Investigation of Swelling Ratio and Textures Analysis of Acrylamide-Nanocellulose Corncobs Hydrogel

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Abstract. Corncobs have a high level of cellulose hence making it suitable to be used as the main ingredient in making hydrogels. Hydrogel are crosslinked polymers capable of absorbing water hundreds to thousands of times their dry weight, but are insoluble in water due to the three-dimensional structure of the polymer network. Hydrogel can be synthesized using corncobs cellulose and acrylate-acrylamide with chemical crosslinking methods. This study aims to determine the effect of adding corncobs cellulose and acrylate-acrylamide on hydrogel ability to swelling ratio, gel fraction and texture analysis. Nanohydrogel were synthesized by cellulose concentration by 5- 25% while acrylamide was varied 10,12 and 16 %. The treatment concentration ratio of nanocellulose solution to acrylamide also showed a significantly different effect at 5% level. The optimum hydrogel synthesis was the treatment of 10 % cellulose ratio and 16% acrylamide ratio which has a swelling ability of 15152.3% (g /g) and gel fraction 56.6%. The increasing the concentration of cellulose caused the hardness value to be higher but the springiness value tends to decrease. Morphology analysis showed the surface of hydrogels that are porous, has lumps and forms a three-dimensional tissue.

1. Introduction

Hydrogel is a polymer network with the ability to store a large of water with a high water absorption capacity [1]. Hydrogels can be synthesized using natural and synthetic polymers. Natural polymers are recommended because their raw materials are abundant, non-toxic and low production costs but have low water absorption ability, while synthetic polymers have high swelling properties. Most of the hydrogels use synthetic polymers excessively, causing the hydrogel to be difficult to decompose in nature because it is not environmentally friendly and toxic [2].

The synthetic and natural polymer determines the properties and characteristics of the hydrogel so that the combination of the two polymers aims to make the hydrogel have good swelling ability and physical properties. An alternative to natural polymers that can be used for hydrogel synthesis is corncobs cellulose [3]. The cellulose content of corncobs is 40% -60%, of the total weight of corncobs. The presence of hydroxyl groups in cellulose is an important factor in the manufacture of good quality
hydrogels [4]. Several previous studies obtained results that the use of natural polymers alone resulted in a low swelling ratio of 514% [5], only using corncobs cellulose, whereas the addition of acrylate synthetic polymer alone resulted in a swelling ratio of 1600% [6] and the addition of acrylamide alone resulted in a swelling ratio of 2500% [7].

In this study, the cellulose was inserted with acrylic acid (AA) and acrylamide (AAm) monomers and crosslinking agent N, N-methylene Bisacrylamide (MBA) by chemical crosslinking method. Both monomers have carboxylate anions which play a role in forming bonds with water through hydrogen bonds [8]. The modification of the cellulose particle size was also carried out because it was able improved hydrogel swelling. The process of grafting monomers to the cellulose polymer chain is carried out by the cross-linking method. In addition, crosslinking also results in a three-dimensional structure which allows the hydrogel to be insoluble in water [9].

2. Materials and Methods

2.1 Materials

The raw material used is corncobs from Wonogiri farmers, Central Java. Chemicals such as acrylamide, acrylate acid, N, N-methylene Bisacrylamide (MBA), Ammonium persulfate (APS), NaOH, sodium hypochlorite (NaClO), and distilled water. Viscometer, Particle Size Analyzer (PSA), Texture Analyzer Texture Pro CT V1.2 Build 9, Ultrafine grinder (Masuko Corp, Japan), and Scanning Electron Microscope (SEM).

2.2 Extraction of Cellulose and Preparation of Nanocellulose Solutions

Corncobs are coarsely chopped, milled and sieved to obtain 60 mesh corncobs powder. Sterilization of corncobs powder using an autoclave at 80 °C for 12 hours, delignification using 8% NaOH at 15 °C for 30 minutes. The bleaching process uses 15 liters of NaClO at room temperature for 1 hour. Preparation of nanocellulose solution using an ultrafine grinder, cellulose was dissolved in distilled water with a concentration of 2% (dry matter). The sample was ultrasonicated for 1 hour. Nanocellulose particle size distribution was characterized by PSA.

2.3 Hydrogel Synthesis

Nanocelluloses was dissolved in 100 ml of distilled water with variations of 5, 10,15, 20 and 25% (w/v) and stirred until homogeneous. Add APS as an initiator 1 ml and stirred for 15 minutes. Dissolve acrylic acid (AA) in the KOH solution in a 1: 1 ratio. Mix 25 ml of acrylic acid (AA) solution in cellulose solution, then stirred until homogeneous for 15 minutes. After that, mix the acrylamide (AAm) solution that has been dissolved in 25 ml distilled water with concentrations of 10, 12, and 16% into the cellulose solution. Reaction grafting occurred for 45 minutes at 45 °C. MBA 1 ml of as agent crosslinker was added. Furthermore, the temperature is increased to 60 °C, kept constant until the sample forms a gel. The hydrogel is dried in an oven at 60 °C and ready to be characterized.

2.4 Hydrogel Characterization

2.4.1 Swelling Ratio/EDS. (Equilibrium Degree of Swelling). The swelling value shows the optimum swelling ability or expands from the hydrogel to absorb water. Dry hydrogel soaked in water for 7 days then weigh it. Swelling ratio can be calculated [10].

2.4.2 Gel Fraction. Gel fraction is the degree of crosslinking formed in the structure hydrogel polymer network. The hydrogel is in a state of optimum swelling dried to determine the remaining fraction. The number of fractions that are not dissolved indicates the number of crosslinks formed. Dry hydrogel soaked in water for 24 hours then dried in an oven at 60 °C for ± 48 hours until constant weight. Then the hydrogel is weighed again. Furthermore, the value of the gel fraction can be calculated [9].

2.4.3 Mechanical Properties. Mechanical properties were measured using a Texture Analyzer including parameters, hardness and springiness.
2.4.4 Morphology. Observation of the surface morphology of samples using Scanning Electron Microscopy (SEM) type JSM-6510LA JEOL with an electron acceleration voltage of 20 kV and magnification 2000 times.

2.5 Data Analysis
Experiments were carried out using a completely randomized design (CRD) pattern factorial. The chemical cross-link synthesis method uses the A (A1, A2, A3, a and A5) factor as a variation concentration of nanocellulose solution dissolved in distilled water with five levels (5, 10, 15, 20,25%) (wt / v) and B (B1,B2 and B6) factor is the acrylamide concentration with 3 level (10, 12, 16%) (wt / v). The experiment was carried out 3 times. The experimental data were analyzed using SAS software using the two-way ANOVA test and Duncan's continued test at the 5% level.

3. Results and Discussion
The increase in cellulose content affects the physical color of the hydrogel. The color of the hydrogel will get darker as the cellulose is added (A5B1 sample). In contrast, hydrogels with smaller cellulose content become more transparent (A2B6 sample). The physical condition after 24 hours of immersion, the hydrogel 10% of cellulose is more transparent and has a gel-like texture (Figure 1a), while the addition of cellulose will make the hydrogel a thick white gel, solid but easily crushed (Figure 1b).

3.1 Swelling Ratio Analysis
The swelling ratio or water absorption capacity is the ratio of the weight of the hydrogel in a state of absorbing water to its dry weight [10]. Increasing the concentration of cellulose, the swelling ratio decreased, inversely proportional to the increase in the acrylamide content to increase the swelling ratio of the nanohydrogel as presented in Figure 2. The highest swelling value was A2B6 with 10% cellulose and 16% acrylamide. The hydrogel with the lowest swelling ability was A5B1 with 25% cellulose and 10% acrylamide concentration.

When the water has entered the hydrogel, it will be difficult for the water to come back out. At the addition of 10% cellulose, the deficiency of acrylamide polymer will be covered by the excess cellulose where the water entry space becomes easier. Meanwhile, when water enters the hydrogel, it will be difficult for the water to escape because it is supported by the structural density of acrylamide [11]. In addition to cellulose above 10%, there is a decrease in water absorption capacity because excess cellulose will reduce the density of the polymer structure due to competition between cellulose and acrylamide monomer for polymerization. The addition of excess cellulose will decrease the ability of the hydrogel to absorb water, because of the hydrogel cavities. getting closer [12]. Based on the ANOVA test, the probability value is <0.05, indicating that the data is significantly different, namely changes in cellulose and acrylamide content have an effect on the swelling value.
3.2 Gel Fraction Analysis
The gel fraction test was carried out to show the number of cross-links formed. the value of the gel fraction was inversely proportional to the hydrogel swelling ability [10]. Too many cross-ties formed will actually decrease the swelling ability due to the reduced volume or space for storing absorbed water. The sample that had the highest gel fraction value was A3B1 15% cellulose and 10% acrylamide.

![Swelling Ratio Nanohydrogel](image1)

![Swelling Ratio Nanohydrogel](image2)

Figure 2. Swelling ratio nanohydrogel, (a) NC versus AAm, (b) AAm versus NC

The increase in cellulose content resulted in an increase in the number of hydrophilic groups, but the density of both intramolecular and intermolecular distances in the polymer matrix also increased (Figure 3a and 3b). The ANOVA test results showed that the variation of cellulose and acrylamide content had a significant effect on the value of the gel fraction.

3.3 Texture Analysis
Swelling is an important factor in the characteristics of the hydrogel which represents the hydrogel's
ability to swell due to absorption and water binding. However, the use of hydrogels in various fields is not only consider the swelling properties but also the polymer resistance to excessive deformation associated with the hardness value, elasticity properties hydrogel which can return to its original state when subjected to outside interference and polymer network structure density [13].

Hardness indicates the resistance of the polymer against excessive deformation In figure 4a, it can be seen that the decreasing trend of the swelling value produces value increased hardness. The increase in hardness value makes the hydrogel even stiffer. This means the hydrogel is resistant to deformation.

![Graph showing gel fraction vs nanocellulose and acrylamide content.](image)

**Figure 3.** Gel Fraction, (a) NC versus AAm, (b) AAm versus NC

The texture of the hydrogel becomes harder, when the cellulose increases but the texture is easily destroyed or does not return to its original shape when subjected to pressure, because the elasticity of the hydrogel is reduced [14].

Springiness demonstrates the ability of the nanohydrogel to return to its original shape after pressure. The more acrylamide content, increase the springiness value. It can be seen in Figure 4b that 16% acrylamide has a high average springiness value compared to other samples. The highest springiness value in the A2B6 sample which also has the best swelling ability.
However, the A2B6 sample has a fairly low hardness. The elasticity of the hydrogel increases, because the hardness of the hydrogel decreases. The high swelling ability also causes the presence of solutes during the immersion of the nanohydrogels so that some of the cross-links on the nanohydrogels weaken and the hardness is low [15].

3.4 Surface Morphology analysis

SEM images of hydrogels provide information about the pore geometry and size at specific locations due to the tissue homogeneity of the hydrogels [14]. Figure 5a and 5b shows the hydrogel morphology of A5B1 and A2B6 as representative samples with the lowest and highest swelling ratios, there are different surface morphologies in both.

Surface morphology forms clumps that cover a pore. The agglomerates are polymers which are not cross linked. Clumps on the hydrogel surface will block the water in the hydrogel, resulting in low hydrogel swelling ability.

The smooth surface also shows that there is less cross-linking between the polymer and the crosslinking agent (Figure 5a). Meanwhile, in Figure 5b, it can be seen that the pores that are formed will make it easier to get out of the hydrogel water. There is a polymer branching pattern that forms a three-dimensional network.
4. **Conclusion**

The addition of acrylamide polymer as a material that is grafted with cellulose greatly affects the performance of the resulting hydrogel. The effect of increasing the concentration of cellulose on the hydrogel composition decreased the swelling ability of the hydrogel, on the other hand, the addition of acrylamide concentration increased the swelling ability of the hydrogel. This is because the cross-links formed will cover the space or volume of water in and out. However, high swelling will cause the hydrogel cross-link to stretch during immersion so that the strength is low. The more crosslinking that occurs the gel fraction value increases and the hydrogel polymer network became tighter and stiffer. Rigid polymer network causes the ability of swelling hydrogel to decrease.

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