INFLUENCE OF SPINNING CONDITIONS ON PROPERTIES OF CHITOSAN FIBERS

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Chitosan fibers were prepared by a coagulation method involving spinning from an acetic-acid solution (2%) of polymer (4%) in basic alcoholic solution. The influence of feed rate and shear rate of the polymer solution and the degree of orientational drawing on the structure and mechanical properties of the fibers were studied. The optimum spinning parameters were determined. The chitosan fibers had an anisotropic structure with the macromolecules oriented primarily along the fiber axis.

Chitosan, which is produced from the natural polysaccharide chitin, is interesting because of its biocompatibility, biodegradation, bactericidal properties, high sorption characteristics, and ecological reprocessing [1-4]. Chitosan is widely used in pharmacology, cosmetology, and the food and textile industries [2, 3, 5]. Promising materials based on chitosan include surgical sutures and matrices for cell technologies [6, 7]. Mixed threads containing chitosan fibers are used in the textile industry and enable textiles and items with improved hygienic properties and enhanced bactericidal properties to be produced.

The structure and properties of chitosan fibers prepared by a coagulation method were reported [3, 7-13]. It was shown that the optimal solvent for chitosan was aqueous acetic acid (2%). The precipitant could be NaOH solutions, alcohol and water mixtures, alcohol and aqueous NaOH solution mixtures, and aqueous NaOH and H_2SO_4 solutions.

The influence of the rheological properties of the chitosan solution on the orientation of the polymer macromolecules and anisotropic filler nanoparticles was first studied by Dobrovol′skaya et al. [7]. Data on the structure of fibers containing two polymorphic chitosan modifications, the salt and basic forms (C- and O-forms), were presented. These fibers and composite fibers in which Mg-chrysotile nanotubes were added as filler were characterized by an anisotropic structure with respect to the orientation of both chitosan crystallites and Mg-chrysotile particles relative to the fiber axis. It could be assumed that the existence of the two structural modifications was due to an insufficient fiber precipitation time during which the C-form of chitosan converted to the O-form. Therefore, the optimal residence time of freshly formed fiber in the precipitation bath during which the fiber was fully precipitated and crystallites of the polymer O-form were formed had to be determined.

The goal of the present work was to study the influence on the chitosan fiber structure and strength and deformation properties of the spinning process parameters such as the polymer solution feed rate, precipitation time, and degree of stretching.

Chitosan (Fluka Chemie, BioChemika line) of molecular weight 255 kDa, degree of de-acetylation 80%, and ash content 0.5% was used to prepare chitosan and composite fibers.

Chitosan was dissolved in aqueous acetic acid (2%) with constant stirring for at least 120 min. The polymer solution concentration was 4 mass%. The resulting solutions were filtered and de-aerated for 3 h at a pressure of 0.1 atm.

Fibers were spun by a coagulation method on the laboratory apparatus of the IHMWC, RAS [14]. The apparatus enabled poly- and monofilament threads to be produced and the degree of nozzle and plastification drawing, temperature and duration of drying, feed rate of polymer solution, and harvesting of finished fiber to be varied. The precipitant was a mixture of alcohol and aqueous NaOH (10%) in a 1:1 ratio. Monofilaments were spun through a nozzle of diameter 0.6 mm. The solution feed rate (Q) was varied from 0.05 to 0.5 mL/min. The residence time of fiber in the precipitation bath was from 50 to 200 s. The degree of nozzle drawing (λ) varied from negative values (-40%, fiber precipitation) to 120%. The fiber was rinsed in distilled water and then dried at 50°C for 3 min.
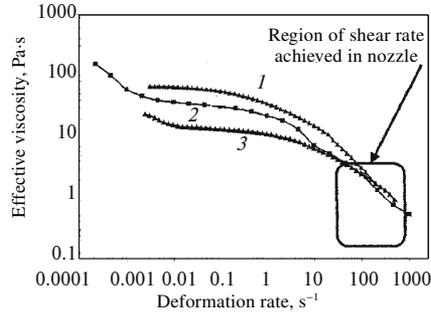

Fig. 1. Viscosities of chitosan solutions η of concentration 3.0
(1), 3.5 (2), and 4.0 (3) (mass%) as functions of shear rate.

Table 1. Chitosan Fiber Production Parameters

Sample No.	Q, mm/min	$\dot{\gamma}$, s^{-1}	τ, s	λ, %
1	0.05	6.29	200	–40
2	0.1	12.59	100	–42
3	0.2	25.18	50	–40
4	0.5	62.95	20	–44
5	0.1	12.59	100	0
6	0.1	12.59	100	50
7	0.1	12.59	100	100
8	0.1	12.59	100	120

Microscopy studies were carried out using a Supra-55 VP scanning electron microscope (Carl Zeiss). The structure was investigated by wide-angle x-ray diffraction on a URS-2 apparatus with point collimation using Cu Kα-radiation.

Rheological properties of chitosan solution in acetic acid were determined on an MCR-301 rheometer (Anton Paar) with a DG26.7-SN4044 measuring attachment (double coaxial cylinders) in shear test mode.

Mechanical properties of fibers were measured on a UMIV stand with test base 15 mm and strain rate 1 mm/min. Fibers were stored under normal climatic conditions (66% relative humidity) for at least 24 h before the tests.

Figure 1 shows viscosities η of chitosan solutions of various concentrations as functions of the shear rate $\dot{\gamma}$. It can be seen that the functions were nonlinear. The slope of the curves increased substantially if the shear rate increased above a certain value. This indicated that the solution viscosities decreased with increasing shear rate. The solution viscosity in the shear-stress field could decrease if the solution structure changed, in particular, if the chitosan macromolecules were oriented and the state transitioned from isotropic to anisotropic. Formation of an anisotropic solution structure under the influence of a shear field is characteristic of most rigid-chain polymers [15].

It is noteworthy that the nature of the $\eta(\dot{\gamma})$ functions persisted if the polymer concentration was varied. The viscosity increased as the chitosan solution concentration increased. The maximum chitosan concentration in the acetic acid solution (2%) was 4 mass%. This solution exhibited the necessary hydrodynamic properties enabling it to be fed through the nozzle over a broad range of rates, preserving the laminar stream in the precipitant.

The influence of polymer feed rate Q, polymer solution shear rate on passing through cylindrical nozzle $\dot{\gamma}$, residence time of fiber in the precipitation bath, and degree of fiber stretching λ on the chitosan fiber properties and structure was studied. The theory of capillary viscometry [16] teaches that the average shear rate for a capillary of radius r is related to the polymer solution feed rate Q by the equation

$$\dot{\gamma} = \frac{2Q}{\pi r^3}.$$

It is easy to calculate the shear rate arising in the nozzle during fiber spinning by substituting the values of Q and nozzle radius $r = 0.3$ mm.
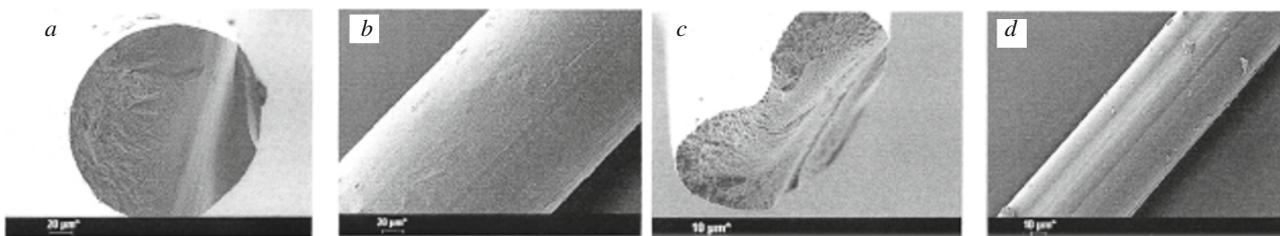
Fig. 2. Photomicrographs of chitosan fibers prepared at solution shear rate Q = 0.1 mL/min: fiber produced under equilibrium conditions (sample No. 2) (a, b); fiber with stretching λ = 100% (sample No. 7) (c, d).

Table 2. Properties of Chitosan Fibers

Sample No.	d, μm	σ, MPa	E, GPa	ε, %
1	170±3	74±9	2.62±0.9	37.2±13.0
2	150±6	102±16	3.36±0.7	44.9±10.4
3	160±8	60±23	1.61±0.9	48.4±10.3
4	180±15	58±14	2.24±0.6	31.4±11.1
5	120±4	168±9	6.33±0.8	12.1±1.4
6	80±6	218±25	7.46±2.3	8.3±1.3
7	70±4	219±17	7.93±1.0	7.2±2.8
8	70±2	225±18	7.20±0.9	4.9±0.8

Table 1 presents the polymer feed rates Q, shear rates $\dot{\gamma}$, precipitation times τ, and degree of stretching λ for which fiber spinning was carried out.

The change of polymer feed rate Q enabled both the shear ratearising during passage of the solution through the nozzle and the residence time of fiber in the precipitation bath to be varied. The results indicated that the fiber cross section was homogeneous and a denser shell and less dense core corresponding to different crystalline modifications were missing if the precipitation time was >160 s. This was evident in electron photomicrographs of fibers prepared at feed rate Q = 0.1 mL/min under equilibrium conditions and fibers subjected to stretching λ = 100% (Fig. 2).

Stretching stresses did not affect the fibers during precipitation, rinsing, and drying if they were prepared under equilibrium conditions (Nos. 1-4). Shrinkage (negative stretching) during precipitation and drying was 40-44%. The resulting fibers had an even and smooth surface. Their cross section was uniform and had a regular round shape (Fig. 2a and 2b). This indicated that the fiber was completely precipitated and the polymer stream was equally coagulated throughout the whole volume.

The surface of stretched fibers was smooth. Fibril formation was visible. The cross section of fibers obtained with stretching was also homogeneous although it had a bean shape (Fig. 2c and 2d). This was characteristic of most fibers prepared by the coagulation method. This was due to the action on the moist fiber located on the uptake reel of compaction stresses arising during stretching.

The studies showed that the fiber diameter d decreased, their strength σ and elasticity modulus E increased, and the ultimate elongation ε decreased as the degree of stretching increased to 100%. Increasing the degree of stretching further led to breakage of the fiber during spinning and instability of the spinning process. The maximum stretching was 120% for polymer feed rate Q = 0.1 mL/min.

The fiber strength depended on the polymer solution feed rate and; therefore, on the shear rate. Table 2 presents mechanical characteristics in comparison with results of rheological studies (Fig. 1). This suggested that the polymer macromolecules were oriented on passage of the polymer solution through the nozzle because of shear stresses. The resulting anisotropic structure was isolated. As a result, an ordered oriented fiber structure was formed. It should be noted that the orientation of the chitosan fiber crystallites was practically independent of the degree of stretching. Such a pattern was characteristic of polymers with rigid and moderately flexible chains [15].

X-ray diffraction analysis confirmed that oriented crystallites were present. Arcing of the (020) reflection toward the axis of the diffraction pattern indicated that the chitosan crystallites were oriented primarily
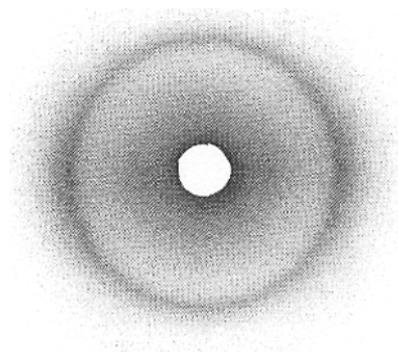
Fig. 3. Wide-angle x-ray pattern of chitosan fiber.

along the fiber axis (Fig. 3). The orientation factor calculated from the (020) reflection by the literature method [17] was −0.3.

As a rule, structuring occurred even at small shear rates. Fibers prepared at solution feed rate 0.1 mL/min ($\dot{\gamma} = 39.3\ s^{-1}$) were the strongest. The polymer stream was uniform during the spinning. The precipitation time was 160 s. Fiber spinning in this mode was stable without breakage of the stream or precipitated fiber.

Increasing the shear rate led to structural ordering. This was evident in the decreased effective viscosity of the solution. However, increasing the polymer feed rate and; therefore, the shear rate, decreased the residence time of the polymer in the precipitation bath. This decreased slightly the mechanical properties of the fibers (samples Nos. 3 and 4). The short residence time of the fiber in the precipitant (35 s) led to incomplete precipitation of the polymer and the formation of the C-form of chitosan in addition to the O-form. As noted earlier [7], fibers with two polymorphic forms exhibit reduced strength of 8-10 cN/tex. Increasing the shear rate to >196.5 s^{-1} led to disruption of polymer solution laminar flow up to its breaking. This complicated considerably the fiber spinning process and could have a negative effect on the fiber strength characteristics.

The results enabled the production of chitosan fibers that could be used as resorbable sutures and as matrices for cell and tissue replacement technologies such as the creation of muscle and cartilage tissues. They provided a foundation for creating vessels and nerves.

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