

Synthesis of Semi Interpenetrating Polymer Network's Hydrogel from Bacterial Cellulose

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Abstract: Semi interpenetrating polymer network's (IPN) hydrogel from bacterial cellulose (BC) has been successfully synthesized. This semi-IPN hydrogel was prepared from a suspension of BC in a solvent system of PEG1000/NaOH in the presence of acrylic acid (AA) as monomer, potassium persulfate (KPS) as initiator, and N,N'-methylenebisacrylamide (MBA) as crosslinker. The obtained semi-IPN hydrogel was characterized using FT-IR and SEM, also its physical property was characterized, i.e. swelling degree and crosslinked percentage. The swelling degree and crosslinked percentage showed the semi-IPN's hydrogel with the addition of 600 mg BC has the maximum value, 1338 and 46%, respectively. The FT-IR analysis exhibited the crosslinked formation between AA and MBA with the presence of band at 1555 cm⁻¹ that assigned as secondary aliphatic amine. The morphological analysis of semi-IPN's hydrogel has a rough and dense surface.

1 INTRODUCTION

Cellulose is an abundance natural polymer that constructed by glucose as the monomer, and it can be easily found as a component in the plants and natural fibers, i.e. cotton and linen. Several bacteria (e.g. *Acetobacter xylinum*) can produce cellulose (exopolysaccharide) (Ross et al., 1991). Cellulose that produced by microbe or bacteria is called as bacteria cellulose which has similar chemical properties with cellulose from plants (Czaja et al., 2007). Cellulose and BC also constructed by glucose unit that linked through 1,4-β-glycoside, this resulted in the highest crystallinity degree of cellulose and BC, and it cannot soluble in water and other common solutions. The different between these two celluloses is the fiber size. Generally, BC has a nanosized fiber but in cellulose-plants, the most common sized of fiber is micro-sized. The other advantage of BC is mostly free from impurities, i.e. pectin and lignin.

Cellulose is found in agricultural waste, including 58% rice husk, 56.86% sago bark, corn cob 44.9%, 40-45% hardwood, 38-49% softwood, oil palm empty fruit bunches 36 - 42%, esparto 33-38%, bagasse 32-44%, wheat straw 29-37%, rice

straw 28-36% and bamboo around 26-43% (Ito et al., 2007).

Cellulose-based hydrogels can be obtained via either physical or chemical stabilization of aqueous solutions of cellulose (Chang et al., 2008). Additional natural and/or synthetic polymers might be combined with cellulose to obtain composite hydrogels with specific properties (Sarkar, 1979).

One polymeric material that currently famous for multipurpose is hydrogel which can be synthesis from natural and synthetic polymer, e.g. cellulose, chitosan, alginate, etc. Hydrogel as the multipurpose material has been utilized for medical, cosmetic, wound healing, agriculture, etc. Hydrogel can be synthesized through several techniques, one of them is semi-IPN. This technique has a lot of advantages, especially to the chemical and physical properties of the obtained hydrogel. The objective of the current study was to determine the physical properties of the hydrogel and learn about its chemical structure through FT-IR data also the morphological from SEM images.

Hydrogels can be produced through the Interpenetrating Polymer Network (IPN) technique. Interpenetrating Polymer Network (IPN) is a polymerization system that is made simultaneously

and sequentially to produce overlapping networks. IPN is made through crosslinked polymeric materials that are synthesized by condensation, addition or propagation using several monomers, then the resulting polymer is polymerized and crosslinked (Banerjee et al., 2010).

The crosslinker used in this study is N, N'-methylene bisacrylamide (MBA) which reacts with carboxyl functional groups in the polymer chain to form a polymer network. The ability of polymers to absorb water is very dependent on the degree of crosslinking (Garner et al., 1997).

Acrylic Acid (AA) is a type of hydrophilic monomer which is the raw material for the manufacture of acrylic polyacetylenes (PAA) polymers. The chemical structure of the acrylic acrylic (PAA) has ionizable -COOH group units. This polymer chain can be crosslinked to the -OH group. By progress in the development of research and technology, in recent years research relating to acrylic acid polymers (PAA) is being intensively developed as a base material for new biomaterials (Billmeyer, 1984).

The combination of biopolymers and synthetic polymers will produce superior hydrogels. Cellulose is one of the basic ingredients of hydrogel which is widely used as a raw material for wound dressing, inexpensive, biodegradable, and biocompatible (Sannino et al., 2009). Cellulose can also be produced by microorganisms, bacterial cellulose (BC) which is purer than cellulose derived from plants because it is free of lignin, hemicellulose, and other biogenic products (Brown, 2007).

2 MATERIALS AND METHODS

2.1 Materials

The chemical in this study were analytical grade, i.e. sodium hydroxide (Merck), acrylic acid (Sigma Aldrich), N,N'-methylenebisacrylamide (Merck), potassium persulfate (Merck), and Polyethylene glycol 1000 (Merck). Bacteria cellulose in this study was obtained by culturing *A. xylinum* in the coconut water medium (Gea et al., 2011).

2.2 Synthesis of Semi-IPN's Hydrogel

About 200 mg of bacteria cellulose powder was suspended in 100 mL of distillate water that contained PEG and NaOH 3:4. The suspension was placed in freezer at -5°C for 24 h. The frozen suspension was melted and homogenized using

magnetic stirrer at room temperature for 2 h, as the result the transparent solution was obtained. About 5 mL of the transparent solution was reacted with 760 mg of AA, 40 mg of MBA, and 54 mg of KPS. These mixtures were stirred at 60°C for 15 min until all components was homogenous. At the end of polymerization, the transparent hydrogel was washed with distillate water until the neutral pH was reached. The obtained hydrogel was dried in oven and kept in desiccator. This procedure was repeated for the other composition of BC (400 mg; 600 mg; 800 mg and 1000 mg).

2.3 Characterization

The obtained hydrogel was characterized using FT-IR (Bruker Opus Alpha 7.5) and SEM (Quorum Model Q150R ES). The physical property of hydrogel also characterized, i.e. swelling degree and crosslinked percentage.

Swelling degree

Five sample replications were dried in oven at 60°C until the constant weight was obtained. These samples were soaked in water for 24 h. The swollen samples were separated from the solvent and weighed (S. K. Bajpai & Swarnkar, 2014). The swelling degree of these samples were determined using the equation (1) below:

$$\text{Rasio Swelling (\%)} = (W_s - W_d) / W_d \times 100\% \quad (1)$$

Where W_s was the weight of swollen sample and W_d was the weight of dried sample.

Crosslinked degree

Five sample replications were dried in oven at 60°C until the constant weight was obtained. These sample were soaked in chloroform for 24 h and then dried at 60°C for 3 h. The dried hydrogel was weighed (S. K. Bajpai & Swarnkar, 2014), and the crosslinked degree was determined using the equation (2) below:

$$\text{Crosslinked degree (\%)} = W_a / W_b \times 100\% \quad (2)$$

where W_a was the dried weight of hydrogel before soaked in chloroform and W_b dried weight of hydrogel after soaked in chloroform.

3 RESULTS AND DISCUSSIONS

3.1 Synthesis of Semi-IPN's Hydrogel

The semi-IPN's hydrogel (Fig.2) was prepared from BC in the combination of poly-AA. As in method,

this hydrogel was prepared by varying the mass of BC. The obtained hydrogel was prepared using free radical polymerization technique, the initiator was KPS and the crosslinker was MBA. The obtained semi-IPN's hydrogel was reacted in the alkaline condition by the using a solvent system of PEG/NaOH.

The chemical structure of semi-IPN's hydrogel was constructed by the crosslinked poly-AA with MBA (crosslinked network of poly-AA). In other hand, the BC in the hydrogel system was overlapped with the crosslinked network of poly-AA. Illustration of making semi-IPN hydrogel and hydrogel can be seen in Fig.1.

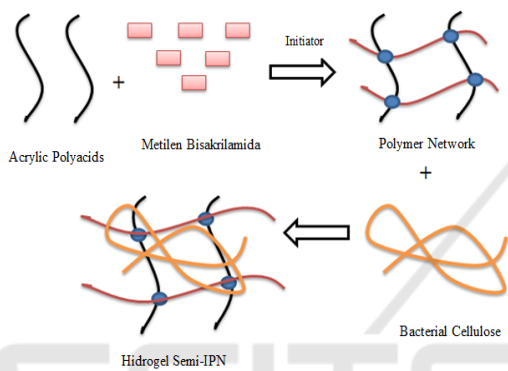


Figure 1: Illustration of Semi-IPN Hydrogel Manufacturing.

3.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

FTIR spectra of BC, poly-AA, and semi-IPN's hydrogel can be seen in Fig.3.

In the FTIR spectrum of bacterial cellulose (Figure 1), there is an absorption peak at 3336 cm^{-1} indicating the presence of hydroxyl (O-H) stretching. Also, there is an absorption peak of 2891 cm^{-1} indicating the presence of -C-H bonds. At the peak of the absorption of 1424 cm^{-1} is the vibration vibrations of $-\text{CH}_2$. There is also an absorption peak of 1157 cm^{-1} where the spectrum shows uptake of -C-O groups originating from bonds between carbon atoms and hydroxyl groups in bacterial cellulose (Suo et al., 2007).

FT-IR spectra of poly-AA and semi-IPN showed a similar band with the spectrum of BC, but only different in their intensities. A significance different can be observed near $1600\text{-}1650\text{ cm}^{-1}$ that assigned as secondary amine group of N,N'-methylenebisacrylamide (MBA). Also, the most dominant band of this kind of sample can be observed at $3000\text{-}3600\text{ cm}^{-1}$ that confirmed the

presence of hydroxyl group from BC and acrylic acid. The presence of secondary amine also can be observed near $715 - 874\text{ cm}^{-1}$.

Based on Fig.3, the shape and absorption band of 600 mg semi-IPN semi-IPN hydrogel did not have a significant difference with the infrared absorption of the hydrogel blank. This proves that the cross-linking process between AA monomers (forming polyacrylic acid) and the MBA cross-linker has been formed. The existence of SB is proven to be able to provide a physical bonding effect characterized by the formation of semi-IPN hydrogels without changing the shape of the absorption band on the hydrogel made. The description of functional groups that were successfully observed by FTIR spectrophotometer between hydrogel blanks and 600 mg semi-IPN hydrogels did not differ much only by shifting wave numbers (Sannino et al., 2009).

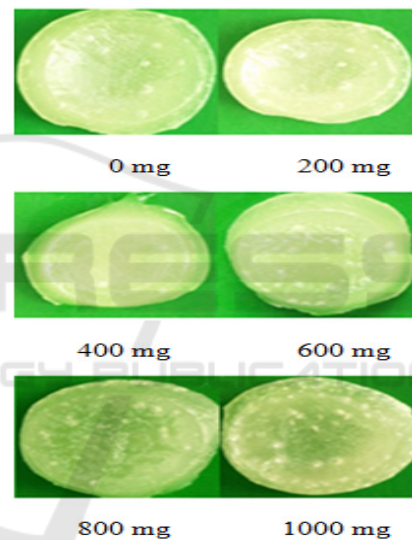


Figure 2: The Obtained Semi-IPN's Hydrogel.

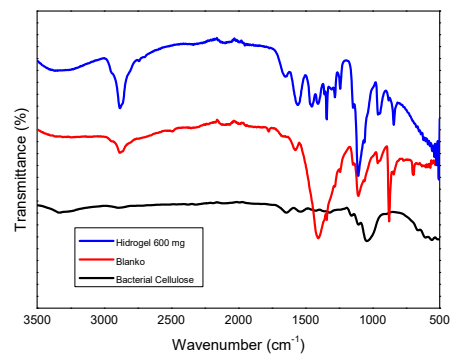


Figure 3: FTIR spectra of (a) BC, (b) poly-AA, and (c) semi-IPN with 600 mg of BC.

3.3 Scanning Electron Microscopy (SEM) Analysis

The morphological analysis using SEM was performed to observe the surface characteristic of the obtained semi-IPN's hydrogel. Fig. 4 (a) the obtained hydrogel poly-AA formed an agglomerate. Hebeish et al. (2014) in his research explained that the formation of agglomerate was twisting effect, an indication of interaction. But a unique result was found in Fig 4 (b), small pores were observed on the hydrogel surface. The presence of this pores in the semi-IPN's hydrogel can enhance the diffusion and swelling degree of hydrogel (Astrini et al., 2016).

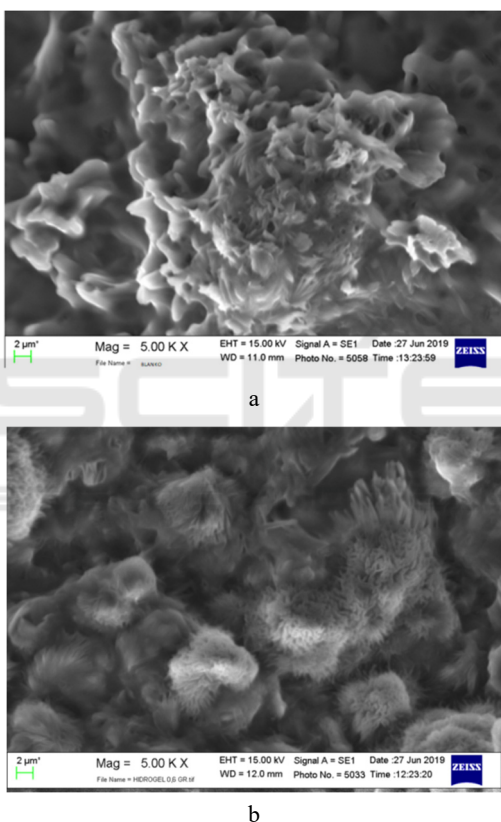


Figure 4: The morphological of hydrogel (a) poly AA and (b) semi-IPN.

3.4 Crosslinked Degree Analysis

The result of crosslinked degree is exhibited in Fig 5.

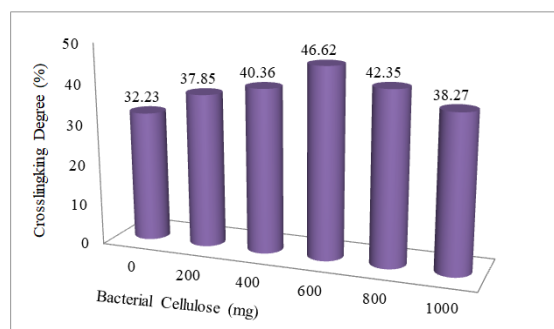


Figure 5: The crosslinked degree of semi-IPN's hydrogel.

The crosslinked degree with the maximum is observed in the addition of 600 mg of BC. This can be assumed as the formation of a long polymer chain and was linkage in the specific positions. But the decrease of crosslinked degree observed in the addition of 800 mg and 1000 mg of BC. This can be assumed at this amount of BC the elasticity modulus of semi-IPN was limited as the van der Waals and hydrogen bonding interactions between BC and AA. This decrease is caused by the occurrence of equilibrium so that the addition of SB can reduce mechanical properties due to irregular polymer chains (Dragan et al., 2012).

3.5 Swelling Degree Analysis

The ability of hydrogel for absorbing water was determined using swelling degree. Hydrogel can be swelling, has a transparent and smooth surface, and flexible (Okay & Sariisik, 2000). The swelling degree of semi-IPN's hydrogel can be seen in Fig.6.

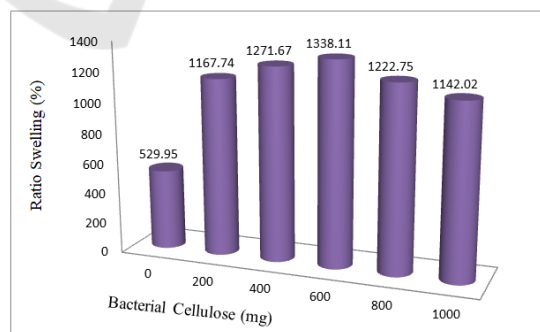


Figure 6: Swelling Degree Of Semi-IPN's Hydrogel.

Based on the Fig.5, the swelling degree increase with the increase of BC in the hydrogel system. But the value decrease when the addition of BC is more than 0.6 g. For the first case, with the increase of BC in the hydrogel system it will have a direct impact to

the number of hydroxyl group. The increase of this hydroxyl group will influence the hydrophilicity of hydrogel. But in the second case, the increase of hydroxyl group may disturb the equilibrium of water, as the impact the water diffusion become low (S. K. Bajpai & Swarnkar, 2014). The other reason of the decrease of swelling degree at the addition of BC of 0.8 and 1.0 g can be caused the ratio between MBA-poly AA and BC was not balanced. It can be assumed, as the impact there are some of BC that will not interact with MBA-poly AA through van der Waals and hydrogen bonding interaction (A. K. Bajpai & Giri, 2003).

4 CONCLUSIONS

Semi-IPN's hydrogel has been successfully synthesis using BC, AA and MBA through free radical polymerization. The maximum value of crosslink degree and swelling degree was found at 600 mg, with the value of 46,62% and 1338%, respectively. The FT-IR spectra confirmed the crosslinked of MBA to AA was found at 1555 cm^{-1} . The morphological surface of semi-IPN's hydrogel showed a rough and dense surface.

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