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Effect of Acrylamide and Potassium Persulfate on The Characteristics of Water Hyacinth-Carrageenan Bead Gel Using Microwave Grafting Method

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ABSTRACT

The cellulose of water hyacinth (Eichhornia crassipes) can be used as raw material in bead gel production. This research prepared hydrogel by grafting acrylamide (AA) monomers onto the water hyacinth cellulose (WH cellulose) as the backbone using the microwave method. This research aimed to determine the influence of adding AA and potassium persulfate (PPS) as initiators of water's swelling capacity characteristics. The WH cellulose was mixed with water and varying additions of 4, 7, and 10 g acrylamide (AA) and 0.05, 0.10, and 0.15 g PPS to undergo a grafting reaction. The obtained gel was washed and soaked in the acetone to remove the unreacted AA and PPS. The resulting precipitated solid was dried and called Water Hyacinth Cellulose Grafted Polyacrylamide (WH cellulose-g-PAA). The mixture of carrageenan with WH cellulose-g-PAA underwent crosslinking using aqueous KCl and $CaCl_2$ after passing through the palm oil layer to form bead gel. The properties of the dried bead gel were tested for functional groups using FTIR and for swelling capacity in water. Based on the FTIR test results, it can be concluded that AA monomers were successfully grafted onto the water hyacinth cellulose backbone due to the appearance of N-H and C=O groups in WH cellulose g-PAA which previously did not appear in WH cellulose. The highest swelling capacity in the AA variation with the cellulose, AA, and KPS mixture were 1, 7, and 0.15 g, respectively. Meanwhile, in the KPS variation, the mixture was 1 g, 10 g, and 1 g, respectively. The addition of AA that is too low or too high will reduce the swelling capacity, as well as PPS.

1. Introduction

Hydrogels have a three-dimensional structure composed of interconnected hydrophilic groups that can absorb and retain water significantly [1]. Hydrogel in the form of granules is called bead gel. In the agricultural sector, hydrogel is used as a growth medium. They can reduce irrigation frequency by up to 50%. Hydrogels can be made from synthetic and natural polymers. Synthetic polymers have good absorption properties and are strong and durable but cannot be broken down [2]. Natural polymers, especially polysaccharides, have been investigated and received much attention due to their biodegradability, biocompatibility, hydrophilicity, and good mechanical strength [1]-[10]. Our laboratory is developing the chemical structure modification of natural polymers to enhance the properties of origin polysaccharides [11]-[16].

In Indonesia, there is an abundant growth of water hyacinth (*Eichhornia crassipes*). This plant is often seen as a severe threat due to its rapid growth [17]. However, water hyacinth has not been fully

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utilized, so it causes negative impacts on the surrounding environment. One of the impacts is blocking lakes' surface and destroying natural ecosystems. Water hyacinth is a valuable material that can be used as a natural raw material for hydrogel production due to its high cellulose content of approximately 40.5%. In the present work, we combined cellulose of water hyacinth and carrageenan as raw materials for bead gels. Carrageenan is a sulfated galactan as a structural polysaccharide belonging to the Rhodophyceae class [18]. Carrageenan is widely used as a thickener, texture modifier, and gelling agent [18]. Carrageenan can be an ingredient in making hydrogels because it increases viscosity [20].

The cellulose structure needs to be modified to become a hydrogel. One of the modification routes is grafting hydrophilic material into cellulose backbone. In Yusof et al.'s previous work [2], hydrophilic acrylamide was grafted onto the cellulose backbone, which was extracted from the waste newspaper. This process was done using microwave radiation, and the Fourier Transform Infrared Spectroscopy (FTIR) test confirmed the success. Using the free radical polymerization technique, Omer et al. [21] also grafted carboxymethyl cellulose (CMC) with acrylamide. That process can improve the swelling degree with a maximal value of 17.770%. The use of initiators in grafting can increase grafting efficiency. Potassium persulfate was chosen as the initiator because this compound has more ability than other types of initiators in terms of forming free radicals at the copolymerization initiation stage. Research conducted by Syafiq et al. shows that using a potassium persulfate initiator provides higher grafting efficiency than using ammonium persulfate [21].

To our knowledge, there is no study preparation of bead gel based on water hyacinth cellulose and carrageenan grafted with acrylamide and potassium persulfate as initiators and using microwave as the energy source. This work contribution is on studying the effect of the amount of acrylamide (AA) and potassium persulfate (PPS) on the swelling capacity of the bead gels. The obtained bead gels were characterized using FTIR and swelling capacity measurement in distilled water.

2. Research Methodology

2.1. Materials

Water hyacinth (*Eichhornia crassipes*) were harvested from Waduk Cengklik, Surakarta, Indonesia. All chemicals, including acrylamide, potassium persulfate ($K_2S_2O_8$), sodium hydroxide (NaOH), potassium chloride (KCl), and calcium chloride ($CaCl_2$), were purchased from Merck. Other chemicals were supplied from the local market, such as carrageenan, 96% technical ethanol (CV. Saba Kimia, Surakarta), acetone, palm oil, and distilled water (CV. Agung Jaya, Surakarta Indonesia).

2.2. Procedures

1) Preparation of Water Hyacinth Cellulose

Freshwater hyacinth was washed using tap water, and the stem was recovered. The stem was chopped and dried in an oven at 90°C to a constant weight. Afterward, the stem was crushed using a miller. The delignification process was done by wetting the water hyacinth powder with a 1.5 N NaOH solution in a 1:10 (w/v) ratio and then heated in a microwave at 90 W for 10 minutes [20]. Then, the cellulose from the stem was neutralized using distilled water and dried in an oven at 45°C to a constant weight.

2) Synthesis of Grafted Polymer

Cellulose from the stem was dissolved in 30 mL of distilled water and then mixed with various amounts of AA, which had been dissolved in 20 mL of distilled water with a stirring speed of 300 rpm for 20 minutes. After that, multiple quantities of PPS were added, and the mixture was stirred for 15 minutes. The amount of cellulose, acrylamide, and PPS are shown in Table 1. The grafting process was done by heating the mixture in a microwave at 630 W for 200 s, with the cooling cycle temperature below 75°C. Every 20 s, the mixture was removed and placed in an ice bath until it reached room temperature. Then, the mixture was left at room temperature for 24 hours. An excess of acetone was added to the mixture and left for 1 hour to remove the unreacted AA and PPS. The mixture was then filtered to obtain the solid part, dried at 45°C to a constant weight, and then weighed and crushed. The grafted polymer product was Water Hyacinth Cellulose Grafted Polyacrylamide (WH cellulose-g-PAA).

Table 1. The varying sample composition

Code[a]	Component		
	Cellulose Mass (g)	*AA (g)*	*PPS (g)*
AC	1	4	0.15
BC	1	7	0.15
CA	1	10	0.05
CB	1	10	0.10
CC	1	10	0.15

[a] The first letter of the code describes various amounts of AA, and the second letter describes various amounts of PPS.

3) Production of Bead Gel

The mixture of WH cellulose-g-PAA powder, 1 g, and carrageenan, 1 g, was dissolved in distilled water and then heated until the temperature reached 85°C and called bead gel solution. After that, the crosslinking solution was made by mixing 100 mL of 0.2 M $CaCl_2$ solution and 100 mL of 0.2 M KCl solution into a 1000 mL beaker glass. Then, 40 mL of palm oil was added to the crosslinking solution. Bead gel solution was injected drops into a syringe into a crosslinking solution. This bead gel formation was done in glass and placed in an ice bath. The formed bead gel was left for 2 minutes and then filtered. The bead gel was soaked in 200 mL of 96% ethanol for 4 hours. Afterward, it was filtered again and dried to a constant weight.

4) Swelling Capacity Test of Bead Gel

Swelling capacity was the ability of a bead gel to expand as the water medium entered its structure. Before the immersion process, three similarly sized bead gels were weighed and called the dry weight (Md). Then, those bead gels were immersed in distilled water for 4.5 hours. The bead gels were weighed every 30 minutes and called the wet weight (Mw). The calculation of the swelling capacity can be described by Equation (1).

$$Swelling\ capacity = \frac{Mw - Md}{Mw} \times 100\% \tag{1}$$

5) Fourier Transform Infrared (FTIR) Spectroscopy Test

FTIR analysis was conducted using an FTIR spectrophotometer to identify the spectra of water hyacinth cellulose, acrylamide, and WH cellulose-g-PAA powder (Shimadzu, IRspirit). The samples were analyzed in the wavelength range between 400 – 4000 cm^{-1}.

3. Results and Discussion

3.1. The Effect of Acrylamide Monomer on Swelling Capacity

Natural water hyacinth cellulose has low swelling capacity and less stable mechanical properties. Therefore, the structure of cellulose needs to be modified. One of the options is microwave grafting of the monomer onto the cellulose backbone, which can improve its properties. Acrylamide monomer forms a covalent bond with the cellulose backbone, producing polymer [22]. Additionally, acrylamide contains hydrophilic groups with high water absorption capacity and quickly reacts to electrophiles and free radicals, thereby increasing the swelling capacity [23], [24]. The data for microwave grafting with various amounts of acrylamide are shown in Table 2.

Table 2. The result of grafted polymer WH cellulose-g-PAA with acrylamide amount variation

Code	WH Cellulose-g-PAA (g)	Form
AC	3.66	Solid
BC	7.89	Solid
CC	5.68	Solid

Sample BC resulted in the highest yield of WH cellulose-g-PAA. In this sample, AA provides enough monomer to be activated by PPS to bind completely to the active sites of backbone cellulose to produce maximum polymer bonding. In the AC sample, the amount of AA is too tiny for a fixed amount of PPS, causing the termination reaction to be faster so that fewer polymer bonds are formed.

There will be ungrafted active sites on the cellulose backbone [1]. For the CC sample, the amount of AA is too much in a fixed amount of PPS, which causes AA to bind to each other, resulting in homopolymerization, so the yield of the grafted polymer decreased [25].

Fig.1. shows the swelling capacity as a function of time immersion (t, min). Fig.1. and Table 3 show the results of swelling capacity in distilled water for 4.5 hours. The swelling capacity was calculated using Equation (1). From 0 to 60 minutes, all variations of AA show a similar increasing trend in swelling capacity. After a minute, sample BC still shows a growing trend, while the samples AC and CC show a decreasing trend. Data collection was stopped at 270 minutes because the gel beads had begun to break slowly.

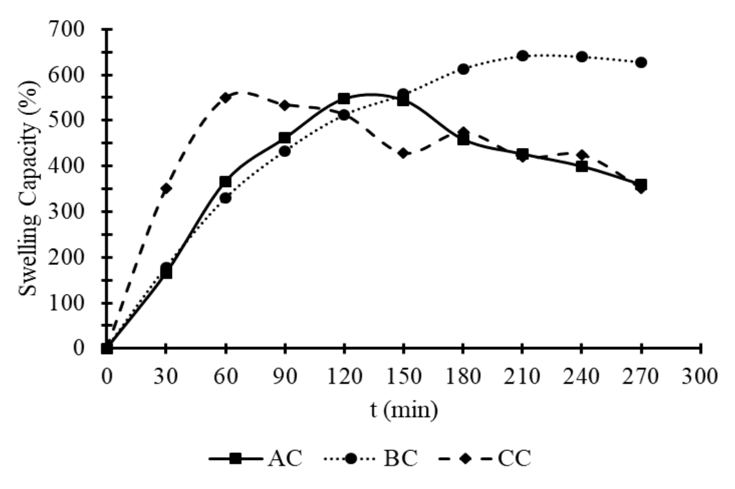

Fig. 1. The Curve of Swelling Capacity Values with Time for Acrylamide Variation

If the amount of AA is too low, there are still active groups from cellulose that have not been polymerized, resulting in a low ability to bind water molecules (sample AC). Otherwise, the monomer tends to form polyacrylamide (homopolymer) and is not wholly grafted onto the cellulose backbone. This also leads to a reduction of the ability to bind water molecules (sample CC). In both samples, swelling capacity tended to decrease after a specific time.

3.2. The Effect of Potassium Persulfate Initiator on Swelling Capacity

As an initiator, potassium persulfate (PPS) forms free radicals that provide active sites between the cellulose backbone and acrylamide monomer in the grafting process, resulting in a higher percentage of grafting [21]. The data for microwave grafting with various amounts of PPS are shown in Table 4. The highest yield of WH cellulose-g-PAA is observed with sample CC. This result is suitable with Omer et al. [21], which suggests that with increasing PPS, the free radicals increased, enhancing the cellulose backbone's active sites.

Table 3. Image bead gel before and after swelling test of 4.5 hours for amount AA variation

Code	Appearance of Bead Gel		Swelling Capacity (%)
	Before	***After***	
AC			547.24
BC			641.09
CC			549.20

Table 4. The result of grafted polymer WH Cellulose-g-PAA with Potassium Persulfate Amount Variation

Code	WH Cellulose-g-PAA (g)	Form
CA	3.32	Solid
CB	7.97	Solid
CC	9.51	Solid

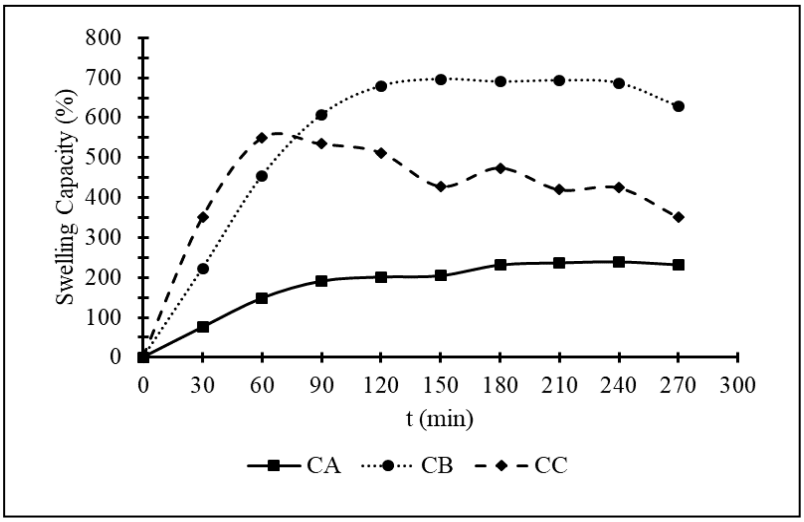

Fig. 2. The Curve of Swelling Capacity Values with Time Immersion for PPS Variation

Table 5. Image bead gel before and after swelling test of 4.5 hours for the amount of PPS variation

Code	Appearance of Bead Gel		Swelling Capacity (%)
	Before	*After*	
CA			239.45
CB			696.35
CC			549.20

The value of swelling capacity is obtained from equation (1) by soaking the bead gel in distilled water for 4.5 hours. Fig. 2 shows that the sample CC dissolved within 3 hours, while the sample CA and CB still absorbed the distilled water within 4.5 hours. Data collection was stopped at 270 minutes because the gel beads had begun to break slowly.

If the amount of PPS is too high, the yield will decrease because of termination reactions, resulting in imperfect grafting of AA onto the cellulose backbone (sample CC). Otherwise, low PPS will only initiate a small amount of AA to be grafted onto the cellulose backbone so that the polyacrylamide chains will be shorter and can only hold a small amount of water as in sample CA. This is supported by a study conducted by Rop et al. [1], which investigated the effect of the initiator ammonium persulfate (APS) on the grafting of monomers onto the cellulose backbone. Low initiator concentration will reduce the polymerization rate, so the initiator is utilized to generate macro-radial sites in cellulose where monomers can be grafted [1].

3.3. FTIR Test Result

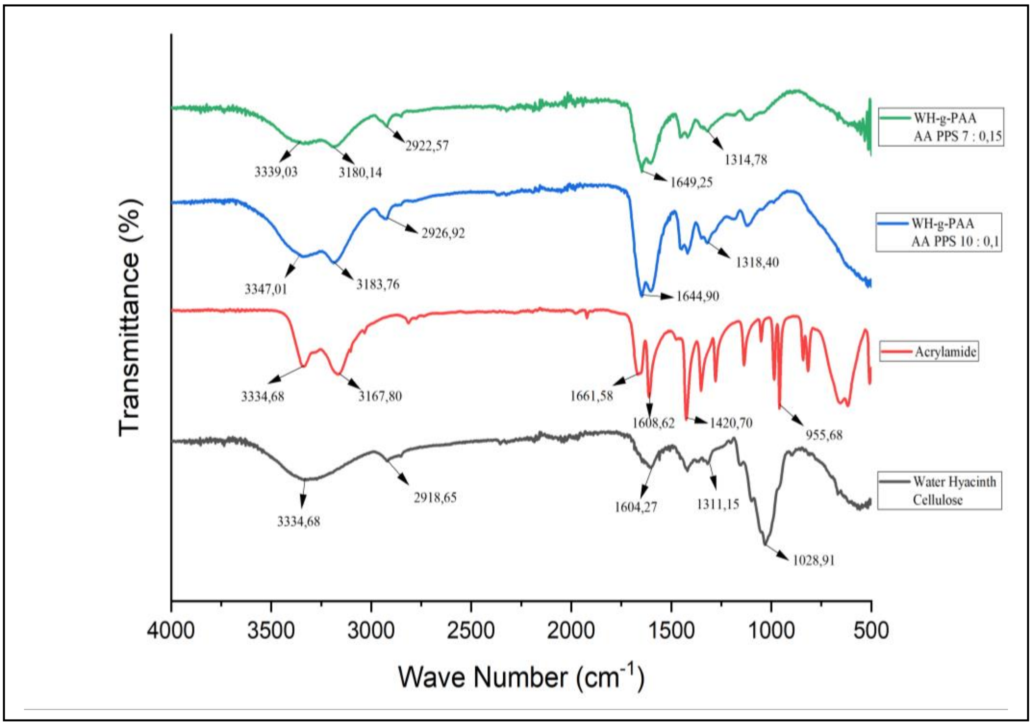

Fig. 3. Comparative of Chemical Functional Groups between Samples BC, CB, Acrylamide, and Water Hyacinth Cellulose

Qualitative analysis using FTIR revealed several stretching peaks, as shown in Fig.3. The FTIR spectrum of WH cellulose-g-PAA, compared to acrylamide and water hyacinth cellulose, showed peaks at 3180.14 cm^{-1} and 3183.76 cm^{-1}, which correspond to the N-H group. Additionally, there were peaks at 1649.25 cm^{-1} and 1644.9 cm^{-1}, corresponding to the C=O group. These groups originated from acrylamide and were not present in WH cellulose. This indicates the successful grafting process of acrylamide onto the water hyacinth cellulose backbone. This result is suitable with the Rop et al. [1], which grafted N, N-methylene-bis-acrylamide onto the cellulose backbone, showing peaks at 3032.1 cm^{-1} (N-H group) and 1647.21 cm^{-1} (C=O group).

4. Conclusion

Water hyacinth is a waste that is rarely used. The cellulose of water hyacinth can be used as a raw material for bead gel. This research was conducted to determine the effect of acrylamide and potassium persulfate on the swelling capacity of water hyacinth-carrageenan-based bead gel. The research results show that the variation amount of AA and PPS impacts the swelling capacity of the bead gel. The high addition of AA and PPS reduced swelling capacity. Likewise, adding too low AA and PPS will lessen the swelling capacity. In the case of AA variation, the highest swelling capacity was attained from a mixture of 1 g cellulose, 0.15 g PPS, and 7 g AA. Meanwhile, the highest swelling capacity was obtained from a mixture of 0.10 g PPS, 1 gram cellulose, and 10 g AA for the PPS variation.

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