

OPTICALLY TRANSPARENT BIOCOMPOSITES: POLYMETHYLMETHACRYLATE REINFORCED WITH HIGH- PERFORMANCE CHITIN NANOFIBERS

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This paper demonstrates the preparation of transparent biocomposites from chitin nanofiber using a series of simple mechanical treatments after the removal of proteins and minerals. Field emission scanning electron microscopy (FE-SEM) images show that the prepared chitin nanofibers are highly uniform with a width of less than 50 nm and a high aspect ratio. Due to the nano-size, the fibers are small enough to retain the transparency of the neat polymethylmethacrylate resin. Light transmission of the obtained chitin/PMMA biocomposite was 90.2%, in comparison to the neat resin, which was 92.6%. Mechanical property tests showed that chitin nanofibers significantly improved the tensile strengths and Young's modulus of the neat PMMA, which increased from 43.8 MPa to 102 MPa and 1.6 GPa to 3.43 GPa, respectively. PMMA resin was found to be well dispersed in the biocomposite and had little effect on the tensile properties of the material. The properties mentioned above qualify the chitin nanofiber as a green and high-performance candidate having potential to be applied in next-generation optical electronic and building systems as a commercially available material.

Keywords: Chitin nanofiber; Polymethylmethacrylate (PMMA); Optically transparent; Biocomposite; Mechanical properties; High-performance

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INTRODUCTION

Nanofibers have received a great deal of attention in the research community because of the recent revolution in nanotechnology. Latest studies have demonstrated that nanofibers can be produced from a number of polymers. The unique characteristics plus the functionalities of the polymers themselves impart nanofibers with many desirable properties for advanced applications (Shams *et al.* 2011). For example, cellulose nanofibers have been shown to be great reinforcement nanocomposites (Siqueira *et al.* 2009; Nakagaito and Yano 2005).

Apart from cellulose, chitin, poly (β -(1-4)-N-acetyl-D-glucosamine), is the most abundant source of polysaccharides found in nature, with an annual bioproduction of around 10^{10} to 10^{11} tons (Gopalan Nair and Dufresne 2003). It is the main component of the exoskeleton of arthropods such as crabs, prawns, and insects. These exoskeletons have a fine hierarchical organization consisting of α -chitin nanofibers and various proteins and minerals (Raabe *et al.* 2005). Recently, Ifuku (2009) succeeded in isolating α -chitin nanofiber from crab shells with a uniform width of approximately 10 to 20 nm and a high aspect ratio by simple process. It shows excellent mechanical properties, including a high Young's modulus and high tensile strength. In particular, Nakagaito and Yano (2005) reported a unique cellulose nanofiber composite film. Because of the nano-size effect, the

nanocomposite, which incorporated with an acrylic resin, was optically transparent. Lately, it has been shown that this finding is applicable for chitin nanofibers to obtain an optically transparent nanocomposite (Ifuku *et al.* 2010b). However, many reports have introduced the preparation of chitin nanofibers under acidic conditions (Ifuku *et al.* 2010a), which are severely damaging to the machines. So this has been a big problem that needs to be solved as soon as possible.

Additionally, chitin has different characteristics from cellulose, such as biocompatibility, wound healing activity, high purity, and hydrophobicity, which strongly distinguishes it from cellulose nanofiber composites (Shams *et al.* 2011). More recently, Ifuku and Shams (2011) demonstrated that chitin nanofibers extracted from crab shells exhibit much higher transparency than cellulose nanofibers. Although native chitin is a semicrystalline biopolymer with microfibrillar morphology and excellent material properties, most of the biomass is thrown away as industrial waste without effective utilization, especially in the case of crab shells. Thus, it is important to make efficient use of this biomass resource as a natural and environmental friendly material.

Because nanocomposites are considered to have great potential, various nanofillers have been used for their preparation, including cellulose, carbon nanofibers, nanoclays, and so on (Johnsen *et al.* 2007). However, a detailed study of composites using chitin nanofiber derived from completely sustainable and renewable natural resources as reinforcement has still not been conducted particularly to the point of discussing its mechanical properties. Specific characterization of the effects of chitin nanofibers on various resins would be especially valuable for designing advanced nanocomposite materials. In this paper, we prepared chitin nanofibers using a series of different mechanical treatments from waste crab shell powder compared with traditional methods, such as just grinding. Then PMMA was selected as the matrix in this study because it presented excellent transparency which could reach as high as 92% compared with acrylic resin which was 91% (Ifuku *et al.* 2011a). At the same time, PMMA is light but with high strength, such that it could be used as a building material. Furthermore, PMMA is a kind of avirulent environmental protection material with good chemical stability. In this paper we compounded PMMA with the obtained chitin nanofiber sheet and characterized its transparency, Young's modulus, tensile strength, and microstructure.

EXPERIMENTAL

Materials

Dried crab shell powder was purchased from Zhejiang Golden-shell Biochemical Co., LTD. at low cost. Polymethylmethacrylate (PMMA, 8N) resin was obtained from Evonik Degussa (China) Co., LTD. The other chemicals and distilled water were all purchased from Nanjing Chemical Reagent Company and used without further purification in this study.

Methods

Removal of matrix components

According to the general methods (Gopalan Nair and Dufresne 2003), crab shell powder was treated with 7% hydrochloric acid (HCl) solution for 24 hours at room temperature

firstly to remove mineral salts such as calcium carbonate. After the suspension filtered and rinsed with an abundance of distilled water, the obtained sample was dispersed in 5% potassium hydroxide (KOH) solution for 6 hours to remove proteins, and this process was repeated four times in order to wipe out all the residual proteins. The pigment composition in the sample was then removed using 95% ethanol at room temperature for 6 hours followed by filtration and washing with distilled water. At last, chitin powder was obtained, as Fig. 1 shows.

Fabrication of chitin nanofibers and chitin sheet

Purified powder was dispersed in water at 1wt%. The suspension was then passed ten times through a grinder (MKCA6-2; Masuko Corp., Japan) at 1500 rpm with a clearance gauge of -1.5 and -3, respectively. The position was determined as the point of slight contact between the two grinding stones. In order to further fibrillate the chitin fibers, the sample was treated with high-pressure homogenization (EmulsiFlex-C3, AVESTIN, Inc, Canada) for 20 min at a concentration of 0.1wt%. Finally, the suspension was placed in a high-speed centrifuge (H-1650, Hunan Xiangyi Laboratory development Co., LTD) and blended for 10 minutes at a speed of 10000 rpm. In the end, the obtained chitin fiber was nano-scalar through the FE-SEM observation. Morphological change of the chitin during the preparation of nanofibers is shown in Fig. 2. Nanofiber suspension, 1000 mL, which was the supernatant removed by decantation after the process of centrifugation, was vacuum-filtered using a polytetrafluoroethylene (PTFE) membrane with a 0.2 μm pore size to produce a thin paper sheet of 11 mm in diameter. The wet sheet was dried at 55 °C under slight pressure overnight and the sample's thickness was 35 μm . Then, another part of the nanofiber suspension was freeze-dried for the purpose of analyzing its diameter distribution later.

Preparation of chitin/PMMA nanocomposite membranes

PMMA was used as a matrix. Five grams of PMMA particles were immersed in 100 mL of dimethyl formamide. After mixing them for 1 hour at 55 °C, a liquid PMMA rein was obtained. The dried sheet, which was vacuum filtered using PTFE membrane were impregnated with neat PMMA resin under reduced pressure for 5 hours. Then, the impregnated sheets were taken out of the solution and oven-dried at 50 °C for 12 hours. Chitin nanofiber reinforced plastic membranes thus obtained were approximately 68 μm thick, and the fiber content was about 60 wt%, calculated based on the dry weights of the chitin nanofiber sheets and nanocomposites. The whole process is shown in Fig. 2.

FE-SEM observation

The morphology of chitin nanofiber and chitin/PMMA nanocomposite was observed using a field emission scanning electron microscope (HITACHI S-4860, HITACHI Japan) and a scanning electron microscope (SEM, FEI, qunta200). The fracture surface of the films was obtained by snap. The sample was freeze-dried in a Freeze Drying Machine (Zhongke, XIANOU-10) at -40 °C for 48 hours, using silica gel to maintain dryness. Then a small part of the specimen was taken to the sample stage and coated with approximately a 2 nm layer of gold using a vacuum sputter coater (SCD 005); the sputtering time was about 30 s, and the electric current was 10 mA.

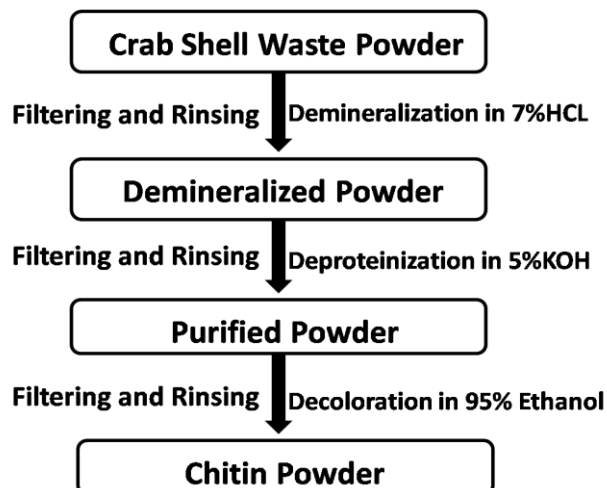


Fig. 1. Process of preparation of chitin from waste crab shell powder

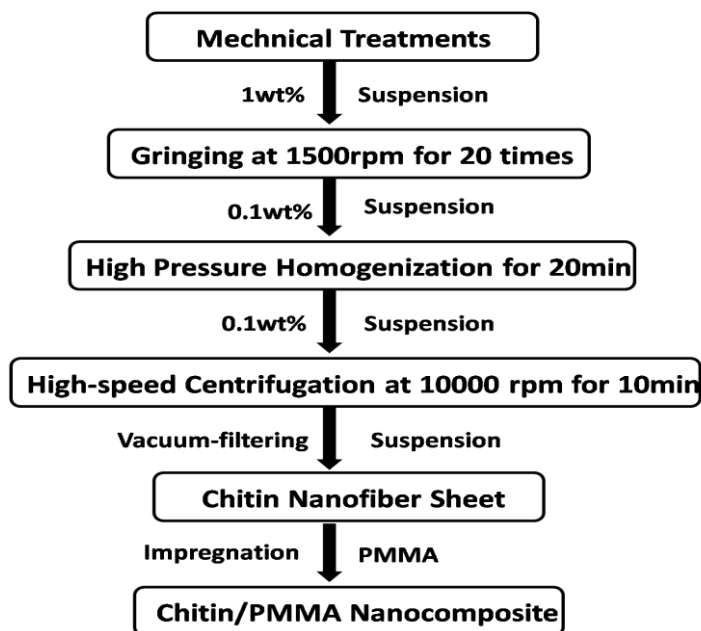


Fig. 2. Overall process of fabrication of chitin nanofibers and their nanocomposite

UV-visible spectra

Light transmittance of the membrane was observed with a UV-VIS near-infrared spectrometer (U-4100.HITACHI) with an integrating sphere 60 mm in diameter from 200 nm to 1000 nm in visible light wavelength range at 20 °C. Three replicates were conducted for each sample. The measurements were carried out three times to ensure the accuracy.

Tensile test

The samples were investigated with a universal material-testing machine equipped with a 100 N load cell (SANS, Shenzhen, China) at room temperature. The

length of the specimen was 20 mm, 5 mm wide, and a crosshead speed of 1 mm/min was used for the tests. Ultimate tensile strength at break of the specimen was evaluated. The results were reported as the average value from measurements of at least five specimens.

RESULTS AND DISCUSSION

Characterization of Chitin Nanofibers

Crab shells are composed of around 20 to 25% chitin nanofibers that are associated with other constituents (Chen *et al.* 2008). Figures 4a and b show photographs of the Burma crab shell, also known as black crab, before and after the removal of matrix components, respectively. Interestingly, after using the same chemical treatments applied in the waste crab shell powder described above, the crab shell turned completely white and kept its original shape and substantial morphological detail, including the eyes. Compared with the raw material, the treated shell feels softer due to the loss of some matrix, and its microstructure is shown in Fig. 5. A number of relatively uniform ellipse-type macropores with dimensions of $1 \times 0.5 \mu\text{m}$ were apparent; these were the spaces that had been occupied by the protein and mineral salts before the treatment. Additionally, the bundles of chitin fiber could also be clearly seen having an oriented arrangement. This image (Fig. 5a) was similar to the one obtained in the latest research performed by Iftekhar *et al.* (2012).

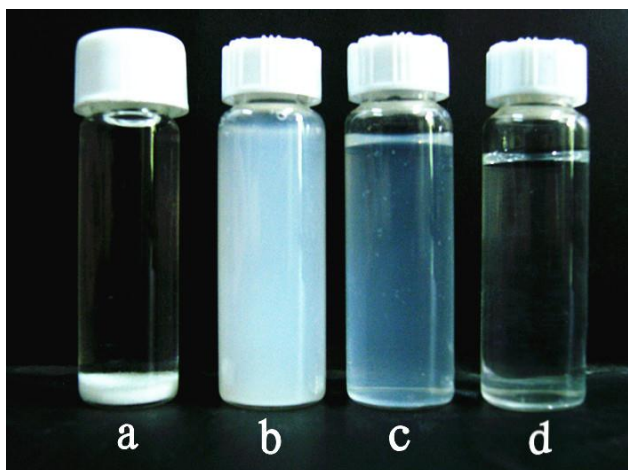


Fig. 3. Morphological change of the chitin during the preparation of nanofibers. (a) chitin powder after chemical treatments, (b) chitin powder turbid liquid after grinding treatment, (c) suspension after high pressure homogenization, and (d) suspension after centrifugation

Thus, in order to obtain nano-scalar chitin fibers with a high aspect ratio, mechanical treatments are necessary to effectively separate the bundles. It can be confirmed via Fig. 3. During the preparation of chitin nanofibers, the fiber suspension was gradually clear and homogeneous. Because of sequential mechanical treatments, fiber bundles are successfully dispersed step by step until reaching the expected nanometer level. Therefore, the final obtained sample, as Fig. 2d represents, is almost transparent through the macroscopic observation.

As many specialists have described (Raabe *et al.* 2005), exoskeletons of crustaceans have a strictly hierarchical organization, and the fracture structure is shown in Fig. 5b. Obvious layers were exhibited and each layer was connected with plenty of chitin fibers. The whole structure looks complex but uniform.

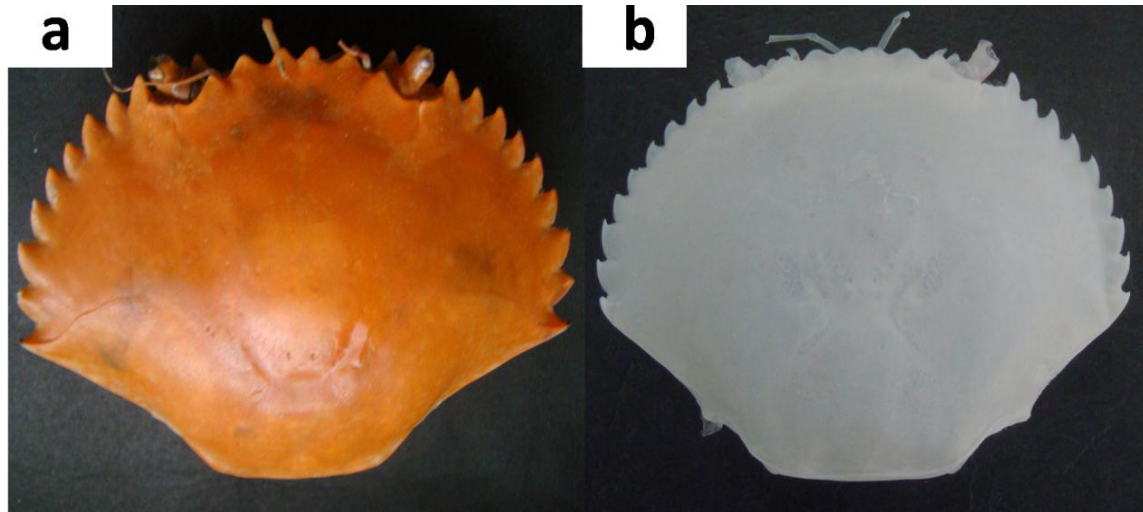


Fig. 4. (a) Raw Burma crab shell and (b) crab shell after removal of matrix components

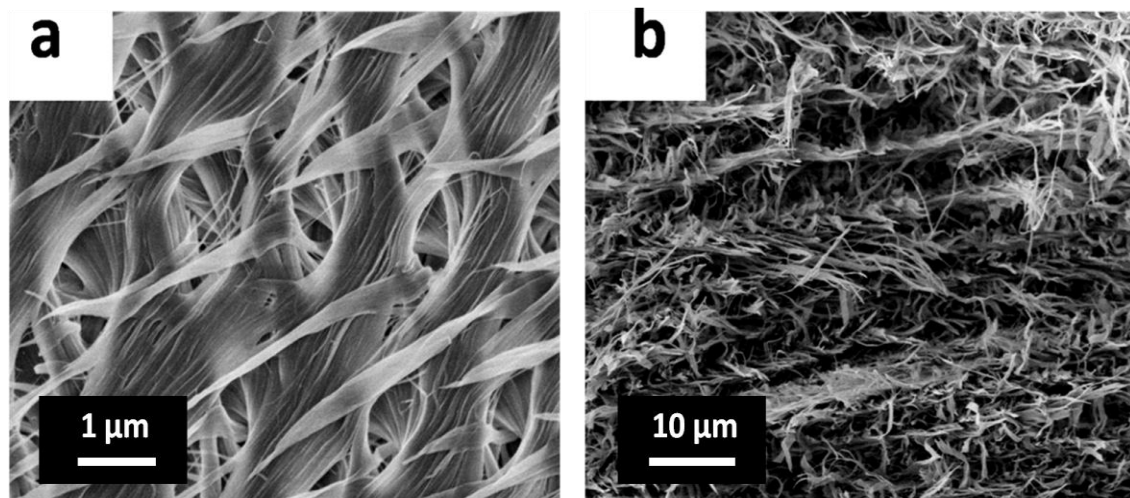


Fig. 5. FE-SEM image of (a) surface of the crab shell and (b) fracture surface of the crab shell

Figure 6 (a and b) shows FE-SEM pictures of the surface of the chitin sheets prepared using the waste crab shell powder as the starting material. Under low magnification ($\times 2000$), it appears very smooth and dense. In the case of mechanical treatments, the chitin fibers were fibrillated successfully with an average width of less than 50 nm. Under 40,000 times magnification, the surface of the sheet exhibited a very fine nanofiber network, which was uniform and compact with a number of holes. This result explains that sufficient mechanical treatments are just enough to separate the bundles into nano-scalar chitin fibers though in neutral condition. This would represent an improvement relative to the conventional methods, which require the addition of acid during the preparation (Ifuku *et al.* 2010a), because acid tends to corrode the equipment.

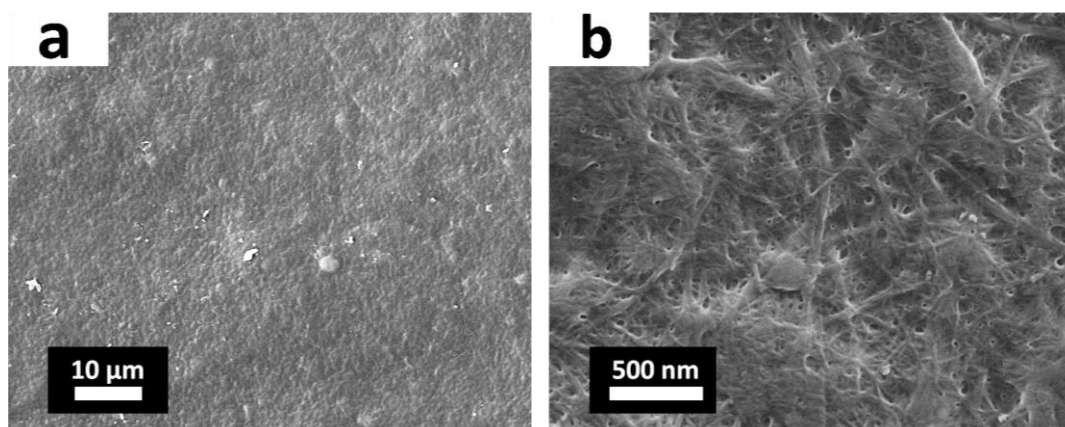


Fig. 6. Surface of the chitin nanofiber sheet (a) $\times 2000$ and (b) $\times 40000$

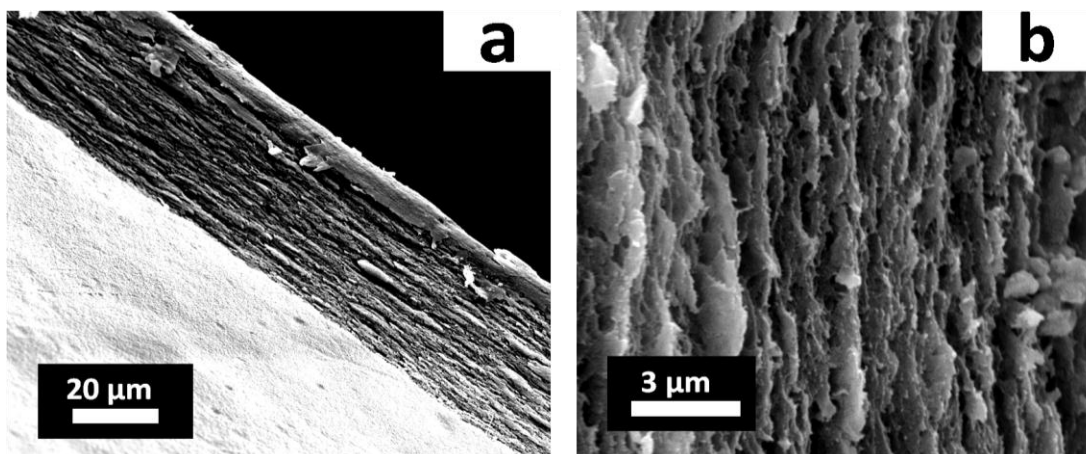


Fig. 7. Fracture surface of the chitin nanofiber sheet (a) $\times 1000$ and (b) $\times 8000$

Similar to the fracture surface of the natural crab shell, the obtained sheet also presents a clear layer structure (Fig. 7). This break happened through snapping, so a lot of tensile traces could be observed. The nodular structure of the fiber domains was torn with ductile failure. This was attributable to the layer structure, which afforded the membrane strong interlaminar fracture toughness. So, the tensile force must break through every layer of the material if the fracture is to happen. Recently one of the authors has published research about preparing bacterial cellulose membrane to establish this result (Chen and Li 2012). In order to analyze diameter distribution of the chitin nanofiber, freeze-drying was conducted on the chitin nanofiber suspension. Compared with oven-dry, this treatment could keep the original shape to a maximum extent. Figure 8 (a-c) shows the morphology of the treated sample in different magnifications. The spaces between fibers are brought about by the sublimation of ice during the freeze-drying process. From Fig. 8d, a detailed distribution of fiber diameter is present. Image-Pro Plus 6.0, which is an image analysis software attached to our optical microscope (Olympus BX-51), was used to explain the diameter distribution. From Fig. 8 a,b,c, 300 data points were acquired, and the final dispersion was about 5%. It can be shown that diameters of less than 50 nm comprised more than 83% of the material, and 46% of the chitin fiber

was less than 25 nm. Only 14% of the fiber exceeded 50 nm. It is suggested that chitin nanofiber prepared in this paper was uniform and fine with a width of less than 50 nm.

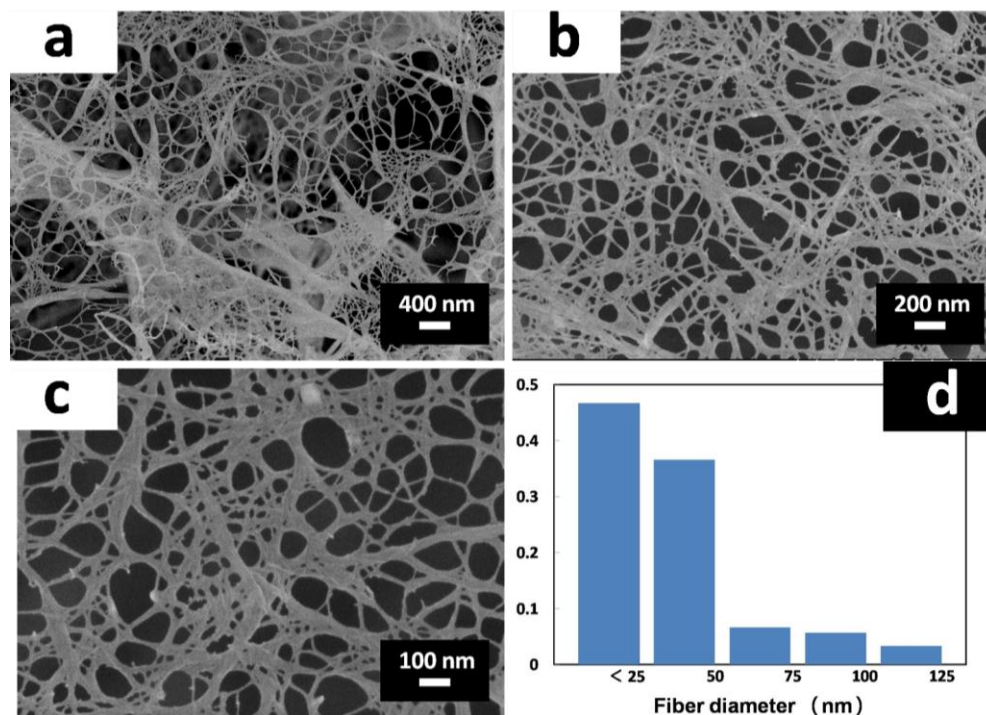


Fig. 8. FE-SEM images of freeze-dried chitin nanofiber: (a) $\times 20000$, (b) $\times 50000$, (c) $\times 80000$, and (d) diameter distribution of chitin nanofiber

Characterization of Chitin /PMMA Nanocomposite

Optical photographs of the raw chitin powder sheet (a) chitin nanofiber sheet, (b) and chitin/PMMA nanocomposite, and (c) are shown in Fig. 9. Backgrounds of the samples could be seen clearly from left to right, indicating that PMMA is effective in improving the transparency of the material. Combining with Fig. 10, at a visible wavelength of 600 nm, which is the center of the visible light spectrum from 200 to 1000 nm, the chitin/PMMA plastic sheet having thickness of 62 μm transmitted 90.2% of the light, including surface reflection. Compared to a neat PMMA sheet, whose transmittance was as high as 92.6%, the totally loss was just about 2.4%, even at high levels of fiber content of 60%. Despite the presence of big and discrete particles (Fig. 9a), the scattering of the visible light is avoided. Furthermore, we can see that the difference of regular transmittance of the chitin powder composite and chitin nanofiber composite was quite small at the wavelength of 600 nm, which is 84% and 88.9%, respectively. The transparency of matrix resin is thus preserved if the particles are nano-element assemblies, which can be impregnated and polymerized with a suit monomer. These improvements are all due to the nano-size effect, as reported by Shams *et al.* (2011). That is, since the width of the chitin nanofiber is much thinner than the wavelength of visible light, light can easily penetrate the nanocomposite.

Surprisingly, through this experimental research, it can be perceived that the chitin nanofiber resin sheet exhibited much higher transparency compared to the cellulose nanofiber resin sheet as introduced by Iftekhhar *et al.* (2011). This high transparency may be attributed to the close affinity between the less hydrophilic chitin nanofiber and the

hydrophobic resin. Also, the PMMA is chemically compatible with the chitin so that it can easily impregnate the substrate despite its nanoporous characteristics. This suggested that chitin nanofiber has more potential to be used as an optical transparent material such as flexible flat panel displays, solar cells, and so on.

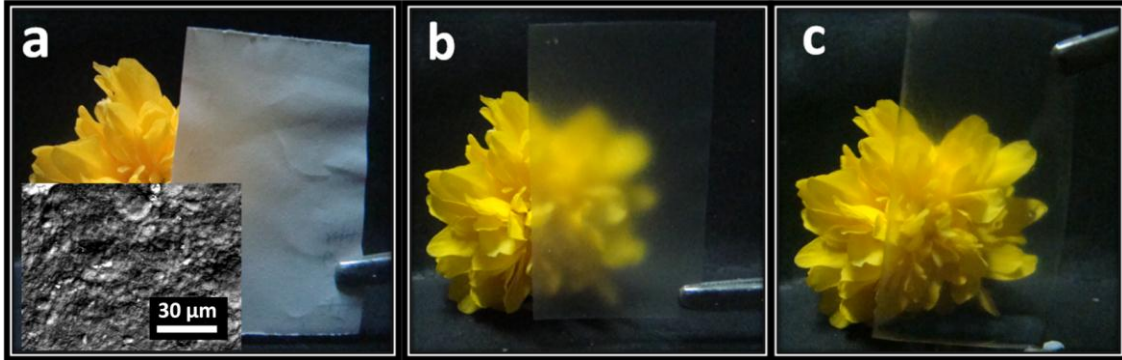


Fig. 9. Optical images of (a) chitin powder sheet only removing the matrix, (b) chitin nanofiber sheet, and (c) chitin/PMMA nanocomposite

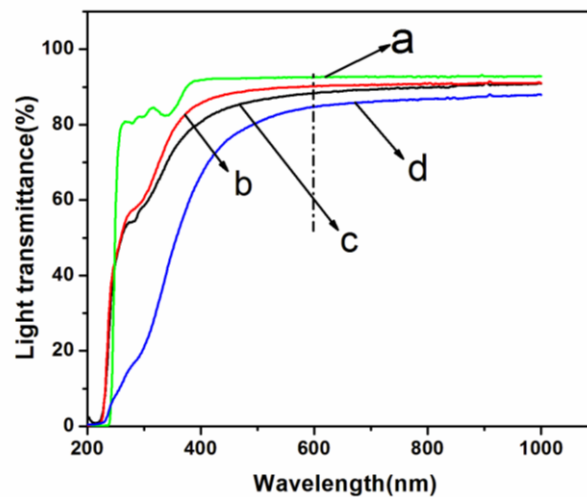


Fig. 10. Regular light transmittance spectra of (a) neat PMMA sheet, (b) chitin nanofiber-reinforced PMMA sheet, (c) chitin nanofiber sheet, and (d) chitin powder composite

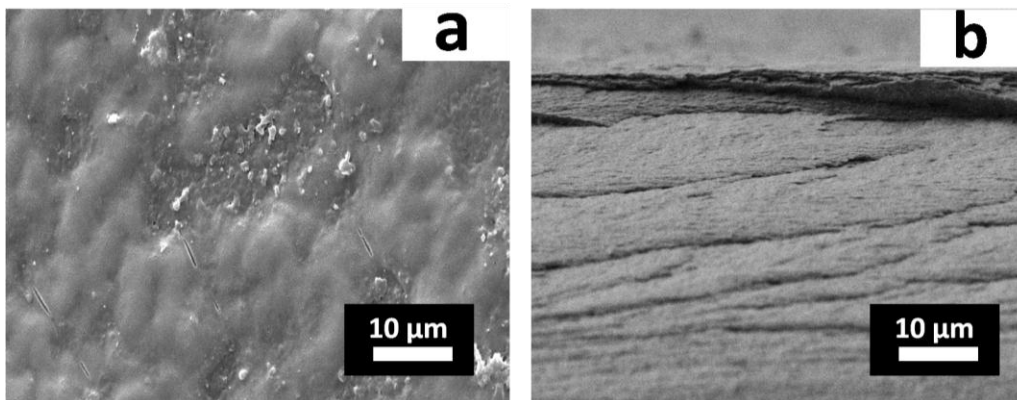


Fig. 11. FE-SEM images of Chitin/PMMA nanocomposite: (a) surface and (b) fracture surface

Figure 11 shows the morphology of chitin nanofiber after being embedded in the PMMA matrix. The lamellar structure is still distinct compared to the neat nanofiber sheet, and PMMA resin appears well covered on the surface and throughout the cross section. The whole FE-SEM micrographs show that dense, layered, paper-like films and nanocomposites were obtained.

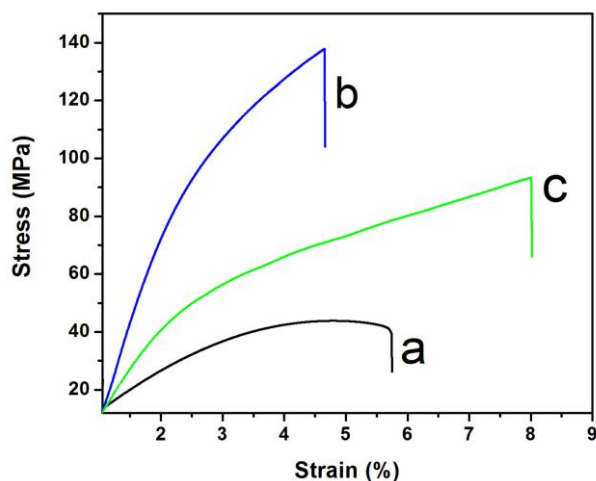


Fig. 12. Stress-strain curves of tensile test results on (a) neat PMMA sheet, (b) chitin sheet, and (c) chitin nanofiber-reinforced PMMA sheet

Since chitin nanofibers have an antiparallel extended crystal structure, they have relatively high mechanical strength and Young's modulus. Therefore, chitin nanofibers are expected to be useful as reinforcing elements to improve the mechanical properties of composite materials. However, there has been little published research involving its mechanical properties. The one paper that was found referring to the mechanical test was that of Ifuku *et al.* (2011). In this paper, the tensile behavior of the neat PMMA and the chitin materials were investigated; the representative stress-strain curves are shown in Fig. 12. The chitin nanofiber-reinforced PMMA sheet exhibited higher tensile strength than the neat PMMA sheet, which increased from 43.8 MPa to 102 MPa. In particular, the average Young's modulus also rose about two times from 1.6 GPa to 3.43 GPa. From the test data, the introduction of PMMA generally had little effect on the tensile properties of the composite. Since PMMA resin is brittle, perhaps the resin acted to bridge the layers of the lamellar structure, preventing crack propagation. Furthermore, fracture values measured here are nearly three times greater than Ifuku (2011) ever tested about the neat chitin nanofiber sheet, which was 2.5 GPa and 42 MPa, respectively. This occurs because fibrillated fibers have a much higher area effectively in the polymer. That is to say suitable mechanical treatments play a key role. The authors' foregoing work about bacterial cellulose (BC)/PMMA showed that chitin nanofibers also can serve as nanofillers (Chen and Li 2012). These outstanding enhancements of mechanical properties strongly support the results that a chitin nanofiber sheet with a Young's modulus of 7.1 GPa and a tensile strength of 137.8 MPa works effectively as an ideal reinforcing element using in developing high-strength composites such as transparent high-performance building materials, OLED displays, and so on.

CONCLUSIONS

1. Through a series of simple mechanical treatments, chitin nanofiber can be successfully extracted from purified waste crab shell powder, achieving a uniform width of less than 50 nm. Compared with the cellulose, this process is easier and faster.
2. Due to the nano-scalar but layered structure and excellent mechanical properties of chitin nanofibers, the chitin nanofiber-reinforced PMMA composites are highly transparent and strong with a high Young's modulus and tensile strength compared with the neat rein. Additionally, the introduction of PMMA generally has little effect on the tensile properties of the composite.
3. Chitin nanofibers, which are derived from completely sustainable and renewable natural materials, can effectively improve the environment caused by a great quantity of waste crab shell every year, especially around the seaside. It strongly represents the notion of waste reclamation and sustainable development. Therefore, preparation of nanofibers from a pure chitin is an important goal for expanding the application of chitin nanofibers as an environmentally friendly bio-nanomaterial with a very high surface-to-volume ratio.

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