（様式２）

学位論文の概要及び要旨

氏　　名　Fantahun Aklog Yihun　　印

題　　目　Preparations, characterizations and applications of chitin nanofiber and its derivatives
（キチンナノファイバーならびにその誘導体の調製と特性評価と応用）

学位論文の概要及び要旨

Introduction

Chitin, the second most abundant carbohydrate polymer on earth next to that of cellulose, is an ideal candidates for various applications due to its remarkable properties such as abundance, biodegradability, biocompatibility, antibacterial activity, and high mechanical performance. Despite these intrinsic advantages, large amount of chitin is still thrown away as industrial waste mainly because of its strong inter and intra hydrogen bonding, which make it insoluble in common solvents. Commercially chitin can be extracted from crab and shrimp shells by treatment with NaOH and HCl aqueous solutions to remove proteins and calcium carbonate components, respectively. A major effluent purification process is then required to purify the abundant calcium carbonate and protein residue, and the expense of this process is passed on in the cost of commercial chitin (currently about 5,000 Yen/kg). Chitin in crab shells possessed an antiparallel molecular alignment forming microfibrils connected with inter and intra hydrogen bonding. In recent years, we have been using mechanical treatments for obtaining nanofibers from chitin and chitin derivatives. We have successfully prepared chitin nanofibers from crab and prawn shells as well as mushroom cell walls using grinder and/or high pressure water jet (HPWJ) system. The thus obtained chitin nanofibers have shown uniform morphology with average width of 10-20 nm, and possessed high mechanical properties due to their high crystalline structure. Though both grinder and HPWJ system have advantages over other methods like ultrasonic or electrospinning techniques for the preparation of nanofibers from polysaccharides, the requirement of repeated passes for complete nano-fibrillation increased the production cost and make the method infeasible for large scale production. In this study, the author prepared chitin and chitin derivatives nanofibers by giving due consideration for the cost and environmental issues. Moreover, we investigated the use of the thus prepared nanofibers for different applications.

Effect of grinder pretreatment for easy disintegration of chitin into nanofiber

Chitin nanofibers were prepared by grinder pretreatments and subsequent mechanical treatment using a HPWJ system. From SEM observations, grinder pretreatment improved disintegration efficiency in subsequent HPWJ treatment. That is, with pretreatment, excellent nanofiber networks were observed after a single HPWJ treatment, and sufficient nano-fibrillation was accomplished with 5 cycles of HPWJ treatments. The characteristic crystalline structure of α-chitin and degree of relative crystallinity were maintained after a series of mechanical treatments. From UV-Vis spectra, grinder pretreatment improved transparency of chitin nanofiber slurry, indicating the pretreatment facilitated subsequent HPWJ mechanical disintegration. Viscosities of chitin nanofiber slurry also showed that the grinder pretreatment and HPWJ treatment disintegrated the chitin into nanofiber very well. However, excessive HPWJ treatment decreased nano-fiber length, resulting in lower viscosity.

Only a single grinder pretreatment could reduce the number of HPWJ treatments needed, which would decrease the production cost of chitin nanofiber. Thus, this easy procedure will enhance the commercial application of chitin nanofiber.

Preparation of chitosan nanofibers from completely deacetylated chitosan powder by a downsizing process

Chitosan nanofibers were easily prepared from fully deacetylated chitosan dry powder using a HPWJ system. From SEM observation, after 10 cycles of treatment, most of the chitosan had been reduced to homogeneous nanofibers measuring tens of nanometers. On the other hand, further mechanical treatment did not show a significant change. Relative crystallinity of chitosan nanofibers gradually decreased as the number of passes increased since HPWJ treatment damaged the crystalline region of chitosan nanofibers. The transmittance of the chitosan nanofiber slurry increased steeply, as the number of passes increased, indicating that the chitosan fibers were disintegrated effectively. Viscosity of chitosan nanofiber slurry also showed that the chitosan disintegrated well into nanofibers up to 10 passes. Above 10 passes, disintegration efficiency was saturated. The molecular weights of the nanofibers steeply decreased due to the depolymerization of chitosan by mechanical disintegration. The Young's modulus and tensile strength of chitosan nanofiber sheets were improved as the number of treatments increased, but further treatments deteriorated the tensile strength.

Preparation of chitin nanofibers by surface esterification of chitin with maleic anhydride and mechanical treatment

Maleated chitin nanofibers were easily prepared by surface esterification of α-chitin powder with maleic anhydride followed by 2 passes grinder treatment. The esterification with maleic anhydride significantly improved the mechanical disintegration of chitin into uniform 10 nm average thickness nanofibers. The nanofibers were homogeneously dispersed in basic water due to the carboxylate salt on the surface. Both the chemical and crystalline structure of the original chitin was maintained after the reaction, since esterification was proceeded on the surface. A cast film of the esterified chitin nanofibers was highly transparent, since the film was free from light scattering.

Protein/$CaCO_3$/chitin nanofiber complex prepared from crab shells by simple mechanical treatment and its effect on plant growth

A protein/$CaCO_3$/chitin nanofiber complex was prepared from crab shells by a simple mechanical treatment with a HPWJ system. The preparation process did not involve chemical treatments, such as removal of protein and calcium carbonate with sodium hydroxide and hydrochloric acid, respectively. Thus, it was economically and environmentally friendly. The nanofibers obtained had uniform width and dispersed homogeneously in water. The nanofibers were characterized in morphology, transparency, and viscosity. Results indicated that the shell was mostly disintegrated into nanofibers at above five cycles of the HPWJ system. The chemical structure of the nanofiber was maintained even after extensive mechanical treatments. Subsequently, the nanofiber complex was found to improve the growth of tomatoes in a hydroponics system, suggesting the mechanical treatments efficiently released minerals into the system. The homogeneous dispersion of the nanofiber complex enabled easier application as a fertilizer compared to the crab shell flakes.