Starch Nanocomposites Reinforced with TEMPO-Oxidized Cellulose Nanofibrils derived from Bamboo Holocellulose

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Bamboo holocellulose was oxidized by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) in water at pH 10 with an addition of 7.5 mmol g^{-1} of NaClO for 2 h. After oxidation, the weight recovery ratio of TEMPO-oxidized bamboo holocellulose (TOBH) was 73% with a carboxylate content of 0.65 mmol g^{-1}. The water-insoluble TOBH was converted to an aqueous dispersion of bamboo TEMPO-oxidized cellulose nanofibrils (TOBCN) through mechanical defibrillation and centrifugation, with the nanofibrillation yield of around 90%. Transmission electron microscopy (TEM) indicated that the widths of TOBCN were estimated to be between 3 and 4 nm and lengths of several micrometers. The TOBCN dispersions had high light-transparencies of 99% at a wavelength of 600 nm. These nanofibrils were used as reinforcing nanoparticles in thermoplastic starch (TPS) films. The TOBCN dispersions were added in dosages of 0, 0.3, 0.6, 0.9, 1.2, and 1.5 wt%. Glycerol was used as a plasticizer. Nanocomposite films were prepared through a solution casting process. The TOBCN/TPS nanocomposite films exhibited high optical transparencies and their tensile strength, Young's modulus, elongation around failure, and work to cause a fracture increased, compared to the TPS films without TOBCN. The presence of TOBCNs, at 1.5 wt%, improved moisture resistance.

Keywords: 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO); Bamboo holocellulose; Oxidation; Cellulose nanofibrils

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INTRODUCTION

Production of materials that are environmentally friendly and sustainable, to substitute petroleum-based synthetic materials, has gained global attention of researchers. The depletion of petroleum resources and environmental legislations and policy are the main factors driving the effort to search for alternative materials. The development of bio-based materials, from renewable plant resources, agricultural crops, and their by-products, can be done to circumvent environmental issues related to the use of petroleum-based products. Their potential use is further justified by the abundant availability, renewability, biodegradability, and non-toxicity (Guimarães Jr *et al.* 2015; Condés *et al.* 2018).

Recently, new biomaterials have been developed from polymeric natural nanofillers. Generally, nano-size fillers have been extensively utilized as reinforcements during the preparation of new polymer nanocomposite and also have applications in non-food industries. The resulting nanofiller-reinforced polymer nanocomposites exhibit the desired mechanical and barrier properties (Angellier *et al.* 2005; Yu *et al.* 2008; Garcia *et al.* 2009; Zheng *et al.* 2009; Fujisawa *et al.* 2013; Le Corre *et al.* 2013). However, such properties strongly depend on the dispersibility of nanofiller in the polymer matrix (Johar *et al.* 2012; Fujisawa *et al.* 2013; Soeta *et al.* 2017).

Among the natural biopolymers, starch has been considered as the most promising material, due to its low cost, biodegradability, and renewability (Wang *et al.* 2003). Starch has been converted into a thermoplastic starch (TPS) by appropriately mixing with water or some plasticizer (*e.g.* glycerol, sorbitol, polyols) (Wollerdorfer and Bader. 1998; Wang *et al.* 2003; Martins *et al.* 2009; Schlemmer *et al.* 2010). However, disadvantages attributed to the hydrophilic properties of TPS in starch-based nanocomposites lead to poor mechanical properties. To overcome such limitations, the use of mineral or cellulosic fillers (*e.g.* talc, kaolin, clay, glass fiber, carbon fiber, cellulose nanofibrils, cellulose nanowhiskers), as reinforcing agent in TPS, is an effective method to solve this issue (Cao *et al.* 2008; Teixeira *et al.* 2009; Ibrahim *et al.* 2014).

Cellulose nanofibrils, with a high aspect ratio (>100) and large specific surface area, can be prepared from plant cellulose, using 2,2,6,6 tetramethylpiperidine-1-oxyl (TEMPO) under aqueous conditions, through successive mechanical treatment. The obtained cellulose nanofibrils from this process have homogeneous widths between 3 and 4 nm and high elastic modulus (145 GPa) (Isogai *et al.* 2011; Isogai 2013). Therefore, these cellulose nanofibrils have interesting reinforcing properties in the matrix at the starch-based nanocomposite.

Bamboo is a renewable resource, is fast growing, short rotation, has a relatively long fiber length, and is found abundantly in Thailand. Bamboo fibers are used in the production of paper, boards, textiles, and other commodities (Liu *et al.* 2010). This study reports the use of TEMPO-oxidized bamboo cellulose nanofibrils (TOBCNs) in a TPS matrix. The TOBCNs/TPS nanocomposite films were prepared with various concentrations of TOBCNs. The resulting films were evaluated for their morphological, moisture absorption, mechanical, and physical properties with respect to the concentration of TOBCNs.

EXPERIMENTAL

Materials

A bamboo holocellulose from *Dendrocalamus asper* (Schult.) was used as the starting material for the preparation of TEMPO-oxidized bamboo cellulose nanofibrils (TOBCNs). Industrial grade tapioca starch (Inter Pacific Paper, Thailand) was used to prepare the TOBCN-starch composites. TEMPO was purchased from Sigma-Aldrich, Germany, while laboratory grade sodium bromide (NaBr), sodium hypochlorite (NaClO) solution, sodium chlorite ($NaClO_2$), glycerol ($C_3H_8O_3$), and other chemicals were purchased from Merck, Thailand.

Methods

Preparation of bamboo holocellulose

A powder was prepared from native bamboo (with an α-cellulose content of 49.2%) following the procedure outlined in Wise *et al.* (1946). The bamboo powder was treated with sodium chlorite with a pH of 4-5 at 75 °C for 1 h. This procedure was repeated four times, with fresh chemicals, in order to prepare bamboo holocellulose. The obtained product was then thoroughly washed with distilled water by passing it through a glass filter and was kept in a wet state at 4 °C before further treatment.

TEMPO-mediated oxidation of bamboo holocellulose powder

The bamboo holocellulose powder, with an α-cellulose content of 68.5% (1 g), which was never-dried previously, was suspended in distilled water (100 mL) containing TEMPO (0.016 g) and NaBr (0.1 g). NaClO solution (7.5 mmol g^{-1} BH) was added to the slurry to start oxidation. The slurry was stirred at room temperature and the pH was maintained at 10 by adding 0.5 M sodium hydroxide for 2 hrs. The TEMPO-oxidized bamboo holocellulose (TOBH) was thoroughly washed with distilled water by filtration using a glass filter and stored in the wet state at 4 °C before further treatment or analysis. The carboxylate content of TOBHs was determined according to technical association of the pulp and paper industry (TAPPI T237 cm-08).

Preparation of TOBCNs

The never-dried TOBHs were suspended in distilled water (50 mL) at 0.1% (w/v) and sonicated at 450 W for 8 min, using an ultrasonic homogenizer, with a probe of 13-mm tip diameter (VCX 750; Sonics & Materials, Newtown, CT, USA), and centrifuged at 7,500 rpm for 25 min to remove the partly or unfibrillated fraction. The nanofibrillation yield was measured through the dry weight of centrifugally fibrillated fraction. (Shinoda *et al.* 2012).

Preparation of TOBCNs/TPS nanocomposite films

Starch-based nanocomposite films, reinforced with TOBCNs, were prepared through the casting solution process (Fig. 1).

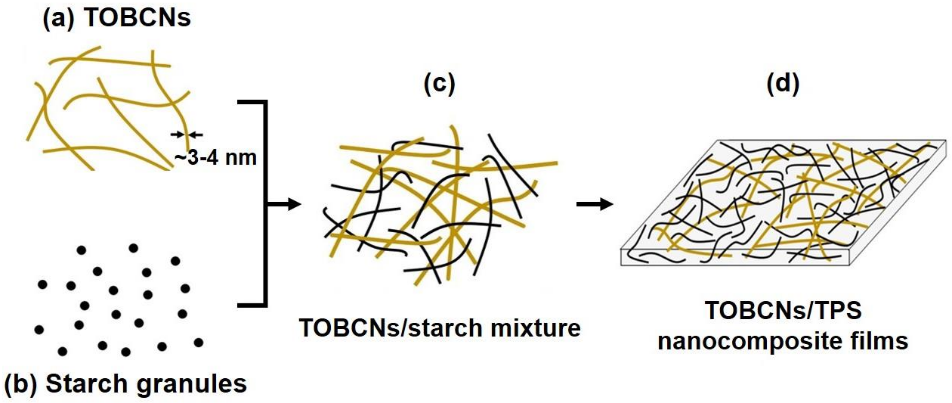

Fig. 1. Schematic of the nanocomposite casting process; (a) TEMPO-oxidized bamboo cellulose nanofibrils (TOBCNs); (b) tapioca starch granules; (c) TOBCNs growing in presence of gelatinized starch; and (d) TOBCNs/TPS networks within the nanocomposite film

A solution of starch and glycerol, with a weight of 5.5 g (starch:glycerol ratio was 4:1), was dispersed in distilled water. Then, the mixture was heated and stirred at 90 °C for 30 min to gelatinize the starch. After cooling down to 40 °C, the mixture was degassed under vacuum to remove the remaining air and was subsequently casted into a square acrylic mold (18×18 cm), followed by drying in a non-ventilated oven at 40 °C for 48 h. The resulting films were peeled off after drying. For processing of nanocomposites, when the mixture had cooled down to 40 °C, the TOBCNs suspension was added to predetermined levels (0.3, 0.6, 0.9, 1.2, 1.5 wt%, based on the amount of tapioca starch).

The nanocomposite films were prepared using a similar procedure. All the films were stored at 23 °C and a relative humidity (RH) of 50% for one week before being tested.

Analyses

Scanning electron microscopy (SEM)

Morphologies of the native bamboo powder and bamboo holocellulose powder were observed through a Hitachi T3030Plus scanning electron microscope (SEM) (Japan) without sample coating. Field-emission SEM (FE-SEM) (SU8020; Hitachi, Japan) was used to determine the surface structure of TOBCNs/TPS nanocomposite films using an acceleration voltage of 1 kV with a platinum coating of 10 nm.

Transmission electron microscope (TEM)

A transmission electron microscope (TEM) (HT7700; Hitachi, Japan) was used to analyze the morphologies of TOBCNs, using an accelerating voltage of 100 kV. A drop of 0.005% (w/v) TOBCNs suspension was deposited on a carbon support grid. Prior to completely drying, a drop of 2% uranyl acetate negative stain was added and kept for 5 min. The excess liquid was blotted with a filter paper and allowed to dry by natural evaporation.

UV-vis spectroscopy

Light transmittance spectra, of the TOBCNs dispersion and TOBCNs/TPS nanocomposite films, were measured at wave lengths between 300 nm to 800 nm using a spectrophotometer (UV-1800; Shimadzu, Japan).

Tensile testing

The mechanical behavior of TOBCNs/TPS nanocomposite films was analyzed using a universal testing machine (M350-5AT; Testometric, UK). Film properties, such as tensile strength, Young's modulus, and elongation at break, were determined following the procedures in ASTM D882-02 (2002), with a 5 KN load cell at a crosshead speed of 12.5 mm/min. The initial gap between the jaws was adjusted to 125 mm.

Thermogravimetric and differential thermogravimetry analysis of the films

Thermogravimetric (TGA) and differential thermogravimetry (DTG) analysis of the films was conducted using a TGA analyzer (Pyris 1; Perkin Elmer, USA). Five mgs of TOBCNs/TPS nanocomposite film was taken with a resolution of around 0.1 µg in a sample pan. The thermograms were obtained at temperatures between 50 and 600 °C at a heating rate of 10 °C/min. All the tests were performed in a nitrogen environment at a flow rate of 20 mL/min.

Water uptake of the films

The water uptake of TPS and TOBCNs/TPS nanocomposite films was also determined on samples with dimensions of 30 mm × 10 mm. The samples were conditioned in desiccators at 0% RH (P_2O_5) and a temperature of 25 °C for 7 days. After weighing, they were conditioned in desiccators at 25 °C under 75% RH (NaCl saturated aqueous solution) for 7 days. The water uptake (W_u) of a sample was calculated as follows,

$$W_u\ (\%) = [(W_1 - W_0)/W_0] \times 100, \quad (1)$$

where W_0 and W_1 are the weights of the sample before exposure to 75% RH and after 7 days, respectively.

Statistical analysis

All data were statistically analyzed using a completely randomized design (CRD). A one way analysis of variance (ANOVA) was performed and the means were compared in each treatment, using the Duncan's new multiple ranges test (DMRT) (at a significance level of 0.05).

RESULTS AND DISCUSSION

Delignification of Native Bamboo Powder

The Wise method was applied as the chemical treatment for delignification of bamboo powder. The color of native bamboo powder changed from brown to white after treatment, which indicated that the non-cellulosic components such as lignin, pectin, and wax present in native bamboo powder were either degraded or removed. This was also in agreement with α-cellulose content of 49.2%. After chemical treatment, the α-cellulose content of bamboo powder increased to 68.5%. A high cellulose content was observed, making bamboo a reliable source for the extraction of cellulose nanofibrils. Moreover, the chemical treatment caused morphological changes. The structure of bamboo powder was observed through an SEM, as shown in Fig. 2. The surface of native bamboo powder is shown in Fig. 2a in which impurities are easily observed on the surfaces. After chemical treatment (Fig. 2b), the surface exposed better packing of cellulose chain which may be due to the removal of residual lignin.

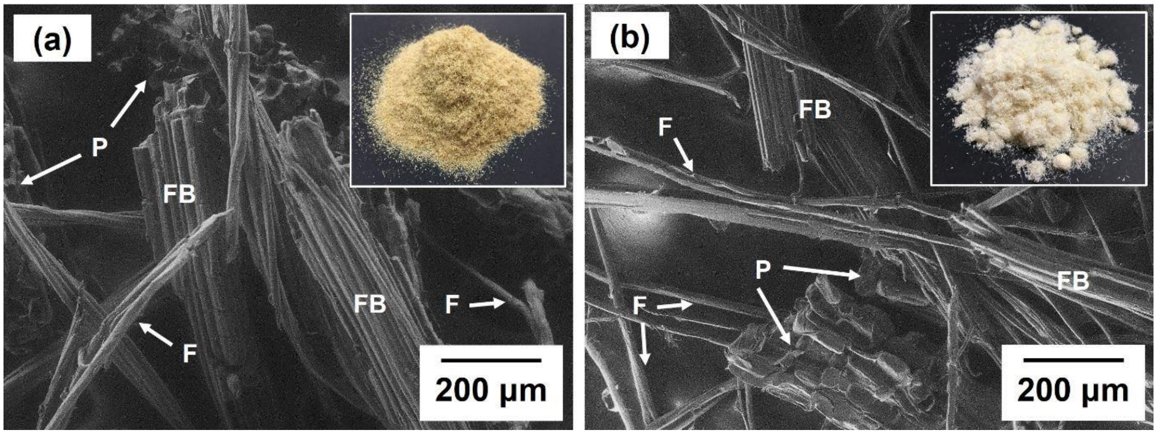

Fig. 2. SEM image and the corresponding photograph of (a) original bamboo powder and (b) bamboo holocellulose powder; the acronyms F, FB, and P stand for fiber, fiber bundle, and parenchymatous cells, respectively

Morphological Investigation of Bamboo TOBCN

TOBHs were prepared from the bamboo holocellulose powder by adding 7.5 mmol g^{-1} of NaClO, using a TEMPO/NaBr/NaClO system in water at a pH 10 for 2 h, after which they mechanically disintegrated in water. TOBHs were obtained with a weight recovery ratio of 73% and carboxylate content of 0.65 mmol g^{-1}. The weight recovery ratios decreased after the TEMPO-mediated oxidation, probably because the hemicellulose in bamboo holocellulose degraded to water-soluble compounds during the oxidation process. A similar behavior was observed in previous studies (Puangsin *et al.* 2013a,b; Kuramae *et al.* 2014). Almost pure TOBCNs can be prepared using this system, with nanofibrillation yields of about 90%. After centrifugation was performed, to remove the unfibrillated fractions (~10%), the TOBCNs dispersions had high transparencies of 99% at a wavelength of 600 nm, as shown in Fig. 3.

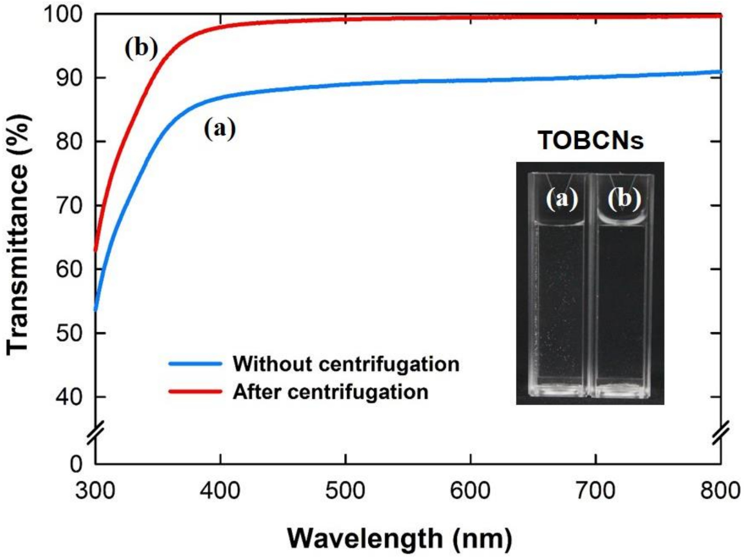

Fig. 3. Light transmittance spectra and the corresponding photographs indicating 0.1% dispersions of (a) never-dried TOBCN before and (b) after centrifugation

After the removal of unfibrillated fractions, the TOBCNs dispersions were subjected to a TEM analysis in order to measure the widths of TOBCNs. TEM observations showed that the TOBCNs had almost uniform widths between 3 and 4 nm and estimated lengths on micrometer scale, as shown in Fig. 4. The present results are in agreement with the values found in literature (Fan *et al.* 2009; Endo *et al.* 2013; Fukuzumi *et al.* 2013).

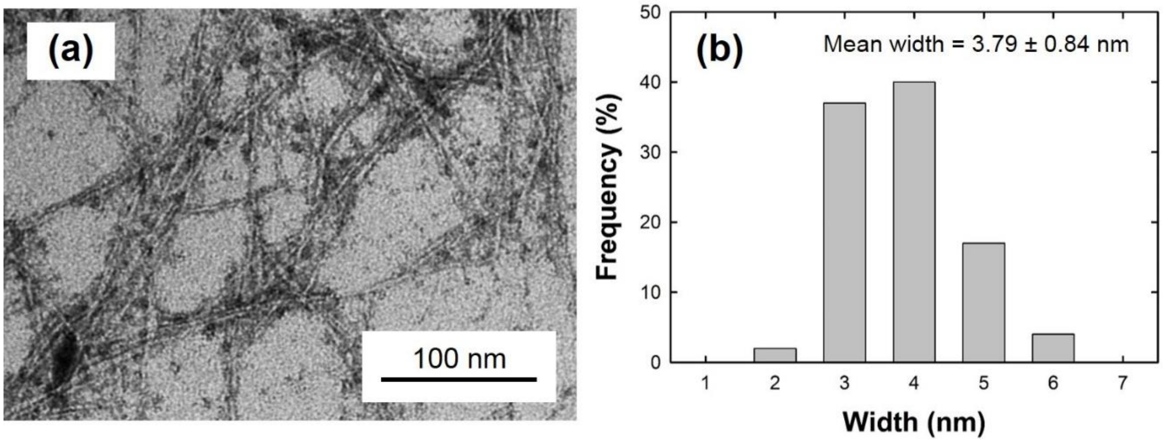

Fig. 4. (a) TEM micrograph of TOBCNs and (b) their width distributions

Optical and Morphological Properties of TOBCNs/TPS Nanocomposite Films

All nanocomposite films, prepared by solution casting with various concentrations of TOBCNs, were homogeneous and transparent. Figure 5a shows the visual appearance of films, and Fig. 5b shows the optical transparencies of the TOBCNs/TPS nanocomposite films. When the TOBCNs loading level increased to 1.5 wt%, the nanocomposite films exhibited high transparencies of 88% at 600 nm, and the neat TPS film showed 85%. The addition of TOBCNs in the composite matrix leads to increase in light transparency (Fujisawa *et al*. 2012). Moreover, this effect is related to the nano-size of the TOBCNs with diameters between 3 and 4 nm, which is much smaller than the optical wavelengths, therefore explaining the transparency of the films (Nakagaito and Yano 2005; Yano *et al*. 2005). Figure 6 shows the FE-SEM micrographs of a TPS and TPS nanocomposite film containing 1.5% TOBCNs. Both films show cracks on the surface. When the TPS matrix was filled with 1.5% TOBCNs, the film showed a smoother surface and smaller crack size than TPS film. This is due to good dispersibility and bonding between the TPS and TOBCNs (Liu *et al*. 2010).

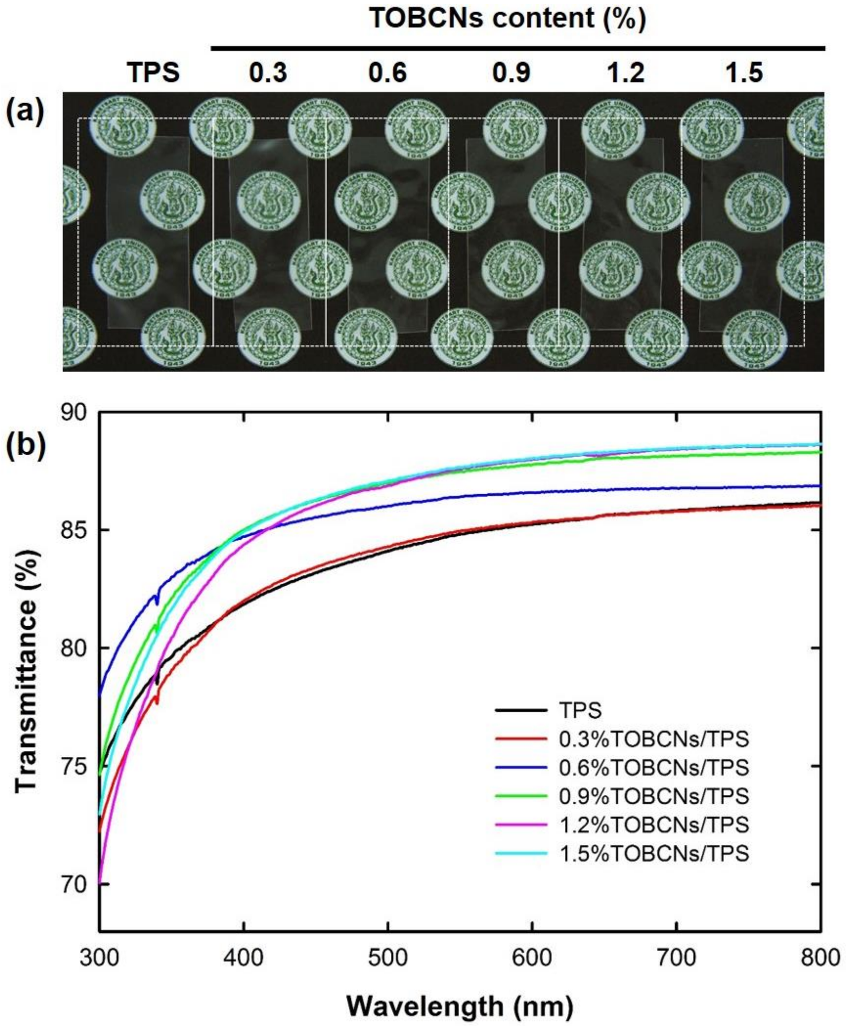

Fig. 5. Photographs of (a) TOBCNs/TPS nanocomposite films with 0, 0.3, 0.6, 1.2, and 1.5 wt% of TOBCN and (b) the light transmittance spectra of nanocomposite films

Film thickness and density of nanocomposite film was approximately 100 µm and 1.3 to 1.4 g cm^{-3}, respectively. The moisture content of nanocomposite films, at 23 °C and 50% RH, ranged between 8.8 and 10.5%. The TPS film had a higher moisture content than TOBCNs/TPS nanocomposite films. Similar results have been reported by Kurihara and Isogai (2014). Statistically, it was found that the nanocomposite film thickness was significantly different from TPS ($P \leq 0.05$), while the film density and moisture content were not affected after the reinforcement with TOBCNs. This indicates that the starch molecules formed disordered regions in the film and more hydroxyl groups were exposed to the moisture.

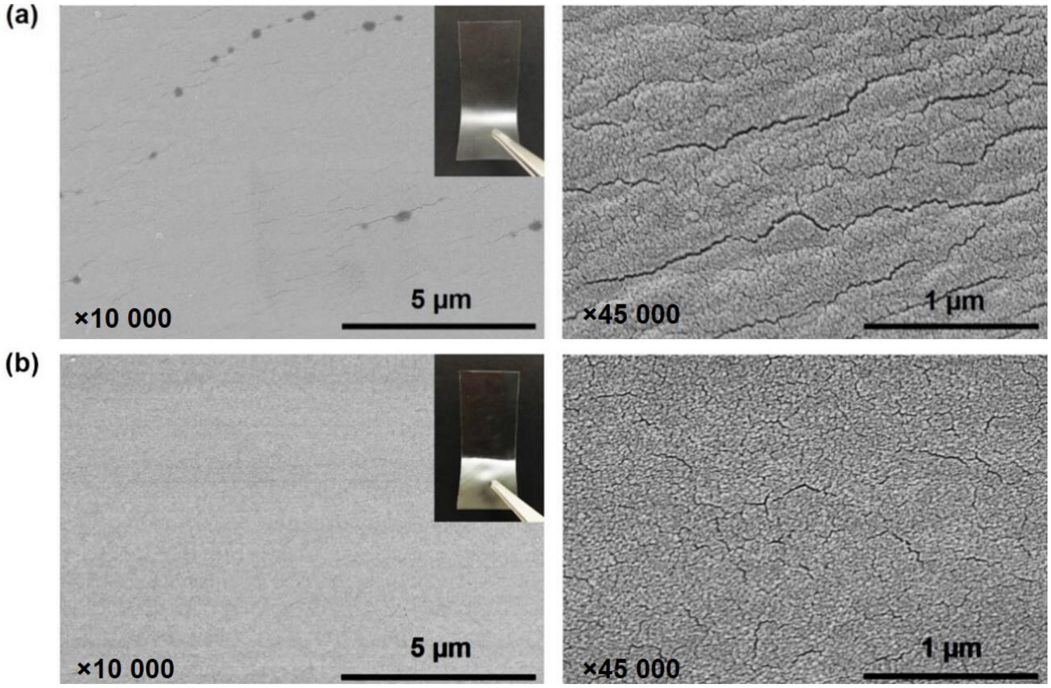

Fig. 6. FE-SEM images and the corresponding photographs of (a) TPS film surface, and (b) TOBCNs/TPS nanocomposite film (with 1.5 wt% of TOBCNs) surface

Mechanical Properties

Figure 7 shows the mechanical properties of the nanocomposite film after the addition of various concentrations of TOBCNs (0, 0.3, 0.6, 1.2, and 1.5 wt%). The TOBCNs reinforcement significantly improved the tensile strength, elongation at break, and work needed to fracture ($P \leq 0.05$), when compared with a neat TPS film. The addition of TOBCNs to the nanocomposite films produced an interesting reinforcement ability. The average Young’s modulus of the film was approximately 1,300 MPa with no significant change observed ($P \geq 0.05$) after the addition of TOBCNs. The film with 1.5wt% TOBCNs/TPS had the highest tensile strength and work needed to fracture, of 21.9 MPa and 0.31 MJ/m^3, while that for the TPS film were 13 MPa and 0.1 MJ/m^3, respectively. This behavior can be attributed to the large surface area of nanofillers in the TOBCNs/TPS film structure, which requires a higher mechanical energy to fracture the structure, as the cellulose nanofibrils can attain a high elastic modulus of up to 140 GPa (Nishiyama 2009) and a strong tensile strength of 2 to 3 GPa (Fujisawa *et al.* 2013). Moreover, a higher level of surface hydroxyls resulted in a strong interfacial bonding between the TPS matrix and cellulose nanofibrils (Babaee *et al.* 2015). The elongation at break was significantly different between TPS and after the addition of TOBCNs (at a concentration of 0.9 wt%, $P \leq 0.05$), indicating that more flexibility and toughness could be achieved at this point. In addition, the nanocomposite film was found to have a dimensional stability within the proper limits during the test.

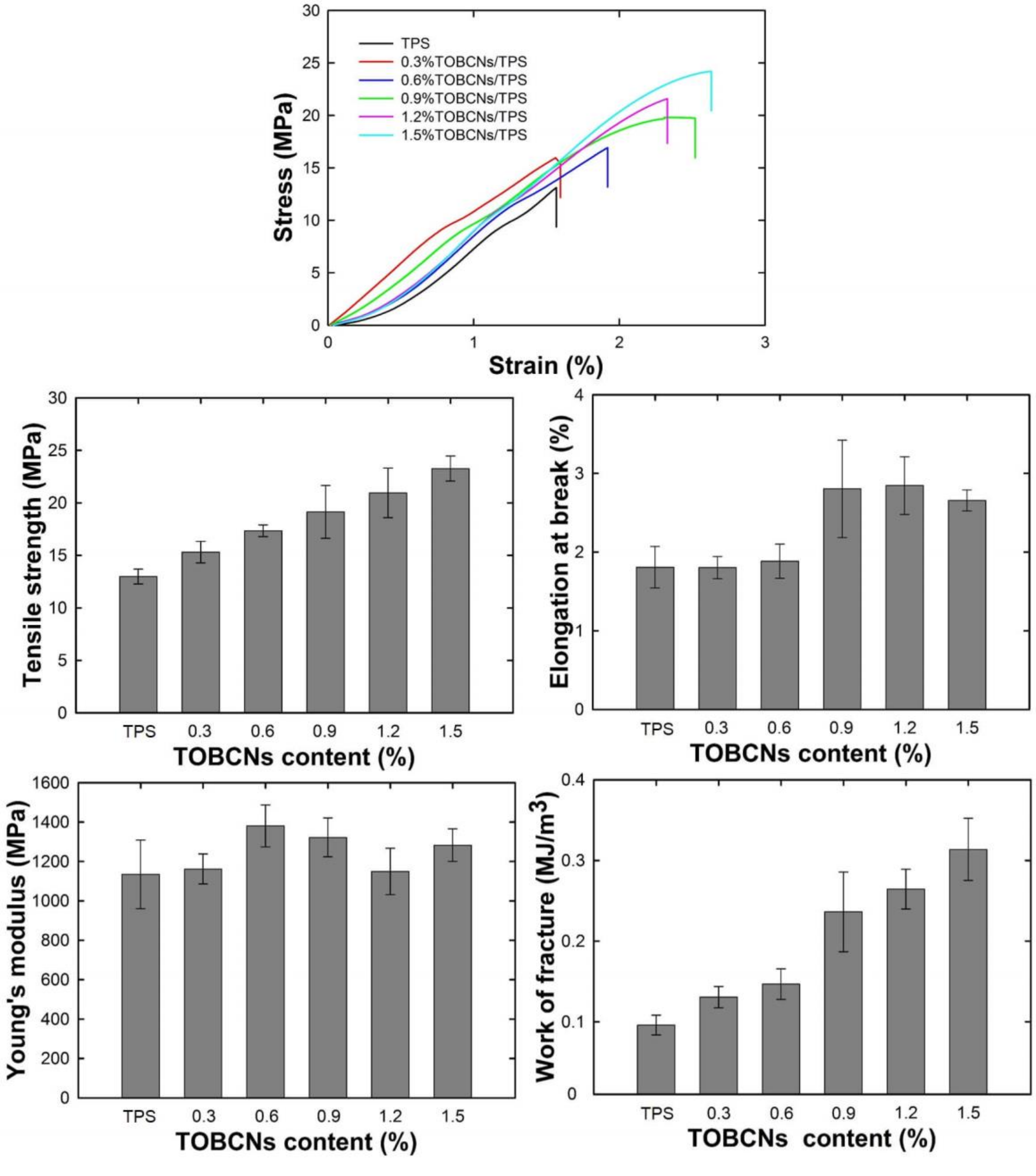

Fig. 7. The mechanical properties of TOBCNs/TPS nanocomposite films at various levels of TOBCNs concentration: (a) stress-strain curves, (b) tensile strength, (c) elongation at failure, (d) Young's modulus, and (e) work needed to fracture

Thermogravimetric and Differential Thermogravimetry Analysis

Figure 8 shows the TGA analysis and the DTG curves of TPS and nanocomposite films. The thermal decomposition and moisture loss were found to be significantly different between the nanocomposites and TPS ($P \leq 0.05$) at concentrations between 0.9 and 1.5 wt%. Temperature at the maximum rate of mass loss ($T_{\max}$) of TPS and nanocomposite films decreased from 344.8 to 336.5 °C. The decrease in degradation stability of the nanocomposite film was caused by the formation of sodium carboxylate groups at the C6 hydroxyls of the TOBCNs surface. These negatively charged groups generated during the TEMPO-mediated oxidation led to the decarbonation of anhydroglucuronate units within the matrix of the nanocomposite films (Isogai *et al.* 2011).

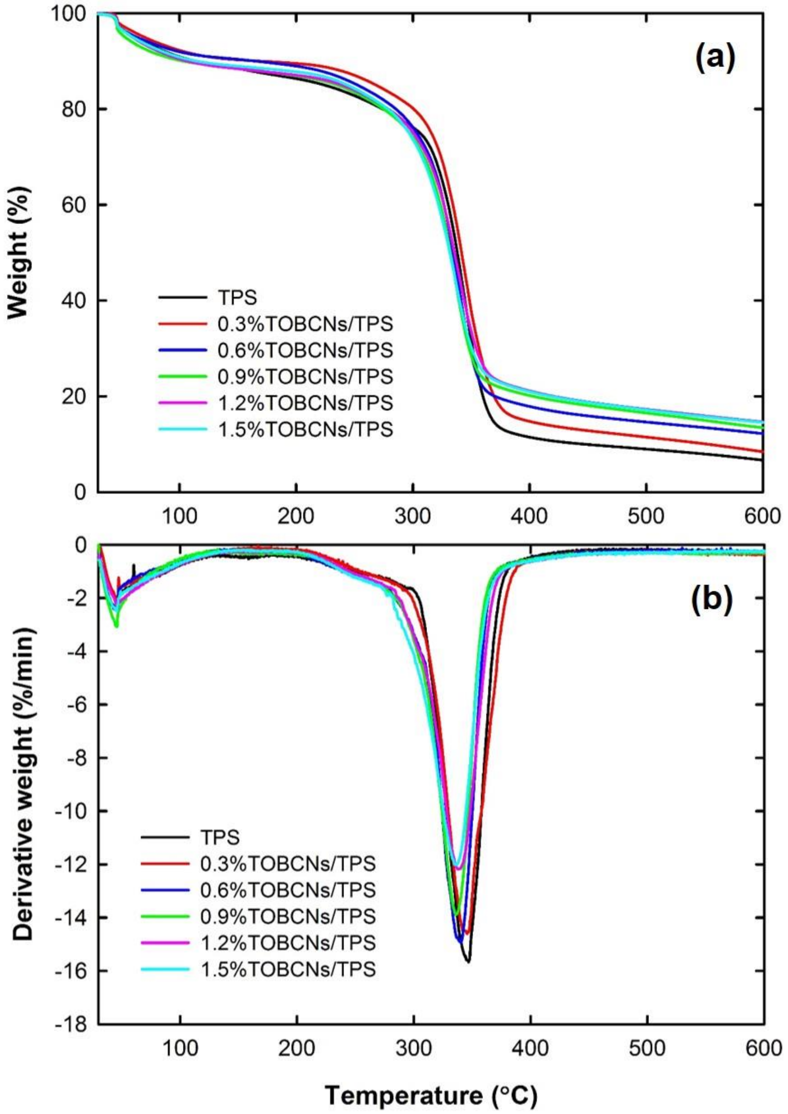

Fig. 8. (a) TGA and (b) DTG curves of TPS and TOBCNs/TPS nanocomposite films

Water Uptake of the Films

Figure 9 shows the water uptake of the TPS and TOBCNs/TPS nanocomposite films, with varying TOBCNs content, under 75% RH for 7 days and evaluated using Eq. 1. TOBCNs reinforcements, between 0.3 to 1.2%, seemed to be ineffective in reducing the water absorption capability of the film. However, at a 1.5% level of TOBCNs, the water uptake of the film started to show a significant difference ($P \leq 0.05$). This improvement at higher TOBCNs content suggests that the presence of TOBCNs content can influence the interaction between TOBCNs and TPS matrix (García *et al.* 2009).

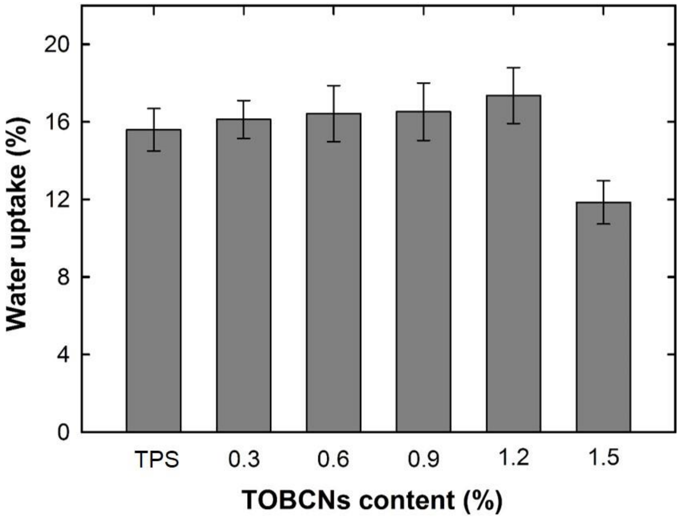

Fig. 9. Water uptake of TPS and TOBCN/TPS nanocomposite films at RH 75% for 7 days.

CONCLUSIONS

1. Cellulose nanofibrils were successfully prepared from bamboo holocellulose powder using the TEMPO-mediated oxidation. The obtained nanofibrils showed individualized nanofibrils with widths of ~ 3 to 4 nm and high aspect ratios.
2. The reinforcing potential was demonstrated for bamboo cellulose nanofibrils, which were individually dispersed and interacted with the TPS matrix. The resultant nanocomposite films had a high transparency, tensile strength, Young's modulus, and work needed to fracture, compared to a TPS nanocomposite without the bamboo cellulose nanofibrils.
3. The present work demonstrates the potential of using bamboo cellulose nanofibril (by TEMPO-mediated oxidation) as a reinforcement in green nanocomposite materials.

ACKNOWLEDGMENTS

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