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Cellulose-based nano hydrogel from corncob by gamma irradiation

Nurfadila¹, A Maddu¹, C Winarti² and M Kurniati^{1*}

¹Department of Physics, IPB University, Bogor, 16680, Indonesia

²Indonesian Center for Agricultural Postharvest Research and Development, Bogor, 16112, Indonesia

*E-mail address: mersikurniati@gmail.com

Abstract. Based on economic nomenclature of Indonesian food crops, corn is the second important commodity after rice. The high corn production correlates with corncob waste produced. The existence of corncob waste is abundant and continuous post-harvest. One alternative to utilize of corncob waste is the high content of cellulose processed to cellulose-based nano hydrogel. In this study, cellulose from corncob was processed into hydrogel by gamma irradiation. Cellulose size reduction is done by the wet milling process. The treatment tested of nano hydrogel control was cellulose dissolved in NaOH/PEG solvent whereas the ratio of cellulose: solvent was 1:2 and 1:4 and nano hydrogel by gamma irradiation that nano-cellulose solution was filtered by vacuum filtration. The aim of this research was to find out the characteristics of nano hydrogel by gamma irradiation. Parameters observed were swelling ratio, gel fraction, texture and morphology. The result showed that the treatment test of nano hydrogel without gamma radiation has 111% and 127% swelling ratio, meanwhile, nano hydrogel with gamma irradiation has a 214% swelling ratio, 99% gel fraction and 1.17 mJ hardness with morphology showed higher porosity. The higher swelling ratio of nano hydrogel by gamma irradiation has the potential for application in agriculture as water absorbent material and fertilizer carrier agent.

1. Introduction

Corn is a cereal plant of the grass family (Poaceae) that can grow well in tropical countries such as Indonesia. Corn production in Indonesia is quite high because corn is the second important commodity after rice. The high production of corn correlates with the corncobs waste produced. According to the Central Bureau of Statistics (BPS), corncobs waste in Indonesia is estimated to increase by 5.7 tons/year [1]. The existence of abundant corncobs is usually discarded and deemed not useful so it can cause environmental pollution because until now, the use of corncobs waste is only used as animal feed ingredients [2]. Actually, corncobs can be reprocessed by utilizing the content contained therein, such as lignin (15%), cellulose (45%) and hemicellulose (35%) [3]. The cellulose content in large quantities has the potential to be used as biodegradable materials.

Cellulose is the most abundant carbohydrates in nature that has many hydroxyl groups and serve a variety of functions, such as water storage because it has high water absorbing ability [4]. Therefore, cellulose in corncobs can be used as a raw material of hydrogels. A hydrogel is a three-dimensional polymer network with crosslinked, which is capable of swelling or storing water [5].

Based on its properties, the hydrogel is used for drug delivery [6], tissue engineering [7], separation [8], and as support carriers in biomedical and agricultural applications [9]. Hydrogels can be synthesized



from synthetic polymers or natural polymers [5]. Synthetic polymers such as polyhydroxyethyl methacrylate (pHEMA), polyacrylamide, and polyvinyl alcohol come from petroleum derivatives so that the resulted hydrogels are difficult to decompose in nature [10]. Therefore, efforts to reduce the use of synthetic polymer-based hydrogels must be carried out by developing natural polymers that have advantages such as environment-friendly (biodegradable), non-toxic (non-toxic) and raw materials are abundant [11].

The process of formed three-dimensional tissue (crosslinking) on hydrogels can be done by using chemical crosslinking and gamma irradiation methods [12]. Both of these methods each have advantages and disadvantages. Some of the advantages of crosslinking methods using gamma irradiation compared to conventional methods included the process can be done quickly, the catalyst was not needed, crosslinker and initiator were not needed during the polymerization, and there is no residue in the process [13]. In addition, the regulation of irradiation doses absorbed by the material can be varied to increase the water-absorbing ability of the hydrogel.

The water absorption capacity of hydrogels can also be increased by reducing cellulose particles to nano-cellulose. Nanocellulose-based hydrogels have a higher absorption rate and degree of swelling compared to micro cellulose [14] because that smaller particle has important characteristics is their large ratio of surface area to volume so more atoms are available to interact with the atoms or ions of other substances [15].

Processing of corncobs waste into nano hydrogel was necessary to be carried out so that nano hydrogel was obtained with the high swelling ability and gel fraction and good mechanical strength so that it can be optimized in various fields. The objective of the study was to analyze the effect of gamma irradiation on the characteristics of the nano hydrogel. We certify that the study is our work that all sources and materials of the product received have been acknowledged.

2. Materials

Corn cob as a raw material in this study was originated from Sukabumi, West Java. Chemicals used were sodium hypochlorite (NaClO), sodium hydroxide (NaOH 8%), and Polyethylene glycol (PEG 4%). Equipment used was magnetic stirrer, digital balance, hot plate, cold room freezer, and oven. Equipment used for hydrogel characteristics testing are Particle Size Analyzer (PSA) Malvern to find out the particle size distribution, Ultrafine grinder (Masuko Corp, Japan) to reduce the size of cellulose, Texture Analyzer Texture Pro CT V1.2 Build 9 and Scanning Electron Microscopy (SEM) Zeiss EVO MA10 to find out the structure and morphological properties of hydrogel. All equipment was supplied by the Indonesian Center for Agricultural Postharvest Research and Development, Cimanggu-Bogor. The other equipment is Irradiator 60Co Gammacell 220 at Isotope were supplied by Radiation Application Center (PAIR) BATAN Cinere, Pasar Jumat.

3. Methods

3.1. Nanohydrogel preparation

The first step was the proximate analyze of a corn cob. Cellulose extraction began with a delignification process to degrade lignin to obtain pure cellulose. The delignification process was carried out for 3 kg corn cobs powder by using 8% NaOH solution of 25 liters, using an autoclave. The temperature was increased to 110 °C and then held for 30 minutes at a pressure of 1.5 bar. Corn cob becomes blackish brown due to the delignification process. Bleaching process was carried out by using a 20-liter NaClO solution at room temperature for 1 hour. After that, the bleached material was rinsed on running water several times until reach neutrality. The cellulose of corncobs was then vacuum pressed to reduce water content. The resulted cellulose of corncobs was then stored in a cold room (4 °C).

Nanocellulose preparation by a wet milling process was carried out by using ultrafine-grinder with a ratio of cellulose: aquadest at 1:10 (2% of its dry weight). The resulted nano-cellulose solution was

dissolved by PEG (4% wt/vol) and NaOH (8% wt/vol) solution. The treatment tested was the ratio of nano-cellulose solution to PEG/NaOH solvents, were 1: 2 known as C2 samples and 1: 4 known as C4 samples. The solution stored in a cold room (4 °C) for 1 day. After that, the solution samples was filtered by vacuum filtration and dried in an oven for 6 hours at 60 °C. The dry sample was a control sample without the effect of gamma irradiation which was then stored for analysis.

The cross-linking process of nano hydrogel was carried out by gamma irradiation technique. The treatment test was nano-cellulose without filtered (G1) and nano-cellulose was filtered by vacuum filtration (G3). Then nano-cellulose was irradiated at the doses 20 kGy by gamma rays at a dose rate of 5.4 kGy/hours. After this process, the solution was filtered by vacuum filtration and dried in an oven for 6 hours at 60 °C. The dry sample was a sample with the effect of gamma irradiation which was then stored for analysis.

3.2. Analysis

Characteristics of nano hydrogel were analyzed by the following parameters: swelling ratio, gel fraction, particle size distribution, surface morphology, and physical analysis were studied by PSA, SEM and texture analyzer, respectively.

3.2.1. Swelling measurements. The swollen nanohydrogels were weighted after wiping out excess water from the surface. The swelling properties were determined by the swelling ratio (%) through the following equation:

$$\text{Swelling Ratio (\%)} = \frac{W_s}{W_d} \times 100 \% \quad (1)$$

where W_s and W_d are the weight of nano hydrogel at swelling and dry state, respectively [16].

3.2.2. Determination of gel fraction. After the swelling experiment, nano hydrogel was dried in an oven until the weight is constant. After that, the nano hydrogel was reweighed. The gel fraction was calculated as follows:

$$\text{Gel Fraction (\%)} = \frac{W'}{W_0} \times 100 \% \quad (2)$$

where W' refers to the dry nano hydrogel when the weight is constant and W_0 is the initial weight of dry nano hydrogel [17].

3.2.3. Texture Analysis. Texture analysis was done by using Texture Analyzer. The sample will be pressed using an analytic probe with the appropriate depth level [18]. Hardness is the strength level of a sample to receive a load until it reaches deformation. Besides hardness, texture analyzer can be analyzed by the following parameters, such as adhesiveness, cohesiveness, and springiness.

4. Results and Discussion

4.1. Proximate and chemical analysis

The raw material of corncobs powder was analyzed proximate included carbohydrate, water, protein, lipid and ash content can be seen in Table 1. The resulted of the analysis was meet to the Indonesian National Standard (SNI) 01-4483-1998 except for lipid and protein [19]. The standard of lipid content minimum 3% and protein content minimum 7.5%. The difference might result from a different variety of corn. However, the corncobs had a high carbohydrate content that was very potential to be further processed.

Table 1. Proximate analysis of corncob

Parameters	Content (%)
Carbohydrate	90.96
Water	3.53
Protein	2.32
Lipid	1.66
Ash	1.54

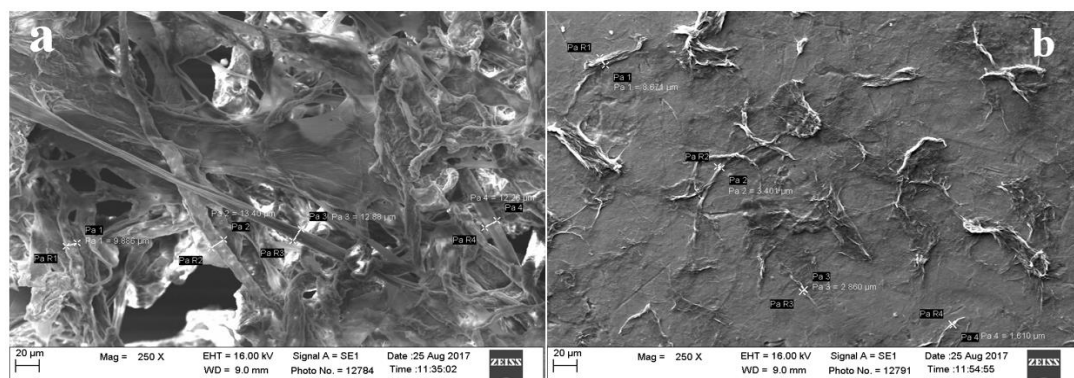
Analysis of cellulose and lignin content in corncobs was presented in Table 2. After the delignification process, corncobs the cellulose content was 96.42% and lignin content of 23.98%, respectively. Meanwhile, the cellulose content of corncobs raw material was 57.60% and lignin content was 10.74%. It can be concluded that lignin was degraded to cellulose due to the delignification process so that the lignin content was decreased and the cellulose content was increased [20].

Cellulose was processed by using an ultrafine grinder with a wet milling process to produce nano-cellulose. After the wet milling process, the resulted nano-cellulose showed much smaller fiber diameter than initial cellulose as can be seen in Figure 1. SEM images showed that corncobs powder initially had rough fiber diameter, however, after the wet milling process, the cellulose has much degraded the size of the fiber diameter was much finer. The nano-cellulose particle size distribution was analyzed by using Particle Size Analyzer (PSA) as can be seen in Figure 2 and Table 3. Nanocellulose had nanometer size with high diversity as can be seen from the high %Pd value.

According to Table 3, the particle size diversity was quite high as is shown in the value of polydispersity index (Pd%) that was above 10%. This particle size is one of the characteristics that can affect the hydrogel swelling properties. Smaller and uniform pore sizes like Nanocrystalline Cellulose (CNC) compared to larger and irregular pore sizes like Microcrystalline Cellulose (MCC) will produce hydrogels with different absorption capabilities. CNC will have a higher degree of swelling than MCC [21].

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

No.	Material	Water content (%)	Lignin content (%)	Cellulose content (%)
1.	Corncoobs before delignification	3.46	23.98	57.60
2.	Corncoobs after delignification	79.10	10.74	96.42

**Figure 1.** Surface morphology of corncoobs powder (a) and nano-cellulose resulted from wet milling process (b) (magnitude 250x)

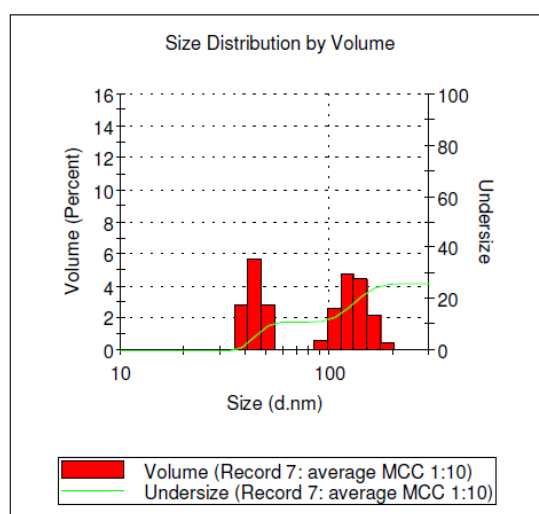


Figure 2. The particle size distribution of nano-cellulose

Table 3. Particle size distribution and polydispersity index of nano-cellulose

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

4.2. Swelling Ratio

One of the important parameters of the hydrogel is the ratio of the weight of the swollen hydrogel to dry hydrogel [22]. Table 4 shows the nano hydrogel swelling ratio. Nanohydrogel has a higher swelling ratio when irradiated. From the data, it can be inferred that the swelling ratio of C2 control nano hydrogel (the ratio of cellulose to solvent was 1: 2) has lower swelling ability than C4 control nano hydrogel (the ratio of cellulose to solvent was 1: 4). C4 nano hydrogel has a higher concentration of solution so that the swelling ability and the crosslinking that formed will increase.

The dose was used for irradiation methods greatly affects the characteristics of the hydrogels produced. Nanohydrogel with gamma-ray irradiation methods has a high swelling ratio value above 200% based on Table 4. Radiation methods utilize high-energy radiation such as gamma radiation that has resulted in the formation of a three-dimensional network of crosslinked hydrogel [23]. Its molecular structure of nano-cellulose which is sensitive to radiation exposure formed free radicals, at the end of the process the free radical reaction formed a hydrogel with an interpenetrating network (IPN) that allows the entry of organic or inorganic substances into it [24]. This showed that if the network contact with water or an aqueous solution, it will absorb water and solutes so that nano hydrogel can swell.

Table 4. The swelling ratio of nano hydrogel

Nanohydrogel	Swelling Ratio (%)
C2	111
C4	127
G1	204
G3	214

4.3. Gel fraction

The evaluation of the gel fraction showed the number of crosslinked was formed [17]. The gel fraction data are presented in Table 5. Control nano hydrogel showed gel fraction value is around 50%. It caused by PEG which is cross-linked with uncontrolled chain-growth (CG) polymerization even without a crosslinking agent. It can occur because the monomers are crosslinked through the polymer kinetic chain [25]. Therefore, the value of the gel fraction was increased. However, there was still a volume or free space to absorb water so that the swelling ratio was decreased [26].

The gel fraction is significantly higher when the polymer was irradiated with a high dose rate [23]. A dose rate of 20 kGy on cellulose-based nano hydrogel has a high gel fraction as presented in Table 5.

When radiation interacts with matter, the material absorbs energy and becomes active such as radicals are produced, thereby, initiating chemical reactions. [27]. High dose radiation resulted in the formation of radicals which uncontrolled so that many crosslinked are formed.

Table 5. Gel fraction of nano hydrogel

Nanohydrogel	Gel Fraction (%)
C2	48
C4	56
G1	99
G3	99

4.4. Texture Analysis

Texture analysis was carried out to determine the physical properties of nano hydrogel which included hardness, adhesiveness, cohesiveness, and springiness. It can be seen from Table 6. G3 nano hydrogel has a lower hardness value than G1. It caused by the presence of substances was dissolved in the water when the hydrogel was swollen so that some crosslinking in the nano hydrogel were weakened and hardness was decreased.

Table 6 showed that the lower hardness, the lower cohesiveness, and springiness, while the higher adhesiveness. It is appropriate that cohesiveness is a measure of the attraction of the group to its members that illustrated the strength of crosslinking on nano hydrogel while springiness illustrated the elasticity properties of nano hydrogel, that its ability to return to its original shape after pressure[28]. Adhesiveness represents inversely characteristics to cohesiveness, that an attraction between non-similar molecules and illustrated how weak the crosslinking is on the nano hydrogel [26].

Table 6. Texture analysis of nano hydrogel by gamma irradiation

Nanohydrogel	Hardness (mJ)	Adhesiveness (mJ)	Cohesiveness (mJ)	Springiness (mJ)
C2	2.35	0.03	0.79	4.76
C4	2.11	0.05	0.71	4.61
G1	1.47	0	0.77	4.56
G3	1.17	0.02	0.69	3.95

4.5. Surface Morphology

The surface morphology of nano hydrogel using SEM at 2000x magnification was shown in Figure 3, the surface of the C4 nano hydrogel has seen a crosslink formed when compared to C2. The effect of the higher solvent ratio showed that one of the polymers used, Polyethylene glycol (PEG) can form polymer complexes on organic molecules [29].

Nanohydrogel with gamma irradiation methods has a uniform surface structure as shown in Figure 4. G1 nano hydrogel and G3 have seen to be cross-linked to the polymer network structure. The high dose of radiation caused many cross-linked formed. The crosslinking in the G1 nano hydrogel looked more formed than the G3. It was caused by the water content in the G1 nanohydrogels that the treatment

was not filtered by vacuum filtration affected the radiolysis process where the water functions as an inductor to formed free radicals [30].

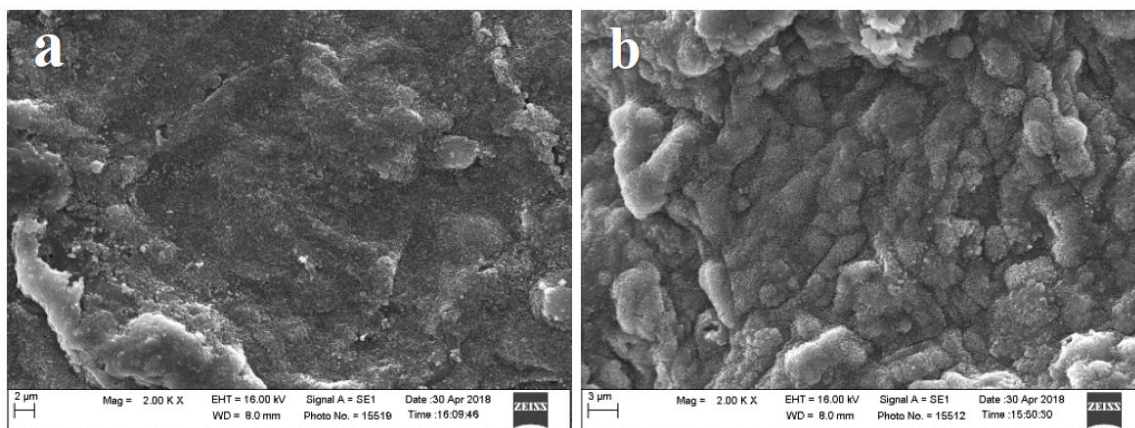


Figure 3. Surface morphology of nanohydrogel C2 (a) C4 (b) (magnitude 2000x)

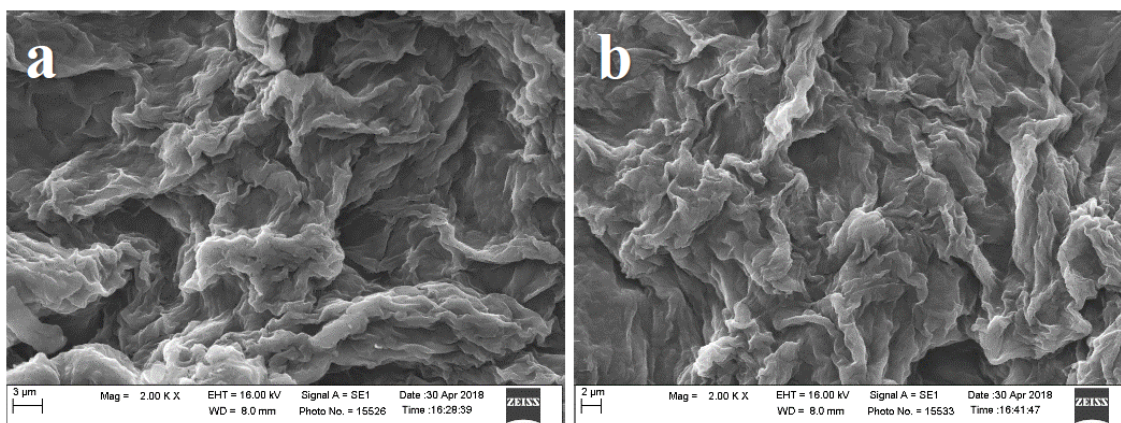


Figure 4. Surface morphology of nano hydrogel G1 (a) G3 (b) (magnitude 2000x)

5. Conclusion

Nanohydrogel with gamma irradiation methods has a high swelling ratio value above 200% and the gel fraction is significantly higher when the polymer was irradiated with a high dose of 20 kGy with a dose rate of 5.4 kGy/hours. The dose was used for irradiation methods greatly affects the characteristics of the hydrogels produced with parameters including swelling ratio, gel fraction, mechanical properties and surface morphology. The higher swelling ratio of nano hydrogel by gamma irradiation has the potential for application in agriculture as water absorbent material and fertilizer carrier agent.

Acknowledgments

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