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Copolymerization of Tapioca Starch Waste through Grafting of Acrylic Acid Monomer with Cerium(IV) Initiator as Super Absorbent Polymer (SAP) Candidate

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Abstract— Indonesia, one of the world's largest tapioca starch producers, generates abundant cassava starch waste (onggok) that remains underutilized. This study aimed to enhance the value of onggok by synthesizing a superabsorbent polymer (SAP) through graft copolymerization using acrylic acid monomer and cerium(IV) initiator. Grafting was optimized by varying monomer concentrations (10–40% w/w) while maintaining the initiator concentration at 1.70% (w/w) and a reaction temperature of 53 °C. The optimal grafting occurred at 20% monomer concentration, yielding a grafting percentage of 14.83% and a monomer conversion of 74.15%. FTIR analysis showed increased absorbance ratios of –OH to C=O functional groups, confirming successful grafting. SEM images revealed a transformation from granular to porous structures, while DSC analysis demonstrated a shift in gelatinization temperature from 45.91 °C (raw onggok) to 46.69 °C (grafted), and retrogradation temperature from 140.67 °C to 141.67 °C. The water absorption capacity of the grafted copolymer reached 4.2450 g/g (5.20 g total), nearly double that of raw onggok (2.2716 g/g or 3.20 g), confirming its effectiveness as a SAP material.

Keywords— *Acrylic acid; Cassava onggok waste; Cerium(IV); Graft copolymerization; Superabsorbent polymer*

1. INTRODUCTION

Indonesia is one of the largest tapioca starch-producing countries in the world. Tapioca starch is widely used in both the food and non-food industries. Making tapioca starch will produce a by-product of solid waste called onggok. The existence of onggok in the central areas of tapioca starch production is abundant, but its existence cannot be utilized optimally to increase economic value. In addition, solid waste that is allowed to continue can cause problems in the form of air pollution because the smell caused is very strong for the surrounding community.

The use of solid waste onggok has been widely carried out, such as enrichment of onggok through fermentation with *Aspergillus niger* can be used as animal feed. In addition, fermented onggok hydrolysis results can be used to manufacture ethanols [1]. Currently, there was very limited research on chemical modification of solid waste substrates with copolymerization techniques that can increase their physical properties and economic value.

Carbohydrate compounds are the main components of the onggok, about 65,90%. Therefore, it is possible to modify the amount of carbohydrate compounds found in solid waste. Modification of the polysaccharide will change the chemical structure of the hydroxyl group of several D-glucopirilosyll units at positions C-2, C-3, and C-6 through chemical reaction of esterification, etherification, and oxidation inside the molecule. This modification can produce changes in gelatinizing properties, decrease retrogradation, and increase water absorption capacity to form Superabsorbent Polymer (SAP) [2].

Research to improve the properties of tapioca starch for SAP has been widely carried out in various methods: blending technique, chemical derivatization, and co-polymerization grafting. Grafting has been widely used in modifying the physical and chemical properties of

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polymers. The formation of radicals in the main chain of starch or polysaccharides is the initial stage of monomer grafting through chemical and γ-ray initiation systems [3]. The choice of initiator is one of the main determining factors in polymerization to produce a large percentage of grafting and grafting efficiency (% conversion). Chemical initiation can be carried out by adding an initiator such as K^+, Fe^{3+}, Cu^{2+}, Co^{3+}, V^{3+}, Ce^{4+}, and so on to activate the polymer. Grafting copolymerization of starch/polysaccharides has been extensively studied with vinyl monomers initiated with cerium salts [4]. The excess initiation of cerium ions can form a very efficient redox system through the formation of complex ions at positions C-2 and C-3 of glucopyranosyl starch/polysaccharide units so that a greater percentage of copolymers are formed and less homopolymers are formed [5].

Cerium(IV) (Ce^{4+}) was chosen as the initiator in the grafting process of acrylic acid onto tapioca starch waste due to its ability to oxidize hydroxyl groups (-OH) on the starch backbone, generating free radicals needed to initiate the grafting reaction. Compared to other initiators like benzoyl peroxide, which are more suitable for synthetic monomers, Ce(IV) is more effective for natural substrates and works well in aqueous systems, making it more environmentally friendly. Additionally, the use of Ce(IV) promotes strong covalent bonding between the starch and monomer, resulting in a more efficient grafting process and producing a stable superabsorbent structure with high water absorption capacity.

This work take attempt on the optimization condition of grafting copolymerization of acrylic acid monomer with Cerium(IV) initiator to produce the superabsorbent polymer (SaP) that never been studied before [6]. The work was focused on the optimization of initiator concentration [Ce(IV)], monomer concentration (acrylic acid), and effect of copolymerization time [7-8]. Further the characterization and the swelling test of the produced SaP was deeply investigated in this paper.

2. EXPERIMENTAL SECTIONs

2.1. Materials & Tools

The materials used in this study include the material to be grafted, the monomer to be grafted, materials for characterization and analysis, and reagents consisting of onggok flour (100 mesh) as a substrate grafted obtained from PT. Sari Alam-Kedung Halang (Bogor, Indonesia), acrylic acid as a monomer to be grafted, $Ce(SO_4)_2.4H_2O$ as an initiator on *grafting*, methanol, n-hexane, acetone, H_2SO_4, aqueducts, and nitrogen gas (*high purity*) to flow at *the grafting* reaction.

The tools used are a set of *grafting* equipment consisting of a three-neck flask, a set of water baths equipped with temperature control, a set of nitrogen gas cylinders, thermometers, condensers, centrifuges, magnetic stirrers, analytical balances, ovens, Soxhlets, FT-IR (*Fourier Transform Infra Red)*-Perkin Elmer Spectrumone series, DSC (*Differential Scanning Calorimetry*)-Metler Toledo type 821, SEM (*Scanning Electron Microscopy*)-JSM 6063LA-JEOL, and glass tools.

2.2. Separation of Fat Cassava Onggok

The cassava flour was cleaned from fat by soaking using n-hexane solvent with stirring for 24 h. The onggok was then dried in an oven at 50 °C. The resulting material was fat-free onggok, which was used as a substrate for copolymer synthesis.

2.3. Grafting Process

A total of 10 grams of onggok as a substrate was weighed and placed into a three-neck flask reactor, followed by the addition of 80 mL of distilled water. The mixture was stirred while nitrogen gas was flowed for 10 minutes. Then, a certain amount of 12.50% cerium(IV) sulfate solution in 0.125 mM sulfuric acid was added while stirring for 20 min. After that, a specific amount of acrylic acid monomer was added to the mixture. The grafting reaction was carried out at 53 °C for 1 h, with nitrogen gas continuously flowing at a rate of 3 mL/min. Upon completion of the reaction, the product was washed with a methanol:water mixture (1:1) and separated by centrifugation. The washing step was repeated twice. The resulting solid was then dried at 60 °C and weighed.

The grafting variables studied included the time and concentration of acrylic acid. The variations in acrylic acid concentrations used were 10%, 20%, 30%, and 40% (w/w) relative to the weight of the substrate. Meanwhile, the weight of the substrate and the initiator cerium(IV) sulfate in 0.125 mM sulfuric acid) were kept constant at 10 grams and 1.7%, respectively.

2.4. Separation of Homopolymers from Copolymers of Grafting Onggok

Soxhlet was performed with 120 mL of acetone:water (1:1) mixture at a temperature of about 100 °C for 8 hours. Several modified dry bags that have been washed with methanol:water (1:1) are weighed, then wrapped in Whatman filter paper, put into a soxhlet tube. The resulting soxhlet was washed with a mixture of acetone:water (1:1), dried at a temperature of 60 °C, and weighed. The reduced weight of the onggok is the weight of a homopolymer (%) and can be calculated by the **Equation (1).**

$$\frac{B}{a} \times \frac{(a-b)}{A} \times 100\% \qquad (1)$$

where A denotes the weight of initial onggok (10 g), B is the weight of grafting result (g), a is the weight taken from B to separate the homopolymer with acetone-water (1:1) (g), b is weight of the separation result using

a soxhlet, and (a-b) is the weight of the homopolymer (g).

2.5. Characterization of copolymers

Characterization is carried out on the standard onggok and *grafting* of the purified onggok. Characterization includes functional group analysis, morphology, thermal analysis, and absorption capacity tests.

2.6. Characterization by Tools

Analysis of functional groups with FT-IR spectrophotometers. A certain amount of copolymers is weighed, add a certain amount of KBr, mixed homogeneously and made a thin film. Furthermore, the sample is entered into the sample place and measurements of the absorption band are carried out in the wave number area of 450-4500 $^{cm-1}$ to determine the functional groups of the sample being analyzed.

Morphological analysis with SEM (*Scanning Electron Microscopy)*. A certain number of samples are taken and attached to the sample holder, then cleaned with a hand blower, given a thin layer (*coating*) of PdAu material. Then the sample is put into the specimen-chamber.

Thermal analysis with DSC (*Differential Scanning Calorimetry).* A 5.40 mg of the sample put into the alumunium pan and tightly closed. The thermal properties of the sample were observed with DSC in the temperature range of 0-250 °C for copolymers and raw parts with a temperature increase per minute of 10 °C.

Test the absorption capacity of acrylic acid copolymers. Ion-free water is weighed approximately 300 grams, put vertically into a 500 cm^3 glass beaker containing 2 grams of dried acrylic acid copolymers wrapped in a tea bag for 3 hours. Then the copolymer is filetered through the aluminium screen until the water does not drip anymore, and then the copolymer is weighed to increase its weight. The amount of water the copolymer retains is calculated as a modified gram of dry water. The same is done to unmodified standards as a comparison. The amount of water absorption can be calculated by the **Equation (2).** Where W1 is final weight and W0 is initial weight.

$$\text{Absorption} = (W1-W0)/W0 \quad (2)$$

3. RESULT AND DISCUSSION

3.1. Grafting on Onggok using Cerium Sulphate Initiator

Onggok, as the main target of grafting, must be treated, one of which is by chemical means through the initiation process using cerium sulfate. Onggok molecules that have received treatment will change chemical properties caused by the interaction between the cerium ion (Ce^{4+}) and the OH group in the onggok molecule so that a high-energy, active centre can be formed react with the acrylic acid monomer vinyl group.

Cerium sulphate ($Ce(SO_4)_2.4H_2O$) 12.5% in H_2SO_4 0.123 mM has a high solubility so that cerium ions (Ce^{4+}) will form. The Cerium ion that acts as an initiator in the grafting polymerization process can form a complex with the OH group of the onggok molecule before the free radicals in the onggok molecule are formed. This happens because cerium ions are transition metals with a high reduction potential so they can oxidize molecules in the area. The formation of a complex of Ce^{4+} ions with an OH group unit of glucose units in polysaccharide compounds can be detected at a maximum wavelength of 320 µm. Onggok has a primary alcohol group and secondary alcohols that cerium ions can oxidize and the result of oxidation is the breaking of the bond at the position of C-2 and C-3, thus forming a free radical that serves as the active center for the subsequent free radical polymerization reaction [9-10].

The substrate in the solution of cerium ions at room temperature will form a complex compound between the OH group and the cerium ions, followed by a change in colour from the onggok suspension solution, which was previously pale white, to a bright white suspension solution. With the heating process (in this study the temperature was 53 °C), the complex compound was easily oxidized and there was a break in the C-2 and C-3 position bonds to produce free radicals.

The method of copolymerization of grafting used is a non-simultaneous method meaning that the substrate to be modified interacts first with the initiator of the cerium ion, and then interacts with the acrylic acid monomer. When the onggok interacts with the cerium ions, it is hoped that free radicals can be formed on the main chain of the onggok so that when the acrylic acid monomer is added, grafting copolymerization will be formed. The method was chosen because it is more effective and can produce reasonable modifications compared to the simultaneous method. The difference is that the onggok is worked together in a solution of the initiator and monomer in the simultaneous or direct method. Monomers that are first oxidized by cerium ions form free radicals that are in the solution system and will hold reactions between monomers that

Table 1. Effect of time and monomer concentration on the percentage of grafting and conversion of monomers at 53 °C

Time (h)	[monomer] (%)	[inisiator] (%)	Grafting (%)	Conversion (%)
1	10	1.7	2.13	21.30
1	20	1.7	12.03	60.15
1	30	1.7	10.73	35.77
1	40	1.7	7.73	19.33
1	20	1.7	12.03	60.15
2	20	1.7	14.83	74.15
3	20	1.7	10.33	51.65

produce homopolymer products, while homopolymers are undesirable products in the grafting copolymerization process. The formed homopolymer must be separated from the grafting copolymer.

The effect of acrylyc acid monomer concentration of the percentage of grafting is shown in **Table 1**. It can be observed that the percentage of grafting increases significantly from an acrylic acid monomer concentration of 10% to a monomer concentration of 20% which is 2.13% and 12.03%, respectively with the number of substates and a fixed initiator concentrations.

Theoretically, the grafting percentage will increase with increasing monomer concentration until a relatively constant grafting result is obtained. The effect of monomer concentration on grafting results can be explained by the phenomenon of diffusion [11-12]. Increasing monomer concentration will increase the amount of monomer that diffuses into the polymer matrix. As a result, the possibility of collisions between monomer molecules and radicals in the polymer matrix will also increase. This collision causes the propagation stage to occur more as long as the conditions are kept constant, thus increasing grafting in the polymer (stump). However, the copolymerization reaction has an optimum monomer concentration. Once the optimum concentration is reached, the grafting result will remain constant or even decrease with increasing monomer concentration due to higher monomer concentrations inhibit monomer diffusion into the polymer matrix. Once most of the monomer forms a graft covering the surface of the polymer matrix (stump), further monomer diffusion into the active centers of the polymer matrix will be inhibited, thereby reducing grafting.

This study proves that at optimum grafting conditions, namely at a monomer concentration of 20%, the grafting percentage is 12.03% with a monomer conversion rate of 60.15%. While at higher concentrations (30% and 40%) there is a decrease in the grafting percentage, i.e. 10.73% and 7.73% with monomer conversion percentage is 35.77% and 19.30%, respectively (**Table 1**). The decrease in copolymers occurs due to the quenching of the active center of the polymer radical by other polymer radicals to form cross-links, followed by a change in the conformation of the polymer molecule (piles) as a whole into a closed form (the main chain structure of the polymer does not expand), which results in difficulty for acrylic acid monomers to diffuse to form copolymers and makes it easier for monomer radicals to form homopolymers with other monomers.

The duration of the grafting copolymerization reaction carried out in this study was 1, 2, and 3 h with fixed initiator and monomer concentrations of 1.7% and 20%, respectively (**Table 1**). It shows that the grafting percentage increase with increasing reaction time and tends to be constant at a certain time. This was because the longer the reaction time, the greater the diffusion of monomers into the cassava polymer matrix. The grafting percentage increased from 12.03% to 14.83% in the 1 and 2 h reactions, but the increase was not significant. The grafting percentage dropped to 10.33% after 3 h of copolymerization. This can be explained by the high number of free radicals produced at the beginning of the reaction, which interact with each other to form copolymers or homopolymers. As time increases, the number of free radicals decreases, and the interaction between the radicals and the monomers decreases, thus lowering the grafting percentage.

3.2. Separation of Homopolymers from Copolymers of Grafting Onggok

Homopolymers were formed due to competition between acrylic acid monomer radicals to react with cassava starch, cassava starch radicals, monomers, or monomer radicals. Reactions with cassava starch or cassava starch radicals form copolymers, and reactions with monomers or monomer radicals form homopolymers. This study separated the homopolymers formed from the copolymerization process using Soxhlet extraction. The solvent used was a mixture of acetone:water (1:1), carried out for 8 hours at 100°C. Observations after Soxhlet extraction showed that the solution in the round-bottom flask became cloudy. This indicated that the homopolymer contained in the copolymer mixture had been extracted. The results of the grafting reaction, after being extracted with Soxhlet, washed with acetone:water (1:1), and dried at 60°C, obtained a coarser powder (granules). The cassava starch granules that had formed grafts with acrylic acid had a brighter color than the standard cassava starch.

Table 2. The effect of initiator, monomer concentration, and time reaction on homopolymer formation

[initiator] (%)	[monomer] (%)	time (h)	homopolimer	
			g	%
0.4	20	1	0.7236	7.24
1.3	20	1	0.7039	7.04
1.7	20	1	0.4098	4.09
2.2	20	1	0.7101	7.10
1.7	10	1	0.6538	6.54
1.7	20	1	0.4098	4.09
1.7	30	1	0.5335	5.34
1.7	40	1	0.6275	6.28
1.7	20	1	0.4098	4.09
1.7	20	2	0.4601	4.60
1.7	20	3	0.6150	6.15

Table 2 shows that the greater the concentration of cerium ion initiator, the smaller the homopolymer formation, meaning that with increasing initiator concentration the copolymer formation is greater, except at a concentration of 2.2% there is an increase in homopolymer formation. This means that at a

concentration of 2.2% there is a decrease in the grafting of monomers formed. This is due to the quenching of the active center in the cassava starch through chain transfer between radical cassava starch polymers or between monomer radicals, so that more homopolymers are formed and conversely grafting decreases. Cerium ion concentrations of 0.4%, 1.3% and 1.7% produce homopolymers of 7.24%, 7.04% and 4.09% respectively, while at a higher cerium ion concentration of 2.2%, homopolymer formation increases (7.10%).

As shown in **Table 2**, at acrylic acid monomer concentrations of 10% to 20%, there was a decrease in homopolymer formation of 6.54% and 4.09%, respectively. This means that more copolymers were formed. Meanwhile, at higher monomer concentrations (30% and 40%), the tendency for homopolymer formation increased (5.34% and 6.28%), meaning that there was a decrease in grafting. This is because as the monomer concentration increases, there is a tendency for reactions between monomer radicals to form homopolymers.

Homopolymer formation also occurs at varying polymerization times. **Table 2** shows the effect of the length of the copolymerization reaction time on homopolymer formation. The length of the reaction time affects the amount of homopolymer formed. The longer the reaction time, the less homopolymer formation and at a certain time the optimum condition will be reached, even homopolymer formation can increase again. However, the results show that for reaction times of 1 and 2 h, homopolymer formation increased by 4.09% and 4.60%, respectively, and was followed by an increase in the grafting percentage of 12.03% and 14.83% as the reaction time increased. Of course, the conversion of monomers to form copolymers increased by 60.15% and 74.15%. Homopolymer formation tended to increase (6.15%) at a reaction time of 3 h. This means that the conversion of monomers to copolymers tended to decrease at longer times (10.33%). This is because under optimum conditions (2 h) for the formation of grafting copolymers, the chance of monomers or monomer radicals reacting with the polymer chain decreases so that the formation of homopolymers from monomers increases.

3.3. Identification of Acrylic Acid Onggok-Acrylyc Acid Grafting Copolymers

Analysis of functional groups using the FTIR spectrophotometer was carried out on samples of raw and grafting onggok with acrylic acid monomers (percentage of grafting 12.03%). By observing and comparing the infrared absorption spectrum of the two samples, it is hoped that an interpretation can be used to conclude that the grafting process between the onggok and the acrylic acid monomer can occur. The spectrum of FTIR absorption of raw and grafting carried out by grafting is shown in Error! Reference source not found..

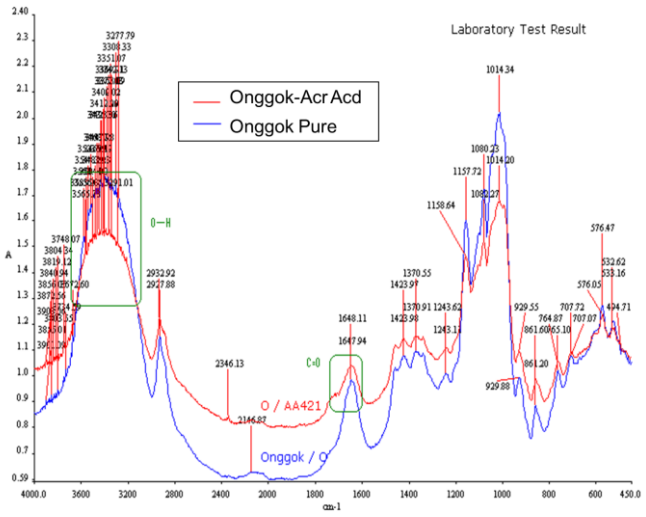

Fig. 1. FT-IR spectrum of onggok pure and onggok-acr acd

Qualitatively, there is a wide absorption peak in the FTIR spectrum at a wave number of 3400.01 cm^{-1}. This absorption band is a typical absorption of the vibration of the –OH and is further emphasized by the absorption band of the bending vibration –OH at a wave number of 1423.98 cm^{-1}. The typical absorption band of the stretch vibration –CH appears at wave number 2927.88 cm^{-1}, while the bending vibration of -CH appears at wave number 1370.91 cm^{-1}.

The C-C stretch vibration absorption band was observed at wave number 1014.34 cm^{-1}, while C-O stretch vibration appeared at wave number 1157.72 cm^{-1}. There is also a sharp band of vibration absorption in the wave number area of 1647.94 cm^{-1}, this absorption band comes from the C=O aldehyde group of the constituent

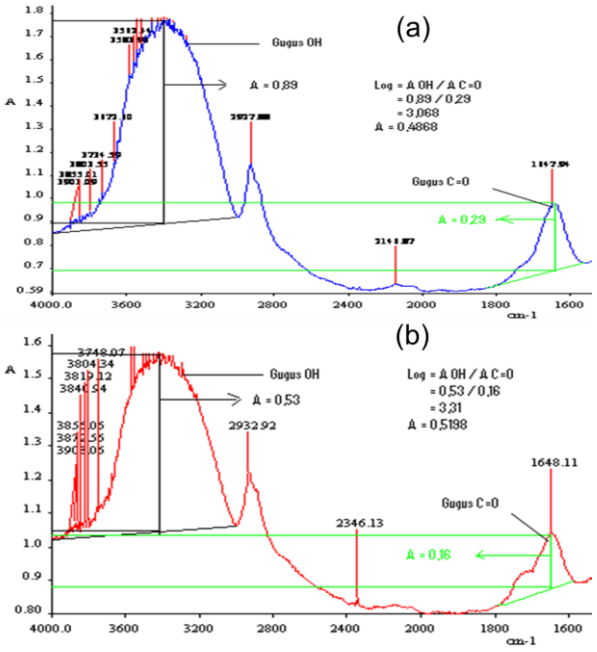

Fig. 2. Absorption ratio of –OH/C=O FT-IR spectrum of (a) onggok pure and (b) onggok-acr acd

glucose unit. **Fig. 1** shows that the absorption spectrum of the onggok that has been graphed by the acrylic acid monomer based on the absorption of functional groups has no significant difference. This is because the acrylic acid monomer and the acrylic acid have relatively similar functional group units. However, the formation of a grafting copolymerization reaction by acrylic acid monomers on the substrate is characterized by a change or shift in the wave number in each functional group. This can be observed in **Fig. 1**, marked by a change in the absorption of the stretch vibration width –OH from the wave number 3400.01 cm^{-1} to 3420.97 cm^{-1} after grafting.

Similarly, there was also a change/shift in the absorption of stretch vibration and bending vibration of the –CH group from the wave number 2927.88 cm^{-1} to 2932.92 cm^{-1} after grafting. Similarly, with the band of absorption of the vibrational vibration of the C=O functional group, after grafting the acrylic acid monomer on the onggok, there is a shift in the absorption of the stretch vibration from the wave number 1647.94 cm^{-1} to 1648.11 cm^{-1}. This shows that the presence of monomers that form grafting in the onggok results in changes in the energy level of the molecule as a whole and has an impact on shifting /change in the vibration energy of the molecular functional group which is characterized by the occurrence of a shift in the wave number even though the shift is small. Meanwhile, quantitatively, in **Fig. 2**, calculations can be made based on the comparison/absorption ratio between the –OH function group and the C = O function group by measuring the magnitude of the uptake of both functional groups through the baseline lines of the spectrum respectively (**Fig. 2**). Based on calculations, acrylic acid grafting has a greater absorption ratio of –OH/C=O functional groups (0.4868) than the onggok pure (0.5198).

The morphology of onggok and onggok polymer substrates that have received grafting treatment with acrylic acid monomers can be seen with SEM imaging potraits so that morphological forms are expected before and after grafting can be distinguished. **Fig. 3**a clearly shows the grains of the onggok, while in **Fig. 3b**, the the grains of grafted onggok by acrylic acid monomer are not clearly visible. The change in surface morphology after grafting is due to the interaction of acrylic acid monomer bonds with the onggok, which is accompanied by a change in shape from single grains to clusters to form porous granules (more clearly can be seen in **Fig. 3c**). The penetration of acrylic acid monomers into the polymer tissue to form grafting copolymers will have a swelling ability related to absorbing water (superabsorbent).

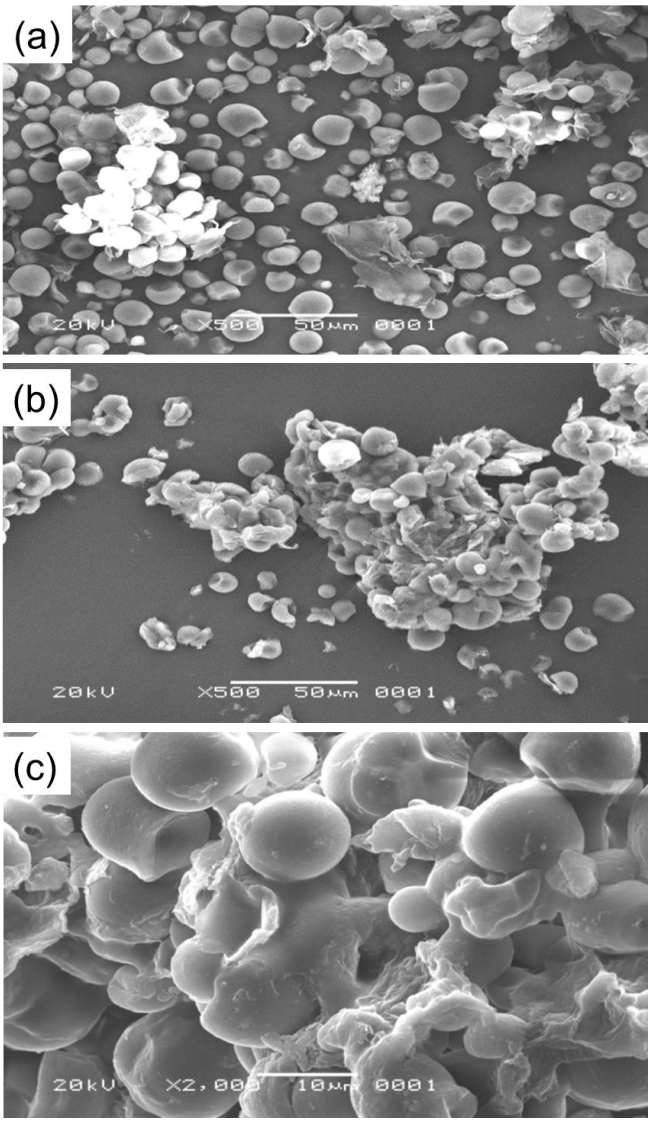

Fig. 3. SEM image of (a) onggok (b) onggok-acr acd copolymer (500x), and (c) onggok-acr acd copolymer (2000x)

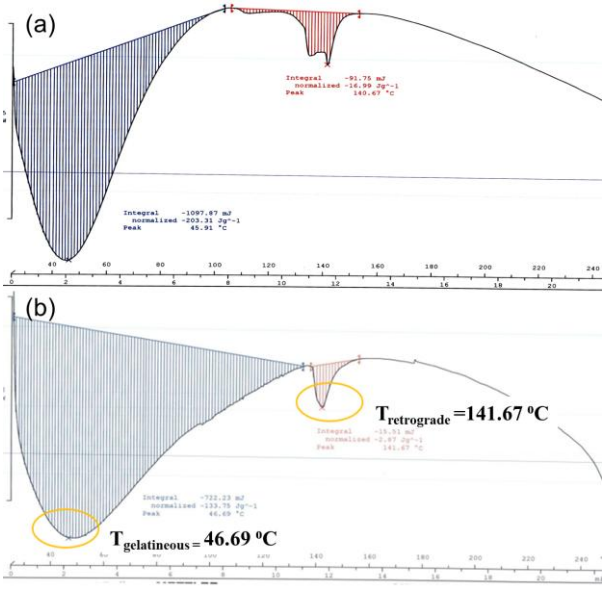

Fig. 4. DSC measurement results of (a) onggok, and (b) copolymer of onggok-acrylic acid

The results of the analysis using DSC on the onggok and copolymer of onggok-acrylic acid are shown in **Fig. 4** It can be seen that there is a difference in the endothermic heating curve between onggok and copolymer of onggok-acrylic acid. **Fig. 4a** shows the presence of a gelatination temprerature curve at a temperature of 45.91 °C, while onggok-g-acrylic acid the temperature of gelatinization at a temperature 140.67 °C is thought to be derived from the absorption of the retrogadation temperature of the amylum compouns and the temperature curve of such retrogradement can be observed also in the copolymer of onggok-acrylic acid i.e. shifted to a higher temperature of 141.67 °C.

Peak area produced by the DSC thermogram is directly proportional to the change in heat of the gelatinization transition. This can be proved in **Fig. 4a** and **Fig. 4b** that the peak area of the heating curve (heat capacity) in the copolymer of onggok-acrylic acid is wider than the heating curve raw ongok, meaning that the presence of acrylic acid that forms grafting in the onggok can increase molecular weight and degree of crystallinity. So, the response to heating the gelatinizing temperature shifts to a higher temperature.

The presence of a hydrophilic group (OH) of acrylic acid can interact with the molecular chains in the area through hydrogen bonds so as to stabilize the crystalline part of the onggok. Acrylate molecules bind to the amorphous part of the polymer molecule chain and produce a second interaction between the molecular chains effectively. The chain bridge between the two molecules will strengthen the flexibility of the

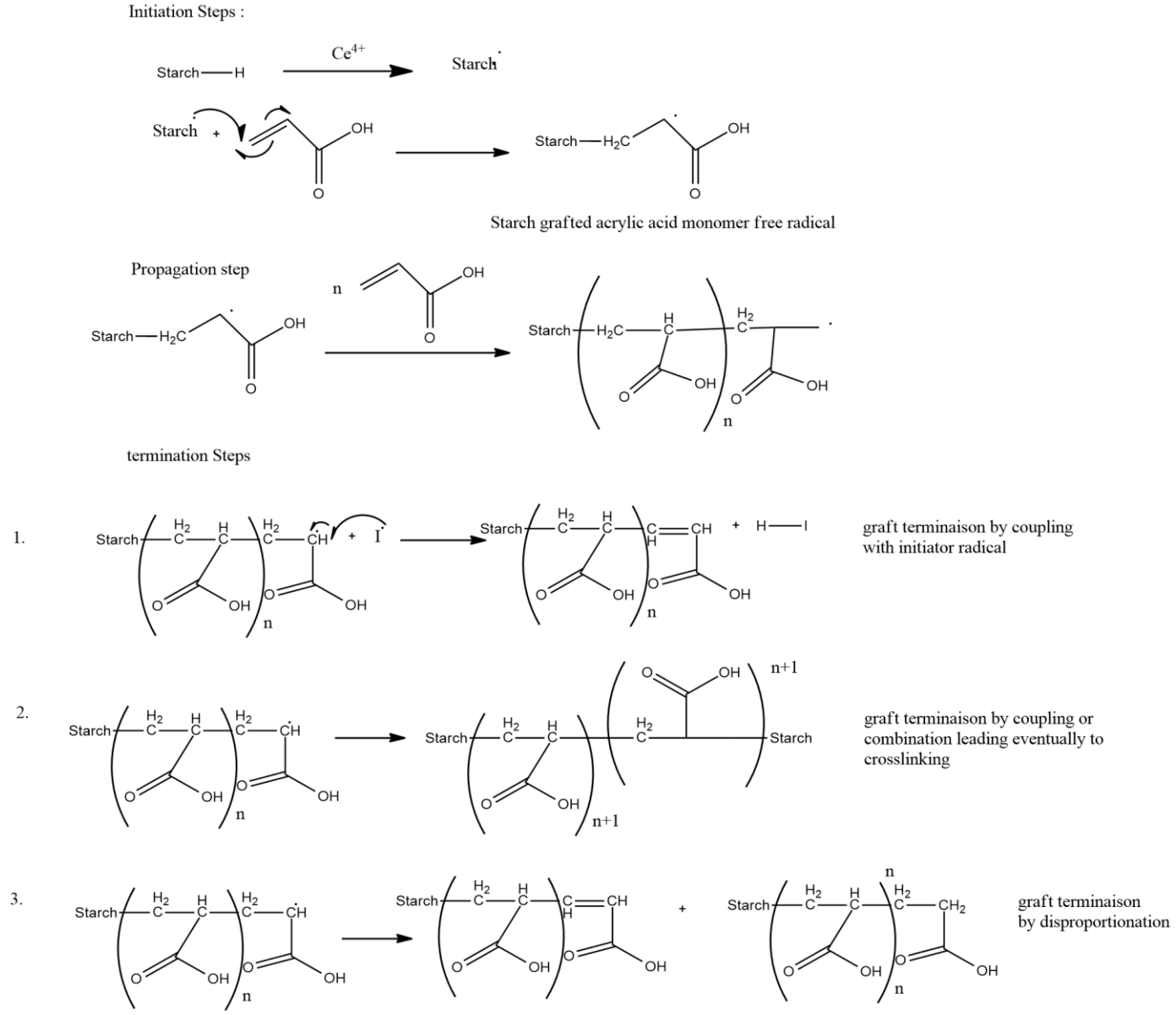

Fig. 5. Schematic mechanism of onggok copolymerization with initiator Ce^{4+}

chain so that greater thermal energy is needed to weaken its degree of crystallinity. This proves that the grafting carried out produces compounds that have been modified, accompanied by changes in their physical properties. The copolymerization of acrylic acid in cassava onggok gives changes to the crystallinity and thermal properties of the onggok.

3.4. Mechanism of Grafting Onggok with Monomers and Initiators

The grafting mechanism of onggok with acrylic acid using cerium(IV) sulfate as an initiator involves a free-radical reaction. Firstly, cerium(IV) ions (Ce^{4+}) oxidize the hydroxyl groups (-OH) present on the glucose units of the starch (onggok) backbone, generating starch-based free radicals. These radicals then act as active sites for the grafting of acrylic acid monomers. The double bonds of the acrylic acid react with the starch radicals, initiating a chain reaction that results in the covalent attachment of the monomer chains onto the starch backbone. This process forms a graft copolymer, where poly(acrylic acid) chains are chemically bonded to the natural starch structure. The presence of nitrogen gas helps maintain an inert atmosphere to prevent unwanted side reactions such as homopolymerization of acrylic acid.

The interaction of water with the synthesized Super Absorbent Polymer (SAP) is primarily governed by the presence of hydrophilic functional groups, especially the carboxyl (-COOH) and hydroxyl (-OH) groups. These groups are found on both the starch backbone (from onggok) and the grafted acrylic acid chains. When the SAP comes into contact with water, the carboxyl groups ionize into carboxylate anions ($-COO^-$) in the presence of water, creating osmotic pressure that draws water into the polymer network. Simultaneously, hydrogen bonding occurs between water molecules and the hydroxyl groups, further enhancing water uptake. The crosslinked structure of the copolymer allows it to retain a large volume of water without dissolving, enabling the material to swell significantly while maintaining its integrity. These interactions are what give the SAP its remarkable water-absorbing and retaining capacity.

The copolymerization reaction involves the grafting of acrylic acid monomers onto the starch backbone (onggok) through a free-radical mechanism initiated by cerium(IV) sulfate. The chemical representation of the process is presented in **Fig. 5**.

3.5. Water Absorption Test

Absorption tests were conducted to determine the hydrophilic properties of standard cassava and cassava-g-acrylic acid. Standard cassava essentially has three hydroxyl groups in its glucose units, making it polar and able to absorb water. Grafting copolymers of cassava-acrylic acid exhibit different absorption performance than standard cassava. The change in hydrophilic properties, chemically speaking, occurs in the acrylic acid-modified cassava due to the addition of hydrophilic groups from the polar acrylic acid. This increases the water absorption affinity of the cassava-g-acrylic acid material, even creating superabsorbent properties [13-14].

Table 3. Effect of time, monomer, and initiator concentration on water absorption of

[inisiator] (%)	Time (h)	[monomer] (%)	Grafting (%)	Absorption (g/g)
0.4	1	20	4.03	3.6196
1.3	1	20	11.33	3.8937
1.7	1	20	12.03	4.1035
2.2	1	20	3.51	3.4645
1.7	1	10	2.13	3.3732
1.7	1	20	12.03	4.1035
1.7	1	30	10.73	3.2632
1.7	1	40	7.73	3.4891
1.7	1	20	12.03	4.1035
1.7	2	20	14.83	4.2450
1.7	3	20	10.33	3.8424

Absorption tests were conducted on both standard onggok (2.2716 g/g) and cassava-g-acrylic acid, with deionized water used. The effect of initiator concentration on absorption is shown in **Table 3**. It shows that the water absorption affinity of cassava-acrylic acid grafting copolymer increases with increasing grafting percentage. A grafting percentage of 4.03% or an initiator concentration of 0.40% can absorb 3.6196 (g/g) of water or equivalent to 4.6 grams of its initial weight (2 g). A grafting percentage of 11.33% or an initiator concentration of 1.3% absorbs 3.8937 (g/g) of water or equivalent to 4.9 g of its initial weight. A grafting percentage of 12.03% or an initiator concentration of 1.7% absorbs 4.1035 (g/g) of water or equivalent to 5.1 g of its initial weight. Meanwhile, with a higher initiator concentration (2.2%) or a grafting percentage of 3.51%, water absorption decreased to 3.4645 (g/g), equivalent to 4.4 g of its initial weight, while the standard cassava pulp absorbed 2.2716 (g/g), equivalent to 3.2 g of its initial weight (2 g). This demonstrates that the cassava pulp-acrylic acid copolymer has a higher water absorption capacity than the standard cassava pulp.

The increase in water absorption with increasing initiator concentration, although not significant, is due to the increased percentage of acrylic acid grafting in the cassava pulp polymer main chain. The addition of monomers covalently bonded to the cassava pulp polymer matrix increases the overall hydrophilicity of the polymer, thereby increasing water absorption through hydrogen bonding. Meanwhile, at a higher initiator concentration (2.2%), the grafting percentage decreased, resulting in decreased water absorption. This is because excess initiator will trigger the formation of active radical centers in the main chain of the polymer matrix, resulting in the formation of

reactions between polymer chains (cross-linking reactions), thereby increasing the polymer density. Increased density in grafting copolymers results in decreased absorption because water has difficulty diffusing into the polymer matrix and reducing swelling.

The effect of monomer concentration on absorption is shown in **Table 3**. It shows that the ability of cassava-acrylic acid grafting copolymer to absorb water increases with increasing grafting percentage (monomer concentration of 10% and 20%). A grafting percentage of 2.13% or a monomer concentration of 10% can absorb water of 3.3732 (g/g) or equivalent to 4.3 grams of its initial weight (initial weight of 2 g). A grafting percentage of 12.03% or a monomer of 20%, absorbs water of 4.1035 (g/g) or equivalent to 5.1 grams of its initial weight. Water absorption decreases at higher monomer concentrations (30% and 40%), at a grafting percentage of 10.73% or a monomer concentration of 30%, absorbs water of 3.2632 (g/g) or equivalent to 4.2 grams of its initial weight. A higher monomer concentration (40%) or a grafting percentage of 7.73% resulted in water absorption of 3.4891 (g/g), equivalent to 4.4 grams of its initial weight, while the standard cassava starch absorbed 2.2716 (g/g), equivalent to 3.2 g of its initial weight (2 g). This demonstrates that the cassava starch-acrylic acid copolymer has a higher water absorption capacity than the standard cassava starch at varying monomer concentrations. The highest water absorption was achieved with the highest grafting percentage (12.03%).

As the grafting percentage increases at monomer concentrations of 10% and 20%, water absorption increases because increasing monomer concentration can increase diffusion into the polymer matrix, increasing the opportunity for monomer collisions/interactions with the polymer's active centers to form copolymers and resulting in increased hydrophilicity. Higher monomer concentrations (30% and 40%) decrease water absorption. This is because the cassava starch polymer matrix, as the main framework, contains active free radical centers that are disproportionate to the monomer. As a result, reactions occur between monomers, resulting in longer branched chains (homopolymers), while the homopolymers are discarded during separation with Soxhlet. The occurrence of reactions between polymer chains through cross-linking and resulting in increased density, is also a cause of decreased absorption, because monomers have difficulty diffusing and reduce the overall hydrophilicity of the grafting polymer.

Table 3 shows the difference in absorption at various reaction times. Absorption increases with increasing copolymerization reaction time. The longer the reaction time, the more copolymer formation increases which results in an increase in its hydrophilicity. A reaction time of 1 h with a grafting percentage of 12.03%, water absorption is 4.1035 (g/g) or equivalent to 5.1 g of its initial weight (initial weight of 2 g). A reaction time of 2 h with a percentage of 14.83%, water absorption is 4.2450 (g/g) or equivalent to 5.2 g of its initial weight and the difference is not significant. Meanwhile, at a longer time (3 h) accompanied by a decrease in the grafting percentage (10.33%), water absorption decreases to 3.8424 (g/g) or equivalent to 4.8 grams of its initial weight. The raw cassava pulp absorbs 2.2716 (g/g) of water or the equivalent of 3.2 g of its initial weight (2 g).

CONCLUSION

This study was successfully demonstrated the chemical modification of cassava starch waste (onggok) via graft copolymerization with acrylic acid using cerium(IV) as an initiator to produce a superabsorbent polymer (SAP) candidate. The optimum grafting conditions—20% (w/w) monomer concentration, 1.70% (w/w) initiator concentration, and 2-h reaction time at 53 °C—resulted in a grafting percentage of 14.83% and a monomer conversion of 74.15%. Characterization through FTIR confirmed successful grafting, supported by an increase in the absorbance ratio of –OH to C=O groups. SEM analysis showed a transition to a more porous morphology, while DSC analysis indicated shifts in thermal properties, with gelatinization and retrogradation temperatures increasing slightly after grafting. Most notably, the water absorption capacity of the grafted product reached 4.2450 g/g—significantly higher than that of raw onggok—demonstrating its potential as an efficient superabsorbent material. These findings highlight the value-added potential of agricultural waste, especially for use in environmentally friendly SAPs. Future applications may include water-retaining agents in agriculture, disposable hygiene products, and biodegradable packaging. Further research could explore crosslinking techniques, biodegradability assessments, and performance under real-world conditions to expand its applicability.

SUPPORTING INFORMATION

This article contains no supporting material. Supporting information can be provided by request to Corresponding Author (TK).

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CONFLICT OF INTEREST

The authors declare that there are not conflicting financial interests or personal relationships that have the potential to impact this study findings. All authors agree the final version of the manuscript.

AUTHOR CONTRIBUTIONS

TK: Conceptualization, Formal analysis, Project administration, Supervision, Validation, and Writing – original draft. **ARP & RP**: Writing early manuscript and revising. **N, RH,** and **A**: Conceptualization and Methodology.

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