

Preparation and Characteristics of Polyvinyl Alcohol-based Hydrogel Containing Natural Microbentonite

Mawarani Manullang¹, Diana Adnanda Nasution² and Basuki Wirjosentono^{2*}

¹Postgraduate Chemistry Study Program, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1 Kampus USU, Medan, Indonesia

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Jl. Bioteknologi No. 1, Medan 20155, Indonesia

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Abstract: In this work, polyvinylalcohol (PVA)-based interpenetrating-hydrogels containing natural microbentonite (NMB) were prepared in a bench scale reflux-reactor using water as solvent in an optimized condition in the presence of constant compositions of acrylicacid (AA) and N,N'-methylenebisacrylamide (MBA) as comono-mers as well as ammoniumpersulphate [(NH₄)₂S₂O₈, APS] as initiator. Results of interpenetrating-hydrogels, with various loadings of NMB (2, 5, 10 and 15%) were moulded and cooled to form film specimens, and then characterized for their properties. First of all, their mechanical properties and chemical structure were measured using tensile testing (ASTM D882) and infrared spectroscopy (FTIR), then their thermal properties were analysed using differential scanning calorimetry (DSC), and their morphological properties were tested using scanning electron microscopy (SEM). Results showed that optimum composition weight ratio of PVA/AA/NMB/MBA/APS = 60/40/10/1/0.5 enhanced highest tensile modulus of the interpenetrating-hydrogel microcomposites 25% in compare to its neat hydrogel counterpart. FTIR analysis of the film specimens after exhaustive extraction in n-hexane still contained stable AA-carbonyl (C=O) peak at 1725 cm⁻¹. Thermal properties of the optimized composition of the hydrogel showed slight improved of thermal stability (decomposition temperature increase from 280 – 285°C). Morphological properties of the interpenetrating-hydrogel microcomposite also showed finely distributed of the microfiller, which is responsible for its improved mechanical and thermal properties. It is recommended that the interpenetrating-hydrogels can be further developed for application as biomedical materials.

1 INTRODUCTION

Along with the increasing industry in Indonesia, all the raw material needs derived from rock materials also increase, one of which is bentonite. Bentonite is a type of clay whose availability is very abundant in Indonesia. Indonesia has a source of local raw materials based on natural polymer hydrogels, namely bentonite. The potential of bentonite in Indonesia is quite large and spread in several locations, namely the island of Java and Sumatra. one of them in the Province of Nanggroe Aceh Darussalam which is located on the western tip of the island of Sumatra. In this area the source of bentonite is still not widely processed by the government and industry. Bentonite used as filler was first made into bentonite nanoparticles using the coprecipitation method. Hydrogel is a hydrophilic polymer network that is cross-linked

and has the capacity to expand (swelling) by absorbing water or biological fluids but is insoluble due to crosslinking. Hydrogel from poly (acrylic acid) -ko-polyvinyl alcohol can be synthesized from cranic acid and polyvinyl alcohol using gamma irradiation (Nesa, 2017). This is indicated by an increase in absorption (Erizal, 1998). The ability of a hydrogel to absorb water that is insoluble in water is indicated by the presence of cross connective tissue when ex-posed to water will form a three-dimensional mac-romolecular network (Zohuriaan-Mehr, 2008).

Cross-linking in bentonite can improve the characteristics of bentonites such as solubility in water, or organic solvents, bacteriostatic effects, chelating ability and complexing. Processing with N, N dengan-methylene bisacrylamide (MBA) acrylic acid as a crosslinker is expected to bind natural

nanobentonite added in the interpenetration network of the formed polyvinylalkyton-polyacrylate hydrogel polymer. Polyvinylalkohol (PVA) is an environmentally friendly polymer that is widely used as a medical polymer, including: soft lenses, absorbents, wound dressings, drug carriers, cosmetics, and so on. PVA applications as absorbents are hampered by their low mechanical properties so they are easily destroyed, especially if applied in excessive water medium (Kobayashi et al.,2008).

2 MATERIALS AND METHODS

2.1 Materials

Bentonite. Other reagents are commercially available. Acrylic acid (AA) and Ammonium Persulfate (APS) are used as initiators of polymerization, Poly-vinylalkohol (PVA), N, N'-metylenbisacrylamide (MBA).

2.2 Preparation PVA 10%

Technical PVA is weighed as much as 10 grams, then dissolved into 100 mL of distilled water, sterilized and heated at 90°C for ± 3 hours until dissolved.

2.3 Making Bionanocomposite Hydro-gel Interpenetration

The reflux device is equipped with a 250 mL 4 neck flask, mechanical stirrer, condenser and thermometer. Entered 6 mL aquadest, added nanobentonite with a variation of weight 0; 0.2; 0.4; 0.6 and 0.8 and heated the mixture at 60°C with a water bath and stirred constantly until it turns into a sticky solution like a transparent paste. Enter 10% PVA solution with variations of 1 ml, 2 ml, 4 ml, 6 ml and 8 ml into the reaction flask. Put 7 ml AA with 0.04 g N, N'-metilenbisakrilamida (MBA) into the reaction flask. After bubbling, nitrogen gas is poured for 30 minutes. 0.05 g of Ammonium Persulfat (APS) was added into the reaction flask with a mechanical stirrer. The reaction mixture temperature is raised to 60°C and the reaction is maintained for 1 hour. Soaked with ethanol products Which is produced for 24 hours. Dried in the oven for 24 hours at 60°C.

2.4 Characterization

2.4.1 Analysis of FTIR

FTIR analysis was used to determine the functional groups found in graphene oxide. Then the sample is prepared in liquid form (suspension), then the sample is dropped between two KBr plates to make a thin film. Then the plate is placed on the sample to be passed by infrared light. FTIR analysis using the Prestige-21 IR device was carried out in the wave number range 4500-450 cm⁻¹.

2.4.2 Morphological Analysis with SEM

The microscopic observation process using SEM was carried out on the sample fault surface. Then after the sample is cleaned with a blower, the sample is coated with gold and palladium in a machine that presses 1492 x 10⁻² atm, the sample is then put into a room (vacuum evaporator) with a pressure of 0.2 Torr using the JSM-35 C Shimadzu machine . Furthermore, the sample is irradiated with a 20 kV electron beam in a special room so that the sample emits secondary electrons and electrons which are bounced can be detected by the Scientor detector which is amplified by an electrical circuit that causes a 4 minute Cathode Ray Tube (CRT) to appear. Then the 400 Armstrong coating is inserted into the Chamber specimen to be carried out by removing secondary electrons and the detectors can be detected by the detector. The shooting results can be adjusted to the desired magnification for shooting.

2.4.3 Test the Percentage of Water Absorption

Testing the percentage of water absorption was carried out by determining the percent swelling ratio by measuring the initial weight (Wd) of the sample which was then immersed in distilled water for 24 hours. use filter paper and measure the final weight again (Ws). Measuring the percentage of water absorption in the hydrogel can be determined by the following formula:

Where:

$$\text{Degree of cross tie (\%)} = \frac{W_a}{W_b} \times 100\% \quad (1)$$

Wa = weight of dry hydrogel after soaking

Wb = weight of dry hydrogel before immersion.

3 RESULTS AND DISCUSSION

FTIR functional group test results on bentonite hydrogel, 2 ml PVA: 7 ml AA, and APS 0.05: NBA 0.2 grams with the addition of MBA as much as 0.04 grams can be seen in Figure 1. Hydrogel that has been made in cluster analysis its function using FTIR. The main functional group of bentonite constituents can be seen through absorption of the OH group at 2985.16 cm^{-1} , Si-OH-Si group at 1027.67 cm^{-1} , Al-O-Si group at 799.30 cm^{-1} , Si-O group at 521.99 cm^{-1} , the O-H group bending at 978.74 cm^{-1} and at 3392.96 cm^{-1} and 1647.54 cm^{-1} are adopted water molecules. The above functional group is the main functional group of bentonite in the hydrogel. This result is in accordance with the research (Darvishi, 2010).

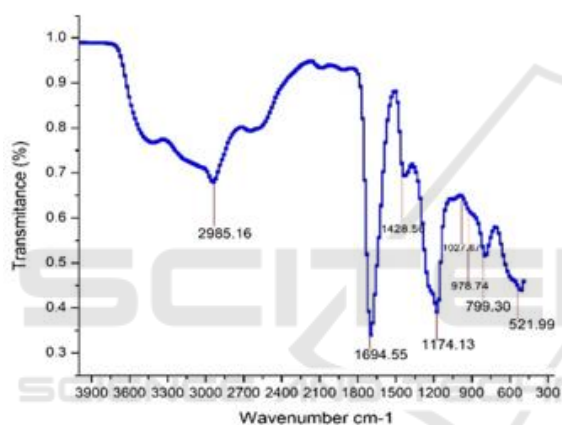


Figure 1: FTIR of hydrogel bentonite 0,2 g.

Figure 2 shows the results of SEM 500x magnification in PVA / AA / APS / NBA / MBA hydrogel composite samples. Because PVA dissolves in water (Gao, 2015). whereas bentonite is a hydrophilic polymer and swelling in water, the three can be mixed like shown in Figure 2. In general, it can be seen that the morphology of the full PVA / AA / APS / bentonite / MBA hydrogel SEM has a rough surface and large density. This shows that the polymer network formed will converge and interact with each other. Irregular shapes provide porous space so that absorption can occur. Heterogeneous surfaces indicate that there are areas that experience interactions between bentonite chains and there are also areas that do not form interactions of the bentonite chain.

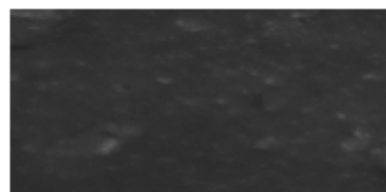


Figure 2: SEM image of NBA 0,4 g.

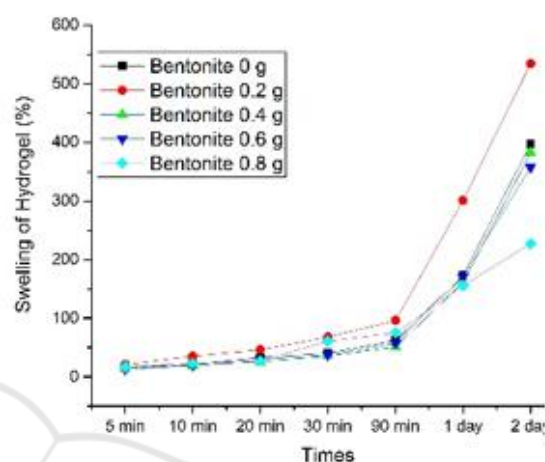


Figure 3: Graph of Absorption Test Results.

Based on the table and graph above, shows that the hydrogel semi-interpenetration polymer network on the weight of the addition of bentonite is 0.4 g; 0.6 g and 0.8 g still have low absorption compared to the blank. It can be said that the more the amount of bentonite used, the smaller the value of the absorbed water. The solvent re-sistance test is carried out to see how far the hydrogel is resistant to solvents such as water. The polymer Material for the build up of the hydrogel should inflate (swell) and retain the water fraction of its structure, but not soluble in water. Both natural and synthetic materials have been widely used to synthesize hydrogels (Dragan et al., 2012), (Matricardi, 2013).



Figure 4: Graph of Absorption Test Results.

Hydrogels with crosslinked structures can absorb water, but are not soluble in water. The process of entering water into the hydrogel matrix results in the development of the hydrogel itself (Yang,2012). Revealed that at the beginning of the absorption process, water diffuses in the network continuously until it reaches equilibrium conditions, with maximum development. After the equilibrium phase, the amount of water absorbed decreases due to the gel liquefaction cycle. In Figure 4, the percent of development increases as a function of time and reaches the maximum condition after \pm 24 hours of immersion, for all bentonite / PVA hydrogel concentrations which are 0 g; 0.2 g; 0.4 g; 0.6 g and 0.8 g.

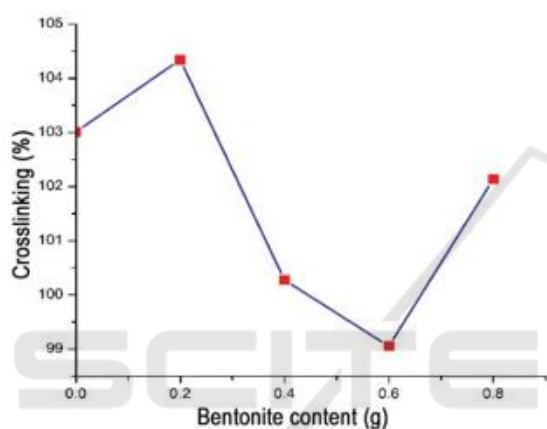


Figure 5: Graph of test results% Crossed.

4 CONCLUSIONS

Optimum condition obtained through hydrogel absorbent power test and superabsorbent cross tie test using full IPN method with a variation of time 5 minutes, 10 minutes, 20 minutes, 30 minutes, 90 minutes 1 day and 2 days with variations of bentonite 0.2 grams. Cross-binding agent concentration of MBA 0.4%, and the concentration of APS initiator 0.5%. The value of this site hydrogel ratio is 533.83% and the cross belt is 104.34%. The power of the bentonite structure can be improved by conducting polymerization using the full IPN method.

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