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CHARACTERISTIC PROPERTIES OF SPINNING SOLUTION AND NANOFIBRES FROM CHITOSAN BIOPOLYMER

Electrospinning from solutions of polymers which is a promising way of nanofibres manufacture in the field of nanotechnologies is reviewed in the paper. Chitosan which possesses wound-healing action was used as polymer, it is also non-toxic, biocompatible and biodegradable. Nanofibres on its basis manifest the superdeveloped surface and voids rating. Taking into account wound healing properties, chitosan is very effective at producing wound textile for burns, long nonhealing wounds, and trophic ulcers. Nanofibres from chitosan were produced according to the Nanospider technology on the NS LAB 500 S (ELMARCO, Czech Republic). During process of nanofibres electrospinning potential difference between electrodes up to 60 kV was created. Positively charged sprays push each other, move and vibrate during electrospinning. Diameter of a spray decreases towards nanosizes because their movement accelerates. The chemical composition, viscosity, and rheological parameters of the solution are developed. The electrospinning technology is optimized; the structure of a nanofiber layer is analyzed by method of scanning microscopy on JSM-5610 LV JEOL. Thus, the prospects of use of Nanospider technology are defined for production of nanofibres based on polymer solutions.

Key words: electrospinning, chitosan, nanofibers, spinning solution, electrode, viscosity, scanning electron microscopy, nanofiber coating.

Introduction. Chitosan is an active chitin substance, amorphous-crystalline biopolymer. High molecular weight chitosan is easily dissolved in solutions of both mineral and organic acids. Some researchers believe formic acid solution with a concentration from 0.2 to 100% to be the best solvent [1]. Reducing the molecular weight allows chitosan to dissolve at neutral pH [2, 3]. Natural chitosan is found only in queen termites (abdominal wall) and in Zygomycetes (cell partition) [4, 5]. Therefore, chitosan is produced from chitin, which is, by contrast, is widely distributed and renewable. It is concentrated in the shells of crustaceans (lobsters, crabs, shrimps, crayfish), as well as in insects (flies, bees, beetles).

Medicinal preparations based on chitosan are increasingly widely used for burn wounds treatment of various etiologies [6]. Thus, synthetic leather (from the highly purified high molecular weight chitosan membranes and films) is used for burns and open exudative wounds treatment [7]. The tests with these films resulted in a significant inhibition of the microflora growth (staphylococcus, proteus, blue pus bacillus) and an accelerated treatment of burn wounds [8]. Universal mechanism of chitosan selective binding with sugar receptors on the cell membrane provides a bacteriostatic effect on almost any kind of microorganisms [9, 10].

In recent years, the production of nano/ultrafine fibre materials is widely used for the manufacture of such medical devices as wound dressings, cell substrates, medical masks, nasal filters, filters for air and liquid filtration, and radionuclides sorbents. This material consists of several layers: an inner layer is made of chitosan nano/ultrafine fibers and the outer layers serve as an elec-trospinning substrate and perform a protective function [11, 13].

There are various methods of nanofibres spinning, but any process consists of the three stages required: the material transfer in viscous flow state (plastic state), molding and curing [14]. Plastic state determines the ability of a material to fiberization and is characterized by specific values of viscosity and surface tension. Polymer and resin solutions or melts show the ability to fiberization [15, 16]. Viscosity and surface tension values are different while using different methods of spinning: due to a temperature change (for hot-melt molding) or concentration (for polymer or resin solutions molding), or the introduction of surfactants. The curing process is performed either by cooling below the glass transition temperature of the polymer or by solvent removal (via evaporation or substitution) [17].

By its implementation and nature the electrospinning technological process is a dry nonspinneret method, in which deformation of the initial polymer solution, followed by transportation of curable upon solvent evaporation fibers and fibrous layer formation are accomplished solely by electrical forces in a single workspace [18].

Spinning polymer solution under its own weight or under extreme pressure of gas, liquid or piston flows out of the container with a predetermined volumetric flow through an injected capillary nozzle. By means of the metal electrode the solution is supplied with a regulated, constant, high and always negative voltage. Further, under the influence of electric force the solution forms a continuous, stationary, accelerating and thinning free

jet, the axis of which coincides with the general direction of the electric field. As a result, the jet is formed as a cone which in the foreign literature is called "Taylor cone" [19–21]. This is the first, relatively easily regulated electrospinning process stage, on the stability and the results of which depend all the subsequent stages.

The second stage consists of several processes that proceed simultaneously: spatiotemporal fluctuations in the volume electric charge density cause fluctuations in value and direction of the electric field intensity leading to the charge deviation from the direction of the jet. At the same time due to a large inertia of the jet there is a hydrodynamic force moment which increases jet deviation, the viscous gas medium acting on the jet (jet speeds are rather high) [22–24]. As a result, the jet turns round across the field and is retarded by an increasing medium resistant force. The jet forms a cloud (in the form of an expanded downward cone) which is pushed apart by the like electric charges.

At the same time, the solvent evaporation which begins at the first stage of the process is sharply intensified. The jet is solidified and the resulting fibrous cloud drifts in an external electric field to the precipitation electrode [25].

At this stage of the process successive jet dissipations into pairs of daughterly jets are also possible, each of these new pairs may undergo further dissipation. This process depends on the balance of viscosity, surface tension and density of the electric charge in the jet volume [25, 26].

It should be noted that in addition to these two instabilities there is one more instability type – surface capillary instability of the jet resulting from competition of surface tension forces and electrostatic forces and leading to the jet surface morphology change and the violation of its cylindricity. As a result, the diameter of the jet becomes variable, constrictions, thickenings and twistings are formed. In the section the jet takes the shape of a dumbbell, ellipsoid, or a more complex shape. According to some theoretical models it is the surface instability that leads to the jet dissipation [25].

The aim of this study was to determine the influence of technological parameters of a spinning solution from the biopolymer chitosan on the structure of nanofibers produced by electrospinning. 70% acetic acid was used as a solvent. To prepare the spinning solution animal chitosan ("BelRos-BioTeh" production) with a molecular weight of 100–200 kDa was used.

Main part. One of the most important properties of the spinning solution is its dynamic viscosity. From the viewpoint of power production, the viscosity appears as an undesirable factor, which increases energy losses to overcome the internal friction in the liquid jet. On the other hand it is not only positive, but, in some cases, significant, and even a decisive factor to achieve the desired result [27, 28]. A higher polymer concentration corresponds to a greater viscosity and hence, a larger weight output of the process. Furthermore, viscosity suppresses capillary waves, destroying the liquid jet and increases its resistance. The dynamic viscosity study was conducted using a Brookfield rotational viscosimeter on the Brookfield DV-II+PRO with a cylinder/cylinder type measurement cell for small volume samples.

Fig. 1 shows the dynamic viscosity dependence of chitosan spinning solution on its concentration in 70% acetic acid at 20°C.

From the literature it is known that polymer solutions with a molecular weight of several tens or hundreds of thousands are generally used in the electrospinning process. Weight concentration of polymer solutions is up to 20% and the corresponding dynamic viscosity is in the range of 0.05 to 1.0 Pa · s.

The graph shows that if the chitosan concentration is 1.5 wt %, the viscosity equals to 65 mPa · s (0.065 Pa · s), and at a maximum concentration of 3.5 wt % – 885 mPa · s (0.885 Pa · s). That is, the viscosity of the spinning solution at concentrations of 1.5–3.5 wt % is in the recommended range for the electrospinning process.

It is seen from the data obtained that the dynamic viscosity at 2.1 wt % of chitosan concentration is 196 mPa · s (0.196 Pa · s), and at a maximum concentration of 3.1 wt % – 604 mPa · s (0.604 Pa · s). Viscosity dependence on concentration is not linear and is described as a parabola.

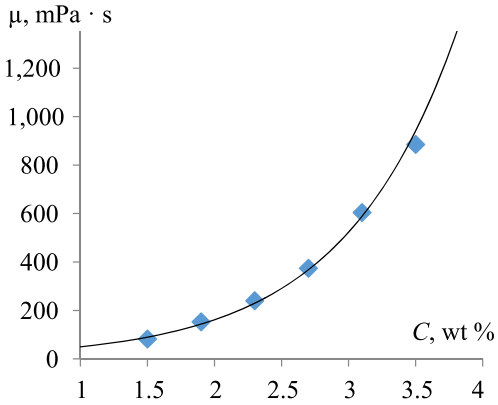


Fig. 1. Dynamic viscosity dependence of the spinning solution on chitosan concentration

Fig. 2 shows the dynamic viscosity dependence of the chitosan spinning solution in 70% acetic acid in a concentration within its optimum at 20°C.

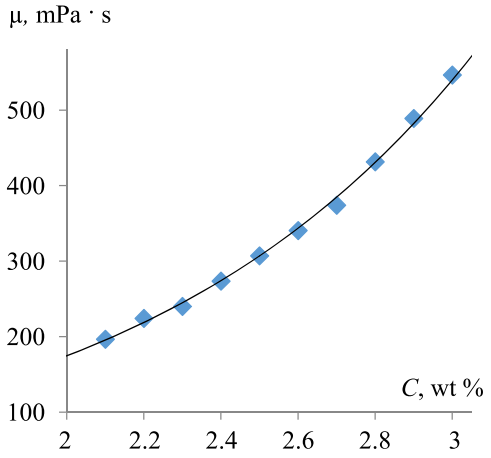


Fig. 2. Dynamic viscosity dependence on chitosan concentration

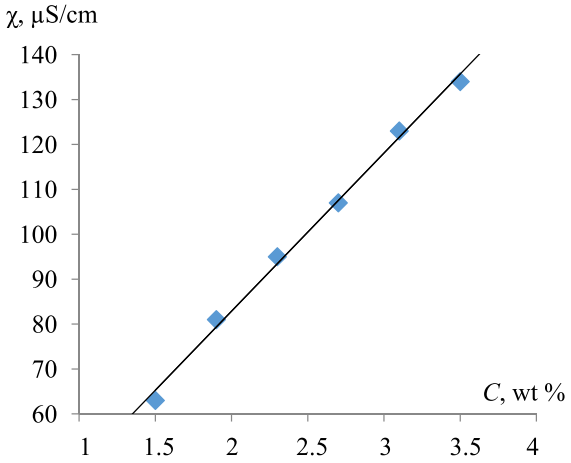


Fig. 3. Specific conductivity dependence on chitosan concentration

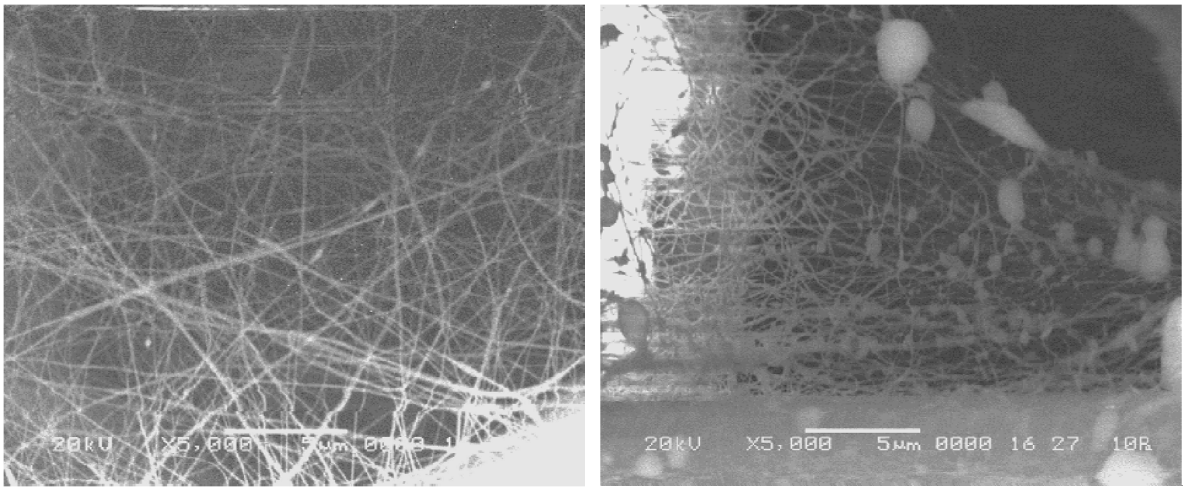
Specific conductivity of a spinning solution greatly influences the electrospinning process. From the literature [26, 27] it is known that specific conductivity of the nanofibres electospinning process has a fairly wide range – from 10^{-6} to 10^{-2} S/cm, where the lower limit is terminated by the gas discharge from the jet, which violates its stability. The increase of specific conductivity leads to the increase of the likelihood and the number of successive dissipations of the jet, which is drifting but is not fully cured. And, consequently, the effective rate of fiberization, i. e. electrospinning productivity increases either.

Fig. 3 shows the specific conductivity dependence of the χ chitosan spinning solution in 70% acetic acid on its concentration.

It is seen from this dependency that at a minimum chitosan concentration of 1.5 wt %, the specific conductivity is 63 μS/cm, and at a maximum chitosan concentration of 3.5 wt % – 134 μS/cm. These values are in the range suitable for nanofibres electrospinning process.

Determination of chitosan nanofibres structure obtained by electrospinning was performed using the electron microscope JSM-5610 LV JEOL (Japan). The obtained data allowed to analyze the structure of the nanofibres being spinned, and to determine the most appropriate process parameters of the spinning solution. Fig. 4 shows photographs of the material surface with nanofibers at different chitosan concentrations in the spinning solution.

The presented data show that at higher chitosan concentration (3.5 wt %) a large number of defects is observed in the spinning solution. Deterioration of nanofibre coating properties probably is due to an excess of chitosan. This leads to a difficulty in the dissipation of polymer jets formed by electrospinning into thinner ones.



a *b*

Fig. 4. Material surface with nanofibres produced from a spinning solution with the chitosan concentration of: *a* – 2.0 wt %; *b* – 3.5 wt %

Conclusion. Studies of the properties of the spinning solution from animal chitosan biopolymer showed that the values of the specific conductivity and dynamic viscosity of the spinning solution at concentrations of 1.5–3.5 wt % are in the recommended range for the electrospinning process. However, nanofiber coating structure analysis revealed the following features of the spinning solution properties, namely an increase up to 3.5 wt % of chitosan concentration can lead to the appearance of defects in the form of droplets. This impairs the coating uniformity of the substrate by nanofibres. It should be noted that the occurrence of the nanofibre coating defects at a given chitosan concentration may also be related to the process parameters of electrospinning.

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