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WET-SPINNING AND APPLICATIONS OF FUNCTIONAL FIBERS BASED ON CHITIN AND CHITOSAN

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SUMMARY: A series of novel human-made functional fibers (biofibers) based on chitin and chitosan are prepared by the wet-spinning and the post chemical modification of chitosan fiber. The wet-spinning gives rise to a series of biofibers: chitin, chitosan, chitin-cellulose, chitosan-cellulose, chitin-silk fibroin, chitin-glycosaminoglycans, chitin-cellulose-silk fibroin, chitosan-tropocollagen, and chitin-cellulose-silk fibroin. The post chemical modification of chitosan fiber gives rise to a series of chemically modified fibers: N-acylchitosans, N-arylidene- and N-alkylidene-chitosans, N-acetylchitosan (chitin)-tropocollagen, and chitosan-transition metal complexes. Some of the current and potential applications of these biofibers are described.

Introduction

Chitin is a linear (1→4)-linked N-acetyl-beta-D-glucosaminan, and chitosan is N-deacetyl derivatives of chitin. Both the polymers are structurally resemble to cellulose. Chitin has two hydroxyl groups at C3 and C6 in the repeating N-acetyl-D-glucosaminide residue, and chitosan has one amino group at C2 and two hydroxyl groups at C3 and C6 in the repeating D-glucosaminide residue. The chemical substitution of these groups with specific groups (Figure 1), which are easily removable under mild conditions. The molding products of chitin and chitosan including filaments, beads, hydrogel and films are artificially manufactured during the removal of these substituted groups.

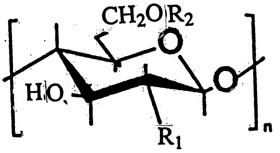

Figure 1. Chemical structures of the repeating residue of chitin and chitosan, and their derivatives appeared in the present article.

	R_1	R_2
Chitin	$-NHC(=O)CH_3$	-H
Chitosan	$-NH_2$	-H
Chitosan acetate	$-NH_3^{+}{}^{-}OC(=O)Me$	-H
Sodium chitin salt	-NHC(=O)Me	-Na
Sodium chitin xanthate	-NHC(=O)Me	-C(=S)SNa
Sodium N-propionylchitosan salt	-NHC(=O)CH2Me	-Na
N-Alkylidene and N-arylidene chitosan	-N=CHR	-H
Sodium cellulose xanthate	-OH	-C(=S)SNa

R: alkyl and aryl groups.

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The present paper aims to review, mainly on the basis of our works, some novel human-made biofibers based on chitin and chitosan, and their current and potential applications in biomedical, biotechnological and textile fields as an environmental and ecological friendly material [1-3].

Generating and regenerating functions

Chitosan (d.s. 0.10-0.12 for NAc) was prepared by chemical N-deacetylation of crab shell chitin, and chitin (N-acetylchitosan, d.s. 1.0 for NAc) was prepared by chemical N-acetylation of chitosan.

Chitosan is dissolved into an aqueous acetic acid solution as chitosan acetate (the generating reaction), and the solution is used as the dope for spinning. The chitosan acetate is treated in an aqueous alkaline solution as the coagulating solution to give rise to chitosan (the regenerating reaction). Chitin is soluble in an aqueous 14% NaOH solution as sodium chitin salt (alkaline chitin) (the generating reaction), and the solution was used as the dope for spinning. The alkaline chitin is treated with carbon disulfide to give rise to sodium chitin xanthate (the generating reaction), which is soluble in an aqueous 5% NaOH solution, and the solution was used as the dope for spinning. Both the chitin solutions are treated in an aqueous H_2SO_4 solution as a coagulation solution to give rise to chitin (the regenerating reaction). The regenerating reactions are performed through a viscose-type spinneret, and the corresponding biofilaments are produced.

Table 1. Some generating and regenerating reactions usable for the wet-spinning of chitin and chitosan fibers.

Reactions	Examples
$R\text{-}NH_2 \leftrightarrow R\text{-}NH_3^{+-}O(C{=}O)Me$	chitosan $\leftrightarrow$ chitosan acetate
$R\text{-}OH \leftrightarrow R\text{-}ONa$	N-acylchitosans $\leftrightarrow$ Sodium N-acylchitosan salts
$R\text{-}OH \leftrightarrow R\text{-}O\text{-}(C{=}S)SNa$	N-acylchitosans $\leftrightarrow$ sodium N-acylchitosan xanthates

[a]The generating ($\longrightarrow$) and regenerating ($\longleftarrow$) reactions.

The generating and regenerating reactions are summarized in Table 1. Both the reactions are usable for the molecular molding of chitin and chitosan into filaments, carving products, beads, hydrocolloids, hydrogels, hydrogels, sheets, membranes, microspheres, non-woven fabrics, polyelectrolyte capsules, sponges, tubes and threads.

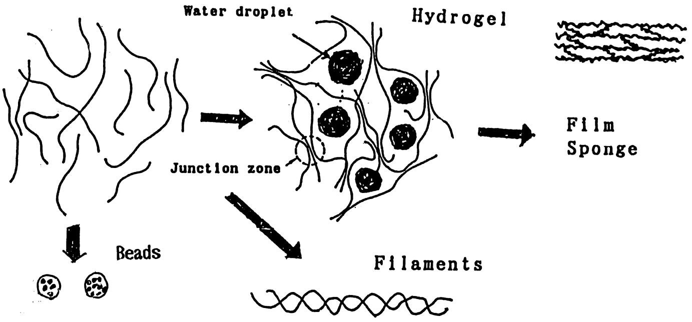

Figure 2. The molecular molding of chitin and chitosan into beads, hydrogels, filaments, sponges and films.

Wet-spinning

A fundamental wet-spinning unit consists of a viscose-type spinneret (0.10 mm in hole diameter), a dope (the derivative or the blends dissolved in the spinning solution), a coagulation bath containing a coagulating solution, and rollers for the winding, drawing and drying of filaments (Figure 3). Each solution of chitosan and chitin in the spinning solution (dope) is spun through the spinneret into the coagulation bath to afford filaments. The filament structure is controlled by the hole size and hole shape of the spinneret and by the post treatments.

The spinning and coagulating solutions are shown in Table 2. After stretching up to 1.4 folds, the filaments are soaked in the corresponding coagulating solution at room temperature overnight, washed with water and methanol, and then air-dried. The solution of sodium chitin salt (alkaline chitin) in aqueous 14% NaOH is usable as the dope, and no harmful carbon disulfide (CS_2) is used in the present method.

Based on the filament constituents, the fibers are classified into a) monoconstituent, b) biconstituent and c) multiconstitutent filaments (Table 3).

Table 2. Spinning and coagulating solutions for the wet-spinning of biofilaments based on chitin and chitosan.

Methods	Spinning solution	Coagulating solution
A	aq. 2% acetic acid	aq. 10% NaOH & 30% Na_2SO_4
A-2	aq. 2% acetic acid	aq. 10% NaOH & 40-43% $(NH_4)_2SO_4$
A-3	aq. 2% acetic acid-MeOH	aq. ca. 5% ammonia & 40-43% $(NH_4)_2SO_4$
A-4	aq. 2% acetic acid-MeOH	aq. 10% NaOH & 30% Na_2SO_4
B	aq. 14% NaOH	aq. 10% H_2SO_4, 32% Na_2SO_4 & 1.3% $ZnSO_4$
B-2	aq. 14% NaOH	aq. 10% H_2SO_4, 40-43% $(NH_4)_2SO_4$
C	aq. 5% NaOH	aq. 10% H_2SO_4 & 25% Na_2SO_4
C-2	aq. 5% NaOH	aq. 10% H_2SO_4 & 40-43% $(NH_4)_2SO_4$
D	Post chemical modification at the fiber state	

Post chemical modification

The post chemical modification of chitosan fiber is carried out by treating with carboxylic anhydrides or aldehydes in methanol, and with transitional metals in water. Amino groups of chitosan are easily N-substituted at the fiber state. The N-substitution reaction occurs not only on the fiber surface but also the fiber inside. The d.s. value for the N-substituents is in the range of 0.7-0.9 per GlcN. The post chemical modification gives rise to a series of N-acylchitosan fibers including N-acetyl, N-propionyl, N-butyryl, N-hexanoyl, N-succinyl, N-(1'-carboxypropionyl), N-(4'-hydroxy-3'-methoxybenzylidene), N-methylene, N-formylmethylene and N-benzylidene fibres. The N-(1'-carboxypropionyl)chitosan fiber, which has hydrophilic carboxyl groups, is soluble in water, but the other N-substituted fibers are insoluble in water. A cross-linked chitosan fiber is also prepared by treatment of chitosan fiber with epichlorohydrin. Chitosan fiber is produced by chemical N-deacetylation of chitin fiber, and the produced chitosan fiber has a relatively weak mechanical strength than the directly wet-spun chitosan fiber. Chitin fiber is also regenerated by the O-deacylation of dry-spun O-dibutyrylchitin fiber. N-Acylchitosan fibers are partially modified with O-alkyl, O-aryl, O-acyl and O-phosphoryl groups.

Table 3. Some human-made biofibers

Biofibers	Derivatives used in the dope	Method[a]
Monoconstituent fibers		
Chitosan	chitosan acetate	A, A-2, A-3
Chitin	a)sodium chitin salt	B, B-2
	b)sodium chitin xanthate	C, C-2
N-Propionylchitosan	a)sodium N-propionylchitosan salt	B
	b)sodium N-propionylchitosan xanthate	C
N-Butyrylchitosan	chitosan fiber	D
N-Propionylchitosan	chitosan fiber	D
N-Pentanoylchitosan	chitosan fiber	D
N-Hexanoylchitosan	chitosan fiber	D
N-Octanoylchitosan	chitosan fiber	D
N-Decanoylchitosan	chitosan fiber	D
N-Lauroylchitosan	chitosan fiber	D
N-(1'-Carboxypropionyl)chitosan	chitosan fiber	D
(N-succinylchitosan)		D
N-(4'-Hydroxy-3'-methoxybenzylidene)chitosan	chitosan fiber	D
N-Methylenechitosan	chitosan fiber	D
N-Formylmethylenechitosan	chitosan fiber	D
N-Benzylidenechitosan	chitosan fiber	D
Transition metal cation-chitosans[a]	chitosan fiber	D
Biconstituent-blended fibers		
Chitosan-tropocollagen	chitosan acetate-collagen	A-2, A-3
Chitin-tropocollagen	chitosan-tropocollagen fiber	D
Chitosan-silk fibroin	chitosan acetate-silk fibroin	A-2, A-3
Chitin-cellulose	a)sodium chitin xanthate-sodium cellulose xanthate	B
	b)sodium chitin salt-sodium cellulose xanthate	B
N-Propionylchitosan-cellulose	sodium N-propionylchitosan xanthate-sodium cellulose xanthate	C
	sodium N-propionylchitosan salt-sodium cellulose xanthate	B
Chitin-silk fibroin	sodium chitin xanthate-silk fibroin	C-2
N-Propionylchitosan-silk fibroin	sodium N-propionylchitosan xanthate-silk fibroin	C-2
Chitin-hyaluronate	sodium chitin salt-hyaluronate	B-2
Chitin-heparin	sodium chitin salt-heparin	B-2
Chitin-chondroitin 4-sulfate	sodium chitin salt-Ch4S	B-2
Chitin-chondroitin 6-sulfate	sodium chitin salt-Ch6S	B-2
Cellulose-silk fibroin	sodium cellulose xanthate-silk fibroin	C-2
Cellulose-hyaluronate	sodium cellulose xanthate-hyaluronate	C-2
Cellulose-heparin	sodium cellulose xanthate-heparin	C-2
Cellulose-chondroitin 4-sulfate	sodium cellulose xanthate-Ch4S	C-2
Cellulose-chondroitin 6-sulfate	sodium cellulose xanthate-Ch6S	C-2
Triconstitutent-blended fiber		
Chitin-cellulose-silk fibroin	sodium chitin xanthate-sodium cellulose xanthate-silk fibroin	C-2
N-Propionylchitosan-cellulose-silk fibroin	sodium N-propionylchitosan xanthate-sodium cellulose xanthate-silk fibroin	C-2

[a] Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mo^{2+}, Cd^{2+} and UO^{2+}.

Biofibers based on chitin and chitosan

The direct wet-spinning method gives rise to chitin, chitosan, chitin-cellulose [4-6], chitosan-cellulose [7], chitin-silk fibroin [8], chitin-glycosaminoglycans (heparin, hyaluronate etc.)[9] chitin-cellulose-silk fibroin, chitosan-tropocollagen [10] and chitin-cellulose-silk fibroin. The post chemical modification gives rise to a series of N-acylchitosans (N-octanoyl, N-hexanoyl etc.) fibers [5.11], N-arylidene- and N-alkylidene-chitosans (N-methylene, N-4-hydroxy-3-methoxybenzylidene (Vanillin) etc.) fibers [12], chitin-tropocollagen [10] and chitosan-transition metal ions complex (Cu^{2+}, Fe^{2+} etc.) fibers (Table 3).

Table 4. Mechanical properties of some biofilaments based on chitin and chitosan.

Filament (% in constituents)	Preparation method	Titer (denier)	Tenacity (g/denier)	Elongation (%)
Chitin	B	3.75-7.89	1.15-1.25	3.6-8.4
Chitosan	A	4.50	1.29	8.2-10.4
N-Acetylchitosan	B	4.35	0.87	6.9
	D	3.08	1.30	11.2
N-Propionylchitosan	B	3.40	0.78	4.9
	D	4.71	0.58	25.9
N-Butyrylchitosan	D	3.22	0.78	15.9
N-Hexanoylchitosan	D	4.30	0.58	15.2
N-(1'-carboxypropionyl)chitosan	D	5.96	0.71	8.0
Chitosan-tropocollagen	A-3			
(90:10)		11.3	1.11	14.4
(70:30)		16.3	1.08	15.7
(50:50)		17.7	1.15	10.9
Chitin-silk fibroin				
(83:17)		9.70	0.67	4.2
(94:6)		3.24	1.05	8.4
Chitin-hyaluronate				
(68:32)		9.90	0.69	8.6
(91:9)		5.87	0.36	7.5
Chitin-heparin				
(78:22)		4.87	0.48	6.7
(91:9)		4.54	0.36	7.2
Chitin-chondroitin 6-sulfate				
(76:24)		6.75	0.37	7.8
(92:8)		5.45	0.31	5.9
Chitin-cellulose				
(62:38)	B	5.32	0.18	4.8
(43:57)	B	6.96	0.26	4.5
(28:72)	B	3.62	0.53	19.1
N-Propionylchitosan-cellulose				
(61:39)	B	2.00	0.76	21.0
(49:51)	B	2.79	1.10	22.6
Cellulose	C	5.01	1.10	54.7

Titer, tenacity and elongation values of the biofilaments prepared under the present conditions are summarized in Table 4. The chitin and chitosan filaments are generally weaker than "Rayon" (regenerated cellulose) in the mechanical strength[13]. With an increase in the carbon number of N-acyl group for the N-acyl derivatives of chitosan fiber, the elongation value increases due to the increase of their hydrophobic interaction, but the tenacity value decreased probably due to the disordering of fibril orientation in the filament. The N-acylchitosan filaments prepared from sodium N-acylchitosan salt have higher tenacity and higher elongation values then those prepared from sodium N-acylchitosan xanthates. The N-acylchitosan filaments are regenerated more smoothly from sodium N-acylchitosan salts than their xanthates. The fibril orientation is disordered by cross-linking with the Schiff's base, resulting in the formation of mechanically weak filaments.

Scanning electron microscopic (SEM) observation

A scaly structure is observed with the surface of the chitosan filament, but this structure disappears on the post chemical N-acylation (Figure 3). A smooth structure appears on the surface of chitosan-tropocollagen, chitosan-silk fibroin and chitin-heparin filaments. The filament diameter as examined by SEM observation and the titer value (denier) for the biconstituent filaments are generally larger than those of the monoconstituent filaments, resulting in the higher filament densities for the biconstituent filaments than those for the monoconstituent filaments.

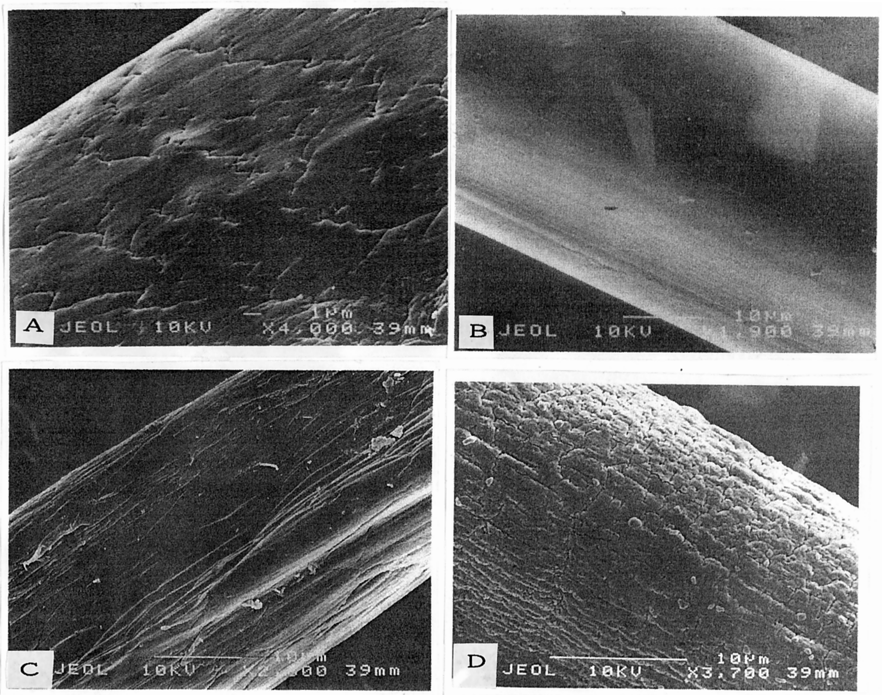

Figure 3. A scanning electron microscopic (SEM) observation on the surface structure of some biofilaments.
A, Chitosan; B, chitosan-tropocollagen; C, N-octanoylchitosan; D, chitin-silk fibroin.

Current and potential applications

The biofibers based on chitin and chitosan have various functions including antithrombogenic, anti-microbial, biocompatible, biodegradable, cell-eliciting, hemostatic, metal-chelating, metal ions-complex, molecular affinity, polyelectrolyte-forming and wound-healing. Those fibers are usable as ecological and environmental friendly materials in agricultural, air-cleaning, medical (digestible sutures, wound-dressings *etc*.), cosmetic (for the slow releasing of perfumes), functional textile, and house interior (for removing formaldehyde) fields [14].

a) Medical and biotechnological materials

N-Hexanoyl and *N*-octanoylchitosan fibers are antithrombogenic, blood compatible [15,16] and resistant to chitinase and lysozyme hydrolyses (Table 5), and are usable as an antithrombogenic biomaterial. Chitosan fiber is hemostatic [17], and is usable as hemostatic and antibacterial materials. Both the fibers are being used as a wound-healing dressing material (artificial skin) for not only human beings and animals but also plants [19-21]. Anionic groups present on the cell surface of pathogenic microorganisms react with the cationic groups of chitosan, resulting in the inhibition of their growth. The growth of *E. coli* is inhibited even at a low concentration of 0.025% chitosan. These functions also effect on the acceleration of wound-tissue healing in animals and plants. A crystal growth of calcium phosphate is stimulated on partially phosphorylated chitin fibers, and the tendon formation is stimulated by implantation of non-woven fabrics into animal tissues [22].

N-Acylchitosan filaments (about 5 um in each diameter) are bundled up into 16-20 filaments, and the bundles are braided, rinsed, coated with a surfactant, attached to a needle, and sterilized with ethylene oxide to produce an *N*-acylchitosan surgical suture [18]. The *N*-acylchitosan suture is digested by lysozyme in the tissue, and the digestion period is controlled by the chemical structure of *N*-acyl groups (Table 5) and their degree of substituents. Their hydrolyzed products (chito-oligosaccharides) enhance macrophages in the tissues, and the wound healing is accelerated. It is not necessary to take out the stitches after the operation.

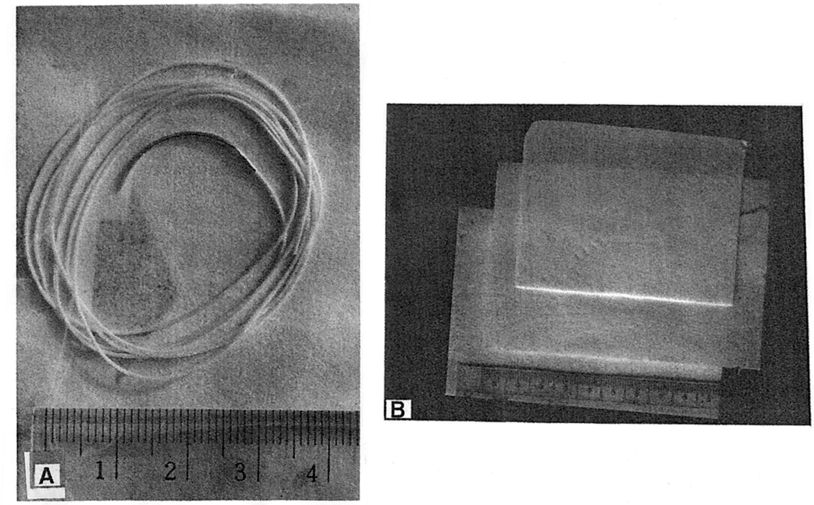

Figure 4. An absorbable chitin suture and a dressing of chitosan-tropocollagen blends for the clinical use.

Their staple fibers are allowed to mix with natural cotton at the fiber state to give rise to various medical suppliers including sanitary cottons, gauzes, bandages, plasters, sanitary pads and cotton swabs.

Table 5. The *in vitro* digestibility of *N*-acylchitosan fibers by lysozyme and chitinase.

Fiber	Increase in reducing sugar value^a	
	Lysozyme (μmol/5h)	Chitinase (μmol/2h)
N-Acetylchitosan fiber	2.44	2.09
N-Propionylchitosan fiber	0.34	0.21
N-Hexanoylchitosan fiber	0.00	0.00
Natural crab shell chitin^b	0.23	0.19

^{a}Expressed as μmole of *N*-acetyl-D-glucosamine.
^{b}Powdered into 100-200 mesh.

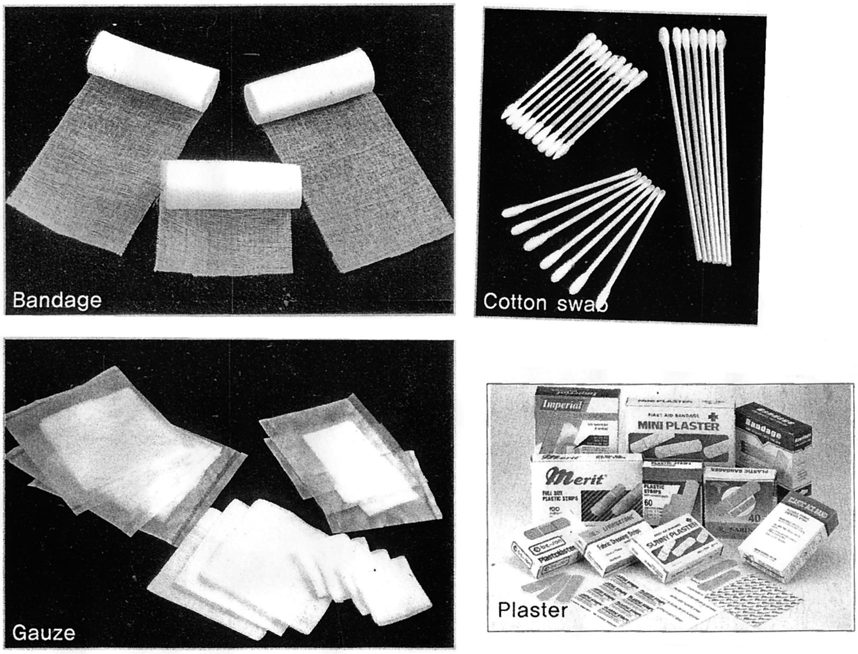

Figure 5. Some medical suppliers manufactured from chitosan fiber.

b) Textile materials

Chitin and chitosan fibers have various functions including non-allergenic, deodorizing, antibacterial, perfume-releasing, and moisture-controlling. Some body care products for sick persons and babies are commercializing, and chitosan-transition metal ion complex fibers are usable as a shielding material for radiations and electromagnetic waves. Chitin-cellulose (Rayon) blend fibers ("Crabyon") have been commercialized as a functional textile material for underwear, sportswear, towels, socks, and non-woven fabrics (Figure 9).

c) Industrial materials Chitosan forms its polyelectrolyte complexes with anionic polymers [23] and its metal ion complexes with transition metal ions. These functions have been used for the waste-water treatment, and for the collection of rare metal ions [24] and proteins. Chitosan fiber is also usable as air- and water-filters.

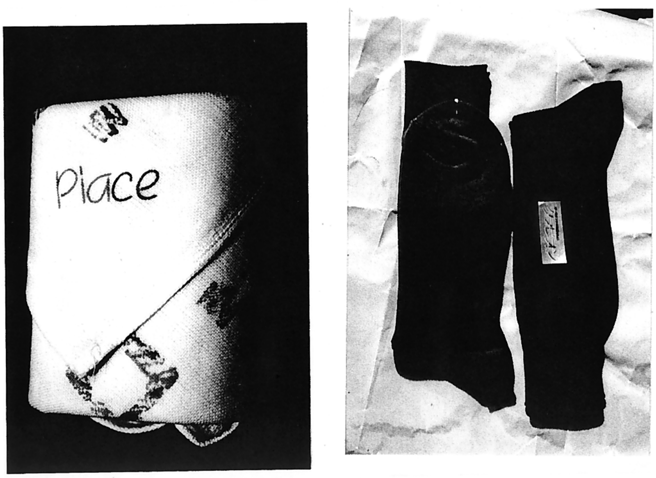

Figure 6. Bath towels and socks manufactured from "Crabyon".

Future prospects

An estimated amount of 1x10^4 tons of chitin is biosynthesized annually on the earth, and is biodegraded at at the same time. These biopolymers are ecological and environmental friendly for all the livings on the earth [25-29]. These biopolymers are circulating in the hydro-, litho- and bio-spheres on the earth. The balanced circulation of chitin and chitosan in these spheres is of importance. We should not disorder the circulation by an excess harvest of chitin and chitosan.

Several tasks for the chemical molecular molding of chitin and chitosan are as followings: 1) The first one is to establish a novel biomimetic template method for the preparation of the parallel oriented fibrils (beta-chitin), as recently demonstrated in "a chitosan-induced conformational transition of silk-fibroin" [30]. 2) The second one is to prepare the biomimetic composite materials based on chitin and chitosan such as crab and shrimp shells, and insect cuticles. 3) The third one is to prepare new artificial intelligent materials which have mechanical movements [31], magnetic functions [32], shape-memorizing, and novel biological functions.

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