Effect of addition polyethylene glycol on morphology and functional groups of composite films bacterial nanocellulose - graphite nanoplatelets

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Abstract. Polyethylene Glycol (PEG) existence on the composite film bacterial nanocellulose (BNC) reinforced with graphite nanoplatelets (GNP) has been analyzed in this research. Pineapple peel waste extract was used to synthesis the bacterial cellulose (BC) pellicle. A 1% NaOH solution was used to remove impurities from the BC pellicle. Mechanical disintegration and a high-pressure homogenization method were used to synthesize BNC. The high-pressure homogenizer (HPH) runs for five cycles at 150 bar before being filtered with a vacuum filter. The composite films are synthesized using a mixture of BNC, PEG 1%, and GNP 2.5%. Then the mixed slurry was dried using an oven for 14 hours at a temperature of 80 degrees Celsius. The morphology of composite BNC film was observed by using SEM. The addition of PEG causes the BC structure to become more porous. GNP is not well distributed in the BNC matrix but still acts as a dispersed filler. FTIR analysis is conducted to see its functional groups. The addition of GNP caused the hydroxyl group to be significantly reduced.

1. Introduction

Eco-friendly polymer composites should be biodegradable and renewable. These polymer composites are simple to compost and do not harm the environment [1,2]. Cellulose is an eco-friendly polymer, and it is an abundant natural polymer, producing many tons per year for paper and textile production [3,4]. Bacterial cellulose (BC) is pure cellulose produced by gram-negative bacteria such as Acetobacter xylinum and Pseudomonas aeruginosa [5,6], naturally formed through the bottom-up approach [7] and can produce cellulose with beneficial physical properties [8]. More than 90% of BC being water. It is made as a white hydrogel and consists of a tangled network of three-dimensional cellulose nanofiber [9] in the form of a band connected through a hydrogen bond tissue [10]. BC’s chemical structure is similar to plant cellulose, but it differs in three-dimensional structure, degree of polymerization, and physicochemical characteristics [11]. Because of the cellulose chain characteristics, BC has a high crystallinity (60–80 percent). It also possesses outstanding mechanical characteristics as well as the capacity to be tuned by an in situ process [12]. Pure BC, on the other hand, is devoid of antimicrobial characteristics, optical transparency, conductivity, magnetism, and...
hydrophobicity [13]. BC has been utilized as a precursor for the synthesis of carbon nanofibers (CNF), which are used as an electrode material in supercapacitors and alkaline metal batteries, in certain prior research [9]. BC is also used as a binder on hybrid nanocomposites [14], and as a reinforcement agent. As a result, there are some possibilities for it to use as a binder such as electrodes of lithium battery [15,16].

As a biodegradable synthetic material, polyethylene glycol (PEG) is a biocompatible and non-toxic polymer. It's soluble in a wide range of organic solvents as well as water. [17]. The presence of polyethylene glycol (PEG) on the BC network has been shown by Liu et al. [18]. Biocompatibility and biodegradability are great in composites made of cellulose, graphene, and PEG. This research will provide a win-win method for developing composite-based environmentally friendly components [19].

The Graphite Nanoplatelet (GNP) is a 2D nano-sized carbon material composed of graphene sheets [20]. GNP can be used to alter thermal properties [21], electrical [22], mechanical [4] and electrochemical [23] in BC films [10]. In this experiment, GNP was used as a filler on the BNC matrix with PEG as a surfactant to produce a composite film of bacterial nanocellulose. Pineapple peel extract was used as the medium for synthesizing the BC pellicle. BNC was synthesized using the mechanical disintegration of BC. Then continue the homogenization process, conducted using a high-pressure homogenizer (HPH) and vacuum filtration. BNC, PEG, and GNP are dissolved and mixed by using a distillate water media. The purpose of this study was to see how adding PEG to BNC, and BNC/GNP composites affected their morphology and functional groups.

2. Materials and methods

2.1. Materials
Pineapple peel extract is used as a medium of BC culture. Other materials in the manufacture of culture media, supplied from CV. Makmur Sejati Malang, are glucose (C6H12O6), PEG 4000, urea, and solid NaOH. A. xylinum bacteria used as a fermentation agent obtained from the Applied Technology Lab of Muhammadiyah University of Malang, Indonesia. GNP was provided from CV. Gamma Scientific Biolab, Malang, East Java, Indonesia.

2.2. Synthesis of BC
Suryanto et al. method is used in this BC synthesis [24]. A high-speed blender was used to mix 300 grams of rotting pineapple peel with up to 1 liter of water for 1.5 minutes. Additional water was poured till the level reached 2 liters. Then mix for 1 minute in the blender. After that, strain the juice to remove the extract and heat until it boils. After boiling, the mixture was mixed with 7.5 wv% glucose and 0.5 wv% urea, then allowed to cool to room temperature. After cooling, 1 v/v% A. xylinum bacterial starter was introduced and cultured for 10-14 days. The BC pellicle was collected and then cleaned with water before being cooked for up to 2 hours at 90°C with a NaOH 1 percent solution. Finally, it was rewashed until it was completely neutral.

2.3. Synthesis of BNC
The steps to synthesize BNC refer to Sardjono et al. [25]. Approximately about 50 gr of pellicle with 300 ml of distilled water was mechanically disintegrated using a high-speed blender for 1.5 minutes. Then 700 ml of distilled water was added and continue to blend for 2 minutes. BC solution homogenized using HPH at 150 bars as much as five cycles. It is then filtered using a vacuum filter.

2.4. Synthesis of composite BNC-PEG films
Ten grams of BNC dissolved using distilled water up to 200 ml and then stirred for 20 minutes. Next, PEG with a percentage of 1% was added. The solution then stirred using a magnetic stirrer for 25 minutes, continuing with the homogenization process in an ultrasonic homogenizer for 20 minutes. The sonication results are placed on a glass mould coated in aluminium foil and dried using an oven for 14 hours at 80°C [17]
2.5. Synthesis of composite BNC-PEG-GNP films
Ten grams of BNC dissolved using distilled water up to 200 ml volume. It was then stirred using a magnetic stirrer for 20 minutes. Next, PEG 1 wt% and GNP 2.5 wt% were added to the solution. Then continue to stir for 25 minutes. The solution is then sonicated using an ultrasonic homogenizer for 20 minutes. Finally, results are placed on a glass mould coated in aluminium foil and dried using an oven for 14 hours at 80°C [17].

2.6. Morphological analysis
The morphological observation was conducted using SEM, type Inspect-S50. Specimens were coated with 10 nm gold before it was observed.

2.7. FTIR analysis
The function group was analyzed at Advanced Mineral and Material Laboratory, Faculty of Science, State University of Malang, Indonesia, using the FTIR Shimadzu IR Prestige-21 Spectrum.

3. Results and discussion

3.1. Morphology
SEM observations are shown in Figure 1. The disintegration and HPH process already has resulted in nano-sized BNC fibers. Figure 1 (a) shows the morphology of BNC at magnification 50,000 times. This treatment can get 30-50 nm in diameter of BNC [25]. Also, the cellulose contact surface becomes wider and strengthens the possibility of interaction between cellulose in BNC and carbon in GNP.

Figure 1 (b) shows the results of an SEM micrograph from a BNC with a PEG 1 wt% film sample. The surface morphology, shown in Figure 1 (b) and (c), is a rough structure and severe wrinkles. PEG makes the BC structure more porous because it increases the distance between the fibers. Figure 1 (c) shows the non-uniform dispersion of GNP in the BNC matrices. This is because GNP has a hydrophobic feature, while PEG is a hydrophilic polymer. Therefore, GNPs are challenging to be dispersed in PEG because of the weak interaction between GNPs and PEG [26].

![Figure 1](image.png)

Figure 1. SEM observations of BNC-PEG-GNP composite film micrographs; (a) pure BNC films; (b) BNC with PEG 1 wt%; (c) composite films of BNC with PEG 1 wt% and GNP 2.5 wt%.

As a dispersed filler, GNP is distributed in the BNC matrix. GNP is hydrophobic, so GNP tends to agglomerate when dispersed in a water-based solution and forms a thicker layer on the interface [25]. The development of cellulose-PEG interaction interactions, which are favored owing to the high concentration of hydrogen bonds, might promote agglomeration of BNC particles [4]. Furthermore, hydrogen bonding between molecules and intramolecular hydrogen bonds between three hydroxyl groups of recurring units cause BNC fibers to cluster [27].
3.2. FTIR analysis

FTIR analysis begins by analyzing the FTIR spectrum graph of the BC/PEG/GNP composite film. The hydroxyl group (O-H) consists of intramolecular and intermolecular hydrogen bonds at wavenumber of 3200-3400 cm\(^{-1}\) [28]. Figure 2 shows that with the addition of PEG and GNP, the number of O-H bonds detected at the peak of 3412 cm\(^{-1}\) decreases. It indicates a reduction in the number of hydrogen bonds when the GNP content in the composite increases. Decreasing the number of hydrogen bonds can reduce the mechanical properties of composite films [4]. Then at 2899 cm\(^{-1}\), a peak belongs to the C-H stretch due to the presence of CH and CH\(_2\) groups in cellulose. A peak appears at 1647 cm\(^{-1}\), corresponding to the –OH bond [29]. O-H and C=O groups strongly decreased. It may be caused by the cross-linking reaction between the O-H group of GNP, BNC, and PEG [1,31]. The C-O cluster that appears at the peak of 974 cm\(^{-1}\) tends to decrease and shift slightly because of the existence of GNP, and the thermal stability of the composite film will increase [13]. With the increasing temperature of the composite film during the drying process, rapid oxygen discharge occurs in CO and CO\(_2\) gases [31]. The –OH functional group did not change and only shifted slightly after PEG was added to BC, while the addition of PEG caused the amount of –OH to decrease significantly.

![Figure 2. FTIR spectroscopy of BNC/PEG/GNP composite films.](image)

GNP is a hydrophobic material. It tends to agglomerate when dispersed in a water-based solution. It also could form a thicker layer on the interface [32]. The O-H group created high surface energy on the surface of nanocellulose, which that surface energy leads to insufficient wetting and weak interface adhesion with hydrophobic polymers [33]. So, it can be predicted that there was no chemical bonding between BNC and GNP. GNP just merged into the BNC matrix and made the structure become conductive film [2].
4. Conclusion
The composite film from combination BNC/PEG/GNP had been produced successfully. GNP agglomeration may cause by the hydrogen bonds that occur between BNC fibres. Since GNP was hydrophobic, most of them agglomerated while dissolved in water solvents. GNP was difficult to distribute throughout the composite film because of the hydrophilic properties of BNC. Low molecular weight PEG addition can increase the porosity of BNC. The addition of GNP caused the hydroxyl group to be significantly reduced.

Acknowledgement
A great appreciation was delivered to LP2M UM through the PNBP-PUI research grant 2021.

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