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BC-g-PAA: Characterization and Establishment of the IPN Hydrogel

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Abstract: A study on the manufacture of bacterial cellulose IPN hydrogel crosslinked poly acrylic acid using the MBA crosslinker. This study aims to characterize and observe the reaction to form bacterial cellulose-based hydrogel IPN. The BC-g-PAA was characterized by the degree of cross-linking, swelling ratio, and FTIR analysis. The results of this study found predictions of the reaction process for the formation of IPN Hydrogel in several process stages, namely 1) The polymerization process of bacterial cellulose chains that form cross-linked networks independently, 2) The process of cross-linking Acrylate monomers with MBA crosslinkers in three steps, i.e. initiation, propagation and termination, 3) Reaction process Formation of IPN network. The results of the characterization test for the degree of crosslinking were 54.55%; Swelling ratio of 1631.25%. FTIR analysis shows that there is a peak that identifies the occurrence of crosslinking.

Keywords: Bacterial cellulose; Characterization; Crosslinking; IPN Hydrogel; MBA

Introduction

In the last few decades, hydrogels have attracted increasing attention of researchers. Its unique features have made hydrogel a biomaterial that can be used in many applications, especially in the medical world (Hu et al., 2019), including for contact lenses, soft tissue engineering (Dutta et al., 2019; Silva et al., 2022), drug delivery and wound healing world (Firlar et al., 2022). In addition, hydrogel research has also been developed in environmental control processes, namely the incorporation of hydrogel-based thermo-responsive compounds (Orlando, 2019). Hydrogel as a hydrophilic material which have the ability to swell in water and develop a 3D network structure but insoluble (Aswathy et al., 2020; Khan et al., 2021). Hydrogel retains its original shape when it swells. It has special surface properties to stimulate tissue as a good biocompatibility when in contact with blood, body fluids and living tissues. Hydrogel is a bioactive material for biological application, care product, and agriculture (Chaiyasat et al., 2018).

IPN hydrogel has advantages in the pharmaceutical industry (Zou et al., 2020), including in engineering bone tissue (C. Wang et al., 2019; Zhang et al., 2019), its good swelling capacity can increase the solubility of hydrophobic drugs, it is effective in controlling drug retention (Lee et al., 2019). This IPN delivery system has low antigenicity, and has good biodegradability properties. IPN Hydrogels have special features in the cross-linking process that occurs. This IPN occurs when 2 or more polymers are connected to form a network that is linked before other polymers without covalent bonds, where the polymers have the same kinetics and are not separated by a dramatic phase (Wu et al., 2020). The formation of IPN occurs in two stages, namely a sequential free radical polymerization process in which the very relative molecular mass is neutral, and the second step is the incorporation of the polymer network onto the first network of swollen heterogeneous polyelectrolytes (Y. Wang et al., 2019). This IPN

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hydrogel is good for use in drug delivery systems of relieved release due to the nature of the multi-polymer chemical–physical combination. IPN hydrogels have superior mechanical strength, are stable phases and produce a synergistic effect of the polymer components (Na et al., 2019).

Hydrogel has been developed from both a) natural include chitosan, gelatin, alginate, agarose, collagen, cellulose etc. and b) synthetic polymers include polyvinyl alcohol, polyethylene oxide, polyphosphazene, polyacrylic acid, etc (Kabir et al., 2018). Hydrogel biopolymer base is a naturally sourced hydrogel. It has biokompatibily, biodegradability, non toxicity. Mainly from naturally polysacharide cellulose.

Cellulose can be used for hydrogel production, several structures and properties to act as a platform for tissue engineering (Dutta et al., 2019; Irham, Marpongahtun, et al., 2023). Bacterial Cellulose was produced by *Acetobacter Xylinum,* it has biodegradablity, and pure cellulose content (Iqbal et al., 2022; Irham et al., 2021; Santosa et al., 2022). Bacterial Cellulose has a high tensile strength, porous and easy to store (Irham, Hardiyanti, et al., 2023; Suryanto, 2017).

In this study, pH-responsive hydrogel based on BC, grafted with AA were synthesized by using gamma radiation polymerization. The grafting monomer of AA were determined and compared between two types of ratio BC: AA. The characteristics of the pH-responsive hydrogel were analyzed using ATR-FTIR. The pH-responsive of the hydrogel was investigated using swelling test in different pH buffer solutions.

Method

Materials

We used NaOH (pa Sigma), H_2O_2 (pa Sigma), sodium hypochlorite (merck), oxalic acid (Merck), sodium hypochlorite (pa Sigma), oxalic acid (pa Sigma), DMSO (pa Aldrich), *N, N'- methylenebisacrylamide* (MBA) (pa Aldrich), potassium persulfate (pa Aldrich).

Preparation of Bacterial Cellulose

500 ml of coconut water, 1 gram of ammonium sulfate and 80 grams of sugar are stirred until homogeneous, added glacial acetic acid (p.a) to be pH 4, poured to a steriled media, added 80 ml of Acetobacter xylinum culture is to the solution, than cooled at 30 ± 2. Check the solution after 7 days. The pellicle produced (nata) are washed by water, NaOH and H_2O_2. Then pressed to removed purified pellicle from water content (Irham et al., 2020).

Preparation of Hydrogels IPN

The bacterial cellulose, 40 mL of distilled water was heated to a temperature of 65^{0}C while stirring with a stirrer, and left for half an hour at this temperature, then 0.25 g of potassium persulfate was added while still heating and stirring, and left for half an hour at 65 ^{0}C.

4 mL of acrylic acid, 10 mL of distilled water were neutralized with 12% NaOH to pH 5. This solution was added to the bacterial cellulose solution which was being heated, while still being heated and stirred, and left for half an hour at a temperature of 65^{0}C. Then 0.25 g of N, N'-methylenebisacrylamide (MBA) was added, while still heating and stirring until thickened. Then pour it into a cup mold, let it cool, then put it in the oven at 65^{0}C until it forms a hydrogel (Aswathy et al., 2022). Then removed from the mold. The obtained hydrogel was washed repeatedly with distilled water to remove residual acid until it reached a neutral pH.

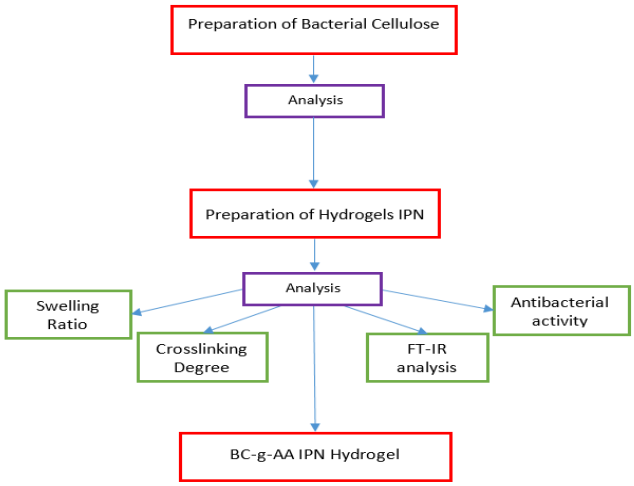

Figure 1. Reasearch flow chart

Result and Discussion

Interpenetrating Polymer Networks (IPN) hydrogels can be formed from at least two independently cross-linked polymers without covalent bonds between networks. Cellulose hydrogels can be prepared from cellulose solutions by physical cross-linking. It cause cellulose has many hydroxyl groups which can form hydrogen bond networks easily.

The predicted reactions accured on hydrogel IPN from this study.

Polymerization Stage of Bacterial Cellulose Chains

The stability of long molecular chains in an ordered system is caused by the presence of functional groups that can interact with one another. OH groups are able to interact with one another. Hydrogen bonds are formed by the H atom from the OH group is close to the lone pair of electrons on the O atom. Hydrogen bonds occur from cellulose OH groups and OH-water. Water molecules attached to the cellulose surface can be single water molecules or groups of water. Water absorption

by cellulose depends on the number of OH groups that are not bound to each other or are called free OH groups. The entry of water into the cellulose structure means swelling of the structure (Smyslov et al., 2022).

The mechanism of bacterial cellulose polymerization is predicted in Figure 1.

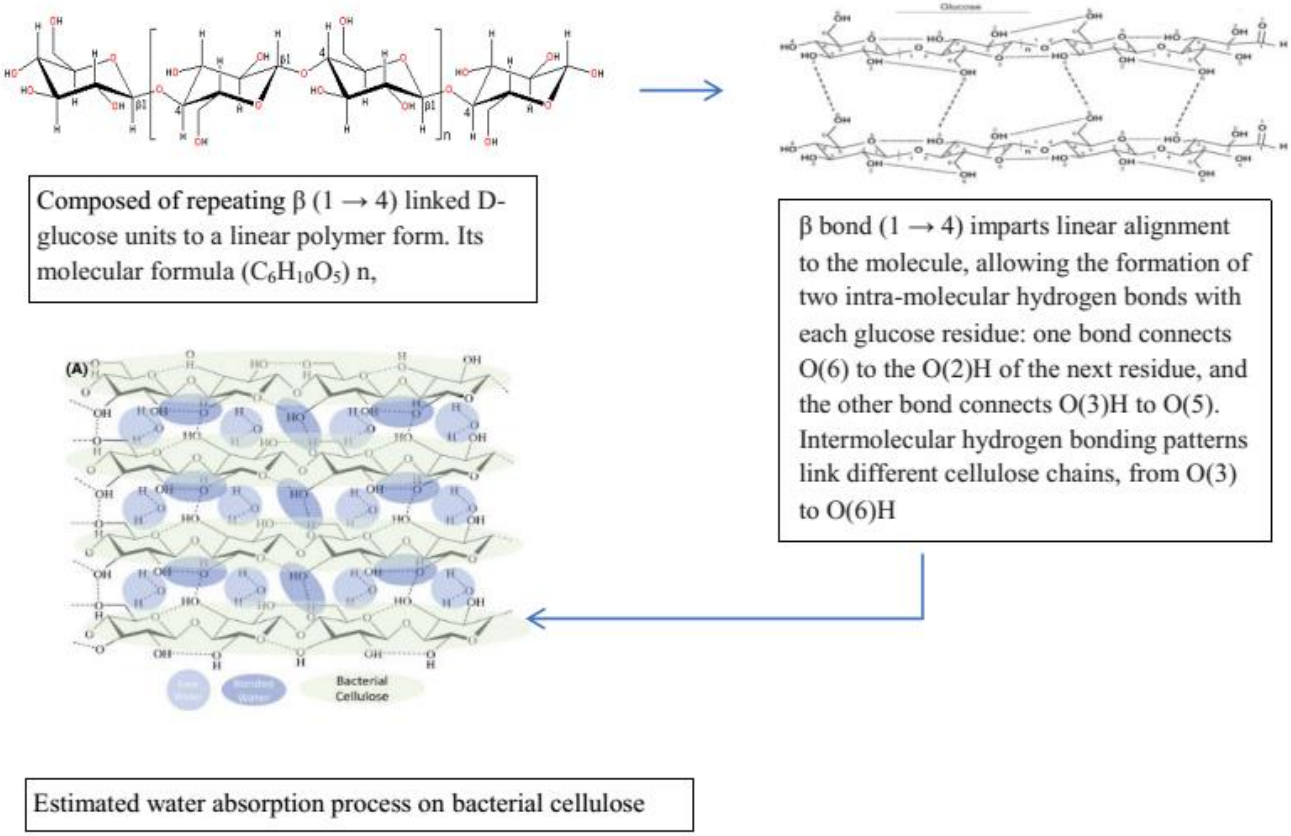

Figure 2. Mechanism of bacterial cellulose polymerization reaction

Crosslinking Reaction Process Acrylate-MBA Initiation

On 60⁰C, potassium persulfate will undergo homolytic bond cleavage and produce sulfate anion radicals. This anion radical adds to the double bond in the monomer. As a result, monomer radicals are formed

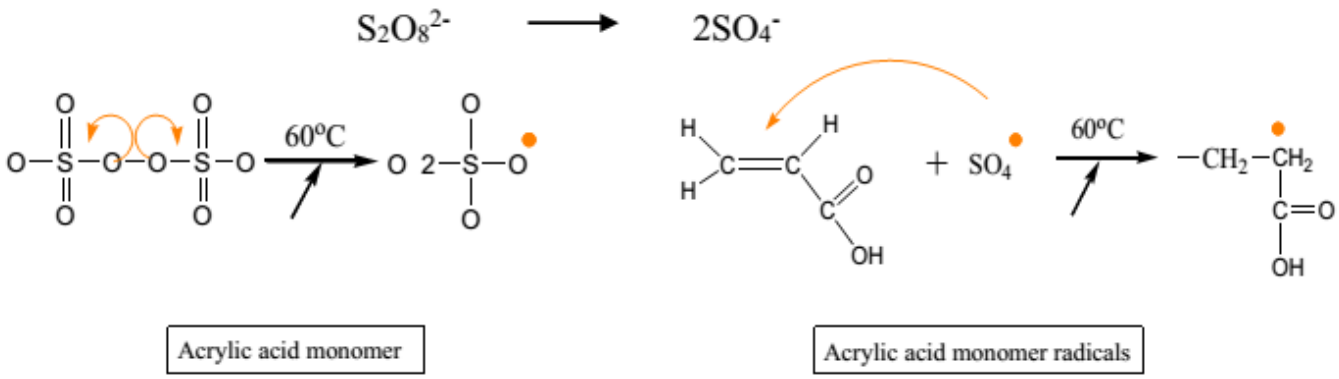

Figure 3. Mechanism of initiation

Propagation

In the propagation stage, monomer radicals will add to other monomers to form oligomers or polymers. Then a radical chain addition of oligomers or polymers occurs to the monomers that are still available. The cross-link has been formed after this. The oligomer or

polymer radical adds a double bond to one of the MBA olefin groups, producing an oligomer or polymer radical that has been cross-linked MBA. This radical will add to other MBA olefin groups so that a polymer network is formed.

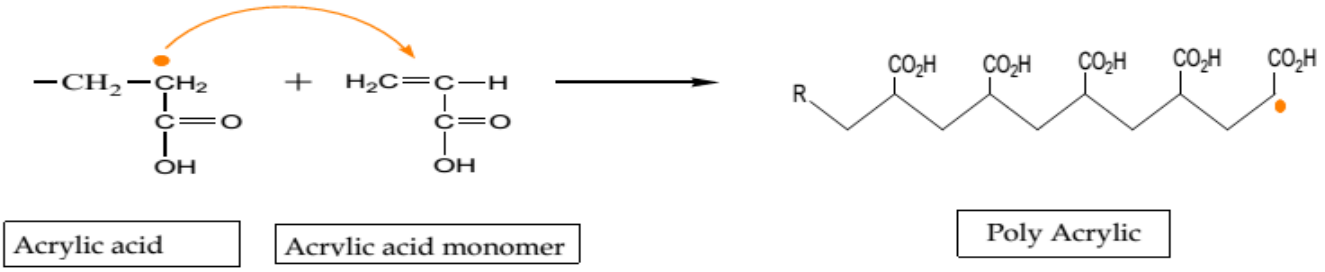

Figure 4. Mechanism of propagation

Termination

The termination stage is the final stage of the polymerization reaction. The propagation reaction will stop when the number of monomers has completely reacted or another reaction has stopped. At the termination stage, two radical polymers will change or transfer hydrogen atoms from one end of to the other (disproportionation).

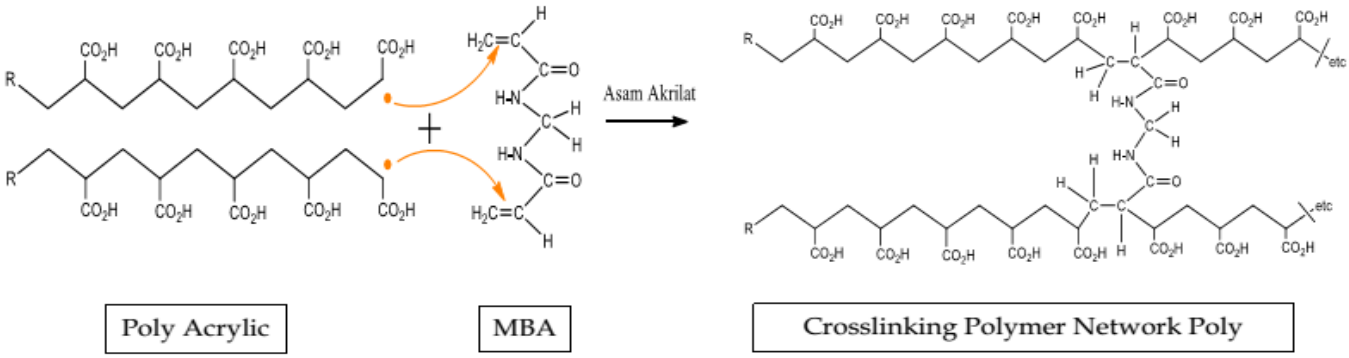

Figure 5. Mechanism of termination findings can happen and to extend to which the research findings can be applied to other relevant problems

Establishment of the IPN Hydrogel

The IPN hydrogel is formed when bacterial cellulose polymer is added to the cross-linked polymer network of poly acrylic acid - MBA, and then forms entanglements the BC-g-PAA IPN hydrogel.

This IPN hydrogel can be depicted by the following illustration.

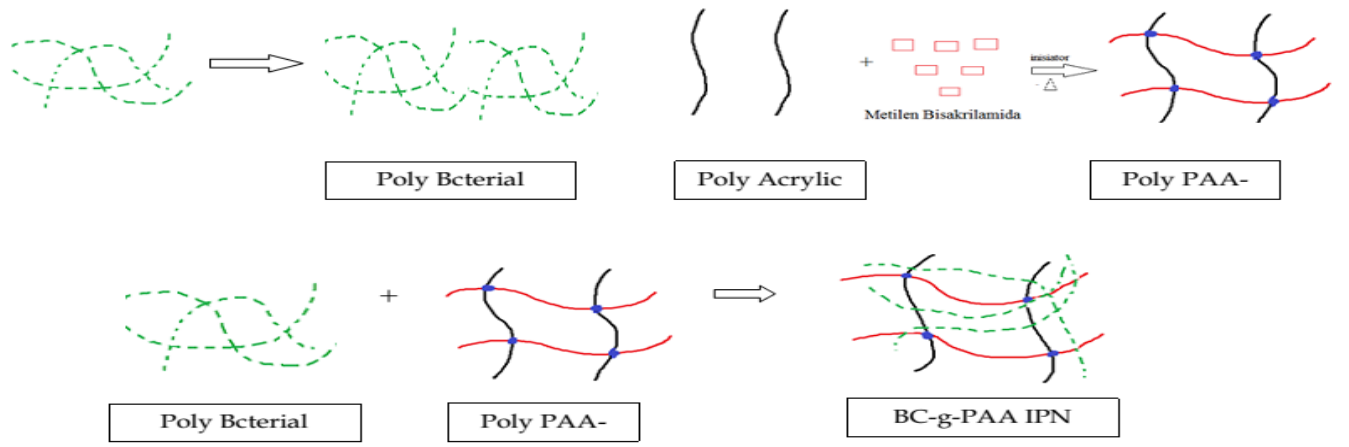

Figure 6. Illustration of establishment of the IPN hydrogel

The cross-linking of bacterial cellulose and PAA-MBA is a chemical bond, and the interaction that occurs of the two polymer networks is a physical interaction by hydrogen bonds, called an IPN network.

Establishment of the IPN Hydrogel will be tested using an FTIR test which will later be able to see the functional groups contained in the spectra and show the characteristics of the BC-g-PAA IPN hydrogel.

Crosslinking Degree

Cross-linked hydrogel functions as a shape memory which allows very large elastic deformations to occur. The desired network is to form a chain as long as possible and cross-linked in several places.

Table 1. Crosslinking Degree Data IPN HBC-g-PAA

Test	Initial Weight (g)	Final Weight (g)	Crosslinking Degree (%)
1	1.10	0.60	54.55
2	1.09	0.61	55.96
3	1.03	0.55	53.40

Determination of Swelling Ratio

Hydrogels are able to absorb water due to the presence of OH groups from cellulose. The hydrogel will reach optimum conditions, which is due to the cross-link density in the hydrogel.

Table 2. Swelling Ratio Data

Test	Initial Weight (g)	Final Weight (g)	Swelling Ratio (%)
1	1.60	27.7	1631.25
2	1.56	26.5	1598.72
3	1.65	28.6	1633.33

Fourier Transform Infrared (FT-IR) Spektroscopy

FTIR analysis is intended to see the success of the IPN hydrogel formation process based on the step-by-step identification of functional groups.

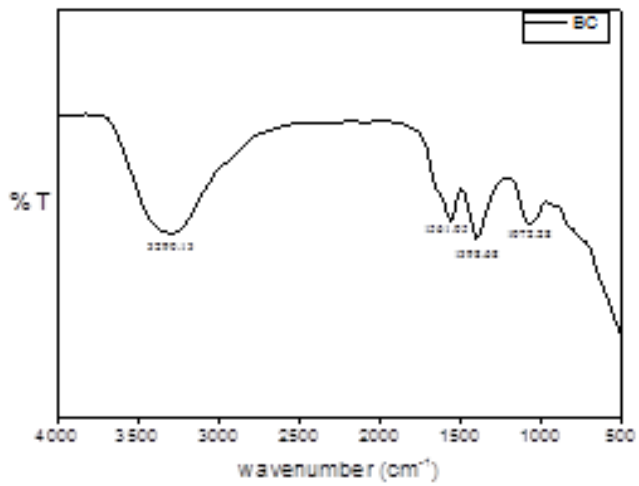

Figure 7. Bacterial cellulose FTIR spectrum

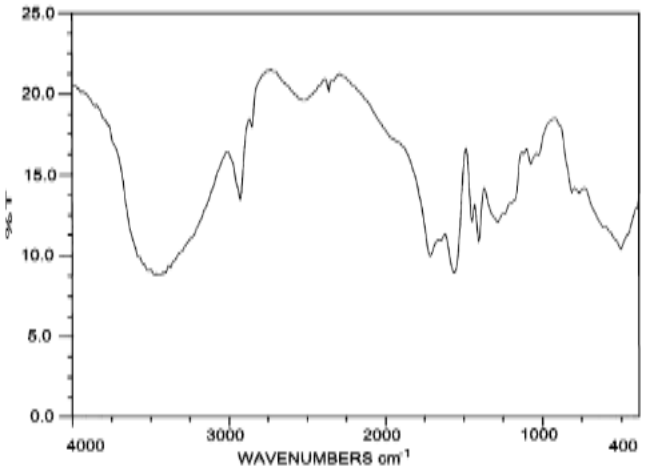

Figure 8. Poly acrylic acid FTIR spectrum

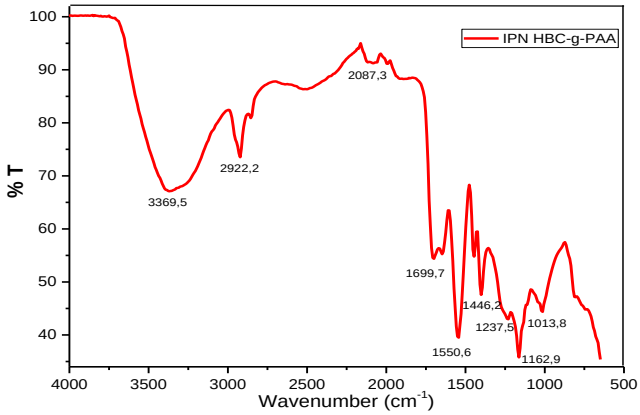

Figure 9. BC-g-PAA IPN hydrogel FTIR spectrum

Based on figure 8 BC-g-PAA IPN Hydrogel FTIR spectrum, the OH functional group can be seen at the peak of 3369.5 cm^{-1} It is bacterial cellulose and also poly acrylic acid (Zhao et al., 2023). Another functional group which is characteristic of poly acrylic acid is sp^3 CH, in poly acrylic acid its peak is at a wavelength of 2920 cm^{-1} and shifts slightly to a wavelength of 2922.2 cm^{-1} after IPN is formed on bacterial cellulose (Abiaziem et al., 2020; Nesrinne et al., 2017).

The presence of bacterial cellulose in the FTIR IPN spectrum of bacterial cellulose-g-poly acrylic acid hydrogel (figure 8) is proven by the absorption peak at a wavelength of 1550.6 cm^{-1} which indicates aromatic C=C bonds from bacterial cellulose. Wave 1237.5 cm^{-1} which indicates the presence of C-O-C bonds from bacterial cellulose, also absorption peaks at wavelengths 1162.9 cm^{-1} and 1013.8 cm^{-1} indicate the presence of the C-OH functional group from bacterial cellulose (Huang et al., 2017).

The peak at a wavelength of 1699.7 cm^{-1} on the FTIR spectrum data of IPN bacterial cellulose-g-poly acrylic acid hydrogel (figure 8) is the C=O functional group which has a higher intensity than the C=O functional group in poly acrylic acid which is at a wavelength of

1750 cm^{-1} (figure 7), this is due to the addition of the C=O functional group apart from acrylic acid, namely there is also C=O which is obtained from bond interactions by the MBA crosslinker. So it can be said that cross-linking of poly acrylic acid with MBA cross-linking has occurred. The PAA-MBA crosslinking process is also proven by the presence of a peak at a wavelength of 2087.3 cm^{-1} which is the C-N group of MBA (Gao et al., 2019).

The peak at a wavelength of 1446.2 cm^{-1} on the FTIR spectrum data of IPN bacterial cellulose-g-poly acrylic acid hydrogel (figure 8) is CH_2 bending which has a higher intensity than CH_2 bending in poly acrylic acid which is at long wave 1400 cm^{-1} (figure 7), this is also due to the addition of CH_2 bending apart from acrylic acid, and also CH_2 bending which is obtained from bond interactions by the MBA crosslinker, namely the PAA radical bond adds to the C=C double bond in MBA, so that PAA-MBA crosslinking process occurs. Besides that, it is also a shift from the CH_3 bending of bacterial cellulose which is at a wavelength of 1398.68 cm^{-1}. This peak indicates that there has been PAA cross-linking with MBA cross-linking, and there has also been an interaction process of forming bacterial cellulose hydrogel IPN with PAA-MBA to form BC-g-PAA IPN hydrogel. This proves that the process of forming an IPN network of bacterial cellulose-g-poly acrylic acid hydrogel network has occurred.

Conclusion

This study has explained establishment and its characteristic of IPN hydrogel. The polymerization by Composed of repeating β (1 → 4) and formating of two intra-molecular hydrogen bonds with each glucose residue. Crosslinking reaction process Acrylate-MBA by Initiation, propagation, and initiation stages, and next reaction process Formation of IPN network. The results of the characterization test for the degree of crosslinking were 54.55%; Swelling ratio of 1631.25%. FTIR analysis showed peaks that identifies the occurrence of IPN Hydrogel.

Authors Contribution

Conceptualization, W.H.I..; methodology, S.W.S..; validation, J.; formal analysis, J..; investigation, W.H.I..; resources, S.W.S..; data curation, J..; writing-original draft preparation, W.H.I..; writing-review and editing, J. all authors have read and agreed tc the published version of the manuscript.

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Conflicts of Interests

The author declares that there is no conflict of interest regarding the publication of this article.

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