EQUILIBRIUM JOURNAL OF CHEMICAL ENGINEERING
*Homepage:*https://jurnal.uns.ac.id/equilibrium

Bead Gel Preparation from Cassava Baggase Grafted Acrylamide and Carrageenan

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DOI: *https://dx.doi.org/10.20961/equilibrium.v8i2.85999*

Article History
Received: 16-04-2024, Accepted: 31-01-2025, Published: 02-02-2025

Keywords:

ammonium persulfate, bead gel, grafting microwave, swelling capacity, cassava bagasse

ABSTRACT. This research intends to prepare bead gels for medium of plant growth. Bead gels were prepared by grafting cassava bagasse by acrylamide with ammonium persulfate (APS) as the initiator using microwave energy. This research aims to examine the effect of the ratio of acrylamide to APS initiator on the swelling capacity. Briefly, cassava bagasse powder 1 g in 80 ml distilled water was mixed with acrylamide and APS to form grafted polymer by applying microwave. The resulted grafted polymer powder then was mixed with carrageenan to create bead gels. The formed bead gel was soaked in distilled water to test the swelling capacity. The highest swelling capacity in this research is 1193% at a ratio of 0.1 g APS (10 g acrylamide). Therefore, the swelling capacity increases with an increase in the ratio of acrylamide and APS. From the results of swelling capacity and FTIR, it can be concluded that the grafting process of cassava bagasse and acrylamide has been successfully conducted.

1. INTRODUCTION

Hydrogel is hydrophilic polymer macromolecule in the form of a cross-linked network and has the ability to expand in water (swelling). It can absorb a lot of water since it has a three-dimensional, interconnected network [1]. For several uses, hydrogels have undergone substantial development and research. For example, in agriculture, hydrogels are used as a growing medium to maintain soil moisture over an extended period and reduce the risk of drought in plants by acting as water reservoirs and releasing water slowly [2].

This research intends to prepare bead hydrogel as growth plant medium in agriculture field. A hydrogel that resembles tiny beads is known as bead gel. Less than 0.4 cm in diameter the size of bead gel, allows for rapid diffusion of solutions within the solid as opposed to mass transfer between phases [3]. Currently the nonbiodegradable synthetic polymers are still used raw material for forming hydrogel. A different strategy is required for preparing bead gel from natural polymers which show biodegradable properties.

Many researchers are interested to develop the use of natural polymers. Natural polymers have demonstrated their sustainability, high biodegradability, and non-toxic base components [4]. Cellulose and starch are kind of natural polymers obtained from renewable sources that is biodegradable and available in abundance [5]. One underutilized source of cellulose is cassava bagasse. Cassava bagasse is a byproduct of the tapioca industry and contains high cellulose content [6]. The cellulose content of cassava bagasse is approximately 39.37%. Raw cassava consists of around 22% cassava bagasse. Its utilization is not yet fully optimized, resulting in an abundant supply [7]. Additionally, its high cellulose content makes cassava bagasse is as a potential raw material for bead gel production. This research developed the underutilization and abundance of cassava bagasse as raw material for preparing bead gel.

Cassava bagasse cellulose have low absorption capacity and less stable mechanical properties. Therefore, modification of structure molecule of cassava bagasse is necessary using a combination of grafting and cross-linking methods to produce hydrogels with high swelling capacity and stable mechanical properties. Grafting is performed by grafting hydrophilic groups of acrylamide onto the main polymer chain of cassava bagasse cellulose. The grafting of monomers onto the polymer structure will alter the main properties of the polymer, such as hydrophilic characteristics, increased elasticity, water absorption, and ion exchange abilities, as well as heat resistance. Subsequently, crosslinking is carried out to create a three-dimensional bead gel structure within the polymer chain.

The synthesis method employed is grafting method, which involves grafting cassava bagasse cellulose with acrylamide using microwave energy. The grafting reaction method using microwave requires relatively shorter time and only requires a small amount of solvent for faster and more homogeneous heating [8]. Like the research conducted by Hosseini [9], ammonium persulfate (APS) and potassium peroxodisulphate (KPS) were used as initiator for the graft copolymerization process with aniline in aqueous media. Initiator acts as a free radical initiator that initiates the cassava bagasse cellulose to form an active radical main chain that reacts with acrylamide monomers.

Based on the literature review, there seems to be no previous research on bead gel production from cassava bagasse and acrylamide with APS as the initiator using microwave energy. In this paper, grafted cassava bagasse was mixed with carrageenan polymer extracted from red seaweed for producing bead gel. The carrageenan was chosen due to carrageenan's thickening properties. The desired properties of the hydrogel are water superabsorbent, meaning it exhibits high water absorption capacity, making it suitable for use as a growing plant medium. The water absorption capacity is indicated by the swelling capacity value. This research aims to examine the effect of acrylamide and APS initiator on the swelling capacity. The success of the grafting reaction is evaluated by changes in functional groups using FTIR analysis.

2. MATERIALS AND METHODS

Cassava bagasse flour, carrageenan, palm oil, distilled water, and technical-grade ethanol 95% (w/w) were purchased from the local market in Surakarta, Indonesia. Acrylamide (C_3H_5NO), ammonium persulfate (APS), potassium peroxodisulphate (KPS), acetone ($(CH_3)_2CO$), potassium chloride (KCl), and calcium chloride ($CaCl_2$) were purchased from Merck and without purification.

2.1 Preparation of Grafted Polymer

The preparation of grafted polymer in this research was carried out by dissolving 1 g of cassava bagasse in 80 mL of distilled water and placing it in a 250 mL beaker glass. Then, acrylamide (AA) with weight variations (5, 10, 15 g) was dissolved in 30 mL of distilled water and then added to the cassava bagasse solution. The beaker glass was covered with aluminum foil and stirred for 30 min at 300 rpm. The solution was added with an APS initiator with weight variations (0.0, 0.05, 0.1 g) and stirred for 15 min. The solution was placed in a microwave with a rotating turntable. Grafting reaction was carried out using domestic microwave oven (Krisbow 20 L). This research utilized microwave irradiation at 630 watts of power and a reaction time of 225 s. The cooling cycle was maintained at a temperature range of 60°C - 70°C to prevent damage to the backbone and excessive side reactions. The liquid phase at the top was collected while the solid phase was immersed in excess acetone and then filtered. The solid was dried at a temperature of 50°C for 12 h. Subsequently, the solid was crushed, sieved using an 80-mesh sieve, and weighed.

This research investigates the effect of APS and KPS initiator in the grafting reaction on the swelling capacity of the obtained bead gel. When KPS was used as an initiator, 1 g of cassava bagasse was dissolved in 80 mL of distilled water and placed in a 250 mL beaker. Then, 10 g of acrylamide was dissolved in 30 mL of distilled water and added to the cassava bagasse solution. The beaker was covered with aluminum foil and stirred for 30 min at 300 rpm. Subsequently, 0.1 g of the KPS initiator was added to the solution and stirred for 15 min. Afterward, the solution was placed in a microwave with a rotating turntable. This research employed microwave irradiation at 630 watts of power for a reaction time of 315 s. The cooling cycle temperature was maintained within the range of 60°C to 70°C to prevent damage to the backbone and excessive side reactions.

2.2 FTIR Analysis

The FTIR test was conducted to find out the changes in chemical compound structure due to chemical reactions during the grafting process. These changes were identified by the peak of the compound groups using FTIR. The FTIR analysis of cassava bagasse cellulose, acrylamide, and grafted polymer variations of APS and AA were recorded by IR-Spirit Shidmadzu FTIR Spectrometer using the QATR method with the spectral range between 500 and 4000 cm^{-1}.

2.3 Bead Gel Preparation

Bead gel was prepared by mixing the carrageenan and powder from the grafted polymer with a total weight of 1 g, using a 1:1 ratio. The mixture of carrageenan powder from the grafted polymer was added to 100 mL of distilled water and stirred with a magnetic stirrer until a homogeneous solution was obtained. The solution was then heated to a temperature of 85°C. The solution was injected into a mixture of 0.2 M $CaCl_2$ solution and 0.2 M KCl solution, with the addition of palm oil to a height of 1 cm in an ice bath. At this stage, physical crosslinking occurred. The formed beads were left undisturbed for 15 min while being stirred, then filtered and soaked in 200 mL of technical-grade ethanol solution for 4 hours. They were subsequently drained and dried at room temperature until a constant weight was achieved.

2.4 Swelling Capacity Test

As for the swelling capacity test on the resulted bead gel, each sample was weighed as the dry weight (Md). Then, the samples were immersed in the swelling capacity medium and weighed every 30 min until a constant weight was achieved. This weight was recorded as the wet weight (Mw). The determination of swelling capacity was repeated for up to 3 h. The success of grafting was indicated by a high swelling capacity value. The calculation of the swelling test value can be described using Eq. (1).

$$\text{Swelling Capacity (\%)} = \frac{(\mathrm{Mw} - \mathrm{Md})}{\mathrm{Md}} \text{ x } 100\% \qquad (1)$$

3. RESULTS AND DISCUSSION

3.1 Effect of APS and KPS Initiator

Fig. 1 expresses the effect of initiator on the time required of grafting reaction to form the thicken product. Based on Fig. 1, it is found that the ammonium persulfate (APS) initiator requires less time for the microwave grafting process compared to the potassium peroxodisulfate (KPS) initiator. From the figure, the total time for APS initiator in microwave grafting is 225 s, while the KPS initiator requires 315 s to form thicken mixture. The microwave grafting results for the APS initiator start to form thickened mixture at 135 s, whereas for the KPS initiator, the microwave grafting results start to form thickened mixture at 225 s. Both APS and KPS are persulfate salts. However, their effects on cellulose degradation vary significantly. Compared to APS, KPS showed higher degradation of cellulose chains than APS [10]. Also, APS is more soluble in water than KPS. This solubility and degradation process may cause the grafting reaction using APS results thickened mixture in shorther time than using KPS. Based on the results of comparison the using of initiator APS and KPS, the further bead gel synthesis based on cassava bagasse used APS initiator in this research.

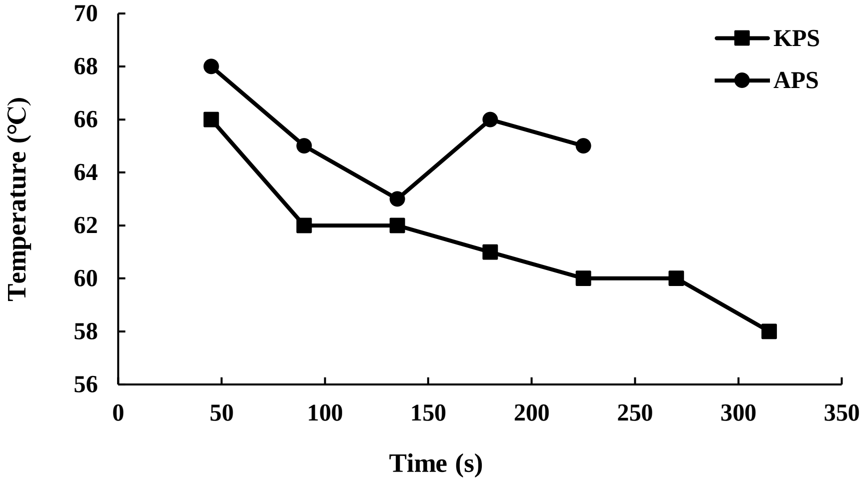


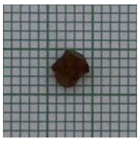
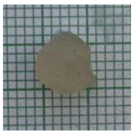
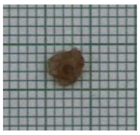
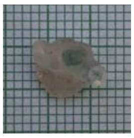
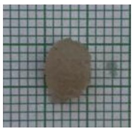
Figure 1. Comparison APS and KPS initiator on microwave grafting temperature and time

3.2 Affect of APS and Acrylamide

The resulting graft polymers using APS initiator were mixed with carrageenan to create bead gel. During formation bead gel process, physical cross-linking occured. The shape and size of the bead gel were influenced by the height of the oil in the cross-linker solution. From the preliminary experiment, if the oil height is less than 1 cm, the bead gel shape will not be perfectly round.

Table 1 shows the appearance and swelling capacity in water of obtained bead gel. In Table 1, the appearance of the bead gel before and after soaking in water can be observed. The dried bead gel color appears darker compared to after immersion in water. The bead gel becomes more transparent and its size increases. Bead gels made from different variations of acrylamide and initiator APS show the different swelling capacities. The more of acrylamide content causes the more hydrophilic content in the bead gel. Till 210 min, the bead gels were able in retaining water, allowing it to continue expanding. At minute 210, the swelling capacity is still high, but after that, it starts to shrink and lose weight.

Table 1. Image and swelling capacity of bead gel before and after swelling

Variation		Appearance of bead gel		Swelling Capacity (%)	Total Swelling Time (min)
APS (g)	Acrylamide (g)	Before	After		
1	5			580	210
	10			787	210
	15			1160	210
0	10			597	210
0.05				860	210
0.1				1193	210

In this research, hydrogels based on cassava bagasse cellulose were synthesized by grafting acrylamide as the monomer and APS as the initiator to allow spontaneous polymerization of acrylamide. Based on Fig. 2, it can be observed that as the amount of acrylamide mixed with cassava bagasse increases, the swelling capacity tend to increase. The hydrophilic groups present in the hydrogel polymer will increase due to the polyacrylamide grafted in cassava bagasse cellulose. The carbonyl and amide functional groups of acrylamide create hydrogen bonds with water resulting in improved hydrogel swelling capacity [5]. However, it is observed that after 180 min, the swelling capacity decreases due to reaching the optimum swelling time.

As reported in the research by Wivanius et al. [11], on the synthesis of chitosan-poly(N-vinylcaprolactam) hydrogel, the optimum swelling time is 2 h, coinciding with an increase in crosslinking degree that leads to a more organized polymer structure, providing sufficient space for reaction with water. However, the swelling capacity decreases with longer swelling times due to an increase in crosslinking degree, which is directly proportional to the increase in time, causing the hydrogel structure to become stiffer and thereby reducing the hydrogel's absorption capacity.

Fig. 2 illustrates that the cassava bagasse:acrylamide ratio (w/w) affects the swelling capacity. With the same immersion time at 210 min, the bead gel with a ratio of 1:5 (w/w) has a swelling capacity of 580%, while the ratio of 1:10 (w/w) has a swelling capacity of 787%, and the ratio of 1:15 (w/w) has a swelling capacity of 1160%. The increase in swelling percentage is due to the availability of a larger amount of acrylamide monomer. Acrylamide can form long polymer chains called polyacrylamide, thus increasing its ability to retain water.

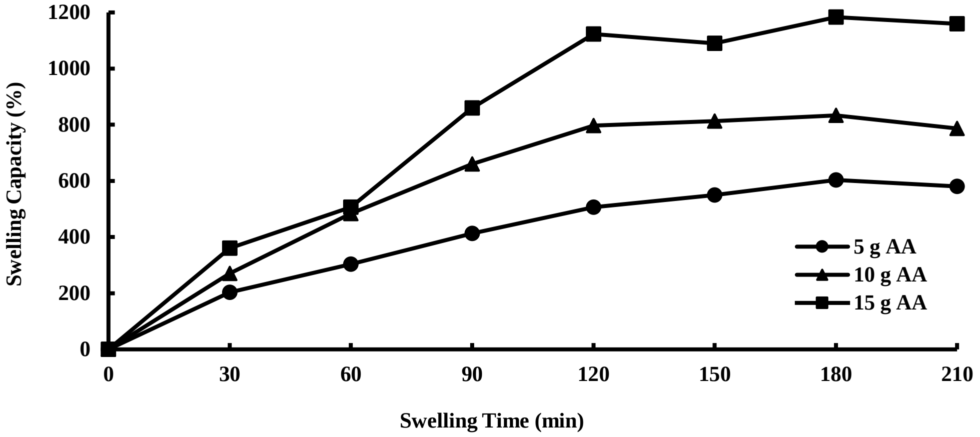


Figure 2. Swelling capacity as function of immersion time of bead gel obtained from various acrylamide amount (5, 10, and 15 g).

Fig. 2. also shows that the swelling capacity increases from 30 to 180 min of immersion. The swelling capacity gradually slows down until it reaches equilibrium swelling. For the ratios of 1:5, 1:10, and 1:15, the swelling capacity starts to decrease after 180 min.

Based on the results of the literature research, the addition of excess acrylamide as a monomer will result in a declining graph. This is because the added monomer reaches its saturation point. Once it reaches saturation, adding more monomer causes the cross-linking between polymer chains to become denser. The denser crosslinking bonds will result in a higher gel fraction value, but it leads to insignificant changes in swelling capacity [11].

Fig. 3. shows the comparison of APS amount variations on the swelling capacity generated within the time range of 0 to 210 min. The 0.1 g APS variation achieves the highest swelling capacity of 1193.33%, while the 0 g and 0.05 g variations exhibit a decrease in water absorption capacity with results of 596.67% and 860.00% respectively. This indicates a consistent trend in the data, as the increased amount of APS added leads to a higher swelling capacity. As reported in the research by Sunardi et al. [12], an increase in the initiator amount can result in an increase in the generated radicals along with the rise in the initiator concentration. Increasing the concentration of the initiator results in higher cross-linking efficiency, leading to a progressively increased swelling capacity due to the expansion of the gel fraction formed [13].

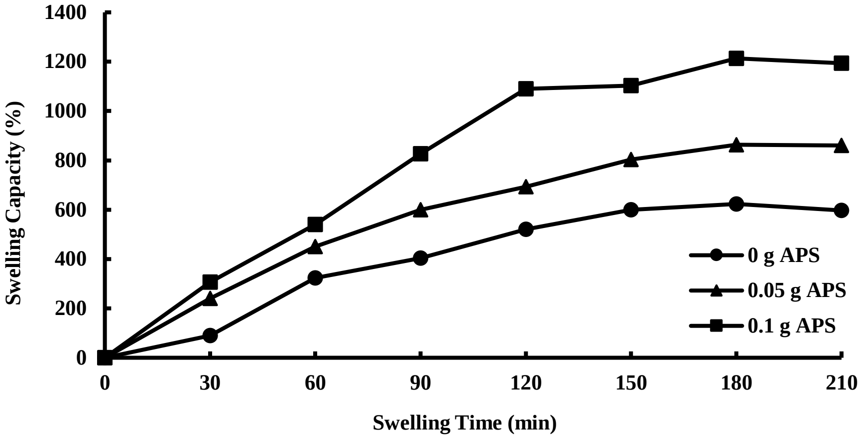


Figure 3. Swelling capacity of bead gel as function of immersion time with APS amount variation.

3.3 FTIR Result

The grafting of acrylamide onto cassava bagasse is confirmed by comparing the FTIR spectra of raw cassava bagasse with the mixture of grafted cassava bagasse-acrylamide-APS performed with the assistance of microwave. The FTIR spectra of cassava bagasse cellulose, which serves as the backbone in this research, as well as acrylamide and the resulting grafted polymer, are shown in Fig. 4. The FTIR analysis in this research aims to analyze the indication of acrylamide grafting onto the cassava bagasse cellulose backbone.

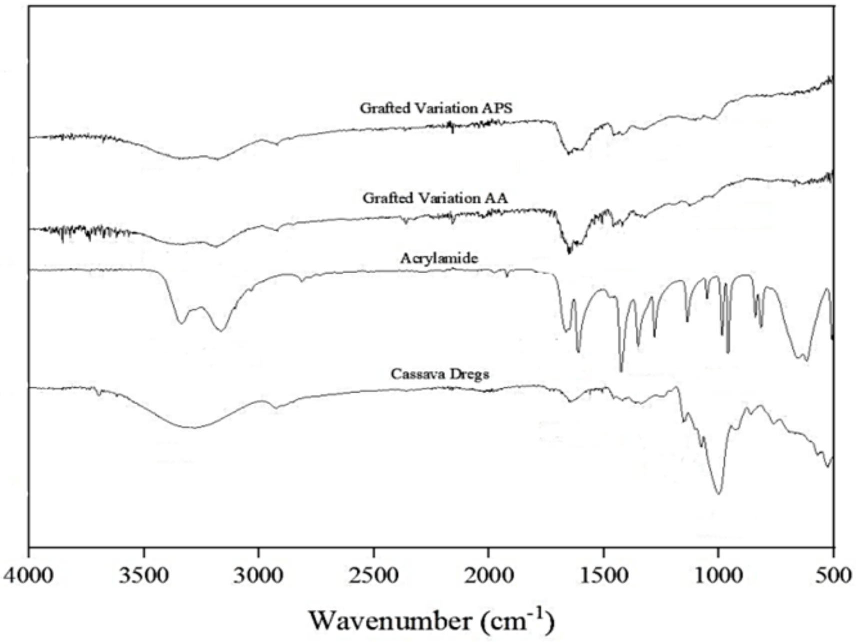


Figure 4. FTIR spectra of cassava bagasse cellulose, acrylamide, grafted cassava bagasse

The FTIR test results for acrylamide show a peak at the wavenumber of 3336.09 cm^{-1}, indicating the stretching vibration of O-H bonds. Additionally, there are other significant absorption peaks observed, such as: 3163.51 cm^{-1} (N-H stretching vibration), 1667.33 cm^{-1} (C=O stretching vibration), 1611.71 cm^{-1} (C=C stretching vibration), 1424.86 cm^{-1} (C-N stretching vibration), and 959.89 cm^{-1} (C-H stretching vibration).

The FTIR test results for cassava bagasse cellulose show a peak at the wavenumber of 3299.01 cm^{-1}, indicating the stretching vibration of O-H bonds in the hydroxyl groups of cassava bagasse and a peak at 1630.25 cm^{-1} indicates the presence of C=O vibration.

The FTIR test results for the grafted polymer variations of APS and acrylamide show similar spectra. This is because the materials used for both variations are the same, resulting in identical functional groups produced in both cases. In the acrylamide variation, the O-H stretching vibration peak is observed at 3346.08 cm^{-1}. A shoulder peak at 3179.2 cm^{-1} indicates the N-H stretching vibration. A small peak at 2925.32 cm^{-1} indicates the C-H stretching vibration. Sharp peaks at 1654.5 cm^{-1} and 1600.3 cm^{-1} indicate the stretching vibrations of C=O and C-N, respectively, as shown in the spectrum at the wavenumber 1342.14 cm^{-1}.

The FTIR test results for the APS variation of the grafted polymer show the O-H stretching vibration peak at 3333.24 cm^{-1}. A shoulder peak at 3177.8 cm^{-1} indicates the N-H stretching vibration. A small peak at 2925.32 cm^{-1} indicates the C-H stretching vibration, which is the same as the C-H stretching vibration in the acrylamide variation. Sharp peaks at 1654.5 cm^{-1} and 1597.44 cm^{-1} indicate the stretching vibrations of C=O and C-N, respectively, as shown in the spectrum at the wavenumber 1327.88 cm^{-1}.

In the research conducted by Tran Boi An et al. [4], which synthesized maize bran with N.N-methylene-bisacrylamide as a crosslinker and ammonium persulfate as solution initiator, the analyzed FTIR spectrum data showed the stretching vibration of O-H at the peak of 3460 cm^{-1}. Furthermore, the peaks for the stretching vibration of C-H and C=O were observed at 2920 cm^{-1} and 1580 cm^{-1}, respectively. Additionally, in the research conducted by Sorour et al. [14], who synthesized cassava starch with KPS initiator, a stretching vibration of C-N was observed at the peak of 1327 cm^{-1}.

Based on the analysis of functional groups in the FTIR spectra, the presence of a new peak corresponding to the N-H group in both grafted polymer samples indicates the successful grafting process. The FTIR data demonstrates that the graft copolymer is formed through the interaction between the free radicals generated from cassava bagasse as the backbone and acrylamide. The obtained peak wavenumbers are consistent with previous research, further confirming the successful grafting of acrylamide onto cassava bagasse cellulose.

4. CONCLUSION

From the FTIR spectrum analysis conducted, it is found that acrylamide grafting onto cassava bagasse using the microwave-assisted grafting method has been successful. The increase in acrylamide amount (5-15 g) leads to an increase in swelling bead gel capacity in water medium. The highest swelling capacity (1160%) was attained by 15 g acrylamide. The more APS amount, the swelling capacity of obtained bead gel will increase. With APS 0.1 g, the swelling capacity was 1193%.

ACKNOWLEDGEMENTS

Sebelas Maret University is thankfully acknowledged for supporting facilities and financial this project through grant research 228/UN27.22/PT.01.03/2023.

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