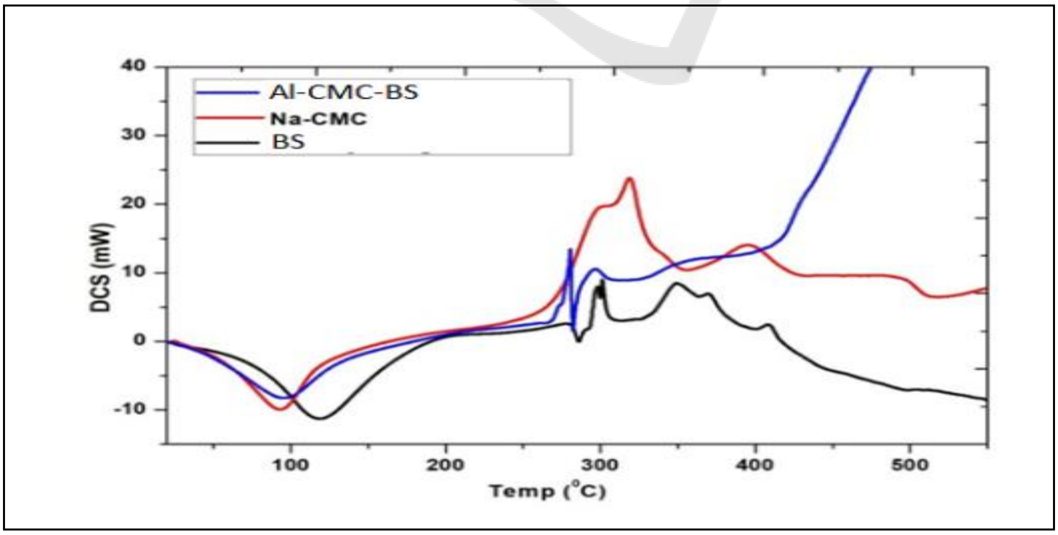
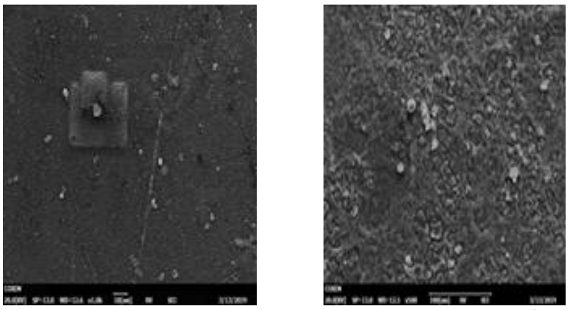


Figure 3: Termogram DSC of Al-CMC-BS, Na-CMC and BS.

Figure 4.is a SEM photo of Na-CMC and Al-CMC-BS with optimum WAG. SEM photos showed that Al-CMC-BS had a coarser and more porous surface observed compared to surface SEM photos from Na-CMC. This shows the formation of polymeric networks that are intertwined and interact with each other. Larger pore presence in the AL-CMC-BS will facilitate more water absorption and retention (Pourjavadi et al., 2007)(Ma et al., 2015)



(a) (b)

Figure 4: (a) Photograph SEM (a) Na-CMC and (b) Al-CMC-

4 CONCLUSIONS

A super absorbent polymer material from CMC, Aluminum sulfate octadecahydrate and BS called Al-CMC-BS superabsorbent polymer has been successfully synthesized. The existence of readfruit starch is very influential in increasing the absorption of it to water which reaches 244.4 g of water / g Al-CMC-BS. Al-CMC-BS super absorbent polymer is a miscible porous blend

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