Preparation and Properties of Optically Transparent Chitin Nanofibers Sheet by Different Simple Mechanical Methods

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Keywords: Chitin nanofibers; Fibrillation; Mechanical method; Optical transparency

Abstract. Chitin nanofibers were prepared from commercially available dried chitin powders by different simple mechanical methods under acid conditions after removal of minerals and proteins. The fibrillated chitin samples were observed by FE-SEM and there was a fine network structure formed by chitin nanofibres with a width of approximately 10-50 nm and high aspect ratio. The mechanical treatment under acid conditions was crucial to facilitate the fibrillation of chitin fibres into nanofibers. The high pressure homogenization in combination with grinding was used to obtain the most transparent chitin nanofibers sheet with a transmittance of 88.5% and tensile strength of 82.34MPa, and the sheet even had a Young’s modulus of 6.17GPa. Thus, chitin nanofibers provide excellent potential as reinforcement of transparent flexible composites to improve the properties of nanocomposites.

Introduction

Chitin is the second most abundant natural polysaccharide next to cellulose and occurs mainly in the exoskeleton of crustacean with a biosynthesis quantity of about $10^{10}$ to $10^{11}$ tons every year. [1] Although chitin is a kind of renewable and biodegradable biomass material with excellent properties, most of biopolymers are abandoned as industrial waste without effective utilization.

Recently, Abe et al. [2] succeeded in preparing cellulose nanofibers with a highly uniform width of approximately 15 nm from wood. The cellulose nanofibers in cell walls of wood are wrapped in matrix substances such as lignin and hemicelluloses, so the cellulose nanofibers can be isolated by a simple mechanical treatment after removal of the matrix substances. In general, the exoskeleton of crustacean has a strictly hierarchical organization including crystalline α-chitin nanofibers and various types of proteins and minerals. [3] Similarly, chitin nanofibers embedded in sufficient matrix may be extracted from commercially available dried chitin powders by the same chemical treatments and mechanical methods used to obtain cellulose nanofibers. The fibrillation of chitin fibers into chitin nanofibers further contributes to the application of the green chitin as reinforcement.

Experimental

Chemical treatments. We designed a flow diagram showed in Fig.1 to remove matrix substances of commercially available chitin powders according to the conventional method [4, 5]. The dried chitin powders were first treated with 7% of hydrochloric acid solution for 24 hours at room temperature to remove minerals and part of proteins. After thoroughly filtering and washing the sample with an abundance of distilled water, the treated sample was dispersed in 4% of sodium hydroxide solution
for 12 hours to remove most of proteins. Next, the sample was filtered and rinsed with distilled water until the residues were neutralized. The above two processes were repeated 4 times to get rid of residual proteins completely. Then, the pigment composition in the sample was further removed using 95% of ethanol at room temperature for 6 hours followed by filtration and rinsing with distilled water.

\[ \text{Fig.1 Flow diagram of preparation of chitin nanofibers sheet.} \]

**Mechanical methods.** The purified chitin powders were dispersed in water at a concentration of 0.5 wt%, and acetic acid was added to adjust pH value to 3 to facilitate fibrillation. According to the flow diagram in Fig.1, the chitin slurry was first passed 15 times through a superfine grinder (MKCA6-2; Masuko Sangyo Co., Ltd., Japan) at 1500 rpm. Grinding was performed with a clearance gauge of -1.5 from the zero position, where was determined as the point of slight contact between the grinding stones. Next, the obtained chitin suspension was diluted into 0.15 wt% followed by dividing it into 3 groups. The first group suspension was treated by ultrasonic cell crusher for 0.5h at an output power of 80% and the treated suspension was called the sample 1. The second group suspension was used for the preparation of the sample 3 by a high-pressure homogenizer (EmulsiFlex-C3, AVESTIN Co., Ltd., Canada) for 0.5h. The third group suspension was processed by ultrasonic cell crusher combined with high-pressure homogenizer to make the sample 5 in the same way as the former procedure. Subsequently, the sample 1, 3 and 5 were centrifuged with a high-speed centrifuge for 10 minutes at 10000 rpm to respectively gain the sample 2, 4 and 6 which were the supernatant liquid separated from the sample 1, 3 and 5.

**Preparation of chitin nanofibers sheet.** The sample 1, 2, 3, 4, 5 and 6, the suspensions of fibrillated chitin fibers, were vacuum-filtered using polytetrafluoroethylene membrane filter (pore size: 0.2μm) to produce chitin nanofibers sheets of 90 mm in diameter. The obtained sheets marked as S1, S2, S3, S4, S5 and S6 were subjected to oven-drying at 55°C for 48 hours.

**Measurements.** The prepared chitin nanofibers and sheets were observed by a field emission scanning electron microscope (S-4800, HITACHI, Japan). The samples were coated with a layer of gold by an ion sputter coater for 30s. The UV-visible transmittance spectra of transparent sheets was recorded on a UV-visible spectrophotometer (U-4100, Hitachi High-Tech Corp., Japan) with an integrating sphere 60 mm in diameter. The regular light transmittances were measured by placing the specimens at the entrance port of the integrating sphere at wavelengths from 200 to 1000 nm. The universal material testing machine (GMT4204, SANS Corp.) was used for the measurement of tensile properties of chitin sheets for specimens 25 mm long and 4-6 mm wide at a crosshead speed of 1 mm/min.
Results and discussion

Fig. 2 Photograph of chitin nanofibers suspension prepared with different mechanical methods.

**Morphology of chitin nanofibers and chitin nanofibers sheet.** The photograph of the sample 1, 2, 3, 4, 5 and 6 is given in Fig. 2. Interestingly, all the samples have slight blue color indicating that they form a relatively stable suspension. However, due to the agglomeration of nanofibers into big aggregations, the sample 1, 3 and 5 are turbid and have some precipitates after a time. The sample 2, 4 and 6 become very clear and limpid after centrifugation, which demonstrates that there may be thinner and more uniform chitin nanofibers in the supernatant liquid.

Fig. 3 FE-SEM micrograph of chitin nanofibers after grinding and ultrasonication under neutral conditions (pH 7). The length of the scale bar is 2μm.

Fig. 3 shows the FE-SEM micrograph of the freeze-dried chitin nanofibers obtained by grinding and ultrasonication under neutral conditions (pH 7) after the chemical treatments. The FE-SEM observation reveals that high intensity mechanical processing results in the change of chitin fibers’ morphology from big bundled-structure to microfibers with a width of 100-500 nm. However, the obtained chitin fibers are still bundles of crystalline chitin nanofibers with strong hydrogen bonding between each thinner nanofibers. Therefore, chitin fibers tend to aggregate and are not fibrillated easily without the action of acid. The desired chitin nanofibers are not thoroughly isolated from the big clustering under neutral conditions.
Fig.4 FE-SEM micrographs of chitin nanofibers sheet (a) surface and (b) section after grinding and ultrasonication under acid conditions (pH 3). The length of the scale bar is (a) 100nm and (b) 4μm, respectively.

In comparison with Fig.3, Fig.4 is the FE-SEM micrographs of the oven-dry chitin nanofibers sheet surface and section produced with fibrillated chitin fibers obtained by grinding and ultrasonication under acid conditions (pH 3). Obviously, we could observe the fine chitin fibers with a width of about 10-50 nm, suggesting that the fibrillation process of chitin fibers into chitin nanofibers is facilitated in acidic solution as reported by Fan et al. It is emphasized that the cationization of the C2 amino groups on the chitin fibers surface at pH 3-4 is very important to maintain the stable dispersion state by electrostatic repulsions to prevent from coacervation. We also see that the network formation among chitin nanofibers and the stacking of abundant network formations estimated to consist of 880 layers at least in Fig.4. Perhaps, the special structure of chitin nanofibers sheet could strongly affect the properties of chitin nanofibers sheet.

**Optically transparency of chitin nanofibers sheet.** Fig.5 shows the regular light transmittance spectra of the S1, S2, S3, S4, S5 and S6 after different mechanical treatments. All the sheets display high transparency in the range of visible light of 400-800 nm with the transmittance from 72.5% to 88.5% at 600 nm, revealing that most of chitin nanofibers made by different mechanical methods with a width of 10-50 nm are much smaller than the wavelength of visible light. Remarkably, the light transmittances of the S2, S4 and S6 undergoing the centrifugation, which are respectively 87.9%, 88.5% and 86.8% at 600 nm, are generally higher than those of the S1, S3 and S5 without the centrifugation and increase by 21.2%, 8.3% and 13.6%. Furthermore, the S3 and S4 all exhibit higher transparency with high pressure homogenization compared to other sheets, suggesting that the high pressure homogenization may be the best mechanical method to fibrillate chitin fibers. These results indicate that the excellent chitin nanofibers could be prepared with different mechanical processes after the chemical treatments and the far finer and much more chitin nanofibers are collected in the supernatant liquid.
Mechanical properties of chitin nanofibers sheet. Fig. 6 presents the stress-strain curve of the S1, S2, S3, S4, S5 and S6 after different mechanical treatments. The tensile strengths of all chitin nanofibers sheets sufficiently reach more than 56.30MPa and Young’s moduli are all more than 4.59GPa. In surprise, the tensile strengths of the S2, S4 and S6 with the centrifugation are 80.48MPa, 82.34MPa and 84.53MPa, which significantly increase by 36.43%, 31.43% and 50.14% compared to those of the S1, S3 and S5 without the centrifugation, respectively. Moreover, the S3 has the highest tensile strength of 62.65MPa among the S1, S3 and S5 and even has the highest Young’s modulus of 6.17GPa compared with all the sheets, which also proves that the high pressure homogenization is most conducive to prepare chitin nanofibers. The outstanding mechanical performances of the sheets are obviously due to the antiparallel extended crystal structure of chitin \([9, 10]\), the network formation among chitin nanofibers and the stacking of abundant network formations as shown in Fig.4. Thus, these results support that chitin nanofibers could work effectively as reinforcement to improve the mechanical properties of composites.

Conclusions

Chitin nanofibers with a width of about 10-50 nm were prepared from commercially available chitin powders after the chemical treatments and different mechanical methods under acid conditions. Meanwhile, the obtained chitin nanofibers sheet exhibited high transparency and excellent mechanical properties, which all increased significantly after centrifugation due to the much thinner and more homogeneous chitin nanofibers collected in the supernatant liquid, and even had a transmittance of 88.5%, tensile strength of 84.53MPa and Young’s modulus of 6.17GPa. In addition, the high pressure homogenization in combination with grinding could be the best one to fibrillate chitin fibers into chitin nanofibers compared with different mechanical methods. Above all, chitin nanofibers were expected to be novel green nanomaterials as reinforcement to improve the properties of nanocomposites which could be applied to transparent substrates of electronic devices in future.
Acknowledgements

This work was financially supported by National Natural Science Foundation of China (NSFC 30871968, 31170514), Doctorate Fellowship Foundation of Nanjing Forestry University (2011YB014), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Graduate Cultivation Innovative Project of Jiangsu Province (CXZZ11-0525) and the Doctorate Program of Higher Education (20113204110011).

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10.4028/www.scientific.net/AMR.634-638.2232