

Tensile and Morphological Properties of Bacterial Cellulose Nanowhiskers Reinforced Polylactic Acid Nanocomposites

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In this study, bacterial cellulose nanowhiskers (BCNW) reinforced polylactic acid (PLA) nanocomposites were prepared using solution casting technique. The BCNW nanofiller was first isolated from bacterial cellulose (BC) using acid hydrolysis treatment. PLA/BCNW nanocomposites were prepared by the addition of various amounts of BCNW [1–4 parts per hundred parts of polymer (phr)] into PLA matrix. The produced PLA/BCNW nanocomposites were then investigated using Fourier transform infrared (FTIR) spectroscopy, tensile testing and atomic force microscopy (AFM). FTIR spectra analysis indicates that the acid hydrolysis of BC did not altered the chemical structure of isolated BCNW. The tensile testing was revealed that the addition of BCNW into PLA improved the tensile properties of PLA/BCNW nanocomposites. The highest tensile strength of PLA/BCNW was obtained with the addition of 3 phr BCNW which dedicated to approximately 27 MPa. The Young's modulus of the PLA/BCNW nanocomposites increased with increasing the BCNW content due to the stiffening effect of the high modulus BCNW reinforcement. However, elongation at break of PLA/BCNW nanocomposites decreased with the addition of BCNW compared to neat PLA. AFM images of PLA/BCNW nanocomposites indicates the presence of BCNW in PLA/BCNW nanocomposites. The relatively good tensile properties of PLA/BCNW shows its suitability in a wide range of applications such as packaging.

1. Introduction

The development of biodegradable polymer composites; combining biodegradable matrices and biodegradable reinforcements are currently of great importance. Polylactic acid (PLA) is being used widely in automobile, food packaging and pharmaceutical industries due to its relatively good mechanical performance. However, PLA has limitations such as low ductility, low thermal stability and high cost (Herrera et al., 2015). Although PLA has relatively good strength and stiffness comparable to other thermoplastics such as PET and PS, continuous effort has been carried out to further enhance the mechanical properties of PLA (Arjmandi et al., 2015a).

Cellulose is one of the most abundant biopolymers on earth. Vegetal resources such as wood, cotton and linter are the most commonly raw materials employed to extract cellulose. Nevertheless, cellulose can be also synthesized by some bacterial species. Although plant-derived cellulose (PC) and bacterial cellulose (BC) have the same chemical structure, they have different structural organization and mechanical properties. BC shows a finer web-like network structure, higher water holding capacity and higher crystallinity (Wan et al., 2007). Furthermore, while PC is naturally associated with other kinds of biopolymers such as hemicelluloses and lignin, BC is practically neat cellulose. Due to its outstanding properties, i.e. high purity, high crystallinity, high mechanical strength, low density and biocompatibility, bacterial cellulose has become an interesting material with applications in biomedicine (Czaja et al., 2006), paper industry, packaging and more recently as a reinforcement agent for polymeric matrices (Gindl and Keckes, 2004).

Inspired by a growing number of environmental concerns, renewable and biodegradable nanomaterials have assumed great significance for reinforcing various polymers. Several investigators have reported the

preparation of cellulose nanowhiskers (CNW) from microcrystalline cellulose (MCC) and were used as a reinforcing material in biodegradable polymers such as PLA (Pettersson et al., 2007). Comparatively, bacterial cellulose nanowhiskers (BCNW) because of their high crystallinity, high modulus and strength were also found to impart superior properties to polymer nanocomposites (Azizi Samir et al., 2005). The most commonly employed method for producing CNW of 10 - 50 nm diameter and 100 - 300 nm length is by subjecting cellulose to sulfuric acid hydrolysis in combination with ultrasonication (Revol et al., 1992). The production of nanocomposite materials has been proven to be an efficient strategy to tune the properties of polymeric materials, as the matrix properties improved with low loadings like concentrations lower than 5 wt% of highly dispersed nanoparticles (Arjmandi et al., 2015a).

To the best of knowledge, no study has been reported on BCNW reinforced PLA nanocomposites. In this study, PLA/BCNW nanocomposites were prepared using solution casting and the effects of BCNW on tensile and morphological properties of PLA nanocomposites were investigated.

2. Experimental

2.1 Materials

Poly(lactic acid) (PLA 3001D) in pellet form was supplied by NatureWorks. The PLA properties include the density of 1.24 g/cm³, range of melting temperature around 145 - 155 °C, crystallinity of up to 37 % and it has an average molecular weight of 220 kDa. Other reagent grade materials used in this project were sulfuric acid (H₂SO₄), acetone (C₃H₆O) and chloroform (CHCl₃) which were purchased from QReC, Asia and used without further purification.

2.2 Preparation of BCNW

BCNW was prepared by acid hydrolysis of bacterial cellulose. The dried bacterial cellulose (BC) was used as a raw material for preparation of BCNW. 5 g of BC was hydrolysed in 64 % of H₂SO₄ solution. The acid to BC ratio was 8.75 mL/g and hydrolysis was carried out at 40 °C for 60 min under strong agitation. The on-going hydrolysis was stopped by adding 4 - 5 times cold distilled water based on the volume of the reacting mixture. The diluted suspension was centrifuged using a Universal 32 Hettich centrifuge (Newport Pagnell, England) at 5,000 rpm for 15 min to get the precipitates. The precipitates were again suspended in distilled water, followed by a centrifugation. This process was repeated until the supernatant solution became turbid. Then, dialysis technique has been carried out using dialysis tube (from Sigma Aldrich) and distilled water in order to remove the remaining acid from colloidal suspension until the distilled water was constant in pH, i.e. about pH 7. Afterward, mechanical treatment was carried out using an ultrasonic bath (Branson 2510). The colloidal suspension collected and sonicated for 30 min. The sonication was carried out in cold water bath to avoid heat-up. Finally, the produced BCNW was stored in a refrigerator at 4 °C.

2.3 Preparation of Poly(lactic acid) Film

10 g PLA pellets were fully dissolved in 64 mL of chloroform by heating in a water bath at 60 °C for 2 h with constant stirring, as described by Martínez-Sanz et al. (2011) and Arjmandi et al. (2015a). The PLA solution was immediately casted onto clean glass plates and was left at room temperature for 48 h to allow the solvent to evaporate. Consequently, the neat PLA films were allowed to evaporate with vacuum-oven drying at 30 °C and pressure of 30 atm for 24 h. The thickness of the resulting cast film was approximately 100 µm.

2.4 Preparation of PLA/BCNW nanocomposites film

PLA/BCNW nanocomposites films were prepared by mixing 10 g of PLA pellets with BCNW at different contents (1, 2, 3 and 4 wt%). The BCNW fillers used were in wet form. Solvent exchange was carried out via centrifugation using a Universal 32 Hettich centrifuge (Newport Pagnell, England). Water was exchanged with acetone and acetone was exchanged with chloroform. The BCNW fillers were sonicated using an ultrasonic bath for 10 min to ensure a homogenous dispersion inside the chloroform. The dispersed BCNW was transferred into a reaction flask containing 10 g PLA pellets. Subsequently, the various PLA/BCNW mixtures were placed in 64 mL of chloroform and then were stirred with vigorous agitation for 2 h at 60 °C until the PLA pellets completely dissolved. The suspensions were then sonicated for 10 min and immediately casted onto a clean glass plate to obtain PLA/BCNW nanocomposites films with ~100 µm thickness. Lastly, the PLA/BCNW nanocomposites films were allowed to evaporate with vacuum-oven drying at 30 °C and pressure of 30 atm for 24 h. The PLA/BCNW nanocomposites films were designated as PLA/BCNW1, PLA/BCNW2, PLA/BCNW3 and PLA/BCNW4.

2.5 Atomic force microscopy analysis

The Atomic Force Microscopy (AFM) analysis, were performed using an SPA-300HV atomic force microscope with a SPI 3800 controller. The neat PLA and PLA/BCNW nanocomposites samples (0.1 mm × 0.1 mm) were analysed directly.

2.6 Fourier transform infrared spectroscopy analysis

Neat PLA and its nanocomposites were characterised by Spectrum One-Perkin Elmer Fourier Transform Infrared spectroscopy (FTIR). The fillers were crushed into small particles and then blended with potassium bromide (KBr) followed by pressing the mixture into ultrathin pellets. In this analysis, ratio of fibres to KBr was approximately 1:100. Scans were recorded in the range 370 - 4,000 cm^{-1} with a resolution of 4 cm^{-1} for each sample.

2.7 Tensile analysis

Tensile testing was performed using Instron 4400 Universal Tester. The tensile tests were carried out at room temperature according to the ASTM D882. A fixed crosshead speed of 12.5 mm/min was utilised in all cases. The mean data had taken as an average from 10 tests and also had included the determination of Young's modulus, tensile strength and elongation at break.

3. Results and discussion

3.1 Production of BCNW

Lu and Hsieh (2012) described that acid hydrolysis of cellulose in sulfuric acid involves rapid protonation of glucosidic oxygen or cyclic oxygen by protons from the acid, followed by a slow splitting of glucosidic bonds induced by the addition of water. Figures 1 (a) and (b) show the photograph images of dried bacterial cellulose and BCNW after acid hydrolysis, respectively. The hydrolysed BC with sulfuric acid involved esterification of hydroxyl groups and yielded acid half-ester. The presence of the induced sulphate groups on the nanowhiskers surfaces can greatly improve the separation of nanowhiskers by charge repulsion. Due to their strong hydrogen bonding, BCNW normally have high tendency to form bundles or aggregates. This is the major challenge in developing the CNW as the reinforcement in the effective nanocomposites regarding to the difficulty in their homogeneous dispersion within the polymer matrix.



Figure 1: Photograph images of a) dried bacterial cellulose and b) BCNW after acid hydrolysis

3.2 Atomic force microscopy

The mechanical performance of nanocomposites is depending to the degree of dispersion of the fillers in the polymer matrix (Thomas et al., 2009). To explore the dispersion behavior of the BCNW fillers inside the PLA matrix, neat PLA and PLA/CCNW nanocomposites were observed using AFM. Figures 2(a) to (c) show typical AFM micrographs of neat PLA and its nanocomposite. It can clearly be seen from Figure 2 (a) that the neat PLA has a smooth surface topography which is typical for an unfilled matrix material.

Figure 2 (b) shows the AFM images of PLA/BCNW2 nanocomposites which provided a good filler dispersion in the matrix, as indicated by arrows. With the incorporation of the BCNW fillers the surface topography of the neat PLA becomes rough, owing to uniform filler dispersion within the matrix (Figure 2(b) and (c)). Similar

observation has been reported by Singha and Thakur (2009). This result is in agreement with tensile properties of the nanocomposites as reported in Section 3.4.

Figure 2 (c) show the AFM images of PLA/BCNW4 surface which was clearly seen that very rough surface. As can be observed from Figure 2 (c), addition of 4 wt% BCNW led to filler aggregation in the PLA matrix, as indicated by circles. This may explain the differences in the mechanical properties of the PLA/BCNW nanocomposites as explained in following sections.

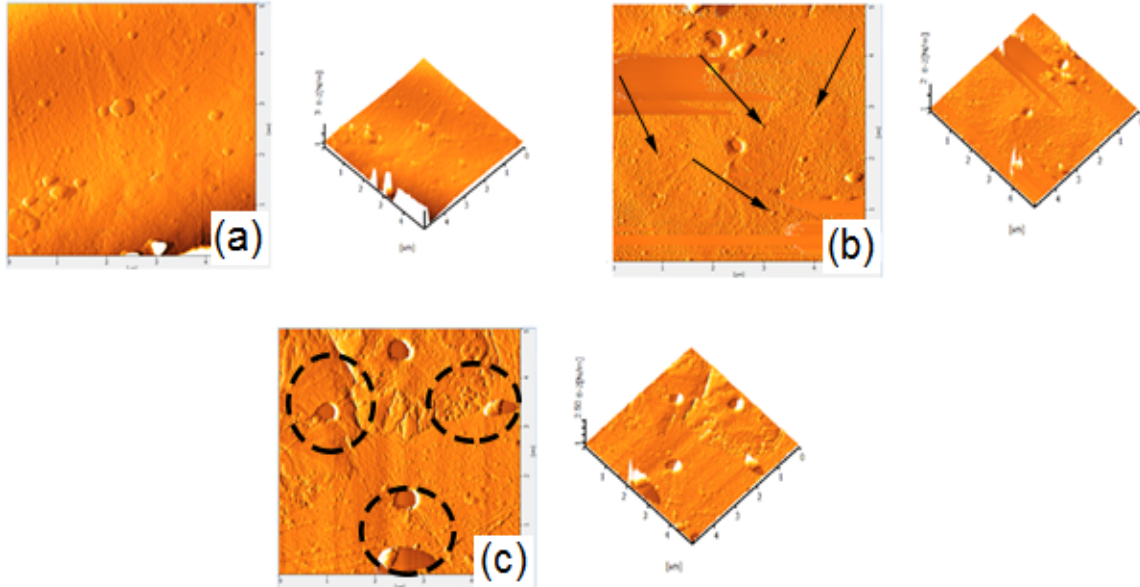


Figure 2: AFM images of (a) neat PLA, (b) PLA/BCNW2 and (c) PLA/BCNW4 nanocomposites

3.3 Fourier transform infrared spectroscopy

The FT-IR analysis has been widely used to identify the interactions and phase behavior by identifying the functional groups of the polymer nanocomposites (Qu et al., 2010). Figure 3 (a) shows that the spectrum of the neat PLA. The stretching vibration peak of the C=O appeared at $1,750\text{ cm}^{-1}$. The peaks at $2,997\text{ cm}^{-1}$ and $2,948\text{ cm}^{-1}$ were asymmetric and symmetric stretching of CH_2 . The peaks at $1,185\text{ cm}^{-1}$, $1,125\text{ cm}^{-1}$, $1,084\text{ cm}^{-1}$ and 1044 cm^{-1} are attributed to the stretching vibration of C-O. The bending of the $-\text{CH}_3$ is located at $1,452\text{ cm}^{-1}$. In addition, the peak of 867 cm^{-1} corresponds to the stretching vibration of the C-C single bond.

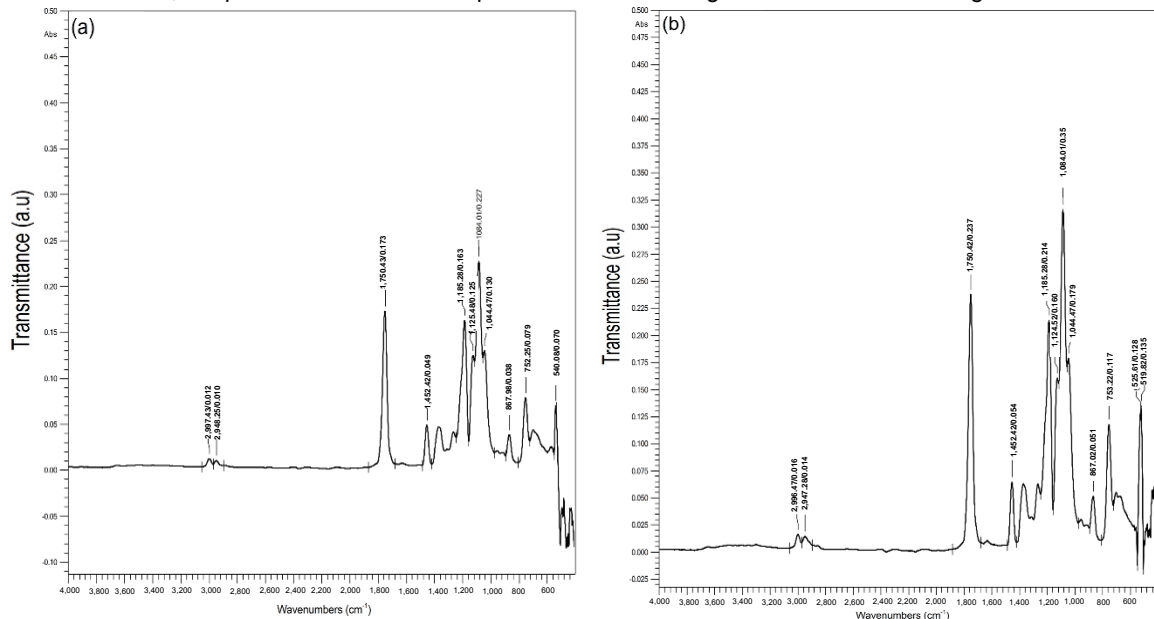


Figure 3: FTIR Spectroscopy Graph of (a) neat PLA and (b) PLA/BCNW2 nanocomposites

Upon the addition of BCNW into PLA (Figure 3(b)), a broad absorption peak was observed at approximately $3,350\text{ cm}^{-1}$ which corresponded to the hydroxyl group of BCNW in PLA/BCNW nanocomposites. This confirmed that the hydrophilicity of neat PLA increased by incorporation of BCNW. In addition, the absorption peaks of CH_2 at $2,948\text{ cm}^{-1}$ and $2,997\text{ cm}^{-1}$ were shifted to lower wavenumbers in PLA/BCNW nanocomposites ($2,947\text{ cm}^{-1}$ and $2,996\text{ cm}^{-1}$) compared to their original position in PLA, which indicated the good interactions between BCNW and PLA matrix.

3.4 Tensile properties

Figure 4 (a) to (c) report the tensile strength, Young's modulus and Elongation at break of PLA/BCNW nanocomposites, respectively. As can be observed from Figure 4 (a), the tensile strength increased with addition of BCNW up to 3 wt%, and subsequently decreased at higher filler contents. The tensile strength of the neat PLA was about 24.9 MPa. The tensile strength for the PLA/BCNW1 nanocomposites at 1 wt% filler content was slightly higher than the neat PLA (about 0.8 %). For the PLA/BCNW2 and PLA/BCNW3 nanocomposites, the tensile strength was 6.4 and 7.3 % higher than the neat PLA, respectively. Hence, these shows good dispersion and interaction between the $-\text{OH}$ groups of the BCNW and the $-\text{OH}/\text{C}=\text{O}$ groups of the PLA. When 4 wt% of BCNW was added to the PLA nanocomposites, the tensile strength of PLA/BCNW4 was approximately 24.6 MPa which was lower than the neat PLA. This finding attributed to poor interfacial bonding between the BCNW and the PLA matrix due to aggregation of the BCNW in the PLA, which then act as stress concentration points.

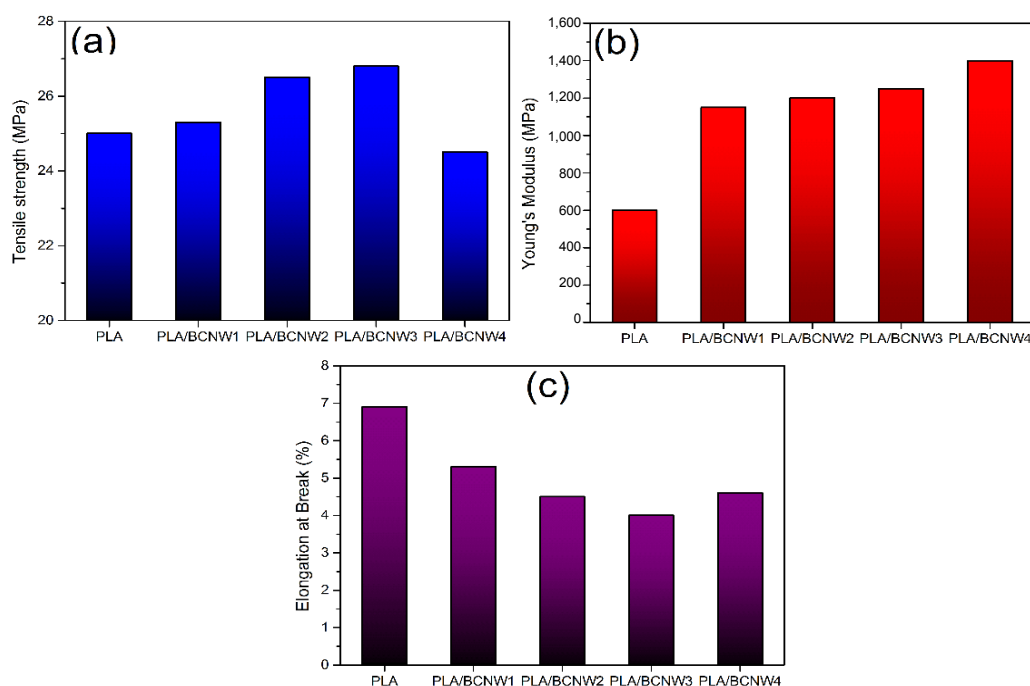


Figure 4: (a) Tensile strength, (b) Young's modulus and (c) elongation at break of neat PLA and PLA/BCNW nanocomposites

Based on the Figure 4 (b), the PLA/BCNW nanocomposites were shown an increasing trend in Young's modulus, where the Young's modulus increased with increasing BCNW content. The Young's modulus for the neat PLA was around 800 MPa while the Young's modulus for the PLA/BCNW nanocomposites at 1 wt% filler content was approximately 1,088 MPa, which showed 36 % improvement compared to neat PLA. For the PLA/BCNW2 and PLA/BCNW3 nanocomposites, the Young's modulus was about 1,205 and 1,346 MPa, which were 51 and 68 % higher than the neat PLA, respectively. In addition, the Young's modulus for the PLA/BCNW nanocomposites at 4 wt% was approximately 1,409 MPa. This increase was attributed to the stiffening effect of the high modulus BCNW reinforcement. Similar results were reported by Arjmandi et al. (2015a) when PLA was reinforced using CNW.

Figure 4 (c) shows the elongation at break of neat PLA and PLA/BCNW nanocomposites. The elongation at break of PLA/BCNW decreased dramatically as compared to the neat PLA. Based on the Figure 4 (c), the elongation at break of PLA/BCNW1, PLA/BCNW2 and PLA/BCNW3 was slightly lower than the neat PLA (21,

38 % and 48 %, respectively). This observation may be attributed to the stiffening action of the filler by restricting the segmental chain movement of PLA during tensile testing. Similar result was reported by Petersson and Oksman (2006). As can be seen in Figure 4 (c), the elongation at break slightly increased at high concentration of BCNW in PLA matrix, which seemed likely to be due to their enhanced hydrophilic character. Thus, the existence of a proportional content of hydrophilic groups may contribute to plasticization leading to enhanced deformability (Arjmandi et al., 2015a and b).

4. Conclusion

BCNW were produced from the dried bacterial cellulose through acid hydrolysis in order to obtain the nano-sized of BCNW. A uniform dispersion of BCNW was readily apparent with the addition of 2 wt% BCNW into PLA matrix, as confirmed by AFM analysis. The tensile strength of PLA/BCNW nanocomposites increased with increasing BCNW content and reached a maximum value at 3 wt%. However, there was slightly decreased in tensile strength of PLA/BCNW when 4 wt% BCNW content was added. In addition, the Young's modulus increased with increasing BCNW content. The increased in Young's modulus could be attributed to the stiffening effect of the high modulus BCNW. Nevertheless, the elongation at break PLA/BCNW nanocomposites decreased with the addition of BCNW compared to neat PLA.

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