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## Nano-Fiber Nonwoven Materials of Polymers with Surface-Active Properties

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**Abstract** A specially assembled electrospinning unit was used to form nanofibers from solutions of fibroin, chitosan, a copolymer of acrylonitrile and to obtain nanofiber nonwovens based on them with surface-active properties.

**Keywords** Fibroin, chitosan, acrylonitrile copolymer, electrospinning, nanofibres, non-woven layered materials, surface-active properties

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### Introduction

The development of modern nanoscience and nanotechnology is closely related to the creation of new nanomaterials, in particular, nanofibres of polymers with unique properties. One of the high-tech methods for producing nanofibers is electrospinning [1], based on the electroforming of this nanomaterial from solutions and polymer mixtures under the influence of a high DC voltage, which implements the “jet-nanofiber” transformations by analogy with “dry” molding in the interval from the anode (die-needle) to the cathode (drum or screen). The conditions for forming nanofibers and their required thickness are selected by adjusting the diameter of the needle (1 - 50 mkm), distance from the anode to the cathode (1 - 20 cm), high voltage (1 - 50 kV), polymer concentration (1 - 25%) in the dope or mixture, thermodynamic quality of the solvent, etc.

The high voltage applied to the anode not only draws polymer molecules from the jet towards the cathode, but also carries out orientation-twisted structure formation of macromolecules in the form of nanofibers. Technically, the adoption of nanofibers on a stationary screen is simple, which allows direct laying of the formed nanofibers on the surface of the screen in the form of a non-woven material. Moreover, the resulting non-woven material is characterized by nanoporosity and surface activity. Such characteristics of nanofibers and nonwovens based on them are largely dependent on the type of polymer. In this aspect, it is of great interest to obtain surface-active nanofibers based on biocompatible, biodegradable local polymers such as chitosan, fibroin, acrylonitrile copolymer, cellulose and its derivatives, etc. [2, 3]. Obviously, nanofibers of chitosan (ChZ) and fibroin (FB) exhibit surface bioactivity due to the presence of functionally active amine (NH<sub>2</sub>) and carboxyl (COOH) groups in the elementary biopolymers of these biopolymers. Usually, nanofibers of chitosan or fibroin are noticeably stiff compared to nanofibers of the synthetic acrylonitrile copolymer (Co-AN). Therefore, the preparation of nanofibers from mixtures of these natural and synthetic polymers or the formation of layered materials based on nanofibers of these high molecular weight compounds seems very practical and promising. The present work is accomplished in this aspect in order to obtain nanofiber nonwoven laminated materials with surface active properties.



### Objects and methods

Spinning polymer solutions for electrospinning nanofibers are characterized by a viscosity of about 10 Pa.s. This was taken into account in the preparation of spinning solutions of selected polymers, which markedly differed in molecular weight (M) and solubility in individual solvents. And so, an FB solution (M = 127000) was prepared in formic acid (HCOOH) with concentrations of C = 15%, a solution of ChZ (M = 108000) in acetic acid (85% CH<sub>3</sub>COOH) with C = 5%, and a solution of Co-AN (M = 115000) in dimethylformamide (DMF) with C = 7%. Since this work was carried out for the first time, this required the use of a specially assembled laboratory installation of electrospinning of nanofibers [4], the circuit diagram of which is shown in Fig. 1. The installation consists of a reservoir - a syringe (R), a die - anode (A) connected to high voltages (15 kV), and a screen nanofiber receiver - a cathode (K). At the beginning of the experiment, the solution (S) is squeezed out of the syringe through a die (needle) to the outside in the form of a drop. Further, a strong electric field arising in the range from the anode to the cathode (5 - 15 sm) under the action of high voltage contributes to the structural-phase transformation of the solution components depending on their molecular characteristics.

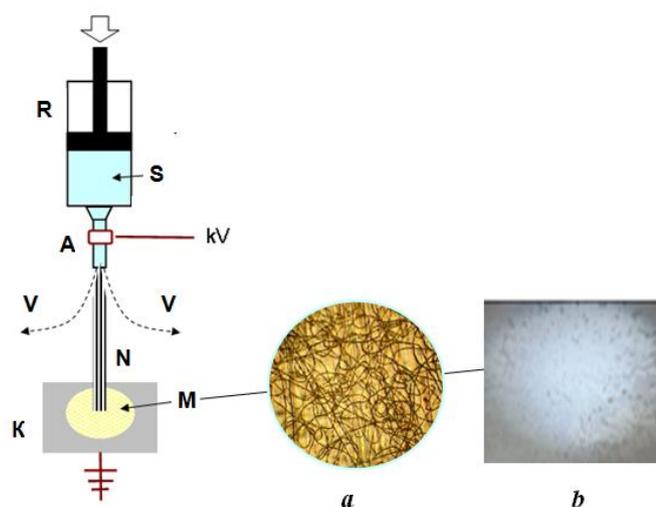


Figure 1: Schematic diagram of electrospinning of nanofibres of polymers: a - SEM image of FB nanofibres; b - micrograph of a nanofiber non-woven layered material based on FB and Co-AN

In this, solvent molecules with other low molecular weight compounds (V) are volatilized, and macromolecules undergo orientation-twisted structure formation of nanofibers (N) and are laid in the form of a nonwoven material (M) on the surface of the screen (K). The structure of the nanofibers (a) was analyzed using electron microscopy (SEM-200).

### Results and Discussion

The optimal conditions for electrospinning for the prepared polymer spinning solutions were revealed, namely, the limiting distances from the anode to the cathode and the specific voltage allowing one to obtain nanofibers in a certain thickness range (table 1). It was found that a decrease in the distance from the anode to the cathode by 1.5–2 times for a given high voltage leads to a decrease in the thickness of the polymer nanofibers by about 3–10 times. The reason for this is an increase in the tensile force of the fiber-forming jet due to an increase in the specific stress by 1.5 - 2 times.

Table 1: Electrospinning conditions for forming polymer nanofibres

Spinning solution			The distance to the cathode, cm	Specific voltage, kV/cm	The thickness of the nanofibers, nm
Polymer	Solvent	Concentration, %			
FB	HCOOH	15	5 - 7,5	3 - 2	100 - 300
ChZ	85% CH <sub>3</sub> COOH	5	5 - 7,5	3-2	100-500
Co-AH	DMFA	7	5 - 10	3 - 1,5	50 - 500



Nonwoven laminates were obtained by sequentially forming nanofibers, i.e. a layer of nanofiber nonwoven fabric of bioactive fibroin or chitosan was formed onto the surface of a preformed nanofiber Co-AN nonwoven fabric layer. Polarization-optical studies of these samples showed that the thickness of the base layer of the materials is about 30–45 mkm, and the thickness of the surface layer varies in the range of 5–20 mkm. It was revealed that these materials are nanoporous, with pore sizes ranging from 0.1 - 1.0 mkm.

It was determined that the nanofibers of the selected polymers are characterized by high optical anisotropy, the value of the chain orientation factor (where  $\Delta n$  is fluid and  $\Delta n_0$  is the maximum birefringence value) [5]. However, nonwoven layered materials do not exhibit pronounced optical anisotropy due to the arbitrary disordered arrangement of nanofibers in the samples. The value of the orientation factor of non-woven layered materials does not exceed. The results obtained suggest that non-woven layered materials, in general, are isotropic due to the ordered packing of nanofibers in them.

It was revealed that the obtained layered materials are characterized by high mechanical strength and resistance to deformation stretching. For example, samples with an average thickness are destroyed at a relative elongation of 15–20% and have a Young's modulus of 5–10 and retain high mechanical flexibility with repeated bending and torsion of the material.

The surface activity of nonwoven laminated materials is mainly determined by the presence of functionally active elements, namely, amine and carboxyl groups, selected polymers. These groups are characterized by specific interactions with oppositely charged elements, ions, groups, etc. This feature is clearly manifested during the flow of gaseous and liquid-phase mixtures through layers of nonwoven material, i.e. when filtering. Such filtering experiments were carried out in order to clean engine oil waste by passing it through non-woven layered materials based on fibroin and CoAN, characterized with average pore sizes of 10, 100 and 300 nm. It was found that waste machine oil (100 ml) flows through a layer of nonwoven material for 80 minutes and is achieved at 95% purification of oil. These results indicate a high surface activity of non-woven layered materials as nanofilters.

The interaction of surface-active elements of non-woven layered materials with metal ions was studied using the electroosmosis method, using an aqueous solution of  $\text{CuSO}_4$  (2%) as a nanoporous membrane of a non-woven layered material and a mobile dispersed phase [6]. We determined the, potential characterizing the stability of the interaction of ions with functional groups of nanofibers when a dispersed medium moves through membranes under the influence of direct current (Fig. 2). It was determined that the value of the potential increases from 40 to 80 mV with an increase in the concentration of  $\text{CuSO}_4$  from 0.5 to 2%.

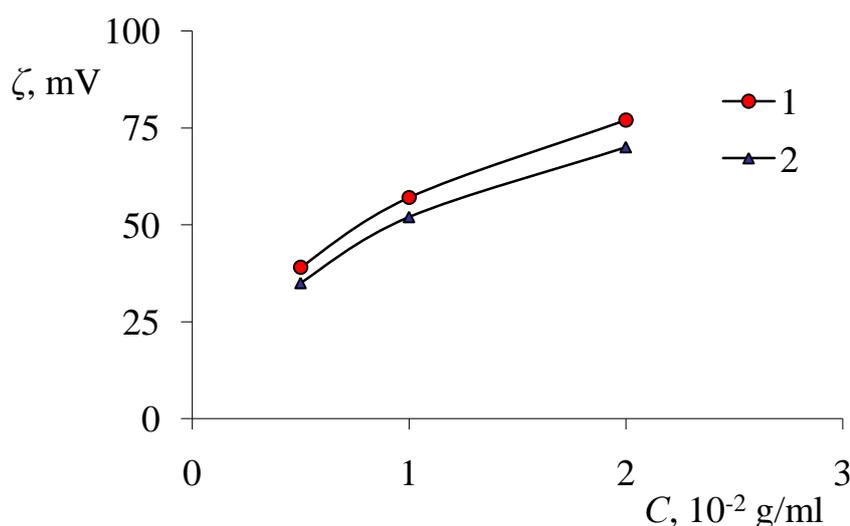


Figure 2: Dependence of the potential value on the concentration ( $C$ ) of a  $\text{CuSO}_4$  solution for nonwoven layered materials based on Co-AN with FB (1) and Co-AN with ChZ (2)



These results indicate a high stability of the interaction of ions with nanowires due to the surface activity of the nonwoven layer of the material.

### Conclusions

Thus, the research results show that on the basis of fibroin, chitosan and acrylonitrile copolymer non-woven layered materials with surface-active properties are possible. The wide possibility of regulating the structure of nonwoven layered materials by varying the conditions of electrospinning of nanofibers, the concentration of polymer solutions, by changing the sequence of forming nanofiber laminated materials is shown.

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