Cellulose-Based Nanohydrogel from Corncob with Chemical Crosslinking Methods

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Abstract. Indonesia is the sixth largest corn producer in the world. The high corn production in Indonesia is correlated with waste corn cob produced. However, corn cob waste is not fully utilized, mainly only disposed and burned that caused environmental pollution. One alternative to utilize of corn cob is to be processed to cellulose based superabsorbent polymer (SAP) hydrogel. In this study, cellulose based hydrogel was prepared using epichlorohydrin (Ech) as cross-linking agent and modified particle size to produce nanohydrogel. The aim of the research was to find out the effect of Ech concentration and cellulose: solvent ratio on the characteristic of nanohydrogel. The treatment tested was Ech concentration of 4%, 16% and 28%; whereas the ratio of cellulose: solvent was 1:2 (A2) and 1:4 (A4). Parameters observed were swelling ratio, gel fraction, texture and morphology of the resulted hydrogel. Result showed that the higher the Ech concentration the swelling ratio increasing. The best treatments were nanohydrogel with Ech concentration 28% and cellulose: solvent ratio 1:2 with characteristics as follows: 514% swelling ratio, 44% gel fraction and 0.33 mJ hardness, with morphology showed higher porosity. This hydrogel has a wide potential as water absorbent material in dry agricultural areas and can be used as fertilizer carrier agent.

1. Introduction

Hydrogels are crosslinked polymers networks with high absorbing water capacity, but are not water-soluble due to the three-dimensional structure of the polymer network [1]. Based on its properties that can absorb large amounts of water and its good biocompatibility, hydrogel have been widely used as wound cover, medical, pharmaceutical, biotechnology, drug and agrochemical delivery system [2] as well as sanitary products. Hydrogels can be synthesized using natural and synthetic polymers. Generally, hydrogels are synthesized using synthetic polymers (petroleum base polymer), namely poly acrylic acid (PAA) or poly acryl amide (PAAM). However, the use of this type of polymer is less environmentally friendly because of its non-biodegradable nature. This kind of polymer is difficult to decompose in nature [3]. Therefore, there have been many studies to modify the hydrogels by utilizing natural polymers, such as polysaccharides that have advantages as non-toxicity, biodegradability, and good biocompatibility. However, they have inferior mechanical properties compared to petroleum based hydrogel. Several techniques to improve the mechanical properties of hydrogels include increasing the cross-linking density and incorporation of inorganic materials or suitable polymers [4].

Cellulose is an abundant polymer available in nature, renewable and is a major structural component of cell walls in plants [5]. The number of hydroxyl groups on cellulose provide factor that
facilitates the production of hydrogels with good structures and properties [6]. In this study, cellulose was extracted from corn cobs. Corn cob has a very high cellulose content of about 40% [7].

Indonesia is the sixth largest corn producer in the world. The high corn production is correlated with waste corn cob produced. According to Statistical Bureau (BPS) production of corn cob in Indonesia reached 5.7 ton/year [8]. Corn cob waste is not fully utilized, mainly only disposed and burned that caused environmental pollution. Data showed that the cellulose content in corn cob is very high reach about 40%.

In recent years, the development of hydrogels from biodegradable and biocompatible biodegradable natural polymers has increasing for being more environmentally friendly. However, to strengthen, its structure, the hydrogel is cross linked by a chemical method such as epichlorohydrin (Ech.) [9]. Epichlorohydrin is the best poly functional reagent compared to other monomers such as POCl 

In this study, hydrogels were made from cellulose with nanometer sizes. Smaller particles, such as nano cellulose which have larger surface area and interstitial volume will increase water absorption [11]. Hydrogel-based nano cellulose has an uptake rate and a higher degree of swelling than micro cellulose. Moreover, hydrogels with nanostructures (nanohydrogels) have a faster ability to respond to environmental changes than in macro form [12]. To dissolve the nano crystalline cellulose to be processed into hydrogel, nano cellulose can be dispersed in several solutions such as NaOH, urea and PEG or mixed NaOH and urea or NaOH and PEG. The aim of the research was to find out the effect of Ech concentration and cellulose: solvent ratio on the characteristic of the resulted nanohydrogel.

We certify that the intellectual content of this paper is the product of our own work and that all the assistance received in preparing this paper and sources have been acknowledged.

2. Methods

2.1 Materials

Raw material used in the research was corn cob originated from Sukabumi, West Java. Chemicals used were sodium hypochlorite (NaClO), NaOH 8%, PEG 4% dan Epiklorohidrin (Ech). The chemicals used as received. Equipment used were digital balance, magnetic stirrer, hot plate, oven, cold room freezer, Texture Analyzer Texture Pro CT V1.2 Build 9, Scanning Electron Microscopy (SEM) Zeiss EVO MA10, Ultrafine grinder (Masuko Corp,Japan), Particle Size Analyzer (PSA) Malvern.

2.2 Nanohydrogel Preparation

The delignification process of corn cob cellulose was conducted general process published elsewhere. Corncob powder of 3 kg powder was soaked in 25 liters of water at 80°C for 12 hours. Then the water was removed and corncobbs was autoclaved in 20 liters of 8% NaOH solution by at 151°C for 30 minutes. This process causes the color of corncob powder to be blackish brown so it needs to be rinsed with running water. The bleaching process was carried out stirring using 15 liters of NaClO at room temperature for 1 hour. This process of rinsing was conducted for several times using running water until the pH reached neutral. Cellulose gel was then stored in a cool room until to be processed.

Reduction of cellulose particle size was performed by cellulose suspension using an ultra-fine grinder (Masuko, Japan) with a ratio of cellulose: aquadest was 1: 10 to produce nano size cellulose. For the formation of hydrogels was carried out according to the method Bajpai [13]. Prior to hydrogel formation, nano cellulose performed a dissolution process. Nanocellulose was dispersed in solution of PEG (4% wt/vol) and NaOH (8% wt/vol) with ratio variation of nanocellulose: solvent was 1: 2 (A2) and 1: 4 (A4). The solution was then stored in refrigerator (4°C) for 24 hours.

The formation of the nanohydrogel was carried out as follows: the cooled nanocellulose solution was stirred at a moderate rate at 55°C. Then epichlorohydrin (Ech) was added with a concentration variation of 0%, 4%, 16% and 28%. The mixing was done until homogeneous for 90 minutes with a
constant temperature of 55°C. Then the solution was allowed to stand for 4 hours at room temperature to form a precipitate. The resulting precipitate was filtered by vacuum filtration and placed in a petri dish to be dried in a 60°C oven for 6 hours. The dry polymer was stored and used as for analysis.

2.3 Analysis
Sample analysis was conducted for raw material, cellulose, nano cellulose as well as hydrogel products. Raw material analysis include proximate analysis and lignin and cellulose content. Nanocellulose was analyzed its surface morphology by SEM and particle size distribution using PSA. Moreover, the nanohydrogel were analyzed its performance such as swelling ratio, gel fraction, physical analysis using texture analyzer, and surface morphology.

2.3.1 Swelling Measurements
Nanohydrogel samples was weighed \( W_d \). The samples were then incubated in distilled water for over 24 h at 25°C until reach the swelling equilibrium \( W_s \). The equilibrium swelling ratio was experimentally determined and percentage of swelling ratio \( (\%) \) is calculated as:

\[
\text{Swelling Ratio (\%)} = \frac{W_s}{W_d} \times 100\%
\]

where \( W_i \) is the weight of the swollen get at 25°C and \( W_d \) is the weight of the gel at dry state [14].

2.3.2 Determination of Gel Fraction
Nanohydrogel samples dried to constant weight \( W_i \) were immersed in distilled water for 24 hours. They were removed from the distilled water, air dried and then further dried to a constant weight \( W_1 \) in an oven. The experiment was repeated three times for each sample, and the average weight of the extracted sample was measured. The gel fraction was calculated as follows:

\[
\text{Gel Fraction (\%)} = \frac{W_1}{W_i} \times 100\%
\]

where \( W_i \) is the weight of dry sample after extraction in water and \( W_1 \) is the initial weight of dry sample [15].

2.3.3 Texture Analysis
Texture analysis was conducted using Texture Analyzer Texture Pro CT V1.2 Build 9. In texture analysis, an analytical probe is depressed into the sample at a defined rate to a desired depth [16]. From the resultant force–distance curve, the mechanical parameters of hardness, adhesiveness, cohesiveness and springiness may be derived. Force necessary to attain a given deformation is called hardness. Adhesiveness is regarded as the work necessary to overcome the attractive forces between the surface of sample and surface of the probe with which the sample comes into contact [16]. Cohesiveness is the strength of internal bonds making up the body of the sample. Springiness is a textural parameter, which is related to elasticity of the sample.

3. Results and Discussion

3.1 Proximate and Chemical Analysis
The proximate analysis included moisture content, ash, lipid, protein and carbohydrates and presented in table 1. The results showed that almost all parameters meet standard (SNI 01-4483-1998, except protein and lipid. Corncob has a high carbohydrate content above 90%. Analysis of the content of cellulose and lignin on corncob before and after delignification process were presented in table 2.
Table 1. Result of proximate analysis of corn cob powder.

| Parameter     | Content (%) |
|---------------|-------------|
| Water         | 3.53        |
| Ash           | 1.54        |
| Lipid         | 1.66        |
| Protein       | 2.32        |
| Carbohydrate  | 90.96       |

Table 2. Analysis of lignin and cellulose content before and after delignification process.

| No. | Material          | Water content (%) | Lignin content (%) | Cellulose content (%) |
|-----|-------------------|-------------------|-------------------|-----------------------|
| 1   | Corn cob powder   | 3.46%             | 23.98             | 57.60                 |
| 2   | Cellulose         | 79.10%            | 10.74             | 96.42                 |

Figure 1. Surface morphology of raw material corn cob powder (a) and nanocellulose resulted from wet milling process (b) (magnitude 250x).

After the delignification, the cellulose content increasing from 57.60% to 96.42% and the lignin decreasing from 23.98% to 10.74% respectively. This showed that a lot of lignin has been rinsed and loss during this process.

Reduction of cellulose particle size was carried out by wet milling process using ultra fine grinder to produces a nanocellulose fiber with smaller diameter than that of raw cellulose, as shown in Figure 2. The results of SEM image (250x magnification) at corn cob powder showed that originally cellulose fiber diameter has decreasing and fragmented into separated fiber and the average fiber diameter decreasing from 16.542 µm becomes 4.1355 µm after wet milling process. The particle size distribution of nanocellulose using the PSA showed that the produced cellulose have nanometer size with range 44.06 – 637.4 nm. However, the particle size diversity was quite high as the Pd% value was above 10%. The size of cellulose particles can affect the performance of hydrogels because there is a significant difference between micro and nano cellulose particle size which become the raw material of hydrogel. Microcrystalline Cellulose (MCC) has an irregular pore and is larger when compared to Nano Kristalin Cellulose (CNC) with a smaller and uniform pore size that will affect swelling ability [5].

Table 3. Particle size distribution and poly dispersity index of nanocellulose.

| Peak | Size (d.nm) | % Vol | Σ    | % Pd |
|------|-------------|-------|------|------|
| 1    | 44.06       | 10.9  | 4.570| 10.4 |
| 2    | 132.1       | 14.4  | 22.26| 16.9 |
| 3    | 637.4       | 23.8  | 17.19| 12.8 |
3.2 Swelling Ratio

The ratio of the hydrogel weight in the water-absorbing (swelling) state to its dry weight is one of the main parameters of hydrogel [12]. Figure 3 showed that increasing the concentration of epichlorohydrin (Ech) increased the ratio of swelling nanohydrogel. Ech is a crosslinking agent which can react with two or more functional groups of different molecules, such as hydroxyl groups of cellulose [9]. The more concentration of Ech, the more crosslinked hydroxyl groups that leads to the increased of nanohydrogel swelling ability. Nanohidrogel A2 (cellulose: solvent = 1: 2) has higher swelling ability than A4 (cellulose: solvent = 1: 4) nanohydrogel because the concentration of nanocellulose solution at A2 hydrogel is higher, ie cellulose: the solvent is 1: 2 so that when added Ech, the crosslinks formed will increase and the swelling ability will also increases.

Figure 3. Effect of Ech. concentration and solvent ratio on the swelling ratio of nanohydrogel.
Figure 4. The kinetics of swelling ratio Nanohydrogel A2 a) Nanohydrogel A4 b)

Figure 4 showed the kinetics of swelling ratio nanohydrogel for 1 hour. A higher swelling rate is required as well as a higher swelling capacity. It is well known that the swelling kinetics for the nanohydrogel is significantly influenced by factors such as swelling capacity, size distribution of particles and specific size area. The influences of these parameters on the swelling capacity have been investigated by various workers. Results indicated that as the particle size became smaller, the rate of absorption increased. This may be attributed to an increase in surface area with decreasing particle size of samples [13].

3.3 Determination of Gel Fraction

The gel fraction could also be used as a quantitative indicator for the efficiency of network formation [23]. Table 4 showed that the higher the Ech concentration (4-28%) the higher the gel fraction. This substantiated that more gelation occurred through the formation of more crosslinking networks in the sample with a higher crosslinker concentration [23]. Gel fraction (52%) was obtained from treatment solvent ratio 1:4 (A4) with Ech concentration of 28%. The amount of solvent on the A4 nanohydrogel leads to the formation of faster radicals resulting in many crosslinks being formed [10].

Nanohydrogel with 0% Ech concentration showed the higher gel fraction. This contain nanohydrogel solvent, PEG that can be crosslinked by (CG) chain-growth polymerization. CG polymerization is generally less controllable without crosslinker like Ech. Because monomers are crosslinked via polymer kinetic chains, the crosslink functionality is hardly controlled and network defects (e.g. loop) are more likely to form [23]. Therefore crosslink and network chain increase but by increasing the latter parameter there is less free volume or room to accommodate water and hence degree of swelling and molecular weight between two successive crosslinks decrease [24].

Table 4. Effect of Ech concentration and solvent ratio on the percentage gel fraction.

| Concentration (%) | Gel Fraction (%) |
|-------------------|------------------|
|                   | A2               | A4               |
| 0                 | 48 ± 0.7 b       | 56 ± 2 d         |
| 4                 | 41 ± 0.3 a       | 44 ± 0.3 a       |
| 16                | 43 ± 0.6 a       | 47 ± 0.6 b       |
| 28                | 44 ± 0.3 a       | 51 ± 1 c         |
3.4 Texture Analysis
Measurement of the physical properties of nanohydrogel was performed using texture analyzer with parameters tested including hardness, adhesiveness, cohesiveness and springiness. The texture of nanohydrogel in Table 5 showed that the higher the concentration of Ech, the lower the nanohydrogel hardness. This suggests that higher swelling ability makes the presence of dissolved substances during immersion of nanohydrogel so that some of the crosslinking of the nanohydrogel weakens. Moreover, the lower the hardness the cohesiveness and springiness will be lower also whereas the adhesiveness tend to be higher. It is appropriate that cohesiveness is an attractive attraction among similar molecules to illustrate how strong the crosslinking of the nanohydrogel is [24]. Meanwhile the springiness shows the ability of the nanohydrogel to return to its original state after get a pressure [24]. Adhesiveness is an attractive attraction between unkind molecules that describe how weak the crosslinking of nanohydrogels [24]. Adhesiveness represent inversely characteristics to cohesiveness.

| Solvent ratio | Ech concentration (%) | Hardness (mJ) | Adhesiveness (mJ) | Cohesiveness | Springiness (mm) |
|---------------|------------------------|---------------|-------------------|--------------|-----------------|
| 1:2           | 0                      | 2.11          | 0.05              | 0.79         | 4.61            |
|               | 4                      | 0.39          | 0.02              | 0.84         | 2               |
|               | 16                     | 0.38          | 0.06              | 0.63         | 1.51            |
|               | 28                     | 0.33          | 0.11              | 0.56         | 1.18            |
|               | 0                      | 2.35          | 0.03              | 0.71         | 4.76            |
|               | 4                      | 1.10          | 0.04              | 0.86         | 1.96            |
| 1:4           | 0                      | 0.47          | 0.04              | 0.79         | 1.60            |
|               | 4                      | 0.42          | 0.06              | 0.74         | 1.62            |

3.5 Surface Morphology
The surface morphology of the nanohydrogel with the chemical crosslinking method was presented in Figure 5. As explained before that the higher the Ech concentration, the more crosslinking formed, appeared from the figure to be more porous Figures 5(c) and 5(f) a which are nanohydrogels from A2 and A4 with a 28% Ech concentration, although their network structure tend to be agglomerated. In Figure 5 (a) nanohydrogel A2 with a 4% Ech concentration is still visible cellulose fibers that have not been crosslinked while Figure 5 b) has seen a cross link formed when the Ech concentration increased to 16%. SEM images support the formation of interconnected pore and capillary channels. A higher concentration of Ech produces a larger degree of polymer chains branching and generates an additional network. The capillary channels were clearly observed from SEM image and this may enable water to enter into the hydrogel networks [24]. Moreover, treatment of Ech crosslinking in cellulose results a macro porous internal structure. Increasing Ech cross linker will increase pore size. They justified this by the crosslinking process that occurred slowly with a strong self-association of the cellulose chains at low temperatures [25].
Figure 5. Surface morphology of Nanohydrogel a) A2 4% ; b) A2 16% ; c) A2 28% ; d) A4 4% ; e) A4 16% ; f) A4 28% (2000x magnitude).

4. Conclusion
The higher the Ech concentration the swelling ratio of the resulted nanohydrogel increasing. The lower solvent ratio tend to produce higher swelling ability. The best treatments were nanohydrogel with Ech concentration 28% and cellulose : solvent ratio 1:2 with characteristics as follows: 514% swelling ratio, 44% gel fraction and 0.33 mJ hardness, with morphology showed higher porosity. This hydrogel has a wide potential as water absorbent material in dry agricultural areas and can be used as fertilizer carrier agent.

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