

Functional Hybrid Fibers of Cellulose/Microcrystalline Chitosan. I. Manufacture of Viscose/Microcrystalline Chitosan Fibers

PERTTI NOUSIAINEN,¹ MARIANNA VEHVILÄINEN,¹ HENRYK STRUSZCZYK,² ELINA MÄKINEN¹

¹ Tampere University of Technology, Institute of Fiber, Textile and Clothing Science, Korkeakoulunkatu 2, FIN-33720 Tampere, Finland

² The Institute of Chemical Fibres, Institute of Chemical Fibres, Sklodowska-Curie 19/27, 90570 Lodz, Poland

ABSTRACT: Blends of microcrystalline chitosan (MCCh) with cellulose xanthate alkaline solutions were prepared to investigate the effects of aqueous MCCh gel concentration and additives on the spinnability of hybrid cellulose/chitosan fibers and their properties. The properties of the spinning solution were mainly dependent on the concentration of MCCh in the aqueous gel-like dispersion and the amount mixed into the cellulose xanthate solution. Sodium alginate chemically close to cellulose and chitosan was used as an additive to improve the miscibility of chitosan due to the ionic bonds formed with chitosan 2-amino groups. Using an optimized ratio of 2 : 1 of MCCh to the sodium alginate, a maximum of 6% of MCCh calculated from alpha-cellulose content could be introduced into the sodium xanthate solution containing originally 9% of alpha-cellulose. The yield of MCCh in the resulting fibers was dependent on the molecular mass, and varied between 73–82%. The strength, elongation, and color of the resulting hybrid fibers were only slightly changed and the WRV remarkably increased compared to standard fibers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1725–1730, 2000

INTRODUCTION

Hybrid polymers represent blends of materials of chemical and physical similarity, where molecular secondary bonds such as hydrogen and van der Waals result in increased adhesion, which actually is close to molecular cohesion forces of a homogeneous compound. Thus, in the manufacture of viscose and regenerated cellulose fibers, the highest effect could be obtained by forming hybrids of cellulose with other polymeric carbohydrates, preferably with anhydroglucosic compounds.

Chitin, poly(*N*-acetyl-2-amino-2-deoxy- β -D-glucopyranose), is a naturally occurring renewable polymer, one of most abundant in nature. Several

billion tons of this polysaccharide are produced annually, mainly by shellfish.^{1,2} Chitosan, poly(2-amino-2-deoxy- β -D-glucopyranose) is produced industrially from chitin by an alkaline dehydrolyzing method from shellfish in the United States, Japan, and Europe.^{1–5} Due to the direct amine salt formation ability and chemical reactivity, several derivatives of chitosan have been investigated to develop its functional properties further.

Chitosan, when regarded as a cellulose derivative substituted at the C2 carbon by the *N*-acetylamine group with a deacetylation degree of at least 70%, shows the structure and properties very close to cellulose; however, the effect of one amine group is very important in biological systems caused by the reactivity and hydrogen bond formation ability.⁶ It has been found to be very attractive in the wound-healing process shown by human clinical tests.^{7–9} Chitosan, in contact with red cell membranes, forms a hemostatic coagulum

Correspondence to: P. Nousiainen.

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that withstands arterial pressure in vascular grafts and leads to growth of a vascularized smooth muscle vessel wall with an endothelial intima. When chitosan is used to treat various tissues, it results in the inhibition of fibroplasma and the regeneration of normal tissue elements. On the promise that the availability of abundant lysozyme at the wound site would gradually degrade chitosan to the active movable *N*-acetyl-2-amino-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glucopyranose oligomers, the sustained release of these compounds provides a long-lasting action.^{8,9}

Chitosan does not dissolve in inorganic acids excluding HCl and HNO₃, and dissolves with ease in dilute organic noncorrosive aqueous acids such as formic, acetic, lactic, propionic, and tartaric acids. Fibers and films obtained from acetic acid aqueous solutions exhibited breaking strengths of 3.81 g/den (4.1 cN/dtex), and 261 Mpa, respectively.¹⁰ Stronger fibers can be manufactured from chitosan derivatives, especially from liquid crystalline solutions of esters. Although fiber tenacities are excellent in the dry state, as high as 7.1 g/den (7.7 cN/dtex), a 10-fold loss of wet tensile strength was obtained.

Standard chitosan powder has been used as an additive in polynosic fibers resulting in a moderate decrease of tensile strength and an increased antibacterial function against *S. aureus*.¹¹ A blend of chitosan and viscose rayon film has been investigated by regenerating NaOH solution of the xanthogenated blend of chitosan and dissolving pulp, including optimum conditions for phase behavior.¹² DSC and DMA are a characterization of the suggested partial compatibility of chitosan with viscose, which could be further improved by the addition of carboxymethylated chitosan into the blend. The phase behavior of chitosan with various polyamide blend films from formic acid have shown partial miscibility with nylon-4, followed by the increase of mechanical properties and relative water contents.¹³ The investigations of calcium alginate–chitosan beads, containing insulin, showed a possibility of providing an excellent gastrointestinal delivery system for insulin.¹⁴

Microcrystalline chitosan (MCCh) as a novel material type reveals a high superiority with many properties in comparison with standard chitosan, for example, in respect to the ability for powerful hydrogen bond formation, water-retention value, direct film forming from the gel, controlled bioactivity, and high metal chelating abil-

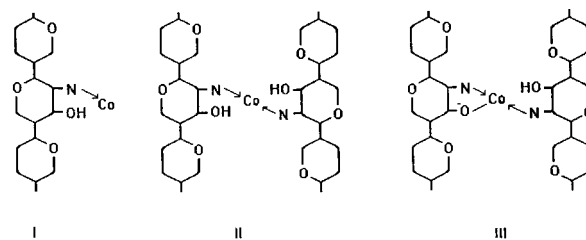


Figure 1 The schematic structure of chitosan and the mechanisms of chelate forming.

ity.^{8,9,15} (Fig. 1). The specific properties of MCCh result from the careful crystallizing by alkali from an acidic solution to recombine molecular chains. Supermolecular structure followed by new combinations of free electron pairs of hydroxyl and amine groups is more accessible to form coordinative bonds in *N*-acetylamine, amine, and hydroxyl groups in the polymer chain.

Although showing direct film-forming properties, the tenacity of MCCh film is lower than 100 MPa due to the lack of orientation of polymer chains, and no strong fibers can be obtained either. However, the possibility of mixing of MCCh with aqueous alkaline polymer solutions for spinning solutions offers a technology for manufacturing multifunctional cellulose fibers, especially using the viscose method.^{16,17} Multifunctional hybrid fibers could be tailored for hygienic nonwoven products, liquid filters for metals and organic substances, and for medical textiles. In earlier trials no success was achieved when mixing 3–6% of MCCh alone in gel form with viscose.

The first objective of this study was to develop a dope addition method for the cellulose xanthate alkaline solution and laboratory scale spinning of the hybrid viscose MCCh fibers by regeneration into a sulphuric acid spinning bath. The second objective of the study was to estimate principal properties and structure of the fibers obtained including strength, elongation, and water-retention values.

MATERIALS AND METHODS

Microcrystalline chitosan samples (MCCh) were obtained from Novasso Oy, Tampere, Finland, in the form of gelatinous water dispersion. The average molecular mass of MCCh was between 0.68–2.83 $\times 10^5$ Daltons, water-retention value (WRV) between 640–1450%, deacetylation degree (DAD) of 71%, and concentration of 3.2%. The

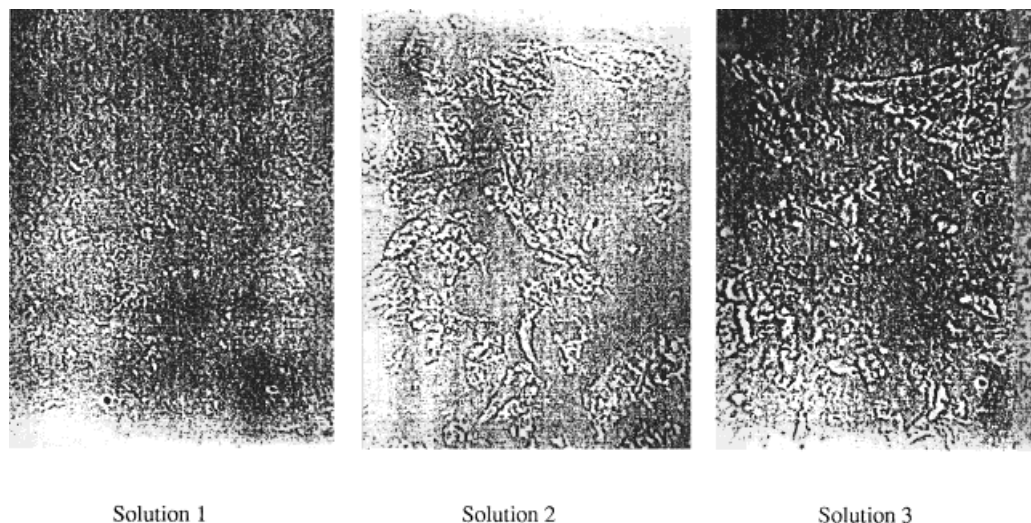


Figure 2 Microscope photographs of MCCCh-viscose spinning solutions with sodium alginate (magn. 160).

particle-size distribution of MCCCh gel was quite large ranging from $50\ \mu\text{m}$ to $3\ \mu\text{m}$, the maximum being at $18\ \mu\text{m}$. Thus, the spinneret of $100\ \mu\text{m}$ was selected for this preliminary study. Sodium alginate viscous solution of 5% by solid content was obtained from Sigma Co., St. Louis, MO.

Ripened sodium cellulose xanthate (viscose) solution for spinning was obtained from Säteri Oy (formerly Kemira Fibres Oy). The raw material was Eucalyptus sulphite (Saiccor) dissolving pulp, alpha-cellulose content of viscose was 9.0%, NaOH of 5.7%, ripeness of 4.5 H, and viscosity of 5.5 Pa s.

MCCCh gel and sodium alginate were mixed in the ratio of 2 : 1 and added into the viscose. The solution was homogenized and deaerated prior to spinning. The fibers were spun using a laboratory wet spinning machine. A coagulation bath contained 90 g/L sulphuric acid, specific gravity was 1.276 g/L, zinc content 22 g/L, and temperature 43°C also containing a minor amount of normal spin bath additive, Berol Spin 644. The spinning line consisted of the pump, capacity 0.3 mL/revolution, spinneret $36 \times 100\ \mu\text{m}$, three godets, one regeneration bath, two washing baths, and a fiber collector. The drawing ratio varied from 1.48 to 1.71 for the MCCCh/viscose samples. One reference spinning without MCCCh was also done. The spinning parameters were as above, and the drawing ratio was 2. After spinning, the hybrid fibers were dried, conditioned at 65% R.H./ 20°C for 24 h, and subjected to titer, tensile strength, elongation, and water-retention value measurements using standard methods.

RESULTS AND DISCUSSION

The MCCCh-viscose spinning solutions were studied under the light microscope after deaeration. Clearly, a smaller number of large particles were detected in spinning solutions containing alginate compared with the reference sample. Some large particles still could be detected originating from the MCCCh raw material (Fig. 2). The dispersive action of sodium alginate can be explained by the attachment of carboxylate anions of the alginate on the protonated amine groups of MCCCh followed by the formation of polymeric quarternary salts. Thus, the further formation of hydrogen bonds and increasing of the particle size is hindered (Fig. 3). In the sulphuric acid spinning bath the alginate forms the water-soluble polycarboxylic acid again, but the chitosan remains insoluble due to the insolubility in sulphuric acid. The presence of zinc in the spinning bath to form chelates with MCCCh is not probable because of the high acidity (<2.5), which causes a blocking of nitrogen, which is in main role in zinc-chitosan chelate formation.¹⁵

Despite the large particle size of the MCCCh gel, the spinning process could be carried out for a rather long time to produce fibers for further research. Taking into account the low efficiency and shear rate of the mixer used, there are further possibilities to manufacture MCCCh with smaller particle size and its distribution. A most important stage is, however, the production of MCCCh and the regulation of chitosan particle size formation during the nucleation process.

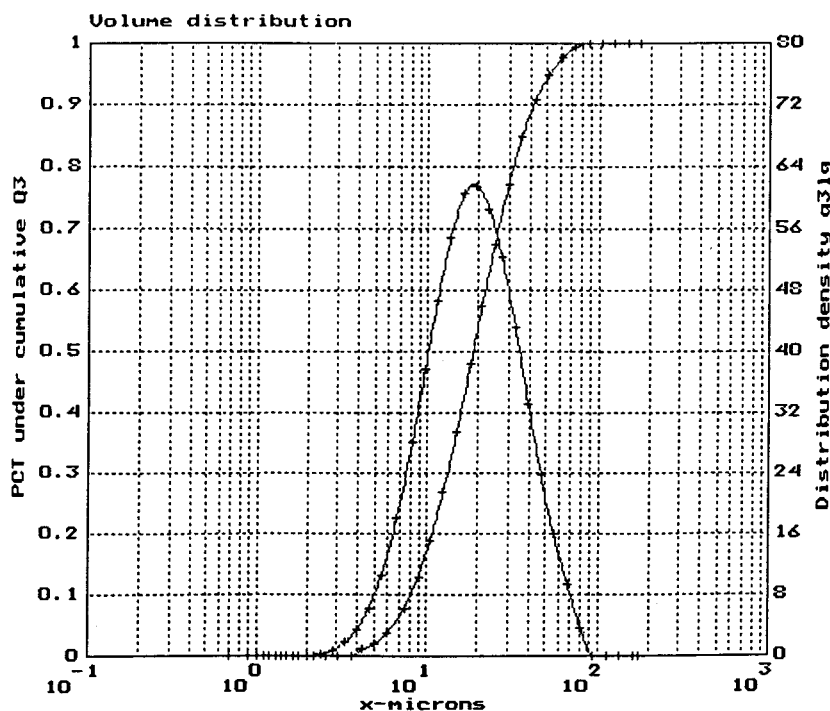


Figure 3 Particle size distribution curve of viscose-MCCh spinning solution after deaeration of 24 h.

The spinning process was not optimized (spinning speed, drawing, desulphurization, finishing) with regard to obtaining the highest possible tenacity of viscose fibers, because the main purpose was to study the behavior of the viscose-MCCh blend. The titer of hybrid fibers was higher (11–74%) than calculated in each trial, as can be seen from Table I. Accordingly, a decrease (7–16%) of the fiber tenacity was obtained, depending on the molecular mass of the starting MCCh additive. In the case of higher molecular masses, the loss of tenacity was higher compared with the fiber containing MCCh of a molecular mass of 68,000.

Determinations of nitrogen by the Kjeldahl method of various fibers showed ranges of 0.30–0.34%, which results in the MCCh content of 4.93–4.35% and yields of 82–73%, respectively. Thus, there seems to be a larger washout effect when using a smaller molecular mass of MCCh. The determination accuracy of nitrogen by the Kjeldahl method was not very high in this case ($\pm 5\%$), and further studies to determine the yields are necessary.

The photographs of fiber cross-sections under an optical microscope show that MCCh is homogeneously precipitated and blended with viscose

to form the hybrid fiber, as seen in Figure 2. The water-retention values are varied in the case of the standard viscose samples between 120–125%, and for the hybrid fiber samples at 132–139%, which possibly can be explained by the increased porosity and hydrogen-bonding capability of the blends. Thus, there is an important effect on increased water uptake; however, due to the specific conditions in fiber spinning the exact effect must be investigated in real production conditions.

CONCLUSIONS

Microcrystalline chitosan (MCCh) has proved to be a new potential additive in neutral and alkaline spinning solutions for manufacturing multifunctional hybrid fibers. It shows a superiority of functional properties as an additive in comparison with initial chitosan due to the high hydrogen bonding and increased accessibility, especially in controlled bioactivity and high metal chelating ability.

Because the usual viscose wet spinning process is not possible by mixing 3–6% of MCCh with the viscose solution due to the particle flocculation on the spinneret, a new method of manufacturing a viscose-MCCh spinning solution by using sodium

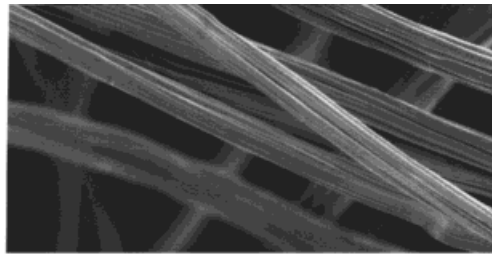
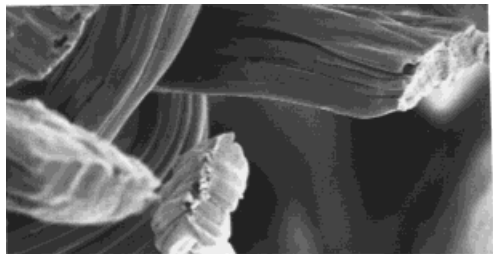


Figure 4 a. Reference viscose fibers

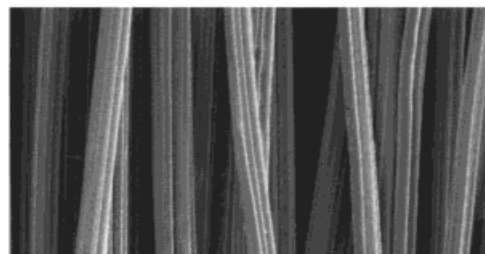
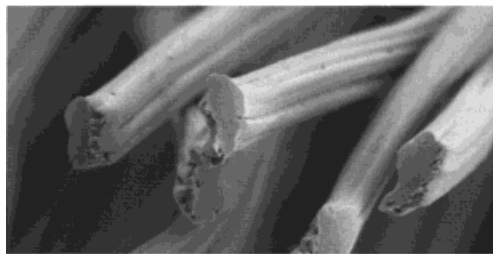


Figure 4b. Viscose-MCCh-fibers, sample 1.

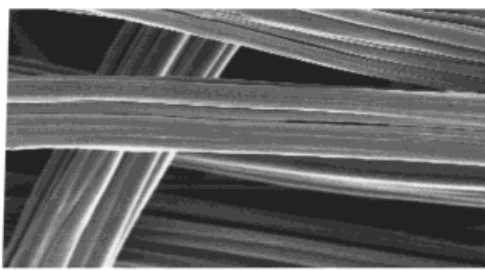
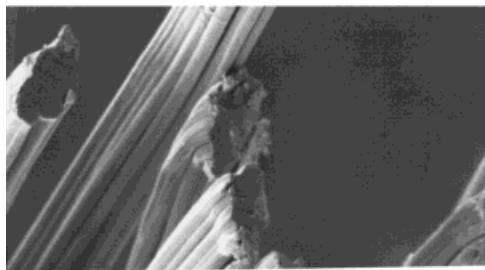


Figure 4c. Viscose-MCCh fibers, sample 2.

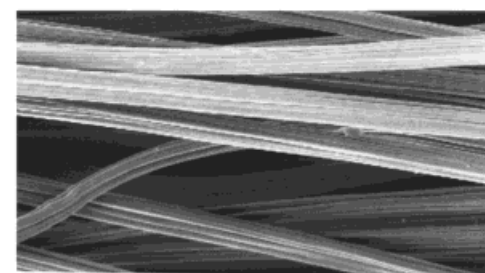
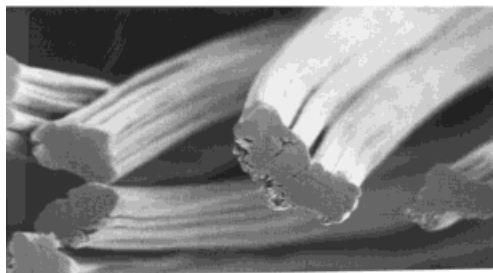


Figure 4d. Viscose-MCCh fibers, sample 3.

Figure 4 Scanning electron microscope photographs of reference viscose fibers (a) and MCCh-viscose fibers of various molecular mass of MCCh: 2.83 MD (b); 2.03 MD (c); 0.68 MD (d), respectively, to samples 1–3 in Table I.

alginate as a dispersing additive was developed. The resulting hybrid fibers showed a normal appearance, slightly reduced tenacity, increased water retention value, titer, and elongation compared

to standard viscose fibers. The yield of MCCh in the fibers was 73–82%, and contents of 4–5% of dry weight could be achieved showing homogeneous distribution in the cross-section's final fibers.

Table I Properties of Viscose-MCCh Spinning Solutions and the Obtained Hybrid Fibers

No.	Spinning Solution (g)	α -Cellulose (%)	MCCh MW $\times 10^5$ (%)	MCCh of α	Na-Alginate (%)	Strength (cN/dtex)	Elongation (%)	Water Retention Value (%)	Titer (dtex)	
Ref.	1000	9.0	—	0	0	1.39	15.30	123	2.95	
1	1165	7.72	2.83	0.46	5.96	0.23	1.17	18.20	132	3.27
2	1179	7.56	2.07	0.46	6.08	0.23	1.30	18.11	134	5.15
3	1145	7.86	0.68	0.47	5.98	0.24	1.25	18.55	139	3.85

REFERENCES

- Muzzarelli, R. A. A. *Chitin*; Pergamon Press: New York, 1978.
- Roberts, G. A. F. *Chitin Chemistry*; MacMillan Press Ltd: London, 1992.
- Chitin/Chitosan Conference Proceedings, Trondheim, Norway, 1988, Princeton, NJ, 1990.
- Muzzarelli, R. A. A. *Chitin Enzymology*; Euechis Ltd: London, 1993.
- Muzzarelli, R. A. A.; Jeuniaux, Ch.; Goodway, G. W. *Chitin in Nature and Technology*; Plenum Press: New York, 1986.
- Allan, G. G.; et al. *INDA J* 1993, 5, 33.
- Cuero, R. G.; et al. In *Advances in Chitin and Chitosan*; Elsevier Appl Sci: London, 1992, p. 419.
- Struszczyk, H. *J Appl Polym Sci* 1987, 33, 177.
- Struszczyk, H.; Owczarek, K.; Niekraszewicz, A. *Bidegradation of Chitosan*, 8th ICCS Symposia, Gdynia, 1994.
- Rathke, T.; Hudson, S. M. In *J.M.S.—Reviews of Macromolecular Chemistry and Physics*; Marcel Dekker Inc.: New York, 1994, p. 422, vol C34.
- Seo, H.; et al. *ibid.*, 93.
- Guan, Y.; et al. *J Appl Polym Sci* 1998, 67, 1965.
- Ratto, J. A.; Chen, C. C.; Blumstein, R. B. *J Appl Polym Sci* 1996, 59, 1451.
- Hari, P. R.; Chandy, T.; Sharma, C. P. *J Appl Polym Sci* 1996, 59, 1795.
- Struszczyk, H.; et al. *ibid.*, 65.
- Nousiainen, P.; Struszczyk, H. *Finnish Pat. WO 9109163* (1991).
- Struszczyk, H.; Nousiainen, P. *U.S. Pat. 5,622,666* (1997).