

## Effect of Graphene Addition on Bacterial Cellulose-Based Nanocomposite

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### ABSTRACT

Bacterial cellulose (BC) is a widespread, low-cost biopolymer that has generally been produced from plants and biomass waste. A method for improving the range of applications for bacterial cellulose is adding graphene material. It has an outstanding feature that can increase the performance of nanocomposite materials. The research aims to observe the effect of graphene on the surface morphology, crystallinity, chemical bonding, and tensile strength of BC/CuO nanocomposite. For this study's synthesis, BC was synthesized by fermenting pineapple peel extract for 10 to 14 days. The produced BC was crushed, homogenized with a nano homogenizer machine, and filtered. Filtered BC, CuO, and graphene were added to obtain a solution, and the mixture was first stirred magnetically, followed by an ultrasonic homogenizer, and finally dried using a freeze-dry method to make a porous nanocomposite. According to SEM analysis, the addition of CuO and graphene can fill porosity nanocomposite. By XRD analysis, the addition of graphene reduces the crystallinity of BC/CuO. The FTIR data showed that adding graphene reduces hydrogen bonding and makes some Cu-O-C bonding. The tensile test has demonstrated that the tensile strength of BC-based nanocomposite with graphene reinforcement tends to decrease.

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**Keywords:** Bacterial cellulose, CuO, FTIR, graphene, SEM, tensile strength, XRD

## I. Introduction

Bacterial cellulose (BC) is a bacterial fermentation product that generates a matrix by hydrogen bonding [1]. Because they include active O-H sites on their chemical chains, cellulose molecules form a network of microfibrils that communicate with each other through hydrogen bonding [2]. BC has the benefits of a high degree of purity, strong mechanical qualities, crystallinity, and distinctive physical characteristics [1], [3]–[6]. Bacterial cellulose is useful for making many materials like paper with high-quality sensors, synthesized artificial skin, packaging with biodegradable capability, and air filters due to its variety of qualities [1], [6]–[10].

Because of this bacterium's poor production under agitated conditions, implementing it in a large-scale fermentation system can be challenging. The creation of techniques to produce BC as cheaply as possible is crucial. Indonesia is one of the largest pineapple producers in the world, producing around 1,396,153 million tons per year [11]. Pineapples are exclusively used on the fruit's flesh, and 23% of it becomes pineapple peel waste [12].



Pineapple peel was easy to obtain, affordable, and environmentally friendly for carbon sources. There have been many attempts to manufacture bacterial cellulose-based nanocomposites. Many material has been added to support BC such as TiO<sub>2</sub>[13], ZnO[14], Fe<sub>3</sub>O<sub>4</sub>[15], Graphite [16], Ag[17], Al<sub>2</sub>O<sub>3</sub>[18] and CuO[19]. This nanomaterial's application is intended following its function, such as enhancing antibacterial, thermal, electrical, and mechanical properties.

The metal substance with antibacterial capabilities is copper oxide (CuO), which enters the microbe network and damages the microbe cell membrane [20]. According to previous studies, the inclusion of CuO may also have an impact on the composite made of chitosan and cellulose's mechanical strength [21]. Furthermore, Cu has the ability to increase mechanical strength to 59.77 MPa [22] because Cu can produce a molecular bonding with a composite matrix.

Graphene is an allotrope of carbon consisting of atoms arranged with a single layer and a two-dimensional honeycomb lattice nanostructure. Graphene is a good candidate for binding metals and other inorganic precursors [23]. According to a different study, bonded silver's antibacterial capabilities could be improved by adding graphene [24], [25]. Another research has also demonstrated that adding graphene can improve CuO antibacterial capabilities [26]. Therefore, there is already a very wide range of possibilities for using graphene in hybrid nanomaterials. The current study was conducted to know the effects of adding graphene on the properties of BC/CuO nanocomposite synthesized from pineapple peel waste.

## II. Material and Methods

### A. Materials

The honey pineapple peel that is used was purchased in the Indonesian city of Malang, in the province of East Java. *Acetobacter xylinum* was the bacteria used to produce bacterial cellulose. The reagents for bacterial fermentation, sugar (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>) as carbon source and urea (CH<sub>4</sub>N<sub>2</sub>O) as nitrogen culturing, were both applied, and Cetyl trimethylammonium bromide (CTAB) with the Merck brand served as the surfactant. CuO was purchased from Guangzhou Hongwu Material Technology Co., Ltd., and graphene, which had a thickness of 1–5 nm, was supplied by SkySpring Nanomaterials, Inc.

### B. BC Pellicle Synthesis

This synthesis referred to the approach utilized in a prior study by Suryanto et al. [27]. Pineapple peel (300 g) was blended at high speed with 2L of water to extract the juice. The pineapple peel extract was boiled, then 150g of sugar and 5g of urea was added to the solution. After the mixture has reached a temperature of 30°C, add 20% of the solution that contains *A. xylinum*. The culture then underwent 10-14 day fermentation. The produced BC pellicle will float on top of the culture medium.

### C. Homogenization Process

The synthesized BC pellicle was sliced and washed with a 1% NaOH solution for 2 hours at 90°C to remove contaminants. The pellicle was rinsed till its pH returned to normal. 5g of pellicle are added to 1L of water and blended for 5 min. at 26,000 rpm in a blender. The material was then homogenized for 5 cycles with 150 bar using a High-Pressure Homogenizer (HPH), and the solution was filtered via Whatman paper 42.

#### D. Nanocomposite Synthesis

3g of crushed BC, 1% CuO, 1% CTAB, and various graphenes (0.1%, 0.3%, and 0.5%) were needed to synthesize a nanocomposite. Such substances were then added to 200mL of water and stirred for 1h 45 min. and homogenize with ultrasonic waves for 30 min. The solution was vacuum filtered with Whatman paper no. 42. The nanocomposite formed on the paper was dried with the freeze-dried method at -62°C for 2 days.

#### E. Surface Morphology

Surface morphology studies were observed under Scanning Electron Microscope with a magnification of 25,000x. Before observation, the surface of nanocomposite was coated by a sputter coater to boost its conductivity.

#### F. Crystallinity Analysis

The diffraction angle of BC/CuO nanocomposite was determined using X-Ray Diffraction (XRD) (PANalytical Expert-Pro). The Segal equations were then applied to calculate a crystallinity degree (Cr) and crystallinity index (CI) of the membrane, as illustrated in equations 1 and 2. The scanning was performed at a diffraction angle of 10°-80°.

$$Cr = \frac{I_{(002)}}{I_{(002)} + I_{(am)}} \times 100\% \quad (1)$$

$$CI = \frac{I_{(002)} - I_{(am)}}{I_{(002)}} \times 100\% \quad (2)$$

Where I(am) represents the diffraction amorf intensity at about 18° and I(002) refers to the highest diffraction intensity at 22°-23°.

#### G. Functional Group Analysis

The Fourier Transform Infra-Red (FTIR) test was conducted to identify the changes in intermolecular interactions and chemical bonding in BC/CuO/graphene nanocomposite membranes. Spectra were collected at a range of 400-4000 cm<sup>-1</sup> and then matched with IR Correlation table to see bond issues of BC/CuO/graphene nanocomposite.

#### H. Mechanical Strength

The mechanical strength of the nanocomposite was performed using an ASTM D638-V tensile test. Tensile testing was performed with tensile test equipment (Techno Lab, Indonesia) at a maximum load of 50 N. The samples were sliced with a scissor according to ASTM D638-V and put between tensile testing holders. For each sample, the rate used was 3 mm/min.

### III. Results and Discussions

#### A. Morphology Analysis

Figure 1 represents the surface morphology of BC control (a), with the addition of CuO on BC nanocomposites (b) and the addition of graphene to BC/CuO nanocomposites.

Surface porosity was created during the synthesis of the BC/CuO/graphene nanocomposite by freeze-dry method. In the vacuum freeze-drying operations, the water content of the BC/CuO/graphene nanocomposite is frozen to restrict the material's mobility and then sublimated, limiting form modifications, resulting in porosity in the nanocomposite surface.

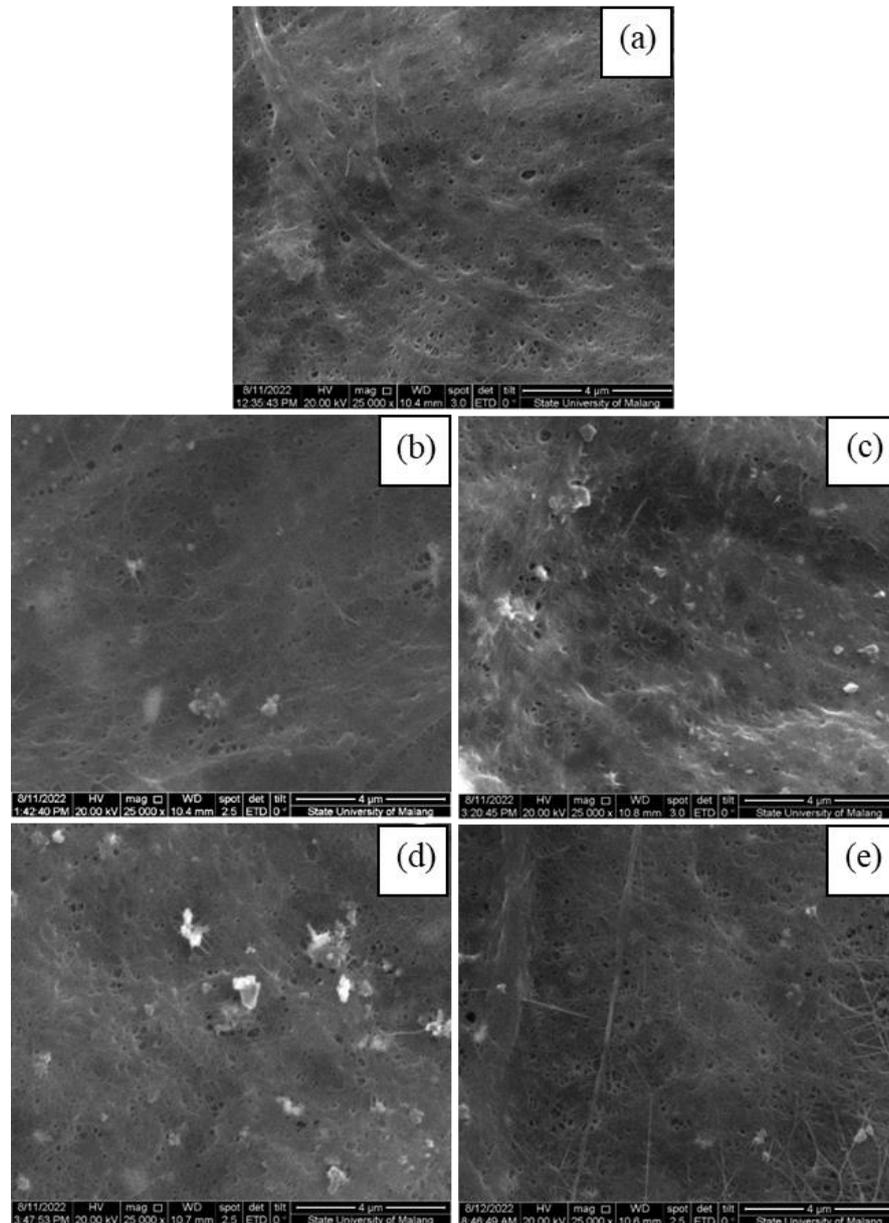


Fig. 1. Surface Morphology of BC nanocomposite with 0% CuO (a), 1% CuO (b), CuO and 0.1% Graphene (c), CuO and 0.3% graphene (d), and CuO and 0.5% Graphene (e)

Figure 1(b) reveals an interaction between CuO and BC. The spherical, dark, aggregated CuO is clearly visible, and 1% CuO is evenly distributed uniformly on the surface. This is owing to the surfactant CTAB's assistance in the binding between BC and CuO, as described in earlier investigations [16]. The graphene was filled porosity by adding graphene to BC/CuO nanocomposite tissue. The porosity of BC was also confirmed in another study, in which the addition of GO/CuO was also able to fill the porosity of bacterial cellulose

membranes [23]. Graphene is represented by a dark, flat plate. As Figure 1 (d), the addition of graphene also makes some bonds with CuO, which is indicated by the sticking of CuO spheres on the graphene sheet [26]. This is indicated by bonding from CuO and graphene and assisted by CTAB as a surfactant [28].

### B. Crystallinity Analysis

Figure 2 shows the diffraction angle obtained from the XRD characterization. In all samples, 4 main peaks can be observed in Figure 2:  $14.4^\circ$ ,  $16.7^\circ$ ,  $22.6^\circ$  and  $26.3^\circ$ , which are indicated the cellulose I by these peaks [29]. BC has a form of cellulose I with crystal planes  $[110]$ ,  $[\bar{1}10]$ , and  $[200]$ . By addition CuO-NPs, new peaks appear at  $35.4^\circ$  and  $38.6^\circ$  [13, 21]. These peaks reflect the monoclinic crystal plane bonding type, which is the index miller is  $[\bar{1}11]$  and  $[111]$  [19]. Table 1 presents further information regarding comparing cellulose crystallinity on BC/CuO/graphene nanocomposite.

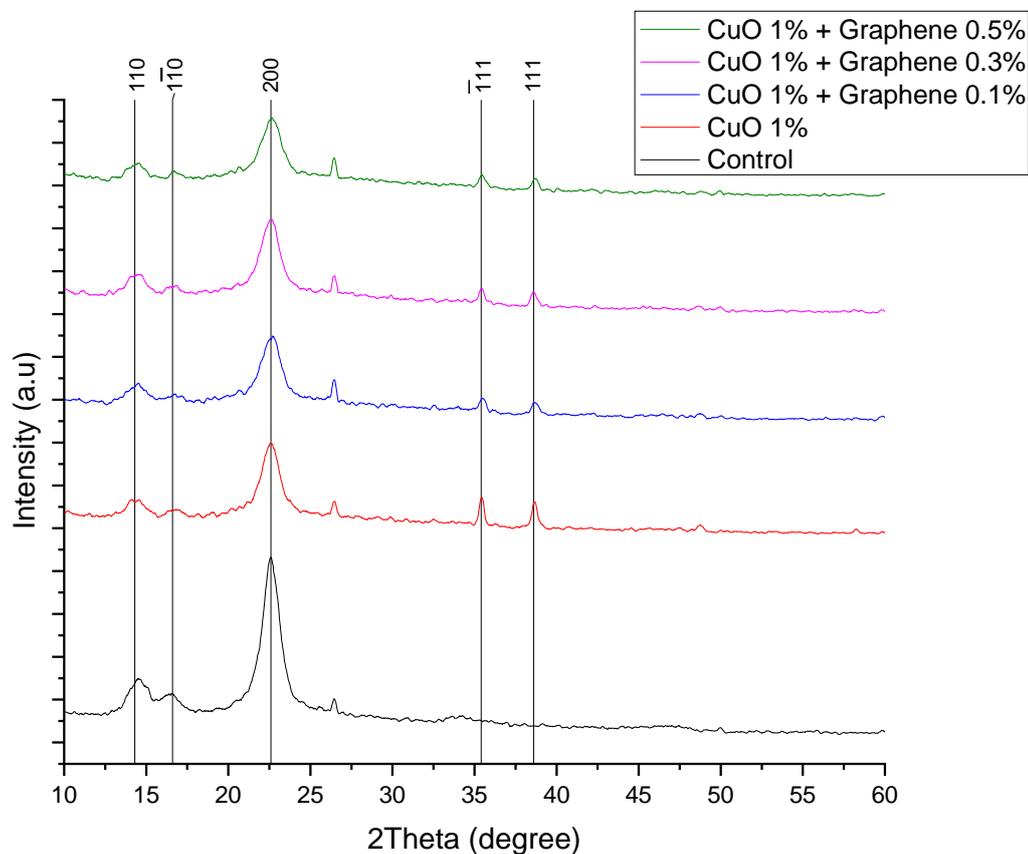


Fig. 2. X-Ray Diffraction Angle of BC/CuO/graphene nanocomposite

Table 1 is a presentation that is used to facilitate a comparison of the effect of the addition CuO-NPs, and graphene in a bacterial cellulose network. The crystallinity of nanocomposite can be described by the crystallinity index (CI) and degree crystallinity (Cr). When the Segal equation is used to compute the degree of crystallinity and crystal index in each sample, the crystallinity of cellulose may be seen at  $22.6^\circ$  [32].

As described in Table 1, the bacterial cellulose peak angle at  $22.6^\circ$  gets the effect of adding graphene where the crystallinity is reduced so that it will result in changes to other properties [27]. The peak angle at  $22.6^\circ$  represents  $[200]$  plane, which is the crystallinity of

cellulose. This peak continues to decrease along increase in the graphene content [28]. This result contrasted with the previous study, which found that adding graphene oxide can increase bacterial cellulose's crystallinity and tensile strength. This is due to the fact that cellulosic polymeric chains are prone to crystalline conformation due to intermolecular interaction between crystal cellulose chains [35]. The conjunction of this fluctuation with increasing nanofibril crystallization might lead to a crystallinity reduction. Although more study is needed to pinpoint the specific mechanisms by which graphene affects crystallinity, the XRD data showed that graphene had an impact on BC's crystal structure.

**Table 1.** Crystallinity and Peak BC/CuO/graphene nanocomposite

Samples	Diffraction Angle (degree)						Crystallinity (%)	
							CI	Cr
BC Control	14.3	16.4	22.5	26.4	-	-	87.4	88.8
BC + 1% CuO	14.3	16.7	22.5	26.4	35.6	38.7	81.1	84.1
BC + 1% CuO + 0.1% Graphene	14.4	16.8	22.6	26.4	35.6	38.7	78.0	81.9
BC + 1% CuO + 0.3% Graphene	14.4	16.5	22.6	26.4	35.6	38.7	77.1	81.4
BC + 1% CuO + 0.5% Graphene	14.3	16.6	22.6	26.4	35.6	38.7	74.6	79.7

### C. FTIR Analysis

Figure 3 represents the intermolecular bonding of BC/CuO/graphene nanocomposites. At 3400-3500  $\text{cm}^{-1}$  range represent intramolecular bonding  $3\text{O} \cdot \cdot \cdot \text{H}-\text{O}5$  of BC [34]. Both the lowered depths indicate that the O-H bond is affected by the contribution of graphene to the BC network. Peaks in absorption at wavelengths about 2900  $\text{cm}^{-1}$  on BC/CuO nanocomposites and graphene in alkyl form reveal the nature of C-H bonds [30].

The spectra of 1595  $\text{cm}^{-1}$  until 1597  $\text{cm}^{-1}$  demonstrate that aromatic carbon (C=O) has a double bond [31]. The findings of the FTIR characterization generally did not show any notable changes. No new peaks or bonds can be identified in the transmittance readings, which just vary little. The graphene was indicated by C=O stretching bonding, which is indicated by the presence of a valley in the wavelength of 1591  $\text{cm}^{-1}$  by BC/CuO/Graphene nanocomposites spectrum. This transmittance demonstrates that graphene is present in the nanocomposite [32]. The molecular bonding between BC, CuO, and graphene is illustrated in Figure 4.

Nonetheless, the bonding of Cu-O-H formation, which come about as a result of the interface among both carboxyl or hydroxyl groups and copper, has a significant impact on the adsorption of graphene on the copper oxide nanoparticles [28]. The formation of bonds between graphene and Cu can be seen with changes in the depth of the Cu-O-H transmittance valley, which decreases, and the hydrogen content is replaced by graphene and forms Cu-O-C bonds [38]. Because there is no free molecular bonding of OH on graphene oxide, the reduced tensile strength of this research assumed that the graphene we used was a substance that potentially ruined and disrupted the bacteria's cellulose chain network [29]. This

interaction damaged the main network of cellulose crystals, causing the tensile strength of the BC/CuO/graphene nanocomposite to continue to decrease.

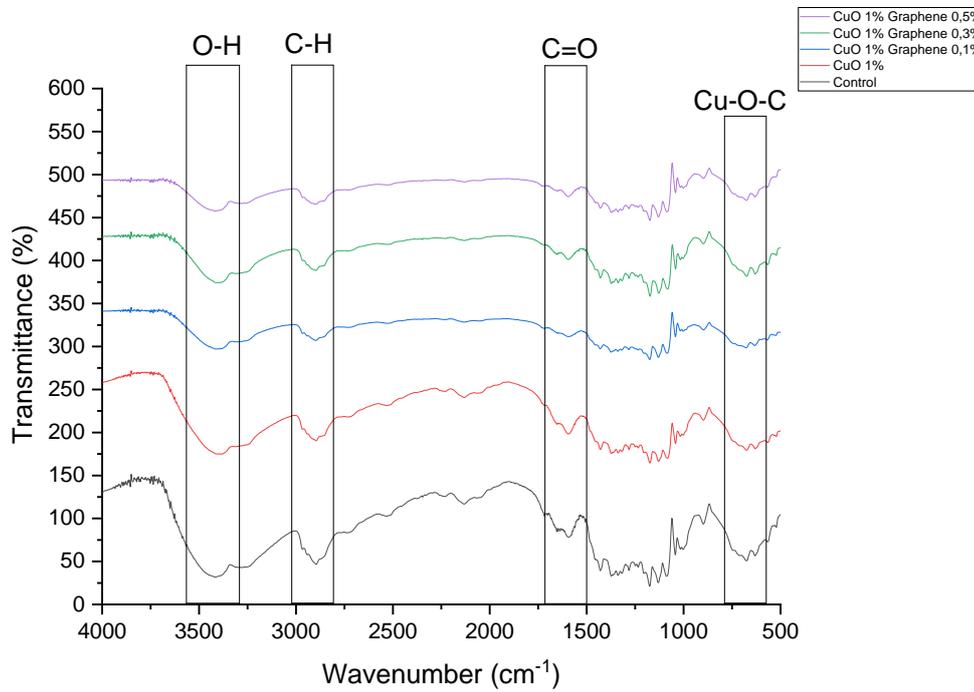


Figure 3. FTIR Spectra of BC/CuO/graphene nanocomposite

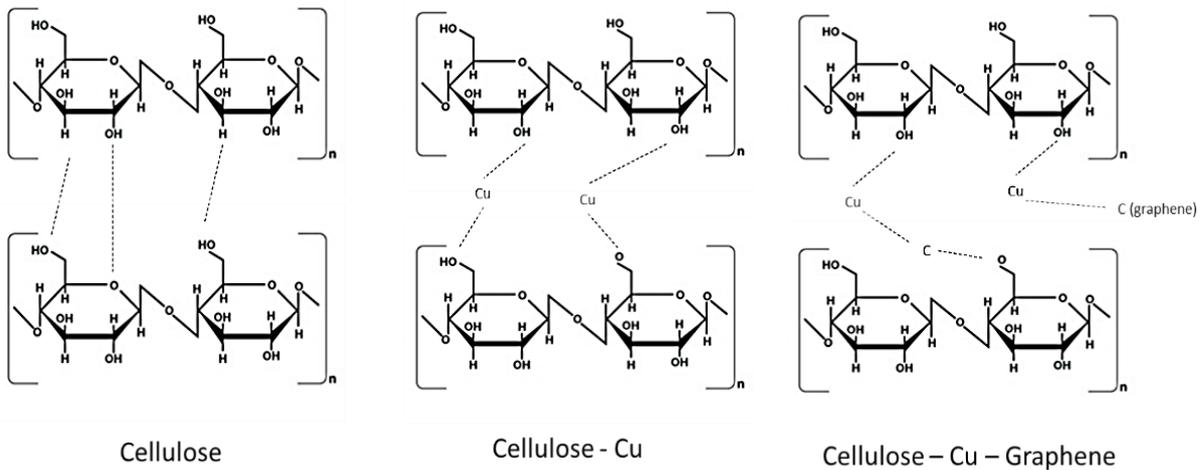


Fig. 4. Illustration of molecular bonding of BC/CuO/Graphene nanocomposite

**D. Mechanical Strength**

The comparison of tensile strength of BC/CuO/ nanocomposite with variations adding of graphene was illustrated in Figure 5. According to the bar graph, a BC with 1% CuO nanocomposite with a tensile strength of 69.643 MPa has the maximum tensile strength. The BC/CuO/ Graphene 0.1% of 54.078 MPa, BC/CuO/Graphene 0.3% was 44.031 MPa after that control material has a tensile strength in 40.652 MPa, and for the last, BC/CuO/Graphene 0.5% was 29.324 MPa.

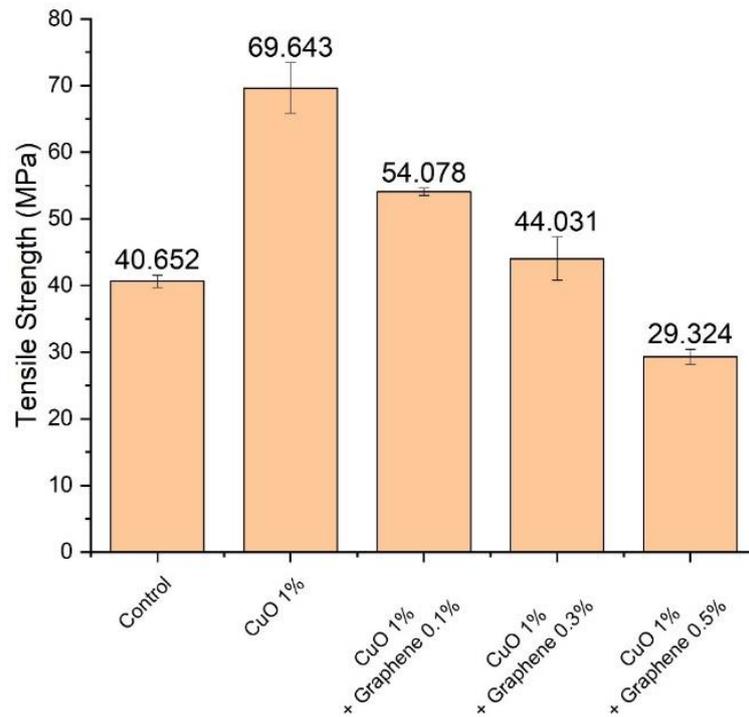


Fig. 5. Comparison Bar of Tensile strength of BC/CuO/graphene nanocomposite

Molecular interactions in BC/CuO/graphene nanocomposites have a significant impact on the variations in mechanical strength. This finding implies that the connection between BC and CuO was strong but that the interaction between BC/CuO and graphene did not contribute much to mechanical improvement. Bonding BC/CuO/graphene makes agglomeration and BC fiber randomly dispersion and makes stress distribution not uniform. The non-uniform distribution of CuO/Graphene bonding causes agglomeration of nanoparticles in the BC network, which makes BC fiber disperse erratically and results in an uneven distribution of stress in BC/CuO/Graphene. Asymmetrical network and distribution stress cause the dispersed load increases only shortly so that accelerating the cracking process and weakening the network on the composite [33].

#### IV. Conclusions

The study of BC/CuO nanocomposites with variations of graphene has been completed properly. A vacuum filtration process and freeze-drying are used to retain porosity. Adding graphene forms some connections with CuO, which is clearly apparent from the CuO spheres' adhesion to the graphene sheet. Also, graphene can reduce crystallinity at a diffraction angle of 22.6°, indicating that the addition of graphene interferes with the cellulose crystals by splitting the molecular bonding bacterial cellulose. Besides, graphene affects O-H, C-H, C≡C, and C=O bonds. The adsorption of graphene on the copper oxide nanoparticles is significantly influenced by the bonding of Cu-O-C formation, which results from the interface between both carboxyl or hydroxyl groups and Copper. But, the mechanical properties of BC/CuO/graphene nanocomposite were reduced from 69.643 MPa

to 29.324 MPa. In the future, the nanocomposite BC/CuO/Graphene potentially be used in a variety of applications, including packaging, the food sector, and medicine.

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