Increasing Electrical Conductivity of Bacterial Cellulose/Polypyrrole Bio Composite Films Prepared Using the Pulling Technique

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Abstract **– this research has found a new approach to improving the conductivity of bacterial cellulose BC/Ppy bio composite films prepared using pulling. A wet BC pellicle is immersed in a liquid Ppy semiconductor for 30 minutes. The wet films was pulled out using a tensile testing machine. The results show that, after pulling, the conductivity of the films became better parallel to the sample drawing direction. Compared to the non-pulled out film, the pulled out film had higher conductivity (σ = 19.2 x 10-3 S/cm), increasing by 153%. The conductivity of films can still improve significantly because deformation during sample preparation in wet conditions.**

Keywords **– Bacterial cellulose; bio composites; conductivities; polymer conductive; polypyrrole; pulling technique; TEMPO.**

1. Introduction

In recent decades, electrical composite materials have been widely studied by researchers in the field of electrical materials, medical technology developments and applications in machining materials [1][2][3].

DOI: 10.18421/TEM121-46
https://doi.org/10.18421/TEM121-46

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Received: 25 August 2022.
Revised: 13 October 2022.
Accepted: 15 November 2022.
Published: 27 February 2023.

Natural fibers have many advantages, and the manufacturing process is relatively low cost and environmentally friendly [4]. Several types of natural fibers, such as oil palm empty fruit bunches, flax, jute, banana, corn, and pineapple leaf, are the major plantation commodities in Indonesia. Plants and some types of bacteria are capable of producing cellulose fibers. One of the advantages of BC was pure cellulose without extraction by chemical treatment. BC fiber has a great physical structure that can create superior mechanical strength.

Bio composites based on BC have many advantages, such as being abundant in nature, renewable, inexpensive, easy to process, environmentally friendly, and biocompatible [5]. Bacterial cellulose pellicles obtained from an Acetobacter xylinum culture were produced cellulose nanofibers [6]. It has high crystallinity, superior thermal properties, non-toxicity, and good mechanical properties [7]. Bacterial cellulose is environmentally friendly, easy to produce, lightweight, and low cost. Its tensile strength is also high, reaching 250.7 MPa [8].

The high strength properties are supported by the long and interconnected chains of the molecules. BC nanofibers form a net-like pellicle with thickness is below 100 nm and diameter is approximately 30 nm [9].

Nanofibers can be produced using various methods, including using high pressure, hydrolyzing them with acid and oxidizing with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl). [10][11]. Nanofibers from bacterial cellulose have a crystallinity rate of 70-80% and a degree of polymerization up to 8000 [10]. Thus, BC was suitable for use as a hybrid nanomaterial for biomedical, biosensing, and supercapacitors [9]. One application of nanofibers was an electrical application for the separator component in batteries with high porosity [12].

Several conductive polymers have been studied. The several types of conductive polymers that have been studied, it is Ppy and PANI have the advantages

of good conductivity, environmental stability, and various color changes according to different redox [7]. However, the processability of PANI was relatively poor because it can be infused and insoluble in common solvents [13]. In contrast to PANI, polypyrrole was used as a conductive polymer because easy to synthesize, environmentally friendly, and has relatively high conductivity [14][15]. The polymerized Ppy can be produced by chemical polymerization/electrochemical using the oxidation of the pyrrole monomer [16]. Polypyrrole (Ppy) was a promising conducting polymer with various applications, including counter electrodes in electrolytic capacitors, actuators, micro actuators, and membrane separations [1][2][3][15][16][17][18][19][20]. However, it also has certain drawbacks, such as the limit of electronic conductivity and poor mechanical strength [10]. Various synthetic and biopolymers have produced Ppy composites with good flexibility and higher conductivity values. One of the potential biopolymers was bacterial cellulose with high flexibility and conductivity.

In this study, BC was oxidized with TEMPO to break hydrogen bonds in bacterial cellulose to make bacterial cellulose fibers do not stick to one another. [21]. TEMPO was used as a coupling agent, reagent for synthesis in organic chemistry, and as a mediator in the control of radical polymerization [22]. It is also widely used in the oxidation of several functional groups.

The previous study reported that Ppy could fill nanogaps and coat the nanofiber because Ppy has flexibility and high conductivity value [23]. The bio composites based Ppy/BC has a high degree of crystallinity, mostly uniform width (3-4 nm), and a large aspect ratio (>50) compared to other nanocellulose [24][25][26][27]. Scanning Electron Microscopy (SEM) observation showed that bio composite based Ppy/BC fibers were tangled and irregular. The advantages of BC used in bio composite were a small elasticity value and increased mechanical strength [28]. Thus, it can be assumed that when pulling the bio composite, the fibers of the bio composite can become straighter and more regular [29]. The straight and regular fibers in the bio composite can increase the absorption of Ppy. It can also increase the conductivity value and minimize the possibility of inhibiting the conductive polymer dispersion in polypyrrole.

This article aims to report the effect of bio composite being pulled on changes in conductivity. First, the cellulose bacterial pellicle was prepared. The cellulose bacteria were then oxidized using TEMPO and soaked in polypyrrole. When the TOBC is wet, it is pulled so that the polypyrrole seeps into the bio composite fibers and covers the straighter fibers.

2. Material and Method

The hypothesis developed is that the strength of the material that occurs is very dependent on the percentage composition of the mixture of polyether and vinyl ester. This is an important object of this research.

A. Material

BC pellicle was purchased from its manufacture in Padang, Indonesia. In terms of size (length equal to 250 mm, width equal to 150 mm and thickness equal to 25 mm). The pellicle was cleaned with distilled water, followed by sodium hydroxide (NaOH). NaOH and the adsorbent (silica gel) were purchased from PT. Brataco, Padang, Indonesia. 5wt% polypyrrole dispersed in H2O with conductivity<0.005 S/cm, FeCl3, Acetone, TEMPO with the formula (2, 2, 6, 6-tetramethylpiperidine-1-oxyl), NaBr 14% NaOCl, and HCl were purchased from Sigma-Aldrich, USA.

B. Preparation of TOBC Film

Water with a volume of 100 mL was mixed with TEMPO weighing 0.016 g and NaBr as much as 0.1 g, then shaken at 500 rpm for 30 minutes. BC pellicle was immersed in acetone, then cut to size (50 mm × 100 mm), then washed with 100 mL of distilled water. The BC pellicle was put into the solution and shaken at 200 rpm for 10 minutes. Add 1.6 g of 14% NaOCl to the solution and shaken at 200 rpm for 15 minutes. Then 0.5% NaOH added to the solution until the pH is 10 and shaken at 200 rpm for 10 minutes at 70 ^{o}C. Boil BC pellicle in solution at 70 ^{o}C for 30 minutes. Then the BC pellicle was cooled, and 5M HCl was added to pH 7.

Three types of bio composites have been made, which are used to see the effect of conductivity after being pulled. The manufacture of bio composites begins with immersing BC using distilled water mixed with NaOH to obtain a pH of 14. The residual precipitate was rinsed using distilled water to clean from the remaining bacteria and to neutralize the pH value of the BC.

Milling was done to remove the water content in the BC pellicle. Furthermore, it aims to get the follicles processed into bio composites using these follicles to get better mechanical strength. After grinding, the strands are immersed in acetone to absorb the remaining water content. This process lasts for one day. After soaking, the follicles were cut into 10 cm x 1.5 cm in size.

C. *Preparation of TOBC/Ppy Bio Composite Before and After Being Pulled*

1.83 mL of Ppy and 4 ml of FeCl3 were mixed and blended in a Petri dish. Then, the TOBC pellicle was added and soaked for 30 minutes. After soaking, TOBC will change color to blackish, which indicates the polypyrrole has been absorbed, coating the TOBC fibers. After that, the bio composite was prepared to be pulled. The pellicle pulling process was similar to the previous work [30]. The purified BC pellicle was cut into a 20 mm × 70 mm rectangular shape. Then pulled in wet conditions was carried out using the COM-TEN Testing Machine 95T Series tensile test equipment.. The sample is placed between filter paper and using a Carver press machine is hot pressed at a temperature of 60 °C for 24 hours. For comparison, the undrawn BC films were made in the same way. Oxidation using Sodium Hypochlorite (NaOCl) and Sodium Bromide (NaBr) at pH 7 with 25 ^{o}C and 0.5% NaOH at 70 ^{o}C.

D. *Characterization*

The Sample was placed on a FESEM (Field Emission Scanning Electron Microscopy). Samples were coated with carbon, then followed gold for two minutes using an Argon plasma metallizer (K575X sputter coating) (Edwards Limited, Crawley, United Kingdom). It aims to reduce sample electron charge. The FESEM type used is FEI Nova NanoSEM 230 FESEM (by FEI, Brno-Černovice, Czech Republic) at 10 kV and at 5,000x magnification.

To measure tensile strength (TS), tensile modulus (TM), and elongation at break (EB) the Com-Ten 95T test machine can be used. In this study, the standard used in the tensile test is ASTM D638-type V. The test was carried out at room temperature and using a tensile speed of 5 mm/min. The sample to be tested is cut to a length of 100 mm and a width of 50 mm. All samples were conditioned at a relative humidity of 50 ± 5% and a temperature of 25 °C for 48 hours. Tensile testing is carried out until the sample breaks. This was done 5 times for each sample.

Samples were stored in a vacuum for 24 hours, with a humidity of 50% or 75% RH. After that, characterize the sample using FTIR. The FTIR used was made by PerkinElmer Frontier. The wavelength used to scan is at 4000-600 cm^{-1} with a resolution of 4 cm^{-1}.

E. *Conductivity Test*

The conductivity is calculated using the formula with the following model; $\sigma = {}^{1}/_{4,53tR}$.

Where is the value of ρ obtained = 4,53tR. The bio composite was analysed at four measurement positions to determine the direction of being pulled (see Figure 1).

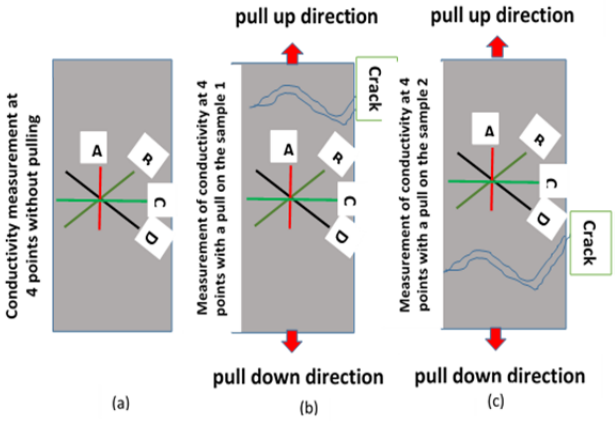


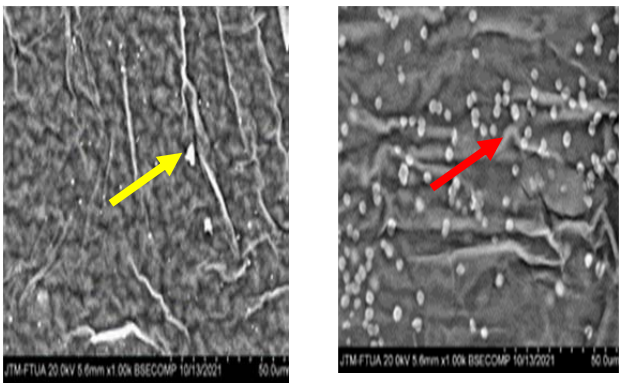
Figure 1. Schematic of conductivity measurement positions

Figure 1 shows the schematic of conductivity with the various position. The probe placed in the drawn direction represents position A. At position B, the probe is placed 45 from probe A. At position C, the probe was placed perpendicular to being pulled. In position D, the probe was placed crossed with probe B.

3. Result and Discussion

A. *Morphology of Bio composite films*

Figure 2 shows the surface of the bio composite films with various treatments (a) without and (b) with pull-out. The surface bio composite film became rough after pull-out. The agglomerates of Ppy nanoparticles crystallized into irregular polymer granules (marked yellow arrow in Figure 2a) on the surface. Ppy particles are uniformly distributed on the surface of the bio composite film (TOBC/Ppy with fiber pull-out), as shown in Figure 2b (marked red arrow). The morphological changes are due to the pulling process. It has changed the electrical conductivity of bio composite film.



a) b)

Figure 2. SEM of the bio composite films, (a) without fiber pull-out, (b) with fiber pull-out

B. Tensile Properties

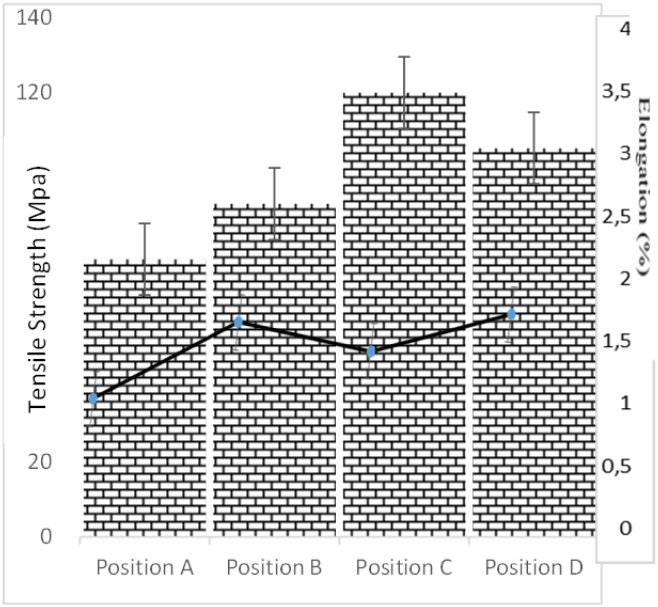


Figure 3. Tensile strength and elongation of the sample

From Figure 3 it can be seen that the tensile strength and relative elongation have the same behavior. The tensile strength of the bio composite at position C is 120 MPa. The tensile strength of the bio composite at position C is 120 MPa. Position C is the best position to get the maximum tensile strength of the bio-composite film. This value increased by 60 % compared to position A. It was because the position of the fiber effectively withstands the maximum load given first before being forwarded to the matrix, thus the maximum tensile strength is obtained. The same phenomenon was also seen for elongation which shows an increase elongation when there was a change in the direction of fiber pulling. The highest elongation was indicated by position B with a value of 1.75 % higher 33.3 % than position A. This tensile strength supports the results of electrical conductivity, where the effect of fiber pull-out treatment can increase the electrical conductivity (see Figure 6).

C. FTIR

FTIR (Fourier Transform Infra-Red Spectroscopy) is used to detect functional groups, identify and analyze organic and inorganic compounds in bio composite films. An FTIR graph can observe the effects of pulling treatment on structural changes in the bio composite film. The principle of FTIR was the interaction between energy and matter [31]. Figure 4 displays an FTIR graph with a similar pattern for all bio composite films.

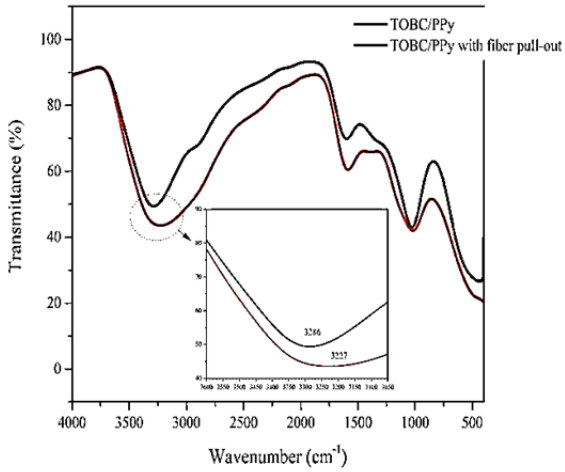


Figure 4. FTIR Graph of Bio composite Films

The range of the FTIR test wavenumber was 4000-500 cm^{-1}. In the FTIR spectrum, there are five leading absorption bands. Bands at about 3200 cm^{-1} (Region I) were associated with stretch vibration O-H. Some shifts in FTIR curves after fiber pull-out from TOBC/Ppy to OH functional group (moisture content). It was due to the hydroxyl group content affecting the conductivity value; therefore, the TOBC/Ppy bio composite film with the fiber pull-out has the highest conductivity (see Figure 6). Bands at about 2900 cm^{-1} (Region II) refer to the CH strain vibration; 1600 cm^{-1} (Region III) was a C=O stretch; 1300 cm^{-1} (Region IV) was associated with C-C-H and C-O-H bending; 1090 cm^{-1} (Region V) was associated with represent stretching vibrations of C-O-C. This is because the TOBC/PPy composite film with tensile test contains more hydroxyl groups (moisture content). The amount of hydroxyl group content affects the conductivity value, therefore the TOBC/PPy composite film with tensile test has the highest conductivity value [32],[33],[34].

D. XRD (X-ray diffraction)

The XRD patterns for TOBC/Ppy bio composite film with and without the fiber pull-out are shown in Figure 5. The peak position for the unstretched TOBC/Ppy bio-composite film was 2 Theta = 22.79° lower than that of the unstretched bio-composite film (2 Theta= 22.92°), this was due to the different lattice spacing [34]. This peak position (200 planes) for the drawn TOBC/Ppy bio-composite film has a larger angle than that of the unstretched film. It was due to the increased polypyrrole absorbed into the bacterial cellulose film. Furthermore, the being pulled on the TOBC/Ppy bio composite film shows a sharp peak, which indicates a large crystal structure. On the other Figure 5. The XRD patterns of bio composite films.

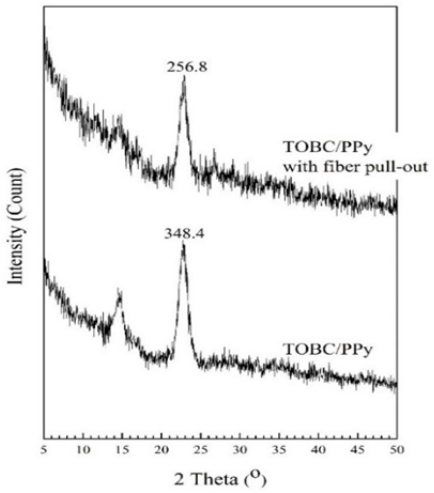


Figure 5. The XRD patterns of bio composite films

E. Conductivity Test

Figure 6 shows the conductivity of the bio composite films with and without fiber pull-out. After drying bio composite films at room temperature (50±5% relative humidity and 25°C), the conductivity test was carried out. At positions A, B, C, and D, conductivity values for bio composite films without fiber pull-out were relatively the same.

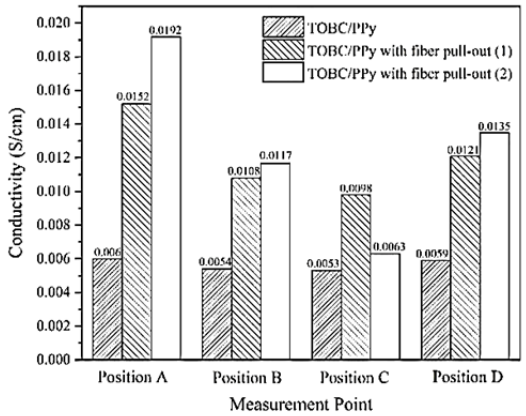


Figure 6. The conductivity of Bio composite TOBC/Ppy with and without fiber pull-out at various positions.

The bio composite without fiber pull-out was not straight. Ppy was not homogenously distributed when tested vertically or horizontally. After fiber pull-out, the fibers become straighter and denser following the pulling direction. This treatment causes Ppy to diffuse homogeneously in the bio composite film.

The conductivity value of the bio composite film at position B was lower than at position A. At position B, there was a 45° shift from position A. At position C, the lowest conductivity value was obtained. It is because the conductivity measurement position is not perpendicular to the pulling direction, causing the electron flow to be slightly blocked compared to positions A, B, and D. At position D, the conductivity value is relatively the same as in position B. The position of the conductivity measurement at D crosses the measurement position at B. This result proves that the BC film will become straighter and unidirectional when pulled, making it easier for the Ppy to diffuse and increase ion transport. It increases the conductivity of the bio composite film [35].

3. Conclusion

The effect of fiber pull-out can improve the electrical conductivity of a bio composite film-based TOBC/Ppy. The conductivity of bio composite with fiber pull-out was about 153% from the before pulling treatment. The conductivity values of TOBC/Ppy bio composite film without a fiber pull-out at position A (in the direction of pull-out), position B (45° from the direction of pull-out), position C (90o to the direction of pull-out), and position D (135° from the direction of pull-out) were relatively the same. This result proves that the bacterial cellulose fiber in the bio composite is still not straight and tight. The highest conductivity value for TOBC/Ppy bio composite with fiber tension was in position A. The Ppy successfully diffused into the BC film when this was stretched. The TOBC/Ppy bio composite with fiber pull-out increased the conductivity value.

Acknowledgment

The researcher would like to thank colleagues who have helped complete this re-search. In particular, the authors would like to thank the Department of Electrical Engineering and the Faculty of Engineering, Andalas University, who have assisted in funding this research.

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