Chitin nanofibers from marine bio-resources

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Chitins are the main components in crab and shrimp shells, in the outer skins or cuticles of other arthropods, and in the molluscan shells of squid, and they are chemically identical to cellulose except that the secondary hydroxyl group on the carbon atom of the cellulose molecule is replaced by an acetoamide group. Chitin in the crustacean shells have the alpha type crystal structure where all molecular chains are arranged in an anti-parallel mode with strong intermolecular hydrogen bonding. The microfibers form layers producing a plywood-like structure. The microfibers recognize each other and arrange themselves in an orderly fashion. The crystalline microfibers contain nanofibrils, approximately 300 nm long and 2-5 nm wide. In this study, we have demonstrated the successful fabrication of chitin nanofibers having a uniform width of 20-30 nm from crab shells using simple mechanical process.

The starting material was dried crab shell flake of *Paralithodes camtschaticus* (Red king crab) sieved through 30-60 mesh. To extract nanofibers efficiently, chitin can be isolated from the cuticle by a series of decalcification and deproteinization steps using acid and alkali treatments, respectively. The wet chitin was suspended in water at 1% concentration and subjected to the high speed blender for 10 min at a rotating speed of 37000 rpm and kept at never dried condition. Despite its water-swollen condition, chitin exhibited a wide-ranging distribution of fiber widths. Thus, we added acetic acid to the pure chitin slurry, adjusted the pH value to 3-4, and then placed the mixture in a high-speed blender for 10 minutes. Surprisingly, a colloidal structure was obtained, indicating that the chitin-fiber slurry was homogeneously dispersed in water. SEM image (Fig.1) reveals that well-constructed chitin nanofibers were fabricated by controlling pH value and simple blending technique. These nanofibers have an average width of about 20-30 nm.

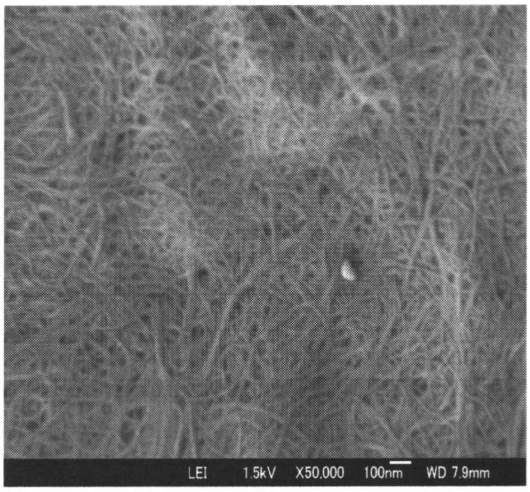

Figure 1. chitin nanofibers extracted from crab shells via high-speed blender under acidic conditions (pH 3-4)

An interesting observation was noticed during the filtration process to produce chitin nanofiber sheet. Possessing both hydroxyl and amine/*N*-acetyl functionalities, water suspension of chitin nanofibers was vacuum filtered 9 times faster compared to cellulose nanofibers to prepare nanofiber sheet. This is a prominent advantage of chitin nanofibers over cellulose nanofibers from the commercial viewpoint. Furthermore, the obtained nanofibers are small enough to retain the transparency of neat acrylic resin. At a visible wavelength of 600 nm; chitin/acrylic resin nanocomposite transmitted 87.3% of light, the fibrillated chitin fiber networks degraded only 3.2% light transmission of neat acrylic resin. Most interestingly, chitin nanofibers acrylic resin films exhibited much higher transparency compared to cellulose reinforced acrylic resin films despite the similar refractive indexes (RI) and width of both kinds of nanofibers. This high transparency of chitin composites may attribute to the close affinity between less hydrophilic chitin nanofibers and the hydrophobic resin. In addition, the incorporation of chitin nanofibers contributes the significant improvement of the thermal expansion and mechanical properties of the neat acrylic resin.

A foldable material with high light transmittance and low thermal expansion is a promising candidate for the substrate of continuous roll to roll process in the manufacturing of various optoelectronic devices such as flat panel displays, flexible displays and solar cells.