

THE MOLECULAR MASS EFFECT ON MECHANICAL PROPERTIES OF CHITOSAN FIBERS

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Abstract: Chitosan fibers have been prepared from acetic-acid solution (2%) by a coagulation method. It was established that optimal concentration of chitosan solution depends on its molecular mass for fibers preparation. The influence of molecular mass value on mechanical properties of chitosan fibers has been studied. The fibers of the best mechanical properties have been obtained from chitosan of 2.1×10^5 g/mol molecular mass, these fibers have strength of 188 MPa and Young modulus of 11.5 GPa.

Keywords: chitosan, molecular mass, fibers, wet spinning, mechanical properties.

1 INTRODUCTION

Chitosan, a derivative of the natural polysaccharide chitin, has a biocompatibility, biodegradability, bactericidal activity and high sorption characteristics. Due to such properties chitosan based materials find a lot of applications in pharmacology and medicine. Recently, fibers, films and porous block materials have been applied as matrices for cellular technologies, tissue engineering and transplantology [1-4]. Chitosan-based fibers as mono- and multifilaments are promising materials for biodegradable surgical sutures, one-dimensional matrices for cellular technologies. Application of yarn or threads containing chitosan fibers makes it possible to obtain textile materials with the improved hygienic characteristics and high bactericidal properties [5].

Method of wet (coagulation) spinning of chitosan-based fibers is described in [4, 6-8]. It has been shown that the optimal solvent for chitosan is 2% aqueous solution of acetic acid [4, 8]. An aqueous solution of NaOH or a mixture of alcohol and an aqueous solution of NaOH or an aqueous solution of NaOH and sulfuric acid can be used as a precipitant.

It is known that spinning conditions as well as initial molecular characteristics such as molecular mass and deacetylation degree can have a significant effect on the properties of the wet spun fibers. The influence of spinning conditions, in particular the factor

of orientation drawing, on mechanical properties of chitosan-based fibers, has been described at the work [6]. The results of some research of the structure and mechanical properties of chitosan fibers are presented in [6, 7]. The studies of the resorption of chitosan fibers *in vivo* are presented in [9].

But, there is no information practically on the influence of molecular characteristics, primarily chitosan molecular mass, on the process of fibers spinning and their properties. Therefore, the aim of the work was to study the influence of the molecular mass of chitosan on fibers wet spinning as well as on the strength and elastic characteristics of the processed fibers.

2 MATERIALS AND METHODS

Chitosan samples of similar deacetylation degree were used for processing of the fibers. The characteristics of polymers are given in Table 1.

Molecular mass M_{SD} of chitosan samples was determined by an absolute method based on sedimentation and diffusion analysis of their dilute solutions in 0.33 M CH_3COOH + 0.2 M CH_3COONa . Velocity sedimentation was investigated using Beckman XLI analytical ultracentrifuge. Translation diffusion coefficients of chitosan molecules were received by means of the isothermal diffusion study in Tsvetkov diffusometer.

Table 1 The characteristics of chitosan samples

	Raw materials	Deacetylation degree DD [%]	M _{SD} [g/mol]	Manufacturer
1	crab	96	6.5x10 ⁴	"Bioprogress" (Russia)
2	crab	92	1.1x10 ⁵	"Chitosan Technologies" (Russia)
3	crab	94	1.5 x10 ⁵	"Biolog Heppe" (Germany)
4	shrimp	91.5	2.1 x10 ⁵	"Biolog Heppe" (Germany)

Sedimentation of chitosan has been studied at the solute concentration range 0.1-0.02 g/dl with the rotor speed 42000 rpm at temperature 298 K. The scans were received using Rayleigh interference optical scheme every 60 s within overall experiment time of around 10 hours. The normalized sedimentation coefficient distributions of chitosan samples (Figure 1), corresponding to their molecular-mass distributions, have been acquired in velocity sedimentation experiments.

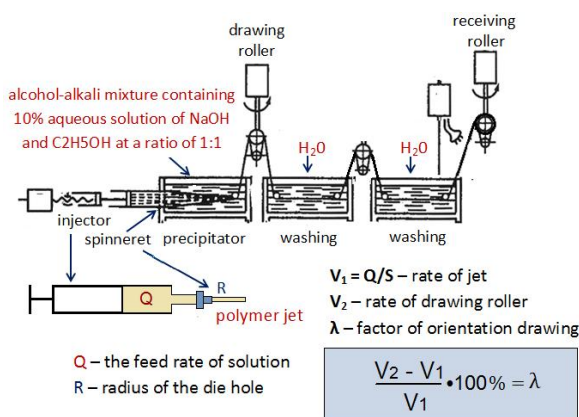
To process fibers the aqueous mixtures (pH = 4-5) of chitosan have been stirred at room temperature for 30 min until the partial dissolution of chitosan and its swelling. The concentration of chitosan in solution was varied from 3.5 to 6.5% and depended on chitosan samples. Then the 2% acetic acid solution in water has been added into the mixtures during a continuous stirring. The mixtures of the solution of chitosan have been stirred in the glass bulb at room temperature during 90 min and then filtered and deaerated for 24 h at the pressure 0.1 atm.

Rheological measurements of polymer solutions were carried out on the rheometer Physica MCR 301 (Anton Paar) at 20°C according to the method of "cylinder in the cylinder" in the regime of shear flow with the shear rates 10⁻⁴ - 100 sec⁻¹. 5 ml of solution was placed into the rheological cuvette and the dependence of viscosity (η) on the shear rate ($\dot{\gamma}$) was obtained.

The fibers were spun by coagulation method [6-8], at the laboratory equipment developed at the Institute of Macromolecular Compounds RAS. The scheme of this processing is presented in Figure 1. Precipitator was the mixture 10% solution of NaOH and C₂H₅OH in the proportion 1:1. Monofilament processing was flowed through the die hole with the diameter of 0.6 mm, the feed rate of the solution through the die hole was 5.5 mm/sec; the time of precipitation was 150 sec. The factor of orientation drawing λ [%] of the monofilament in the coagulation bath was varied from - 20% (shrinkage) up to +100%. The fibers were washed in the distilled water and then dried at a temperature of 50°C during 10 min.

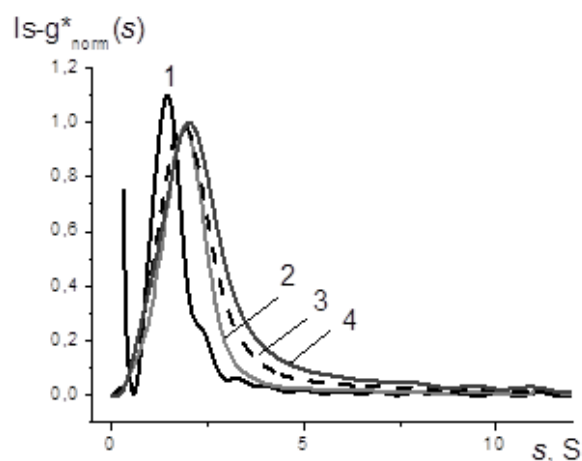
The studies of the structure were conducted on the microscope Supra-55 VP (Carl Zeiss). The measurements of the mechanical properties of the processed fibers were carried out with Instron 5943 at room temperature and the load speed of 10 mm/min; basic length of the fibers was 100 mm. The cross section S [m²] of the monofilaments was estimated by the formula $S = T/\rho$, where T is

the linear density [tex] of monofilament and specific gravity ρ of chitosan is equal 1400 kg/m³. Prior to the mechanical testing fibers were placed in special box with relative humidity 66% for 24 hours.

**Figure 1** The scheme of chitosan fibers processing

3 RESULTS AND DISCUSSION

All investigated chitosan samples were similar in deacetylation degree but its molecular masses (Table 1) and sedimentation coefficient distributions (Figure 2) were quite different. Sample 2 was characterized by the narrowest distribution among the studied chitosans 2-4, when sample 1 had another type of distribution.

**Figure 2** The normalized sedimentation coefficient distributions for samples 1-4 at $c = 0.02$ g/dl. On x-axis, the values of sedimentation coefficient s are expressed in Svedbergs (S); where one Svedberg unit corresponds to 10⁻¹³ second

To optimize the process of wet spinning the information about the rheological properties of the chitosan solution is necessary. Figure 3 represents the dependences of the viscosity on the shear rate for the 4% chitosan solutions in 2% acetic-acid solution.

It is obvious that the molecular mass of chitosan has a significant influence on the effective viscosity (η) of solutions and the dependence of the viscosity on the shear rate ($\dot{\gamma}$). The viscosity of solutions increases with increasing molecular mass. The optimum concentration of a solution of chitosan for processing decreases with increasing molecular mass. The dependences of viscosity on shear rate for solutions with similar viscosities and different concentrations of chitosan are shown in Figure 4.

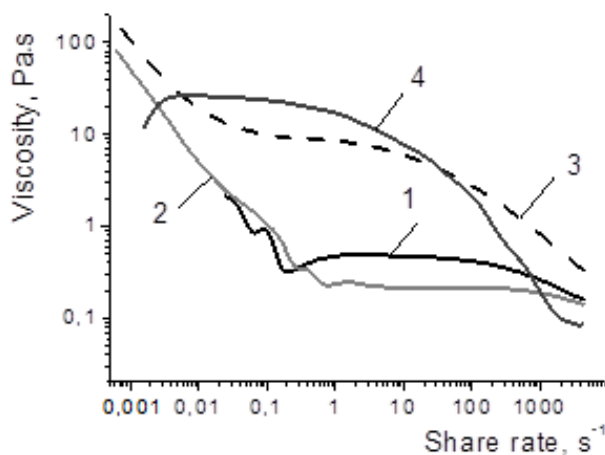


Figure 3 Dependences of viscosity on shear rate for 4% chitosan solutions. The numbers correspond to the sample numbers shown in the Table 1

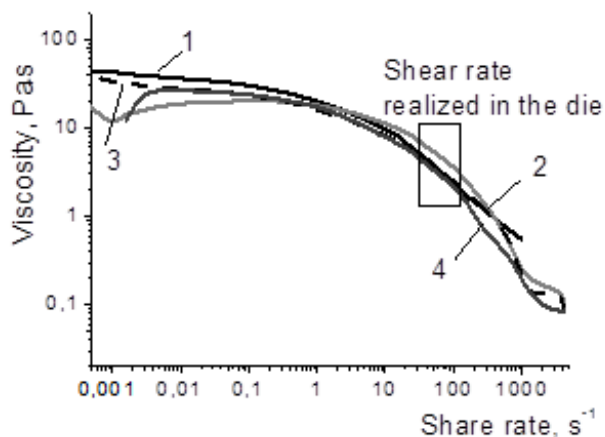


Figure 4 Dependences of viscosity on shear rate for chitosan solutions with different concentrations of chitosan: sample 1 – 6.3%, sample 2 – 5.5%, sample 3 – 5%, sample 4 – 4%

As seen in Figure 4 the dependences of viscosity on shear rate for these solutions are similar and have a nonlinear behavior. The slope of the curves increases substantially with an increase in the shear

rate, the significant decrease of viscosity is observed at the shear rate of 10 s^{-1} or more. The decrease in viscosity upon an increase in the shear rate is related to the destruction of the initial structure of the polymer solution and the creation of a new oriented structure that means transition from isotropic state to anisotropic one. The formation of the anisotropic structure of the polymer solution under the action of shear field is typical of the majority of rigid-chain polymers.

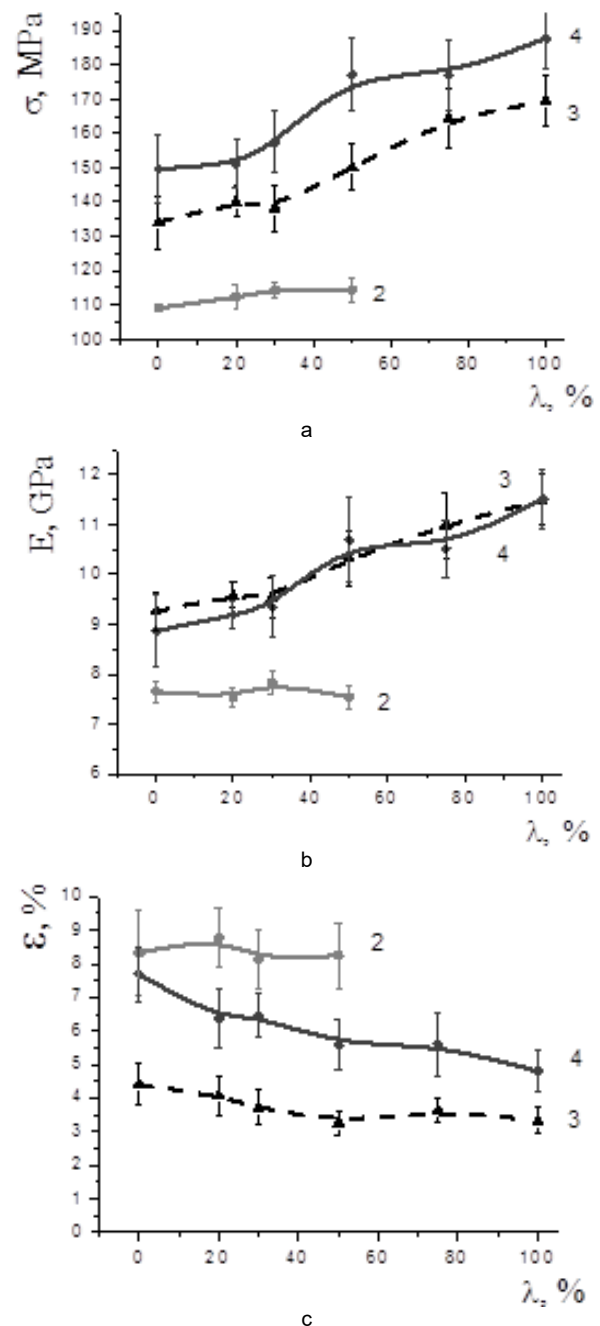


Figure 5 Dependences of the tensile strength (a), Young modulus (b) and elongation at break (c) of the chitosan fibers obtained from 4% solutions on the factor of orientation drawing (λ)

Studies of rheological properties have allowed determining the optimal concentrations of chitosan for processing (Table 2) and the feed rate of solution through die hole. It is shown in [4, 6] that oriented structure of the chitosan fibers is formed during flowing of the solution through the die hole. In turn, the orientation of the macromolecules depends on the shear stress occurring in the die hole. The optimum feed rate Q [mL/min] of the polymer solution through the die hole of the radius R can be calculated according to the proportion $Q = \pi \dot{\gamma} R^3 / 2$ which is correct for Newtonian liquids [10]. The shear rate $\dot{\gamma}$ should be quite high in order to provide good orientation of the macromolecules but not too high in order to make possible the complete coagulation of the fiber in the alkali/ethanol bath. Thus, the Q has been chosen to ~ 0.1 - 0.3 mL/min. This value corresponds approximately to the $\dot{\gamma} \sim 100 \text{ s}^{-1}$ as indicated in Figure 4. The solutions have possessed the necessary rheology characteristics preserving the laminarity of the jet in the coagulation bath after the flowing of the solution through the die hole.

It has been found [3, 4, 6] that optimal concentration of chitosan with $M_{SD} = 2.1 \times 10^5 \text{ g/mol}$ for processing is 4%. In connection with this to study the molecular mass effect on mechanical properties, fibers from 4%

chitosan solutions for samples 2-4 have been prepared (Figure 5). The fibers from 4% chitosan solutions for sample 1 could not be spun due to low viscosity of its solution.

It has been shown that molecular mass influences factor of orientation drawing (λ) and the mechanical properties of fibers. Maximum factor of orientation drawing for sample 2 was 50%, the maximum strength of fibers did not exceed 120 MPa. But, the fibers from sample 3 and 4 have been spun with factor of orientation drawing up to 100%, wherein the strength and Young modulus of these fibers grows considerably and elongation at break decreases with an increase in the drawing up to maximum factor of orientation drawing 100%. Fibers spun chitosan with molecular mass $2.1 \times 10^5 \text{ g/mol}$ have highest mechanical properties: strength is $188 \pm 9.1 \text{ MPa}$, Young modulus is $11.5 \pm 0.6 \text{ GPa}$, elongation at break is $4.8 \pm 0.6 \%$.

The mechanical properties of chitosan fiber spun from solution with optimal concentrations of chitosan for each sample are given in the Table 2.

The molecular mass of chitosan doesn't effect on appearance of the fibers. All obtained fibers have a smooth surface and homogeneous internal structure (Figure 6).

Table 2 Properties of chitosan fibers

№ of chitosan sample	Optimal concentration of chitosan in solution [%]	Maximum orientation drawing [%]	Mechanical properties		
			Strength [MPa]	Young modulus [GPa]	Elongation at break [%]
1	6.3	40	110 ± 8.3	7.7 ± 0.6	3.9 ± 0.7
2	5.5	80	156 ± 4.4	10.3 ± 0.4	4.1 ± 0.8
3	4.0-5.0	100	169 ± 7.3	11.5 ± 0.5	4.6 ± 0.8
4	4.0	100	188 ± 9.1	11.5 ± 0.6	4.8 ± 0.6

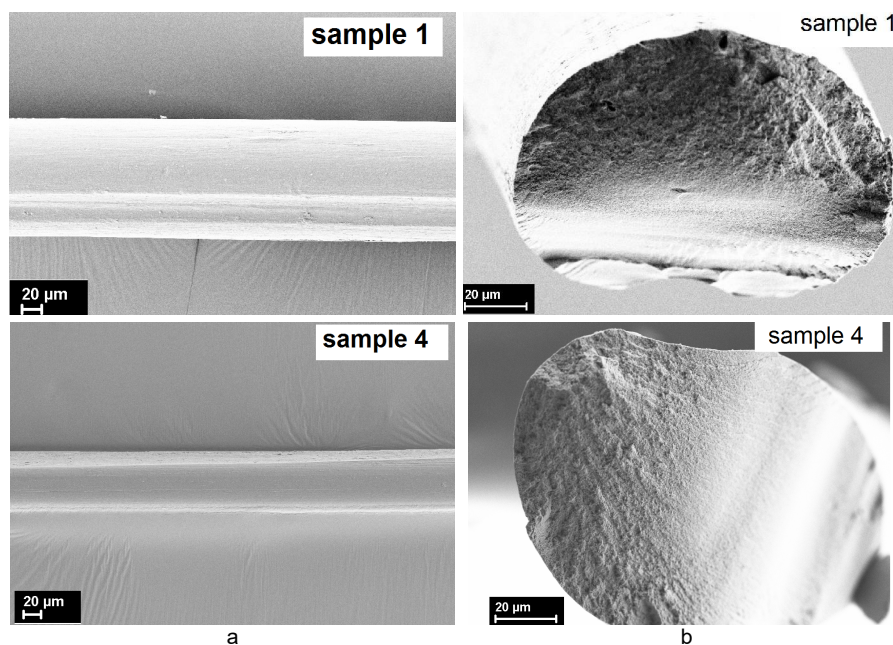


Figure 6 SEM micrographs of chitosan fibers: longitudinal view (a) and cross-section (b)

4 CONCLUSIONS

The molecular mass has a significant influence on the effective viscosity of chitosan solutions. The viscosity of solutions increases with increasing molecular mass, at the same time the optimum concentration of the solution for fibers processing decreases with increasing molecular mass.

The chitosan fibers have been prepared from an aqueous solution of 2% acetic acid by coagulation method. The concentration of polymer was optimal for each chitosan sample:

- 6.3% for chitosan with $M_{SD} = 6.5 \times 10^4$ g/mol,
- 5.5% for chitosan with $M_{SD} = 1.1 \times 10^5$ g/mol,
- 4-5% for chitosan with $M_{SD} = 1.5 \times 10^5$ g/mol
- 4% for chitosan with $M_{SD} = 2.1 \times 10^5$ g/mol.

The fibers with highest factor of orientation drawing ($\lambda = 100\%$) have been prepared from chitosan with $M_{SD} = 2.1 \times 10^5$ g/mol, an increase in the strength ceases at $\lambda \sim 40\%$ for chitosan sample with $M_{SD} = 6.5 \times 10^4$ g/mol and $\lambda \sim 80\%$ for chitosan sample with $M_{SD} = 1.1 \times 10^5$ g/mol respectively. Fibers of the best mechanical properties have been spun with $M_{SD} = 2.1 \times 10^5$ g/mol chitosan sample, whose fibers have a strength 188 ± 9.1 MPa and Young modulus 11.5 ± 0.6 GPa, elongation at break is $4.8 \pm 0.6\%$.

The obtained fibres may be used for preparing the matrices for cell replacement technologies and tissue engineering, biodegradable surgical suture materials or hemostatic material.

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