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学 位 論 文 の 概 要 及 び 要 旨

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題　　目　Preparation of nanochitin by break-down and bottom-up approaches
（ブレイクダウンならびにボトムアップアプローチによるナノキチンの調製）

学位論文の概要及び要旨

Introduction

Chitin is the major component of crab and shrimp shells and is one of the most abundant polysaccharides found in nature. The structure is composed of (1,4) linked 2-acetamido-2-deoxy-β-D-glucopyranose repeating units. Most of the chitin resource was discarded as waste without any utilization. The chemical structure is similar to that of cellulose except for the replacement of C-2 hydroxy group by the acetamide functional group. The two hydroxy and acetamide functional groups of chitins significantly affect the chemical and physical properties. The hydrogen bonding limits the solubility of chitin in a common solvent. α-chitin from crab shells exists as hierarchically arranged nano-size fibers in an antiparallel fashion. Chitin can be processed into nanochitin using the processing technology of nanocellulose. Various biological functions of nanochitin were already clarified. For instance, wound healing, skin inflammation suppression, hair growth promotion, inflammatory bowel disease curing, anti-hepatic and antioxidative effects were reported. In this study, we have applied both the downsizing and bottom-up methods to prepare nanochitin. The produced nanochitin showed different morphology, crystallinity, and chemical properties compared to the conventional one. Thus, this experiment adds value in widening the characteristics of nanochitin and improves the industrial manufacturing process. More emphasis was given to the improvement of the technical, environmental, and economic feasibility of the industrial manufacturing process.

Optimum preparation conditions for highly individualized chitin nanofibers using ultrasonic generator

α-Chitin derived from crab shells was treated with 30% sodium hydroxide to prepare partially deacetylated chitin with a deacetylation degree of 36%. Partially deacetylated chitin nanofibers were prepared by applying weak ultrasonic energy generated by a domestic ultrasonic cleaner. The deacetylated chitin was easily disintegrated into nanofibers with the aid of electrostatic repulsion and osmotic pressure effect of amino cations on the chitin surfaces. The nanofibers were characterized in terms of yield, morphology, crystallinity, viscosity, and dispersibility. After a series of characterizations, ultrasonication with 45 kHz frequency and 20 min treatment was found to be the optimum conditions for obtaining fine nanofibers with a high yield.

Optimization of chitin nanofibers preparation by ball milling for fillers in composite resin

Chitin nanofiber is a nanomaterial produced by pulverizing chitin, the main component of crab shells. Since it has excellent mechanical properties, it is expected to be used as a reinforcing material to strengthen materials. Chitin was mechanically ground in water using a ball mill to prepare nanofibers. The ball size, total ball weight, and milling time were varied, and the resulting water dispersion and the cast film were analyzed to optimize the conditions for efficient preparation. The length and width of the nanofibers were also measured by SEM and AFM observations. The size of the balls affected the level of grinding and the intensity of impact energy on the chitin. The most efficient crushing was achieved when the diameter was 1 mm. The total ball weight directly affects the milling frequency, and milling proceeds as the total weight increases. However, if too many balls occupy the container, the grinding efficiency decreases. Therefore, a total ball weight of 300 g was optimal. Regarding the milling time, the chitin becomes finer depending on the increase of that time. However, after a specific time, the shape didn't change much. Therefore, a milling time of approximately 150 minutes was appropriate.

Production of chitin nanoparticles by bottom-up approach from alkaline chitin solution

Most of the series of nanochitins have been produced by the break-down process. In this study, chitin nanoparticles were prepared by a bottom-up process. Chitin was treated with sodium hydroxide to obtain an alkaline chitin aqueous solution. The alkaline chitin was regenerated by neutralization and then vigorously stirred to obtain chitin nanoparticles. The average particle size of the chitin nanoparticles was 7 nm. The individual particles were stably dispersed in water. Chitin nanoparticles had lower crystallinity than the raw material chitin and the surface of the chitin nanoparticles regenerated in water were presumed to be hydrophilic. The low crystallinity and the high hydrophilicity of the surface contributed to the high dispersibility of the chitin nanoparticles in water. Chitin nanoparticles had higher heat resistance than the raw material chitin, suggesting a large change in the higher-order structure associated with dissolution and subsequent regeneration of chitin. Since chitin nanoparticles interact with each other less than chitin nanofibers produced by mechanical treatment, the viscosity of nanoparticles was smaller than that of nanofibers. Therefore, it can be prepared at a high concentration. In addition, the chitin nanoparticles can be easily redispersed in water after being concentrated by centrifugation.

Preparation of partially deacetylated chitin nanoparticles by a bottom-up approach

Partially deacetylated chitin nanoparticles were prepared by using a bottom-up approach. For preparation, partially deacetylated chitin was dissolved in water as alkaline chitin and regenerated by neutralization to produce nanoparticles with a 28% deacetylation degree and an average particle size of 4 nm. The particles were homogeneously dispersed in water due to the positive charge on the surface and consisted of an amorphous structure, resulting in characteristic thermal behavior. The thin film was easily prepared by casting of nanoparticle dispersion and was optically transparent due to the smooth surface and densely packed amorphous structure.