（様式２）

学位論文の概要及び要旨

氏　　名　Ajoy Kumar Dutta　　印

題　目　Preparations and characterization of chitin nanofiber and the related materials

学位論文の概要及び要旨

Introduction

Chitin is the second most abundant biopolymer. However, most chitin is thrown away as industrial waste because it is completely insoluble in water. In recent years, our group have prepared chitin nanofibers from crab and prawn shells as well as from mushroom cell walls. The chitin nanofibers have a highly uniform network morphology with a 10–20 nm width and strong mechanical properties owing to its extended crystalline structure. A grinder instrument has been utilized to obtain chitin nanofibers. Recently, high pressure water jet system (HPWJ) called Star Burst was developed by Sugino Machine Co., Ltd. The system applies high-pressure water jet technology to downsize several materials. Chitin nanofibers from the HPWJ system are more advantageous in high-volume production, maintaining the product quality, and allowing less contamination than occurs with the use of a grinder. Thus, the HPWJ system will be a strong candidate for the commercial production of chitin nanofibers. In this study, we prepared chitin nanofibers and the related materials by using HPWJ system, and characterized them in detail.

Preparation of *α*-Chitin Nanofibers by High Pressure Water Jet System: Impact of Number of Passes on Nanofibrillation

The author studied the effects of the nanofibrillation of α-chitin by the HPWJ system on the morphology, chemical structure, crystallinity, and several physical properties of chitin nanofibers. SEM images showed that the nanofibrillation of chitin powder significantly affected by the number of passes and at around 10 passes disintegration ended remarkably. The thickness of nanofibers decreased as the number of passes increased gradually up to 30 passes. The light transmittance of the chitin nanofiber slurry and the nano-composite with acrylic resin showed the same trend. On the other hand, above 30 passes, the nanofibers started to break. However, X-ray diffraction profiles of the chitin nanofibers showed that the HPWJ treatment did not reduce crystallinity, even with the high collision force caused by super-high-pressure water. Therefore, mechanical properties were improved by nanofibrillation, and extensive cycles of treatment did not reduce their properties. The HPWJ system is advantageous in the commercial application of chitin nanofibers from the standpoints of quality stability, high-volume production, and low contamination. We expect that this detailed characterization will play an important role in the commercial use of chitin nanofibers.

Simple Preparation of *β*-Chitin Nanofibers from Squid Pen

The authors studied the influence of HPWJ system on β-chitin from dry squid pen powder to transform into nanofibers. We highlighted the nanofibers morphology, chemical structure, crystallinity, viscosity, mechanical properties and thermal expansion. SPM images revealed that chitin nanofibers fibrillated to thinner fibers uniformly up to 10 passes. Light transmittances and viscosity of chitin nanofibers slurry also supported the above statement. Nanofibers with a cross-sectional width of 3-4 nm were possible to isolate. Extensive cycles of treatment, although, reduced the fibers lengths. The original β-chitin structure was unchanged by the HPWJ system, and the crystallinity of chitin nanofibers did not reduce. As a result, the mechanical properties were improved by nano-fibrillation up to an extensive range of treatments. We expect that this detailed characterization will play a vital role in developing commercial applications for the β-chitin nanofibers.

Novel Preparation of Chitin Nanocrystals by H_2SO_4 and H_3PO_4 Hydrolysis

The authors used H_2SO_4 and H_3PO_4 for the first time to prepare chitin nanocrystals (CNCs) from chitin powder. After examining the results of SPM, we discussed the influences of hydrolysis conditions on the CNCs' morphology. Irrespective of the nature of acids and reaction conditions, a high yield of CNCs was achieved in all cases. We were able to isolate CNCs with an average thickness of 7.3-8.0 nm. S- and P-CNCs showed higher crystallinity than the conventional H-CNCs. So, the present hydrolysis conditions might be suitable for preparing highly crystalline CNC. Moreover, TGA results showed P-CNCs have higher thermal stability than H- and S-CNCs. All types of CNCs formed stable dispersions in water and had high transparency. High-pressure water jet technology emerged as a powerful disintegration tool for preparing nanomaterials. We expect that a thermally stable P-CNC prepared by a lower reaction temperature and with lower acid volume might be appropriate as filler in the design of polymer nanocomposites, together with some other applications.

Simple Preparation of Chitosan Nanofibers by High Pressure Water Jet System

The authors studied the effects of the nano-fibrillation of chitosan by the HPWJ system, paying particular attention to the morphology, chemical structure, crystallinity, viscosity, mechanical properties, and thermal expansion of chitosan nanofibers. The chitosan powders turned into thinner nanofibers through the HPWJ system, as the nanofiber aggregate structure was still maintained after deacetylation treatment. Extensive cycles of treatment reduced the fiber length and crystallinity due to the high collision force caused by super high-pressure water. As a result, the mechanical and thermal expansion properties were improved by nanofibrillation up to 10 passes, while further treatment resulted in a degradation of these properties. This detailed characterization is expected to play an important role in developing commercial applications for the nanofibers. Naturally rare cationic-charged nanofibers can be obtained from chitosan flakes. The HPWJ system could therefore be a key tool for designing smart materials by means of ionic complex or self-organization approaches. In addition to the chitin and cellulose nanofibers, the chitosan nanofibers have been now listed in bio-nanofibers.

Facile Preparation of Surface *N*-halamine Chitin Nanofiber to Endow Antibacterial and Antifungal Activities

N-halamine-based CNF film was prepared successfully by using easily available diluted sodium hypochlorite. The concentration of sodium hypochlorite and the reaction time strongly affected the active chlorine content on the films. FT-IR, UV-Vis, XRD, and TGA analyses showed the presence of a N-Cl bond on the CNF surface. Chlorine was rechargeable onto CNF by the same sodium hypochlorite treatment. All the microbes of *E. coli* and *S. aureus* died within 30 min of contact with the chlorinated CNF film. Moreover, 100% of *A. alternata* and 80% of *P. digitatum* fungal spore stopped their germination upon 24 h treatment with the chlorine-containing CNF films. Here, CNF acquired antibacterial and antifungal properties in addition to various characteristics, such as nanostructure, high surface area, excellent mechanical properties, and several biological properties. Chlorination will expand the range of commercial applications of CNF, especially in medical, food, and cosmetics fields.