

# Electrospinning of Composite Nanofibers Based on Chitosan, Poly(ethylene oxide), and Chitin Nanofibrils

I. P. Dobrovolskaya<sup>a,b\*</sup>, I. O. Lebedeva<sup>b</sup>, V. E. Yudin<sup>a,b</sup>, P. V. Popryadukhin<sup>a,b</sup>,  
E. M. Ivan'kova<sup>a,b</sup>, and V. Yu. Elokhovskii<sup>a</sup>

<sup>a</sup>*Institute of Macromolecular Compounds, Russian Academy of Sciences, Bol'shoi pr. 31 (V.O.), St. Petersburg, 199004 Russia*

<sup>b</sup>*St. Petersburg Polytechnic University, Politekhnicheskaya ul. 29, St. Petersburg, 195251 Russia*

\**e-mail: dobrov@hq.macro.ru*

Received June 25, 2015; Revised Manuscript Received November 2, 2015

**Abstract**—Composite chitosan nanofibers containing 20 wt % chitin nanofibrils and 10 wt % PEO are obtained via the electrospinning method. Additions of 0.5–20.0 wt % chitin nanofibrils into chitosan solutions with concentrations of 3–7 wt % in acetic acid (70 vol %) insignificantly increase the electrical conductivity, surface-tension coefficient, and viscosity of these mixed solutions. Decreases in the viscosities of chitosan solutions containing chitin nanofibrils with increases in shear rate provide evidence for the structuring of solutions and the orientation of chitosan macromolecules and chitin nanofibrils in the shear flow. The effects of shear stress and a high-voltage electric field on chitosan solutions containing chitin nanofibrils and PEO result in a decrease in the imperfection of composite nanofibers. The introduction of chitin nanofibrils allows the content of PEO in the composite nanofibers to be reduced.

DOI: 10.1134/S0965545X1602005X

## INTRODUCTION

A topical problem of modern materials science is the development of bioresorbable materials based on natural [1–6] or synthetic [7, 8] polymers that may be used in tissue engineering as matrixes for cell technologies [9] and as wound dressings [1]. Materials for tissue engineering should be biocompatible, and there should be no cytotoxicity of both the materials themselves and their resorption products [10]. For the proliferation of cells in the matrix bulk and the formation of a tissue identical to the patient tissue, the presence of tens to hundreds of micron-sized pores is required [11]. A number of methods are used for the preparation of porous polymer materials: irradiation of polymer films with high-energy particles [12], phase separation of polymer solutions [8], and introduction of various porogen additives [13].

Recently, the method of electrospinning of nanofibers has been used to prepare materials with pores of tens to hundreds of micron in size [14]. As was shown in [8, 15], mesenchymal stem cells are well fixed on the surfaces of nanofiber materials and a high rate of their proliferation is observed in this case. The essence of the method is as follows. A polymer solution or melt is supplied through a spinneret electrode in a high-voltage field (15–30 kV). Under the application of the electric field, the jet flowing out of the spinneret is split into microjets that are deposited on a collector as fibers with diameters of up to hundreds of nanometers.

It is known [14, 16] that the rate of formation, the diameters of fibers, and their imperfectness are substantially affected by the electrical conductivity of the polymer solution and its viscosity as well as surface tension.

The polymer chitosan is widely used to produce biomedical materials [1]. It is biocompatible and biodegradable, it is a derivative of chitin polysaccharide, and its macromolecules consist of  $\beta$ -(1-4)-D-glucosamine units and N-acetyl-D-glucosamine. The products of chitosan biodegradation are nontoxic and readily involved in natural biochemical reactions in the body. It is known that the electrospinning of chitosan nanofibers is an extremely complicated process because the electrical resistance of its solutions is lower than that of other polymers, this fact being a consequence of chitosan's polyelectrolytic properties. For the electrospinning of chitosan-based nanofibers, water-soluble polymers—such as PEO, PVA, methyl cellulose, and polyvinylpyrrolidone—are introduced into chitosan solutions [17–23]. However, the additives of flexible-chain polymers worsen the properties of the resulting material: It becomes more hygroscopic, and its mechanical properties decrease.

In [21, 22], the capillary-free electrospinning method was utilized to obtain a nanofibrous material from a mixture of chitosan and PVA. The conditions of its transformation into the insoluble state via heat treatment and the effect of cosolvent additives

(DMSO and ethanol) on the values of electrical conductivity and surface tension and the structural-rheological properties of the chitosan solutions being formed were investigated.

As was shown in [6], chitosan- and chitin-nanofibril-based composite fibers obtained via the coagulation method have enhanced tensile and elastic characteristics. The introduction of chitin nanofibrils with diameters of 20 nm and lengths of 600–800 nm into a chitosan solution [24] promotes the orientation of polymer macromolecules in shear-stress fields that arise when the mixed solution containing nanoparticles passes through the spinneret. Moreover, the introduction of chitin nanofibrils into a chitosan solution provides a laminar jet flow in the spinneret and stabilizes the fiber-spinning process. It may be assumed that the introduction of chitin nanofibrils into a chitosan solution will increase the efficiency of electrospinning of composite nanofibers and make it possible to decrease the amount of the water-soluble polymer in the chitosan-based composite nanofibers.

Thus, the aim of the present study is to investigate the effect of chitin nanofibrils on the values of electrical conductivity, surface tension, and viscosity of chitosan solutions in order to optimize the electrospinning of composite nanofibers based on chitosan and chitin nanofibrils and to reduce the content of water-soluble polymers in chitosan-based composite nanofibers.

## EXPERIMENTAL

### *Materials*

Chitosan with a molecular mass of  $M_w = 2.2 \times 10^5$  and a degree of deacetylation of 80% (OAO Bioprogress, Russia) was used. PEO (Unioncarbait) had a molecular mass of  $M_w = 9 \times 10^5$ . Mixed solutions containing chitosan and chitin nanofibrils were prepared with the use of an aqueous dispersion of chitin nanofibrils (SRL Mavi Sud, Italy) with a concentration of chitin nanofibrils of 31.9 mg/mL, an electrical conductivity of  $\sigma = 116 \mu\text{S/cm}$ , and a pH of 4.87. Acetic acid was purchased from ZAO Vekton (Russia).

Chitosan solutions were prepared according to the following procedure. A chitosan powder was placed in water in an amount providing a polymer concentration in solution of 3–7 wt %. This aqueous dispersion of chitosan was stirred for 40 min at 200 rpm until chitosan became partially swollen. Afterward, glacial acetic acid was added under continuous stirring at a velocity of 1000 rpm in an amount providing a solvent concentration of 70 vol %. According to [23], this concentration of acetic acid reduces the electrical conductivity of a chitosan solution. The mixture of chitosan with the solvent was stirred for 40 min at a velocity of 500 rpm. Before spinning, the solution was kept for a day at 4°C.

In order to obtain the mixed solution of chitosan and PEO in an amount providing its concentration of 5–20 wt % with respect to chitosan, PEO was dissolved in water, chitosan was added, and their mixture was prepared as described above.

Composite nanofibers based on chitosan and chitin nanofibrils were spun from an aqueous dispersion of chitin nanofibrils with a concentration of nanoparticles of 0.1–20.0 wt % with respect to chitosan. The dispersion was subjected to ultrasonic treatment for 40 min. Afterward, chitosan and/or PEO was introduced into this dispersion, and the solution was prepared according to the scheme described above.

### *Equipment and Analytical Methods*

Chitin nanofibrils were dispersed on a UZV-1.3 ultrasonic disperser (Russia) at a frequency of 40 kHz.

Rheological investigations were performed on a Physica MCR 301 rheometer (Anton Paar) at 20°C via the “cylinder-in-cylinder” method in the shear-flow regime at a shear rate of  $10^{-2}-(4 \times 10^3) \text{ s}^{-1}$ . For measurements, 5 mL of a solution was placed in a measuring cell. The viscosity dependence on shear rate for each sample was measured at an increasing frequency of rotation of the cylinders.

The electrical conductivities of chitosan solutions and their mixtures were determined with a Seven Multi electrometer–pH-meter (Mettler Toledo Co., Switzerland). The surface-tension values were found via the anchor-ring method (the du Noüy ring method) on a laboratory setup developed at the Institute of Macromolecular Compounds, Russian Academy of Sciences [25]. The setup was calibrated against a standard fluid (water). Each point was measured at least five times.

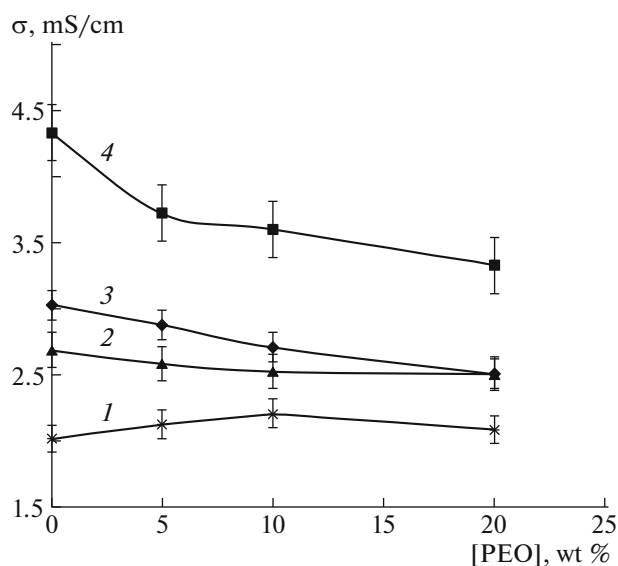
The structures of nanofibers were investigated with a Supra 55VP scanning electron microscope (Carl Zeiss, Germany).

The electrospinning of fibers was performed on a NANON-01A setup (MECC Co., Japan). A solution was extruded by an injection pump through the spinneret electrode with a radius of 0.3 mm in an electric field at a voltage of 18 kV. The distance between the spinneret electrode and the receiving electrode, on which fibers were deposited, was 0.2 m.

## RESULTS AND DISCUSSION

### *Electrical Conductivities of Chitosan Solutions and Their Mixtures with PEO and Chitin Nanofibrils*

It is known that, to spin chitosan-based nanofibers, water-soluble fiber-forming polymers—in particular, PEO, PVA, and methyl cellulose—are added to a solution [11, 19–21]. In the present study, the effect of PEO on the electrical conductivities of chitosan solutions is investigated. The results of electrical-conductivity measurements are presented in Fig. 1. It is seen

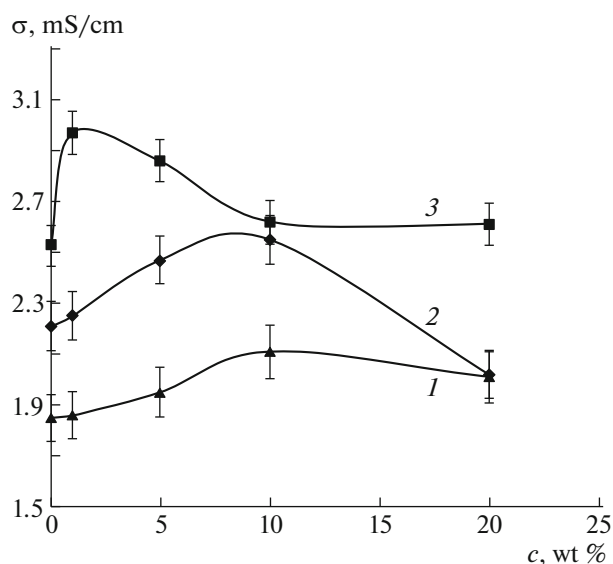


**Fig. 1.** Electrical conductivity vs. the content of PEO for chitosan solutions with concentrations of (1) 3, (2) 4, (3) 5, and (4) 7 wt %.

that the introduction of PEO causes a slight decrease in the electrical conductivity of a solution with a chitosan concentration of 7 wt %, but has almost no effect on the electrical conductivities of solutions containing small amounts of chitosan (3 or 4 wt %). These data agree with the results reported in [22]. Slight changes in the electrical conductivities of PEO-containing chitosan solutions occur because PEO macromolecules lack ionogenic groups that can block the ionogenic  $\text{NH}_3^+$  groups of chitosan.

Note that the electrical conductivities are three to four orders of magnitude higher than the analogous values obtained for polymers with good spinning abilities in electric fields, in particular, an aliphatic copolyamide with  $\sigma = 16.61 \mu\text{S}/\text{cm}$ . As was shown in [8], the process of electrospinning of fibers from solutions of this polymer is highly stable and film and tubular samples based on nanofibers of this aliphatic copolyamide possess flawless structures.

In order to enhance the spinning ability of chitosan-based nanofibers, aliphatic polymers, in particular, PEO, are introduced into its solutions [16, 26–28]. The process of electrospinning of fibers from the aqueous solutions of PEO is highly stable, and film materials based on PEO nanofibers, like those based on aliphatic copolyamides, are free of defects, such as drops and tapered structures. The introduction of 10–40 wt % PEO into a chitosan solution makes it possible to spin chitosan-based nanofibers in an electric field. The effect of the molecular mass of PEO on the spinning ability of nanofibers was studied in [28]. It was shown that an increase in the molecular mass up to  $(2\text{--}5) \times 10^6$  makes it possible to decrease the amount



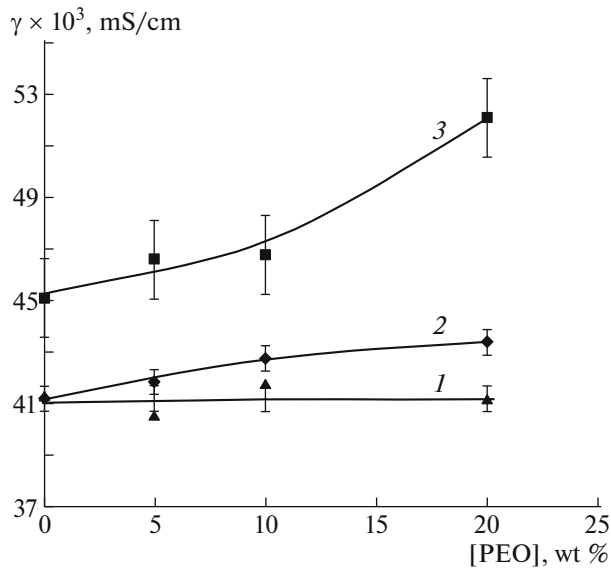
**Fig. 2.** Electrical conductivity vs. content  $C$  of chitin nanofibrils for (1) chitosan solutions with a concentration of 4 wt % and (2, 3) chitosan solutions containing 10 wt % PEO at chitosan concentrations of (2) 4 and (3) 5 wt %.

of the flexible-chain polymer in the composite to 1 wt %. Further investigations were conducted with the use of the composite based on a chitosan solution containing 10 wt % PEO ( $M = 9 \times 10^5$ ) as the most accessible solution.

The introduction of chitin nanofibrils into chitosan solutions facilitates stabilization of the spinning process performed via coagulation of composite fibers based on chitosan and chitin nanofibrils and promotes increases in their tensile and elastic characteristics [5, 6]. Consequently, it may be assumed that chitin nanofibrils will promote the formation of nanofibers during the electrospinning process.

Figure 2 plots the conductivity of a 4 wt % chitosan solution versus the content of chitin nanofibrils in it. This dependence is nonmonotonic. In accordance with [6], the arrangement of chitosan macromolecules along the surfaces of chitin nanofibrils is the most preferable energetically. This conclusion was made on the basis of molecular-dynamics simulations; therefore, an increase in the electrical conductivity of the composite may be due to a more pronounced ordering of the chitosan solution under the effect of anisometric nanoparticles of the filler and the orientation of chitosan macromolecules on the surfaces of filler particles. Similar nonlinear dependences of electrical conductivity on the content of chitin nanofibrils were observed for 4 and 5 wt % chitosan solutions containing 10 wt % PEO.

It may be proposed that an insignificant increase in electrical conductivity with the content of nanofibrils and a shift of its maximum towards lower chitin concentrations in solutions are caused by the adhesion of



**Fig. 3.** Surface-tension coefficient vs. content of PEO for chitosan solutions with concentrations of (1) 3, (2) 4, and (3) 5%.

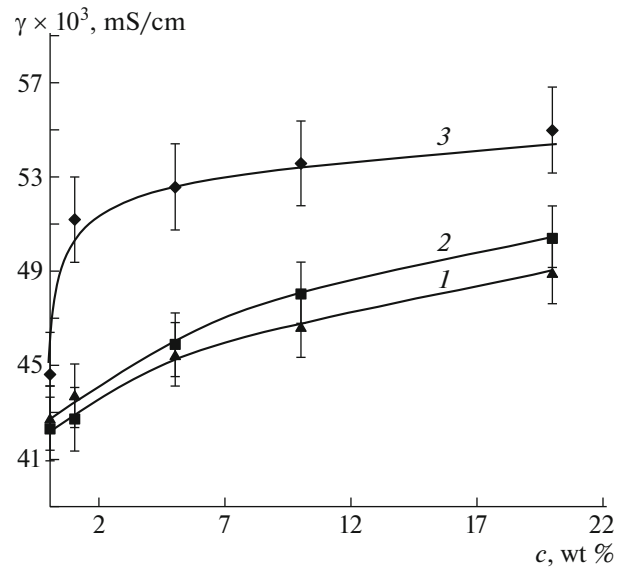
chitosan macromolecules on the surfaces of anisometric chitin particles as well as by their enhanced orientation.

Thus, chitosan solutions in acetic acid have high conductivities of  $\sigma = 2\text{--}4$  mS/cm. The introduction of PEO into chitosan solutions leads to certain decreases in the electrical conductivities of the mixtures. The conductivity of a mixed solution likewise increases insignificantly via the addition of 1–10 wt % chitin nanofibrils with respect to chitosan. Therefore, it may be inferred that the introduction of 10 wt % PEO into a 4–5% chitosan solution in 70% acetic acid, as well as the addition of 5 to 20 wt % chitin nanofibrils, insignificantly affects the conductivity of the mixed solution. The latter parameter remains at a level of 2–4 mS/cm, that is, three to four orders of magnitude higher than the values for aliphatic copolyamide-like polymers characterized by good spinning abilities in an electric field.

#### *Surface-Tension Values of Chitosan Solutions Containing PEO and Chitin Nanofibrils*

It is known [14, 16] that the electrospinning ability of a solution is another important parameter determining the magnitude of the surface-tension coefficient. Therefore, how the surface-tension coefficients of chitosan solutions depend on the contents of PEO and chitin nanofibrils was investigated.

Figure 3 shows surface-tension coefficients of chitosan solutions of various concentrations against the contents of PEO. As is seen, for 3 and 4 wt % chitosan solutions, surface-tension coefficients  $\gamma$  remain prac-



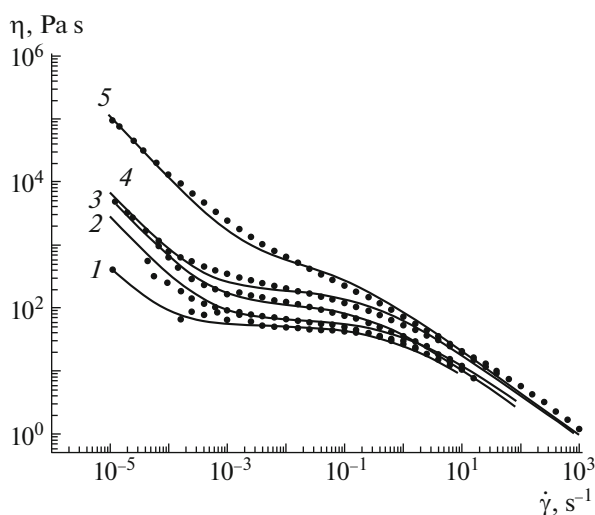
**Fig. 4.** Surface-tension coefficient vs. content  $C$  of chitin nanofibrils for (1) a 4% chitosan solution and (2, 3) chitosan solutions containing 10 wt % PEO at chitosan concentrations of (2) 4 and (3) 5 wt %.

tically the same with increases in the amounts of PEO (curves 1, 2). For the 5 wt % chitosan solution (curve 3), the surface-tension coefficient increases with an increase in the PEO content. Note that these values are higher than the values for solutions of PEO and an aliphatic copolyamide, for which  $\gamma$  is  $\sim 30$  N/m.

The addition of chitin nanofibrils to the chitosan solution results in its structuring in shear-stress fields, that is, in the orientation of chitin nanofibrils and chitosan macromolecules along the force-field direction [6]. This effect promotes stabilization of the wet spinning of fibers and increases in their tensile strength and elastic modulus.

The dependence of the surface-tension coefficient of a 4% chitosan solution on the content of chitin nanofibrils is presented in Fig. 4. An increase in the content of nanoparticles in chitosan solutions up to 10 wt % leads to a noticeable growth of the surface-tension coefficient of the composite, while a further increase in the filler concentration up to 20 wt % exerts only a weak effect on this parameter. Increases in the surface-tension values of chitosan solutions containing chitin nanofibrils, as well as increases in the electrical conductivities, are probably due to the structuring of solutions and adhesion of chitosan macromolecules on the surfaces of chitin nanofibrils.

In addition, surface tension increases after the introduction of chitin nanofibrils into a chitosan solution containing 10 wt % PEO (Fig. 4). Note that the introduction of 10 wt % PEO into 4 and 5 wt % chitosan solutions has practically no effect on the surface-tension coefficients of the mixtures.



**Fig. 5.** Viscosity vs. shear rate for (1) a chitosan solution and (2–5) mixtures with contents of chitin nanofibrils of (2) 1, (3) 7, (4) 10, and (5) 20 wt %.

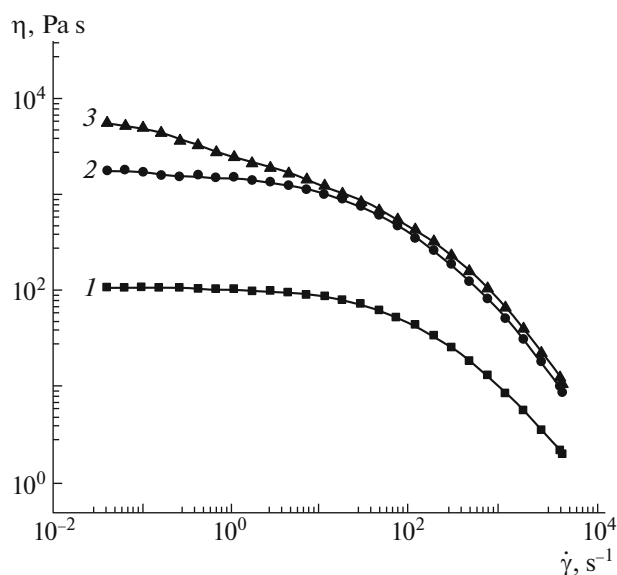
From the above data, it follows that the surface-tension values of solutions grow with an increase in the concentration of chitin nanofibrils. For a 4% chitosan solution, this dependence is monotonic, while at a 5 wt % concentration of chitosan, it jumps abruptly, even after the introduction of 1 wt % chitin nanofibrils.

Thus, the addition of 10 wt % PEO to chitosan solutions has almost no effect on the surface-tension values of the chitosan solutions. At the same time, even small additives of chitin nanofibrils (1 wt % with respect to chitosan) lead to noticeable increases in the surface-tension coefficients. The surface-tension values obtained for chitosan solutions and their mixtures with PEO and chitin nanofibrils ( $\gamma = (45\text{--}55) \times 10^3$  N/m) are higher than the values known for aliphatic copolyamide solutions ( $\gamma = 33 \times 10^3$  N/m), which have a highly stable electrospinning ability.

#### *Rheological Properties of Chitosan Solutions and Their Mixtures with Chitin Nanofibrils and PEO*

In [27, 28], the viscosities of chitosan solutions and of their mixtures with other polymers were investigated and changes in the intrinsic viscosities were analyzed. These data are important for estimation of the molecular characteristics of the polymer. The dependence of intrinsic viscosity on concentration for chitosan solutions, the properties of PEO, the contents of PEO in solutions, and the effect of viscosity on the diameter of nanofibers were studied [28].

In order to investigate the structuring of a solution in a shear field, which is important for the fiber formation process, the dependences of viscosity on shear



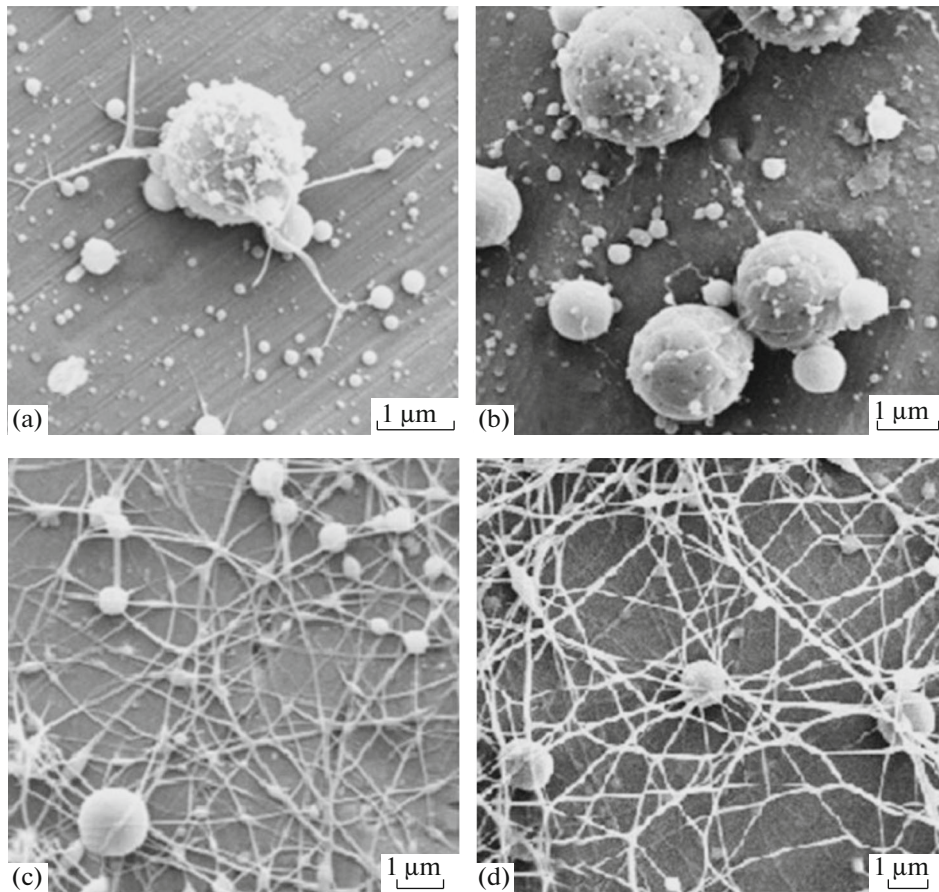
**Fig. 6.** Viscosity vs. shear rate for (1) a 4% chitosan solution and (2, 3) 4% chitosan solutions containing (2) 10 wt % PEO and (3) 10 wt % PEO + 20 wt % chitin nanofibrils.

rate were examined and data were obtained for chitosan solutions of various concentrations and containing additives of chitin nanofibrils and PEO.

Chitin nanofibrils were used as fillers to prepare resorbable composite nanofibers and to improve their moisture resistance. Figure 5 plots viscosity versus shear rate for a chitosan solution and for its mixtures with chitin nanoparticles.

The results of rheological measurements make it possible to state that the dependence of viscosity on shear rate is linear for each of the investigated solutions. For the filler-free solution (Fig. 5, curve 1), a significant decrease in viscosity is observed when the shear rate is above  $10 \text{ s}^{-1}$ . The viscosity of the chitosan solution increases with the content of chitin nanofibrils. This effect is especially noticeable at filler contents above 1 wt % (curves 3–5). As the content of chitin nanofibrils is increased, the threshold value of the deformation rate shifts toward lower  $\dot{\gamma}$  values. For the mixture containing 20 wt % filler, dependence  $\eta(\dot{\gamma})$  approaches a linear dependence in a wide range of shear rates. A decrease in viscosity with an increase in shear stress is due to the fact that the structure of the initial solution is destroyed and a new one is created with oriented chitosan macromolecules and chitin nanofibrils in a solution; this effect is typical in particular for most rigid-chain polymers [29].

An increase in the filler content in a chitosan solution is accompanied by increases in viscosity and shear stress. This phenomenon is especially noticeable at low shear rates. This fact is evidence for a good interaction of chitin particles with chitosan macromolecules and a high adhesion between the filler and the matrix. Low filler contents in solutions (below 1 wt %)



**Fig. 7.** Micrographs of the materials obtained via the electrospinning of (a) chitosan solutions with a concentration of 4 wt % and (b–d) mixtures containing (b) 5, (c) 10, and (d) 20 wt % PEO.

weakly influence the rheological properties of chitosan solutions.

Figure 6 shows the dependences of viscosity on shear rate for a 4% chitosan solution containing 10 wt % PEO (curve 1) and for a similar solution additionally containing 20 wt % chitin nanofibrils (curve 2). As is seen, the addition of chitin nanofibrils increases the viscosity of the composite at low (below  $1 \text{ s}^{-1}$ ) shear rates. The second marked difference is that the viscosity of the solution containing chitin nanofibrils decreases with an increase in the shear rate in the range  $0.05\text{--}5.0 \text{ s}^{-1}$  and that such a dependence is absent for the composite containing no nanofibrils. A decrease in the viscosity of the solution in the shear-stress field indicates that “structuring” of the solution, that is, the orientation of chitosan macromolecules and anisometric chitin nanoparticles, occurs.

As was shown in [5, 6], the oriented structure of chitosan fibers prepared via the coagulation method is formed at the stage of extrusion of the solution or its mixture with nanoparticles through the spinneret. The orientation of filler particles and polymer macromolecules depends on the flow rate of the polymer solution

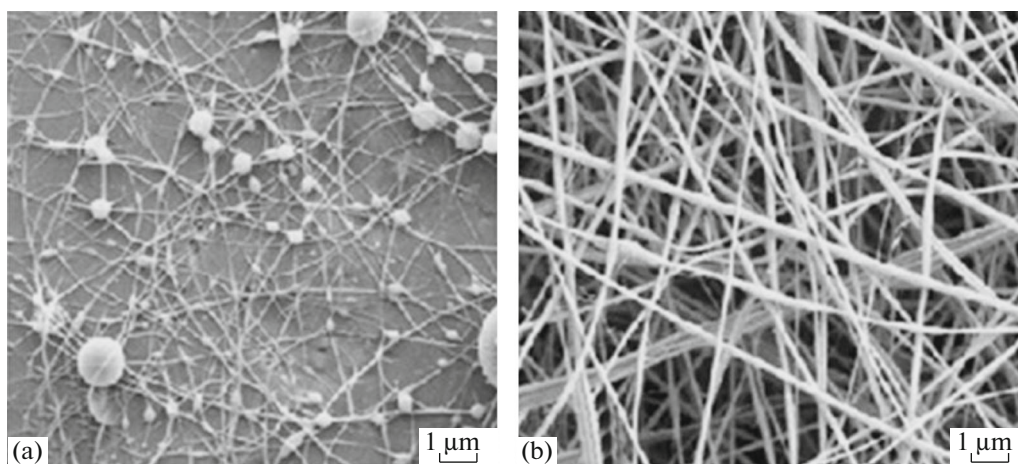
and the spinneret diameter, which determine the value of the shear rate in the spinneret. This value of the shear rate provides the structuring of the solution during its extrusion through the spinneret.

The regime of fiber spinning was adjusted according to the following equation [30]:

$$\dot{\gamma} = \frac{2Q}{\pi R^3},$$

where  $Q$  is the polymer-flow rate and  $R$  is the spinneret radius.

Note that, for the “wet spinning” of pure chitosan fibers, the values of  $\dot{\gamma}$  are  $10^1\text{--}10^2 \text{ s}^{-1}$ . Inprecisely this range, the highest slope of the viscosity dependences on shear rate is observed (Fig. 5). The spinning of such fibers proceeds at the high rate  $Q = 0.1 \text{ mL/min}$ . During electrospinning, the polymer-flow rate is much lower ( $Q = (3\text{--}8) \times 10^{-4} \text{ mL/min}$ ); in this case, the shear rate is  $\dot{\gamma} = 0.12\text{--}0.31 \text{ s}^{-1}$ . In this range of shear rates, as is seen in Fig. 6, there likewise are slopes of curves, but they are absent on the analogous dependences for solutions containing no chitin nanofibrils.



**Fig. 8.** Micrographs of the materials obtained via the electrospinning of 4% chitosan solutions containing (a) 10 wt % PEO and (b) 10 wt % PEO + 20 wt % chitin nanofibrils.

It follows from Figs. 5 and 6 that the viscosities for chitosan solutions containing chitin nanofibrils decrease in the shear-stress field. This effect is especially noticeable at a high content of nanofibrils (20 wt %). It should be emphasized that the addition of nanofibrils to the PEO-containing chitosan solution, on the one hand, increases the viscosity and, on the other hand, considerably increases its dependence on the shear rate relative to those of solutions free of chitin nanofibrils.

After passing through the spinneret, the mixture containing PEO and chitin nanofibrils enters the electric field. Acting on the three-component mixture (chitosan–chitin–PEO), this high-voltage field most substantially affects PEO macromolecules and chitin nanofibrils that possess good dielectric properties. As a result of the combined orientation effect of both the shear field and the electric field on the chitosan solution containing PEO and chitin nanofibrils, a fibrous structure that is characterized by the absence of droplike defects is formed.

The introduction of chitin nanofibrils into chitosan solutions stabilizes the electrospinning of fibers and makes it possible to reduce the content of the water-soluble PEO in nanofibers. It may be supposed that this circumstance will improve the properties of materials, and, above all, their moisture resistance.

#### *Structuring of Composite Nanofibers Based on Chitosan, PEO, and Chitin Nanofibrils*

Figure 7 presents micrographs of the materials prepared via the electrospinning of 4 wt % chitosan solutions and mixtures containing 5, 10, and 20 wt % PEO. During electrospinning of a pure chitosan solution and its mixture containing 5 wt % PEO (Figs. 7a, 7b), spherical particles with radii of 0.5–2.0 μm appear,

while fibrous structures are absent. Fibers with diameters of 60–150 nm and spheres with radii of 1.0–2.0 μm (Fig. 7c) are formed during spinning of the solution containing 10 wt % PEO.

Fibers with diameters of 80–200 nm with inclusions containing small amounts of spherical particles with radii of 80–200 nm (Fig. 7d) are formed from the mixture containing 4 wt % chitosan and at least 20 wt % PEO. After the introduction of less than 20 wt % PEO ( $M_w = 9 \times 10^5$ ), the amounts of defects (drops, microspheres) in nanofibers increase considerably (Figs. 7a–7c). Moreover, these defect nanofibers are formed only at a very low polymer-flow rate, while an increase in this rate leads to the formation of even larger droplike defects and causes a substantial decrease in the fraction of nanofibers.

After the introduction of chitin nanofibrils into the chitosan solution containing 10 wt % PEO, defect-free structures of nanofibers may be obtained. As follows from Fig. 8a, a significant amount of droplike defects with sizes of 1 μm or less are formed during electrospinning of the composite without chitin nanofibrils. Meanwhile, nanofibers containing 20 wt % chitin nanofibrils have an almost defect-free structure (Fig. 8b).

It was shown in [5, 6] that the orientation of chitosan macromolecules and chitin nanofibrils occurs during the coagulation spinning of composite fibers from chitosan solutions containing chitin nanofibrils. Such “structuring” of a solution is caused by the presence of shear stresses arising during solution extrusion through the spinneret. Therefore, during the electrospinning of chitosan solutions containing chitin nanofibrils, an easier splitting into microjets that form nanofibers on the surface of the receiving electrode may be expected. Chitosan solutions without chitin nanofibrils are almost completely unstructured in the

spinneret. Thus, no orientation of chitosan macromolecules occurs. The formation of chitosan fibers during electrospinning may be promoted by the addition of PEO macromolecules to the chitosan solution, as has already been shown in a number of papers (e.g., [28]). A high-molecular-mass PEO, owing to its dielectric properties, is capable of orientation and fiber formation under the application of a high-voltage electric field. In turn, the orientation of PEO macromolecules may promote the orientation of chitosan macromolecules; as a result, successful electrospinning of chitosan nanofibers is provided. Nevertheless, a decrease in the concentration of PEO with  $M_w = 9 \times 10^5$  in chitosan solutions (below 20 wt % with respect to chitosan) gives rise to the formation of defective fibers. The quality of nanofibers being spun with a decrease in the concentration of PEO may be recovered only via the introduction of chitin nanofibrils instead of PEO into chitosan solutions. As was shown in our studies, the introduction of up to 20 wt % chitin nanofibrils into chitosan solutions considerably accelerates the spinning of nanofibers in electric fields and decreases the amounts of defects in them.

## CONCLUSIONS

The electrical conductivities of chitosan solutions and liquid mixtures containing PEO are 2–4 mS/cm, that is, three to four orders of magnitude higher than the values for polymers with good spinning abilities in electric fields (aliphatic copolyamides and PVA). The surface-tension coefficients of chitosan solutions with concentrations of 3–4 wt % remain practically the same after the addition of small amounts of PEO. The addition of chitin nanofibrils into a chitosan solution containing 10 wt % PEO insignificantly increases the electrical conductivity and surface tension of the mixture. At the same time, the introduction of chitin nanofibrils into a chitosan solution substantially affects the dependence of the viscosity of the polymer solution on the shear rate. This fact is evidence for the orientation of chitin nanoparticles and chitosan macromolecules in the shear field. Therefore, it may be suggested that the rheological characteristics of chitosan solutions with PEO and chitin nanofibrils are crucial for predicting the manufacture of high-quality nanofibers via the electrospinning method.

## ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 14-03-00003.

## REFERENCES

1. R. A. A. Muzzarelli, P. Morganti, G. Morganti, P. Palombo, M. Palombo, G. Biagini, *Carbohydr. Polym.* **70**, 274 (2007).
2. J. Ok, J. M. Lee, J. H. Kim, J. Kim, H. Y. Kweon, Y. Y. Jo, and Ch. H. Park, *J. Biomed. Mater. Res., Part A* **100** (8), 2018 (2012).
3. E. I. Shishatskaya, T. G. Volova, and S. N. Efremov, *J. Mater. Sci., Mater. Med.* **15**, 719 (2004).
4. A. Rahmanian-Schwarz, M. Held, T. Knoeller, S. Stachon, T. Schmidt, H.-E. Schaller, and L. Just, *J. Biomed. Mater. Res. A* **102** (4), 1173 (2014).
5. I. P. Dobrovol'skaya, E. N. Dresvyanina, A. N. Yudenko, P. V. Popryadukhin, E. M. Ivan'kova, and V. E. Yudin, *Nauch.-Tekhn. Vedomosti SPbGPU. Fiz.-Mat. Nauki*, No. 4 (206), 74 (2014).
6. V. E. Yudin, I. P. Dobrovolskaya, I. M. Neelov, E. N. Dresvyanina, P. V. Popryadukhin, E. M. Ivan'kova, V. Yu. Elokhovskii, I. A. Kasatkin, B. M. Okrugin, and P. Morganti, *Carbohydr. Polym.* **108**, 176 (2014).
7. H. Seyednejad, D. Gawlitta, R. V. Kuiper, A. Bruin, C. F. van Nostrum, T. Vermonden, W. J. A. Dhert, and W. E. Hennink, *Biomaterials* **33**, 4309 (2012).
8. I. P. Dobrovolskaya, P. V. Popryadukhin, V. E. Yudin, E. M. Ivan'kova, V. Yu. Elokhovskiy, Z. Weishauptova, and K. Balik, *J. Mater. Sci., Mater. Med.* **26** (1), 1 (2015).
9. D. C. Surrao, S. D. Waldman, and B. G. Amsden, *Acta Biomater.* **8**, 3997 (2012).
10. M. S. Shoichet, *Macromolecules* **43**, 581 (2010).
11. B. Duan, C. Dong, X. Yuan, and K. Yao, *J. Biomater. Sci., Polym. Ed.* **15**, 797 (2004).
12. G. N. Flerov and V. S. Barashenkov, *Sov. Phys. Usp.* **18**, 783 (1975).
13. M. Mulder, in *Basic Principles of Membrane Technology Center for Membrane Science and Technology* (Academic, 1996), p. 564.
14. P. K. Baumgartner, *J. Colloid Interface Sci.* **36**, 71 (1971).
15. P. V. Popryadukhin, I. P. Dobrovol'skaya, V. E. Yudin, E. M. Ivan'kova, A. B. Smolyaninov, and N. V. Smirnova, *Cell Tissue Biol.* **6**, 82 (2011).
16. R. Rošic, J. Pelipenko, P. Kocbek, S. Baumgartner, M. Bešter-Rogač, and J. Kristl, *Eur. Polym. J.* **48**, 1374 (2012).
17. J. D. Schiffman and C. L. Schauer, *Polym. Rev.* **48**, 317 (2008).
18. K. Ohkawa, D. Cha, H. Kim, A. Nishida, and H. Yamamoto, *Macromol. Rapid Commun.* **25**, 1600 (2004).
19. M. Spasova, N. Manolova, D. Paneva, and I. Rashkov, *e-Polym.* **56**, 1 (2004).
20. L. Li and Y.-L. Hsieh, *Carbohydr. Res.* **341**, 374 (2006).
21. A. N. Sonina, G. A. Vikhoreva, I. E. Veleshko, A. N. Veleshko, M. G. Drozdova, E. A. Markvicheva, and L. S. Gal'braikh, *Fibre Chem.* **45** (2), 79 (2013).
22. A. N. Sonina, G. A. Vikhoreva, G. K. Morgunov, and L. S. Gal'braikh, *Fibre Chem.* **44** (2), 79 (2012).
23. A. Yu. Khomenko, P. V. Popryadukhin, T. B. Bogomolova, I. P. Dobrovol'skaya, V. G. Mamagulashvili, A. D. Shepelev, S. N. Chvalun, V. E. Yudin, and E. M. Ivan'kova, *Nanotechnol. Russ.* **8** (9–10), 639 (2013).



24. I. A. Dobrovol'skaya, I. Kasatkin, V. Yudin, and V. Yu. Elokhovskii, *Polym. Sci., Ser. A* **57** (1), 52 (2015).
25. I. S. Lishanskii, A. Yu. Men'shikova, T. G. Evseeva, E. E. Komarovskaya, V. E. Shubin, and N. A. Sakharov, *Vysokomol. Soedin., Ser. B* **31** (6), 413 (1991).
26. J. W. Gatti, M. C. Smithgale, S. M. Parajape, R. J. Rolfes, and M. Parajape, *Biomed. Microdevices* **15**, 887 (2013).
27. E. V. Kozyreva, Yu. A. Dmitriev, A. B. Shipovskaya, and L. Yu. Kossovich, *Izv. Saratov Univ. Nov. Ser. Ser. Khim., Biol., Ekol.* **11** (1), 22 (2011).
28. Yu. A. Dmitriev, Candidate's Dissertation in Chemistry (MITKhT, Moscow, 2011).
29. G. I. Kudryavtsev, V. Ya. Varshavskii, A. M. Shchetinin, and M. E. Kazakov, *Reinforcing Chemical Fibers for Composite Materials* (Khimiya, Moscow, 1992) [in Russian].
30. K. E. Perepelkin, in *Carbochain Synthetic Fibers*, Ed. by K. E. Perepelkina (Khimiya, Moscow, 1973), p. 165 [in Russian].

*Translated by A. Yakimansky*