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Effect of Acrylamide And Potassium Peroxodisulphate on The Quality of Bead Gel Based on Cassava Bagasse-Carrageenan Using Microwave Grafting Method

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ABSTRACT. Hydrogels are widely used for drug delivery systems, immuno-chemotherapy applications, preventing dry soil, and increasing soil infiltration. Generally, hydrogels are derived from synthetic polymers which are non-biodegradable and toxic. Cassava bagasse is an alternative cellulose to make hydrogels. The purpose of this research was to determine the effect of the amount of acrylamide and potassium peroxodisulphate (KPS) initiator on the quality of bead gel based on cassava bagasse-carrageenan. The chemical structure of the hydrogel was studied using FTIR spectroscopy. Cassava bagasse was immersed in a solution of n-hexane to separate the fat. Then, fat-free cassava bagasse was grafted with mass ratios of cassava and acrylamide 1:5, 1:10, and 1:15 in 110 mL water. The solution was added with a KPS initiator with weight variations (g) 0.04; 0.08; 0.12 then stirred 15 min. The solution was put in the microwave with 630 watts of irradiation for 450 s with the cooling cycle temperature maintained at 65-70^{o}C. The aqueous grafted polymer and carrageenan was injected into a beaker glass that contained 1 cm of palm oil and a mixture of 0.2 M $CaCl_2$ and 0.2 M KCl in an ice bath. Results showed that the highest average swelling capacity was found in the bead gel variation 1:15 with the number of initiators 0.04 g of 1797.8% at a time of 210 minutes of immersion. From FTIR spectrum, it was found that there was success in grafting acrylamide into bagasse's backbone using the microwave grafting method with KPS as the initiator.

1. INTRODUCTION

Hydrogel is a hydrophilic polymer and able to absorb large amounts of water (up to 10 – 1000 times its size). Hydrogels are widely applied to drug delivery systems [1], immuno-chemotherapy [2], and soil conditioners that can increase the efficiency of water use, prevent dry soil, and increase soil infiltration. Hydrogel has several forms such as powder, film, granules, and others. Bead gel is a hydrogel in granules form.

Generally, bead gel is still produced from synthetic polymers that are non-biodegradable and toxic. One of the alternatives is to replace synthetic polymers with cellulose from natural polymers that are biodegradable, renewable, and low prices [3]. The starch industry in Indonesia is not widely developed so the waste can cause a smell and air pollution if not treated properly. One of them is cassava bagasse. The cellulose in cassava bagasse is 65.90%, which is quite high [4]. Thus, cassava bagasse can potentially be used as raw material for bead gel.

Bead gel as a superabsorbent polymer from a natural polymer such as cellulose, starch and chitosan suffer from low water absorption rate [5]. Therefore, it needs to be modified by polymer synthesis. Polymer synthesis is obtained by two methods, conventionally and heating with microwaves [6]. The grafting method with microwave irradiation has been chosen because it is easy to use, energy-efficient increases production yields, and environmentally friendly [7]. Anwar et al. [3] found copolymerization microwave grafting bacterial cellulose Nata de soya – acrylic acid using potassium peroxodisulphate (KPS) as initiator and N, N'-methylene bis-acrylamide (MBA) as crosslinker with the result of swelling capacity in distilled water was 26.0 g/g. Matovanni et al. [8] also synthesized cassava starch-grafted polyacrylamide hydrogel by microwave method for polymer flooding with acrylamide as a monomer, and potassium peroxodisulphate KPS as initiator. The result of the highest grafting percentage and water solubility, which was 1565.53 and 96.06%, respectively.

Depending on previous research [3,8], can be known that the initiator can accelerate the grafting process. Thus, this research used the microwave grafting method by grafting acrylamide into the cassava bagasse as a backbone with potassium peroxodisulphate (KPS) as an initiator to produce bead gel. KPS as a free radical initiator can

initiate cassava bagasse cellulose to form a main chain of active radicals that react with acrylamide monomers. Acrylamide can form long polymer chains known as polyacrylamide which will form a gel when mixed with water. The result of grafting is grafted polymer mixed with carrageenan to make bead gel. Carrageenan functions as a gel base, stabilizer and viscosity-increasing agent. As far as we known that the synthesis of bead gel based on cassava baggage-carrageenan using microwave grafting method with KPS as initiator has been not investigated. This study aims to determine the effect of the ratio of cassava bagasse: acrylamide (w/w), the ratio of cassava bagasse:KPS (w/w) on the quality of bead gel, and characterize the functional group using Fourier Transform Infrared (FTIR).

2. MATERIALS AND METHODS

The materials used cassava bagasse was purchased from CV Phan Jaya Supplier Bagasse, Indonesia. Ethanol technical (95%) was purchased from CV Cipta Kimia, Surakarta, Indonesia. Acrylamide (> 99% w), potassium peroxodisulphate ($K_2O_8S_2$) (> 99%), potassium chloride (KCl) (> 99,5%), calcium chloride ($CaCl_2$) (>99% w) were purchased from E. Merck, Germany. Hydroquinone (>99%) was purchased from Loba Chemie Pvt Ltd, India. Acetone was purchased from Saba Kimia, Surakarta, Indonesia. Palm oil brand Tropical, carrageenan, n-hexane, and distilled water were used without further purification.

2.1 Bead Gel Synthesis

Cassava bagasse (20 g) was dissolved in 115 mL of n-hexane for 2 hours at 100 rpm and then waited for 24 hours. Dried the bagasse until constant weight. Fat-free bagasse (1 g) was dissolved in 80 mL of distilled water and added to an acrylamide (AA) solution (with variations in the weight of 5, 10, 15 g in 30 mL of distilled water). The beaker glass was covered with aluminum foil and stirred for 30 min at 300 rpm. Added the KPS initiator with a weight variation (g) of 0.04; 0.08; 0.12 to the solution (bagasse-acrylamide) then stirred for 15 minutes. Microwave irradiation was run at 630 watts and a reaction time of 450 seconds with the cooling cycle treatment maintained at 65-70ºC. Add 5% w/v saturated hydroquinone solution to stop the reaction. The solution was stirred for 5 minutes and waited for 30 minutes. The liquid phase at the top was removed and added excess acetone. The solids were dried in an oven at 50ºC to constant weight. After it dried, the solids were crushed into powder size, then filtered and weighed. Figure 1 shows the main steps of the process microwave grafting synthesis. The variation of grafted polymer made is presented in Table 1.

Table 1. Variation of Polymer Grafting Samples with Microwave

Sample Code	Weight Ratio of Bagasse : Acrylamide	KPS (g)	Power (watt)
A1	1 : 5	0.04	630
A2	1 : 10	0.04	630
A3	1 : 15	0.04	630
B1	1 : 15	0.08	630
B2	1 : 15	0.12	630

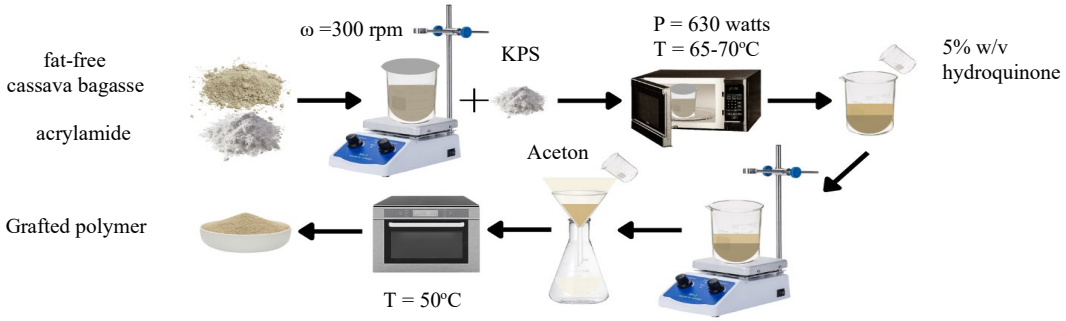

Figure 1. Process of Microwave Grafting Synthesis

Bead gel was made by mixing carrageenan-grafted polymer powder in a ratio of 1:1 then stirred until homogeneous and heated to a temperature of 85ºC. The mixture of grafted polymer and carrageenan was injected

into a beaker glass that contained 1 cm of palm oil and a mixture of 0.2 M $CaCl_2$ and 0.2 M KCl in an ice bath. The granules were formed and stirred for 15 min, after being filtered and immersed in 200 ml ethanol solution for 4 hours, drained and dried at room temperature in a desiccator until constant weight. Figure 2 shows the main steps process of preparation of bead gel.

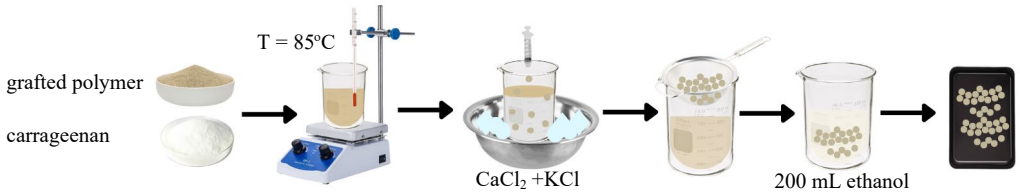

Figure 2. Process of preparation bead gel

2.3 Swelling Test the Bead Gel on Water

Each sample was weighed as dry weight (Md). Then the sample was immersed in distilled water and weighed every 30 minutes until the weight was reduced at a certain time. This weight is expressed as wet weight (Mw). Determination of swelling capacity was repeated 3 times by using Eq. (1).

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

3. RESULTS AND DISCUSSION

3.1 Grafted Polymer from Cassava Bagasse-Acrylamide

In the microwave grafting process, cellulose from bagasse acts as the backbone while acrylamide is a monomer because it has double bonds that allow copolymerization to occur. The acrylamide has double bonds that allow copolymerization during grafting. KPS is an initiator to initiate cassava bagasse cellulose to form a radical main chain, then the active side of the cellulose chain reacts with the acrylamide monomer. During the process, polymerization, grafting, and cross-link bond were formed. There are 3 possible cross-links, cross-link between monomers at monomers that have been grafted into cellulose, cross-link between cellulose, and cross-link between monomers at homopolymers.

3.2 Bead Gel from Grafted Polymer-Carrageenan

Bead gels were made by grafted polymer-carrageenan in a 1:1 weight ratio. The solution was injected into 0.2 M $CaCl_2$ and 0.2 M KCl with a 1 cm high layer of palm oil. During the process injection in $CaCl_2$ and KCl solution, physical cross-linking occurs. This causes the bead gel to be round and not shatter. Table 2 and 3 show the appearance of the bead gel before and after being immersed in water. The color of the bead gels were getting transparent and the size of the bead gel is getting bigger than the dry bead gel. Bead gel samples A1 and A2 took 180 min before shrinking. Meanwhile, the bead gel samples A3, B1, and B2 took 210 min. Bead gel with a perfect granular shape has the highest swelling and long absorption time. It causes the surface area of bead gel more extensive and the absorption process maximized. The change in shape and size of bead gel to swell prove that bead gel can be produced from grafted cassava bagasse-carrageenan.

In Table 2 & 3 there are three repetitions in each sample so we can see the trend of the data. Then, the three data are averaged so the value that represents the sample is obtained.

Table 2. Size of bead gel before and after swelling test acrylamide variation (using 0,5 x 0,5 cm scale)

	Appearance of bead gel		Swelling Capacity (%)	Swelling test (min)
Sample	Before	After		
A11			1435.63	180
A12			1948.08	180
A13			1356.19	180
A21			1357.91	180
A22			2512.62	180
A23			1500.98	180
A31			1573.53	210
A32			2436.78	210
A33			1383.56	210

Table 3. Size of bead gel before and after swelling test KPS variation (using 0,5 x 0,5 cm scale)

	Appearance of bead gel		Swelling Capacity (%)	Swelling test (min)
Sample	Before	After		
B11			1253.56	210
B12			1174.64	210
B13			872.036	210
B21			1438.88	210
B22			1124.08	210
B23			1383.56	210

3.3 *Effect of Cassava Bagasse Ratio:Acrylamide (w/w) on Swelling Bead Gel Capacity*

Cassava bagasse has low swelling capacity and less stable mechanical properties. Therefore, it is necessary to modify it using the grafting method to produce hydrogels with high swelling and stable mechanical properties. Grafting with microwave irradiation was carried out to produce a three-dimensional structure in the polymer chain. Monomer grafting on the polymer structure will change the main properties of the polymer such as hydrophilic and hydrophobic character, elasticity, water absorption, ion exchange, and resistance to heat [9].

Based on Figure 3, with more amount of acrylamide mixed with cassava bagasse, the hydrophilic groups in the hydrogel polymer will increase. This causes the hydrogel absorption ability will increase. At constant reaction time, bead gel 1:5 (w/w) had a swelling capacity of 816.5%, while 1:10 (w/w) had a swelling capacity of 1022.4% and 1:15 (w/w) had a swelling capacity of 1797.8%. Matovanni et al [8] has been synthesized 1 g cassava starch, acrylamide 10 g, KPS 0.3 g, and an irradiation time of 180 s. The result swelling ratio is 9.58 g/g (958 %). Compare to the research [8], the result of this research is better. The swelling percentage is increased because there are more acrylamide monomers. Acrylamide can form long polymer chains called polyacrylamide, so its ability to hold water will increase.

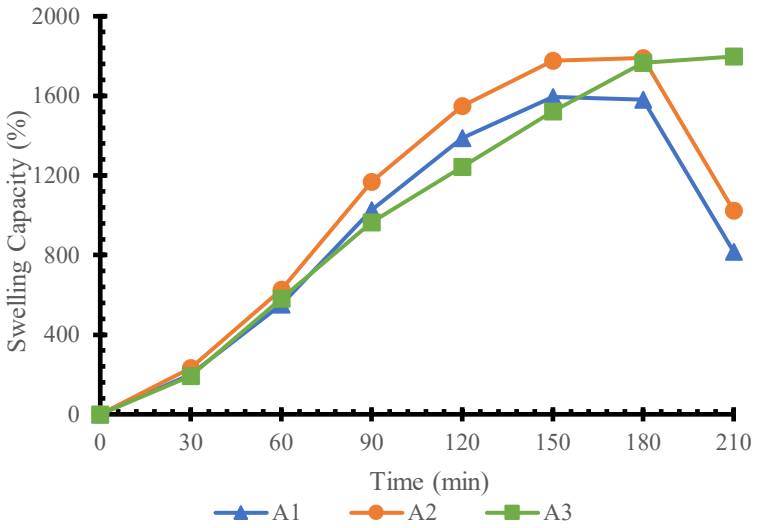

Figure 3. Comparison of swelling capacity acrylamide variation (%) vs time (min)

3.4 Effect of Cassava Bagasse:Potassium Peroxodisulfate (KPS) (w/w) Ratio on Swelling Bead Gel Capacity

Figure 4 shows the effect of cassava bagasse:potassium peroxodisulfate (KPS) (w/w) ratio of swelling bead gel capacity. The best swelling result in KPS variation is 0.04 g. The grafting solution turned into a gel at 300 s of grafting with microwave irradiation. This is because of KPS as initiator activates the acrylamide group instead of the backbone group. The swelling capacity has an absorption time of 210 minutes. The ratio of acrylamide:KPS initiator 15:0.04 (g) resulted in a larger swelling capacity of 1797.8%, while variations of 0.08 g and 0.12 g showed a decrease in water absorption by 1100.08% and 1315.51%.

Anwar et al [3] has been synthesis neutralized AA (9.5g), Nata de Soya bacterial cellulose (0.5g), KPS (0.008g), and N,N'-methylene bisacrylamide (MBA) in irradiation time 4.5 minutes and 180 W. The result swelling ratio is 26 g/g (2600 %) while in this research with 1 g bagasse,10 g AA, 0.04 KPS had a swelling capacity of 1022.4%. The result on this research is lower because in research [3] uses crosslinker 0.4 g MBA that can affect a large number of cross-linked acrylic acid monomers so that the hydrophilicity groups also increase. But, the data trend is the same, because the increase in initiator use can produce more radical groups [10]. High radical groups can affect the polymerization rate during grafting which causes a decrease in system density and swelling capacity of the polymer [11].

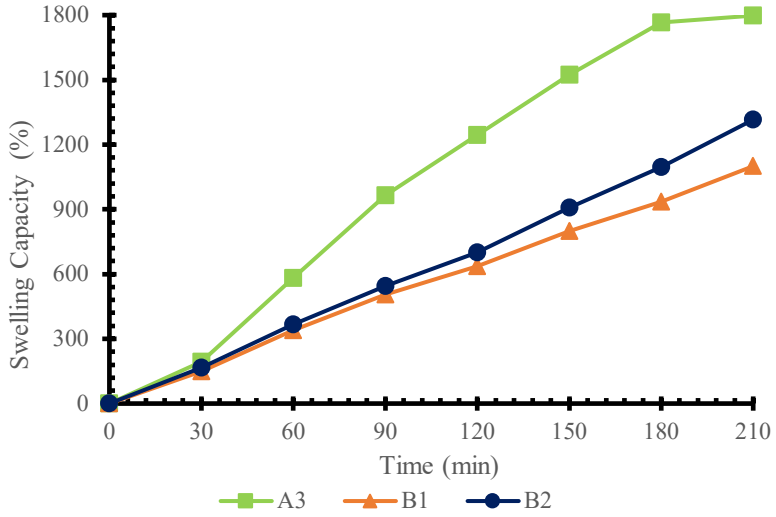

Figure 4. Comparison of swelling capacity KPS variation (%) vs time (min)

3.5 *Effect of Acrylamide:Potassium Peroxodisulfate (KPS) (w/w) Ratio on Swelling Bead Gel Capacity*

The spectrum of cassava bagasse grafted with variations of acrylamide and KPS showed identical profiles. The FTIR results of cassava bagasse as a backbone, grafted polymer acrylamide variations in sample A3 and KPS variations in sample B2 are shown in Figure 5. In FTIR results, the main absorption peaks were: 3333.95 cm^{-1} (O-H strain vibration), 2910.95 cm^{-1} (C-H strain vibration), 1139.35 cm^{-1}, 1080.43 cm^{-1}, 1006.42 cm^{-1} indicated the presence of C-O-C strain vibration.

The results of FTIR on the grafted polymer acrylamide variation show absorption indication in peaks: 3333.95 cm^{-1} and 3185.21 cm^{-1} (asymmetric and symmetrical N-H bond vibrations). In the peak of 3347 cm^{-1}, O-H and N-H functional groups is appear [12]. The presence of a small peak of 2916.77 cm^{-1} indicates the presence of C-H vibrations, a sharp peak of 1647 cm^{-1}, 1608.62 cm^{-1} (C=O strain vibration) and the graft product peaks 1319.13 cm^{-1}, 1020.93 cm^{-1} indicates the presence of C-N stretch. The FTIR results on the grafted polymer KPS variation showed almost the same spectrum because the materials used for both variations were the same. The O-H strain vibrations of the heap hydroxyl group and N-H strain vibrations overlap each other with a peak of 3352.09 cm^{-1} and a shoulder peak of 3178.68 cm^{-1}. The small peak of 2928.37 cm^{-1} indicates the presence of C-H strain vibrations. The presence of a sharp peak of 1652.88 cm^{-1} and 1604.99 cm^{-1} of a stretching vibration of C=O and a peak of 1312.60 cm^{-1} indicates a strain of C-N vibration.

The results of the functional group analysis of the FTIR spectrum showed that there were strain vibrations of C=O, N-H, and C-N at -$CONH_2$ which indicated the success of the grafting process. FTIR data showed the interaction between free radicals and the O-H groups on the cassava backbone replaced by polyacrylamide chains. The results of the spectrum showed that the peak of the C-O vibration was at the peak of 1675 cm^{-1}, while the peaks of the N-H, C-H and C-N strains were at the peak of 1615 cm^{-1} and 1410 cm^{-1}, respectively [13]. Suka [9] explained that the absorption band of the carbonyl group (C=O) combined with the N-H and C-N groups was at 1640^{-1} and 1550 cm^{-1}, respectively. These peaks appear in the analyzed FTIR spectrum data. From this explanation, it can be confirmed that the success of grafting.

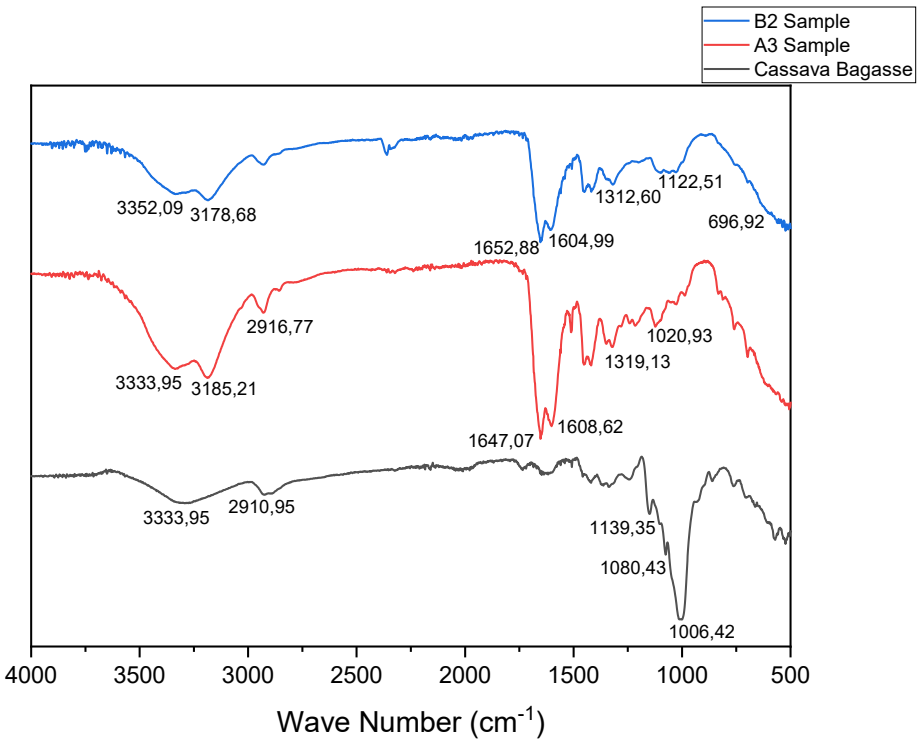

Figure 5. FTIR Spectrum

4. CONCLUSION

Based on the results of the study, it can be concluded that the amount of acrylamide and KPS (w/w) affects the swelling capacity. The increased amount of acrylamide causes the higher swelling capacity of the bead gel. The variation of acrylamide 15 g with an initiator of 0.04 g has a swelling capacity of 1500 - 2000 % at an immersion time of 210 minutes. Meanwhile, the more KPS causes the lower of the swelling capacity. From the results of the FTIR spectrum, it was found that there was success in grafting acrylamide into cassava bagasse using the microwave grafting method with KPS as the initiator.

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REFERENCES

[1] S. Bashir, Y. Y. Teo, S. Naeem, S. Ramesh, and K. Ramesh, “PH responsive N-succinyl chitosan/Poly (acrylamide-co-acrylic acid) hydrogels and in vitro release of 5-fluorouracil,” PLoS One, vol. 12, no. 7, July. (2017). doi: 10.1371/journal.pone.0179250.

[2] X. Wu, Y. Wu, H. Ye, S. Yu, C. He, and X. Chen, “Interleukin-15 and cisplatin co-encapsulated thermosensitive polypeptide hydrogels for combined immuno-chemotherapy,” Journal of Controlled Release, vol. 255, pp. 81–93, June. (2017). doi: 10.1016/j.jconrel.2017.04.011.

[3] B. Anwar, R. Nurkomarasari, and Y. Sunarya, “Pengaruh crosslinker N,N’-Metilenbisakrilamida (MBA) terhadap kinerja kopolimer superabsorben selulosa bakterial nata de soya-asam akrilat yang disintesis menggunakan radiasi microwave,” Chemica Isola, vol. 1, no. 1, pp. 1-8. June, (2021).

[4] M. Apriyani and D. E. Sedyadi, “Sintesis dan karakterisasi plastik biodegradable dari pati onggok singkong dan ekstrak lidah buaya (Aloe vera) dengan plasticizer gliserol,” J. Sains Dasar, vol. 4, no. 2, pp. 145-152. September, (2015).

[5] L. Chang, L. Xu, Y. Liu, and D. Qiu, “Superabsorbent polymers used for agricultural water retention,” Polymer Testing, vol. 94, February, (2021). doi: 10.1016/j.polymertesting.2020.107021.

[6] T. Erceg, S. Cakić, M. Cvetinov, T. Dapčević-Hadnađev, J. Budinski-Simendić, and I. Ristić, "The properties of conventionally and microwave synthesized poly(acrylamide-co-acrylic acid) hydrogels," Polymer Bulletin, vol. 77, no. 4, pp. 2089–2110, April, (2019). doi: 10.1007/s00289-019-02840-w.

[7] A. Abdulhameed, H. M. Mbuvi, and E. O. Changamu, "Synthesis of cellulose-based superabsorbent hydrogel from rice husk using a microwave," American Journal of Materials Science, vol. 10, no. 1, pp. 1–8, (2020). doi: 10.5923/j.materials.20201001.01.

[8] Matovanni, M. P. N., Distantina, S., & Kaavessina, M. "Synthesis of cassava starch-grafted polyacrylamide hydrogel by microwave-assisted method for polymer flooding," Indonesian Journal of Chemistry, vol. 22, no. 3, pp. 791 – 804, (2022). doi : 10.22146/ijc.71343

[9] I. Ginting Suka, "Kopolimerisasi cangkok (graft copolymerization) n-isopropilakrilamida pada film selulosa yang diinduksi oleh sinar ultraviolet dan karakterisasinya," Makara, Sains, vol. 14, no. 1. pp. 1-6. April, (2010).

[10] S. Sunardi, "Pengaruh penambahan jumlah inisiator amonium persulfat (APS) terhadap karakteristik polimer superabsorben asam akrilat dan selulosa batang alang-alang (Imperata Cylindrica)," Prosiding Seminar Nasional Penelitian, Pendidikan, dan Penerapan MIPA. May, (2013). doi: 10.13140/2.1.5170.2561.

[11] L. Anah, N. Astrini, and A. Nurhikmat dan Agus Haryono, "Studi awal sintesa carboxy methyl cellulose-graft-poly(acrylic acid)/monmorilonit superabsorben polimer hidro gel komposit melalui proses kopolimerisasi cangkok," Berita Selulosa, vol. 45, no. 1, pp. 1-8. June, (2010).

[12] W. Tanan and S. Saengsuwan, "Microwave assisted synthesis of poly (acrylamide-co-2-hydroxyethyl methacrylate)/poly(vinyl alcohol) semi-IPN hydrogel," Energy Procedia, vol. 56. pp. 386-393. (2014). doi : https://doi.org/10.1016/j.egypro.2014.07.171

[13] S. Chami, N. Joly, P. Bocchetta, P. Martin, and D. Aliouche, "Polyacrylamide grafted xanthan: Microwave-assisted synthesis and rheological behavior for polymer flooding," Polymers, vol. 13, no. 1484. March, (2021). doi : https://doi.org/10.3390/polym13091484