Creation of Bio-Inspired Fiber Materials and Their Biodegradation

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Abstract

The new method for preparing hybrid fibers from aqueous solution is described. The method is based on interfacial polyionic complexation between the counter-charged polymers. Polysaccharides, chitosan and gellan, and polypeptides, poly(L-lysine) and poly(L-glutamic acid) were utilized as the components of the fibers. The chitosan-gellan and poly(L-lysine)-gellan hybrid fibers exhibited a high level biodegradability.

Introduction

The design of new bio-inspired materials is closely related to the interfacial phenomena in life [1]. The recent advances in the surface chem-istry of polypeptides and polysaccharides offer an insight into the material science, of which the strategy features mediation of water, like as nature does [2]. Thus, the biological surface events, including the interpolymer complexation and cross-linking reaction, have been the interplay between biopolymer chemistry and textile/fiber science.

We present here the simple and innovative principle for developing the new biological fiber materials, which is based on the self-assembling of two counter-charged natural polysaccharides and/or synthetic polypeptides (Fig. 1). The self-assembling is driven by the polyionic complexation, and the process occurs at interface between two aqueous solutions of cationic and anionic polymers. Using this principle, we have already reported the creation of the polycation-polyanion hybrid fibers by combinations of chitosan-gellan [3], poly(L-lysine)-gellan [4], chitosan-poly(L-glutamic acid) [5], poly(L-lysine)-poly(L-glutamic acid) [6], and chitosan-poly(acrylic acid) [7].

One of the current requisites in the application of fiber materials is the biodegradability. Naturally occurring polysaccharides and synthetic polypeptides possess an attractive potential as a biodegradable material. With respects to the environmental application, the biodegradation properties of the chitosan-gellan and the poly(L-lysine)-gellan hybrid fibers were examined using the soil filamentous fungi.

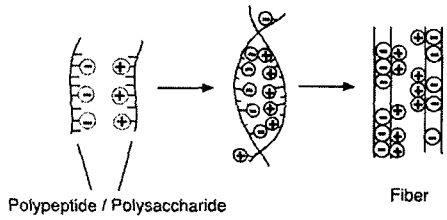

Fig. 1 Illustrative drawing of hybrid fiber formation by zipping up their counter-ions.

Experimental

Poly(L-lysine) (PLL) and poly(L-glutamic acid) (PLG) were synthesized via *N*-caboxyanhydride methods. Commercial chitosan and gellan were used. The details for spinning condition of each hybrid fiber have been reported in the corresponding references [3-7]. The spinning apparatus, the polymer compositions, and the spinning procedures were described in [8].

The biodegradation experiments were reported in the previous article [9]. The biodegradation percentage was calculated as follows,

$$\text{Degradation (\%)} = (BOD^t - BOD^b)/TOD \times 100$$

where BOD^t and BOD^b are the sample and blank data in biochemical oxygen demand (BOD) test, respectively. TOD is the theoretical oxygen demand, which was estimated from the total carbon contents of the fiber samples.

Results and Discussion

Preparation and Characterization of Hybrid Fibers

A fabric method via polyionic complexation is a unique strategy that realizes the formulation of hybrid fibers from their aqueous solutions. Our attempt at the development of new-type hybrid fibers is a kind of reactive spinning.

For example, a 0.75% gellan aqueous solution was slowly added to 1.0% chitosan in a diluted acetic acid/water solution at 60°C. Immediately chitosan and gellan spontaneously associated to form the transparent film at the interface between

the two polymer solutions. The transparent film was drawn by pincettes to spin a wet thread. The formed thread was passed through an ethanol bath, dried with hot air and rolled up.

The chitosan-gellan hybrid fiber was shown in Fig. 2. The chitosan-gellan fibers possess a silk-like luster. Long mono-filament fibers can be obtained.

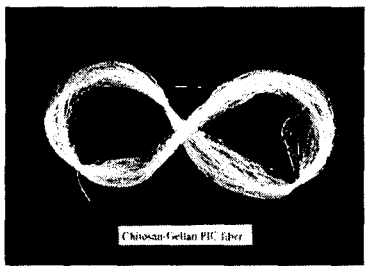

Fig. 2 chitosan-gellan hybrid fiber.

Biodegradation Properties

The degradation of two kinds of hybrid fibers, the chitosan-gellan and PLL-gellan fibers, by seven species of soil filamentous fungi has been investigated. All of the pure-cultured soil filamentous fungi, *Aspergillus oryzae*, *Penicillium caseicolum*, *P. citrinum*, *Mucor* sp., *Rhizopus* sp., *Curvularia* sp., and *Cladosporium* sp. grew on the chitosan-gellan and PLL-gellan hybrid fiber materials. These results indicate that the chitosan-gellan and PLL-gellan hybrid fibers have no toxicity towards the fungal growth.

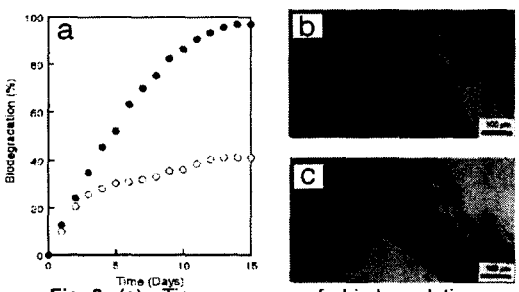

Fig. 3 (a) Time course of biodegradation percentage during the BOD tests of chitosan-gellan (open circles) and PLL-gellan (closed circles) hybrid fibers using *P. caseicolum*. (b) Before and (c) after biodegradation of PLL-gellan hybrid fiber.

In the BOD test, the biodegradation percentages of the PLL-gellan and the chitosan-gellan hybrid fibers by *P. caseicolum* exceeded 97% and 41% carbon dioxide evolution, respectively (Fig. 3a), after a 14-days cultivation. The biodegradation per-centage of the chitosan-gellan hybrid fiber by *A. oryzae* was 59%. Microscopic observations of the biodegradation processes revealed that *P. caseicolum* on PLL-gellan grew with the accom-panying collapse of the fiber matrices (Figs. 3b, c).

Conclusions

The characteristic features of the hybrid fibers are as follows: i) a simple operation for spinning, ii) low-cost media, iii) enhanced tensile and knot strengths due to cross-linking agents, iv) dyeing properties with many colors, v) environmental biodegradabilities.

More recently, we reported vi) the adsorption of anionic medicines and endocrine disruptors, vii) mechanical reinforcement by photochemical and enzymatic cross-linking reactions, and viii) improvement of spinning apparatus for mass-quantity production. The combinations of these characteristics further inspire the multipurpose applications of hybrid fibers.

Acknowledgement: This work was supported by Grants-in-aid for 21st Century COE Program and for Scientific Research (No 13555178, No 13556057) by the *Ministry of Education, Culture, Sports, Science and Technology of Japan.*

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