



Original Article

A simple strategy in enhancing moisture and thermal resistance and tensile properties of disintegrated bacterial cellulose nanopaper



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ABSTRACT

Cellulose-based nanopaper with high moisture and thermal resistance and high tensile properties has many applications in the food packaging industry, electronics, and biosensors. The objective of the present work is to produce and characterize the disintegrated bacterial cellulose-based nanopaper film and its ZnO bionanocomposite prepared without and with compression. Addition of ZnO nanoparticles into nanopaper and compression improved the tensile and thermal properties and moisture resistance of the bionanocomposite. Compressed nanopaper film with 1.2 wt% ZnO had the highest tensile strength (TS) of 94.2 MPa and tensile modulus (TM) of 10.1 GPa. These TS and TM values were 109% and 172% higher than those of non-compressed film due to an increase in the crystal structure. Surprisingly this bionanocomposite also demonstrates higher elongation at break in comparison to the nanopaper film. All samples show good rollability and bendability. Compressed bionanocomposite had higher moisture resistance than non-compressed one. This work promotes an environmentally friendly bionanocomposite film which has good potential for food packaging applications.

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1. Introduction

Nanopaper and nanocellulose based bionanocomposites have been attracting attention for their foldability, biodegradability, lack of adverse ecological impact, and potential commercial

applications [1]. Nanocellulose from renewable sources has a high specific strength and modulus, large specific surface area, high aspect ratio, environmental benefits and low cost. Generally, nanocellulose has been isolated from natural sources such as pineapple leaf [2], water hyacinth fiber [3], sugar palm fibers [4,5], and ramie fiber [6] using acid hydrolysis. This disintegrated cellulose has been used to harvest energy from both ambient thermal and mechanical sources [7] and electrodes of flexible electronics [8].

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Pure nano-sized cellulose can also be obtained from bacterial cellulose (BC) without the need for acid hydrolysis providing more environmental benefits (fewer chemical and physical treatment steps), and lower cost (less energy consumption) in comparison to the isolation of the nanocellulose from plant cell walls. One economical source of BC is *Acetobacter xylinum*, a bacterium commonly used in South East Asia to produce a food product *Nata de coco*. This is composed of BC in the form of a pellicle formed from a porous tridimensional network of cross-linked fibers immersed in a liquid matrix. BC has some unique properties with a high degree of crystallinity, high mechanical strength and a highly pure nanofibrillar network structure [9]. BC has fiber diameters range from 10–15 nm and a low coefficient of thermal expansion [10,11].

The potential of this bacterial nanocellulose has been explored in a wide range of applications for, i.e., blood vessels [12], skin and meniscus replacements, and wound-dressing material [13], and flexible substrates for electronic devices [14,15], flexible organic light-emitting diode (OLED) devices [16]. Preparation of a film from disintegrated BC can be carried out using a compression method to increase the tensile and physical properties of the film. These resulting properties also can be improved when added with ZnO nanoparticle [17]. Recently, ZnO nanoparticle was used for the development of BC/ZnO bionanocomposite with improved thermal and tensile properties [18].

Although many works have reported characterizations of BC-based bionanocomposites, however, the role of compression treatment in the increase of tensile and thermal properties of disintegrated BC/ZnO nanoparticle bionanocomposite remains unclear [19–22]. Therefore, the aim of the present work is to prepare and characterize the disintegrated bacterial cellulose-based nanopaper film and its ZnO bionanocomposite without and with compression. Morphology of these films is observed using both field emission scanning electron microscopy (FESEM). Tensile properties were measured. Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transparency, thermal resistance, and moisture absorption of the nanopaper and bionanocomposite film are characterized.

2. Experimental details

2.1. Materials

Nata de coco pellicle in the form of cubes (250 mm × 150 mm × 25 mm) was purchased from a production home industry in Padang, Indonesia. Analytical grade sodium hydroxide (Brataco Brand), ≥98%, and distilled water used in the purification of the pure BC were supplied by the Andeska Laboratory and PT. Brataco, Padang, Indonesia. ZnO nanoparticles (<100 nm particle size (TEM)), ~80% Zn basis were obtained from Sigma-Aldrich Pte. Ltd. Singapore.

2.2. Preparation of sample

2.2.1. Preparation of disintegrated BC nanopaper without and with compression

The preparation of disintegrated BC nanopaper was conducted as described previously [23]. Briefly, the *nata de coco* pellicle was rinsed with distilled water until pH 7 then cut into rectangles (50 mm × 100 mm) with a steel knife. The clean pellicle was soaked in 5% NaOH for 12 h and rinsed repeatedly with distilled water until pH 7. The wet pellicle was pressed in a mould and rinsed with distilled water until pH 7 then disintegrated in a wet electrical blender (Philips, HR2115, Nederland) at 12000 rpm for 1 h. A 400 mL suspension of this was sonicated using an ultrasonic probe (Ningbo Yinzhou SJIA-1200W, China) at 600 W, 100% amplitude and 20 kHz for 1 h. The temperature of the suspension due to ultrasonication was limited to a maximum of 60 °C using thermocouple integrated to the equipment. 110 mL of this disintegrated BC suspension was poured onto Teflon dish (120 mm diameter), then dried in a drying oven (Mettler UN-55) at 60 °C for 24 h. The resulting dried nanopaper was the sample prepared without compression. For the nanopaper sample with compression, the dried film was clamped using a metal flange which was further compressed using a hydraulic press at a pressure of 86.7 MPa for 5 min at 25 °C. The clamped film was stored with the metal flange still in place in a drying oven (Mettler UN-55) at 100 °C for 72 h for further drying of the film.

2.2.2. The preparation of disintegrated BC/ZnO nanoparticle bionanocomposite without and with compression

The preparation of the BC/ZnO bionanocomposites without and with compression was similar to the preparation of the nanopaper. A 400 mL suspension of disintegrated BC was mixed with 1.2 wt% ZnO. The mixture was prepared with and without compression as for the pure BC nanopaper samples.

2.3. Characterization

2.3.1. FESEM observation

The samples were placed on the FESEM sample stub and coated with carbon followed by gold for two min to reduce the electron charge. A model JFIB 4610 SEM from JEOL, Japan was used with 5 kV to optimize observation of the surface morphology of the sample.

2.3.2. Film transparency

The transparency of films was measured using a spectrophotometer (Shimadzu UV 1800, Japan). Rectangular samples 10 mm × 25 mm were prepared and placed in the spectrophotometer. ASTM D1003-00 was used as a testing standard [24]. Transmittances were measured at wavelengths from 400 to 800 nm. The process was repeated three times for each film.

2.3.3. Tensile properties

A Com-Ten testing machine 95T (Comten Industries Inc., Manufacturer in Pinellas Park, Florida) was used to measure

tensile properties (tensile strength, tensile modulus, and elongation at break) performed with a tensile speed of 5 mm/min at room temperature. ASTM D638- type V is the standard used for tensile testing [25]. Before testing, all samples were conditioned for 48 h at $50 \pm 5\%$ relative humidity and 25°C in a desiccator. Thickness and width of the film were measured using a dial micrometre to $1\ \mu\text{m}$ accuracy. Tensile tests were repeated five times for each sample.

2.3.4. FTIR

The aim of FTIR characterization was to determine the functional groups of the bacterial cellulose nanopaper prepared without and with ZnO and compression. It was performed by using PerkinElmer Frontier equipment (PerkinElmer, Inc., Waltham, MA, USA). The dried samples were formed into a sheet film and scanned at a frequency range of $4000\text{--}600\ \text{cm}^{-1}$.

2.3.5. X-ray diffraction

PANalytical Xpert PRO (Philips Analytical, Almelo, The Netherlands) at 25°C , 40 kV and 30 mA was used to perform X-ray diffraction testing. The samples were scanned from $2\theta = 5^\circ$ to 60° . The crystallinity index (CI) percentage was measured using Eq. 1 [26]:

$$\text{CI (\%)} = \frac{(I_{200} - I_{\text{am}})}{I_{200}} \times 100 \quad (1)$$

where I_{200} (22°) is the intensity of the peak corresponding to cellulose I, and I_{am} (18°) is the intensity of the peak of the amorphous fraction.

2.3.6. Thermogravimetry analyzing (TGA), derivative (DTG), and differential scanning calorimetry (DSC)

This method is similar to the one reported in more detail in a previous study [27]. A thermal analysis instrument Mettler-Toledo AG, Schwerzenbach, Switzerland was used to measure TGA, and DTG of samples. The sample was input into the instrument which was set up with a nitrogen flow rate of $20\ \text{mL/min}$. The heating rate was 10°C/min . DSC was measured using TA Instrument (Model Q20) from room temperature up to 500°C at 10°C/min with nitrogen flow rate of $50\ \text{mL/min}$. The weight of each sample was $5\text{--}10\ \text{mg}$.

2.3.7. Moisture absorption

A method for measuring the moisture absorption (MA) was based on work described in a previous study [27]. All samples were dried in a drying oven (Memmert Germany, Model 55 UN) at 50°C until a constant weight was achieved. The dried sample was stored in a closed chamber with 75% relative humidity at 25°C . After 300 min in the chamber, the samples were weighed every 30 min for 3 h with a precision balance (Kenko) with a $0.1\ \text{mg}$ accuracy. MA was measured five times of each sample and calculated using Eq. 2.

$$\text{MA} = (w_h - w_o)/w_o \quad (2)$$

where w_h is the final weight and w_o is the initial weight of the sample. MA determination was repeated 5 times for each sample.

2.3.8. Statistical analysis

Experiment data were analyzed using IBM SPSS Statistics 25.0 (IBM Corporation, Chicago, USA). One-way analysis of variance (ANOVA) and p-test were used to identify the significance of any effects of treatment on tensile properties and moisture absorption of the bacterial cellulose nanopaper prepared without and with ZnO and compression. Duncan multiple range test was used using a 95% ($p \leq 0.05$) confidence level. The values with statistically significant differences were marked with different letters.

3. Results and discussions

3.1. FESEM morphology

Fig. 1 shows the FESEM morphology of the fractured surface of the tensile specimen. The dried nanopaper without compression (Fig. 1a) displays many layers of cellulose fiber networks and crevices between the layers (red arrow). Compression and heating at 100°C for 72 h allow the increased connection of the fibers through hydrogen bonding (red arrow in Fig. 1b). Both these treatments provided more energy for increasing the amount of the intra- and interconnected polymer chains. Fig. 1c shows good dispersion of the nano-sized ZnO (red arrow) resulting from ultrasonication treatment which effectively destroyed the agglomerations of ZnO [28]. The mechanism of the interconnection of BC nanofiber and ZnO nanoparticle has been reported previously [29]. The presence of this ZnO in the sample was also evidenced by diffraction peaks at 2θ of 32° , 34° , 36° , 48° and 56° in the XRD pattern (Fig. 4). Some ZnO were bonded strongly via hydrogen bonds presumably between the oxygen atoms and the hydroxyl groups on the fiber surface (red arrow in Fig. 1d) and others can be trapped among two fibers [30]. Evidence of this hydrogen bonding can be observed from the shifting OH functional group bands in FTIR spectra (see Fig. 3). This is in agreement with previous work [31]. The greater amount of hydrogen bonding between fibers and the increased number of hydrogen-bonded and trapped ZnO nanoparticles result in an increase in obstruction for fiber mobility. Even unbonded ZnO nanoparticles can prevent fiber movement. A fiber passing around a ZnO particle even if it is not bonded to it must follow a longer tortuous path. These phenomena lead to an increase in the tensile and physical properties of the bionanocomposite film.

3.2. Flexibility and transmittance value

Fig. 2 shows the flexibility and transparency of each film. All samples are rollable (Fig. 2a), and bendable (Fig. 2b). This is probably attributed to strong inter- and intra-molecular hydrogen bonds [32]. When compressed, the transmittance value of the film (Fig. 2c) increased as a result of a decrease in the fraction of the cavities [33]. This higher translucence can also be attributed to more ordered molecular structure as observed using X-ray diffraction (XRD) for the compressed film. Table 1 shows an increase in CI value after compression. The presence of ZnO nanoparticles scatters the light leading to the

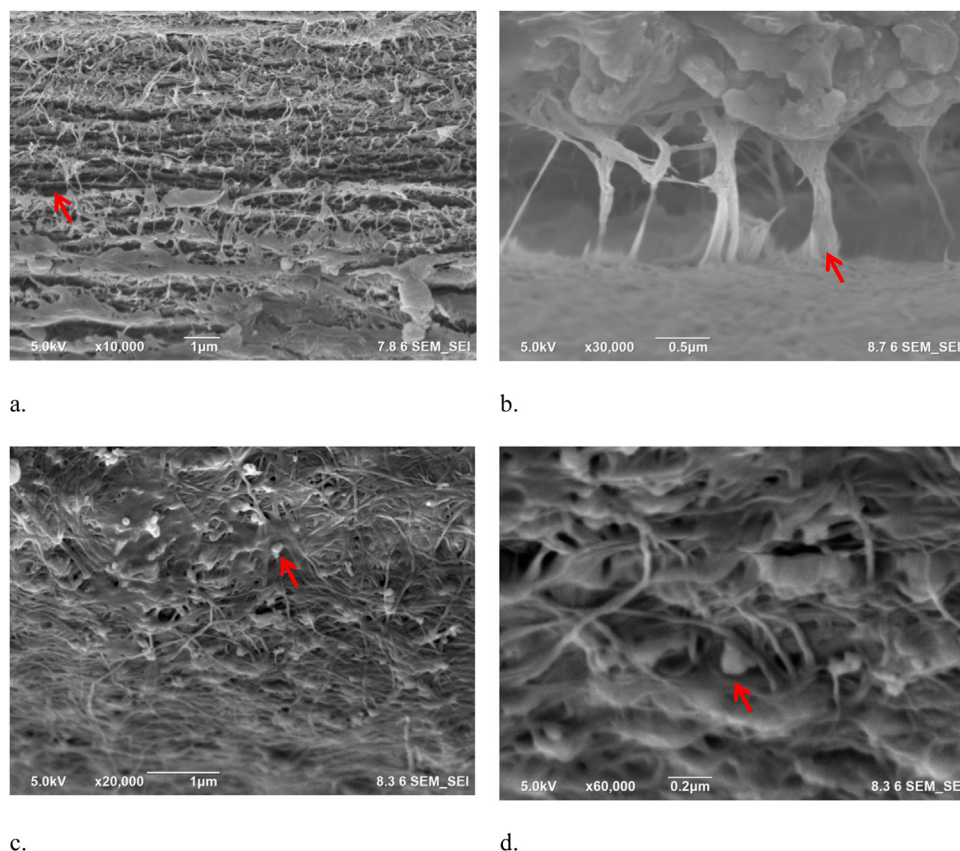


Fig. 1 – The fracture surface of non-compressed nanopaper film (a), Compressed nanopaper film (b), Well-dispersed ZnO in cross-section of compressed bionanocomposite (c), ZnO nanoparticle bonded on fiber surface (red arrow) of compressed bionanocomposite (d).

Table 1 – CI (from Fig. 4), T_o , T_m (from Fig. 6b) of all samples.

Samples (abbreviation)	CI (%)	T_o (°C)	T_m (°C)
Compression + ZnO (WC + ZnO)	83.4	337	361
Without compression + ZnO (WOC + ZnO)	79.4	330	358
Compression and without ZnO (WC)	82.3	315	348
Without compression and without ZnO (WOC)	78.7	314	347

bionanocomposites having lower transparencies. This trend is also in agreement with past report [34].

3.3. FTIR spectra

Fig. 3 displays the FTIR spectra of the functional groups from the average values of three measurements on FTIR spectra for each sample. All FTIR curves show a similar pattern (Fig. 3a). More detailed changes in the functional groups can be seen in the Fig. 3(b–f).

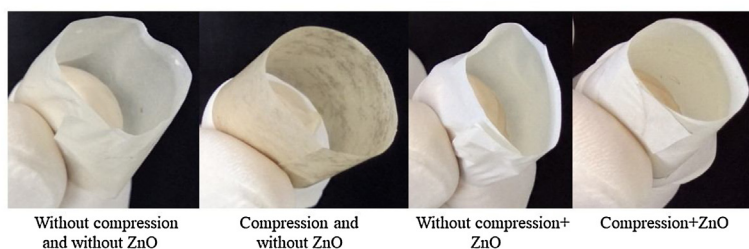
Fig. 3(b) is the band at about 3325 cm^{-1} assigned to O–H stretching vibration [35,36]. The non-compressed films had the strongest intensity. The peak shape was the broadest as a result of the strongest disruption of crystal structure due to ultrasonication [37]. Wavenumber value was shifted

from 3337 cm^{-1} (WOC film) to 3339 cm^{-1} (WOC + ZnO film) resulting from the increasing interlayer spacing. After compression, the WC + ZnO film displays the sharper peak shape and the weaker peak intensity. The wavenumber of this film was shifted to a lower value (3336 cm^{-1}) attributed to the reduction of interlayer spacing and the formation of hydrogen bonding interaction between cellulose and ZnO [38,39]. This reduced wavenumber corresponds to a decrease in molecular vibrations in the OH groups, the decreased number of free OH groups available in the sample, and the increased hydrophobicity of the bionanocomposite [40–42].

Fig. 3(c) is the band at about 2900 cm^{-1} corresponding to C–H stretching vibration [43]. The peak position of the non-compressed films was the most left with a wavenumber of 2900 cm^{-1} (WOC film) the intensity was the strongest and the shape the broadest. These functional groups were under nonhomogeneous strain condition and the crystals highly disoriented. The peak of the band shifted to the lower wavenumber value about $3\text{--}4\text{ cm}^{-1}$, the shape became sharper due to an increase in crystal after compression and addition of ZnO nanoparticles.

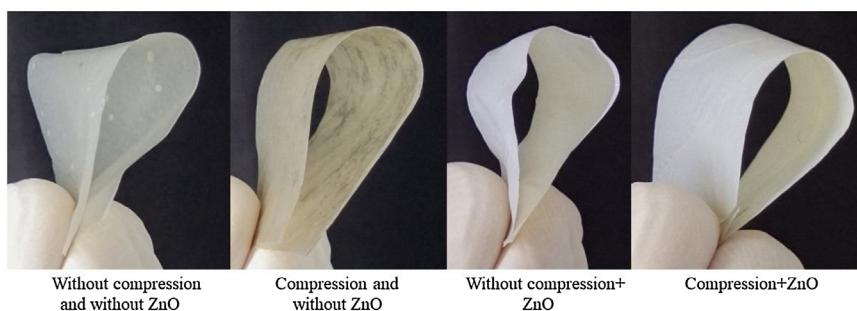
A similar phenomenon with O–H stretching vibration is also presented by peaks at the region of $1644\text{--}1647\text{ cm}^{-1}$ assigned to O–H of absorbed water (Fig. 3d) [44]. The shifting wavenumber to lower value about 1 cm^{-1} was observed on the compressed bionanocomposite film compared to non-

Rollable

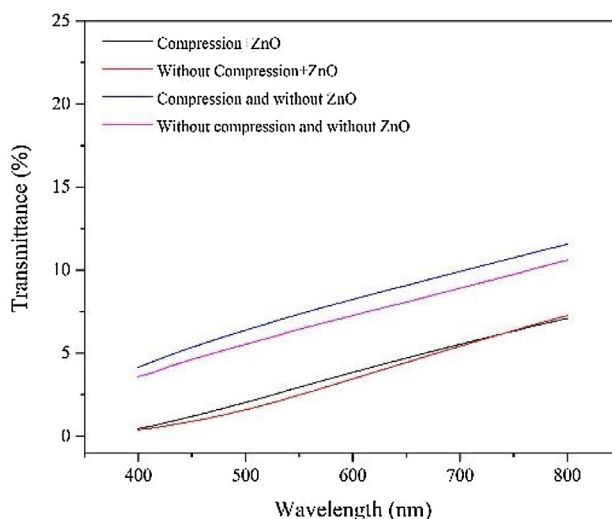


a)

Bendable



b)



c)

Fig. 2 – The appearance of the flexibility of the samples during rolling (a), bending (b), and the transmittance value (c) of the film.

compressed one. This corresponds to the increasing intra- and interconnection among the fibers as well as between ZnO nanoparticles and fiber via hydrogen bonding after compression [45,46]. This higher intersections of OH groups cause a lower molecular vibration as a result of a decrease in the number of free hydroxyls [47]. The weakest intensity was observed in the WC+ZnO film, probably caused by the

lowest degree of hydrophilicity. This result is in good agreement with result in Fig. 7 showing the lowest MA for this film.

The band at 1430 cm^{-1} (Fig. 3e), assigned to CH_2 bending vibration, is known as the crystallinity band [48]. The least intensity of this band reflects the lowest degree of crystallinity in the WOC sample [49]. After compression

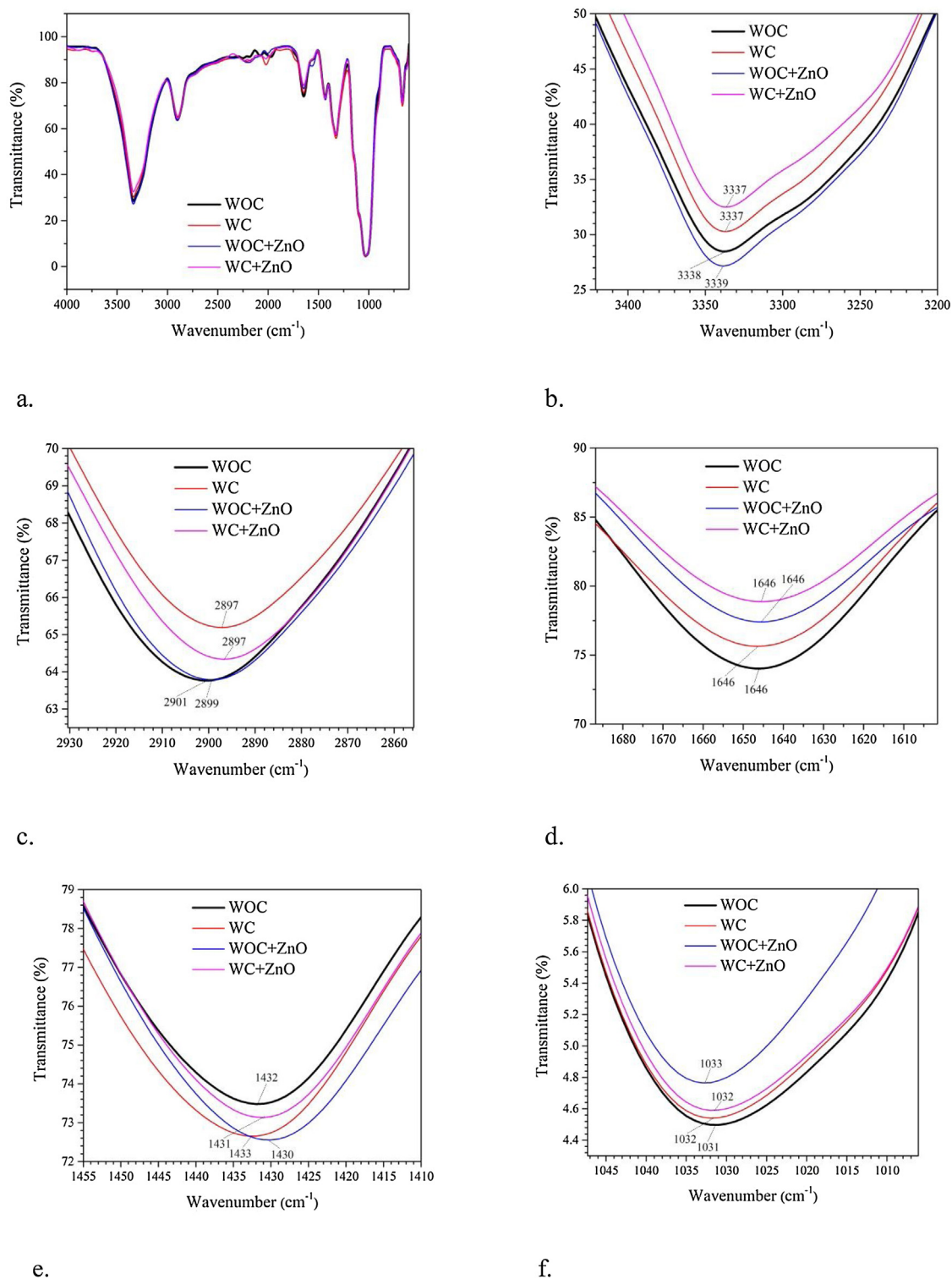


Fig. 3 – FTIR curves of the bacterial cellulose nanopaper prepared without and with ZnO nanoparticles and compression; (a) the full spectrum from 4000–250 cm^{-1} , (b–f) sections of the spectrum expanded to show changes in peaks related to specific functional groups.

and/or addition of ZnO, the intensity of the samples became higher, which corresponds to a higher crystallinity index in the samples. The C–O stretching band at about 1031 cm^{-1} is associated with the backbone structure of cellulose as

shown in Fig. 3(f) [50]. The broadest shape was observed on the WOC sample, related to the lowest crystal structure and the most highly disoriented crystal, probably due to ultrasonication treatment. This sample had a wavenumber value

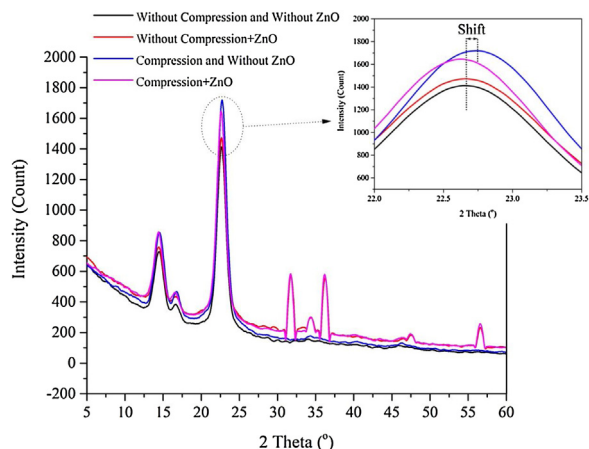


Fig. 4 – X-ray diffraction patterns of the bacterial cellulose nanopaper prepared without and with ZnO nanoparticle and compression.

of 1031 cm^{-1} lower than WC film (1032 cm^{-1}). For the WC film, the shape was sharper and the intensity was reduced probably due to an increase in hydrogen bonding after compression at 100°C for 72 h. The lowest wavenumber value and the weakest intensity of WC+ZnO film represent the highest degree of hydrogen bonds between ZnO and cellulose.

3.4. X-ray diffraction

Fig. 4 shows the X-ray diffraction pattern of nanopaper and bionanocomposite without and with compression. BC film has typical cellulose I diffraction pattern with peaks at $2\theta = 14^\circ$, 16.6° and 22° [23] corresponding to (-101) , (101) and (002) crystal plane respectively [6,51]. This is consistent with the diffraction pattern type reported previously [52]. Bionanocomposite film exhibits diffraction peaks at 2θ of 32° , 34° , 36° , 48° and 56° which correspond to the presence of ZnO nanoparticles [53]. Each sample shows an obvious difference in intensity, shape and diffraction angle of these peaks (see inset). WOC film had the lowest peak intensity and broadest shape corresponding to the lowest crystallinity index (Table 1). This phenomenon is attributable to the greatest disruption of the cellulose crystal structure due to ultrasonication during sample preparation [54–56]. Compression of BC film led to an increase in crystallinity index as shown by WC film with greater intensity and sharper peak shape than WOC film. The cellulose chains of WC film became more closely packed in an ordered and parallel arrangement. Compression also caused a shift of the peak at $2\theta = 14.5^\circ$ and 22.6° to a higher 2θ value. This corresponds to a decrease in interlayer spacing of the crystal structure, consequently, the molecular structure of the WC film was strained compressively [57]. In this case, WC film had higher compressive residual stress than WOC film [54,58]. The presence of ZnO nanoparticle in WC film led to an increase in CI of 83.4%. The peak shift of WC+ZnO film to lower 2θ value resulted from an increased crystal plane spacing [20,59].

3.5. Tensile properties

Fig. 5 shows the tensile properties of the nanopaper and bionanocomposite prepared without and with compression. The error bars represent the standard deviation of five tests. The range of these bars is related to the different values from testing. The treatments of this present work results in a significant increase ($p \leq 0.05$) in the tensile properties of the film. BC nanopaper after compression had the higher TS (56.4 MPa) than that before compression (44.3 MPa) an increase of 27%. This is what might be expected considering the increased hydrogen bonding and CI after compression as shown in Table 1 [7]. The presence of the compressive residual stress which is presented in Fig. 4 also contributes to improving the tensile properties [54]. The external tensile stress must overcome the compressive residual (negative tensile) stress before the crack tips experience sufficient tensile stress to propagate. After the addition of 1.2 wt% ZnO, the TS was significantly increased ($p \leq 0.05$) to almost twice that of BC nanopaper. This is because the hydrogen-bonded and trapped ZnO nanoparticles obstructed the movement of individual cellulose nanofibers. As shown in Fig. 5(a), the maximum TS was obtained on the compressed bionanocomposite (92.4 MPa) corresponding to a higher fraction of hydrogen bonds among fibers and an increase in the number of hydrogen-bonded ZnO nanoparticles after compression [60]. Similarly, TM of the bionanocomposite almost tripled from $3,708.7\text{ MPa}$ to $10,105.8\text{ MPa}$ after compression. This result is in agreement with previous work [61]. Even though TS and TM increased, elongation at break (EB) of the bionanocomposite was also increased. This is attributable to the longer tortuous paths of the cellulose nanofiber due to the presence of the trapped ZnO. This result is consistent with the high flexibility of film as shown in Fig. 2a, and 2b. However, the EB value decreased after compression resulting from an increase in the number of hydrogen-bonded ZnO nanoparticles.

3.6. Thermal properties

Fig. 6(a–b) show TGA and DTG curves of nanopaper and bionanocomposites as a function of temperature. All curves have a similar pattern (3 stages of weight loss of the sample). However, the peaks at the first and second stage in Fig. 6(b) were shifted and affected by the presence of ZnO and compression. The first weight loss region below 100°C is due to the release of moisture present in the sample [62,63]. Each sample displays different weight losses resulting from the different amounts of water evaporated. The non-compressed bionanocomposite had the highest evaporation as evidenced by the deepest peak at this first step (Fig. 6b). This is because this film has the highest number of voids in the structure for the water to escape through. The weight loss for the second stage at $250\text{--}360^\circ\text{C}$ is related to the decomposition of the ZnO and cellulose [64,65]. In the temperature range of $360\text{--}570^\circ\text{C}$ a third weight loss was measured due to a final decomposition to ash [38,66]. The nanopaper shows the lowest thermal resistance. Addition of ZnO nanoparticles and compression both increased it (Fig. 6a and b). This was evidenced by the temperature of the onset of degradation (T_o) and the maximum decomposition rate (T_m) were shifted from 314 to 337 , and $347\text{--}361^\circ\text{C}$,

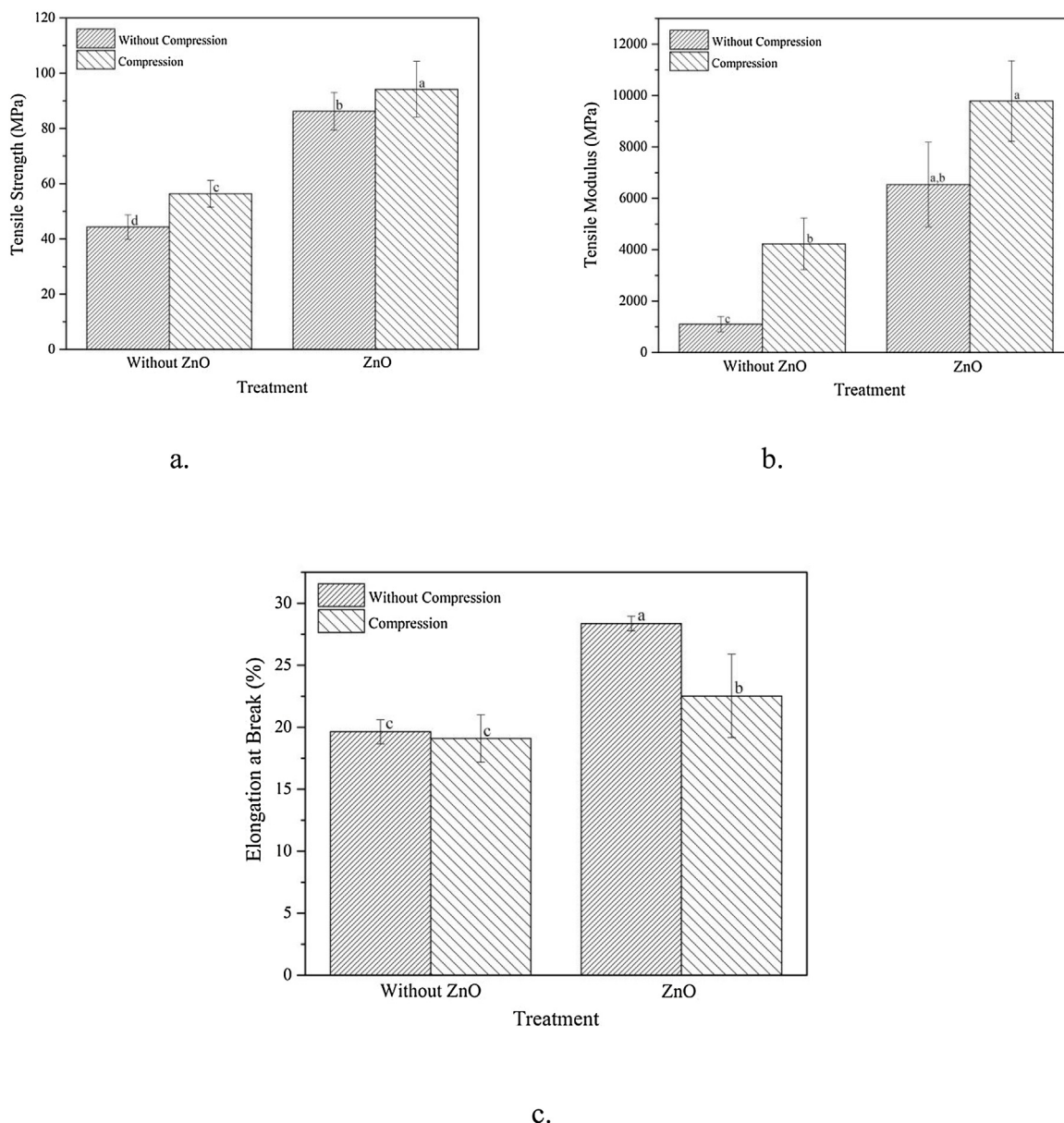


Fig. 5 – The average value of a) tensile strength (TS), b) tensile modulus (TM), and c) elongation at break of each sample as a function of adding ZnO and compression; RH 50% 25 °C. Different letters a, b, c, d in the vertical bar chart indicate significant differences at $p \leq 0.05$.

respectively. This shift corresponds to the higher activation energy for decomposing the bionanocomposite, resulting from stronger bonding energy among fibers as well as between ZnO and fibers, and the presence of ZnO which has higher thermal properties than pure fiber [67]. This is consistent with FTIR pattern (Fig. 3b) showing the formation of hydrogen bonding interaction between cellulose and ZnO. The increased thermal resistance was also affected by the increase in CI after compression (Table 1) and is in good agreement with a previous study [68]. A similar result is demonstrated by Fig. 6(c) displaying the DSC curves of each sample. The non-compressed nanopaper shows the lowest peak in regions between 50 and 125 °C, corresponding to the highest water vaporization [69]. The presence of ZnO and compression in the films decreased

the intensity of the endothermic peaks in the DSC curve between 325 and 375 °C due to higher thermal stabilization.

3.7. Moisture absorption (MA)

Figure 8 shows the average MA at saturation point for all samples measured every 30 min for 3 h. The error bars indicate the standard deviation of five tests. The large size of some of these error bars, particularly for the addition of ZnO and without compression, could be due to the non-homogenous dispersion of the ZnO nanoparticles (1.2 wt%) throughout the sample. The change of weight gain for all samples is typical of Fickian diffusion behaviour [70]. As expected, the highest MA is found in non-compressed bionanocomposite. The presence of trapped

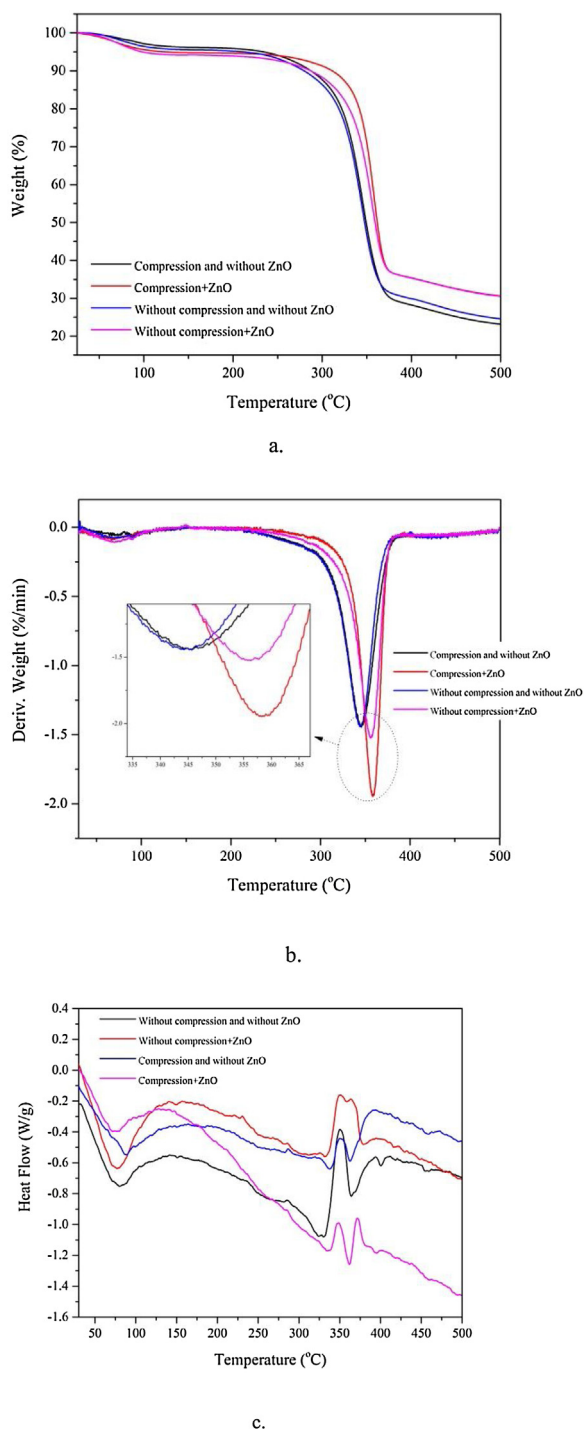


Fig. 6 – a) TGA, b) DTG, and c) DSC curves for nanopaper and bionanocomposite before and after compression.

ZnO among BC nanofiber can produce larger-scale voids which can be occupied by more water molecules via diffusion as described by Fick's second law [71]. This is consistent with the result in Fig. 6 showing the highest evaporation of absorbed water at the first weight loss region for the non-compressed bionanocomposite film. After the addition of ZnO and compression, MA reduced significantly ($p \leq 0.05$). In this case, the compressed bionanocomposite (WC + ZnO sample) had the

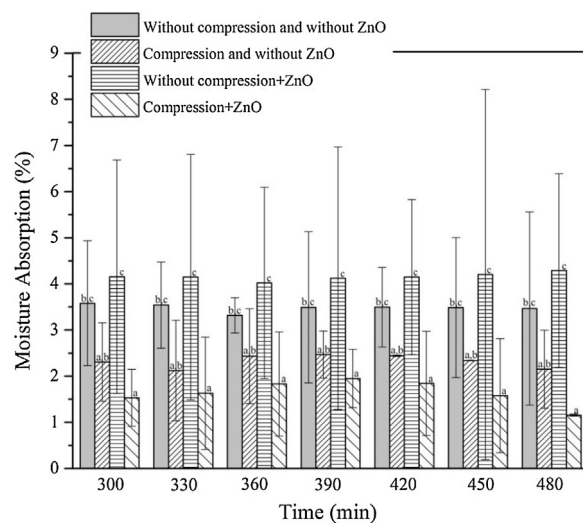


Fig. 7 – Moisture absorption of all samples. Different letters a, b, c in the MA indicate significant differences at $p \leq 0.05$.

lowest MA resulting from the most hydrophobic nature among samples. This is because the compression reduced the size and the number of voids in the film leading to a decrease in water diffusion. This result is consistent with the FTIR pattern of the corresponding WC + ZnO sample showing the shallowest peak of OH stretching at about 3339 cm^{-1} (Fig. 3b) and the weakest intensity of O–H absorbed water at 1645 cm^{-1} (Fig. 3d).

4. Conclusions

This work reported successful fabrication and characterization of a disintegrated bacterial cellulose/ZnO bionanocomposite prepared with and without compression. Addition of 1.2 wt% ZnO nanoparticles into BC nanopaper and compression improved TS (109%) and TM (172%) compared to non-compressed BC nanopaper. This bionanocomposite also displayed higher thermal and moisture resistance and higher elongation at break in comparison to the nanopaper film. All samples had good rollability and bendability. These results suggest that compressed films from these materials provide many advantages as environmentally friendly biopolymers for industrial applications.

Conflicts of interest

We affirm that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere. Also, there is no conflict of interest.

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REFERENCES

- [1] Meng Q, Wang TJ. Mechanics of strong and tough cellulose nanopaper. *Appl Mech Rev* 2019;71:040801–30, <http://dx.doi.org/10.1115/1.4044018>.
- [2] Mahardika M, Abrial H, Kasim A, Arief S, Hafizulhaq F, Asrofi M. Properties of cellulose nanofiber/bengkoang starch bionanocomposites: effect of fiber loading. *LWT - Food Sci Technol* 2019;116:108554, <http://dx.doi.org/10.1016/j.lwt.2019.108554>.
- [3] Asrofi M, Abrial H, Kasim A, Pratoto A, Mahardika M. Isolation of nanocellulose from water hyacinth Fiber (WHF) produced via digester-sonication and its characterization. *Fibers Polym* 2018;19:1618–25, <http://dx.doi.org/10.1007/s12221-018-7953-1>.
- [4] Ilyas RA, Sapuan SM, Atiqah A, Ibrahim R, Abrial H, Ishak MR, et al. Sugar palm (Arenga pinnata [Wurmb.] Merr) starch films containing sugar palm nanofibrillated cellulose as reinforcement: water barrier properties. *Polym Compos* 2020;41:459–67, <http://dx.doi.org/10.1002/pc.25379>.
- [5] Ilyas RA, Sapuan SM, Ibrahim R, Abrial H, Ishak MR, Zainudin ES, et al. Effect of sugar palm nanofibrillated cellulose concentrations on morphological, mechanical and physical properties of biodegradable films based on agro-waste sugar palm (Arenga pinnata (Wurmb.) Merr) starch. *J Mater Res Technol* 2019;8:4819–30, <http://dx.doi.org/10.1016/j.jmrt.2019.08.028>.
- [6] Syafri E, Kasim A, Abrial H, Asben A. Cellulose nanofibers isolation and characterization from ramie using a chemical-ultrasonic treatment. *J Nat Fibers* 2019;16:1145–55, <http://dx.doi.org/10.1080/15440478.2018.1455073>.
- [7] Kumar A, Gullapalli H, Balakrishnan K, Botello-Mendez A, Vajtai R, Terrones M, et al. Flexible ZnO-cellulose nanocomposite for multisource energy conversion. *Small* 2011;7:2173–8, <http://dx.doi.org/10.1002/smll.201100458>.
- [8] Xu X, Zhou J, Jiang L, Lubineau G, Ng T, Ooi BS, et al. Highly transparent, low-haze, hybrid cellulose nanopaper as electrodes for flexible electronics. *Nanoscale* 2016;8:12294–306, <http://dx.doi.org/10.1039/c6nr02245f>.
- [9] Yoshinaga F, Tonouchi N, Watanabe K. Research progress in production of bacterial cellulose by aeration and agitation culture and its application as a new industrial material. *Biosci Biotechnol Biochem* 1997;61:219–24.
- [10] George J, Ramana KV, Bawa AS, Siddaramaiah. Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites. *Int J Biol Macromol* 2011;48:50–7, <http://dx.doi.org/10.1016/j.jbiomac.2010.09.013>.
- [11] Nishino T, Matsuda I, Hirao K. All-cellulose composite. *Macromolecules* 2004;37:7683–7, <http://dx.doi.org/10.1021/ma049300h>.
- [12] Andrade FK, Costa R, Domingues L, Soares R, Gama M. Improving bacterial cellulose for blood vessel replacement: functionalization with a chimeric protein containing a cellulose-binding module and an adhesion peptide. *Acta Biomater* 2010;6:4034–41, <http://dx.doi.org/10.1016/j.actbio.2010.04.023>.
- [13] Klemm D, Schumann D, Udhardt U, Marsch S. Bacterial synthesized cellulose-artificial blood vessels for microsurgery. *Prog Polym Sci* 2001;26:1561.
- [14] Watanabe K, Eto Y, Takano S, Nakamori S, Shibai H, Yamanaka S. A new bacterial cellulose substrate for mammalian cell culture. *Cytotechnology* 1993;13:107–14.
- [15] Nogi M, Yano H. Transparent nanocomposites based on cellulose produced by bacteria offer potential innovation in the electronics device industry. *Adv Mater* 2008;20:1849–52, <http://dx.doi.org/10.1002/adma.200702559>.
- [16] Ummartyotin S, Juntaro J, Sain M, Manuspiya H. Development of transparent bacterial cellulose nanocomposite film as substrate for flexible organic light emitting diode (OLED) display. *Ind Crops Prod* 2012;35:92–7.
- [17] Alavi M, Nokhodchi A. An overview on antimicrobial and wound healing properties of ZnO nanobiofilms, hydrogels, and bionanocomposites based on cellulose, chitosan, and alginate polymers. *Carbohydr Polym* 2020;227:115349, <http://dx.doi.org/10.1016/j.carbpol.2019.115349>.
- [18] Xiao Y, Liu Y, Kang S, Wang K, Xu H. Development and evaluation of soy protein isolate-based antibacterial nanocomposite films containing cellulose nanocrystals and zinc oxide nanoparticles. *Food Hydrocoll* 2020;106:105898, <http://dx.doi.org/10.1016/j.foodhyd.2020.105898>.
- [19] Shahmohammadi Jebel F, Almasi H. Morphological, physical, antimicrobial and release properties of ZnO nanoparticles-loaded bacterial cellulose films. *Carbohydr Polym* 2016;149:8–19, <http://dx.doi.org/10.1016/j.carbpol.2016.04.089>.
- [20] Ul-Islam M, Khattak WA, Ullah MW, Khan S, Park JK. Synthesis of regenerated bacterial cellulose-zinc oxide nanocomposite films for biomedical applications. *Cellulose* 2014;21:433–47, <http://dx.doi.org/10.1007/s10570-013-0109-y>.
- [21] Dinca V, Mocanu A, Isopencu G, Busuioac C, Brajnicov S, Vlad A, et al. Biocompatible pure ZnO nanoparticles-3D bacterial cellulose biointerfaces with antibacterial properties. *Arab J Chem* 2020;13:3521–33, <http://dx.doi.org/10.1016/j.arabjc.2018.12.003>.
- [22] Alavi M, Nokhodchi A. An overview on antimicrobial and wound healing properties of ZnO nanobiofilms, hydrogels, and bionanocomposites based on cellulose, chitosan, and alginate polymers. *Carbohydr Polym* 2020;227:115349, <http://dx.doi.org/10.1016/j.carbpol.2019.115349>.
- [23] Abrial H, Lawrensius V, Handayani D, Sugiarti E. Preparation of nano-sized particles from bacterial cellulose using ultrasonication and their characterization. *Carbohydr Polym* 2018;191:161–7.
- [24] ASTM D1003-00. Standard test method for haze and luminous transmittance of transparent plastics. *Am Soc Test Mater* 2000.
- [25] ASTM D882-12. Standard test method for tensile properties of thin plastic sheeting. *Am Soc Test Mater* 2002.
- [26] Segal L, Creely JJ, Martin AE, Conrad M. Empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Text Res J* 1958;786–94.
- [27] Abrial H, Putra GJ, Asrofi M, Park J, Kim H. Effect of vibration duration of high ultrasound applied to bio-composite while gelatinized on its properties. *Ultrason - Sonochemistry* 2018;40:697–702.
- [28] Abrial H, Anugrah AS, Hafizulhaq F, Handayani D, Sugiarti E, Muslimin AN. Effect of nanofibers fraction on properties of the starch based biocomposite prepared in various ultrasonic powers. *Int J Biol Macromol* 2018;116:1214–21, <http://dx.doi.org/10.1016/j.jbiomac.2018.05.067>.
- [29] Gimenez AJ, Yáñez-Limón JM, Seminario JM. Paper-based photoelectrical devices. *J Intell Mater Syst Struct* 2013;24:2255–61, <http://dx.doi.org/10.1177/1045389X12457836>.
- [30] Abrial H, Ariksha J, Mahardika M, Handayani D, Aminah I, Sandrawati N, et al. Effect of heat treatment on thermal resistance, transparency and antimicrobial activity of sonicated ginger cellulose film. *Carbohydr Polym* 2020;240:116287, <http://dx.doi.org/10.1016/j.carbpol.2020.116287>.

- [31] Lefatshe K, Muiva CM, Kebaabetswe LP. Extraction of nanocellulose and in-situ casting of ZnO/cellulose nanocomposite with enhanced photocatalytic and antibacterial activity. *Carbohydr Polym* 2017;164:301–8, <http://dx.doi.org/10.1016/j.carbpol.2017.02.020>.
- [32] Poletto M, Ornaghi Júnior HL, Zattera AJ. Native cellulose: structure, characterization and thermal properties. *Materials* (Basel) 2014;7:6105–19, <http://dx.doi.org/10.3390/ma7096105>.
- [33] Jonoobi M, Aitomäki Y, Mathew AP, Oksman K. Thermoplastic polymer impregnation of cellulose nanofibre networks: morphology, mechanical and optical properties. *Compos Part A Appl Sci Manuf* 2014;58:30–5.
- [34] Abiral H, Hartono A, Hafizulhaq F, Handayani D, Sugiarti E, Pradipta O. Characterization of PVA/cassava starch biocomposites fabricated with and without sonication using bacterial cellulose fiber loadings. *Carbohydr Polym* 2018;206:593–601, <http://dx.doi.org/10.1016/j.carbpol.2018.11.054>.
- [35] Hafizulhaq F, Abiral H, Kasim A, Arief S, Affi J. Moisture absorption and opacity of starch-based biocomposites reinforced with cellulose fiber from bengkoang. *Fibers* 2018;6:1–11, <http://dx.doi.org/10.3390/fib6030062>.
- [36] Ilyas RA, Sapuan SM, Ishak MR, Zainudin ES. Sugar palm nanofibrillated cellulose (*Arenga pinnata* (Wurmb.) Merr): effect of cycles on their yield, physic-chemical, morphological and thermal behavior. *Int J Biol Macromol* 2019;123:379–88, <http://dx.doi.org/10.1016/j.ijbiomac.2018.11.124>.
- [37] Chen W, Yu H, Liu Y, Hai Y, Zhang M, Chen P. Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. *Cellulose* 2011;18:433–42, <http://dx.doi.org/10.1007/s10570-011-9497-z>.
- [38] Asrofi M, Abiral H, Kurnia Y, Sapuan SM, Kim H. Effect of duration of sonication during gelatinization on properties of tapioca starch water hyacinth fiber biocomposite. *Int J Biol Macromol* 2018;108:167–76.
- [39] Kaewtatip K, Thongmee J. Studies on the structure and properties of thermoplastic starch/luffa fiber composites. *Mater Des* 2012;40:314–8.
- [40] Ghule K, Ghule AV, Chen BJ, Ling YC. Preparation and characterization of ZnO nanoparticles coated paper and its antibacterial activity study. *Green Chem* 2006;8:1034–41, <http://dx.doi.org/10.1039/b605623g>.
- [41] Abiral H, Ariksha J, Mahardika M, Handayani D, Aminah I, Sandrawati N, et al. Transparent and antimicrobial cellulose film from ginger nanofiber. *Food Hydrocoll* 2020;98:105266, [doi:10.1016/j.foodhyd.2019.105266](https://doi.org/10.1016/j.foodhyd.2019.105266).
- [42] Abiral H, Ariksha J, Mahardika M, Handayani D, Aminah I, Sandrawati N, et al. Highly transparent and antimicrobial PVA based bionanocomposites reinforced by ginger nanofiber. *Polym Test* 2020;81:106186, <http://dx.doi.org/10.1016/j.polymertesting.2019.106186>.
- [43] Abiral H, Atmajaya A, Mahardika M, Hafizulhaq F, Handayani D, Sapuan SM, et al. Effect of ultrasonication duration of polyvinyl alcohol (PVA) gel on characterizations of PVA film. *J Mater Res Technol* 2020;9:2477–86, <http://dx.doi.org/10.1016/j.jmrt.2019.12.078>.
- [44] Thiripura Sundari M, Ramesh A. Isolation and characterization of cellulose nanofibers from the aquatic weed water hyacinth - *Eichhornia crassipes*. *Carbohydr Polym* 2012;87:1701–5.
- [45] Guerrero P, Kerry JP, De La Caba K. FTIR characterization of protein-polysaccharide interactions in extruded blends. *Carbohydr Polym* 2014;111:598–605, <http://dx.doi.org/10.1016/j.carbpol.2014.05.005>.
- [46] Anitha S, Brabu B, John Thiruvadigal D, Gopalakrishnan C, Natarajan TS. Optical, bactericidal and water repellent properties of electrospun nano-composite membranes of cellulose acetate and ZnO. *Carbohydr Polym* 2012;87:1065–72, <http://dx.doi.org/10.1016/j.carbpol.2012.12.020>.
- [47] Abiral H, Soni Satria R, Mahardika M, Hafizulhaq F, Affi J, Asrofi M, et al. Comparative study of the physical and tensile properties of jicama (*Pachyrhizus erosus*) starch film prepared using three different methods. *Starch/Stärke* 2019;71:1–9, <http://dx.doi.org/10.1002/star.201800224>.
- [48] Oh SY, Dong IY, Shin Y, Hwan CK, Hak YK, Yong SC, et al. Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy. *Carbohydr Res* 2005;340:2376–91, <http://dx.doi.org/10.1016/j.carres.2005.08.007>.
- [49] Giolacu D, Giolacu F, Popa VI. Amorphous cellulose – structure and characterization. *Fall Tech Meet East States Sect Combust Inst* 2011;45:13–21.
- [50] Wiley JH, Atalla RH. Band assignments in the raman spectra of celluloses. *Carbohydr Res* 1987;160:113–29, [http://dx.doi.org/10.1016/0008-6215\(87\)80306-3](http://dx.doi.org/10.1016/0008-6215(87)80306-3).
- [51] Zhao J, Zhang W, Zhang X, Zhang X, Lu C, Deng Y. Extraction of cellulose nanofibrils from dry softwood pulp using high shear homogenization. *Carbohydr Polym* 2013;97:695–702.
- [52] Lv P, Wei A, Wang Y, Li D, Zhang J, Lucia LA, et al. Copper nanoparticles-sputtered bacterial cellulose nanocomposites displaying enhanced electromagnetic shielding, thermal, conduction, and mechanical properties. *Cellulose* 2016;23:3117–27.
- [53] Shankar S, Teng X, Li G, Rhim JW. Preparation, characterization, and antimicrobial activity of gelatin/ZnO nanocomposite films. *Food Hydrocoll* 2015;45:264–71, <http://dx.doi.org/10.1016/j.foodhyd.2014.12.001>.
- [54] Epp J. X-ray diffraction (XRD) techniques for materials characterization. Elsevier Ltd 2016, <http://dx.doi.org/10.1016/B978-0-08-100040-3.00004-3>.
- [55] Biswas D, Sinha AK, Chakraborty S. Effects of oxygen partial pressure and annealing temperature on the residual stress of hafnium oxide thin-films on silicon using synchrotron-based grazing incidence X-ray diffraction. *Appl Surf Sci* 2016;384:376–9, <http://dx.doi.org/10.1016/j.apsusc.2016.05.015>.
- [56] Amanov A, Umarov R, Amanov T. Increase in strength and fretting resistance of Alloy 718 using the surface modification process. *Materials* (Basel) 2018;11:1–13, <http://dx.doi.org/10.3390/ma11081366>.
- [57] Bandyopadhyay R, Selbo J, Amidon GE, Hawley M. Application of powder X-ray diffraction in studying the compaction behavior of bulk pharmaceutical powders. *J Pharm Sci* 2005;94:2520–30, <http://dx.doi.org/10.1002/jps.20415>.
- [58] Brown EN, Clausen B, Brown DW. In situ measurement of crystalline lattice strains in phase IV polytetrafluoroethylene. *J Neutron Res* 2007;15:131–8, <http://dx.doi.org/10.1080/10238160701372620>.
- [59] Palaniandy S, Azizli KAM. Mechanochemical effects on talc during fine grinding process in a jet mill. *Int J Miner Process* 2009;92:22–33.
- [60] Abiral H, Dalimunthe MH, Hartono J, Efendi RP, Asrofi M, Sugiarti E, et al. Characterization of tapioca starch biopolymer composites reinforced with micro scale water hyacinth fibers. *Starch/Stärke* 2018;70:1–8, <http://dx.doi.org/10.1002/star.201700287>.
- [61] Abiral H, Kadriadi, Mahardika M, Handayani D, Sugiarti E. Characterization of disintegrated bacterial cellulose nanofibers prepared with a high shear homogenizer and their PVA bionanocomposites. *Int J Biol Macromol* 2019;135:591–9.

- [62] Abrial H, Basri A, Muhammad F, Fernando Y, Hafizulhaq F, Mahardika M, et al. A simple method for improving the properties of the sago starch films prepared by using ultrasonication treatment. *Food Hydrocoll* 2019;93: 276–83.
- [63] Ilyas RA, Sapuan SM, Ishak MR, Zainudin ES. Development and characterization of sugar palm nanocrystalline cellulose reinforced sugar palm starch bionanocomposites. *Carbohydr Polym* 2018;202:186–202, <http://dx.doi.org/10.1016/j.carbpol.2018.09.002>.
- [64] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* 2007;86:1781–8, <http://dx.doi.org/10.1016/j.fuel.2006.12.013>.
- [65] Yang Y, Chen H, Zhao B, Bao X. Size control of ZnO nanoparticles via thermal decomposition of zinc acetate coated on organic additives. *J Cryst Growth* 2004;263:447–53, <http://dx.doi.org/10.1016/j.jcrysgro.2003.12.010>.
- [66] Ilyas RA, Sapuan SM, Ishak MR. Isolation and characterization of nanocrystalline cellulose from sugar palm fibres (*Arenga Pinnata*). *Carbohydr Polym* 2018;181:1038–51, <http://dx.doi.org/10.1016/j.carbpol.2017.11.045>.
- [67] Feng Y, Feng N, Wei Y, Zhang G. An in situ gelatin-assisted hydrothermal synthesis of ZnO-reduced graphene oxide composites with enhanced photocatalytic performance under ultraviolet and visible light. *RSC Adv* 2014;4:7933–43, <http://dx.doi.org/10.1039/c3ra46417b>.
- [68] Kim UJ, Eom SH, Wada M. Thermal decomposition of native cellulose: influence on crystallite size. *Polym Degrad Stab* 2010;95:778–81, <http://dx.doi.org/10.1016/j.polymdegradstab.2010.02.009>.
- [69] Garrido T, Peñalba M, de la Caba K, Guerrero P. A more efficient process to develop protein films derived from agro-industrial by-products. *Food Hydrocoll* 2019;86:11–7, <http://dx.doi.org/10.1016/j.foodhyd.2017.11.023>.
- [70] Kushwaha PK, Kumar R. Studies on water absorption of bamboo-epoxy composites: effect of silane treatment of mercerized bamboo. *J Appl Polym Sci* 2010;115:1846–52, <http://dx.doi.org/10.1002/app.31317>.
- [71] Wan YZ, Luo H, He F, Liang H, Huang Y, Li XL. Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. *Compos Sci Technol* 2009;69:1212–7, <http://dx.doi.org/10.1016/j.compscitech.2009.02.024>.