

# Optimization of Polymer Networks using Variations in Molecular Weight of Polyethylen Glycol in the Manufacture of Semi – IPN Hidrogels from Coconut Water Cellulose Bacteria

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**Keywords:** Hydrogel IPN, Coconut Water, Bacterial Cellulose.

**Abstract:** Research have been done to find out the effect of variation molecular weight polietylen glikoln 1000; 3000 and 6000 on manufacture semi interpenetrating polymer networks hidrogel from bacterial selulose with sytem fermentation using acetobacterial-xylum in based coconut water. IPN hidrogel by polietilenglikol 6000 has more croslinks compared using peg 3000 and peg 1000. Analysis thermal hidrogel IPN using peg 6000 is 457,14 °C, compared PEG 3000 is 252, 80 °C and PEG 1000 is 249,30 °C. semi-IPN hidrogel formed was characterized by, crosslink percentage, chemistry structural analysis using Fourier Transform Infrared (FT-IR) spectroscopy, water absorption test and thermal resistance using Differential Thermal Analysis (DTA). From the analysis, they showed Semi Interpenetrating Polymer Network Hydrogel with using PEG 6000 the highest crosslink percentage (64,3%) for PEG 3000 is 42.5 % and PEG 1000 is 15. 7 %. Characterization results of FTIR indicate the occurrence of crosslinking between Polyacrylic acid and MBA. This shown in existence of 1403  $\text{cm}^{-1}$  and 1560  $\text{cm}^{-1}$  (COO<sup>-</sup>) and 3413  $\text{cm}^{-1}$  (NH amine). Thermal analysis using Differential Thermal Analysis (DTA) shows thermal optimum thermal stability at the addition of Polietilenglikol 6000 to semi-IPN hidrogel which was completely degraded at 680°C, reaction that occurs during the decomposition process is endothermic and exothermic reaction.

## 1 INTRODUCTION

Hydrogel is a hydrophilic polymer with a network structure that has crosslinking. Hydrogels have the ability to absorb a certain amount of water without the dissolution process and have hydrodynamic properties of cells in many ways (Lee, 2009).

Making hydrogels can be done by several methods, namely graft polymerization methods, crosslinking physics, chemical crosslinking, and crosslinking radiation (d). One way to improve the mechanical properties of the hydrogel is to make modifications through the formation of the Interpenetration Polymer Network (IPN) (Rimmer, 2011).

Making semi-JPI hydrogels for biomedical applications can be mixed with natural ingredients. Another natural material that may be developed as an alternative to biomedicine is *Centella asiatica* plant. Gotu Kola is believed to cure various types of diseases because it has bioactive components that are useful for the body. The chemical content of

gotu kola including Triterpenoid: asiaticosida, madekasosida, cyanic acid, indosentoat acid, bayogenin; Flavonoids: kaemferol, kuesertin; Saponins: sentelasapogenol A, B and D; and Tanin (BPOM RI, 2010). Bioactive components contained in gotu kola have a function for health, one of which is antibacterial. Bioactive components of gotu kola which have antibacterial properties are flavonoids, tannins and saponins (Zhao et al., 2009). The mechanism of flavonoids inhibits bacterial growth by denaturing bacterial cell proteins, causing all bacterial cell metabolism to stop, tannins can inhibit bacteria by changing the permeability of the cytoplasmic membrane. Saponins can form complex compounds with cell membranes through hydrogen bonds so that they can destroy the permeability of bacterial cell walls.

Zhao et al, (2009) stated that Pegagan ethanol extract had higher antimicrobial activity than petroleum ether and water extract. The results showed that Gotu kola ethanol extract had a minimum inhibitory content (MIC) of 125  $\mu\text{g} / \text{ml}$  in *Propionibacterium vulgaris*, *Staphylococcus aureus*,

*Escherichia coli*, *Aspergillus niger* and *Candida albicans*. Whereas in *Bacillus subtilis* and *Aspergillus flavus* is 62.5 µg / ml. (Heibesh et al., 2013) found antimicrobial activity of asiatic acid which is a saponin derivative in gotu kola against several gram positive and gram negative bacteria. Gotu kola is also used as a toothache medicine in the general public, but until now there has been no research or clinical data that supports it.

Heibesh (2013), has made a semi-JPI hydrogel by mixing isopropyl acrylamide and cellulose. From the results of Heibesh's research, it was obtained semi-JPI because cellulose was used in the form of a linear carbon chain which was optimum at the addition of cellulose by 20%.

Bajpai (2014), has made a semi-JPI hydrogel from microcrystalline cellulose and acrylic acid with N crosslinking, N'-Methylene Bisacrylamide. Microcrystalline cellulose produced from cellulose bacteria was dissolved in PEG (1000, 3000, and 6000) / NaOH solvents which were then polymerized.

This study aims to make semi-JPI hydrogels using various types of polyethylene glycol and analyze how the crosslink degree and absorption power obtained in PEG / NaOH solvent systems with acrylic acid using N, N'-Methylene Bisacrylamide crosslinking and the effect of adding bacterial cellulose which functions as a biopolymer which can improve the nature of hydrogel absorption.

## 2 EXPERIMENTALS

Bacterial cellulose is made from coconut water with the help of *Acetobacter-xylinum* bacteria. put into a beaker glass containing 100 mL solvent system Polyethylene Glycol 1000 (6% wt / vol) and NaOH (8% wt / vol). The dispersion that occurred in the refrigerator at -5°C for 24 hours. The frozen solid obtained was left at room temperature with stirring for 2 hours. The clear solution produced is then filtered with ordinary filter paper which will be used to make hydrogels. The same method is carried out using 3000 polyethylene glycol and polyethylene glycol 6000.

### 2.1 Hydrogel Preparation

A total of 5 mL of bacterial cellulose (BC) 1000 solution was put into a glass beaker then added 10.75 mmol of Acrylate Acid monomer, 200 µmol of initiator of Potassium Per Sulfate, then added

little by little 260 µmol N crosslinking, N'-Methylene bisacrylamide. Then stir for 15 minutes at 60°C. After the polymerization is complete, the results of the spring JPI hydrogel are poured into a test tube, then heated into the oven at 60°C for 2 hours. After that, the results of the hydrogel were released and flowed with distilled water and then stored in a desiccator for 3 days.

Table 1: Comparison of Additions of BC 1000.

Sample	BC (g)	Aac (mmol)	MBA (umol)	KPS (umol)
A	0.2	10.75	260	200
B	0.4			
C	0.6			
D	0.8			
E	1.0			

Table 2: Comparison of Additions of BC 3000.

Sample	BC (g)	Aac (mmol)	MBA (umol)	KPS (umol)
A	0.2	10.75	260	200
B	0.4			
C	0.6			
D	0.8			
E	1.0			

Table 3: Comparison of Additions of BC 6000.

Sample	BC (g)	Aac (mmol)	MBA (umol)	KPS (umol)
A	0.2	10.75	260	200
B	0.4			
C	0.6			
D	0.8			
E	1.0			

### 2.2 Test of Water Absorption

Testing of water absorption was carried out by determining the percent swelling ratio by measuring the initial weight (mo) of the sample which was then immersed in distilled water for 24 hours. The samples that have been soaked are then filtered using filter paper and measured again heavily (me). The amount of water absorbed in the hydrogel can be calculated using the following equation:

$$E = (me - mo) / mo \times 100\% \quad (1)$$

### 2.3 Percentage Test of Crosslinks

The percentage of crosslinking was carried out by determining the crosslink percent percent where the dry weight of the resulting hydrogel was weighed. Then the hydrogel is soaked with a solvent (chloroform) for 24 hours. After immersion, the hydrogel is heated at a temperature of 60°C to dry for 3 hours. The dry weight of the hydrogel after immersion is determined by weighing using an analytical balance. The degree of crosslinking can be determined by the following equation:

$$\% DC = Wg / (Wo) \times 100 \quad (2)$$

Where Wg is the weight of the dry hydrogel after immersion and Wo is the weight of the dry hydrogel before immersion.

### 2.4 FTIR Analysis

The specimens are clamped at the place where the sample is then placed on the tool in the direction of infrared light. The results will be recorded on a paper scale of the wave number curve to the beam intensity in the form of a spectrum graph.

### 2.5 TGA Analysis

Weighed ± 10 mg of sample, then put into aluminum cell then pressed. The pressed cell is placed in a position adjacent to the reference cell. After the instrument is in equilibrium, the analysis device is operated with a temperature of 40°C to 600°C with a speed of heating increase of 10°C / minute and the gas used is nitrogen. The results obtained are in the form of graphs of % of mass lost to temperature.

## 3 RESULTS AND DISCUSSIONS

Making semi-JPI hydrogels was obtained through free radical polymerization of acrylic acid monomers (AA) in the presence of MBA crosslinkers and dissolved cellulose polymers. The polymer network formed consists of crosslinked covalent poly (acrylic acid) chains that are physically entangled with cellulose and parts of PEG macromolecules. The illustration of making a semi-JPI hydrogel is shown in Figure 3.1. The crosslinking used in this study is N, N'-Metilen Bisakrilamida (MBA) which reacts with carboxyl functional groups in the polymer chain so that a polymer network is formed as shown in Figure 1 and 2.

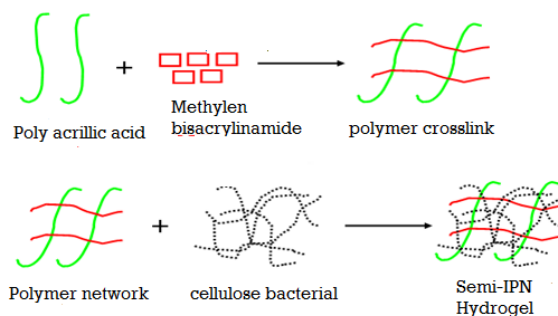


Figure 1: Manufacture of Semi-IPN Hydrogel.

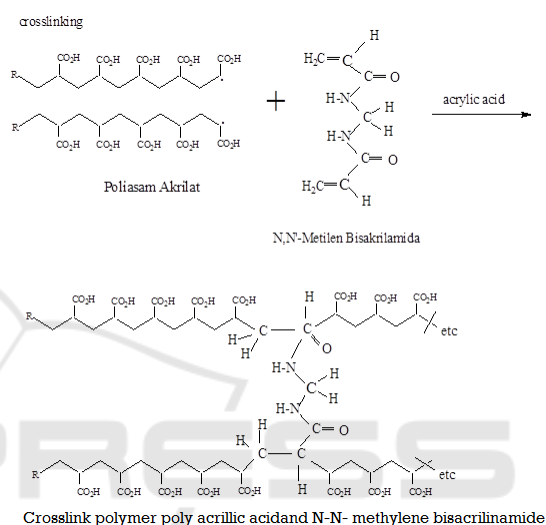


Figure 2: Polyacrylic crosslinking process.

Figure 3 showed the final form of the semi-IPN Hydrogel.

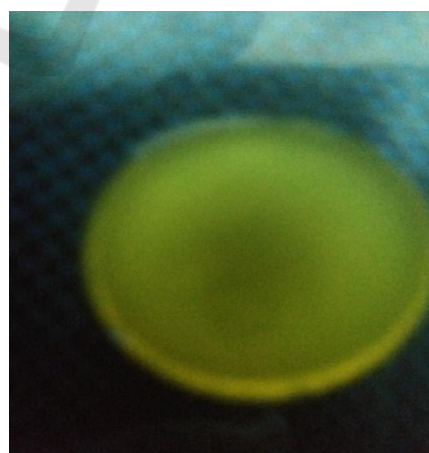


Figure 3: Semi-IPN hydrogel with the addition of KMS as much as (a) 0.2 g (b) 0.4 g (c) 0.6 g (d) 0.8 g (e) 1.0 g for polyethilen glycol 6000.

The percent value of cellulose hydrogel swelling ratio can be seen in Table 4

Table 4: Percentage of Semi-IPN Hydrogel Swelling Ratio Data.

Weight KMS (g)	Initial Weight (g)	Final Weight (g)	Swelling (%)
0.2	0.83	4.00	382
0.4	0.83	5.40	551
0.6	0.98	6.51	564
0.8	0.83	6.50	683
1.0	0.71	5.05	611

Based on Table 4, it is seen that the percent value of the swelling ratio increases with increasing KMS weight. This is because the amount of weight of KMS in the polymerization mixture affects the percent value of the swelling ratio in the hydrogel.

The more the number of KMS, the -OH group also increases, causing high hydrophilicity. Therefore, the water in the hydrogel increases. However, at the addition of 1.0 grams of KMS, the percent swelling ratio decreases again, this is due to the optimum physical interaction which causes the diffusion of water in the hydrogel to decrease, according to Bajpai's research (2014) that cellulose hydrogels can absorb water due to the presence of -OH group of cellulose.

Data determination of the degree of crosslinking can be seen in Table 5.

Table 5: Data on the degree of crosslinking of Semi-JPI Hydrogels.

Weight KMS (g)	Initial Weight (g)	Final Weight (g)	Crosslink (%)
0.2	0.55	0.18	32.70
0.4	0.71	0.25	35.21
0.6	0.54	0.20	37.03
0.8	1.37	0.58	42.30
1.0	1.57	0.61	38.80

Based on Table 5, it can be seen that the percent degree of crosslinking increases with the increase in the number of KMS used. This is because the more number of KMS used, the hydrogel will be more dense but still elastic. Cross ties play an important role in determining elasticity. The expected network is the formation of chains as long as possible and cross-bound only in a few places. On the addition of KMS 1.0 gram percent crosslinking degree has decreased. This is due to physical interactions or the formation of hydrogen bonds between hydrogen

groups from KMS with hydrogen bonds from acrylic acid, these bonds are like hydrogen bridges or vanderwalls thus increasing the limited elasticity properties. In this case the physical bond that occurs has been optimum and so there is a decrease in mechanical properties (addition of 1.0 gram KMS) as shown in table 5. This decrease is due to the occurrence of equilibrium so that the addition of KMS can reduce mechanical properties due to irregular polymer chain chains.

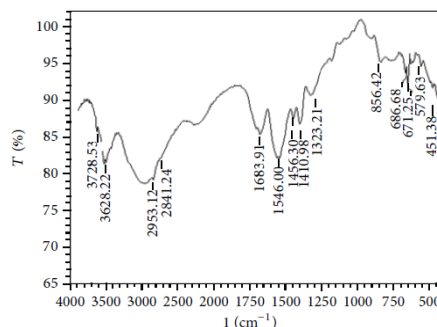


Figure 4: Commercial and Semi-IPN Hydrogel KMS Spectrum.

In the FTIR spectrum of commercial carboxymethyl cellulose it was seen that the absorption area of 1635  $\text{cm}^{-1}$  and 1427  $\text{cm}^{-1}$  showed the presence of COO-carboxyl strain vibrations and CH<sub>2</sub> bonds originating from the ester group. This shows the characteristic of carboxymethyl cellulose compounds containing carboxyl groups as a substitution between monochloro acetate and cellulose compounds. So based on the results of the FTIR analysis it can be concluded that true commercial carboxymethyl cellulose is a carboxymethyl cellulose compound.

In the FTIR spectrum of Semi-JPI Cellulose Hydrogel it was seen that the absorption area at wave number 1403  $\text{cm}^{-1}$  and 1560  $\text{cm}^{-1}$  showed stretching by Karaaslan simetry and asymmetry of carboxylic anions (2001). In the absorption area with wave numbers 1636  $\text{cm}^{-1}$  and 2110  $\text{cm}^{-1}$ , the presence of C = C and CH<sub>2</sub> groups originating from crosslinking. OH wave number 3600  $\text{cm}^{-1}$  to 2400  $\text{cm}^{-1}$  is OH group carboxylic acid, and OH group absorption alcohol about 3400  $\text{cm}^{-1}$  (Sadeghi and Yarahmadi, 2011). So that the absorption of the OH group carboxylic acid covers uptake of OH KMS groups and OH groups from PEG 1000 and NH amide groups from the MBA.

DTA is used to study thermal properties and phase changes due to enthalpy changes of a material. DTA analysis has been performed on the optimum

semi-JPI Hydrogel sample which can be seen in Figure 5.

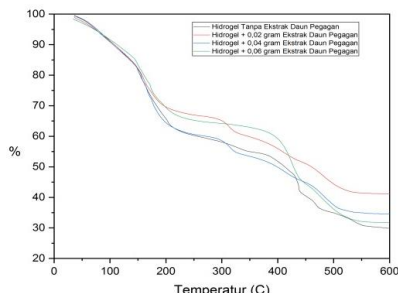


Figure 5: DTA results from optimum Semi-IPN Hydrogels.

In Figure 5 shows the thermogram of DTA for semi-JPI hydrogels with the addition of 0.8 grams of KMS. DTA analysis is carried out at a temperature of 20-650°C. The endothermic reaction occurs at 120°C, the first exothermic point occurs at 380°C, and the second exothermic point occurs at 650°C which shows that the hydrogel has completely degraded. Hydrogel with the addition of 0.8 gram KMS has the highest thermal stability (optimum) this is directly proportional to the crosslinking degree of the hydrogel, where the higher the percent degree of crosslinking the hydrogel has a high thermal resistance as well.

According to Bajpai (2014), hydrogels at temperatures below 350°C of water molecules bound to the polar group are released, and decarboxylation of COO groups associated with Poly (Sodium Acrylate) occurs. When the temperature is above 350-433°C, the number of PEG is low. At temperatures of 415-510°C, the loss of CO and CO<sub>2</sub> groups with a small amount of each other overlap. In the end, slowly and gradually at temperatures above 510°C carbonization or degradation of the process into ash.

## 4 CONCLUSIONS

1. The optimum mixture concentration in making semi-JPI hydrogels between KMS and Acrylate Acid in the presence of crosslinking N, N-Methylene Bisacrylamide and initiator of Potassium Per Sulphate is in comparison of KMS: KPS: MBA (0.8: 0.05: 0.041 b / b) where as much as 0.8 gram KMS is dissolved into the PEG 1000 / NaOH solvent system which is then added to 0.05 grams of KPS initiator and 0.041 grams of the MBA crosslinker.

2. Effect of variation molecular polyethylen glycoln weight 1000; 3000 and 6000 on manufacture semi interpenetrating polymer networks hydrogel from bacterial cellulose with fermentation systems using acetobacterial-xylinum in based coconut water. IPN hydrogel by polyethylene glycol 6000 has more crosslinks compared to peg 3000 and peg 1000. Analysis of IPN thermal hydrogel using peg 6000 is 457.14°C, compared to PEG 3000 is 252, 80°C and PEG 1000 is 249.30°C. Semi-IPN hydrogel formed was characterized by, crosslink percentage, chemistry structural analysis using Fourier Transform Infrared (FT-IR) spectroscopy, water absorption test and thermal resistance using Differential Thermal Analysis (DTA). From the analysis, they showed the highest Semi Interpenetrating Polymer Network Hydrogel with polyethylene glycol 6000 crosslink percentage (64.3%) for crosslink polyethylene glycol 3000 is 42.5% and polyethylene glycol 1000 is 15. 7%. Characterization results of FTIR indicate the occurrence of crosslinking between Polyacrylic acid and MBA. This is shown in existence of 1403 cm<sup>-1</sup> and 1560 cm<sup>-1</sup> (COO<sup>-</sup>) and 3413 cm<sup>-1</sup> (NH amine). Thermal analysis using Differential Thermal Analysis (DTA) shows that it was completely degraded at 680°C, the reaction that occurs during the decomposition of the process is endothermic and exothermic reaction.

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