MECHANICAL PROPERTIES OF ELECTROSPUN SILK FIBROIN NANOFIBER MATERIALS

Abstract. In this paper, we investigate the mechanical properties of nanofiber materials obtained by the method of electrospinning based on silk fibroin. The deformation properties of these nanofiber materials, as well as the optimal parameters of the electrospinning process, have been determined. We also analyzed the change in the geometric shape of a silk fibroin nanofiber material under the action of deformation, leading to a morphological change, that is, the mechanical properties of molecules during the transition from the initial isotropic state to the forced anisotropic state.

Introduction. One of the main issues of nanotechnology is producing materials with new properties. The dynamic development of modern nanoscience and nanotechnology is closely related to the development of new nanomaterials, in particular, polymer nanofibers with anisotropic properties by electrospinning [1].

Electrospinning or electrostatic spinning is the process of producing fibrous structures in nanometer range (diameter 40 to 2000nm) by subjecting a fluid jet to a
high electric field [2]. The conventional process of fibre spinning is based on the principle of pressure-driven extrusion of a viscous polymer into fibres of diameter ranging from 10 to 500µm². It is based on the basic principle of effect of electrostatic force on liquids i.e. when a suitably electrically charged material is brought near to a droplet of liquid held in a fine capillary, it would form a cone shape and small droplets would be ejected from the tip of the cone if the charge density is very high [3].

In the electrospinning, the process parameters such as spinning voltage, spinning distance and the type of collectors have been examined as the crucial elements to control the fibre diameters and morphology. However, the effect of these parameters on fibre formation was at variance for different polymer solutions due to their differences in solution properties such as conductivity and viscosity [4]. The nano fibrous materials produced by electro spinning process exhibit novel and significantly improved physical, chemical and biological properties.

Electrospun nanofibres are normally collected as randomly oriented nonwoven mat. These fibres have smaller pores and higher surface area than regular fibres. The pronounced nano and micro structural characteristics of nanofibres enable to develop advanced materials with sophisticated applications [5].

Silk fibroin (FS). This natural polymer is the basis of natural silk fibers and can be isolated by washing from sericin, fat wax, etc. The resulting fibroin, being a fibrillar protein, is a complex tertiary and quaternary structure in the fiber. The fibroin molecule has an empirical structure C_{13}H_{23}N_{5}O_{6} and its elementary link is characterized by an average molecular weight of 345. Since the elementary links of fibroin consist of amino acid residues, they have such groups as carboxyl and amide, which, being very active, contribute to various structural organizations, in particular, formation of alpha and beta structure, gelation and crystallization [6].

Methods. Electrospinning of SF solution in the electrospinning process, a high electric potential was applied to a droplet of SF solution at the tip (0.5 mm) of a syringe needle, as shown in Fig. 1. The electrospun nanofibers were collected on a target drum which was placed at a distance of ~10 cm from the syringe tip. A voltage of 15 kV was
applied to the collecting target by a high voltage power supply. The flow rate of polymer solution was 1.5 mL h⁻¹ [7-8].

A sample of fibroin was isolated from the composition of the fibers of natural silk cocoon by washing bio-glue-sericin in water at a temperature of 90 °C for 4 hours, as well as fatty waxes in ethanol and acetone on a Soxhlet apparatus. A 50% aqueous CaCl₂ solution at a temperature of 90 °C was used as a solvent capable of destroying the crystalline regions of purified fibers without destruction of the FS molecules.

Ca and Cl ions from the FS solution were removed by dialysis using a semipermeable cellulose xanthate membrane. In this case, purified FS was precipitated with an amorphous state of chains. FS spinning solutions were prepared in formic acid (FA) and it was found that the concentration (C) of this biopolymer of about 12–18% is optimal for the formation of nanofibers with a diameter of 50–500 nm. For comparative studies, we selected purified cotton cellulose fibers and spinning solutions of this sample prepared in trifluoroacetic acid (TFA) [9-11].

*Results and discussion.* The surfaces generated by electrospinning have novel and high performance properties. Electrospun nanofibers possess noticeable differences in their mechanical, electrical and thermal properties as compared to normal fibres. Control of the composition of the solution and mixture is also important in the manifestation of the special properties of nanofibers. The following tab.1. shows important parameters for creating optimal polymer-solution conditions for the electrospinning process [12].
Table 1

List of materials and their solutions used for electrospinning

<table>
<thead>
<tr>
<th>№</th>
<th>Name of polymer</th>
<th>Solvent</th>
<th>Physical properties of solvents</th>
<th>Result electrospinning</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Density, g/cm³</td>
<td>Boiling temperature, °C</td>
</tr>
<tr>
<td>1</td>
<td>Cotton cellulose</td>
<td>Trifluoroacetic acid (TFA)</td>
<td>1.49</td>
<td>72.4</td>
</tr>
<tr>
<td>2</td>
<td>Silk fibroin</td>
<td>Formic acid (FA)</td>
<td>1.220</td>
<td>101</td>
</tr>
</tbody>
</table>

Mechanical properties. The mechanical properties of nanofibers such as tensile strength, elongation and modulus are affected by the surface morphology, pore size and distribution. The thickness of the samples was from 0.30 mm. The gauge length was set to be 60 mm and the rate of the crosshead was 10 mm/min. The reported data of breaking stress and strain represent the average results of ten tests. Mechanical studies were carried out on a ZWESK tensile testing machine. The breaking stress was calculated according to the formula [13-14].

\[
\sigma = \frac{F}{A_0}
\]

where \(\sigma\) - is the breaking strength (MPa), \(F\) - is the tensile strength (N), \(A_0 = b \cdot d\)

\(A_0\) - is the cross-sectional area, \(b\) - is the thickness, \(d\) - is the width of the samples.

\[
x(\%) = \frac{\Delta l}{l_0} \cdot 100\%
\]

where \(x\) - is the breaking strain (%), \(l_0\) - is the original length, \(\Delta l\) - is the increase in length at break.

The mechanical properties of the samples are listed in tab. 2. [15].

Table 2

Mechanical properties of as-spun SF nanofiber materials

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration (%)</th>
<th>Stress (MPa)</th>
<th>Breaking strain (%)</th>
<th>Fiber diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12</td>
<td>16.56±2.21</td>
<td>14.4±2.64</td>
<td>152.8</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>14.44±3.28</td>
<td>21.2±3.78</td>
<td>196.4</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>12.82±2.25</td>
<td>26.8±2.82</td>
<td>234.2</td>
</tr>
</tbody>
</table>
Thick nanofibers have relatively low values of Young’s moduli, however, with a decrease in their diameter below 100 nm, the moduli begin to increase exponentially, indicating the inclusion of intermolecular interaction associated with the orientation of FS molecules [16].

**Conclusions.** Despite the non-orientation of silk fibroin, we will be able to see the change in the diameter of nanofibers depending on the concentration dependence under mechanical action, and the material easily demonstrates the change in mechanical deformations. In the case of applied voltage, the diameter of nanofibers tends to decrease with increasing electrospinning voltage. When studying the mechanical, structural and anisotropic properties of nanofiber material based on silk fibroin using the electrospinning method, it was shown that these materials can be used in various applications.

**References:**