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Synthesis and Characterization of Bacterial Cellulose-Acrylamide Hydrogel Prepared from Banana Peels

RAUDHATUL FADHILAH* and RIZMAHARDIAN ASHARI KURNIAWAN

Department of Chemistry Education, Muhammadiyah Pontianak University, Jl. Jenderal Ahmad Yani No. 111, Kalimantan Bar 78124, Indonesia

*Corresponding author: Tel/Fax: +62 561 764571;E-mail: raudhatul_fadhilah@yahoo.com

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The synthesis of bacterial cellulose hydrogel prepared from banana peel chemically cross-linked with acrylamide is reported. The cross-linkage is proven by Fourier transform infrared spectroscopy. The highest gel fraction value was 90 % in the bacterial cellulose with the addition of acrylamide by 15 %. Hydrogel performance is shown by the degree of swelling in the NaCl and water solvent. The results show that before bacterial cellulose was cross-linked with acrylamide in the water, it has a much larger swelling degree (1228.57) than in NaCl (847.62). Acrylamide involvement affects the swelling degree of bacterial cellulose hydrogels with the trend in the 0.5 M NaCl solvent is the higher the concentration of acrylamide, the greater the swelling degree; the highest degree was 882.35 (C acrylamide = 15 %). While by water solvent, the degree of swellingdecreases along with the increase of acrylamide concentration. The highest degree of swelling by water solvent is 925.86 when the concentration of acrylamide is 10 %. The presence of acrylamide causes an increase of hydrogel cross-linking density, which means that water to hydrogel tissue diffusion power decreased and lead to relatively lower hydrogel swelling ratio.

Keywords: Bacterial cellulose, Banana peels, Degree of swelling, Hydrogels.

INTRODUCTION

Hydrogel is one of bio-materials widely used in medical field. Hydrogel is a cross-linked hydrophilic polymer and is capable of storing water or body fluids [1]. Hydrogel has the ability to swell and hold a large volume of fluid up to 1000-100.000 % [2]. One of the applications of hydrogel in medical field is as a wound dressing. Nowadays, wound dressing is not only used to cover wound but also help in the healing process. Bioactive wound dressings such as hydrogels, capable of changing the area around wound and interacting with wound surface to optimize healing [3].

Hydrogels wound dressing can be made in the form of viscous gel or layer, but the layer one is preferable to viscous gel because it has advantages such as: minimize exudate from burns [3], absorbs water and wound fluids in large volumes, cannot be penetrated by bacteria without damaging the material [4] and can be used for localized wound [5]. Hydrogels are generally synthesized from biopolymers, synthetic polymers, or a combination of both. Combination between biopolymers and synthetic polymers will produce a superior hydrogel.

One of the polymers widely used to make hydrogel wound dressing is cellulose. This is due to the fact that cellulose are biodegradable, low-cost and biocompatible [6]. Cellulose can also be produced by microorganisms, such as bacterial cellulose (BC) which is purer than derived-plant cellulose because it is free of lignin, hemicellulose and other biogenic products [7]. Differences in basic materials to produce bacterial cellulose will affect the tensile strength, degree of polymerization and crystallinity of the resulting hydrogel [8].

Bacterial cellulose in this study produced from a banana peel waste with the help of bacteria *Acetobacter xylinum*. Banana peel waste is good enough to use as a raw material for making hydrogel. Some of the nutrients contained in the banana peel are the sucrose sugar 1.28 %, diverse mineral resources, such as Mg^{2+} (3.54 g/L), as well as the growth promoting factor which is a compound that can boost the growth of bacteria *Acetobacter xylinum*. The sucrose sugar substance in banana peel will be used by *Acetobacter xylinum* as a source of energy, as well as the source of carbon to form the metabolites. One of the metabolites is cellulose that will be use as a base material to form hydrogel which is more useful and has a higher selling price.

Bacterial cellulose has a high tensile strength in both the dry state and the wet state, eco-friendly, has a thermal stability [7], bacterial cellulose porous structure can accelerate wound healing process, has a high absorption of the liquid (albumin) and can absorb fluid emitted from chronic wounds [4].

However, the characteristic of bacterial cellulose which is not elastic [7] and easily unravel causing its use to be not durable [9]. Augmentation of other compatible polymers to a homo polymer will raise its physical properties to obtain a new hydrogel with relatively large absorption capability [10]. Although the water absorption is limited [10], hydrogels from synthetic polymers such as polyacrylamide (PAM) can be used for the matrix water storage with characteristics of elastic and durable [11]. Polyacrylamide is also biocompatible with the body and does not cause skin sensitivity [12] so that polyacrylamide can be cross-linked with bacterial cellulose.

Several studies have discussed the combination between bacterial cellulose and polyacrylamide. Zhang *et al.* [13] has chemically synthesized bacterial cellulose hydrogels which cross-linked with acrylamide, the result was; water expands ability of 1.390 % is reached after 20 h, can increase the thermal stability from 320 to 385 °C and increase the tensile strength from 130 kPa up to 2350 kPa. Pandey *et al.* [14] found that cross-linked bacterial cellulose with polyacrylamide has greater mechanical strength than polyacrylamide with bacterial cellulose. Therefore, this study combines bacterial cellulose synthesized from waste of banana peel with acrylamide to produce wound dressings hydrogels.

EXPERIMENTAL

Instruments used in this study were FTIR Shimadzu Prestige-21, oven, Buchner funnel, thermometer and pH meter. In this study, waste of banana peel obtained from the seller of fried bananas and from Flamboyan traditional market in Pontianak, Indonesia. *Acetobacter xylinum*, sugar, filter paper, distillation water of sigma, $(NH_4)_2SO_4$ (Sigma), acetic acid 98 % (Sigma), acrylamide (Sigma) were used as such.

General procedure

Bacterial cellulose manufacture of waste banana peel: The first step was by scraped the inside of waste banana peel off then pulverized to obtain a slurry out of it, then the slurry is squeezed using gauze to get the extract. The banana peel extract still contains a lot of sediment or impurities, in order to get a good extract need to be filtered using filter paper with the help of vacuum pump-Büchner funnel. In next step, the banana peel extract is diluted with water at a ratio of 1:4, then the solution is boiled. After boiling, add some sugar (0.75 g) in as a carbon source and 0.5 g of $(NH_4)_2SO_4$. The solution was stirred until it becoming homogeneous, then the pH adjusted to 4.5 by adding 98 % of acetic acid. After the pH adjustment, the solution placed into each container then closed. The next day *Acetobacter xylinum* was added and incubated for 8-15 days at 32 °C. On day 8, bacterial cellulose (BC) ready to be harvested with the thickness of 0.5-1 cm.

Dried sample preparation of bacterial cellulose [15]: Bacterial cellulose layer is then washed with water and cut with a knife to make a size of 10 × 10 cm^2 layer. The layers boiled for 20 min to kill any remaining or attached bacteria. If there is no need to use it, these small bacterial cellulose layers can be stored in a plastic bag and put them in a refrigerator. The next step, bacterial cellulose layers were put in into Buchner funnel for vacuum filtered to remove the water. Thin layers formed after this step were dried by using oven at 60 °C till it reach its constant weight.

Manufacture of bacterial cellulose-acrylamide hydrogel: Chemically manufactured of hydrogels was done by modifying the procedure of Rimdusit *et al*. [9]. The first stage begins with soaking each bacterial cellulose layer 10 × 10 cm^2 in an acrylamide solution with a composition of 10, 12.5 and 15 %, respectively by using the water solvent for 2-3 h. The second stage, each of BC-AM Layer packed in a sealed polyethylene plastic bag size of 10 × 15 cm^2 with a thickness of 0.5 cm. The last, the mixed solution was dried in an oven at a 60 °C temperature.

Determination of gel fraction [9]: Three layers of BC-AM hydrogel which have been dried with size of (1 × 1) cm^2 then weighed (W_0). Furthermore, the hydrogels soaked and shaken in distilled water at a speed of 100 rpm for 24 h at room temperature to remove unreacted substances. The hydrogel then being taken out and dried in an oven at a 60 °C temperature till it reach its constant weight. Hydrogel then reweighed (W_1).

Gel fraction was calculated by the equation of:

$$\text{Gel fraction } (\%) = \frac{W_1}{W_0} \times 100$$

where, W_1 = dry weight of BC-AM hydrogel after 24 h soaking (g), W_0 = dry weight of BC-AM hydrogel before soaking (g).

Determination of hydrogel performance: Three layers of BC-AM hydrogel which have been dried with size (1 × 1) cm^2 then weighed (W_d). Furthermore, the dried hydrogel soaked in 50 mL of water for 60 min. The hydrogel being taken out afterwards and the water in the hydrogel surface wiped with a filter paper, then it reweighed (W_s). Measurements were carried out on bacterial cellulose layers as a control and on BC-AM layers with various acrylamide concentrations for 24 h with intervals of 60 min. Measurement of hydrogel swelling power ratio of a test results at each soaking timewas calculated by the equation of:

$$Q\ (\%) = \frac{W_s - W_d}{W_d} \times 100$$

where, Q = Power expands ratio (%). W_s = Weight of wet BC-AM hydrogel (g), W_d = Weight of dry BC-AM hydrogel (g).

Measurement of hydrogel expansion ratio in NaCl: Three layers of dried BC-AM hydrogel with size of (1 × 1) cm^2 (W_d) soaked in a solution of 0.5 mL NaCl for 60 min. The hydrogel being taken out afterwards and NaCl solution on the hydrogel surface wiped with a filter paper, then it reweighed (W_s). Measurements were carried out on bacterial cellulose layers as a control and on BC-AM layers with various acrylamide concentrations for 24 with intervals of 60 min. Measurement of hydrogel swelling power ratio of a test results at each soaking time was calculated by the equation of:

$$Q\ (\%) = \frac{W_s - W_d}{W_d} \times 100$$

where, Q = Power expands ratio (%), W_s = Weight of wet BC-AM hydrogel (g), W_d = Weight of dry BC-AM hydrogel (g).

Analysis using Fourier transform infrared spectroscopy (FTIR): 10 mg sample of powder hydrogel and 100 mg of KBr mixed so it become pellets. Subsequently, the pellets are placed in the sample compartment.

RESULTS AND DISCUSSION

Manufacture of bacterial cellulose-acrylamide hydrogels: Bacterial cellulose-acrylamide hydrogels (BC-AM) was made into 3 different concentration; 10, 12.5 and 15 %. Acrylamide concentration which successfully cross-linked to bacterial cellulose can be determined by measuring the difference in weight of bacterial cellulose before and after soaked in acrylamide. Table-1 shows that the higher the acrylamide concentration used, the greater the acrylamide cross-linked into bacterial cellulose.

TABLE-1
BACTERIAL CELLULOSE WEIGHT BEFORE AND AFTER SOAKED WITH ACRYLAMIDE

AM conc. (%)	BC cellulose (g)	BC-AM (g)	AM (g)
10.0	0.021	0.049	0.028
12.5	0.021	0.058	0.037
15.0	0.021	0.063	0.042

AM = acrylamide; BC = bacterial cellulose

Determination of gel fraction: Gel fraction of the hydrogel showed the grafting level and cross-links in the hydrogel [14]. Gel fraction was calculated based on the ratio of bacterial cellulose-acrylamide (BC-AM) dry weight before and after soaked for 24 h in the water. Three concentration variations of acrylamide (AM) as the results of soaking are shown in Table-2.

TABLE-2
GEL FRACTION

AM conc. (%)	BC-AM (W_0) (g)	BC-AM (W_1) (g)	Gel fraction (%)
10.0	0.049	0.082	59.76
12.5	0.058	0.07	82.86
15.0	0.063	0.07	90.00

AM = acrylamide; BC = bacterial cellulose

The higher the acrylamide concentration, the greater the gel fraction percentage (Table-2). This shows that the 15 % acrylamide concentration is the best concentration in forming the hydrogel. This is slightly different from the results of Mulijani *et al*. [15] research which reported that when the acrylamide concentration was 15 %, the percentage of gel fraction was decreasing. This might be occurred because of the differences in the basic materials used in forming the hydrogel and method of making BC-AM.

Determination of hydrogel's degree of swelling (Q) in a NaCl water and solvent: Measurement of expansion degree of swelling of bacterial cellulose and BC-AM in a NaCl and water solvent wasconducted in 1 h intervals for 12 h. The results are shown in Table-3. It shows that the hydrogel swelling power, both in the water and NaCl solvent keep increasing along the soaking time getting longer. In an NaCl solvent, the swelling of bacterial cellulose hydrogel without acrylamide is much smaller (847.62) than in water (1228.57). This is due to changes in osmotic pressure and reduction of the repulsive force at higher ionic strength. The difference of osmotic pressure between the water and the hydrogel is greater than the pressure between saline and hydrogel. Thus, the hydrogel swelling in water is much higher than in NaCl. The presence of salt reduces the difference in osmotic pressure of saline solution [16]. The decreasing of the swelling in higher ionic strength could also be explained due to the neutralization of carboxylate anion because of the presence of Na^+, resulting in decreased strength of the repulsive electrostatic force, which is the controlling factor for the swelling [17].

This phenomenon also occurs in bacterial cellulose that cross-linked to acrylamide. The highest swelling degree of BC-AM in water solvent was 925.86 on acrylamide concentration of 10 %, while in NaCl solvent, the highest degree of swelling was 882.35 during acrylamide concentration of 15 % (Table-3). On BC-AM, in the NaCl solvent, the higher the acrylamide concentration, the greater the swelling degree of hydrogel. On the contrary, on the water solvent, the higher the concentration of acrylamide, the lower the swelling degree of hydrogel. Highly concentration of acrylamide resulting to hydrogel swelling force in the water decreasing, unlike in the NaCl. This is caused by the infusion of acrylamide into

TABLE-3
DEGREE OF SWELLING OF HYDROGELS IN THE NaCl AND WATER SOLVENT

Time (h)	NaCl (%)				Water (%)			
	BC-AM 10 %	BC-AM 12.5 %	BC-AM 15 %	BC	BC-AM 10 %	BC-AM 12.5 %	BC-AM 15 %	BC
1	98.72	105.45	105.88	285.71	181.03	169.38	84.28	238.09
2	180.77	216.36	210.29	342.86	263.79	240.82	100.00	366.67
3	215.38	270.91	255.88	366.67	367.24	285.71	144.28	400.00
4	237.18	285.45	319.12	376.19	456.89	340.82	168.57	461.90
5	257.69	332.73	400.00	447.62	500.00	395.92	178.57	547.62
6	317.95	356.36	455.88	485.71	527.58	400.00	227.14	566.67
7	373.07	409.09	507.35	571.43	605.17	432.65	230.00	690.47
8	476.92	452.73	607.35	671.43	694.83	455.10	280.00	761.90
9	532.05	498.18	710.29	709.52	737.93	506.12	341.42	804.76
10	538.46	527.27	751.47	714.28	813.79	540.82	384.28	890.47
11	591.03	580.00	861.76	766.67	865.52	591.84	392.85	1019.05
12	652.56	667.27	882.35	847.62	925.86	634.69	415.71	1228.57

AM = acrylamide; BC = bacterial cellulose

the bacterial cellulose structure resulting in a hydrogel cross-linking density increases. So, the water diffusion ability into the hydrogel tissue is decreasing and causing the hydrogel swelling ratio relatively lower [10].

Fourier transform infrared spectroscopy analysis: FTIR spectra before and after cross-linked with acrylamide are shown in Fig. 1. There are some peaks on bacterial cellulose at 669, 1058.8 and 3373 cm^{-1}, represented OH out of phase bending, CO stretching vibrations and OH intra molecular bond O(3) HO(5), respectively [14,18]. While the presence of acrylamide in bacterial cellulose confirmed by the emergence of strong and sharp peaks at 1612.4 and 1674.1 cm^{-1} due to CO stretching, 1429.2 due to CN stretching and two peaks at 3190 and 3354 cm^{-1} due to OH stretching and NH stretching [14].

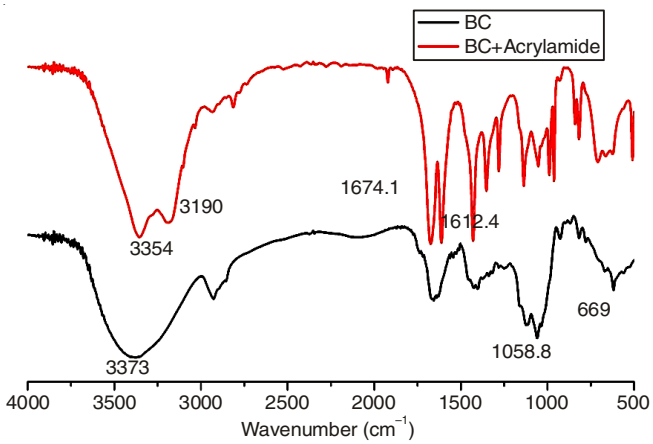

Fig. 1. FT-IR spectra of bacterial cellulose before and after crosslink with acrylamide

Conclusion

Bacterial cellulose-acrylamide hydrogel made from banana peel has been successfully synthesized by chemical methods. Hydrogel performance demonstrated by the highest swelling degree of bacterial cellulose in the water at 1228.57. The presence of acrylamide causing in bacterial cellulose bond becomes tight, which makes the hydrogel swellingabilityin the water is getting lower. The presence of Na^+ ions decrease the strength of repulsive electrostatic force, which is the controlling factor for the swelling. BC-AM shows a high degree of swelling, both in the water or NaCl which can be used as a wound dressing.

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