Synthesis and Characterization of Composites-Based Bacterial Cellulose by Ex-Situ Method as Separator Battery

Maria Ulfa¹, Inda Noviani¹, Emmy Yuanita¹, Ni Komang Tri Dharmayani¹, Sudirman¹, Sarkono²

¹ Chemistry Department, Faculty of Mathematics and Natural Sciences, University of Mataram, Indonesia.
² Biology Department, Faculty of Mathematics and Natural Sciences, University of Mataram, Indonesia.

Abstract: Many studies have been conducted and developed on cellulose-based battery separator materials, including bacterial cellulose, which has characteristics like plant cellulose. This research aims to synthesize BC/Al2O3 composite and analyze its potential as a battery separator. The synthesis of the composite with the ex-situ method is to immerse BC from tofu liquid waste (fermentation time variation of 6, 7, and 8 days) into Al2O3 suspension. The characterization results showed that the immersion of Al2O3 in BC can increase porosity, electrolyte absorption, and conductivity, indicating that the composite has the potential to be used as a battery separator.

Introduction

The separator is a component part of the battery that functions as a separator between electrodes for the transfer of ions in the electrolyte and ensures that there is no short-circuit between the electrodes in the battery (Lee et al., 2018; Lu et al., 2018). Materials commonly used as commercial battery separators are based on polyolefins such as polypropylene (PP), polyethylene (PE), and tri-layer PP/PE/PP (Mun et al., 2021). However, there are some drawbacks, namely non-degradability, low porosity (36.31-44.00 %), electrolyte absorption, and low conductivity (Lee et al., 2018; Xu et al., 2017).

The search for separator materials has been extensive to address such weaknesses, and cellulose is one of the biopolymers that has been extensively studied as a separator battery because it has high porosity and affects ion conductivity (Ginting et al., 2023; Pan et al., 2019; Tanpichai et al., 2019; Wang et al., 2018; Xu et al., 2017; Zhu et al., 2021). Cellulose produced by bacteria, or bacterial cellulose (BC), has characteristics such as porosity, electrolyte absorption, conductivity, tension strength, and thickness that are not much different from the standard (Choi et al., 2022; Li et al., 2021; Muddasar et al., 2022; Xu et al., 2017), so it has the potential to be a separator battery (Ginting et al., 2023; Li et al., 2021; Qian et al., 2022).

The thickness and low tensile strength of the separator can affect battery safety (Hao et al., 2022). The selection of fermentation media used in the manufacture of BC greatly affects the thickness and tensile strength. The use of tofu and corn liquid waste media produces BC with a thickness 4-52 times greater than that of non-waste and is accompanied by low tensile strength (> 98.06 MPa) (Costa et al., 2019; Yasa et al., 2020). Several studies have conducted the addition of ceramic oxide-based fillers (SiO₂, Al₂O₃, TiO₂, and others) to overcome this weakness (Huy et al., 2021; Wei et al., 2019; Xu et al., 2017; Yu et al., 2021). The study by Xu et al. (2017), added
Al(NO₃)₃·9H₂O to BC with a simple in situ thermal decomposition method and produced BC/Al₂O₃ composites that have porosity, electrolyte absorption, thickness, tensile strength, and conductivity that can meet commercial separator standards.

According to the explanation above, the chemical and physical properties of BC and BC/Al₂O₃ composite were investigated to establish its potential as a separator battery. BC synthesis has been performed using Gluconacetobacter xylinus bacteria based on tofu liquid waste media, and BC/Al₂O₃ composite synthesis have been carried out ex-situ.

Method

Preparation of BC and BC/Al₂O₃ composites

The production of BC in this study was carried out following the procedure used by Sarkono et al. (2014) with modifications. In this research, tofu liquid waste was used as a production medium, with nutrient compositions of 10.0, 0.5, and 0.5% (w/v) sugar, ammonium sulfate, and yeast extract in 100 mL production scale. The pH of the media was set to 5 and sterilized for 15 min in an autoclave at 121°C and 2 atm. The media were inoculated with coconut water-based starter culture (10% v/v) and static fermented for 6, 7, and 8 days at 30°C. BC hydrogels were harvested and cleaned with cold water to remove residual media before being boiled for approximately 15 min and soaked in 0.5 M NaOH for 24 h.

![Figure 1. The schematic representation of a ex situ method to synthesize BC/Al₂O₃ composite](image)

Characterization

Chemical characterization of BC and BC/Al₂O₃ composites performed with FTIR-ATR and Raman (Bruker). Porosity was measured by immersing BC and BC/Al₂O₃ composites in n-butanol 80% (v/v) and calculated based on equation (1).

\[ \phi = \frac{(M_d - M_w)}{\rho B V_k} \times 100 \% \]  

(1)  

where \( M_d \) and \( M_w \) are dry and wet mass of the sample, \( \rho B \) is density of n-butanol (g/cm³), and \( V_k \) is dry volume of the sample (cm³). Electrolyte absorption was measured by immersing the sample in NaOH (1 M) electrolyte solution for 1 h and calculated using equation (2).

\[ A_e = \frac{M_2 - M_1}{M_1} \times 100 \% \]  

(2)  

where \( A_e \) is electrolyte absorption, \( M_1 \) and \( M_2 \) is sample mass before and after immersion. The conductivity of BC and BC/Al₂O₃ composites measured and calculated based on equation (3).

\[ \sigma = \frac{1}{\rho} \]  

(3)  

where \( \rho \) is resistivity. Tensile strength is measured based on ASTM D638 with Tensilon RTG-1310 at load cell capacity 5.0 kN with a sampling rate of 5 mm/min. Composite surface morphology analysis using Scanning Electron Microscopy (FEI, Inspect-S50).

Result and Discussion

Figure 2 shows the FTIR-ATR spectra for BC and the BC/Al₂O₃ composite. Based on the absorption bands obtained, the spectra of BC and BC/Al₂O₃ composite have similarities with the difference in wavenumber magnitude as shown in Table 1. The difference in wavenumber for reference BC with the research results as shown in Table 1, may be due to the base BC media used, where Galdino et al. (2020) and Güzel et al. (2019), using corn waste media, and orange peel.

![Figure 2. FTIR-ATR BC and BC/Al₂O₃ composite](image)
show any difference in absorption at wavenumbers 881–558 cm\(^{-1}\) (confirms the existence of Al–O–Al vibrations) with the BC membrane (Atrak et al., 2018). The spectrum of the BC/Al\(_2\)O\(_3\) composite displays a narrower peak compared to the spectrum from BC. This difference is made possible by the increased degree of crystallinity that occurs in the BC/Al\(_2\)O\(_3\) composite. The increase in crystallinity causes molecular vibrations in the BC/Al\(_2\)O\(_3\) composite more districts compared to BC. The increase in crystallinity was also caused by using ultrasonication in the Al\(_2\)O\(_3\) dispersion process.

**Table 1. Absorption Bands of FTIR-ATR BC and BC/Al\(_2\)O\(_3\) Composites**

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Reference</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H</td>
<td></td>
<td>3286(^{[1]}); 3270; 3400–3440(^{[2]})</td>
</tr>
<tr>
<td>C–H</td>
<td></td>
<td>2921(^{[1]}); 1277(^{[2]}); 2800–2900(^{[2]})</td>
</tr>
<tr>
<td>C–OH</td>
<td></td>
<td>1399(^{[1]}); 1375(^{[2]}); 1440–1310(^{[2]})</td>
</tr>
<tr>
<td>C–O–C</td>
<td></td>
<td>1111(^{[2]}); 1040–1068(^{[1]})</td>
</tr>
</tbody>
</table>

\[1\] Galdino et al. (2020); \[2\] Guzel & Akpinar (2019)

Spectroscopy Raman was performed on BC and BC/Al\(_2\)O\(_3\) composites to reconfirm the possibility of some vibrations not being recorded by the FTIR-ATR, with a maximum laser power of 50 mW. The spectrum results for the two composites are shown in Figure 2.

Spectroscopy Raman BC and BC/Al\(_2\)O\(_3\) composites in Figure 3 shows the absorption with wavenumbers that are not much different. The vibrational region shows a similarity to the spectrum Raman for BC from apple cider waste media, with higher and narrower spectrum readings indicated by BC/Al\(_2\)O\(_3\) composites.

**Figure 3. Spectral comparison Raman BC and BC/Al\(_2\)O\(_3\) composites**

Visualization of BC and BC/Al\(_2\)O\(_3\) composites produced in this study gave a different appearance, namely in the form of transparent white sheets for BC and opaque white for BC/Al\(_2\)O\(_3\) composites. This difference indicates the dispersed Al\(_2\)O\(_3\) into BC at the time of fermentation for 6, 7, and 8 consecutive days at 14.00; 6.36; and 24.58% of 33.00% suspension-Al\(_2\)O\(_3\).

**Table 2. Porosity and Absorption of BC Electrolyte, BC/Al\(_2\)O\(_3\) Composite, and Separators Standard**

<table>
<thead>
<tr>
<th>Fermentation Time (Days)</th>
<th>Porosity (%)</th>
<th>Electrolyte Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>BC/Al(_2)O(_3)</td>
<td>BC</td>
</tr>
<tr>
<td>6</td>
<td>54.99</td>
<td>41.56</td>
</tr>
<tr>
<td>7</td>
<td>89.56</td>
<td>87.20</td>
</tr>
<tr>
<td>8</td>
<td>59.91</td>
<td>61.61</td>
</tr>
</tbody>
</table>

Standard: 51.2\(^{[1]}\) 167\(^{[2]}\)/225\(^{[2]}\)

\[1\] Wang et al. (2019); \[2\] Xu et al. (2017)

Porosity and electrolyte absorption test results on BC and BC/Al\(_2\)O\(_3\) composites can be observed in Table 2. The porosity of BC and BC/Al\(_2\)O\(_3\) composite for 7 days of fermentation is about 2 times higher than the standard separator, as well as the electrolyte absorption is higher than the standard. The existence of Al\(_2\)O\(_3\) which dispersed the most in BC fiber at 8 days of fermentation (24.58%) resulted in greater absorption of electrolytes than without Al\(_2\)O\(_3\). This is in line with the increased porosity of the BC/Al\(_2\)O\(_3\) composite.

**Table 3. Conductivity, Tensile Strength, and Thickness**

<table>
<thead>
<tr>
<th>Fermentation Time (Days)</th>
<th>Conductivity (× 10(^4) S/cm)</th>
<th>Tensile Strength (MPa)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC</td>
<td>BC/Al(_2)O(_3)</td>
<td>BC/Al(_2)O(_3)</td>
<td>BC/Al(_2)O(_3)</td>
</tr>
<tr>
<td>6</td>
<td>0.340</td>
<td>2.460</td>
<td>102.92</td>
</tr>
<tr>
<td>7</td>
<td>0.129</td>
<td>0.519</td>
<td>121.87</td>
</tr>
<tr>
<td>8</td>
<td>0.251</td>
<td>2.02</td>
<td>166.08</td>
</tr>
</tbody>
</table>

Standard: 0.5\(^{[1]}\) 58.1\(^{[1]}\) 20\(^{[1]}\)

\[1\] Wang et al. (2019)

This increase is also influenced by the hydrophilicity of Al\(_2\)O\(_3\) and properties of Al\(_2\)O\(_3\) having moisture, wettability, and excellent electrolyte absorption (Xu et al., 2017). The separator must absorb and retain large amounts of liquid electrolyte to achieve low internal resistance and high ionic conductivity. The high tensile strength is also influenced by sonication during the dispersion of Al\(_2\)O\(_3\) into BC fibers. This is because the use of prolonged ultrasonication increases the possibility of single BC fibers reacting with the microbubbles generated in the sonication process (acoustic cavitation effect), which can loosen the fiber surface and cause bond breakage to destroy the micro-sized microcrystalline cellulose fibers into nanocrystalline cellulose. The presence of Al\(_2\)O\(_3\) through the dispersion process in BC fibers, can increase the
thickness of BC/Al₂O₃ composites compared to BC (Fauza et al., 2019).

The surface morphology of BC and BC/Al₂O₃ composites gives a difference in fiber arrangement with an average BC fiber diameter of 65.59 nm. BC/Al₂O₃ composite showed better crystallinity with Al₂O₃-coated fibers so that it shows a different visual from BC, this can be observed in the SEM image (Figure 4). BC/Al₂O₃ composite in the SEM image with cross sections shows cellulose fibers that are arranged in stacks but not as dense as the cellulose arrangement in BC, this is due to the presence of Al₂O₃ in BC fiber, as well as the sonication process during Al₂O₃ dispersion into the BC fiber which can loosen the BC fiber so that it provides a distance between the cellulose piles in the BC/Al₂O₃ composite. Morphological comparison of BC and BC/Al₂O₃ composites indicates that the dispersion of Al₂O₃ gives a change in the physical properties of BC.

Conclusion

BC/Al₂O₃ composite tofu liquid waste-based was successfully synthesized by ex-situ method through immersed Al₂O₃ in BC with variations in fermentation time. The crystallinity of the BC/Al₂O₃ composite has increased compared to BC, this can be observed in the FTIR-ATR and Raman spectra. The existence of Al₂O₃ in BC through the ex-situ method can increase the porosity, electrolyte absorption, and conductivity of BC/Al₂O₃ composite, so it can potentially be developed as a battery separator.

Acknowledgments
We thank our colleagues from State University of Malang (UM) and ITB for contributing SEM images and FTIR-ATR and Raman results, and the research team for working on this study.

Author Contributions
Maria Ulfa, and Sudirman organized and planned the research stages. Maria Ulfa, Sarkono and Inda Noviani carried out sample preparation and made BC and BC/Al₂O₃ composites and characterized the physical properties. Sudirman, Emmy Yuanita, and Ni Komang Tri Dharmayani contributed to data processing, analysis, and interpretation. Maria Ulfa led the manuscript writing. All authors actively provided feedback, and assisted in the research, data analysis and in writing the manuscript.

Funding
This research and APC are funded by the University of Mataram with PNBP (Non-Tax State Revenue) grants in 2023.

Conflicts of Interest
The authors declare no conflicts of interest. The funder had no role in the design of the study; in the collection, analysis, or interpretation of the data; in writing the manuscript; or in the decision to publish the results.

References


