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Research Article

Synthesis and Characterization of Amino Modified Bacterial Cellulose from Sugar Beet Molasses

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Abstract – In this study, amino-modified bacterial cellulose was produced and characterized from sugar beet molasses. Bacterial cellulose (BC) was produced from sugar beet molasses using *G. xylinus* NRRL B-759 in a static culture. It was used to synthesize a composite material with N-(2-Aminoethyl)-3-aminopropyl methyldimethoxysilane (AEAPDMS). The bacterial strain was cultured in Hestrin & Schramm (HS) media. pH was adjusted to 5 using 1 N acetic acid. The culture experiments were carried out in 250 mL with a working volume of 50 mL at 30 °C for 7 days. Static BC production experiments were conducted in 79 g/L molasses concentration, 13 % inoculation ratio, and 130 mL culture volume for ten days. The characteristic properties of the produced BC-AEAPDMS were determined. From X-Ray diffraction analysis (XRD) results, it was seen that the BC-AEAPDMS material was predominantly in the structure of typical crystalline cellulose and a small amount of amorphous cellulose. It was concluded from scanning electron microscope (SEM) images that silane molecules filled the pores in the nanofibril BC structure. From the energy dispersive X-ray (EDX) results, it was understood that the synthesized composite material contained, as expected, a large amount of carbon (C) and oxygen (O), as well as smaller amounts of nitrogen (N) and Silicon (Si) elements. Fourier-transform infrared spectroscopy (FTIR) results showed the presence of CH_2, CH_3, NH_2, mesoporous silica, ether, and alcohol groups in the synthesized BC-AEAPDMS composite material. It can be said that the produced composite material in this study might be used to remove carbon dioxide (CO_2) from gas streams.

Keywords – Bacterial cellulose, amino-modified biocomposite, AEAPDMS, sugar beet molasses, static culture

I. INTRODUCTION

Regulations to remove and reduce the use of compounds that have harmful effects on the environment, especially global warming, have continued to increase. Since the 1990s, precautions applied to climate change mitigation, reducing greenhouse gas emissions, and researching or using renewable energy sources have been taken by many countries against such environmental problems. The latest example is the European Green Deal aiming to reduce greenhouse gas emissions to net zero by 2050 [1]. When it comes the global warming gases, it might be said that the first compound coming into mind is carbon dioxide. Global carbon dioxide levels have reached alarming levels. This affects life directly or indirectly [2-4]. It is reported that human-induced CO_2 emissions are around 40 billion tons per year[5].

There are several techniques to remove or recover and they can be classified as absorption absorption in aqueous solutions of alkanolamine, adsorption, cryogenic distillation, and membrane separation [3, 6]. The removal of CO_2 using absorption is currently a widely used technology. However, there are some disadvantages such as large-sized equipment, high cost of solvent regeneration, and difficulties in separation at high water content [5]. Cryogenic distillation and membrane separation are relatively expensive techniques. It should be noted that the membrane technique might be a good option for specific separation processes [4]. It is reported that adsorption technique has two most important advantages among many advantages: wide operating range and low cost. Carbon materials, zeolites, porous silica, metal oxides, porous polymers, porous aromatic cages, and metal-organic frameworks (MOFs) are commonly adsorbents used [7]. There are some important limitations of powder form and low workability adsorbent materials in industrial applications [8]. It was shown that some of these limitations have been eliminated by adding various structural and functional materials to the adsorbents. Cellulose, amine-immobilized silica nanoparticles, amine-modified mesoporous silica, amine-impregnated natural fibers, and basic ion exchange resins are good examples of materials used for this purpose [9-11]. It is important that such materials, which can be produced in the form of beads, membranes, foams, and aerogels, are biodegradable.

The support material of amine-based adsorbents was previously inorganic matter. But, renewable material applications such as nanfibrillated cellulose and cellulose acetate are now promoted [6, 12]. Cellulose-based metal-organic frameworks (MOFs) and zeolite imidazole frameworks (ZIFs) have also been used for CO_2 adsorption in cellulose matrix [13]. However, the limited compatibility between cellulosic substrate and MOF fillers always restricts the stability and reusability of composites resulting from leakage or aggregation during use. Therefore, the use of bacterial cellulose in MOFs or ZIFs has been reported as an alternative [4]. Gebald et al. showed that CO_2 can be removed using the material synthesized with nanofibril cellulose (NFC) hydrogel and N-(2-Aminoethyl)-3-aminopropyl methyldimethoxysilane (AEAPDMS, Figure 1).

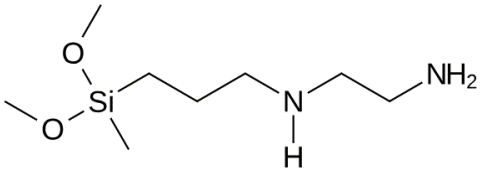


Figure 1. Chemical structure of AEAPDMS

In this study, some properties of the BC-AEAPDMS composite material synthesized have been determined. The BC has been produced from sugar beet molasses.

II. MATERIAL AND METHOD

Reagents

The sugar beet molasses was supplied from Elazığ Sugar Factory. AEAPDMS (97%) was obtained from ABCR (Germany). The chemicals used in the experiments were glucose (Tekkim), glycerol (Merck), Na_2HPO_4 (Tekkim), acetic acid (Merck), sucrose (Carlo Erba), and fructose (Carlo Erba). The bacterial strain in order to BC was *Gluconacetobacter xylinus* NRRL B-759.

BC Production

Bacterial Strain and Culture

Bacterial culture experiments were carried out using *G. xylinus* ARS Culture Collection (NRRL B-759). For this purpose, Hestrin & Schramm (HS) medium (2% glucose, 0.5% peptone, 0.5% yeast extract, 0.27% Na_2HPO_4, and 0.15% citric acid) was used [14]. The initial pH of the fermentation medium was 5. The culture medium was firstly autoclaved at 121 °C for 15 min. The culture *G. xylinus* NRRL B-759 was conducted aerobically in the volume of 50 mL at 30 °C for 7 days. At the end of the culture time, 100 µl stock with glycerol (60%) was kept at -80 °C.

BC Production from sugar beet molasses

BC production was carried out using a static culture system. Molasses concentration, inoculation ratio, and culture volume of the fermentation medium for BC production experiments were approximately 79 g/L, 13%, and 130 mL, respectively [15]. The yield of BC produced under these conditions was 8.6%

Purification of BC

Produced BC pellicles were separated from the fermentation broth at the end of the fermentation time (7 days). Then, the pellicles were washed with distilled water were subjected to centrifugation using NUVE-Nf 800 R at 4100 rpm. So, the removal of culture medium residues and cells in the produced cellulose was achieved. The centrifuged cellulose samples were kept in a water bath at 90 °C with 0.1 N NaOH for 1 h. At the end of this period, the cellulose was neutralized with 0.1 N acetic acid and washed thoroughly. The final product was stored in the refrigerator at +4 °C for the production of composite material in gel form.

BC-AEAPDMS composite material synthesis experiments

AEAPDMS was added to the purified BC hydrogel to obtain a total silane concentration of 4 wt.%. The BC-AEAPDMS suspension was stirred using a magnetic stirrer for 24 h and centrifuged at 3600 rpm for 20 min. After centrifugation, the solid pellet was kept at -80 °C for 1 day to increase the porosity of the composite produced. Finally, the BC-AEAPDMS was dried using a moisture analyzer (Shimadzu MOC63u) at 100 °C.

Characterization Tests

Produced BC-AEAPDMS was subjected to a series of characterization tests. These were XRD (Rigaku), SEM-EDS (Hitachi), and FTIR (SchimadzuIR Spirit Spectrophotometer QATR-S)

III. RESULTS AND DISCUSSION

XRD results

The XRD spectrums of BC-AEAPDMS composite material synthesized from sugar beet molasses is shown in Figure 2.

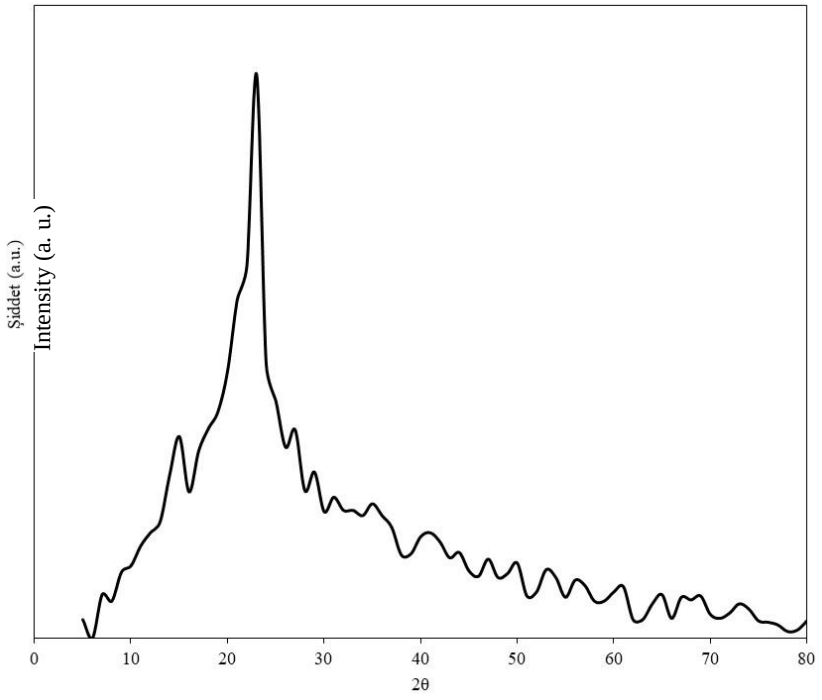


Figure 2. XRD spectrums of produced BC-AEAPDMS composite from sugar beet molasses

As seen in Figure 2, the distinct peak at 2θ=22.5 belongs to the characteristic Cellulose I crystal structure. It can be said that the relatively smaller peak at 2θ=14.9 is the peak indicating the amorphous cellulose structure [15, 16]. XRD results indicate that synthesized BC-AEAPDMS contains the expected cellulose structures.

SEM-EDX results

The SEM images of the BC-AEAPDMS produced in this study are shown in Figure 3. From the figure, it is understood that the porosity of amino-modified BC-AEAPDMS is poor. It is thought that the reason for this situation is the pores formed by the -80 °C application are filled with hydrolyzed silane molecules. Gebald et al. (2011) encountered a similar situation in a study they conducted with beech wood [11]. They noted that silane molecules pushed into the voids in the nanofibril structure formed dense silane aggregates. In this study, the elemental analysis of developed BC-AEAPDMS composite matter was also introduced using SEM-EDX results. The SEM-EDX layered graph and EDX spectrums of BC-AEAPDMS are illustrated in Figure 4. As seen in Figure 4, the elemental content of BC-AEAPDMS produced from sugar beet molasses is given in Table 1. From Table 1, it is clear that there are C, O, Si, and N elements in the content of BC-AEAPDMS synthesized in this study. It can be said that amino modified cellulose structure was formed in the composite material where N and Si are thought to come from AEAPDMS. FTIR analyses performed to reveal the functional groups in more detail were discussed in the next section.

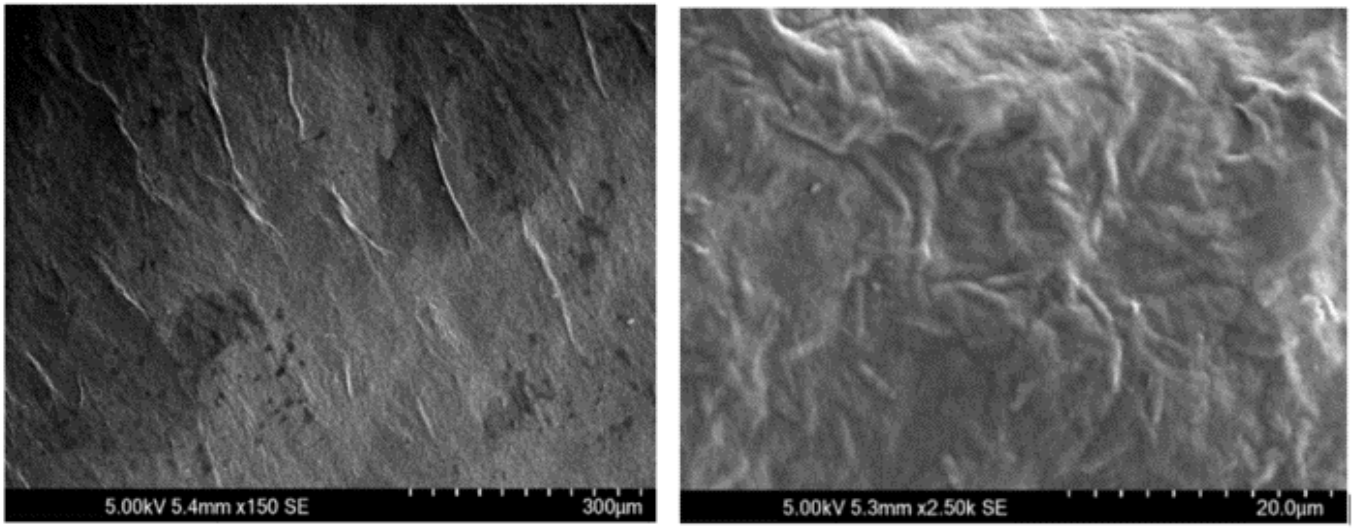
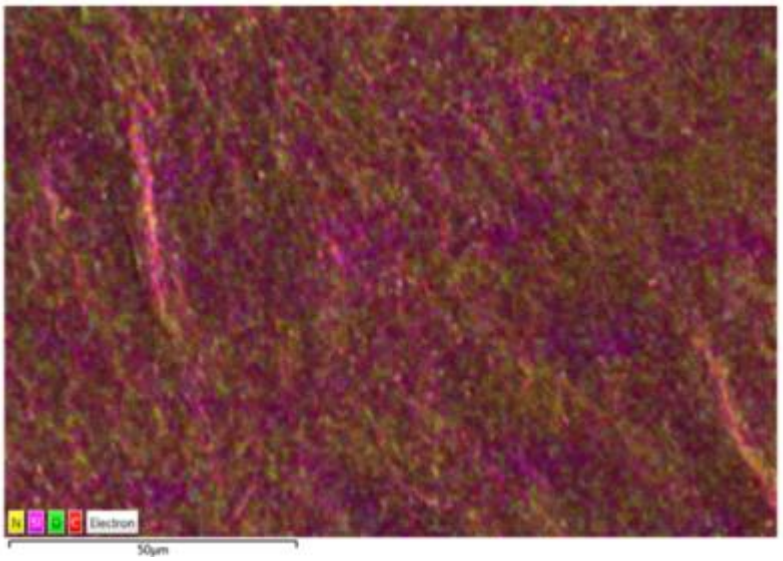
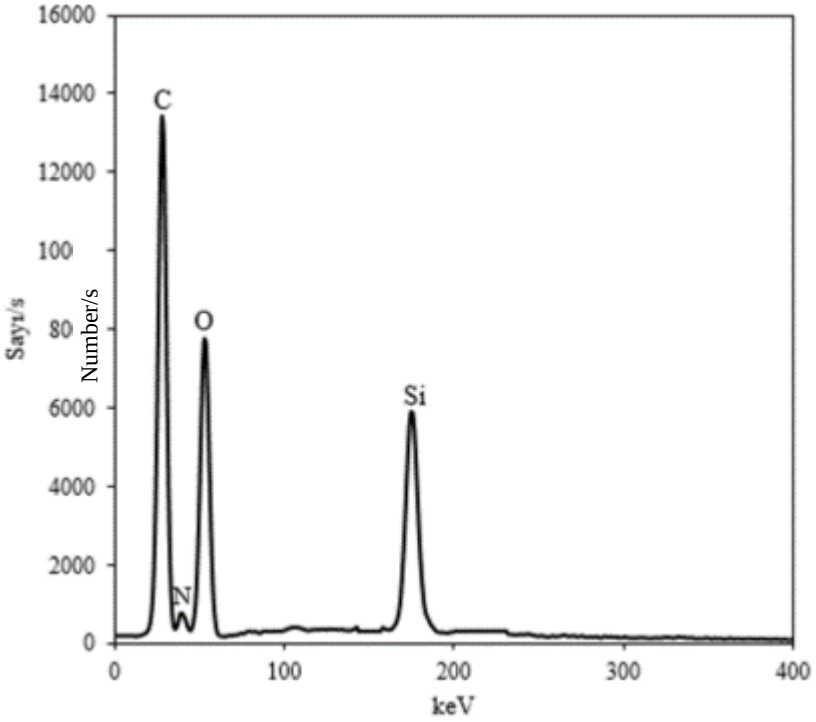


Figure 3. SEM images of the BC-AEAPDMS composite material synthesis (150X and 2500X)



(a)



(b)

Figure 4. SEM-EDX layered graph (a) and EDX spectrums (b) of synthesized the BC-AEAPDMS composite material

Table 1. Elemental content of BC-AEAPDMS composite material produced from sugar beet molasses

Element	Atomic percentage
C	55.72
O	33.17
Si	2.40
N	8.71

FTIR spectra results

FTIR spectrums of produced BC-AEAPDMS is shown in Figure 5. As seen in Figure 5, the peaks in the wavenumber range of 3400-3500 cm^{-1} belong to low acid-free hydroxyl (-OH) groups [17]. The peaks at 3000–2800 cm^{-1} represent the symmetric and asymmetric C-H stretching vibrations of CH_2 (aliphatic hydrocarbons) and CH_3 groups. A peak is seen at 2300 cm^{-1} in the FT-IR spectrums of the produced BC-AEAPDMS pellicle. It is thought that the peak at this wavenumber is due to the large CO_2 impurity during the measurement [18]. From Figure 5, it is observed that NH_2 and mesoporous silica groups are at 1600 cm^{-1} and 1662 cm^{-1}, respectively. It was reported that similar FTIR peaks at 1600 cm^{-1} and 1662 cm^{-1} were also obtained for nanofibril cellulose composite [11]. As can be seen, the presence of amine and silane groups from AEAPDMS in the composite material was proven by FTIR analysis. Finally, the peaks at 1430 cm^{-1}, 1367 cm^{-1}, and 1055 cm^{-1} correspond to CH_2 symmetric bending or surface carboxylate groups, CH_2 waving and C-O-C (ether) functions, and C-OH (alcohol) stretching vibration, respectively [19, 20].

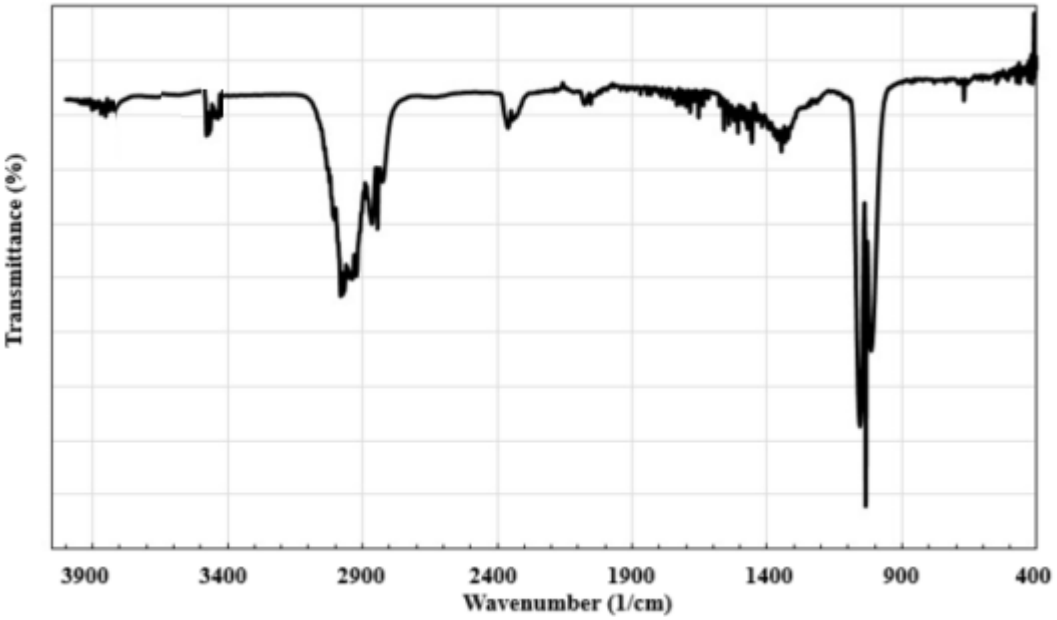


Figure 5. FTIR spectrums of the BC-AEAPDMS composite from sugar beet molasses

Conclusions

This study reveals the production of BC-AEAPDMS from sugar beet molasses in a static culture fermentation and determines its physical and chemical properties. The production yield (as a percentage) of BC produced at 79 g/L molasses concentration, at an inoculation ratio of 13%, and in the working volume of 130 mL was determined as 8.6%. XRD results showed that cellulose I and amorphous forms exist in the synthesized BC-AEAPDMS. From the SEM image, it was observed that the composite material had a low porous structure. Also, it was determined that the nanofibril structure formed dense silane aggregates. From SEM-EDX analyses, the elemental contents of BC-AEAPDMS are composed of C, N, O, and Si. This indicated that the developed material had amino modified. FTIR results showed that the functional groups in the produced BC-AEAPDMS composite material from sugar beet molasses were aliphatic hydrocarbons, CH_3 groups, NH_2, mesoporous silica groups, surface carboxylate groups, ether functions, and alcohol stretching vibration.

In light of all these results, it was concluded that the synthesized material was amine-modified and could be evaluated as an adsorbent in the removal of CO_2 from gas streams. In future studies, it is recommended that employees conduct CO_2 removal experiments.

Acknowledgments

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