Structure and Properties of Chitin Whisker Reinforced Papers for Food Packaging Application

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In recent years, concerns about environmental waste caused by petroleum-derived chemicals as well as the consumer's demand for high quality food products, have prompted people to pay more attention to developing biodegradable food packaging materials using natural resources such as cellulose fibers and chitin derivatives. In this study, chitin whiskers have been successfully generated by hydrolyzing the α-chitin sample. Then the synthesized nano-sized chitin whiskers were used at ratios from 0.1% to 2% (wt%) for improving strength properties of paper sheets by the dip-coating method. Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) were used to investigate the morphology of chitin whiskers and cellulose fiber compounds. The results showed that coating with chitin whiskers brought about an increase in tear strength, burst strength, and wet and dry tensile strength, with a decrease in Zeta-potential value.

Keywords: Chitin whisker; Reinforced paper; Food packaging application

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INTRODUCTION

As the main constituent of wood and crops, cellulose is the most abundant polysaccharide in nature. Paper and paperboard is a sheer material that is largely composed of cellulosic fibers and has been considered to be a renewable and sustainable resource (Hubbe 2006). Paper is an indispensable part of modern life as packaging material, owing to its characteristics of printability, biodegradability, renewability, recyclability, and mechanical flexibility (Hubbe and Bowden 2009; Nassar and Youssef 2012). However, continuous improvement in the quality of paper grades is essential to meet the consumer's demand for high-grade food packing paper. There is an increasing interest to develop the utilization of natural fibers and improve the strength by adding natural strength additives, such as cationic starch (Ghasemian *et al*. 2012), hemicelluloses (Hamzeh *et al*. 2013), sugarcane molasses (Ashori *et al*. 2013), gelatin (Khakalo *et al*. 2014), and chitosan (Chen *et al*. 2013a). Although biodegradable polymers like starch, sugarcane molasses, and gelatin are good raw-materials for preparation of packaging materials, their applications are constrained due to their hydrophilic nature and limited mechanical properties (Tankhiwale and Bajpai 2012). As the second most abundant natural biopolymer after the cellulose group, chitin is well-known as 2-acetamido-2-deoxy-(1→4)-β-D-glucopyranan; it is obtained from shellfish, insects, and microorganisms (Paillet and Dufresne 2001). Chitosan is N-acetylated chitin and has been widely used in the papermaking industry in recent years due to its nontoxicity, biodegradability, and antibacterial properties (Jayakumar *et al*. 2010). According to reported studies, chitosan is effective as a dry and wet strength agent in the pulp and paper industry (Chen *et al*. 2013b; Hamzeh *et al*. 2013).

The strengthening agent can interact with fibers in a number of ways such as van der Waals forces, hydrogen bonding, ionic attractions, and covalent bond formation (Ghasemian *et al*. 2010). However, its poor solubility in aqueous water and most commonly used organic solvents limits its utilizations. Chitin whisker, a kind of crystallite in nanoscale prepared by removing the amorphous phase in chitin, is an emerging nanofiller which could enhance the mechanical and barrier properties of composites (Uddin *et al*. 2012; Rubentheren *et al*. 2015). But to the best of the author's knowledge, there is no report in literature about the chitin whisker enhancing the mechanical properties of paper sheets. In this work, we aim to develop a convenient approach to enhance the strength properties of paper through the electrostatic assembly between chitin whisker and cellulosic fiber in an aqueous medium. The chitin whisker was deposited *via* dip-coating on wet paper sheets, rather than mixing with the cellulose fibers in pulp suspensions. This treatment resulted in a significant improvement in wet strength and dry strength of cellulose fiber network.

EXPERIMENTAL

Materials

Eucalyptus bleached chemi-mechanical pulp (BCTMP) was supplied by Shandong Huatai Paper Co., Ltd. (China). α-Chitin, carboxymethyl cellulose sodium salt (CMC), calcium chloride ($CaCl_2$), and hydrochloric acid were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). All aqueous solutions were prepared with ultrapure water (>18 MΩ cm) from a Milli-Q Plus system (Millipore, USA).

Methods

Preparation of chitin whiskers

Chitin whiskers were prepared following a previous procedure (Morin and Dufresne 2002; Guan *et al*. 2014). The chitin whiskers suspension was prepared by hydrolyzing the purified chitin sample with 3 M HCl at the boiling point while stirring for 1.5 h. After acid hydrolysis, the suspensions were diluted with distilled water followed by centrifugation at 10000 revolutions per minute for 15 min for separation, and decanting the supernatant. This process was repeated three times. After that, the chitin was recovered by centrifugation and resuspended in ultrapure water. The obtained chitin suspension was dialyzed against flowing ultrapure water for 2 h and then dialyzed against ultrapure water for 12 h. Dialysis was performed with a dialysis membrane. At last, the chitin suspension was freeze-dried.

Preparation of CMC-treated cellulose fibers and paper sheets

The eucalyptus BCTMP was placed into a fiber mill beater (Mark V1- PFI, Norway) at 2000 rpm until the beating degree reached 30 °SR. It was then treated with CMC, based on a published method (Wu and Farnood 2014). Briefly, pulp suspension (2 g dried pulp) was prepared in a glass flask, then carboxymethyl cellulose salt solution (2 wt%) was added to the suspensions to obtain the desired CMC content, and ultrapure water was added until the pulp suspension 1.0 wt%. The mixture was heated at boiling temperature for 2 h with 6 mL of 1 M $CaCl_2$. The CMC-treated cellulose fibers were washed three times to remove excess CMC by filtering and re-dispersing them in Milli-Q water. The paper sheets were prepared according to the TAPPI Standard T205 sp-02 (2002), using the model Rapid-Koethen sheet former (RK3AKWT, Sweden) with a target basis weight of 60 g/m^2.

Coating of chitin whiskers

The chitin whiskers suspension with different concentrations of CMC (*i.e.*, 0.1, 0.5, 1.0, and 2.0 wt%) was prepared and homogenized by sonication. Then CMC-treated cellulose fiber sheets were immersed into the colloidal suspension for 10 min and washed using Milli-Q water three times. Finally, the modified papers were conditioned for 48 h at 25 °C, 50% relative humidity, and cut into square pieces for subsequent physical properties test.

Field-Emission Scanning Electron Microscope (FE-SEM)

Freeze-dried samples were sputter gold coated and imaged using a field emission scanning electron microscope (FE-SEM) (ZEISS Merlin, Germany) at a 5 mm working distance and a 5kV accelerating voltage.

Transmission electron microscopy (TEM)

Chitin whisker samples were prepared by depositing 10 μL of 0.1% suspensions onto glow-discharged carbon-coated TEM grids (300-mesh copper), negatively stained with 2% uranyl acetate solution for 5 min, and blotted with a filter paper to remove excess staining solution. The samples were elucidated on the TEM (JEOL, Japan) at an accelerating voltage of 200 kV.

FTIR spectroscopy

The Fourier transform infrared (FTIR) spectra were obtained on a Nicolet FT-IR 5700 Spectrophotometer (Bruker, Germany) using KBr pellets and scanned against a blank KBr pellet background within a wavenumber range 4000 to 500 cm^{-1}, with a resolution of 4.0 cm^{-1} at 25 °C.

X-ray diffraction (XRD)

The crystallinities of crude chitin and chitin whisker were measured using a D8 Advanced X-ray Diffractometer (Bruker AXS Corporation, Germany) operating at 50 mA and 40 kV with a Cu Kα radiation (λ = 0.15418 nm). The scattering angle (2θ) was varied from 5° to 40°, with a step width of 1 °/min.

Zeta-potential and elemental analysis

Potential charges on the surface of cellulose fibers, chitin whisker, and their compounds at different concentrations in pure water were measured with a Malvern 3000 Zetasizer (UK). Cellulose fibers and chitin whisker suspensions (0.10 wt%) were previously dispersed with ultrasonic dispersion for 5 min.

Physical properties of the finished paper

The paper sample was kept in a conditioning room at a temperature of 25 ± 1 °C and a relative humidity of 50% ± 2% for 24 h. The tear and bursting strengths were measured according to ISO 1974 (2012) and ISO 2758 (2001), respectively, by using Lorentzen and Wettre tear testers (Sweden) and a Lorentzen and Wettre Burst-O-Matic (Sweden). The dry and wet tensile index of samples was measured using a Lorentzen and Wettre tensile tester according to TAPPI T 456 (2003) and T494 (2006), respectively. Experimental errors were calculated in accordance with respective standards.

RESULTS AND DISCUSSION

Morphological Analysis

Figure 1a shows the nanostructure of the chitin whisker. The concentration of chitin whisker suspension in the sample plasma bottle was 0.5% (w/v %) (Fig 1a, inset). The SEM micrograph shows the aggregation of whiskers, implying the packing of whiskers after lyophilization. Apparently, the chitin whiskers were stacked as a nanofiber bundle.

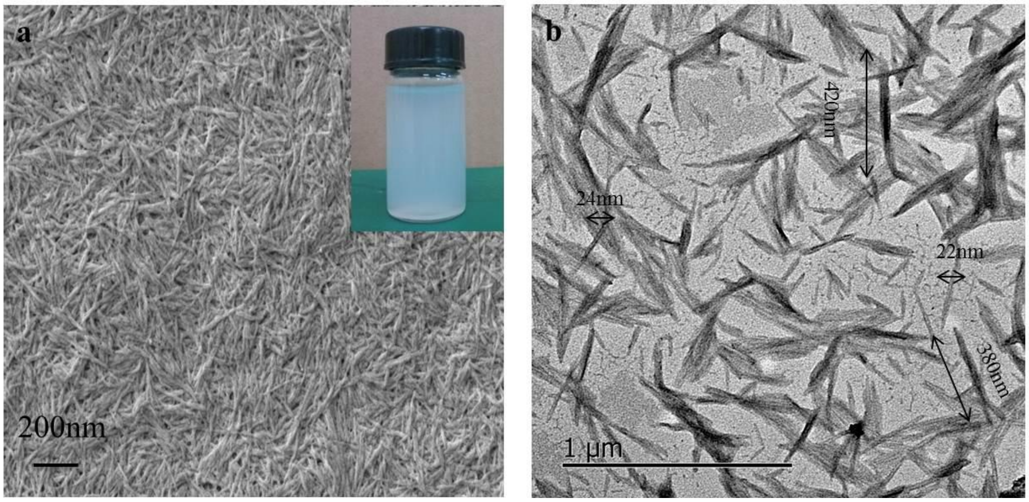

Fig. 1. (a) SEM micrograph of chitin whisker, with 0.5% chitin whisker suspension (inset) and (b) TEM micrograph of chitin whisker

Transmission electron microscopy gave adequate information to determine the morphology in detail in Fig. 1b. Two primary modes of chitin whisker existed in the suspension, individual microcrystals, and aggregated microcrystals. The chitin fragments, which consisted of chitin nanofibrils, were measured to have a length from 380 to 750 nm and a width from 18 to 34 nm and thus a broad distribution in size. The average aspect ratio of these whiskers was about 20. These dimensions are consistent with previous research (Wongpanit *et al.* 2007).

FTIR Analysis

Fourier transform infrared spectroscopy was employed to investigate the changes of the functional groups on chitin whiskers after hydrolysis. Figure 2 shows the FTIR spectra of the crude chitin and chitin whiskers. The peaks at 1655 and 1621 cm^{-1} are assigned to the amide I region of α-chitin, and the peak at 1551 cm^{-1} is attributed to the amide II region of α-chitin, in accordance with the past findings (Guan *et al.* 2014).

The spectra of chitin whiskers exhibited characteristic absorption peaks of chitin. The spectrum of chitin whiskers providing a broad peak at 3460 cm^{-1} was attributed to the –OH stretching vibrations. The peaks at 3250 and 3115 cm^{-1} were attributed to –NH stretching vibrations. The bands at 2900 to 2800 cm^{-1} were -CH anti-symmetric and symmetric stretching vibrations. When chitin was converted to chitin whiskers, the characteristic peaks of the amide groups still existed. The peaks in the chitin whiskers spectrum were sharper than those of crude chitin; this is due to its higher crystallinity (Pereira *et al.* 2014). These FTIR data confirmed that the acid hydrolysis did not alter the chemical nature of α-chitin as expected.

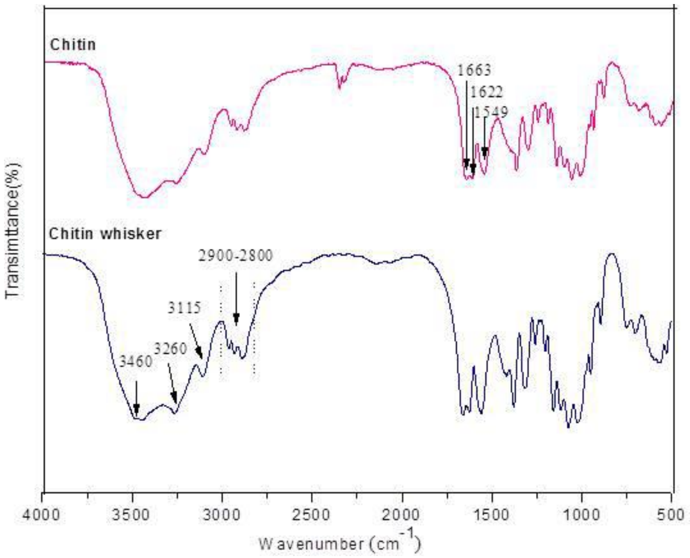

Fig. 2. FTIR of crude chitin and freeze-dried chitin whiskers

Crystallinity Changes

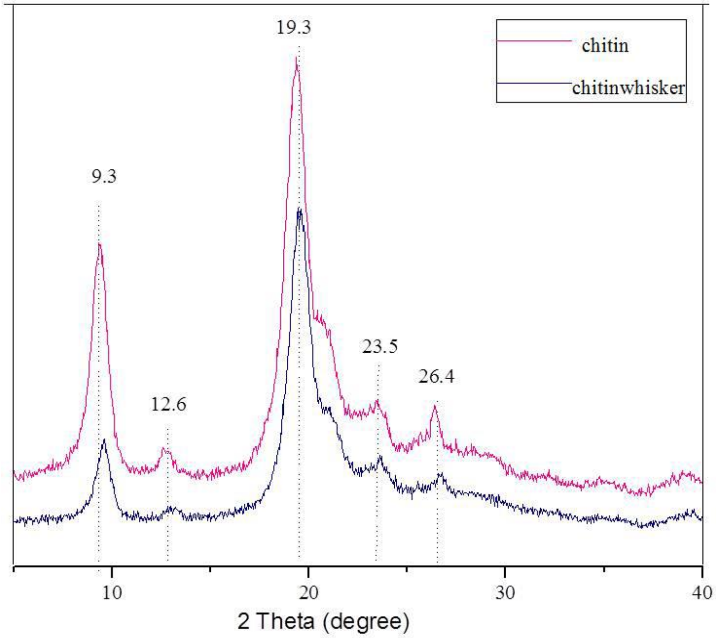

Fig. 3. XRD of crude chitin and chitin whisker

Figure 3 shows the X-ray diffractograms (XRD) of the crude chitin and chitin whiskers. Chitin displayed characteristic diffraction crystalline peaks, with 2 major peaks located at $2\theta = 9.3°$ and 19.3°. Three other minor peaks were located at 12.6°, 23.5°, and 26.4°. These two major peaks suggest that they presented very low qualitative apparent degrees of crystallinity. Chitin whiskers still presented two major diffraction peaks at 2θ of 9.4° and 19.4°, as well as three other weak peaks at about 12.6°, 23.5°, and 26.5°. It is clearly seen that the major peaks at 9.4° and 19.4° were significantly sharper after the crude chitin was hydrolyzed. This result indicates that the chitin whiskers possess relatively high apparent degrees of crystallinity (Phongying *et al*. 2007). The increase in crystallinity was due to the removal of the amorphous domain. Whiskers with high crystallinity could provide better reinforcement to the flexible polymeric matrices because of the high modulus of elasticity of the crystal domain (Pereira *et al*. 2014).

Zeta-Potential Analysis

Table 1. Average Values and Standard Deviation of the Zeta-Potential of the Cellulose Fibers and Chitin Whisker, and their Compounds

Sample	I	I coated with 0.25% II	III	I coated with 1.85% III	I coated with 4.84% III	I coated with 5.67% III	I coated with 6.07 % III
Zeta-potential (mV)	-39.4±0.8	-41.2±0.8	+8.5±1.1	-35.3±0.3	-29.4±0.5	-26.8±0.6	-24.5±0.3
Note: I represents cellulose fibers, II represents CMC, and III represents chitin whisker % represents the dry mass of chitin per dry mass of paper.							

Table 1 depicts the average values and standard deviation of zeta-potential for cellulose fibers and chitin whisker suspensions. As expected, chitin whiskers have a positive zeta potential value in neutral aqueous media, and the cellulose fibers have a negative zeta potential value (Tonoli *et al*. 2012). After treatment with CMC, the modified fibers presented a higher electronegativity. When chitin whisker was deposited *via* dip-coating on cellulose fibers, the zeta potential of fibers became decreasingly negative. The experimental results proved that the cellulose fibers and chitin whisker were intertwined by electrostatic attraction.

Surface Morphology of Composites

SEM was used to determine the surface morphology of cellulose fibers before and after the treatment, as shown in Fig. 4. Interleaving between fibers was loose when the cellulose fibers were not treated (Fig. 4a). The single fiber was intact and the fiber surface was smooth (Figs. 4b and 4c). Figures 4d through 4f show images of fibers after PFI beating. Surface morphology of cellulose was drastically changed after refining. As the result of refining, the fiber underwent fine cutting, associated with mild fibrosis. The surface fibrillation caused the fine fibers to remain loose on the surface to increase the roughness of the outside of the fiber, to increase bonding capabilities, and retain an amount of fine fibers with fluffy surface. Figures 4g and 4i show FE-SEM micrographs of paper sheet coated with a 1 wt% chitin whisker suspension. At the microscale, the fiber is visible, whereas chitin whisker components are not individually seen. Chitin whiskers filled micro voids and increased connectivity within the fiber network.

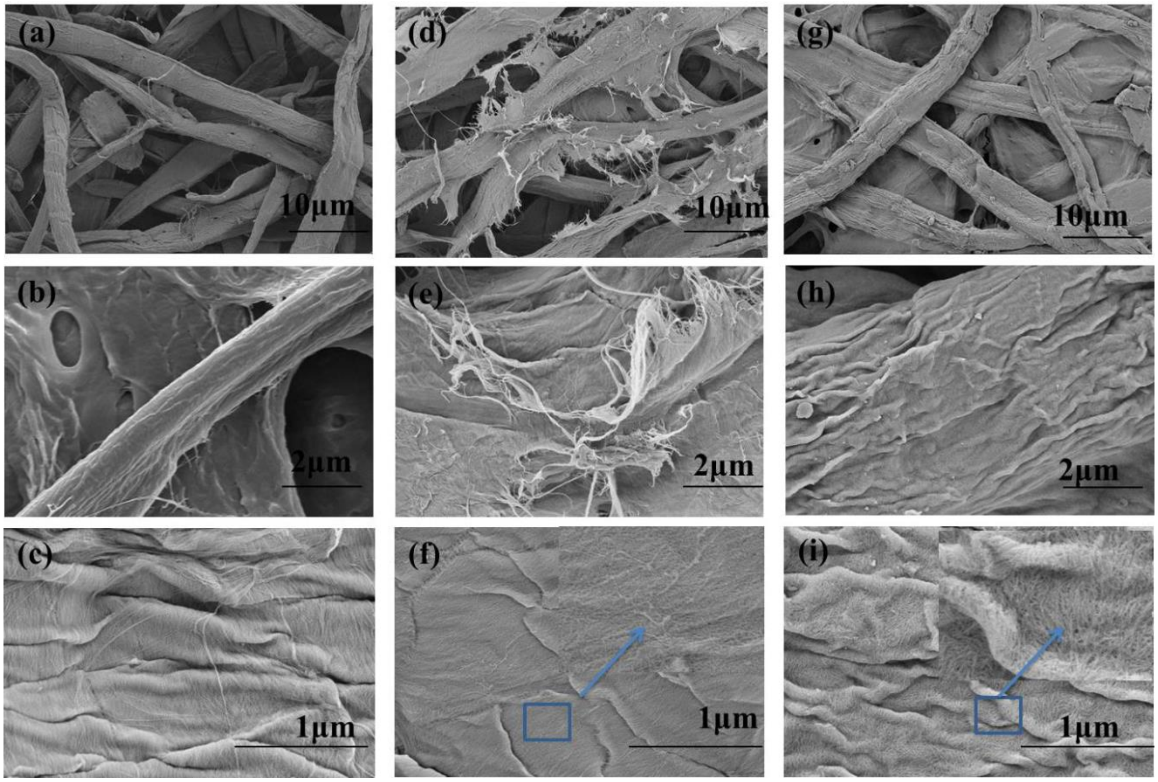

Fig. 4. FE-SEM micrographs of cellulose fibers at three states of (a-c) as-received without any treatment, (d-f) after PFI refining, and (g-i) coated of chitin whiskers; Boxes in (f) and (i) show enlarged details

Effect of Coating of Chitin Whiskers on Physical Properties of Paper Sheets

Chitin could be used as a paper strength additive because it has similar molecular structure to cellulose fiber and forms a number of hydrogen bonds with fibers (Liu *et al*. 2014). Physical properties of paper sheets are expected to be improved by the addition of chitin whiskers as a result of having a more compact and tight structure than those made from regular fibers (Hassan *et al*. 2015). In this study, the effects of chitin whiskers coated with different concentrations of CMC have been studied relative to paper strength; the results are shown in Fig. 5. The CMC coating of chitin whiskers could improve physical properties of the coated paper. For instance, it can be seen from Fig. 5a that the tearing index for the control sample (made of fibers after PFI refining and treated with CMC) was relatively low (24.5 N mN· m^2/g), and the tearing index of modified paper increased from 25.2 to 54.0 mN· m^2/g with increasing concentration of chitin whiskers. The maximum increase in tearing index was 118.6% more than the control sample at 2 wt% concentration of chitin whiskers. Similarly increased trends for tensile and bursting indices were observed in Figs. 5b and 5c, respectively. The increase could be interpreted as the charge-charge attraction between chitin whiskers and CMC-treated cellulosic surfaces enhanced the bonding force between cellulosic fibers, and the electropositive chitin whisker would be expected to form a denser layer during evaporative drying. As shown in Fig. 5d, the wet tensile strength for treated samples was obviously higher than those for the control sample. The results demonstrate that the CMC coating of chitin whiskers can considerably increase mechanical properties of a paper sheet.

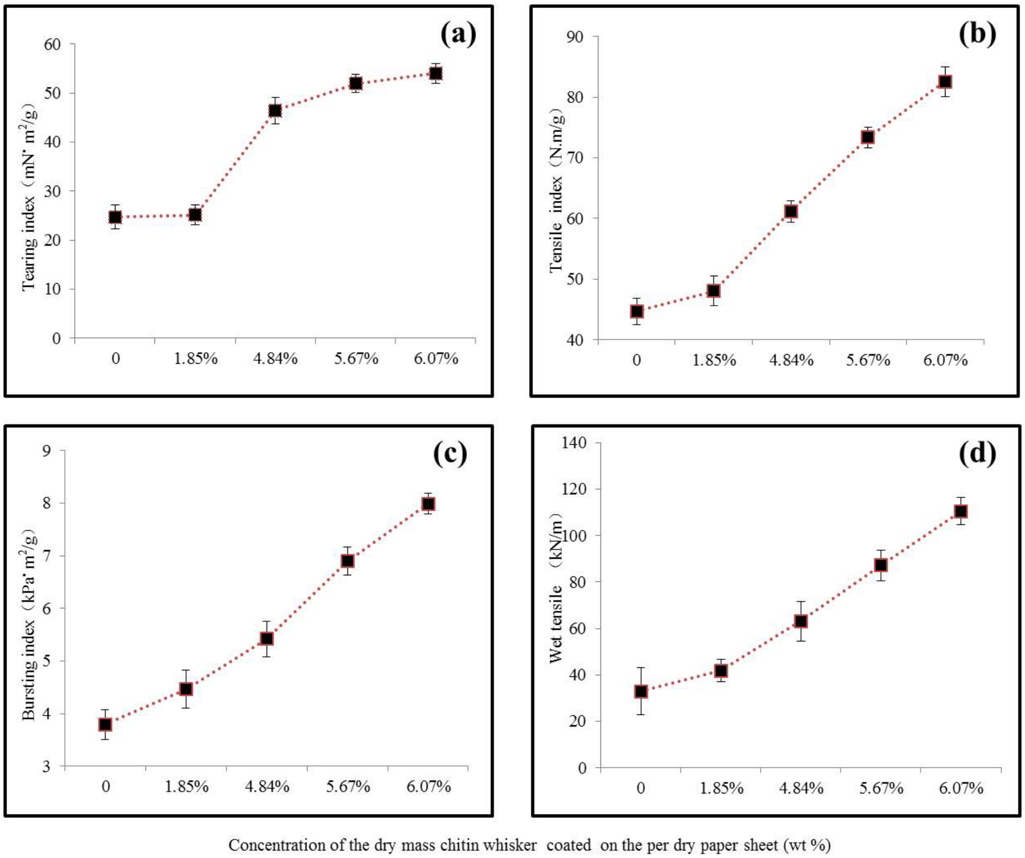

Fig. 5. Effect of coated with chitin whisker on the mechanical properties of paper sheets. Data reported as the average ± standard deviation.

CONCLUSIONS

1. Chitin whiskers with a relatively uniform width of 18 to 40 nm and length of 380 to 750 nm were successfully prepared from α-chitin by acidolysis.
2. A new kind of composite material based on natural cellulose fibers and chitin whiskers was prepared for food packaging applications. Eucalyptus cellulose fibers were first treated with CMC to increase the negative charge density of fiber surface and form paper sheets. Then paper sheets were further dip-coated with different concentrations of chitin whisker suspension. The results of zeta potential analysis and FE-SEM suggest the electrostatic attraction between cellulose fibers and chitin whisker can aid in retention, making it possible for hydrogen bonds to form between the solid surfaces during drying such that the connectivity within cellulose nanostructures is increased.
3. Coating with chitin whiskers can obviously improve the physical properties of paper sheets that could be used as food packing materials.

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REFERENCES CITED

Ashori, A., Marashi, M., Ghasemian, A., and Afra, E. (2013). “Utilization of sugarcane molasses as a dry-strength additive for old corrugated container recycled paper,” *Composites Part B: Engineering*, 45(1), 1595-1600. DOI: 10.1016/j.compositesb. 2012.09.030

Chen, Z. C., Zhang, H., Song, Z. Q., and Qian, X. R. (2013a). “Combination of glyoxal and chitosan as the crosslinking system to improve paper wet strength,” *BioResources* 8(4), 6087-6096. DOI: 10.15376/biores.8.4.6087-6096

Chen, Z. C., Zhang, H., Song, Z. Q., and Qian, X. R. (2013b). “Preparation and application of maleic anhydride-acylated chitosan for wet strength improvement of paper,” *BioResources* 8(3), 3901-3911. DOI: 10.15376/biores.8.3.3901-3911

Ghasemian, A., Ghaffari, M., and Ashori, A. (2012). “Strength-enhancing effect of cationic starch on mixed recycled and virgin pulps.” *Carbohydrate Polymers* 87(2), 1269-1274. DOI: 10.1016/j.carbpol.2011.09.010

Guan, Y., Bian, J., Peng, F., Zhang, X. M., and Sun, R. C. (2014). “High strength of hemicelluloses based hydrogels by freeze/thaw technique,” *Carbohydrate Polymer* 101, 272-280. DOI: 10.1016/j.carbpol.2013.08.085

Hamzeh, Y., Ashori, A., Khorasani, Z., Abdulkhani, A., and Abyaz, A. (2013). “Pre-extraction of hemicelluloses from bagasse fibers: Effects of dry-strength additives on paper properties,” *Industrial Crops and Products* 43, 365-371. DOI: 10.1016 /j.indcrop. 2012.07.047

Hamzeh, Y., Sabbaghi, S., Ashori, A., Abdulkhani, A., and Soltani, F. (2013). “Improving wet and dry strength properties of recycled old corrugated carton (OCC) pulp using various polymers,” *Carbohydrate Polymers* 94(1), 577-583. DOI: 10.1016/ j.carbpol.2013.01.078

Hassan, M. L., Bras, J., Mauret, E., Fadel, S. M., Hassan, E. A., and El-Wakil, N. A. (2015). “Palm rachis microfibrillated cellulose and oxidized-microfibrillated cellulose for improving paper sheets properties of unbeaten softwood and bagasse pulps,” *Industrial Crops and Products* 64, 9-15. DOI: 10.1016/j.indcrop.2014.11.004

Hubbe, M. A. (2006). “From here to sustainability,” *BioResources* 1(2), 172-173. DOI: 10.15376/biores.1.2.172_173

Hubbe, M. A., and Bowden, C. (2009). “Handmade paper: A review of its history, craft, and science,” *BioResources* 4(4), 1736-1792. DOI: 10.15376/biores.4.4.1736-1792

ISO 1974 (2012). “Paper; Determination of tearing resistance - Elmendorf method,” *International Organization of Standardization*, Geneva, Switzerland.

ISO 2758 (2001). “Paper; Determination of bursting strength,” *International Organization of Standardization*, Geneva, Switzerland.

Jayakumar, R., Prabaharan, M., Nair, S. V., and Tamura, H. (2010). “Novel chitin and chitosan nanofibers in biomedical applications,” *Biotechnol. Adv.* 28(1), 142-150. DOI: 10.1016/j.biotechadv.2009.11.001

Khakalo, A., Filpponen, I., Johansson, L.-S., Vishtal, A., Lokanathan, A. R., Rojas, O. J., and Laine, J. (2014). “Using gelatin protein to facilitate paper thermoformability,” *Reactive and Functional Polymers*, 85, 175-184. DOI: 10.1016/j.reactfunctpolym. 2014.09.024

Liu, K., Xu, Y., Lin, X., Chen, L., Huang, L., Cao, S., and Li, J. (2014). “Synergistic effects of guanidine-grafted CMC on enhancing antimicrobial activity and dry strength of paper,” *Carbohydrate Polymer* 110, 382-387. DOI: 10.1016/j.carbpol.2012.02.052

Morin, A., and Dufresne, A. (2002). "Nanocomposites of chitin whiskers from riftia tubes and poly(caprolactone)," *Macromolecules* 35(6), 2190-2199. DOI: 10.1021/ma011493a

Nassar, M. A., and Youssef, A. M. (2012). "Mechanical and antibacterial properties of recycled carton paper coated by PS/Ag nanocomposites for packaging," *Carbohydrate Polymers* 89(1), 269-274. DOI: 10.1016/j.carbpol.2012.03.007

Paillet, M., and Dufresne, A. (2001). "Chitin whisker reinforced thermoplastic nanocomposites," *Macromolecules* 19(34), 6527-6530. DOI: 10.1021/ma002049v

Pereira, A. G., Muniz, E. C., and Hsieh, Y. L. (2014). "Chitosan-sheath and chitin-core nanowhiskers," *Carbohydrate Polymer* 107, 158-166. DOI: 10.1016/j.carbpol. 2014. 02.046

Phongying, S., Aiba, S.-i., and Chirachanchai, S. (2007). "Direct chitosan nanoscaffold formation *via* chitin whiskers," *Polymer*, 48(1), 393-400. DOI: 10.1016/j.polymer. 2006.10.049

Rubentheren, V., Ward, T. A., Chee, C. Y., and Tang, C. K. (2015). "Processing and analysis of chitosan nanocomposites reinforced with chitin whiskers and tannic acid as a crosslinker," *Carbohydrate Polymer* 115, 379-387. DOI: 10.1016/j.carbpol. 2014.09. 007

TAPPI T205 sp-02. (2002). "Forming handsheets for physical tests of pulp," *TAPPI Press*, Atlanta, GA.

TAPPI T456. (2003). "Tensile breaking strength of water-saturated paper and paperboard (wet tensile strength) revised and reinstated," *TAPPI Press*, Atlanta, GA.

TAPPI T494. (2006). "Tensile breaking properties of paper and paperboard," *TAPPI Press*, Atlanta, GA.

Tankhiwale, R., and Bajpai, S. K. (2012). "Preparation, characterization and antibacterial applications of ZnO-nanoparticles coated polyethylene films for food packaging," *Colloids Surf. B Biointerfaces* 90, 16-20. DOI: 10.1016/j.colsurfb.2011.09.031

Tonoli, G. H., Teixeira, E. M., Correa, A. C., Marconcini, J. M., Caixeta, L. A., Pereira-da-Silva, M. A., and Mattoso, L. H. (2012). "Cellulose micro/nanofibres from Eucalyptus kraft pulp: Preparation and properties," *Carbohydrate Polymer* 89(1), 80-88. DOI: 10.1016/j.carbpol.2012.02.052

Uddin, A. J., Fujie, M., Sembo, S., and Gotoh, Y. (2012). "Outstanding reinforcing effect of highly oriented chitin whiskers in PVA nanocomposites," *Carbohydrate Polymers* 87(1), 799-805. DOI: 10.1016/j.carbpol.2011.08.071

Wongpanit, P., Sanchavanakit, N., Pavasant, P., Bunaprasert, T., Tabata, Y., and Rujiravanit, R. (2007). "Preparation and characterization of chitin whisker-reinforced silk fibroin nanocomposite sponges," *European Polymer Journal* 43(10), 4123-4135. DOI: 10.1016/j.eurpolymj.2007.07.004

Wu, T., and Farnood, R. (2014). "Cellulose fibre networks reinforced with carboxymethyl cellulose/chitosan complex layer-by-layer," *Carbohydrate Polymer* 114, 500-505. DOI: 10.1016/j.carbpol.2014.08.053

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