

# PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS

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## Abstract

This paper analyzes experimental studies on producing fibers based on the natural polymer chitosan. It discusses how different parameters affect the resulting natural fibers. The paper also includes theoretical calculations of the fiber diameters and compares them with experimental data.

**Keywords:** chitosan, fiber, electrospinning, modeling.

## Introduction

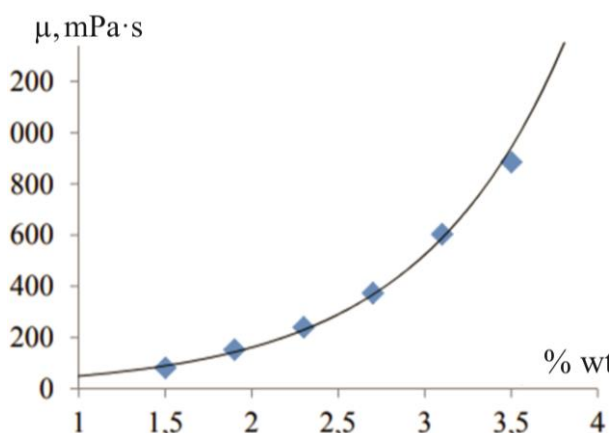
### Process Parameters

Various methods exist for spinning nanofibers, but any fiber production process typically comprises three essential stages: transitioning the material to a viscous-fluid state, spinning, and curing [1]. The viscous-fluid state dictates a material's capacity to form fibers and is characterized by specific viscosity and surface tension values. Polymers and resins in solution or molten form demonstrate fiber-forming capabilities [2]. Different fiber spinning techniques alter the viscosity and surface tension of these materials through temperature adjustments (for spinning thermoplastics), concentration changes (for spinning polymer solutions or resins), or surfactant introductions. Subsequently, the curing process is executed either by cooling below the polymer's glass transition temperature or by solvent removal (via evaporation or substitution) [3].

Literature [4] indicates that electroforming processes typically employ polymer solutions with molecular weights ranging from tens to hundreds of thousands, weight concentrations up to 20%, and corresponding dynamic viscosities ranging from 0.05 to 1.0 Pa·s.

Exploring one promising avenue for nanofiber production discussed in literature [5]—the electrospinning method using polymer solutions—chitosan emerges as a notable polymer base. Chitosan not only possesses wound-healing properties but also stands out for its non-toxicity, biocompatibility, and biodegradability.

Figure 1 illustrates the relationship between the dynamic viscosity of a chitosan molding solution in 70% acetic acid and its concentration at 20°C.



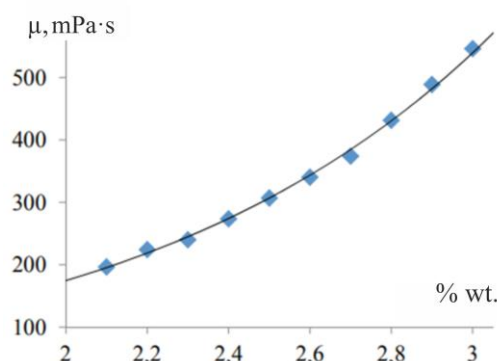
**Figure 1.** Dependence of the dynamic viscosity of the molding solution on the concentration of chitosan

## PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS

The graph illustrates that at a chitosan concentration of 1.5% wt., the viscosity is 65 mPa·s (0.065 Pa·s), while at the maximum concentration of 3.5% wt., it reaches 885 mPa·s (0.885 Pa·s). This indicates that the viscosity of the molding solution within the 1.5–3.5% wt. concentration range falls within the recommended levels for conducting the electrospinning process.

In Figure 2, the dependence of dynamic viscosity of the chitosan molding solution in 70% acetic acid is depicted within the optimal concentration range at 20°C.

From the obtained data, it is evident that at a chitosan concentration of 2.1% wt., the dynamic viscosity is 196 mPa·s (0.196 Pa·s), while at the maximum concentration of 3.1% wt., it measures 604 mPa·s (0.604 Pa·s). Notably, the relationship between viscosity and concentration is not linear but follows a parabolic trend.

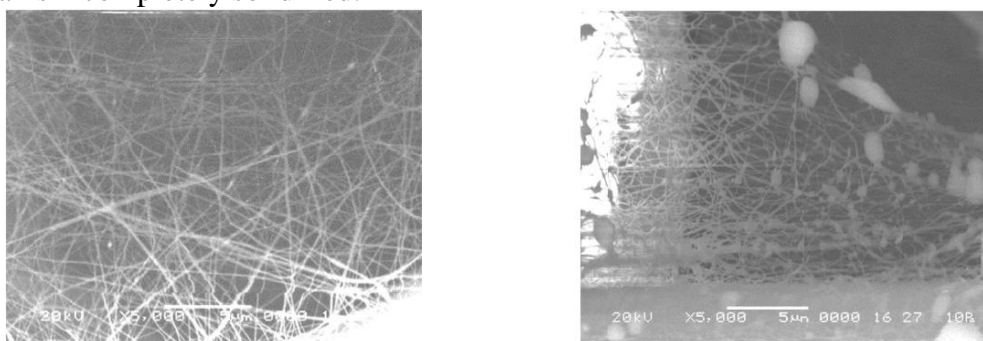


**Figure 2.** Dependence of dynamic viscosity on chitosan concentration

In the literature [6], it's established that in the electrospinning process of nanofibers, specific electrical conductivity spans a wide range—from  $10^{-6}$  to  $10^{-2}$  S/cm. The lower limit is constrained by the threshold for gas discharge from the jet, which compromises its stability. As electrical conductivity increases, the likelihood and frequency of successive jet splits rise, promoting effective fiber formation and, consequently, enhancing the productivity of the electrospinning (ESP) process.

Regulating the electrical conductivity of the spinning solution can be achieved in two primary ways: through minor additions of ionic substances, provided the polymer and solvent are relatively pure, or by purification if they are heavily contaminated with such substances.

Additionally, it's understood that as electrical conductivity increases in the electrospinning process of nanofibers, the probability and frequency of successive splits rise, although the jet remains incompletely solidified.



**Figure 3.** The surface of the material with nanofiber obtained from a spinning solution with a chitosan concentration: a – 2.0% wt.; b – 3.5% wt

In Fig. 3, the relationship between specific electrical conductivity and chitosan concentration is depicted. It's evident from this graph that at a minimum chitosan concentration of 1.5% wt., the electrical conductivity measures 63  $\mu\text{S}/\text{cm}$ , while at the maximum chitosan concentration of 3.5% wt., it reaches 134  $\mu\text{S}/\text{cm}$ . These values fall within the suitable range for conducting the electrospinning process of nanofibers.

In Fig. 4, microphotographs display the surface of a material with nanofibers obtained from a spinning solution with chitosan concentrations of a) 2.0% wt. and b) 3.5% wt. The data presented indicate that at a higher chitosan concentration (3.5% wt.) in the molding solution, a notable increase in defects is observed. This deterioration in the nanofiber coating's properties is likely attributed to an excess of chitosan, hindering the splitting of polymer jets formed during electrospinning into thinner ones.

Investigations into the properties of the molding solution derived from the animal biopolymer chitosan reveal that the dynamic viscosity and electrical conductivity values within the 1.5–3.5% wt. concentration range align with the recommended parameters for electrospinning. However, an analysis of the nanofiber coating's structure unveils a noteworthy aspect: an increase in chitosan concentration to 3.5% wt. may result in the appearance of droplet defects, compromising the uniformity of the nanofiber coating on the substrate. It's worth noting that such defects in the nanofiber coating at this chitosan concentration may also stem from the technological parameters of the electrospinning process.

Surface tension forces of molding solutions play a crucial role in producing films and fibers from chitosan. However, this aspect has received limited attention in the literature. Nonetheless, surface properties not only significantly impact polymer processing processes but also influence its ability to form films or fibers fundamentally. A study [7] delves into the surface properties of chitosan aminopolysaccharide.

The study encompasses industrial and laboratory samples of the chitosan homologous series, with a viscosity-average molecular weight ( $M\eta$ ) ranging from 9 to 700 kDa and a similar degree of deacetylation ( $DD$ ) at approximately 80 mol. %. Laboratory samples were procured through the oxidative degradation of chitosan-700. Aqueous solutions of acetic acid with concentrations ranging from 2% to 96% were selected, prepared using chemically pure-grade glacial acetic acid and distilled water, alongside a 1.9% acetate buffer consisting of 1.6%  $\text{CH}_3\text{COONa}$  and 1.6%  $\text{CH}_3\text{COOH}$ , and solutions of cold concentrations ranging from 0.1 to 0.75 g/dl.

The surface tension coefficient was measured using a stalagmometer with a diameter ( $d$ ) of 0.6 mm. Prior to measurement, both the solution and the solvent underwent filtration using a Schott filter No. 160. The experimental determination of the number of drops ( $n$ ) of liquid formed as it flowed through the stalagmometer's capillary, from the top mark to the bottom, was conducted. Four to five measurements were performed for each solution portion, and the arithmetic average values of  $n$  were utilized for calculations. The surface tension coefficient ( $\sigma$ ) was then determined using the formula:

$$\sigma = \sigma_0 \frac{n_0}{n}$$

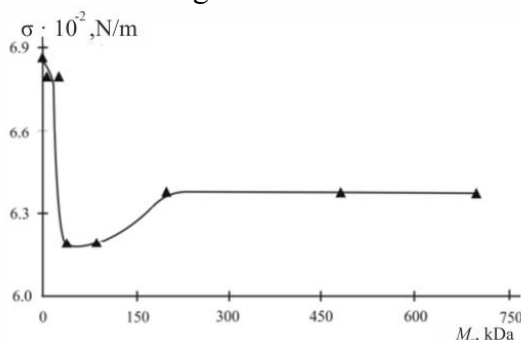
Here,  $n$  and  $n_0$  represent the number of droplets of solution and solvent formed, respectively, and  $\sigma_0$  (in  $\text{N}/\text{m}$ ) denotes the coefficient of surface tension of the solvent. When examining solutions of acetic acid, water served as the solvent, whereas solutions of chitosan employed acetic acid and acetate buffer.

To quantify a substance's ability to reduce surface tension through adsorption at the interface, the surface activity ( $g$ ,  $\text{N}\cdot\text{m}^2/\text{mol}$ ) of chitosan was calculated based on its concentration in the volume. The value of  $g$  was determined graphically from the tangent drawn to the

# PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS

initial straight section of the surface tension isotherm, originating from the point corresponding to the surface tension of the solvent.

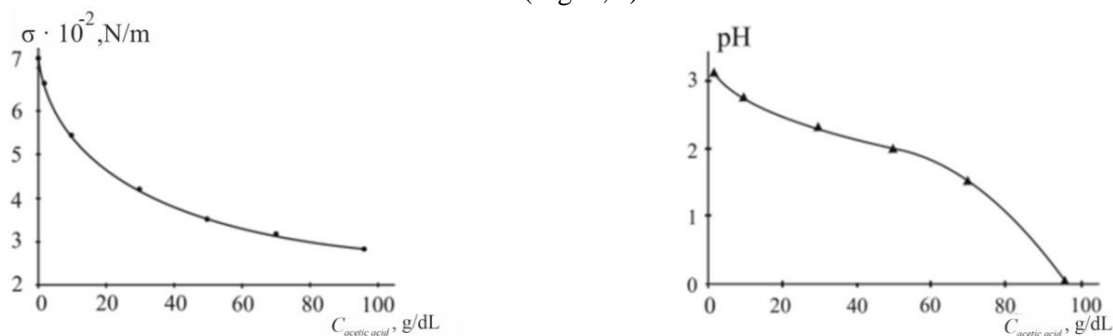
Surface tension within rows of chain molecules sharing the same chemical structure of the repeating (monomeric) unit, but differing in molecular weight (i.e., within a homologous series), is contingent upon the size of the homolog molecule. Accounting for this factor, the initial stage of the study focused on examining the dependency of the surface tension coefficient on the molecular weight of chitosan. Solutions with concentrations ranging from 0.10 to 0.50 g/dl in 2% acetic acid were utilized. Figure 5 illustrates the dependency  $\sigma = f(M_\eta)$  for the investigated samples of the homologous chitosan series. It's observed that as the molecular weight of the sample increases, the surface tension coefficient decreases, ultimately stabilizing at a constant value around  $M_\eta \sim 200$  kDa. Within the region  $M_\eta \approx 35$ -100 kDa, the dependency  $\sigma = f(M_\eta)$  exhibits a minimum of  $\sigma$  values. This observation does not contradict the classical concepts of physical and colloidal chemistry of polymers and remains subject to ongoing research. For subsequent investigations, a chitosan sample with  $M_\eta = 200$  kDa was chosen, representing the molecular mass range where  $\sigma$  remains constant.



**Figure 5.** The dependency of the surface tension coefficient of chitosan solutions in 2% acetic acid on the molecular weight of the samples was examined. For samples with molecular weights ( $M_\eta$ ) of 9 and 27 kDa, the chitosan concentration in the solution was set at 0.50 g/dL, while for  $M_\eta$  ranging from 38 to 700 kDa, the concentration of chitosan was 0.10 g/dL.

Before delving into the study of concentration-dependent surface tension coefficients of chitosan solutions, experiments were conducted to determine certain physicochemical parameters of solvents. Specifically, the surface tension coefficient ( $\sigma$ ) of the acetate buffer and the concentration-dependent variations in  $\sigma$  and pH of aqueous solutions of acetic acid at different concentrations were investigated.

The surface tension coefficient of the acetate buffer was measured to be  $6.7 \times 10^{-2}$  N/m. For acetic acid solutions, a gradual change in surface tension was observed as the concentration of the solution varied from that of the solvent to that of the solute (Fig. 6, a).



**Figure 6.** The concentration dependence of the surface tension coefficient (a) and pH (b) of aqueous solutions of acetic acid.

The obtained dependency  $\sigma = f(C_{\text{acetic acid}})$  of acetic acid solutions follows the typical pattern observed in surface tension isotherms of aqueous solutions of surfactants. Additionally, as anticipated, the pH of the solutions decreases with an increase in the concentration of acetic acid (Fig. 6, b).

A study [8] presents findings on the production of chitin and chitosan nanofibers, addressing key challenges such as the aggressive and environmentally harmful nature of solvents. Table 1 provides initial data on the properties of the polymers used for nanofiber production, while Table 2 outlines the characteristics of chitosan nanofibers.

Table 1.

Properties of chitin and chitosan.

Property	Chitin	Chitosan
Molar weight	$(1-1.03) \times 10^6$ to $2.5 \times 10^6$	$10^5$ to $5 \times 10^3$
Deacetylation Degree	~10%	60–90
Viscosity of 1% solution (1% acetic acid)	-	200–2000
Moisture content		6–7
Solubility	Dimethylacetamide–LiCl/ Trichloroacetic acid–dichloromethane	Dilute acids Trichloroacetic acid – dichloromethane

Table 2.

Characteristics of chitosan nanofibers.

Property	Value
<b>Mechanical:</b>	
Title, dtex	1.5–3.0
Strength under standard conditions, cN/tex	10–15
Strength in wet conditions, cN/tex	3–7
Loop strength, cN/tex	3–7
Elongation under standard conditions, %	>10
<b>Structural:</b>	
Average molecular weight, kD	150–300
Polydispersity (Pd)	3,6–6
Crystallinity index, %	35–50

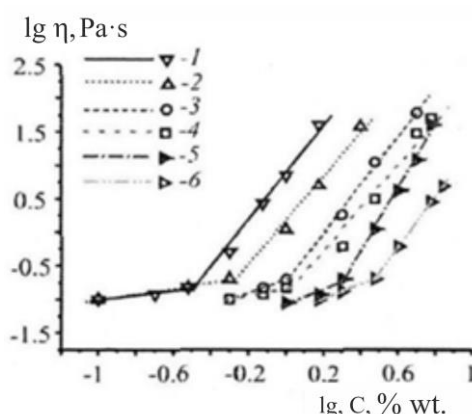
The high viscosity of chitin solutions in certain solvents poses challenges in fiber processing. However, despite these obstacles, fibers have been produced with superior properties, often surpassing those of cellulose. Notably, the best tensile strength (4 g/d) and modulus (100 g/d) for chitin have been achieved with mixed chitin ester or chitosan acetate. Chemical modification stands as another viable approach to enhancing fiber properties.

In [9], a spinning solution formulation based on chitosan, acetic acid, and ultra-high molecular weight polyethylene oxide (PEO) as a technological additive was proposed. This formulation facilitated the electrospinning process of chitosan-based fibers, with a PEO content in the dry matter not exceeding 1 wt. %.

The study focused on chitosan samples with viscosity-average molecular weights of 87 kDa and 200 kDa, with degrees of deacetylation of 83.6% and 82%, respectively (sourced from JSC "Bioprogress"). Additionally, polyethylene oxide with a molecular weight of 900 kDa was utilized as the technological additive (procured from MO®, Yes, 2-10®, and 5-10® series from Sigma Aldrich). Chemically pure acetic acid from JSC Vekton served as the solvent.

Figure 7 illustrates the dependency of dynamic viscosity of PEO and chitosan solutions with varying molecular weights in 70% acetic acid on the polymer concentration in the solution.

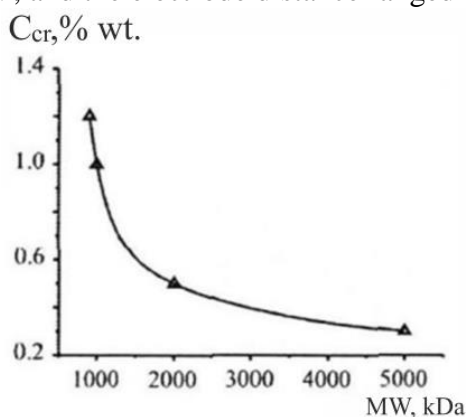
# PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS



**Figure 7.** Dependence of the viscosity of solutions of PEO with MW  $5 \cdot 10^6$  Da (1),  $2 \cdot 10^6$  Da (2),  $1 \cdot 10^6$  Da (3), 900 kDa (4) and chitosan with MW 200 kDa (5), 87 kDa (6), in 70% acetic acid from the polymer concentration in logarithmic coordinates. Viscosity measurements were carried out at a constant temperature of the studied solutions equal to  $25^\circ \text{C}$

Based on the inflection point in the viscosity-concentration curve of solutions, the critical polymer concentration ( $C_{cr}$ ) values were determined. For PEO with molecular weights of 900 kDa,  $1 \cdot 10^6$  Da,  $2 \cdot 10^6$  Da, and  $5 \cdot 10^6$  Da, the  $C_{cr}$  values are 1.2%, 1.0%, 0.5%, and 0.3% (by weight), respectively. For chitosan with molecular weights of 87 kDa and 200 kDa, the  $C_{cr}$  values are 2% and 3% (by weight), respectively. The increase in viscosity at concentrations greater than  $C_{cr}$  is attributed to the formation of a stable, continuous network of molecular coils or their associates. Consequently, the rheological properties of solutions change, leading to increased resistance to deformation under the influence of physical fields and, notably, the formation of continuous liquid jets during the processing of polymer solutions into fibers and monofilaments.

The value of  $C_{cr}$  depends on the molecular mass of PEO, the size of molecular coils in solution, and their spatial arrangement within the volume (see Fig. 8). In Fig. 8, the coordinate of the inflection point occurs at a molecular weight of  $2 \cdot 10^6$  Da, with  $C_{cr}$  equal to 0.5% (by weight). When utilizing polyethylene oxide with a molecular weight exceeding  $2 \cdot 10^6$  Da as a spinning solution modifier, a stable process of fiber electrospinning can be achieved. The electrospinning of fibers was conducted under the following technological parameters: the volume flow rate varied from  $0.033 \text{ cm}^3/\text{min}$  to  $0.1 \text{ cm}^3/\text{min}$ , the voltage applied to the capillary ranged from 20 kV to 40 kV, and the electrode distance ranged from 200 mm to 350 mm.



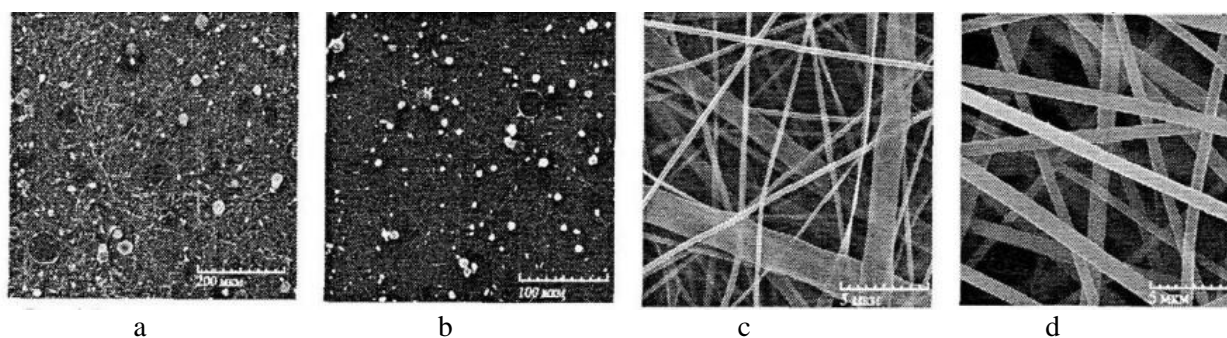
**Figure 8.** Dependence of the viscosity of solutions of polyethylene oxide in 70% acetic acid on the concentration of polymer with MW  $5 \cdot 10^6$  Da (1),  $2 \cdot 10^6$  Da (2),  $1 \cdot 10^6$  Da (3) and 900 kDa (4) in logarithmic coordinates



It has been observed that a solution of chitosan with a concentration ranging from 3% to 7% by weight generates a fine aerosol when subjected to electrical influence, depositing a layer of spherical particles with diameters ranging from 50 nm to 2  $\mu\text{m}$  on the precipitation electrode.

In the process of electrospinning fibers from a chitosan solution with the addition of 1% polyethylene oxide (PEO) by weight (with a molecular weight of 900 kDa) and a total polymer mixture concentration of 5.31% by weight in 70% acetic acid, a pulsating spinning nature was noted. This was accompanied by dripping of the polymer solution within a specified range of volumetric flow rates and applied electrical voltage. The resulting fibrous mesh exhibited numerous defects, including dried droplets and spindle-shaped thickenings on the fibers (refer to Fig. 4).

Upon introducing 1% by weight of polyethylene oxide with a molecular weight of  $5 \times 10^6$  Da into a 6% solution of chitosan in 70% acetic acid, the electrospinning process was notably improved, yielding a homogeneous fibrous structure devoid of defects across a wide range of technological parameters (see Fig. 9). This enhancement in the fiber-forming ability of the spinning solution, attributable to the addition of higher molecular weight PEO, is linked to the solution's increased capacity for highly elastic deformation.



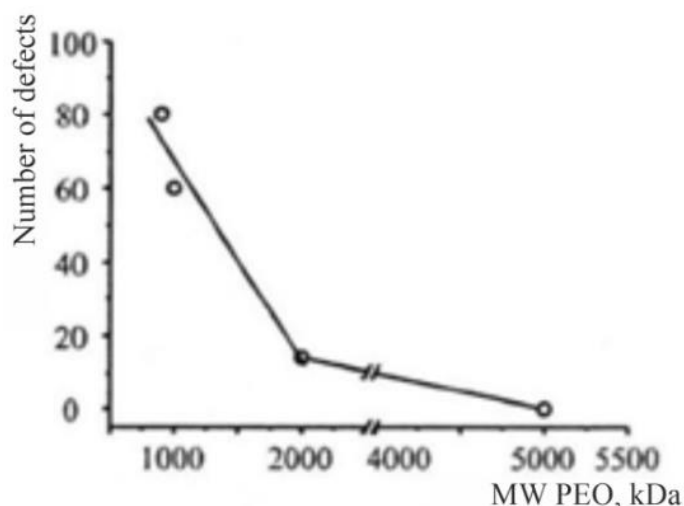
**Figure 9.** The result of applying an electric field to a spinning solution based on chitosan with the addition of 1 wt.% PEO of various molecular weights 900 kDa (a),  $1 \cdot 10^6$  Da (b),  $2 \cdot 10^6$  Da (c),  $5 \cdot 10^6$  Da (d). Scanning electron microscopy. Electroforming parameters: volume flow 0.067 cm<sup>3</sup>/min, voltage 30 kV, interelectrode distance 200 mm.

The presence of multiple defects in the form of dried droplets within the fibrous layer significantly compromises the physical and mechanical properties of nonwoven fibrous materials, thereby limiting their range of applications.

In Figure 10, the dependence of the number of defects during the electrospinning of fibers from freshly prepared chitosan solutions with the addition of polyethylene oxide of various molecular weights (in a ratio of 99:1 wt.% in dry matter) is illustrated. The technological parameters were kept constant: volume flow at 0.067 cm<sup>3</sup>/min, capillary voltage at 30 kV, and interelectrode distance at 200 mm.

As the molecular weight of polyethylene oxide increases, an enhancement in the process of fiber electrospinning is observed, coupled with a reduction in the number and size of defects.

## PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS

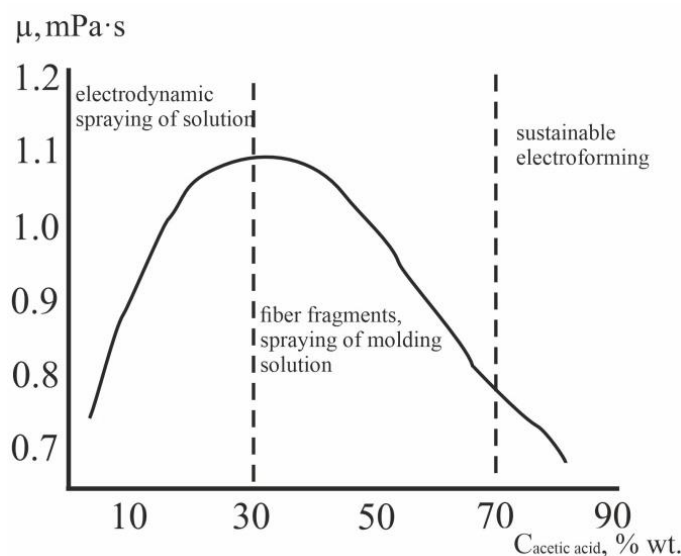


**Figure 10.** Dependence of the number of visible defects on a section of material with an area of 0.04 mm<sup>2</sup> during electrospinning of fibers from solutions with the addition of 1 wt. % polyethylene oxide of various molecular weights

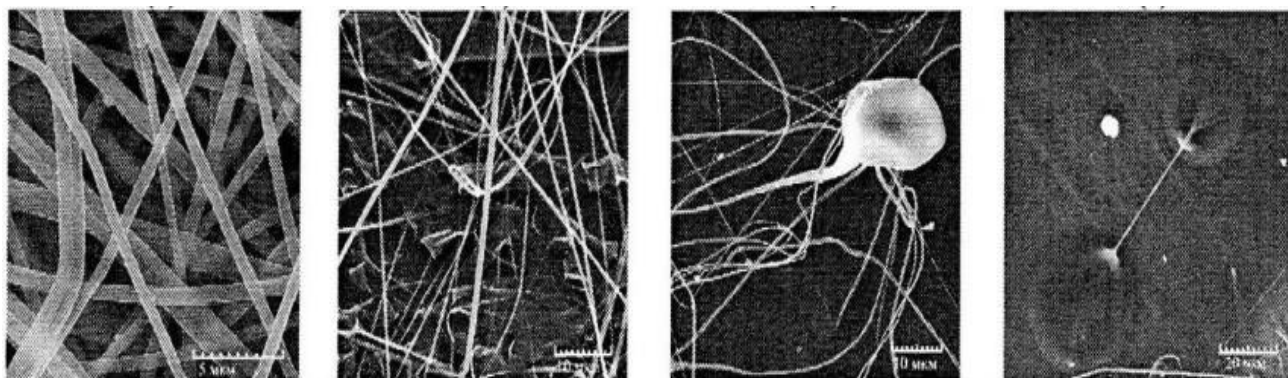
It has been determined that electrospinning fibers from a solution based on chitosan, with a total polymer concentration of 5.31 wt.%, and a ratio of chitosan (200 kDa, degree of deacetylation 82 mol.%) to PEO ( $5 \times 10^6$  Da) at 99:1 wt.% in dry matter, results in the formation of a defect-free fibrous structure on the collecting electrode. The molding solution exhibits the following characteristics: Brookfield viscosity of 0.8 Pas and specific volumetric electrical conductivity of 1.5 mS/sm.

When using acetic acid with concentrations ranging from 30% to 70% as a solvent, with an equal concentration of the polymer mixture in the spinning solution, fibers with defects in the form of dried drops are formed. A decrease in the concentration of acetic acid below 30% leads to electrohydrodynamic spraying of the polymer solution (see Fig. 11). The inclusion of 1 wt.% PEO ( $5 \times 10^6$  Da) in the spinning solution yields favorable fiber-forming ability (refer to Fig. 12, a). However, reducing the mass concentration of PEO to 0.5 wt.% results in the formation of a fibrous layer with defects such as dried drops and fibers resembling ribbons (see Fig. 12, b). This fibrous structure exhibits localized inhomogeneities within the network and a significant variation in fiber diameters. Further reduction of the concentration of PEO to 0.25 wt.% leads to the dripping of the polymer solution during electrospinning, alongside the formation of thickenings on the fibers (depicted in Fig. 12, c). Lastly, decreasing the mass concentration of PEO in the initial chitosan solution to 0.1 wt.% results in a decline in the fiber-forming ability of the solution, leading to dripping and electrospaying of the polymer solution (as illustrated in Fig. 12, d).





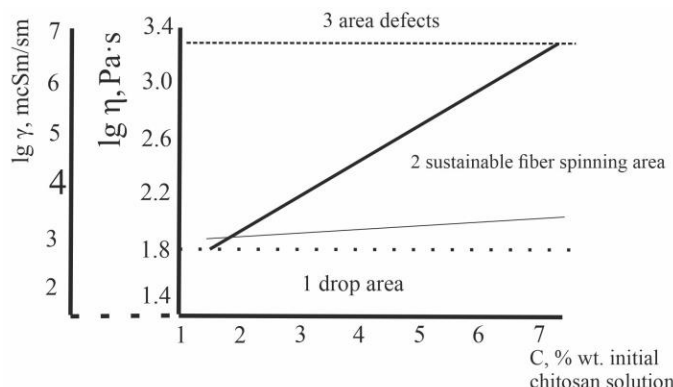
**Figure 11.** Effect of  $\text{CH}_3\text{COOH}$  concentration on the dynamic viscosity of chitosan solutions (MW 200 kDa, SD 82 mol%) with the addition of PEO (MW  $5 \cdot 10^6$  Da) 1 wt.%. The total concentration of the polymer mixture in solutions is 5.31 wt.%.



**Figure 12.** Microphotographs of chitosan fibers with different mass ratios of PEO  $5 \cdot 10^6$  Da in the spinning solution, a-1 wt. %, b-0.5 wt. %, c, d -0.25 and 0.1 wt. % respectively. Parameters of the electroforming process; volumetric flow;  $0.033 \text{ cm}^3/\text{min}$ , voltage 30 kV, interelectrode distance 200 mm.

The utilization of solutions with relatively low viscosity solely results in electrohydrodynamic spraying of the polymer solution, as depicted in Region I (Fig. 13). Moving on to Region II, which encompasses solutions with concentrations approximately ranging from 2.1 to 7 mass % and viscosities from 0.8 to  $1.8 \text{ Pa}\cdot\text{s}$ , stable, pulsation-free formation of a homogeneous, defect-free fiber is observed. Region III pertains to solutions with concentrations exceeding approximately 7.5 wt.% and viscosities surpassing  $1.9 \text{ Pa}\cdot\text{s}$ . Here, an elevation in the chitosan concentration in the molding system beyond 7.5 wt.% leads to a notable increase in the solution's viscosity.

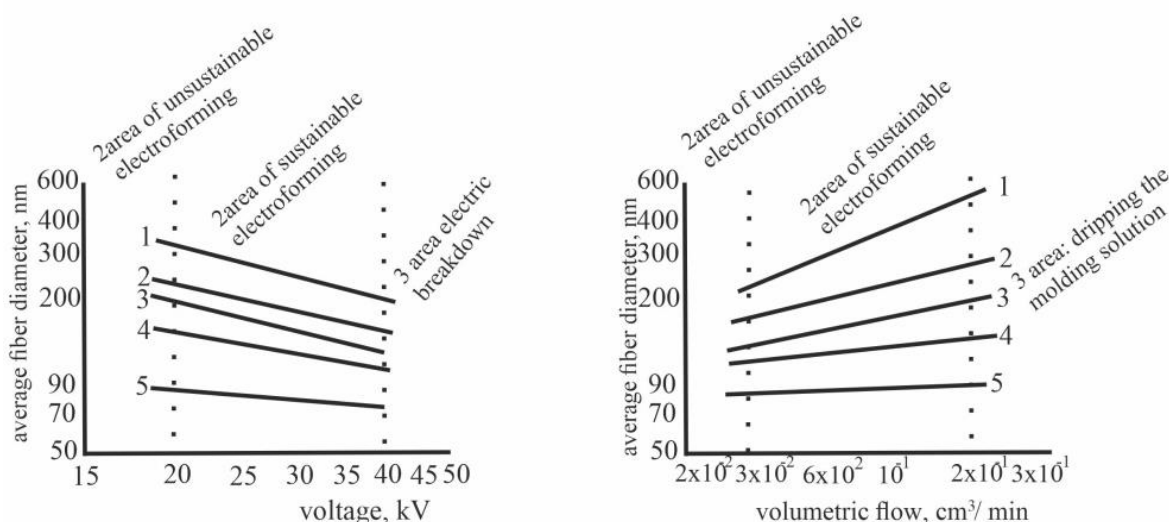
# PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS



**Figure 13.** Concentration dependence of the highest Newtonian viscosity (1) and specific volumetric electrical conductivity (2) for the chitosan (200 kDa)-PEO (5•106 Da)-70% acetic acid system. Chitosan ratio; PEO 99:1.

Optimal technological parameters for stable electrospinning of defect-free chitosan fibers with a diameter of  $250 \pm 50$  nm have been determined: a shelf life of no more than 2 days from the moment of preparation, a volume flow rate ranging from 0.033 to 0.1  $\text{cm}^3/\text{min}$ , a voltage between 25 and 35 kV, and an interelectrode distance of 200 mm.

It was found that the dependence of the fiber diameter on the voltage applied to the capillary is  $D \sim U^{0.22 \pm 0.05}$  for a freshly prepared solution and a solution stored for one, two, or three days. Regarding the dependence of the fiber diameter on the voltage applied to the capillary, it was observed that  $D \sim U^{-0.1}$  is noted (as shown in Fig. 14, a). The average diameter of the resulting fiber also exhibits a dependence on the volumetric flow rate of the spinning solution, as depicted in Fig. 14, b. This dependence diminishes over time, with values of  $D \sim Q^{0.37}$  for the initial solution,  $D \sim Q^{0.23}$ ,  $D \sim Q^{0.2}$  and  $D \sim Q^{0.12}$  for solutions stored for 1, 2, and 3 days, respectively. After 4 days of storing the solution, the dependence of the fiber diameter on the volume flow rate becomes practically absent, and an increase in the volume flow rate to 0.2  $\text{cm}^3/\text{min}$  destabilizes the electrospinning process, transitioning from a jet flow to electrohydrodynamic spraying of the polymer solution.



**Figure 14.** Dependence of the average fiber diameter on the voltage supplied to the capillary at a fixed flow rate  $Q = 0.033 \text{ cm}^3/\text{min}$  (a) and on the volumetric flow rate of the spinning solution at a fixed voltage and  $U = 30 \text{ kV}$  (b), 1 - initial (freshly prepared) solution, 2 - 5 - stored under static conditions for 1, 2, 3 and 4 days, respectively.

The current carried by the jet was measured using a single-capillary setup. A positive voltage was applied to the capillary, through which the molding solution was dosed into the interelectrode space, while the collecting electrode, in the form of a plate, was grounded through a universal voltmeter. The parameters of the fiber electrospinning process were an interelectrode distance of 300 mm, with the voltage varied in the range of 20-36 kV, and the volumetric flow rate of the spinning solution set to 0.06 -0.33 cm<sup>3</sup>/min. The current carried by the jet was measured under the condition that the fiber electrospinning process remained stable and the polymer solution did not dry out at the tip of the capillary.

In the experiments, a 5.31 wt% solution of a mixture of chitosan (200 kDa, degree of deacetylation 82 mol%) and PEO (5×10<sup>6</sup> Da) in 70% acetic acid was utilized. The mass ratio of polymers in the molding solution was chitosan: PEO (99:1). It was determined that over time, the viscosity of the chitosan molding solution decreased by more than 30%, while the specific electrical conductivity of the solution remained unchanged.

Several significant findings were made in this study:

A formulation of a spinning solution based on chitosan, acetic acid, and ultra-high molecular weight polyethylene oxide (PEO) as a technological additive was proposed, enabling the electrospinning process of chitosan-based fibers with a PEO content in the dry matter of no more than 1 wt%.

Properties of chitosan solutions in mixtures of acetic acid and water were investigated across a wide range of acetic acid concentrations (5-96%), with the optimal solvent from a technological perspective determined to be a mixture containing 70% acetic acid and 30% water. The relationship between the fiber diameter and the viscosity and electrical conductivity of the spinning solution was established, and the process of obtaining fibers of a desired diameter was optimized.

A technical solution was found for producing fibrous nanomaterials based on chitosan with an average fiber diameter of 160 nm and a technological additive content in dry matter of no more than 1 wt%.

Using a spinning solution based on chitosan (MW 200 kDa, degree of deacetylation 82 mol%), it was recommended to limit the shelf life of the spinning solution to 2 days, during which good fiber-forming ability is maintained during the electrospinning process. It was suggested that the aging of the molding solution is associated with the chemical degradation of chitosan.

### **Theoretical approach to the fiber electrospinning process**

The purpose of this part is a new approach to developing a process for electrospinning polymer nanofibers. The presented approach can be useful in filling the lack of regular and fully described experimental observations, as well as the theoretical features necessary to control the effective results obtained. Complex physical relationships were not considered; the methodology presented is related to process parameters.

The flow model of the electrospinning process can be represented as follows:

$$m \frac{d^2 P}{dt^2} = f_Q + f_E + f_V + f_S + f_A + f_g$$

Where  $m$  is the equivalent mass,  $P$  is the position coordinate,  $f_Q$  - Coulomb forces,  $f_E$  - electric field forces,  $f_V$  - viscoelastic forces,  $f_S$  - surface tension forces,  $f_A$  - air resistance forces,  $f_g$  - gravitational forces.

In particular, these forces can be described by physical relations:

# PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS

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$$f_C = \frac{e^2}{l^2}, f_E = -\frac{eV_0}{h}, \frac{d\sigma_V}{dt} = \frac{G}{l} \frac{dl}{dt} - \frac{G}{\mu} \sigma_V, f_S = \frac{\alpha \pi R^2 k}{\sqrt{x^2 + y^2}} [i|x| \sin(x) + j|y| \sin(y)],$$

$$f_A = 0,65 \pi R \rho_{air} v^2 \left( \frac{2vR}{v_{air}} \right)^{-0,81}, f_G = \rho g \pi R^2$$

where:  $e$  - charge,  $l$  - length of an ideal straight jet,  $V_0$  - applied voltage,  $h$  - distance to the collection drop,  $\sigma_V$  - viscoelastic stress,  $G$  - elastic modulus,  $\mu$  - viscosity,  $\alpha$  - surface tension coefficient,  $R$  - jet radius,  $k$  - jet curvature,  $\rho$  - density,  $v$  - kinematic viscosity.

## Task1.

The calculate the fiber diameter and bead width for each concentration value polymer 1 (P1) and polymer 2 (P2).

For this problem, we will assume that the surface tension coefficient  $\gamma$  for the solution is constant. Now let's substitute the values into the formulas to determine the fiber diameter and bead width in the electrophilic fiber process (EFP), the following formula is used:

$$d = \frac{2\gamma V}{U(1 - C)}$$

$d$  - fiber diameter,  $\gamma$  - surface tension coefficient,  $V$  - feed speed,  $U$  - applied voltage,  $C$  - polymer concentration in solution.

The bead width  $W$  can be defined as:

$$W = \frac{2U}{\rho}$$

where  $\rho$  is the distance between the tip and the collector.

Considering the given process parameters:

- Flow rate ( $V$ ) = 1 ml/h = 1/3600 ml/s.
- Applied voltage ( $U$ ) = 15 kV = 15000 V.
- Distance between tip and collector ( $\rho$ ) = 10 cm = 0.1 m.
- Inner diameter of the needle (needle dineedle) = 0.4 mm = 0.0004 m.

Now, given the change in polymer concentration in solution ( $C$ ), we can determine the fiber diameter and bead width for each concentration value.

Let's assume that  $\gamma$  is 0.072 N/m (this is a typical value for many organic solvents).

Now we can substitute the values into the formulas and calculate the fiber diameter and bead width for each concentration value of P1 and P2.

## Task 2.

The concentration of polymer 1 (P1) and polymer 2 (P2). The indicated concentration of polymer 1 varied from 10–25% (w/v relative to the solvent), and the concentration of polymer 2 varied from 1 to 50% (w/v relative to the polymer). The process parameters take the following values: - feed rate = 1 ml/h; - applied voltage = 15 kV, - distance between tip and collector = 10 cm, - inner diameter of needle = 0.4 mm. Determine the fiber diameter [nm] and bead width [ $\mu$ m].

To determine the fiber diameter ( $D$ ) and bead width ( $W$ ), it is necessary to use the Taylor-Coles equation for electrostatic spinning:

$$D = \frac{2\gamma Q}{\varepsilon U}, W = \frac{\gamma Q}{\varepsilon U},$$

where  $D$  is the diameter of the fiber,  $W$  is the width of the beads,  $\gamma$  is the coefficient of surface tension of the solution,  $Q$  is the flow rate of the solution,  $\varepsilon$  is the relative dielectric constant,  $U$  is the applied voltage.

To find the value of  $\gamma$ , you can use the following expression:

$$\gamma = \frac{\sigma}{\rho},$$

$\sigma$  is the surface tension of the solution,  $\rho$  - solution density.

Now let's plug the data into the equations. For fiber diameter:

$$D = \frac{2\gamma Q}{\varepsilon U}, D = \frac{2\left(\frac{\sigma}{\rho}\right)Q}{\varepsilon U}, D = \frac{2\left(\frac{\sigma}{\rho}\right)\left(\frac{m}{V}\right)}{\varepsilon U}, D = \frac{2\left(\frac{\sigma}{\rho}\right)\left(\frac{m}{V\pi r^2 l}\right)}{\varepsilon U}$$

Where  $m$  is the mass of the polymer,  $V$  is the volume of the solution,  $r$  is the radius of the needle,  $l$  is the distance between the needle and the collector.

For bead width:

$$W = \frac{\gamma Q}{\varepsilon U}, W = \frac{\left(\frac{\sigma}{\rho}\right)\left(\frac{m}{V}\right)}{\varepsilon U}, W = \frac{\left(\frac{\sigma}{\rho}\right)\left(\frac{m}{\pi r^2 l}\right)}{\varepsilon U}$$

Now let's substitute the values:

Let the solution density  $\rho=1$  g/ml (this is a typical value for organic solvents). Let  $Q=1$  ml/h (solution supply rate). Let  $\varepsilon=1$  (for simplicity, this value can be used for organic solvents).  $U=15$  kV (applied voltage).  $r=0.2$  mm (half the inner diameter of the needle, i.e.  $0.4/2$ ).  $l=0.1$  m (distance between the needle and the collector).

We must now determine the  $\sigma$  values for both polymers. Let's assume we have access to this information or can use typical values for similar polymers.

Once we have determined all the parameters, we can calculate the values of  $D$  and  $W$ .

#### Calculation of D and W values based on experimental data

Chitosan with a molecular weight of 700 kDa and a degree of deacetylation of 84%. The concentration of the chitosan solution for the formation of nanofibers was 1%. Solution viscosity - 1.4-2.5 Pa·s, surface tension coefficient - 31-35 mN/m and electrical conductivity no more than 2.3 mS/cm. The process parameters take the following values: - feed rate = 1 ml/h; - applied voltage = 15 kV, - distance between tip and collector = 10 cm, - inner diameter of needle = 0.4 mm. Determine the fiber diameter [nm] and bead width [ $\mu$ m].

First, let's determine the density of the chitosan solution:

$$\rho = \frac{c \times M}{N_A \times V_S}$$

Where:  $c$  is the concentration of the chitosan solution (1% or 0.01),  $M$  is the molecular weight of chitosan (700 kDa or  $700 \times 10^3$  g/mol),  $V_S$  is the volume of the solution (the volume of the solution will be approximately equal to the volume used per unit of time, in this case, 1 ml/hour),  $N_A$  - Avogadro's number ( $6.022 \times 10^{23}$  molecules/mol)

$$V_S = \frac{1 \text{ мл/ч}}{3600 \text{ sec/h}} = \frac{1}{3600} \text{ m}^3/\text{sec}$$

$$\rho = \frac{0.01 \cdot 700 \times 10^3}{6.022 \times 10^{23} \cdot \frac{1}{3600}} \approx 3.437 \times 10^{-9} \text{ kg/m}^3$$

Now that we have the density value ( $\rho$ ), let's find the surface tension coefficient ( $\gamma$ ). Since we are given a range of values, let's take the average:

$$\gamma = \frac{31 \text{ mN/m} + 35 \text{ mN/m}}{2}$$

$$\gamma = 33 \text{ mN/m}$$

We can now use these values to calculate the fiber diameter ( $D$ ) and bead width ( $W$ ):

$$D = \frac{2 \cdot V \cdot \gamma}{L \cdot Q}, W = \frac{4 \cdot \gamma}{\sqrt{3} \cdot \pi \cdot \rho \cdot V}$$

$V$  - applied voltage (15 kV),  $L$  - distance between tip and collector (10 cm or 0.1 m),  $Q$  - solution supply rate (1 ml/hour),  $\gamma$  - surface tension coefficient of chitosan solution (should be



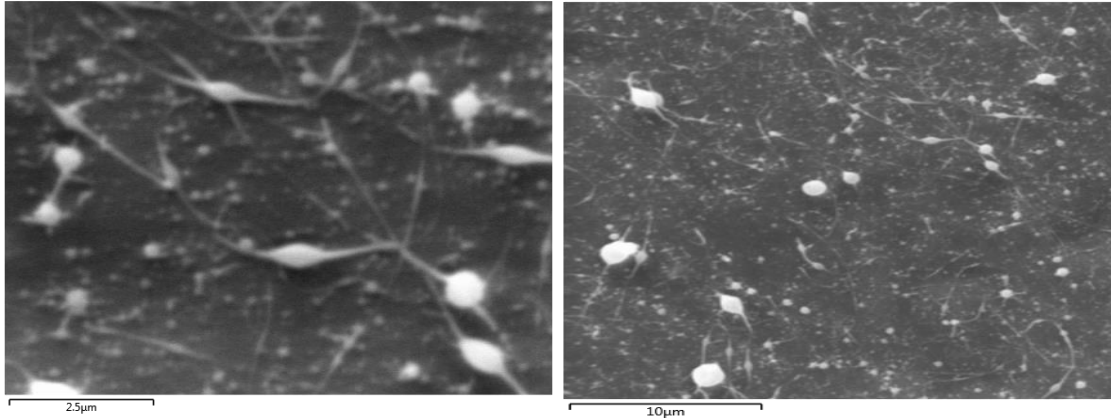
# PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS

determined in the range of 31-35 mN/m),  $\rho$  - density of chitosan solution,  $D$  - fiber diameter,  $W$  - bead width.

Substituting known values:

$$D = \frac{2.15 \cdot 10^3 \cdot 33 \times 10^3}{0.1 \cdot \frac{1}{3600}} \approx 356 \text{ nm}$$

$$W = \frac{4 \cdot 33 \times 10^3}{\sqrt{3} \cdot \pi \cdot 3.437 \times 10^9 \cdot 15 \times 10^3} \approx 0.676 \text{ mkm}$$



**Figure 15.** SEM images of chitosan nanofibers

Electron microscopic studies have shown that the thickness of the resulting chitosan nanofibers ranges from 80 to 300 nm. When electrospinning a 5% solution of chitosan dissolved in 80% acetic acid, along with nanofibers, sections of the polymer in the form of nodes (globules) are found (Fig. 15), and when using a solution with a concentration of 3% and 4%, only sections in the form of drops.

## Conclusions

Analysis of many literature data [10-17] indicates the feasibility of producing and modifying nanofibers using chitosan and other polymers. Typically, a 70% acetic acid solution is employed as the solvent to facilitate fiber formation under the influence of electricity, thus favoring it over the formation of droplets. Preparation of the molding solution involves using chitosan with a molecular weight ranging from 100 to 200 kDa, at concentrations between 1.5% and 3.5% by weight, which falls within the recommended range for electrospinning. The viscosity of the molding solution ranges from 65 mPa·s (0.065 Pa·s) at a chitosan concentration of 1.5% by weight to 885 mPa·s (0.885 Pa·s) at a maximum concentration of 3.5% by weight.

The surface tension coefficient of the polymer solution should not exceed  $5 \times 10^{-2}$  N/m. Specifically, at a chitosan concentration of 2.1% by weight, the dynamic viscosity is 196 mPa·s (0.196 Pa·s), and at a maximum concentration of 3.1% by weight, it is 604 mPa·s (0.604 Pa·s). The specific electrical conductivity exhibits a broad range, from  $10^{-6}$  to  $10^{-2}$  S/cm, with the lower limit constrained by the threshold for gas discharge from the jet, which compromises its stability.

Regarding the general parameters of the electrospinning process, an electrical voltage ranging from a few to one hundred kilovolts (typically 10-60 kV) is applied to the polymer

solution or melt. A lower surface tension coefficient of the spinning solution ensures greater stability of the liquid jet, with values typically below 0.05 N/m.

In the electrospinning process, polymer solutions with molecular weights ranging from tens to hundreds of thousands, weight concentrations up to 20%, and dynamic viscosities between 0.05 and 1 Pa·s are typically used. The deformation time during electrospinning typically ranges from  $10^{-3}$  to  $10^{-4}$  s. The electrical conductivity of the spinning solution can be regulated by adding small amounts of ionic substances, provided the polymer and solvent are sufficiently pure, or by purification if heavily contaminated.

Under normal conditions, the preferred boiling point range is between 50°C and 120°C, with a relative saturated vapor pressure between 0.02 and 0.2. The distance between electrodes varies from 20 to 50 cm, and the distance from electrodes to walls is typically 50 cm or more, with the walls electrically insulated.

The volume flow rate typically ranges from 0.03 to 1 cm<sup>3</sup>/min per injection nozzle, although in some injector designs, the volume flow rate can reach 100 cm<sup>3</sup>/min. For an installation with a single nozzle and an interelectrode distance of 30 cm, a stationary jet exists within a range of nozzle voltages from 22 to 28 kV, with voltage at the nozzle ranging widely from 0.1 to 5  $\mu$ A.

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## References

- [1]. Perepelkin K.E. Fiziko-himicheskie osnovy processov formovaniya himicheskikh volokon. M.: Himiya. 1976, 320. [In Russian]
- [2]. Aragwal S., Wendorff J.H., Greiner A. Use of electrospinning technique for biomedical applications. Polymer. 2008. Vol. 49. P. 5603–5621.
- [3]. Liao S., Chan C. K., Ramakrishna S. Electrospun nanofibers: Work for medicine? Front. Mater. Sci. China. 2010, 4, 29–33. DOI 10.1007/s11706-010-0009-0
- [4]. Papkov S. P. Fiziko-himicheskie osnovy pererabotki rastvorov polimerov. M.: Himiya, 1971. 346 s. [In Russian]
- [5]. Matveev A.T., Afanasov I.M. Poluchenie nanovolokon metodom yelektroformovaniya. M.: Himiya. 2010, 83. [In Russian]
- [6]. Prokopchuk. N. R., SHashok ZH. S., Vishnevskiy K. V., Pris`hepenko D. V. Osobennosti svoystv formovochnogo rastvora i nanovolokon iz biopolimera hitozana//Trudy BGTU, Himiya, tehnologiya organicheskikh ves`hestv i biotehnologiya. 2015, 4S. 42-. [In Russian]
- [7]. Filatov YU.N. YEлектроformovanie voloknistykh materialov (YEFVprocess). Pod redakciey V. N. Kirichenko. ? M.: Neft` i gaz, 1997. ? 297 str. [In Russian]
- [8]. Kozyreva E. V., YUkina O. V., SHipovskaya A. B. Poverhnostnoe natyazhenie rastvorov hitozana. Sovremennyye problemy nauki i obrazovaniya - 2012. - <sup>1</sup> 4. S. 1-8. [In Russian]
- [9]. Pillai C.K.S., Paul W., Sharma Ch. P. Chitin and chitosan polymers: Chemistry, solubility and fiber formation. Progress in Polymer Science, 34, 2009, 641–678. <https://doi.org/10.1016/j.progpolymsci.2009.04.001>
- [10]. Dmitriev Yu. A. Tehnologiya yelektroformovaniya voloknistykh materialov na osnove hitozana (05.17.06 - tehnologiya i pererabotka polimerov i kompozitov) 2011 avtoreferat dissertatsii na soiskanie uch. st. kand. tehn. nauk. Moskva, 2011, 25. [In Russian]
- [11]. Korabel`nikov A.R. Analiz yetapov processa formirovaniya nanovolokon. YEtap obrazovaniya ochagov struynogo techeniya rastvora. Izvestiya vysshikh uchebnykh zavedeniy. Tehnologiya tekstil`noy promyshlennosti. 2014, 5 (353), 120-124. [In Russian]
- [12]. Korabel`nikov A.R., Shutova A.G., Smirnov M.M., Semenova K.A. Model` transportirovaniya zhidkostnoy plenki cilindricheskimi vras`hayus`himsiya yelektrodom, pogruchennyim v rastvor polimera v ustanovke dlya yelektroformirovaniya nanovolokon. Izvestiya vysshikh uchebnykh zavedeniy. Tehnologiya tekstil`noy promyshlennosti. 2016, 6 (366), 191- 195. [In Russian]

## **PRACTICAL AND THEORETICAL ASPECTS OF ELECTROSPINNING CHITOSAN-BASED FIBERS**

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- [13]. Smirnov M.M. Razrabotka sposoba polucheniya mikrovloknistyykh kompozitsionnykh netkanykh materialov metodom yelektroformovaniya (05.19.02-Tehnologiya i pervichnaya obrabotka tekstil'nykh materialov i syr'ya). Dissertatsiya na soiskanie uchenoy stepeni kandidata tekhnicheskikh nauk. Kostroma, 2021, 123. [In Russian]
- [14]. Ponomar M., Krasnyuk E., Butylskii D., Nikonenko V., Wang Y., Jiang C., Xu T., Pismenskaya N. Sessile Drop Method: Critical Analysis and Optimization for Measuring the Contact Angle of an Ion-Exchange Membrane Surface. *Membranes*, 2022, 12, 765. <https://doi.org/10.3390/membranes12080765>
- [15]. Smirnov M.M., Tihomirov S.A. Opredelenie svoystv rastvorov polimerov razlichnoy koncentracii, ispol'zuyus'hihsya dlya polucheniya volokon metodom yelektroformirovaniya. *Vestnik Kostromskogo gosudarstvennogo tekhnologicheskogo universiteta*. 2016. 1(36), 41-44.
- [16]. Li J., Fu J., Tian X., Hua T., Poon T., Koo M., Chan W. Characteristics of chitosan fiber and their effects towards improvement of antibacterial activity. *Carbohydrate Polymers* 2022, 280, 119031. <https://doi.org/10.1016/j.carbpol.2021.119031>
- [17]. Ilyas R.A., Aisyah H.A., Nordin A.H., Ngadi N., Zuhri M.Y.M., Asyraf M.R.M., Sapuan S.M., Zainudin E.S., Sharma S., Abral H., Asrofi M., Syafri E., Sari N.H., Rafidah M., Zakaria S.Z.S., Razman M.R., Majid N.A., Ramli Z., Azmi A., Bangar S.P., Ibrahim R. Natural-Fiber-Reinforced Chitosan, Chitosan Blends and Their Nanocomposites for Various Advanced Applications. *Polymers (Basel)*. 2022, 14(5):874. DOI: 10.3390/polym14050874.