Synthesis and characterization of composite gels starch-graft-acrylic acid/bentonite (St-g-AA/B) using N’N-methylenebisacrylamide (MBA)

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Abstract. Composite gels are three-dimensional hydrophilic polymer networks that can absorb high amount of water, and eco-friendly. In this study, composite gels starch-graft-acrylic acid/bentonite (St-g-AA/B) was successfully synthesized by graft copolymerization using starch as natural polymer and bentonite. The acrylic acid that neutralized 40% parts with NaOH was used in copolymerization process. The graft copolymerization process uses potassium persulfate (KPS) as a free radical initiator and N,N-Methylenebisacrylamide (MBA) solution as a crosslinker. The synthesis process was conducted at 70°C for two hours under nitrogen atmosphere. Factor influencing of water absorbency such as amount bentonite in the weight and volume ratio were investigated. The results show that composite gels starch-graft-acrylic acid/bentonite (St-g-AA/B) had an optimum bentonite value of 2%wt acrylic acid with water absorbency obtained were 205.94 g/g and 157 mL/mL. The graft copolymerization reaction was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and morphological structure of product was evidenced by Scanning Electron Microscopy (SEM).

Keywords: Bentonite; Composite gels; Graft copolymerization; Starch; Water absorbency

1. Introduction
Composite gels are three-dimensional hydrophilic polymer networks that can absorb large amounts of water as high as 10 to 1000 times their own weight and eco-friendly [1]. With the ability to absorb and retain water, composite gels can be applied such as in health and agricultural [2], pharmaceuticals, biomedicine, controlled drug delivery [3], and diapers [4]. Synthetic polymers with crosslinking agent and biopolymers are commonly used in the manufacture of composite gels. Synthetic polymers with crosslinkers have properties that are not resistant to high temperatures and depend on renewable raw materials. Biopolymers are resistant to high temperatures but they are expensive [5].

Copolymerization is a method for modifying the structure of natural polymers so that they have properties suitable as polymer gels. Graft copolymers from these materials and the like have a three-dimensional hydrophilic network structure. Starch is very potential to be used as a natural polymer in the manufacture of polymer gel because it is abundant, cheap, and eco-friendly (biodegradable). Bentonite as a filler in polymer gel can be useful to improve the properties of polymer gel such as having a high water absorbency [6].

Ren et al. [7] synthesize polymer gel using gelatinized starch as a backbone which was added by potassium persulfate (KPS) as an initiator at the first stage. Then added monomer acrylic acid and acrylamide and NN-methylenebisacrylamide as a crosslinker material to form a three-dimensional network. From the results in the study, the water absorbency is 699 g/g [7]. Kulkarni et al. [8] synthesizes
gel polymers using gelatinized starch, added acrylic acid, bentonite (to increase water absorbency), and used N’N-methylenebisacrylamide (MBA) as a crosslinker. In the last stage, the potassium persulfate (KPS) as an initiator is added to start the grafting reaction. In the study, the water absorbency is 725 g/g and maximum water absorbency in 0.2% salt solution is 640 g/g [8]. From the study, it was proved that by adding bentonite in a three-dimensional network, it increased water absorbency. The polymerization process to get these properties not only influenced by the addition of bentonite but also influenced by the composition of the raw materials and the arrangement of the polymerization stage so that further research is needed to get a polymer gel that has better properties. In this research, composite gel polymer synthesis will be carried out by modifying the two stages of the polymerization process from Ren et al. [7] and Kulkarni et al. [8] and determine the effect of bentonite composition on water absorbency based on weight and volume ratio. In addition, the functional groups and product morphological structures were analyzed.

2. Materials and Methods
Starch (powder, PT. Sungai Budi, Jakarta, Indonesia), acrylic acid (AA, chemically pure, Shanghai Wulian Chemical Factory, Shanghai, China), N,N-methylenebisacrylamide (MBA, analytical grade, Promega Corporation, USA), potassium persulfate (KPS, analytical grade, Merck KGaA, Darmstadt, Germany), sodium hydroxide (NaOH, analytical grade, Merck KGaA, Darmstadt, Germany), nitrogen gas (N₂ supplied by Samator Gas, Sidoarjo, Indonesia) was high purity nitrogen, bentonite (powder, Research Unit for Mineral Technology, LIPI, Indonesia). All solution was prepared with distilled water.

![Figure 1. Equipment for synthesis of composite gels St-g-AA/B.](image)

Note:
1. Stirring motor
2. Stirrer
3. Condenser
4. Retort stand and clamp
5. Temperature indicator
6. N₂ inlet
7. Three neck flask
8. Glycerine bath
9. Heater
10. N₂ tube
11. Temperature controller
12. Glycerine stirrer

Fig. 1 showed that the equipment of synthesis St-g-AA/B. 10% starch solution were put in a three-neck flask as a reactor with a stirrer, condenser, N₂ inlet, and temperature controller. After that 10% starch solution heated to 95°C for 30 minutes. The starch solution was cooled at room temperature. The addition acrylic acid monomer (composition of acrylic acid: starch is 1:2) which had been neutralized with NaOH 40% (degree of neutralization) then added bentonite. The mixture was heated to 60°C with stirring and purging of nitrogen gas. Potassium persulfate (KPS) in aqueous solution as an initiator was added, then MBA in aqueous solution was added in the mixture. Let the mixture for 2 hours at 70°C. After that, the system was cooled at room temperature. The products were washed with ethanol and distilled water and then dried in an oven at 60°C until constant weight. Dry products were mashed up to
40-80 mesh [9]. To determine water absorbency in weight and volume ratio, dry products were immersed in distilled water for 4 hours so that the initial and final weight of the St-g-AA/B product can be known. Water absorbency is determined based on the volume and weight ratio so that the composite gel St-g-AA/B ability to absorb water and free volume for bonded water can be known and the amount of water absorbed by the product can be known in units of weight and volume. Water absorbency in volume and weight ratio can be calculated by the following equation (1) and (2):

\[
\text{Water absorbency (mL/mL)} = \frac{(V' - V)}{V} \tag{1}
\]

where \(V'\) is volume of swollen St-g-AA/B (ml) and \(V\) is volume of dry St-g-AA/B (ml)

\[
\text{Water absorbency (g/g)} = \frac{(W' - W)}{W} \tag{2}
\]

where \(W'\) is weights of swollen St-g-AA/B (g) and \(W\) is weights of dry St-g-AA/B (g)

Composite gel Starch-graft-Acrylic Acid/Bentonite (St-g-AA/B) was characterized using Fourier Transform Infrared (FTIR) and Scanning Electron Microscopy (SEM).

### 3. Results and Discussions

Fig. 2 shows the FTIR spectra of starch, acrylic acid, MBA, bentonite and composite gel St-g-AA/B. Since the composite gel St-g-AA/B was a mixture of starch, acrylic acid, MBA, and bentonite, the functional groups present in all four compounds should be present in the St-g-AA/B. That matter because composite gels in the result of an acrylic acid grafting on a starch backbone using MBA as a crosslinker and used bentonite. The FTIR spectra of starch show the peak of the wide and strong \(\text{O-H}\) wave numbers at 3277.84; and 2927 cm\(^{-1}\), while the wave number 1076.3 cm\(^{-1}\) indicates the presence of a C-O group on the starch. Spectrum FTIR for acrylic acid shows the presence of \(\text{OH}\) groups at the peak of wave number 2987.92 cm\(^{-1}\), whereas wave number 1694.07 cm\(^{-1}\) shows the indicates that C=O groups, while the C=C groups are at wave number 1634.46 cm\(^{-1}\). Spectrum FTIR for MBA shows \(\text{N-H}\) groups at peak of wave number 3302.56 cm\(^{-1}\), wave number 1655.79 cm\(^{-1}\) indicates that C=O groups, while wave number 1538.23 cm\(^{-1}\) indicates existence of C=C groups on MBA. While the FTIR spectrum for bentonite shows a sharp and wide \(\text{O-H}\) groups at a wave number of 3621.05; and 3360.15 cm\(^{-1}\), \(\text{Si-O}\) groups are at wave number 1627.76 cm\(^{-1}\), wave number 996.09 cm\(^{-1}\) shows that \(\text{Si-O-Si}\) groups, wave number 911.14 cm\(^{-1}\) indicates that Al-O-Al groups, as well as Al-O-Si groups are at wave numbers 510.05 cm\(^{-1}\). Spectrum FTIR for composite gel St-g-AA/B shows the wide and strong \(\text{O-H}\) and \(\text{N-H}\) wave peaks at 3331.77 cm\(^{-1}\), the wave peak C=O at 1694.60 cm\(^{-1}\), the peak of the bond wave N-H at 1557.11 cm\(^{-1}\), as well as the peak of the \(\text{Si-O}\) groups wave length is at say wave 1015.81 cm\(^{-1}\).
Figure 2. FTIR of starch, acrylic acid, MBA and composite gels St-g-AA/B.

From the above figures we can compare the FTIR spectra of the four materials with the composite gel St-g-AA/B where seen several peaks at the same point indicating the same groups. This groups proves that the starch, acrylic acid, and MBA are present in composite gel St-g-AA/B. Moreover, FTIR spectra result there is no wave number indicating the presence of C=C groups on the product, it proves that the reaction of graft copolymerization between starch and acrylic acid was successfully and occurs in the C=C group on acrylic acid. The wave number 1015.81 cm$^{-1}$ indicates that Si-O groups present on composite gel St-g-AA/B, its indicates that bentonite can chemically bind to COOH groups on acrylic acid monomer which has been grafted on the starch backbone. This shows that bentonite not only trapped in three-dimensional polymer networks.

Apart from the observed functional groups in the FTIR spectra, the success of grafting and crosslinking copolymerization was also observed by the SEM which compares starch and bentonite micrographs with composite gel St-g-AA/B micrographs. Fig. 3 shows that the surface morphology of starch and bentonite is very different from the composite gel St-g-AA/B modified starch and bentonite. The appearance of starch looks like a ball-shaped granule with varying granule size with smooth surface [10]. While the appearance of bentonite looks like a fragment of small stones with irregular shapes and a rough surface. The composite gel product of St-g-AA/B, granules were no longer found, but a rough surface, undulant [11] and full of folds were found. This indicates that the graft and crosslink copolymerization was successfully. The rough product surface indicates that the bentonite was spread evenly on the composite three-dimensional polymer gel network. In addition, the folds in the product are areas where water can seep and interact with hydrophilic groups in three-dimensional polymer network [12].
Figure 3. Micrographs of (a) starch (b) bentonite and c) composite gels St-g-AA/B.

Fig. 4 shows that the effect of bentonite concentration of water absorbency of composite gel St-g-AA/B. At 2%wt bentonite concentration, the maximum water absorbency 205.94 g/g and 157 mL/mL were obtained, and the water absorbency increased with the increase of bentonite concentration from 0.5%wt to 2%wt. When the bentonite concentration was higher than the optimum point (2%wt acrylic acid) the water absorbency of composite gel St-g-AA/B decreased with further increase of the bentonite concentration. It can be seen that the bentonite particle in the composite gel network acts as an additional crosslinking point (the carboxylic group in acrylic acid reacts with the -OH group on the bentonite surface) so that bentonite can also add hydrophilic network in the polymer [13]. However, the increasing amount of bentonite particles in the polymer network, causing the composite gel network points to become more and more tight, causing the composite gel to be rigid [14]. In addition, bentonite can prevent the growth of polymeric acid chains and produce a little group of COO− acrylic acids in polymeric network causing water absorbency to be less.

Figure 4. Effect of bentonite concentration on water absorbency.
4. Conclusion
In this study, composite gels Starch-Graft-Acrylic Acid/Bentonite (St-g-AA/B) was successfully synthesized by graft copolymerization. Composite gel Starch-graft-Acrylic Acid/Bentonite (St-g-AA/B) had an optimum bentonite value of 2%wt acrylic acid with a maximum water absorbency of 205.94 g/g and 157 mL/mL. The product was characterized with Fourier Transform Infrared Spectroscopy (FTIR), it was found that characteristic groups of starch, acrylic acid, N’N-methylenebisacrylamide (MBA), bentonite, and there were no C=C groups from acrylic acid monomers on composite gels St-g-AA/B. The Scanning Electron Microscopy (SEM) show that bentonite has been spread evenly to the polymer network and the presence of folds on the surface is an area where water can seep in and interact with hydrophilic groups in a three-dimensional polymer network.

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