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Suwardiyanto, M.Si,. Ph.D

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University of Jember

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Effect of Zeolite Concentration on Hydrogel Characteristics of Arrowroot-Based Starch-G-Poly(Acrylic Acid)/Zeolite Composite

Achmad Sjaifullah,*[a] Beny Akhmat Saputra, [a] Agung Budi Santoso, [a] Busroni, [a] I Nyoman Adiwinata,[b] and Muhammad Reza[a]

Abstract: This study aims to synthesize a hydrogel zeolite composite of arrowroot starch graft copolymerized with acrylic acid through a radical polymerization reaction in a water. Various scenarios were tested using different natural zeolite concentration to determine the impact on swelling/water absorption of the composite. The resulting product was a solid gel—the test results showed that the swelling increased as the ratio of starch to acrylic acid decreased. Increased starch concentrations generally lead to decreased water absorption (swelling capacity). Adding a zeolite improved swelling to some extent and the optimum zeolite concentration was 60%. The increased concentration of zeolite also hardened the hydrogel composite. The highest swelling in the hydrogel composite of starch-g-poly(acrylic acid)/zeolite 60% is 1056.25 $g.g^{-1}$. FTIR analysis of functional groups was conducted to determine differences in the IR spectra of arrowroot starch, acrylic acid, hydrogels, zeolites, and composite hydrogel. Si-O signal appearing on the IR spectra of hydrogel composite with wave number 1030 cm^{-1} indicates that composite hydrogel with zeolite was synthesized.

Keywords: Arrowroot starch, composites hydrogel, compressive strength, swelling capacity.

INTRODUCTION

Indonesia is a country that has abundant natural resources, such as arrowroots (*Marantha arundinacea L*). Arrowroot tubers are a source of carbohydrates, in which most of the constituent carbohydrates are starch. Therefore, arrowroot starch is a food ingredient because of its carbohydrate content. In addition, by looking at its chemical structure, arrowroot starch can be used as an ingredient in the manufacture of hydrogel composites.

Hydrogels are three-dimensional polymers capable of absorbing water/swelling. Hydrogels are formed as a result of cross-linking between the main polymer chains. These cross-links make the hydrogel structure rigid and resistant to certain pressures and forces[1]. The ability of hydrogels to absorb water is due to the presence of hydrophilic groups attached to the main polymer chain. Hydrogels are widely applied in various fields such as agriculture, health, food, and others. Various research on hydrogels made from starch have been developed[2], such as KGM-graft-poly(acrylic acid-co-trimethyl allyl ammonium chloride)[3] and Starch-Polyacrylate as superabsorbent hydrogels[4] for controlled drug release applications[5], potato starch-acrylic-acid hydrogels for dye adsorption[6], and others[7,8].

Starch-based hydrogels are generally graft polymerized with vinyl monomers such as acrylic acid and chemically crosslinked using crosslinking agents[9]. The crosslinking agent commonly used is methylene bisacrylamide (MBA). The presence of crosslinking agents can strengthen the structure of the hydrogel. In addition to chemical crosslinking, hydrogels can be stronger by physical crosslinking. Physical crosslinking can occur by adding several natural minerals such as zeolite[10], $CaCO_3$, bentonite, silica, and others. The natural mineral used in this research is natural zeolite. Hydrogels physically crosslinked with natural minerals are referred to as composites. The composite that is formed will be stronger and not easily broken.

Many studies on manufacturing starch-based hydrogel composites have been carried out and reported. For example, starch-g-poly (acrylic acid)/organo-mordenite hydrogel composite has the maximum ability to absorb water at the addition of 10 wt-% zeolites[11], namely 655 $g.g^{-1}$. Hydrogel composites based on starch-g-PNaMA/eggshell particles as dye biosorbent[12], starch, and clay for the preparation of superabsorbent composite[13], can absorb water up to 1077 $g.g^{-1}$. From the description above, it is necessary to conduct further research on arrowroot starch-based composite hydrogels, considering that using starch as a hydrogel material has never been reported. Arrowroot starch, which is easily available in traditional markets, is cheap and has the potential to be used as an ingredient in hydrogel production, which is one aspect that supports this research. Arrowroot starch with a concentration of 10% is still liquid compared to other starches so it can be polymerized. Natural zeolite was added in this study, reaching 100% by hydrogel weight compared to existing studies. Adding zeolite resulted in a strong composite with a heavier density.

METHODS

Materials

The materials used in this study included arrowroot starch obtained in traditional markets, natural zeolite, 100% acrylic acid (AA), methylene bis-acrylamide (MBA) (Merck), potassium persulfate ($K_2S_2O_8$) (Merck), methanol (technical 96%), and technical NaOH.

[a] A. Sjaifullah, BA. Saputra, AB. Santoso, Busroni, INA Winata, M. Reza
Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Jember
*e-mail: sjaiful.fmipa@unej.ac.id

Preparation of arrowroot starch and zeolite

Arrowroot starch (Marranta arundinacea L) was washed several times with water, then washed with 0.1 M NaOH and soaked for 24 h. Arrowroot starch was then neutralized with distilled water and dried. The dry arrowroot starch was measured for water content.

Natural zeolite was washed several times using water until clean. Washing was continued using distilled water and then filtered and dried at 60°C for 24 h. Finally, the washed, dry zeolite was crushed.

Synthesis of starch-g-poly(acrylic acid)/zeolite composite

Starch-g-poly(AA) was prepared by copolymerization reaction with MBA as a crosslinker. First, a starch solution was prepared by diluting 8 g of starch in 100 g of water. The solution was heated in a bath until a gel formed (like glue). Next, 0.4 g of potassium persulfate ($K_2S_2O_8$) was added, and the mixture was put in the oven at 55-60°C for 10 min. Then, 16 g of AA and 0.01 g of MBA were added. The mixture was stirred and heated at 55-60oC for ± 5 min. Followed with the addition of zeolite with various concentrations (0, 30, 60, and 100% (w/w) of the total mass – starch and acrylic acid). The mixture was stirred, shaken and then heated at 55-60°C for ±3 h to stimulate the polymerization reaction and shaken occasionally to make it homogeneous[11]. The product was then immersed in methanol to remove residual reactants and homopolymers that may be formed. Next, the product was washed with distilled water and dried in an oven at 55-60°C until dry. The dry product was weighed to determine the mass of the product.

Characterizations

Water absorption was measured by weighing the sample before and after water immersion. Soaking was carried out for 8 days. The difference in mass was divided by the initial mass multiplied by 100 to obtain the percent value (%) of water absorption.

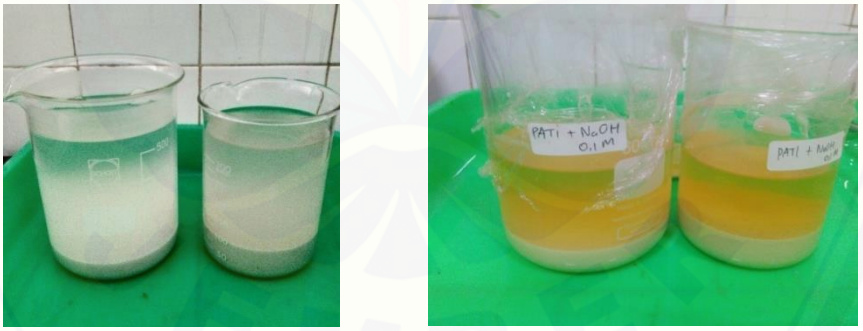
The compressive strength test was carried out using the LLOYD Material Testing A1 series Texture Analyzer. Samples that experienced maximum swelling were pressed until broken, and the required force was recorded. Furthermore, the force value was converted into the form of pressure as the compressive strength value of the sample.

Functional group analysis[14] was measured using the FTIR instrument FTIR ATR Germanium Bruker Alpha at wavenumber of 400-4000 cm^{-1}.

RESULT AND DISCUSSION

Preparation of arrowroot starch

The washing results showed a reduction in starch mass from 500 g to 491 g, or about 2% of the initial mass. It showed that several impurities, such as arrowroot fibers and sand, have been successfully removed. The loss of impurities can be seen in the water used for washing (distilled water and 0.1 M NaOH), which was brownish after the first wash and becomes clearer after several wash. Clearer washing water indicates the disappearance of impurities. 0.1 M NaOH was used to clean the starch from other impurities that cannot be removed with water. The presence of impurities in arrowroot starch was not expected in this study because the components needed were starch carbohydrates (amylose and amylopectin). The following is a picture of the starch washing process with water (Figure 1a) and continued washing with 0.1 M NaOH (Figure 1b). The brownish-yellow color when washing using NaOH indicates that impurities that cannot dissolve in water have been successfully removed with NaOH. Impurities were completely removed after rinsing with water.



(a) (b)

Figure 1. Washing process of arrowroot starch by (a) water and (b) 0.1 M NaOH

Swelling capacity

The effect of the addition of zeolite on the water absorption capacity of the synthesized hydrogel composite is shown in Figure 2. Adding 30% of zeolite can increase the ability of the hydrogel composite to absorb water (swelling) more than one and a half times. The water absorption capacity also increased with the concentration of zeolite. The maximum water absorption capacity of the addition of 60% (w/w) zeolite is 1056.25% ($g.g^{-1}$). And the water absorption decreased with the addition of 100% (w/w) zeolite with a value of 638.24% ($g.g^{-1}$).

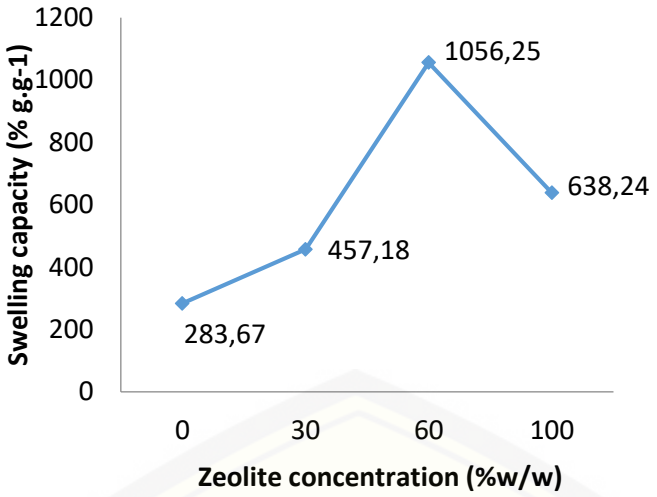


Figure 2. Swelling capacity profile of starch-g-poly(AA)/zeolite composite as a function of zeolite concentration

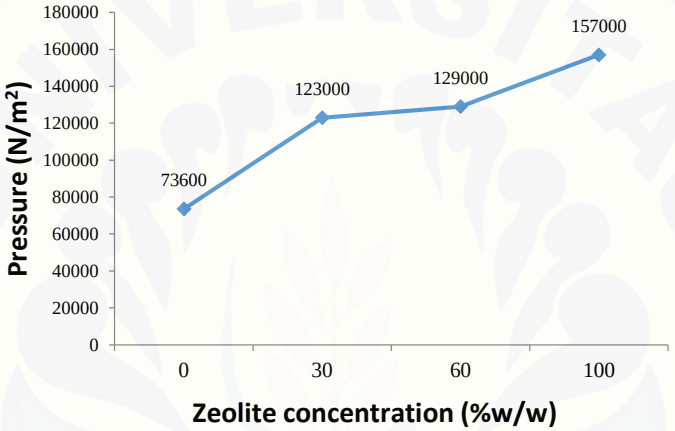


Figure 3. Compressive strength profile of starch-g-poly(AA)/zeolite composite as a function of zeolite concentration

As seen in Figure 2, increasing the concentration of zeolite can increase the ability of water absorption to a certain extent. Water absorption then decreased with the addition of more zeolite. Water absorption increased with 60% (w/w) zeolite and decreased with the addition of 100% (w/w). This phenomenon can be attributed to the role of zeolites in polymerization reactions. When zeolite is added below 60% (w/w), the water absorption increases as the number of zeolites increases. Zeolite contains many hydroxy groups (-OH) which can interact with water molecules, so zeolite also plays a role in increasing the water absorption capacity of hydrogel composites[15]. However, the water absorption will decrease with the addition of more zeolite. It is because the excess amount of zeolite may physically accumulate on the hydrogel network and block the entry of water molecules due to the interaction of the zeolite with the hydroxy groups (-OH) on the hydrogel.

Compressive Strength Test

The compressive strength test was carried out to determine the difference in the hardness level of the synthesized composite[16]. This hardness value is expressed in terms of pressure in units of newtons per square meter (N/m^2). Based on these data, the greater the addition of zeolite the higher the pressure required to suppress the sample. The starch-g-poly(AA)/zeolite 60% composite had the highest compressive strength value of 1.57 x 10^5 N/m^2. The effect of the addition of zeolite on the compressive strength of the hydrogel composite is presented in Figure 3. Figure 3 shows that the increase in the addition of zeolite causes the compressive strength (pressure) possessed by the sample to also increase. The greater the compressive strength value, the harder the texture of the hydrogel composite. It is due to the interaction between zeolite and hydroxyl groups (-OH) of the hydrogel, causing the zeolite to be dispersed and fill the space in the hydrogel network. The more zeolite added, the higher the hydrogel structure density. Therefore, hydrogel composites with the addition of more zeolite tend to have a harder texture.

Functional group analysis

The analysis of obtained FTIR bands can be seen in Figure 4, where the functional groups are theoretically predicted based on the most likely hypothetical structure of the hydrogel composite. The IR absorption bands of each spectrum were analyzed, and their functional groups were determined. Stretching O-H appeared at wave number 3396.7 cm^{-1}. In starch[17], C-O signals also appeared at wave numbers around 1000 cm^{-1} and stretching C-H alkanes at 2931.9 cm^{-1}. Meanwhile, stretching O-H appeared in the IR spectra of acrylic acid, widened in the 2500 – 3500 cm^{-1}, which characterizes acidic O-H. In the IR spectra of acrylic acid, Stretching C=O appeared at around 1700 cm^{-1} and stretching C=C at wave numbers around 1639.5 cm^{-1}. In the IR spectra of the starch-g-poly(AA)/zeolite 0%, the signal that

appeared is an O-H signal in the area of 2500-3500 cm^{-1}. This O-H signal comes from an acrylic acid monomer successfully grafted onto starch.

Meanwhile, the starch O-H signal was not visible because the absorption of acrylic acid is greater than that of starch. Based on the monomers' composition, the amount of available acrylic acid is more than the amount of starch, so more absorption groups appear from acrylic acid. The loss of acrylic acid C=C signal in the IR spectra of the starch-g-poly(AA)/zeolite 0% and starch-g-poly(AA)/zeolite 100% composites indicated that the acrylic acid grafted successfully. The C=C double bond formed a radical and binded to starch radicals forming a C-O-C bond which appeared at 1024 cm^{-1} in the composite IR spectra (43K0). C-H bending appeared in the starch-g-poly(AA)/zeolite 0% composite IR spectra at wavenumber of 1452 cm^{-1}. In the zeolite IR spectra, the Si-O signal appeared at a wavenumber of around 1000 cm^{-1}.

Meanwhile, in the starch-g-poly(AA)/zeolite 100% IR spectra, the Si-O signal also appeared at wave number 1024 cm^{-1}. The N-H signal from the MBA that should appear on the IR spectra of the starch-g-poly(AA)/zeolite 0% and starch-g-poly(AA)/zeolite 100% composites was not visible. The MBA composition, which was very small, causes very low uptake. The Si-O signal's presence in the starch-g-poly(AA)/zeolite 100% composite's IR spectra indicated an interaction between the zeolite and the hydroxy groups (-OH) on the hydrogel to form a composite.

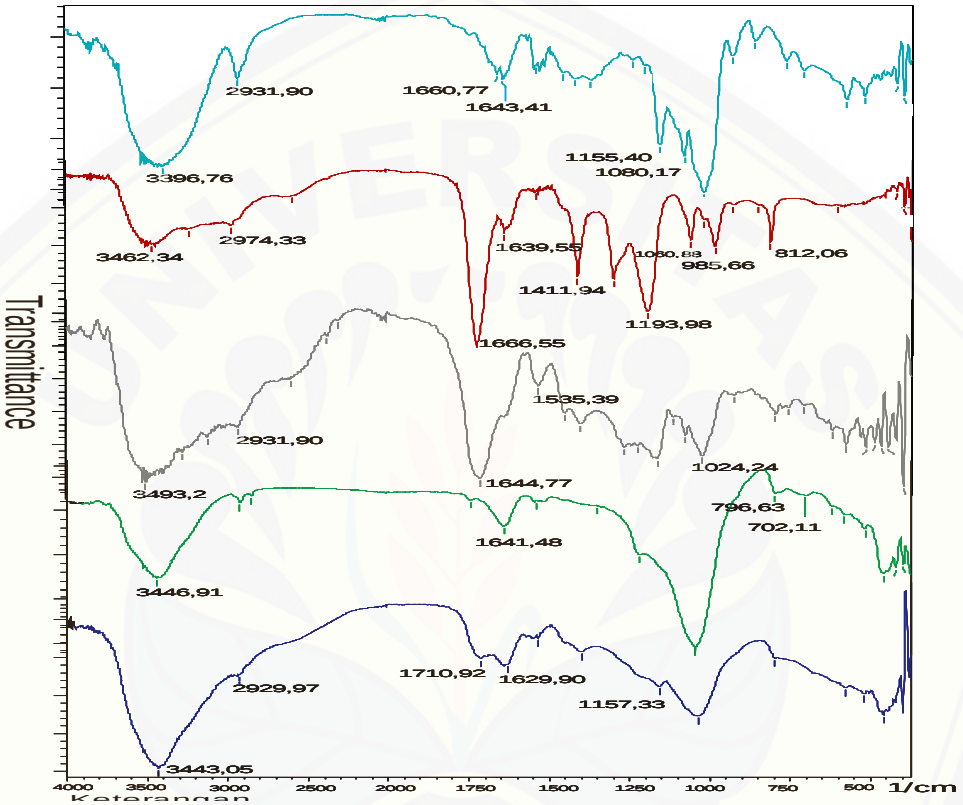


Figure 4. FTIR spectra of (a) arrowroot-based starch, (b) acrylic acid, (c) starch-g-poly(AA)/zeolite 0%, (d) natural zeolite, and (e) starch-g-poly(AA)/zeolite 100%.

CONCLUSION

We have discovered the effect of zeolite concentration on hydrogel characteristics of starch-g-poly(acrylic acid)/zeolite composite. The addition of zeolite in the polymerization reaction will increase the ability of the composite to absorb water (swelling) to a certain extent and harden its texture. The optimum zeolite concentration was 60 %w/w leading to the highest swelling capacity of 1056.25% (g.g-1) and the highest compressive strength value of 1.57 x 105 N/m2.

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