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CHEMICAL MODIFICATION AND SOME ALIGNED COMPOSITES OF CHITOSAN IN A FILAMENT STATE

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A silkworm spins a silk thread, in which a bundle of two pieces of silk fibroin filament is coated with sericin (Fig. 1), and builds a cocoon. The "raw-silk" threads are reeled off the several cocoons. Some blend filaments based on chitin [1] and chitosan [2] have been reported. However, little is known about the raw-silk-mimic threads based on chitosan with their chemical modification.

The present paper reports 1) the preparation of novel raw-silk-mimic threads based on chitosan, chitin, sericin and silk fibroin, 2) their chemical N-modification in filament and thread states from a view-point of their molecular organizations, and 3) some of their molecular and biological functions.

1. Mono-filaments

The mono-filament (N_o) of chitosan was wet-spun through a viscose-type spinneret (ϕ 0.1-mm), and chitin filament (N_2) was prepared by the N-acetylation of chitosan filaments. The long mono-filaments of chitosan-collagen, chitin-collagen and chitin-silk fibroin blends were prepared in the study [1](Table 1).

Table 1. Some long mono-filaments

Filaments	Titer (denier)	Tenacity (gf/denier)	Elongation (%)
Chitosan (N_oI)[a]	4.2	0.67	3.8
Chitin (N_2I)	3.1	0.87	6.9
Silk fibroin (FI)	1.3	2.54	7.2
Chitosan-collagen (87:13, w/w)	11.3	1.11	14.4
Chitin-silk fibroin (83:17, w/w)	9.7	0.67	4.2

[a] N_oI, one chitosan filament; N_2I, one chitin filament; FI, one silk fibroin filament.

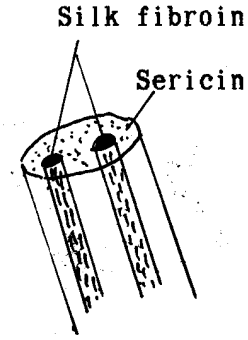

Fig. 1. A model Se(FII) for raw-silk-mimic threads

2. Raw-silk-mimic threads

The mono-filament of chitosan or chitin was aligned on a straight line with two (FII) silk fibroin filaments. A bundle of the aligned composite filaments was coated with chitosan, N-hexanoylchitosan (N_6), N-octanoylchitosan (N_8) or sericin (Se) to give rise to the present raw-silk-mimic threads [3] (Table 2). The thickness of the coating layers was controlled. The elongation (gf/denier) was at 0.67-0.87 for the original chitin and chitosan filaments, and at 0.67-2.46 for the composite threads. The softness of the original threads was decreased by coating the threads with chitosan.

Table 2. Some raw-silk-mimic threads

Threads[a]	Titer (denier)	Tenacity (gf/denier)	Elongation (%)	Filament contents(%)[b]
N_o(N_oI-FII)	87.7	2.31	17.0	8
N_o(N_2I-FII)	46.2	0.67	7.81	10
N_2(N_2I-FII)	37.1	0.92	9.14	10
N_8(N_2I-FII)	40.1	0.73	6.48	14
Se(N_oI-FII)	27.4	2.46	25.0	25
Se(N_2I-FII)	26.2	3.36	11.8	22

[a]N_o, chitosan; N_oI, one chitosan filament; FII, two silk fibroin filaments; N_2I, one chitin filament; N_8, N-octanoylchitosan; Se, sericin.
[b]Calculated on the basis of the titer values of the component filaments and thread.

3. Chemical modification in filament and thread states
Chitosan-collagen filament was N-acylated with acetic anhydrides but not with higher acid anhydrides. Chitosan filament was N-acylated with acetic to lauric anhydrides. The chitosan layer on the threads was N-modified with by treatment with each of carboxylic anhydrides, fragrant aldehydes and transition metal ions. Transition metal ions coordinated on the filaments of chitosan and chitosan-collagen blends. The metal coordination weaken their tenacity.

4. Molecular organization
The apparent density (denier/um in filament diameter) was at 0.49 for chitosan-collagen (1:1, w/w) blend filament, 0.42-0.45 for N_o(N_2I-FII), 0.40 for chitin-silk fibroin blend filament (67:33, w/w), and 0.14-0.18 for the filaments of cellulose (rayon), chitosan and chitin [4]. In the blend filaments, chitosan filament plays as a skeleton, and blend polymers fill in the porous space among chitosan filaments.

5. Some functions
Chitin and chitosan are ecologically and environmentally not only friendly but also functional[5]. 1) The threads exhibited a blood thrombogenic or antithrombogenic functions. 2) The thread underwear enhanced the lysozyme activity of the wearer's saliva and blood due to a stimulation of body immunity. 3) Transition metal ions coordinated on the chitosan layer over the threads, resulting in dyeing the threads in various colors.

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