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NANOFIBERS BASED ON CHITOSAN BOMBYX MORI: FABRICATION AND STRUCTURAL CHARACTERISTICS

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Abstract: It was obtained nanofibers based on chitosan Bombyx mori using electrospinning method and studied their structural and thermodynamic characteristics by AFM, IR-spectroscopic, X-ray, sorption methods. The obtained results indicate that significant structural changes during the formation of nanofibers, which are manifested in the sizes of crystallites, thermodynamic parameters and sorption characteristics. These structural changes and consequent changes in the surface properties can lead to enhanced bactericidal properties of chitosan nanostructures.

Keywords: Nanofiber, chitosan Bombyx mori, electrospinning, chitosan nanostructures.

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Introduction

Natural polysaccharides, such as chitin and chitosan have attracted a lot of attention in different areas of research due to their unique physical, chemical and biological properties. These polymers have biological activity and they are compatible with human and animals tissues. In addition, these materials are ecological safe and are easily decomposed by microorganism enzymes [1].

Electrospinning is universal and efficient method to produce nanofibers with diameters ranging between a few nanometers to a few hundred nanometers [2]. Polymer nanofibers obtained from solutions or melts have many potential applications [3]. These nanofibers have advantages such as higher surface areas than regular fibers, have small pore size, high porosity and high surface area. There is also the advantage to control the nanofiber composition to achieve the desired property or functionality, offering more flexibility in surface functionalities.

These outstanding properties make the polymer nanofibers to be good candidates for many applications, which extend to filtration, tissue engineering, scaffold constructions, wound dressings, energy conversion and storage, catalysts and enzyme carriers, protective clothing, sensors, drug delivery, cosmetics, electronic and semi-conductive materials. [4].

Nanofibers based on chitosan are more effective than conventional fibers in using their natural bactericidal properties. The advantages of chitosan-based nanofibers become more pronounced in treating complex surgical wounds, trophic ulcers and etc. [5]. Chitosan nanofibers have several outstanding properties for different significant pharmaceutical applications such as wound dressing, tissue engineering, enzyme immobilization, and drug delivery systems. [6].

In this work, we studied the process and conditions of formation of nanofibers based on chitosan Bombyx mori by the electrospinning process and investigated their structures and thermodynamic properties.

Experimental

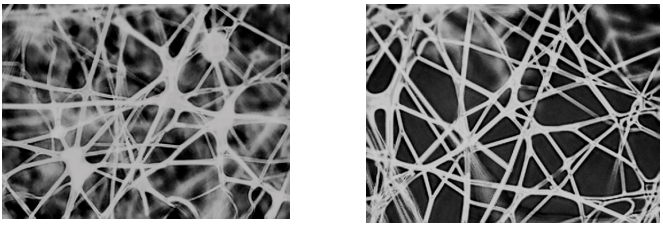
The base material for the nanofiber fabrication was chitosan Bombyx mori with a molecular mass of 90 kDa obtained from silkworm pupae. The characteristic viscosity was determined using an Ubbelohde viscometer at room temperature. The molecular weight was calculated using Mark-Kuhn-Hauwink equation [7]: . The experiments were conducted in a specially assembled device, which enables one to regulate the diameter of the nanofibers by varying the distance between anode (spinner) and cathode (screen) [8, 9].

Structural analysis were carried out using scanning electronic (SEM-200) and atomic-force microscopy (scanning probe microscope Agilent 5500) at room temperature. Silicon continents with a stiffness of 9.5 N/m with a frequency of 145 cps were used during the experiment. The maximum scanning area on the AFM (along X and Y direction) was 5?5 ?m2 and 1 ?m along the Z-direction. X-ray diffraction analyzes were performed using a DRON-3M diffractometer. The CuK? radiation emitted by the nickel filter with a wavelength ? = 1.542 ? is used. The operating voltage was 22 kV and the anode current was 12 mA. Sorption studies were carried out in a high vacuum installation with mercury closures and calibrated quartz weights of Mac-Ben, sensitivity 0.35x10-4 mm/kg. The measurements were carried out at 25°C and a residual air pressure of 10-3-10-4 Pa.

Results and Discussion

The electron microscopic studies show that the thickness of the obtained chitosan nanofibers vary in the range of 100-500 nm, and depends on the solvent and molding conditions (Fig. 1). It is seen that during the electroforming processes of nanofibers dissolved in 85% acetic acid polymer sites are present as

knots (globules) along with nanofibers (Fig. 1 (a)). In the mixture of trifluoroacetic acid and methylene chloride (80/20) these areas were not observed (Fig. 1 (b).



a **b**

Fig. 1. SEM images of chitosan Bombyx mori nanofibers, obtained with using different solvents: a) acetic acid; b) trifluoroacetic acid: methylene chloride (80/20).

Next, we have conducted AFM studies to determine the dimensions of the nanofibers using semicontact methods. Scanning in the topography mode gives the size of the chitosan Bombyx mori nanofibers to be in the range 100-500 nm (Fig. 2).

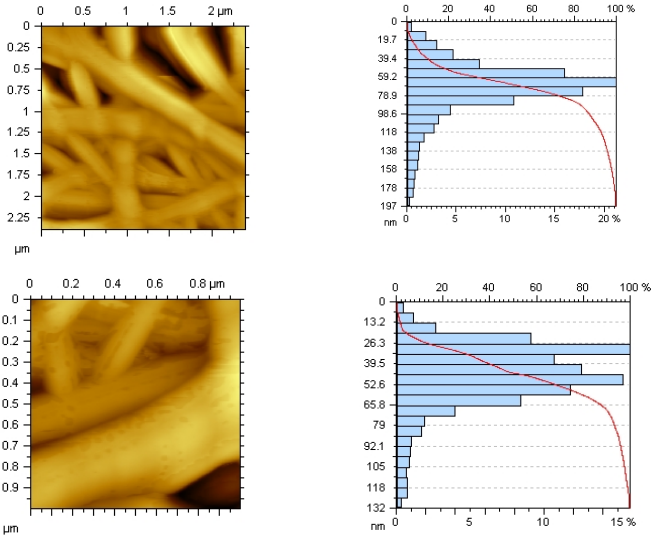


Fig.2. AFM investigations of chitosan Bombyx mori nanofibers in topography mode, and their distribution.

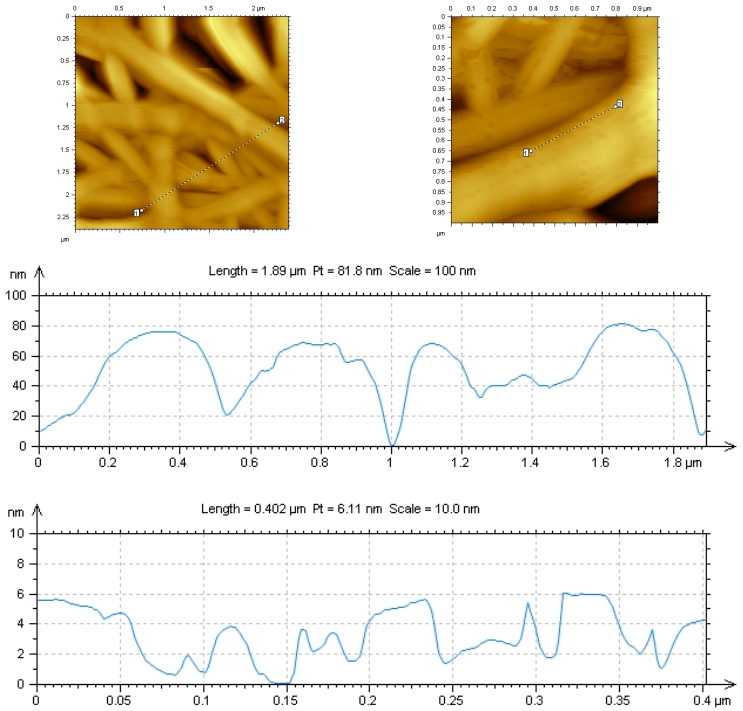
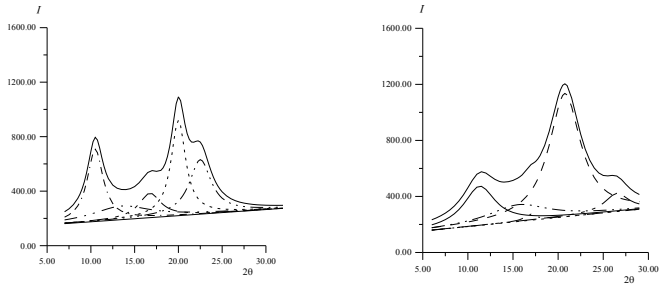


Fig.3. Section profile of chitosan Bombyx mori nanofibers in topography mode

Fig. 2 and 3 show the thickness distribution and profile of the scanned nanofibers in the topography mode. Section profiles show pores in the nanofiber of size ranging from 5 nm to 50 nm, which can be form during the electroforming process due to evaporation of the solvent.

X-ray diffraction analysis has shown that in the initial chitosan sample, obtained from pupae of the silkworm, exhibit characteristic reflections of the crystal structure at 2??11°, 20° and 26° related to the interplastic distances (100), (111) and (211), and the shoulder shape at 16.5° related to (110) (see Fig. 4).



a **b**

Fig.4. X-ray diffractions of chitosan Bombyx mori: a) nanofibres; b) initial sample

A change in the intensity and width of the coherent scattering region is observed for nanofibers, and a more pronounced shoulder is observed near (111) plane of the crystal structure associated with interplanar spacings (110) and (200), but no reflex at 26° (Table 1). In the process of the elementary cell parameters identification, it was determined that the selected objects have an orthorhombic syngony with cell parameters for the initial sample a = 7.85 ?, b = 8.02 ? and c = 10.02 A, and for nanofibers a = 8.01 A, b = 8.2 A and c = 10.1 A, which are in good agreement with the previous reports [10].

Table 1: Structural parameters of chitosan and nanofibers of chitosan

Parameters	Samples							
	Chitosan				Chitosan nanofiber			
	Crystal reflexes							
	100	110	111	211	100	110	111	200
Position of the maximum is 2θ, (deg.)	11.3	16.5	20.75	26.5	10.9	16.75	20	22.5
Interplanar spacing d, (Å)	7.83	5.37	4.28	3.36	8.117	5.29	4.439	3.95
Peak width at 0.5 of height β, (rad.)	0.037	0.037	0.03	0.028	0.019	0.017	0.026	0.026
Size of crystallite L, (Å)	42.27	42.76	52.5	56.72	80.64	89.70	60.04	59.52

Such changes in the cell parameters may be explained by the physical processes occur during electroforming, which determine the orientation of the macromolecules.

Experimental results show the increase of the lattice parameters of the crystals during the electrospinning process. This indicates to more favorable conditions for the crystal growth during the electroforming.

The obtained sorption curves have S-shape behavior (Fig. 5). This S-shaped nature of sorption indicates that the process is developing simultaneously in two ways [11]. At low concentrations of the sorbate, its molecules are predominantly fixed on the active centers of the polymer. The increase in the concentration of the sorbent the sorption becomes more pronounced. The latter processes is qualitatively different than the first one where clear specific interactions between the polymer and sorbate do not exist.

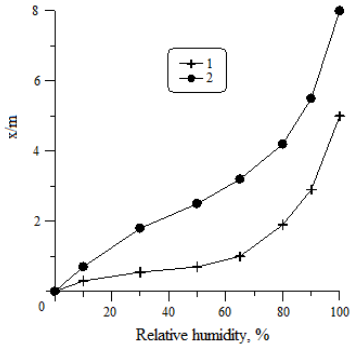


Fig.5. Water vapor sorption isotherm for chitosan fibers: 1-nanofibre, 2 -initial

Basing on the water vapor sorption data, monolayer capacity (Xm), specific surface area (Sun), total pore volume (W0), and average radius of the submicroscopic capillaries (rk) were determined (Table 2). As shown in the Table 2, the nanofibres absorb significantly less water in compare to the original sample, despite their larger average pore size. This could be explained by sorption occurring on different stages; for nanofibers it is caused by a denser packing of chitosan macromolecules in nanofibers, due to which at low relative humidity the amount of absorbed sorbate is of less importance; increasing of the relative humidity due to capillary condensation has a greater significance, and this affects on the average pore size.

Table 2. Sorption characteristics of chitosan fibers

Samples	Xm, gr/gr	$S_{un,m}^2$/gr	W_o,sm^3/gr	r_k, Å
Chitosan	0.0194	68.14	0.080	23.0
Chitosan nanofiber	0.0054	19.11	0.057	52.3

For the initial sample and nanofibers of chitosan the thermodynamic parameters, such as chemical potential, and mixing energy were calculated. It was shown that the chemical potential for nanofibers has a minimum at $p/p_0 \approx 0.30$ relative humidity, and the value of the mixing energy was $\Delta g_m = -3.806$. For the initial sample, the chemical potential has a maximum at $p/p_0 \approx 0.65$ relative humidity, and the mixing energy $\Delta g_m = -1.546$ due to differences in the surface energies of these samples.

The significant structural changes occurring in the formation of chitosan nanofibers are manifested in the sizes of crystallites, thermodynamic parameters, and sorption characteristics. Of course, these structural changes connected with the surface properties can lead to increasing of the chitosan bactericidal activity.

Conclusion

Nanofibers of chitosan Bombyx mori were obtained by electrospinning and their structural characteristics were investigated. The morphology of chitosan nanofibers obtained by electrospinning depends on the used solvent and the thickness of nanofibers varies from 100 to 500 nm. It was found that the size of crystallites increases during electrospinning, which is explained by the fact that more favorable conditions are created for the improvement of crystallites in the process of electrospinning. The thermodynamic parameters of chitosan nanofibers were calculated, and it was shown that the chemical potential for nanofibers has a minimum $p/p_0 \approx 0.30$ at relative humidity, and the value of the mixing energy has $\Delta g_m = -3.806$.

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