Preparation of bacterial cellulose-based adsorbent by simultaneous irradiation method: synthesis and characterization

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Abstract. The adsorbents based on bacterial cellulose matrices, i.e. bacterial cellulose-co-(poly)acrylamide (BC-PAAM) and bacterial cellulose-co-(poly)acrylic (BC-PAA) has been successfully synthesized using polymerization radiation technique by gamma rays. The irradiation doses used in this study were 25, 50, 75, 100, and 150 kGy, with the dose rate of 5 kGy/h. The results showed that the optimum dose for synthesizing the BC-PAAM by using the simultaneous technique was 50 kGy, with the optimum gel fraction was 90.04 % obtained for mass ratio among acrylamide (AAM) and bacterial cellulose (BC) was 1:4. Meanwhile, the optimum dose for synthesizing the BC-PAA by using the similar technique was 75 kGy, with the optimum gel fraction was 94.27 % for the mass ratio between acrylic (AA) and bacterial cellulose (BC) was 2:3. The Fourier Transform Infrared spectroscopy (FTIR) spectra showed that the AA and AAM had been successfully grafted onto the BC. The increasing of heat resistance of the grafted adsorbent was indicated by Differential Scanning Calorimetry (DSC) analysis.

1. Introduction

Cellulose and cellulose-based materials have been applied for heavy metal ion removal [1–5]. Recently, the interest in the utilizing of bacterial cellulose (BC) as matrices for toxic metal adsorbent increases significantly since the production of BC by the biotechnology process could reduce the undesirable impact on the environment [6–11]. Naturally, the BC product is free of impurities such as lignin and extractive compound. Accordingly, previous studies proposed that BC as a better choice for manufacturing cellulose products [12]. The chemical structure of BC is identical to that produced by plants. However, it has excellent properties, such as higher crystallinity (up to 95%), water-adsorption capacity, degree of polymerization, and mechanical strength compared to cellulose derived from the plant [10-13]. However, the adsorption capacity of BC needs to be improved to satisfy the requirements in the application as toxic metal adsorbent.

Hence, to optimize the performance of BC, it usually can be modified by the addition of monomer containing hydrophilic groups such as acrylic acid (AA) and acrylamide (AAM) using graft copolymerization [14-15]. In this study, we systematically studied the effect of irradiation dose and the ratio of BC to the monomers i.e. acrylic acid and acrylamide to get an understanding of the optimum condition for the gel formation which resulting good physical and mechanical properties. Meanwhile, the gel was characterized by Fourier Transformed Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC).
2. Materials and Methods

2.1. Materials

BC was prepared by the method developed elsewhere [16]. Acrylic acid and acrylamide of analytical grade were kindly supplied by Merck, used as monomers.

2.2. Preparation of BC-co-PAAM and BC-co-PAA

A certain amount of BC was mixed with 30% acrylamide, with the various ratios of acrylamide and BC. Then, the homogeneous mixture was transferred into a plastics seal. Subsequently, the samples were exposed to gamma-rays irradiation at room temperature. The dose rate was 5 kGy/h and irradiation doses were 25, 50, 75, 100, and 150 kGy. The irradiated samples were washed several times with boiling water to eliminate the homopolymer and unreacted monomer. Then, the samples were dried in the oven with a temperature of 60°C and cut into small pieces before the grinding process. A similar procedure was applied by using acrylic acid as a monomer.

2.3. Determination of gel fraction

The irradiated sample was dried in the vacuum oven at 60°C for 24 hours to obtain the constant weight ($W_0$). Furthermore, it was soaked in the distilled water and shaken by using a shaker incubator for 24 hours. Then, the sample was washed by hot water. Subsequently, it was dried until it reached a constant weight ($W_1$). The gel fraction was calculated by the following equation:

\[
\text{Gel fraction (\%)} = \frac{W_1}{W_0} \times 100 \%
\]

2.4. Characterizations

2.4.1. Fourier Transformed Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) was performed on the FTIR spectrometer (IR Prestige-21 Shimadzu, Japan), and the spectra were obtained between 4000 and 400 cm$^{-1}$. The sample was dispersed in dry KBr and it was analyzed by FTIR.

2.4.2. Differential Scanning Calorimetry (DSC) Analysis

In Differential Scanning Calorimetry (DSC) analysis, the adsorbent was characterized by a DSC-60 analyzer (Shimadzu, Japan). In detail, the adsorbent (approximately 5 mg) was placed in a platinum crucible and the heating temperature was from room temperature to 600°C at the rate of 20°C min$^{-1}$ under a nitrogen purge.

3. Results and Discussion

Synthesis of bacterial cellulose-co-(poly)acrylamide (BC-PAAM) and bacterial cellulose-co-(poly)acrylic (BC-PAA) is attempted by radiation-induced radical polymerization in the room temperature and oxygen atmosphere using the simultaneous technique. Consequently, the peroxide radicals formed during the irradiation process. The peroxide radicals react with the double bond of the monomer chain and induced polymerization [14-15]. The visual observation of BC-PAAM and BC-PAA formed after the polymerization can be seen in Tables 1 and 2.

The data of visual observations of the irradiated sample showed different gel’s texture with varying irradiation doses. By increasing the irradiation dose, the texture of the gel was not sticky and the gelation was performed well. However, the ratio between BC and monomers are also needed to be considered. The optimum ratio of AAM and BC is 1:4 with the irradiation dose was 50 kGy while the optimum ratio for AA: BC was 2:3 by using an irradiation dose of 75 kGy.
Another method to characterize the formation of the gel obtained after graft polymerization is the determination of the gel fraction of BC-PAAM and BC-PAA. Gel fraction reflects the fraction of the amount of material both monomers and polymers that have been converted into gel after the polymerization process. Gel fraction is determined by washing the gel formed after graft polymerization with the proper solvent for the monomer and homopolymer. The homopolymers formed during graft polymerization was eliminated during the washing process. Homopolymers are formed due to the competition between acrylamide and acrylic monomer radicals to react with cellulose or monomers. If they react with cellulose or cellulose radicals, copolymers were formed. But, if they react with monomers or radicals’ monomers, consequently, homopolymers will be formed. The gel fraction of BC-PAAM and BC-PAA are shown in Figures 1 and 2.

### Table 1. The visual observation of BC-co-PAAM

| Ratio of AAm:BC | Irradiation dose (kGy) | 25  | 50  | 75  | 100 | 150 |
|----------------|------------------------|-----|-----|-----|-----|-----|
| BC             |                        | -   | -   | -   | -   | -   |
| 1:4            |                        | +++ | +++ | +++ | +++ | +++ |
| 2:3            |                        | +++ | +++ | +++ | +++ | +++ |
| 3:2            |                        | +++ | +++ | +++ | +++ | +++ |
| 4:1            |                        | +++ | +++ | +++ | +++ | +++ |
| Aam            |                        | +++ | +++ | +++ | +++ | +++ |

Note: (-) no gelation; (+) soft gel; (++) soft and sticky gel; (+++) strong gel formed partially; (++++) strong gel; (++++*) strong and sticky gel

### Table 2. The visual observation of BC-co-PAA

| Ratio of AA:BC | Irradiation dose (kGy) | 25  | 50  | 75  | 100 | 150 |
|---------------|------------------------|-----|-----|-----|-----|-----|
| BC            |                        | -   | -   | -   | -   | -   |
| 1:4           |                        | +   | +   | +++ | +++ | +++ |
| 2:3           |                        | +   | +   | +++ | +++ | +++ |
| 3:2           |                        | ++  | ++  | +++ | +++ | +++ |
| 4:1           |                        | ++  | ++  | +++ | +++ | +++ |
| AA            |                        | ++  | ++  | +++ | +++ | +++ |

Note: (-) no gelation; (+) soft gel; (++) soft and sticky gel; (+++) strong gel formed partially; (++++) strong gel
The greater the ratio of AAM to BC, the percentage of gel fraction was greater. By increasing the irradiation dose, the greater the percentage of gel fraction was attained (Figure 1). The optimum gel fraction obtained was 90.04% at the dose of 50 kGy, with the ratio of AAM:BC was 1:4. On the other hand, the optimum gel fraction obtained for AA:BC ratio of 2:3 was 94.27% at the irradiation dose of 75 kGy (Figure 2). The data obtained for the gel fraction of BC-PAAM and BC-PAA correspond to the visual observation in which the strong gel was formed in the optimum gelation condition.

![Figure 1](image1.png)

**Figure 1.** Effect of irradiation dose on the gel fraction on the different ratios of AAM and BC

![Figure 2](image2.png)

**Figure 2.** Effect of irradiation dose on the gel fraction on the different ratios of AA and BC

In Figure 3, the spectrum of the bacterial cellulose evidently showed the presence of C–H and –OH functional group, indicated by the broad absorption band at around 2920 cm⁻¹ and 3600 cm⁻¹. The spectrum of grafted bacterial cellulose shows N–H stretching and the N–H bending of the
amide bonds, which are characteristic of the –CONH₂ group present in the acrylamide band at 3500 cm⁻¹ and 1710 cm⁻¹. The presence of absorption bands at 2339 and 2360 cm⁻¹ indicate the presence of amide secondary of the amine group. These changes provide evidence of the grafting of acrylamide onto bacterial cellulose.

Figure 3. FTIR spectra of AAM, BC, and BC-co-PAAM

Figure 4 showed the FTIR spectra of PAA, BC, and BC-co-PAA. The band at 2906 cm⁻¹ for PAA was correlated with the characteristic stretching vibration CH in the methylene group. The protonated carboxyl groups band arose in 1715 cm⁻¹. The broadband ranging from 3100 to 3700 cm⁻¹ was due to the presence of intramolecular hydrogen bonds formed by the carboxylic moieties of AA.

Figure 4. FTIR spectra of PAA, BC, and BC-co-PAA

DSC analysis was carried out for the analysis of thermal transitions of the copolymers synthesized in this study. We studied the heat absorbed or released by a material as a function of temperature. Glass transition temperature (Tg) of BC films was found to be 25.28 °C (Figure 5a). And the Tg for BC-co-PAAM and BC-co-PAA were 49.48 and 43.22°C, respectively (Figure 5b dan5c). The copolymers have
higher Tg due to the amorphous site increased after copolymerization. The thermogram shows that BC fully degraded, while BC-co-PAAM and BC-co-PAA partially degraded at the temperature higher than 480°C.

Figure 5. DSC thermogram of BC (a), BC-co-PAAM (b), BC-co-PAA (c)

4. Conclusion
BC grafted AAM copolymer absorbent material was successfully synthesized by simultaneous irradiation technique using gamma rays with 50 kGy irradiation dose and reached the optimum gel fraction was 90.04 % obtained for the mass ratio of AAM and BC was 1:4. Meanwhile, the optimum dose for synthesizing the BC-PAA by using a similar technique was 75 kGy, with the optimum gel fraction was 94.27 % for the mass ratio between AA and BC was 2:3. The characterization using FTIR showed that the AA and AAM had been successfully grafted onto the BC. In addition, DSC analysis showed the increasing of heat resistance of the grafted adsorbent.

Acknowledgment
The authors acknowledge the Center for Isotopes and Radiation Application, National Nuclear Energy Agency of Indonesia (PAIR, BATAN) for the support and facilities provided to the authors. The authors also thank the staff of the irradiation facility of PAIR, BATAN for irradiating the samples.

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