Surface-Active Properties of Nanofibers on the basis of Fibroin Silk and Copolymer Acrylonitrile

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Abstract

Fibroin silk (FS) and Copolymer acrylonitrile (Co-AN) nanofibers are obtained by the electrospinning method and investigated their surface-active properties. The possibility of regulating the thickness of nanofibers of fibroin in the range of 100-300 nm has been revealed by changing the concentration of (5 – 20%) electrospinning solution of FS in HCOOH and the effects of high voltage 3-6 KV/cm relative to the distance from die (anode) to the screen (cathode). At such high voltage range obtained nanofibers with a thickness of 50 – 500 nm from a solution of Co-AN in DMFA at concentrations of 5 – 10%. Using a stationary screen with an area of 400 cm² as a receiver contributed to the arbitrary nanofibers storage in the form of non-woven material with a thickness of up to 10 mkm. It was found that, nonwoven materials are characterized by nanopores 50-300 nm, depending on the condition of forming nanofibers. Physical properties of nanofibers are investigated and it is shown that the nanofiber nonwoven materials (on the basis of these polymers adsorb water comparatively more than ethanol), demonstrates high efficiency in the filtration of waste engine oil, and interacts stably with metal ions at electro-osmosis, showing bioactivity as the nanocoating for open wounds.

Key words: fibroin silk, copolymer acrylonitrile, nanofiber, electrospinning, surface activity, sorption, nanofiltration, Zeta-potential.

INTRODUCTION

The development of modern nanonanoscience and nanotechnology is closely related to the creation of new nanomaterials, in particular, nanofibers by the method of electrospinning (forming) of solutions and mixtures of polymers [1]. In this formation nanofibers is carried out under the action of high constant voltage (1-30 KV), realizing pulling out of a thin stream of a polymeric solution (or a mix of polymers) from an anode (die) to a cathode (a screen). Thus, the solvent practically completely evaporates and nanofiber is laid in the form of the non-woven foliate material on a surface of a screen. Depending on the conditions of forming are nanofibers with a thickness of 5-500 nm, and the thickness of non-woven material can be adjusted from 10 µkm to tens mm. In the case of polyelectrolytes, the high voltage facilitates the localization of mobile ionic groups of macromolecules on the surface of nanofibers and as a result, the resulting nanofiber non-woven material has a pronounced surface activity [2]. Special attention is drawn to the following points:-forming of nanofibers on the basis of biopolymers (for example, fibroin, collagen, chitosan) containing positively charged amino groups allows receiving non-woven bactericidal materials because amine groups block negatively charged bacteria. Such materials may be used as biodegradable bandages or coatings for open wounds [3]. In case of forming nanofibers on the basis of ionic biocompatible polymers, in particular, copolymer acrylonitrile (AM: MA: IR) are obtained non-woven materials with high flexibility and expressed surface activity, showing interaction with different substances [4]. Such non-woven materials can be used as high-efficiency nanofilter for

gaseous and liquids substances. Based on the actuality of the present work is devoted to the study of surface-active properties of nanofibers on the basis of fibroin silk and copolymer acrylonitrile.

OBJECTS AND METHODS OF RESEARCH

The research objects were selected silk fibroin (FS) and purified from sericin and fatty acids, as well as fibers of copolymer acrylonitrile (co-AN), produced in JSC "Navoiyazot".

The fibers of FS dissolved in 50% CaCl_2 in order to eliminate possible destructions chains. Further, dialysis was performed against CaCl_2 ions, and the resulting powder amorphous fibroin dissolved in the form of formic acid (HCOOH). Experiments have shown, that solutions FS with concentration $c = 5\text{-}20\%$ in HCOOH are suitable for reception of nanofibers with thickness 100-300 nm by the method of a power electrospinning at a voltage 3-6 KV/cm.

Electrospinning solutions were prepared in DMFA with $C = 5 - 10\%$. It is revealed that at the same voltage range 3-6 KV/CM are formed nanofibers co-AN, but the thickness of nanofibers thus varies in the interval of 50-500 nm. Moulding nanofibers carried out on the installation of the electrospinning (Fig. 1) in Erlangen-Nuremberg University (Germany). By means of a special syringe (1) installed on the installation, the polymer solution is issued to the outside through the die (needle) connected to the high voltage (2).

Fig.1. Installing electrospinning (a) and SEM picture of FS nanofibers (b).

Solution, outward die (anode) is drawn to the screen (cathode) under the influence of a strong electric field. The solvent evaporates, and the polymer turns into nanofiber (3) and is placed on the screen in the form of non-woven material. The thickness of nanofibers and porosity of non-woven material is regulated by change of concentration of a solution, a value of high voltage, distance between an anode and a cathode.

Concentration of ionic groups of macromolecules on the surface of nanofibers, therefore, manifestation of the expressed superficial activity of them in contact with the elements of the environment. Such features of nanofibers were investigated by methods of physical chemistry, in particular, sorption vapours, nanofiltration liquids, electric osmosis ζ -potential, and also tested as a bio-coating [5-8].

RESULTS AND DISCUSSION

- a) Sorption vapours. Experiments were carried out on a highly vacuum installation with mercury shutters and quartz weights Mac-Ben at 298 K and residual pressure of air $10\text{-}3\text{-}10\text{-}4$ Pa. As sorbata chose ethanol and water. Received S-shaped isotherms sorption, which are shown in Fig. 2 in the form of dependence of the indicator sorption (x/m) from the relative humidity (P/P_0).

Fig. 2. Sorption isotherms of ethanol vapor (1, 2) and water (1', 2') for nanofibers Photoshop (1, 1') and co-AN (2, 2').

It can be seen that nanofiber samples are relatively more absorb water vapor than ethanol. Moreover, such a phenomenon is noticeably brighter in the case of the sample FS. This difference seems to be due to the dense packaging of flexible chain molecules of co-AN compared FS molecules in nanofibres. And the presence of relatively large numbers of hydrophilic groups in FS chains. Similar differences were found in the calculation of capillary-porous and structural indicators of nanofibers, namely, sorption Volume (X_m), the specific surface ($S_{y\partial}$), the total volume of pores (W_o), the average radius of pores (r_k) nanofibers are shown in the Table. 1.

It can be seen that the value of the indicators is relatively low in the case of ethanol vapors than water for both co-AN and FS. Noticeably curtailed value in the case of FS, i.e. large volumes of pores are caused by presence in molecules of fibroin large amino acid residues of type aspartic and glutamic which do not stack both in α -spiral, and in β -structural forms of the given protein in fibers.

Table 1. Capillary-porous and structural characteristics of nanofibers

Samples	FS	co-AN	FS	co-AN
	Ethanol		Water	
$X_m, \text{g/g}$	0,0045	0,0041	0,0054	0,0052
$S_{y\partial}, \text{m}^2/\text{g}$	14,72	12,91	23,04	18,33
$W_o, \text{cm}^3/\text{g}$	0,028	0,020	0,042	0,037
$r_k, \text{\AA}$	38,27	31,41	45,26	36,55

However, the radiuses of pores are large enough to penetrate atoms and not large molecules into the volume of nanofibers.

Thus, the obtained results are followed by that nanofibers of FS and co-AN are nanomaterials capable of absorbing vapours of atoms and molecules with dimensions of no more than 30-40 Å keeping their forms without significant deformation changes.

(b) Nanofiltration. Clearly, non-woven nanoporous materials on the basis of surface-active nanofibers show specific interactions with gaseous and liquid-phase substances and can selectively fix or retain their constituents depending on chemical nature, structure and dimension. Such selectivity is most vividly manifested when the colloidal and molecular-dispersed system is passed through the surface-active nanoporous material. This is a necessitating of the present experience in order to detect the effectiveness of nanofibre nanoporous material of the co-AN as a nanofilter, skipping through it the spent machine oil containing micro and nanoscale particles. Moreover, the machine oil is chemically neutral relative to the nanofibers of the co-AN. This provided an additional opportunity to carry out comparative experiments of samples of non-woven materials of the co-AN, differing in size of pores: 50, 100, 300 nm. The thickness of non-woven material was $d_n = 0.5$ mm. The study was carried out as follows, i.e. through nanofilter mass (MN), which is in a long funnel, passed $m_o = 100$ ml of spent machine oil, which has brown colour. At the output, i.e. after the oil flow through the nanofilter had a light yellow colour and its mass decreased (m_i), i.e. a certain part of the mass (m_p), from the composition was retained on the nanofilter.

This testified to the flow filtration of the oil, which flowed intensively within 60 -80 min. At the same time, the effectiveness of filtration was judged in relation to m_i/m_o by time (t) observations, building the graphs presented in Figure 3. 3. It can be seen that the filtration process is kinetic character, i.e. with the increase of time and size nanopoures the mass of the filtration product (m_i) is increased monotonically to 60-80 minutes, banners stabilise. Moreover, the reduction of nanofilter pores helps to increase the efficiency of impurities retention.

Fig. 3. Dependence of relative change of mass (m_i/m_o) from time (t) at passing of machine oil through nanofilter co-AN with different sizes of pores: 1 – 50 nm, 2 – 100 nm, 3 – 300 nm.

d) Electro-osmosis. Interaction of surface-active elements of nanofiber non-woven materials with metal ions was investigated using the method of electro- osmosis and determined the values of ζ -potential, characterizing of the stability of these interactions [6]. According to the method as nanoporous membrane used nanofiber of non-woven material on the basis of FS and movable dispersion phase of aqueous solution CuSO_4 (2%). It is visible from the results which presented in Fig. 4. that the value of ζ -potential is increased from 40 to 80 mV with the growth of CuSO_4

concentration from 0.5 to 2%. These results indicate the stability of ion interactions with nanofiber elements due to surface activity of non-woven material.

Fig. 4. Dependence of ζ -potential value on concentration (c) CuSO_4 solution for nanofiber of non-woven material on the basis of FS.

Thus, results show that on the basis of fibroin it is possible to receive nanofiber non-woven materials with surface-active properties, sufficiently stable interacting and holding metal ions in dispersed environments. Surface-active non-woven materials of co-AN are biocompatible, and on the basis of FS not only biocompatible, but also bioactive. It was of interest to carry out medico-biological tests as a cover of open wounds.

For this purpose from nanomaterials co-AN and FS cut squares with sizes $2 \times 2 \text{ cm}^2$ and according to [8] conducted sterilization by means of ethyl alcohol. Further, in a medico-biological laboratory condition on a surface of open wounds in rats have put data of blanks of squares and have fixed them from edges by means of plasters. Comparative observations of wound healing were carried out in other equal conditions with the use of 10 rats for each sample of nanomaterials within 30 days. The results of the observation found that the bioactive nanocoating FS contributed to the almost complete healing of wounds within 14 days, while the healing of wounds under the biocompatible sample of the co-AN lasted up to 21 days.

At the end of the healing wounds nanomaterials coating fell off without any extra effort. Separated from nanomaterials wounds were analyzed for the preservation of the structure. Polarizing-optical and electron-microscopic observations have shown that in general nanofiber structures of samples have remained. Control observations of the physical and medico-biological state of the healing sites of rats, carried out within three months, were not characterized by any serious structural change.

Thus, tests of nanofiber materials of co-AN and FS showed the principal possibility of their application as coatings for open wounds.

CONCLUSION

The conducted researches it is shown, that on the basis of fibroin silk and copolymer acrylonitrile, available functional-active groups it is possible to receive nanofiber non-woven materials with the expressed surface-active properties. The study of these materials for the purpose of detection of

sorption characteristics, filtering abilities, kinetic sustainability, and bioactive coatings gave positive results, on the basis of which at a subsequent stage it is possible development of new nanomaterials with special properties.

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