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IMPACT OF ELECTROSPINNING TECHNOLOGICAL PARAMETERS ON CHITOSAN NANOFIBERS COATING MORPHOLOGY AND SURFACE DENSITY

Electrospinning from solutions of polymers as a perspective way of nanofibres manufacture in the field of nanotechnologies is reviewed in the paper. Chitosan which possesses a wound-healing effect is used as nanofiber-forming polymer; it is also non-toxical, biocompatible and biodegradable. Nanofibres on its basis manifest a superdeveloped surface, and voids rating. Taking into account curative properties, chitosan is very effective at creation ambustial, long non-healing wound 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 potencial difference between electrodes up to 60 kV was created. Impact of electrospinning technological parameters on chitosan nanofibers coating morphology and surface density are described. Most preferred electrospinning process parameters are selected. The structure of a nanofiber layer is analyzed by method of scanning microscopy on JSM-5610 LV JEOL. SEM images of nanofibres are presented. The results of work can be used on medical devices production.

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

Introduction. Electrospinning is one of the methods of obtaining fibers from a polymer solution by the action of an electrostatic field. Despite the complexity of understanding and study of electrospinning physical processes, this method features instrumental simplicity, high energy efficiency of nanofibres production, general versatility to the material and flexibility in the process parameters management. All these factors make electrospinning process attractive for industrial production of nanofibres [1].

A promising area of nanotechnology is Nanospider technology; it is electrospinning of nanofibres from free surface of polymer solutions. Nanofibers that are obtained with this technology feature high surface area, which lead to their high efficiency in filtration processes, biomedical applications; they provide anti-virus and anti-microbial barrier properties; regulation of water permeability and water vapor permeability; creating dressings for the treatment of extensive burn surfaces of different origin, non-healing wounds and trophic ulcers. "Wound dressings" from chitosan obtained by the electrospinning method are particularly promising [1].

Chitosan is deacetylated derivative of chitin. Unlike scarcely insoluble chitin, chitosan is soluble in acidic solutions, both mineral and organic acids. Chitosan molecular weight reducing allows it to dissolve at neutral pH [2]. The substance based on chitosan is a powder from white to white with a yellowish shade, or present in the form of a whitish, translucent beads.

Chitosan exhibits haemostatic, bacteriostatic, fungistatic properties. Immunomodulating and anti-tumor effects are detected, biodegradability, complete withdrawal from the body and biostimulation of regenerative processes, lack of immunoreactivity is proved [3].

It is shown that chitosan in the body is decomposed by specific group of enzymes and quickly deduced [3]. The end product of the decomposition of chitosan is a 2-aminoglyukan, a natural polysaccharide component of the body, a part of the molecules of hyaluronic acid and heparin [4]. It perforates well into the biological environment such as blood, lymph tissue and joint fluid, and it is absolutely non-toxic [5].

Chemistry and technology of chitosan nanofibers has a special role in the "medical nanotechnology" development [6–7]. Chitosan has high sorption properties, it is able to adsorb small polar molecules, peptide and protein drugs. Chitosan combines chemical and radiation resistance, [8] it is compatible with different substances – antiseptics, antibiotics, sulfonamides, and other local anesthetics [9].

Medicinal products based on chitosan are increasingly used for the treatment of burn wounds of various etiologies. Chitosan membranes and films are used for treatment of burns and open exudative wounds. Such films showed a significant inhibition of the microflora growth (staphylococcus, Proteus, Pseudomonas shelves) and accelerated healing of burn wounds [10]. Universal mechanism of selective chitosan binding to sugar receptors on the cell membrane provides a bacteriostatic effect on virtually any form of microorganisms [11].

Analysis of experimental data studying the effect of several forms of chitosan (solution, gel, film) on the healing process of skin wounds in rats

and rabbits showed that the use of the gel provides a significant acceleration of the repairing process of the skin and mucous membranes [12].

Chitosan is used for the production of biodegradable sutures. These sutures stay long enough to heal tissue, but then slowly dissolve, therefore they do not have to take out. Unlike many other biodegradable sutures, these do not cause allergic reactions, and do not lose their strength [13].

Thus, chitosan has unique properties and biological activity, which allows its wide use in medicine and pharmacy [1].

Electrospinning is based on polymer solution (melt) drawing in the thin jets of polymer under the influence of an electric voltage from a few to hundred kilovolts. High voltage induces electric charges in the polymer solution, which leads to the formation of the Taylor cone and further electrostatic stretching of the polymer solution. Polymer stream in the process of stretching may undergo a series of successive splitting into thinner jet. The resulting jet cured by solvent evaporation or by cooling, turning into fiber, and under the action of electrostatic forces drifts to the substrate having the opposite electric potential value.

The main impact on the process of electrospinning is to provide spinning solution properties and electrospinning process parameters. Optimum selection of all of the above properties of the spinning solution and electrospinning process technological parameters is the research task in each case [1].

Main part. Resulting nanofiber coating properties are directly affected by such technological parameters as voltage, electrode spacing, spinning electrode rotation speed. The main purpose of this paper is investigation of influence of these parameters on nanofibers average diameter and chitosan nanofiber coating surface density. To prepare spinning solution it was used chitosan produced by "KitoZyme" with molecular weight 30–50 kDa. Chitosan concentration in spinning solution was 7 wt %, acetic acid (70%) was used as solvent. Polyethylene oxide (0.3 wt %) with molecular weight 400 kDa was used as a processing additive. Electrospinning was performed on the day of the solution preparation. Spunlace and SpunBel nonwoven materials were used as substrates. Electrospinning was preformed on NS LAB 500S equipment.

Produced nanofiber was examined by the scanning electron microscope JSM-5610 JEOL LV. Nanofibers average diameter was calculated from the obtained SEM images using Image J software. Density of the nanofiber coating was gravimetrically measured on samples sized $10 \cdot 10$ cm.

Table 1 shows dependence of fungal chitosan nanofibers average diameter from electrode spacing, spinning electrode rotation speed, when SpunBel and Spunlace nonwoven materials were used as a substrate.

The analysis of the research data showed no significant differences between nanofibers average diameters during electrospinning of solution based on fungal chitosan at different voltages. The maximum value of nanofibers average diameter is 280 nm (when the inter-electrode voltage is 65 kV), while voltage increased up to 70 kW average diameter of nanofibers changed slightly – 270 nm. At the same time, further voltage increase (75, 80 kV) reduces the value of the nanofibers average diameter to 220 nm. This can probably be attributed to greater spinning solution jet stretched due to increased voltage, electric field strength and consequently Coulomb force increase.

Experimental data shows an increase in nanofiber coating surface density with voltage increasing when Spunlace and SpunBel are used as a substrate. When voltage was 60 kV nanofiber coating surface density was 0.15 and 0.18 g/m^2, and at 80 kV – 0.38 and 0.45 g/m^2 for SpunBel and Spunlace respectively. For maximum nanofiber coating surface density it is necessary to use maximum voltage.

Table 1

Dependence of fungal chitosan nanofibers average diametr on electrode spacing, spinning electrode rotation speed, when SpunBel and Spunlace nonwoven materials are used as a substrate

Characteristics	SpunBel					Spunlace				
Voltage, kV	60	65	70	75	80	60	65	70	75	80
Average diametr, nm	280	280	240	240	200	310	320	280	250	220
Coating surface density (ρ), g/m^2	0.15	0.23	0.31	0.34	0.38	0.18	0.27	0.37	0.41	0.45
Electrode spacing, mm	100	125	150	175	200	100	125	150	175	200
Average diameter, nm	390	260	240	230	200	410	280	250	190	280
Coating surface density (ρ), g/m^2	1.16	0.31	0.20	0.15	0.10	1.31	0.37	0.30	0.15	0.10
Spinning electrode rotation speed, rpm	4	7	10	13	16	4	7	10	13	16
Average diameter, nm	270	250	240	260	290	260	250	280	250	280
Coating surface density (ρ), g/m^2	0.20	0.26	0.31	0.23	0.24	0.27	0.32	0.37	0.31	0.34

Increase in voltage reduces spinning time; it may cause fibers not to dry fully before laying the substrate and the appearance of defects [14, 15, 16, 17]. It is also not recommended to use voltage value close to the maximum for the high-voltage source [16, 17]. Increasing the voltage in most cases leads to a greater spinning solution jet stretching due to Coulomb forces and increasing the electric field intensity. Thus, there is a decrease in average fibers diameter [19, 20, 15] and also acceleration of the solvent evaporation from the jet [16]. However, the increase in voltage reduces jet flight time. At higher values of flight time jet has more time for stretching and orientation, which may contribute to obtain finer fibers [21]. At higher voltages there is possible formation of defects. Shape defects can vary from spherical to beads [17]. In some cases [18] the number of defects decreased due to increased voltage, when jet spinning solution is drawn stronger. When low-viscosity spinning solutions are used, higher voltages contribute jet splitting, which leads to decrease of nanofibers average diameter [22].

Regarding these data the most appropriate voltage value to produce chitosan nanofiber coating is 70 kW, because under these conditions there is high equipment productivity under the normal mode and produced nanofiber coating has relatively high density. The obtained data are generally relevant to the literature data.

Electrode spacing is an important process parameter. It has a direct impact on jet flight time and electric field strength.

It was studied that the electrospinning at electrode spacing 100 mm, nanofibers average diameter is 390–410 nm, and at 200 mm - 201 and 280 nm for Spunlace and SpunBel, respectively.The most significant decrease in average fiber diameter is observed with increasing electrode spacing from 100 to 125 mm and from 390 to 260 nm for SpunBel and 410 to 280 for Spunlace. From these results, it was found that the nanofiber coating density with increasing distance between electrodes decreases, made it impossible to obtain products with satisfactory combination of properties. Increasing the distance between electrodes can lead to decrease of average diameter in produced fibers [20]. This is due to the fact that a larger distance between electrode jets has more time for stretching. However, average fiber diameter increase is possible with increasing distance between electrodes due to lower electric field intensity [15]. The obtained data are generally relevant to the literature data.

To form a single fiber, jet flight time should be sufficient to ensure evaporation of the major part of the solvent. When reducing electrode spacing the jet will have to travel shorter distance to reach the substrate. However, if the electrode spacing reduces, electric field force acting on the jet increases, which leads to its acceleration increase. As a result, the jet may not have enough time for solvent evaporation before placing the substrate [18]. When there is insufficient electrode spacing, fibers may stick together due to high solvent content [23]. Low values of the electrode spacing can result in the formation of defects in the form of beads [19]. This is because the reduction of the electrode spacing has a similar effect with increasing voltage between the electrodes, increasing the strength of the electric field, while increasing the jet instability. This promotes the formation of defects in the form of beads.

The data shows increase in chitosan nanofiber coating surface density when spinning electrode rotation speed increases, but at certain value of spinning electrode rotation speed, decrease is observed. Maximum density occurs at spinning electrode rotation speed 10 rpm, which is probably due to the creating the most appropriate conditions for forming nanofiber coating, because at low spinning electrode rotation speed there is a shortage of forming solution on the surface, which reduces the productivity of the process, and at high spinning electrode rotation speed the spinning solution does not have time to fully spun from electrode surface. Therefore, there is an excess initiation of new Taylor cones; however, the spinning was still possible from the available cones. This has a negative impact on production. The average diameter varies insignificantly and ranges within the 250–280 nm for Spunlace and SpunBel substrates, respectively.

To obtain chitosan nanofiber coating with maximum surface density electrospinnig should be preformed at spinning electrode rotation speed 10 rpm for nonwoven substrate Spunlace and Supbel.

Fig. 1 and 2 show SEM images of chitosan nanofiber coating surface on Spunlace and SpunBel nonwoven materials in the most suitable mode: voltage 70 kV, electrode spacing 125 mm, the spinning electrode rotation speed 10 rpm.

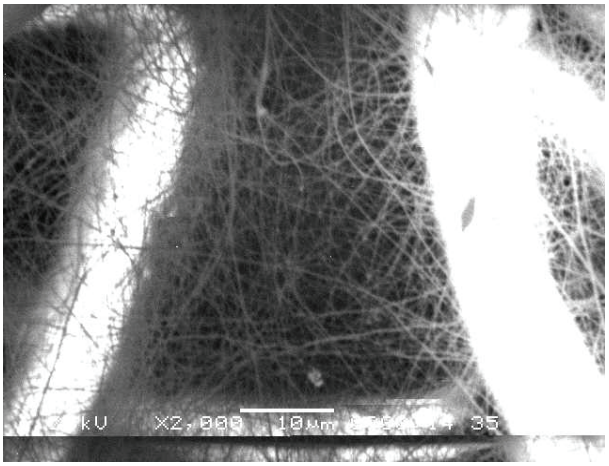

Fig. 1. SEM images of chitosan nanofiber coating surface on Spunlace

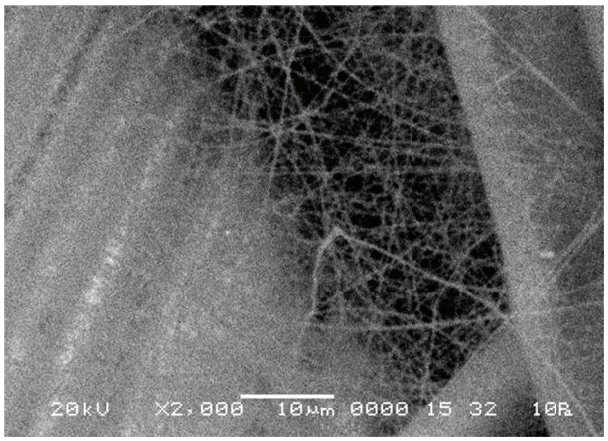

Fig. 2. SEM images of chitosan nanofiber coating surface on SpunBel

Conclusion. The studies of process parameters impact on electrospinning process have shown that the highest density of chitosan nanofibers coating can be with minimum electrode spacing of 100 mm. However, nanofiber coating structure analysis revealed a sharp increase in the average diameter of the fibers to 390–410 nm. The most appropriate electrode spacing is between 125–150 mm, wherein the average diameter of the fibers is 240–280 nm, and nanofiber coating density is 0.2–0.4 g/m^2. When voltage increases, the decrease in the average diameter of nanofibers and nanofiber coating density increase is observed. Since high voltage source operation is not recommended at the maximum output, the most appropriate voltage is 70 kV, when the nanofiber diameter is 240–280 nm, and the nanofiber coating density is 0.31–0.37 g/m^2. Spinning electrode rotation speed does not have a significant influence on the diameter of the produced nanofiber coating. Maximum density of the coating is observed at spinning electrode rotation speed 10 rpm.

The resulting data can be used at JSC "Mineral Wax Plant" in production of medical devices with chitosan nanofibres. Preclinical trials on laboratory animals showed their greater efficiency if it is compared to conventional means. Preliminary costing shows that the product obtained by the electrospinning method is 2–3 times cheaper than foreign analogues.

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