KAUNAS UNIVERSITY OF TECHNOLOGY

JURGITA ŠATEIKĖ

INVESTIGATION OF NATIVE AND CATIONIC STARCH INSERTION INTO FIBRE FORMATION VIA ELECTROSPINNING TECHNIQUE

Summary of Doctoral Dissertation
Technological Sciences, Materials Engineering (T 008)

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JURGITA ŠATEIKĖ

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INTRODUCTION

Research problem justification and relevance of the work

Nanotechnology is no longer a novelty in the modern context. It is incorporated in household, medicine, textile, automotive and many other industries. Electrospinning is a versatile and effective nano-micro fibre formation technique, which produces fibres with excellent mechanical properties, large surface area and high porosity. These properties make this technique widely applied in many applications. Electrospinning technique can form a nanofibre from a wide variety of native polymers as well as from different natural polymer blends or low molecular weight, non-volatile materials (Mendes, Stephansen and Chronakis, 2017).

Polysaccharides as biopolymers are of great interest to scientists and industry representatives for the possibility to change synthetic polymers to the native polymers. These interests in polysaccharides-based polymers are influenced by positive properties such as biocompatibility, biodegradability, nontoxicity and economic price. The formed fibres with polysaccharides are as well promising due to their wide application possibilities. The excellent properties make them very suitable in the biomedical field.

It can be stated that from all the polysaccharides, starch is one of the most abundant and lowest price polysaccharides. The formation of native polymer by electrospinning technique generally depends on the degree of their chain entanglements. Subsequently, the chemical structure, concentration and shear thinning properties affect their electrospinning processing.

The beginning study and the analysis of the possibilities of starch formation by electric spinning technique started in 2010, when very few researchers performed experiments with starch. The first step in the formation of fibre with modified starch via electrospinning technique were made by a group of researchers led by KTU Prof. A. Žemaitaitis and Prof. R. Milašius in 2009; they studied the possibilities of PVA and cationically modified starch KOEK formation (Adomavičiūtė et al., 2009). The results showed that the PVA/KOEK solution, with a weight ratio of 75/25, was able to form fibres by electrospinning technique. For this reason, the research on this topic continued, and the possibilities of the fibre formation were analysed.

The fibre formation with pure starch by using electrospinning technique is complicated. Over the recent years, researchers have been analysing the pure starch fibre formation by using electrospinning technique. Kong and Zielger introduced the method of producing pure starch fibres by electrospinning that involves using an appropriate solvent for native high amylose starch and spinning starch with a modified electrospinning setup. Additionally, a post-spinning heat treatment and cross-linking were employed to further improve the starch fibre properties, including water stability. The spinning solution was prepared by dissolving (15 % w/w) corn starch in 95 % aqueous DMSO solvent. This group of scientists (Kong, Ziegler, 2012, 2013, 2014) have formed smooth and uniform micron size fibres from starch.

On the basis of various research results provided in different literature sources, it can be stated that the fibre formation of pure starch is possible but in general difficult to electrospun. In order to improve the electrospinning process of the starch as polymer, it can be modified, i.e., its chemical structure is modified, which allows the formation of the fibre with this polysaccharide. Starch can be blended with synthetic polymers that have excellent spinning properties as well.

The goal of the dissertation is to investigate the possibility to form fibre structures with the native and cationic starch component in poly(vinyl alcohol) solution by electrospinning technique and determine the influence of native and cationic starch content in the mixture with poly(vinyl alcohol) on the electrospinning process and the structure of the fibres web.

The objectives of the research:

1. To investigate the possibility to form fibres via electrospinning technique with potato starch in a mixed poly(vinyl alcohol) solution.
2. To determine the influence of ethanol on the electrospinning process and the structure of the fibre web from poly(vinyl alcohol) and potato starch polymer solution.
3. To investigate the possibilities of incorporation of cationic starch and poly(vinyl alcohol) into fibres structures and the influence of technological parameters of the electrospinning process.
4. To investigate the possibility of forming fibre structures with poly(vinyl alcohol) and cationic starch, when the cationic starch makes more than 50 % of the amount.

Research novelty and practical importance

The electrospinning technique is increasingly used in the formation of nano-microfibre due to its large specific surface area, high porosity, small pore size and simple operation principle. This fibre formation method offers unique opportunities to produce natural fibres with a controlled pore structure.

Polysaccharides are polymers of natural origin that have a wide variety of applications, excellent physical and chemical properties, easy extraction and low cost, which is very cost-effective. Over the last decade, the application of polysaccharides in various fields has attracted an increasing interest from both industry and researchers. However, the main challenges in forming filaments from polysaccharides still complicate the formation of fibres and the size of the fibres that are formed.

Starch is a polysaccharide that has a property with good iodine absorption, which can be an excellent antiseptic with antimicrobial properties and is widely used in the treatment of wounds. Chitosan, which as well has antimicrobial properties and is used in wound healing, can be replaced with a starch/iodine mixture, which would be more cost-effective, knowing that chitosan is a relatively expensive polysaccharide. However, starch has its chemical nature that complicates the electric spinning process. In order to improve the electrospinning process of this polysaccharide, it can be blended with synthetic polymers, which have good properties for the nano-microfibre formation. Poly(vinyl alcohol) PVA is one of the most widely used synthetic polymers and has a great interest due to its positive properties suitable for pharmaceutical, biomedical applications. However, one of the most important advantages of this synthetic polymer is its relatively low cost. Thus, the economic aspect can be one of the many other benefits of this synthetic polymer.

On the basis of various research results provided in different literature sources, it has been noticed that the possibility of forming nano size ranges fibres using electrospinning method with starch as biopolymer still has not been achieved. Therefore, the formed nano size fibre polysaccharides are modified or blended with synthetic polymers.

Starch was the main objective of this dissertation. In order to achieve the improvement of electrospinnability and formed nano-micro size fibres, starch was cationically modified and mixed with synthetic polymer.

The novelty of the work lies in using electrospinning technique to form fibre with modified starch as polymer solution and blend with PVA when the cationic starch KOEK content is more than 50 %. When analysing the literature sources, there are no studies in which fibres were formed with cationic starch using the electrospinning method with a rotating electrode. All studies were made by using the needle electrospinning method or modifying this method into so-called wet electrospinning for the fibre web formation. In this work, the fibres were formed using electrospinning method with a rotating electrode, and the influence of different rotating electrodes (plain and electrode with tines) on the formed fibres nonwoven web was analysed.

Approbation of the research results: the results of the research were presented in 3 scientific publications and 4 conferences.

Structure of the dissertation: the dissertation consists of an introduction, 3 chapters, conclusions, a list of references (134 positions) and a list of scientific publications.

CONTENT OF THE DISSERTATION

In the Introduction chapter, there is a short description of the topicality and novelty of investigations, the aim and the tasks of the dissertation.

The first chapter Literature Review contains a short survey of literature on the theme of the dissertation. This part presents the analysis of the electrospinning process parameters including polymer solution parameters, ambient parameters during the process that affect the formation of fibre webs. Moreover, the most significant achievements of scientists are observed as well as the application possibilities of fibres that are formed via electrospinning technique with polysaccharides.

The articles concerning native polysaccharides and the possibilities to electrospun are analysed as well as the main difficulties that occur during the formation of fibres. In addition, the articles, where solvents have been used in order to increase the electrospinnability and achieve uniform nanofibres, were observed. Based on the investigation results provided in different literature sources, there have been observed the possibilities in fibre formation with the pure starch as a spinning solutions and the main difficulties regarding the electrospinning process and solution preparation. Different starch modification possibilities and synthetic polymers that can be blended with this polysaccharide have been observed as well. In addition, articles by different authors, concerning the polysaccharides, especially starch applications in medical field, are taken into consideration as well.

The second chapter Research Methodology describes the methodology of experimental investigations.

Experimental materials and methods. During the researches, there were used different types of spinning solutions. To carry out the experiments, a polymer solution obtained by dissolving the PVA powder (CARL ROTH, Germany) was used, under the constant stirring for 2 hours with a magnetic stirrer. PVA powder was dissolved in the deionized water of 70 ºC temperature. This way, the solution with 7 and 8 % concentration was attained.

In the 7 % PVA and water solutions were added different amounts of starch: 0 % (native solution), 1 %, 3 % and 5 %. A small amount of potato starch (Alvo & Co, Lithuania) was dissolved in cold water. In the 8 % PVA and water solution, different amount of ethanol, i.e., 0 % (native solution), 1 %, 3 % and 5 %, was added. Ethanol (75 % medical spirit) was added to the spinning solution just before the electrospinning process due to the evaporation.

Cationic starch was prepared by chemical reaction of hydroxyethylated starch with 2,3-epoxypropyltrimethylammonium chloride in the presence of sodium hydroxide (molar ratio of starch: epoxy compound: NaOH was 1:0.35:0.04) at 45 ºC for 24h. After the reaction, the KOEK was washed (5 times) with isopropanol and dried at 50 ºC. The nitrogen content in KOEK was estimated by the Kjedahl method after the purification by Soxhlet extraction with methanol for 16 h. PVA/KOEK solutions with mass ratio 75/25, 50/50 and 35/65 were prepared. The experiments were carried out using: 8, 10, 12 % concentration PVA/KOEK spinning solutions with the mass weight ratio 75/25, and 12 % concentration was used for the same polymer composition solution but with different mass ratio 50/50 and 35/65. Moreover, the pure PVA solution was prepared with the following concentrations: 8, 10 and 12 %.

All polymers solutions with cationic starch were prepared by Prof. A. Žemaitaitis and J. Bendoraitienė (Department of Polymer Chemistry and Technology, KTU)

The dynamic viscosity was measured by using a rotational viscometer RheoTec RC02-R (Germany) equipped with a small-sample thermostated adapter, spindle TR8 at 25 ± 0.1 °C. The conductivity measurements of the spinning solutions were performed with Radelkis OK-102 conductometer (Hungary). The surface tension of the solutions were measured using Dataphysics DCAT21 (Germany) apparatus with Wilhelmy plate.

The fibre web was manufactured by using the Nanospider™ (Germany) electrospinning equipment. The fibres that were manufactured in this equipment used two different kinds of rotating electrode: cylindrical and electrode with the tines. The rotating electrode is partially immersed in a tray with polymer solution, towards the upper electrode, which is attached to the collection part.

During the electrospinning process, under conditions of increasing voltage, on the rotating bottom electrode, the hemispherical-shaped droplets start to form, from which, under conditions of further increase in voltage, cone-shaped droplets, called Taylor Cones, are formed. After the electrostatic forces have exceeded the surface tension, a solution jet is formed from the cone-shaped droplets (Taylor Cones). This jet, while moving towards the collection screen, stretches and splits into nano-micro fibres.

During all the experiments, the distance between the electrodes was 13 cm, the applied electrical potential varied between 35 and 70 kV, the temperature of electrospinning environment was T = 20 ± 2 °C, and the relative air humidity was φ = 40 ± 2 %.

Scanning Electron Microscopy (SEM) with SEM-FEI Quanta 200 (The Netherlands) was used to observe and identify the morphology and structure of nonwoven material from nanofibres. A small section of the nanofibre mat was used in SEM with the use to determine the morphology of nanofibres. Lucia 5.0 software was utilized to measure the diameter of nanofibres and calculate the average diameters of the observed fibres. The average of nanofibres diameter was calculated from 3 SEM images with the same scale and magnification. All nanofibres were measured from every SEM image.

The third chapter Results of the Research presents theoretical and experimental investigations and their analysis.

Fibre formation with poly(vinyl alcohol) and small amounts of potato starch spinning solution

While analysing the structure of fibres, it was observed that the presence of starch in 0 % and 1 % of PVA solution did not have a significant effect; however, with increasing starch content of 3 % and 5 %, there was observed a lower amount of fibre that has formed on the nonwoven material. SEM images of 7 % PVA without starch and the addition of 5 % starch are presented in Fig. 1. From the presented data, it has been observed that, compared with the SEM images (Fig. 2) of 8 % PVA with additional ethanol in the polymer solution, a lower number of spots on nonwoven mats with a PVA solution containing starch were formed.

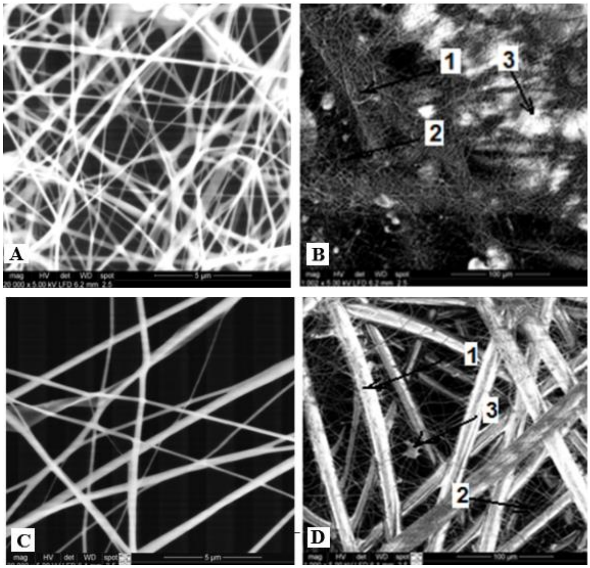

Fig. 1. SEM images of nonwoven mats, formed from 7 % PVA solutions containing various amounts of starch at 65kV voltage: A – 0 % starch (scale 5 μm); B – 0 % starch (scale 100 μm); C – 5 % starch (scale 5 μm); D – 5 % starch (scale 100 μm) (1 – fibres of support material, 2 – fibres, 3 – spots of spinning solution)

In the next specimen part, it was analysed how ethanol influences the electrospinning process and what amount of ethanol in the electrospinning solution is preferred for the procedure. The amounts of ethanol in PVA solutions (8 % PVA) were as follows: 0 % (native solution), 1 %, 3 % and 5 % ethanol in solution (Fig. 2). From the presented data, it can be noticed that by increasing ethanol in the electrospinning solution, the fibres with more defects, i.e., spots of PVA solution, were formed. It can be presumed that because of the decreased conductivity of PVA solution with higher amount of ethanol, more spots of PVA solution could be formed.

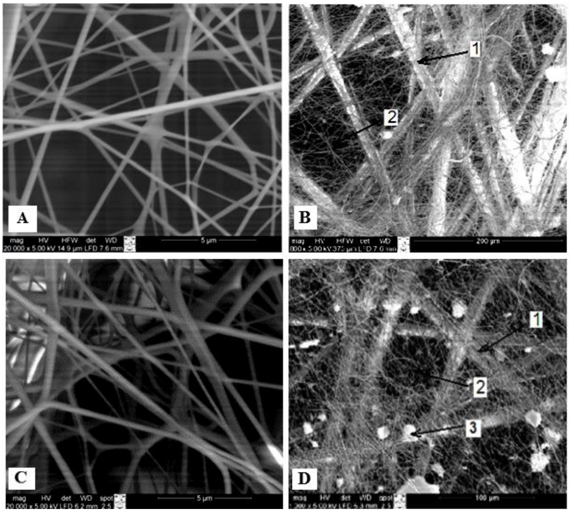

Fig. 2. SEM images of nonwoven mats formed from 8 % PVA solutions containing various amounts of ethanol at 55kV voltage. A – 0 % ethanol (scale 5 µm); B – 0 % ethanol (scale 100 µm); C – 5 % ethanol (scale 5 µm); D - 5 % ethanol (scale 100 µm) (1 – fibres of support material, 2 –fibres, 3 – spots of spinning solution)

In order to confirm the assumption that the electrospinning solution with starch formed fibres containing less spots, for the next specimens, there were electrospun fibres with starch (0, 1, 3 and 5 %) and the addition of 5 % of ethanol form all polymer compositions. SEM images display 7 % PVA solution with different amounts of starch and the addition of 5 % ethanol as shown in Fig. 3.

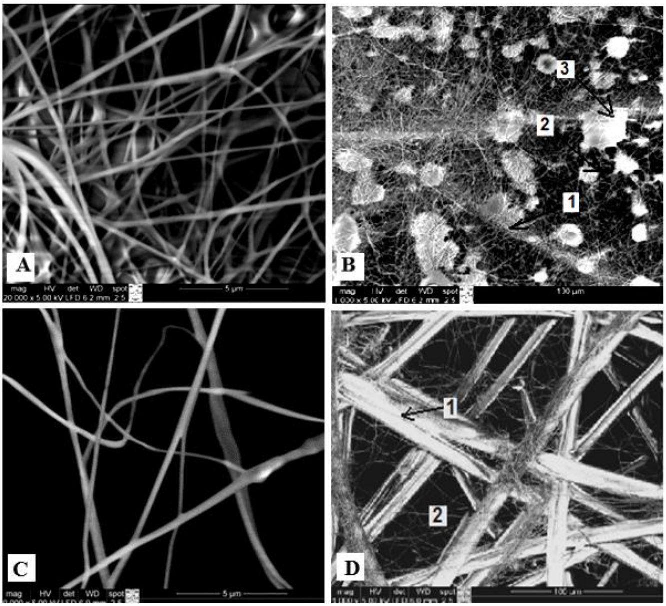

Fig. 3. SEM images of nonwoven mats formed from 7 % PVA solutions containing various amounts of starch and 5 % ethanol at 65 kV voltage: A – 0 % starch and 5 % ethanol (scale 5 µm); B – 0 % starch and 5 % ethanol (scale 100 µm); C – 5 % starch and 5 % ethanol (scale 5 µm); D – 5 % starch and 5 % ethanol (scale 100 µm) (1 – fibres of support material, 2 – fibres, 3 – spots of spinning solution)

The presented data has confirmed the assumption that the lower density of fibres was formed, but with a smaller number of defects. After the results have been analysed in this experiment part, it was noticed that it is possible to form fibres with PVA containing potato starch in the spinning solution but with the lower density of fibre that was formed. Moreover, it was confirmed that when adding an additional 5 % of starch and 5 % of ethanol into the polymer solution, fibre with lower number of spots of PVA solution were formed.

Formation of fibres with poly(vinyl alcohol) and cationic starch solution blends

The purpose of this experiment part was to form fibres PVA/KOEK when mass weight ratio is 75/25 and find the preferable concentration. Furthermore, it was aimed to analyse the different rotating electrode (Fig. 4) influence on the electrospinning process and formed nano-micro fibre morphology and structure.

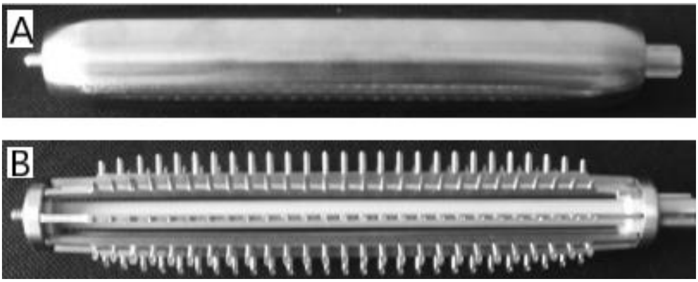

Fig. 4. The rotating electrode of electrospinning process: A – plain cylindrical electrode, B – electrode with tines

The results showed that the rotating electrode with tines (Fig. 4 B) had a positive influence on the electrospinning process: it was possible to form nano-micro fibres at higher voltage.

It is known that the parameters of solutions have significant influence on the electrospinning process and the structure of the fibre. The parameters of spinning solutions are presented in Table 1. The viscosity of the solution, which directly depends on the solution concentration, is one of the main factors that have influence on the diameter, morphology and structure of the forming fibre.

Table 1. The measurements of polymer solution parameter and the average diameter of fibre PVA/KOEK with mass ratio 75/25 at different concentrations

Concentration (%)	**Viscosity (mPa*S)**	**Surface tension (mN/m)**	**Conductivity (S*cm)**	**Average diameter (nm)**	
				Plain electrode	**Electrode with tines**
12	1320	46.78	$3.515 * 10^{-3}$	310	280
10	610	46.68	$3.515 * 10^{-3}$	260	230
8	190	47.08	$3.156 * 10^{-3}$	275	215

From the presented data, it was noticed that the diameter of electrospun fibres formed lower when the concentration of PVA/KOEK polymer solution decrease 8 %. The difference of solution viscosity from 1320 Pa*s to 190 Pa*s influenced the formation of fibre with a smaller diameter at a concentration of 8 %. An assumption is made that the type of rotating electrode had a positive influence on the diameter of the fibre.

In order to analyse the rotating electrode impact on the electrospinning process, Table 2 shows the ranges of applied voltage for all PVA/KOEK (mass ratio 75/25) polymer concentrations. The results show that the highest applied voltage for electrospinning process was 70 kV for all polymer solutions. It was noticed that 12 % polymer solution using rotating electrode with tines starts form fibres at 35 kV, which was not noticed with the plain electrode. Using plain rotating electrode, the lowest applied voltage was 50 kV. The type of rotating electrode has influence on the electrospinning process, using electrode with tines, it was possible to form fibres at lower voltages.

Table 2. The solution PVA/KOEK with mass ratio 75/25 electrospinning process ranges of applied voltage

75/25 PVA/CS polymer solutions	Ranges of applied voltages, kV (plain electrode)	Ranges of applied voltages, kV (electrode with tines)
12 %	70–50	70–35
10 %	70–40	70–40
8 %	70–45	70–40

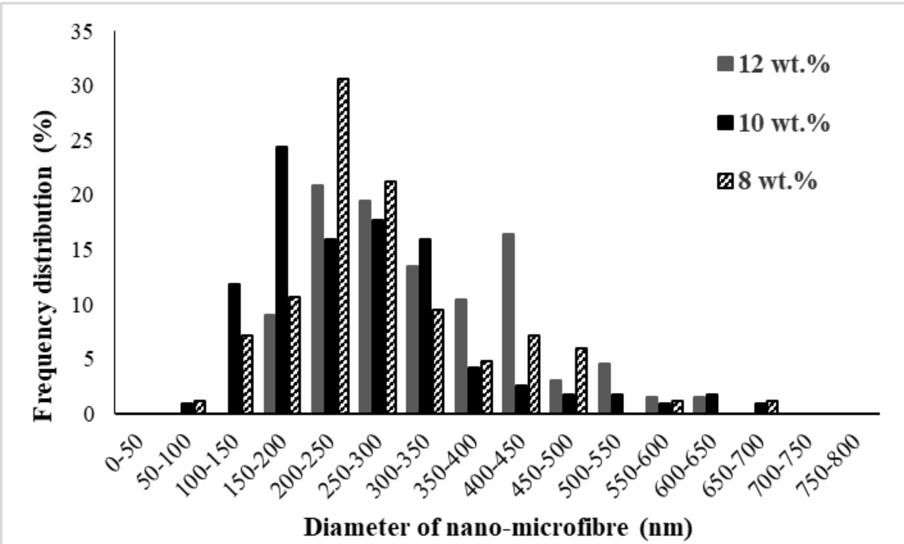

Fig. 5. The diameter distribution of fibres formed from PVA/KOEK solutions (mass ratio 75/25) with concentrations (8, 10, 12 %) using plain rotating electrode

In Figure 5 and 6, the distribution of the 75/25 PVA/KOEK fibres formed from the spinning solutions with various concentrations (8, 10, 12 %) by using cylindrical and electrode with tines are presented. From the presented data, it can be observed that by using cylindrical electrode, the majority of PVA/KOEK fibres were formed from the solutions with concentrations of 8 % and 10 % are 100–200 mm in diameter. However, the majority of fibres formed from the solution with 12 % concentration appear to be 200–300 mm in diameter. In the case of electrode with tines, the majority of nanofibres formed are 200–300 mm in diameter for all concentrations (8, 10 and 12 %). Moreover, it was noticed that when using cylindrical electrode, more fibres were formed with the diameter higher than 500 mm. From this, it can be concluded that electrode with tines is more appropriate for the electrospinning of PVA/CS fibres, and the best concentration of the spinning solution for the accepted conditions is 8 %.

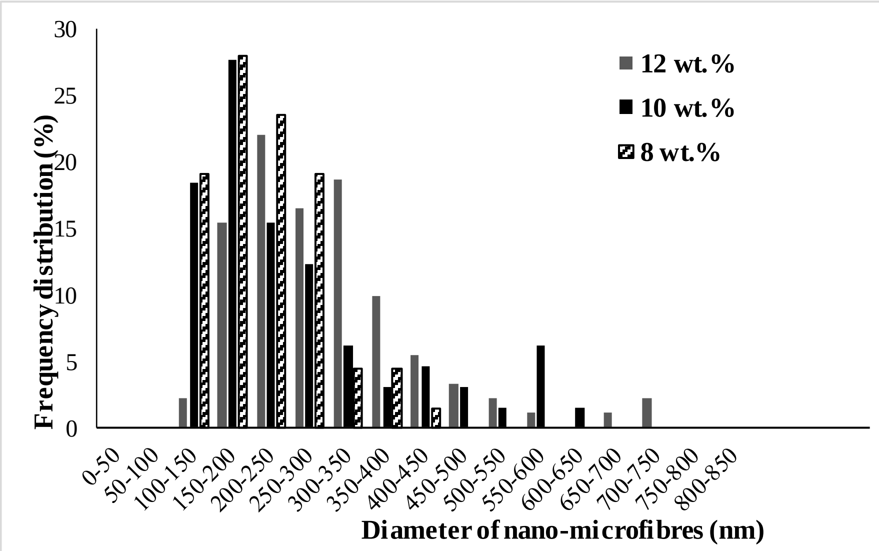

Fig. 6. The diameter distribution of nano-microfibres formed from PVA/KOEK solutions (mass ratio 75/25) with concentrations (8, 10, 12 %) using rotating electrode with tines

From this experiment part, it can be concluded that the type of rotating electrode has an influence on the electrospinning process, diameter and structure of the form of fibre.

In the first part of the experiment with potato starch, the analysis revealed a positive influence of a small amount of ethanol on the electrospinning process. In order to confirm the assumption from the previous experiments, 8 % PVA/CS with the mass weight ratio 75/25 and ethanol (3%, 6% and 9%) in the solution were electrospun.

The results of applied voltages and average diameter of fibres of 8 % PVA/KOEK with mass weight ratio 75/25 is presented in Table 3. The lower voltage at which the electrospinning process formed fibres with the PVA/KOEK solution and 9 % of ethanol was 30 kV. However, it is known that electrospinning process is intensive at higher voltages; thus, this did not affect the fibre structure and morphology, since at the low voltage, the electrospinning process is less productive. Increasing ethanol to 9 % in the spinning solution, the electrospinning process forms fibres at the highest applied voltage 60 kV, while adding 3 % and 6 % of ethanol electrospun fibre webs at 70 kV.

Table 3. 8 % PVA/KOEK with mass weight ratio 75/25 average diameter of fibre and ranges of applied voltages of electrospinning process

Amount of ethanol (%)	**Surface tension (mN/m)**	**Average diameter (nm)**	**Ranges of applied voltages (kV)**
0	47,34	260	70–40
3	48.32	210	70–40
6	46.85	260	70–40
9	41.97	275	60–30

The distribution of the fibre diameters (Fig. 7) that are presented shows that added ethanol in the electrospinning polymer solution had no significant effect on the fibre diameter. It is necessary to note that fibres with higher diameter than 500 nm were formed by increasing the ethanol amount in the polymer solution, which did not occur with fibres containing 3 % of ethanol or without ethanol. Thus, it can be concluded that in this case, the increasing of ethanol in the spinning solution increased the diameter of the fibre.

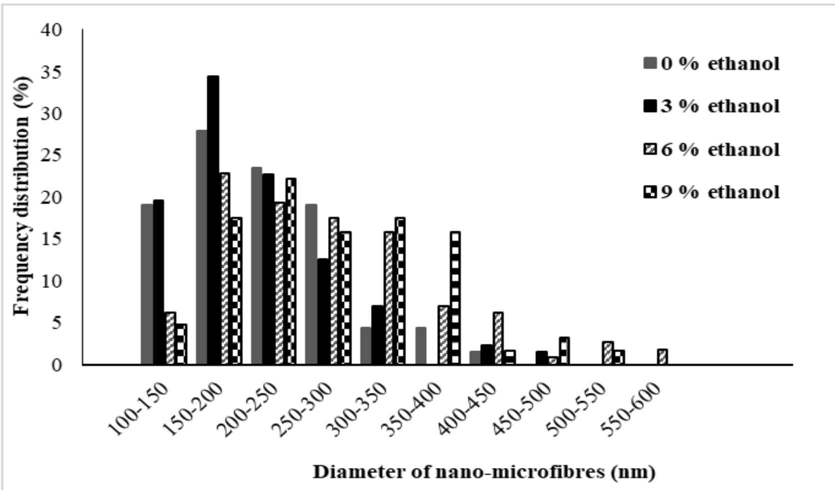

Fig. 7. The average value of the distribution of 8 % PVA/KOEK with mass ratio 75/25 and different amount of ethanol in the polymer solution

For the next experiments, the rotating electrode with tines was used due to the positive results described above.

In the next part of the experiment, the fibres with PVA/KOEK solutions with a different mass weight ratio 50/50 and 35/65 were formed to compare the results with 75/25 PVA/CS and pure PVA. The concentration of the electrospinning solution was 12 % for all polymer compositions.

In Figures 8 and 9, the distributions of the PVA and PVA/KOEK with mass ratio 75/25 distribution of the fibre diameters and SEM images with formed fibres are presented. From the presented data, it can be seen that the majority of formed fibres were in the range of 200–350 nm and formed higher diameter than 500 nm for both solution compositions PVA and PVA/KOEK with mass ratio 75/25.

Analysing the distribution of the fibre diameters electrospun from PVA/KOEK polymer solution with mass ratio 50/50 (Fig. 10) and 35/65 (Fig. 11), it was noticed that fibres were formed with the lower diameter than in the case of PVA and PVA/KOEK with mass ratio 75/25. In the solution composition 50/50 PVA/KOEK, the majority of fibres formed in the range of 100–200 nm, and there are no fibres formed with higher diameter than 500 nm. By increasing KOEK amount to 65 % in the PVA solution, it can be noticed from the SEM image that the lower density of fibres was formed, and the distribution show that the majority of fibre diameter formed in the range of 150–250 nm but more fibres stuck together.

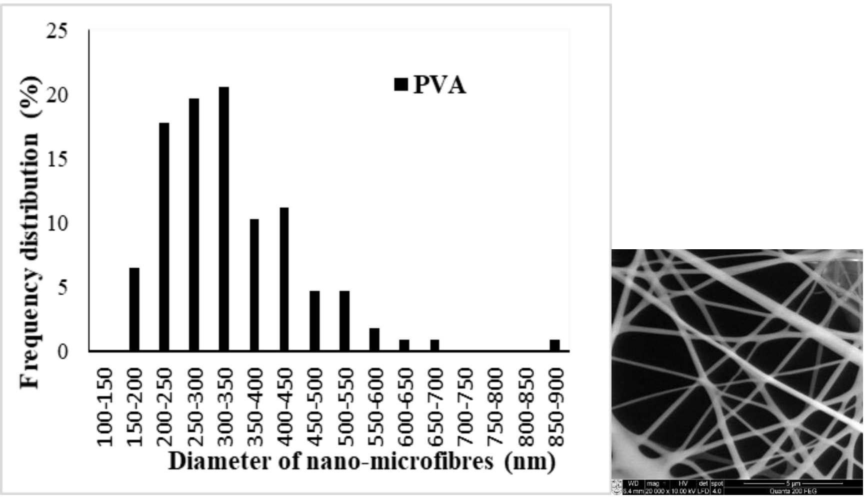

Fig. 8. The average value distribution and SEM image with fibres 12 % pure PVA solution at 65 kV

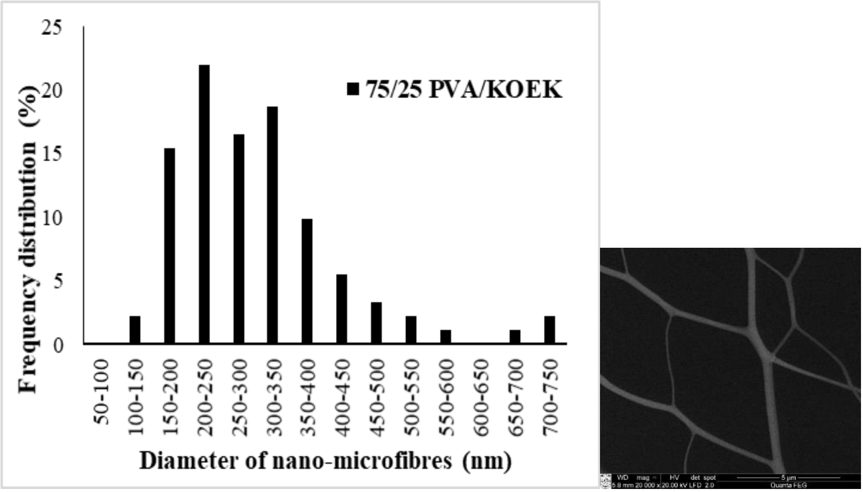

Fig. 9. The average value distribution and SEM image of fibres 12 % PVA/KOEK with mass weight ratio 75/25 at 65 kV

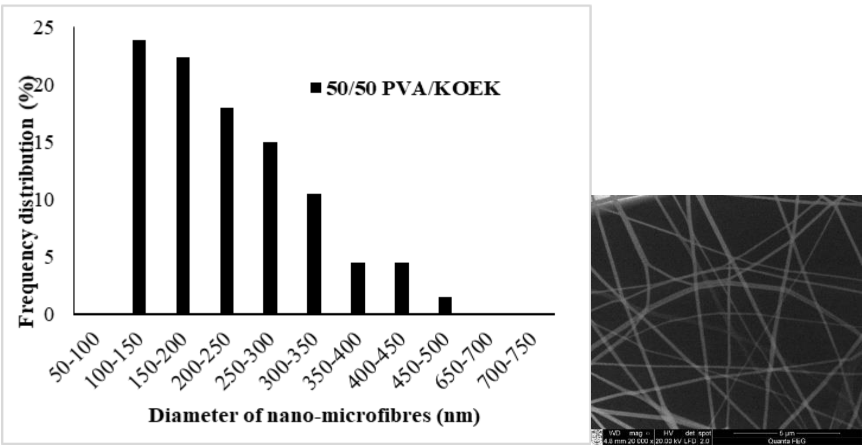

Fig. 10. The average value distribution and SEM image of fibres 12 % PVA/KOEK with mass weight ratio 50/50 at 65 kV

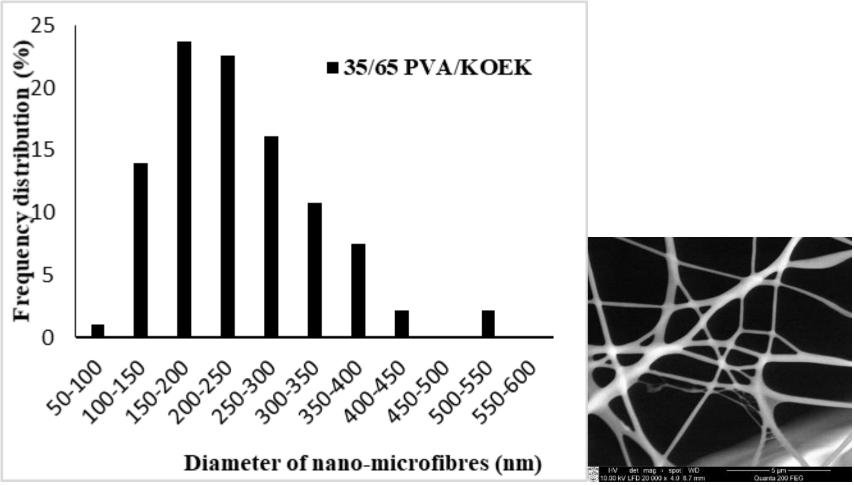

Fig. 11. The average value distribution and SEM image of fibres 12 % PVA/KOEK with mass weight ratio 35/65 at 65 kV

CONCLUSIONS

1. It was established that it was possible to form fibres with 7 % poly(vinyl alcohol) with the addition of a small amount of starch via electrospinning technique. It was noticed that starch in the spinning solution negatively affects the electrospinning process. Due to the high viscosity of the solution, it was not possible to form fibres with 5 % of starch in the poly(vinyl alcohol) solution. However, a 7 % poly(vinyl alcohol) solution with 5 % of starch and 5 % of ethanol was suitable for the fibre formation by electrospinning. The starch in the poly(vinyl alcohol) solution influenced the higher average diameter of fibres: in 7 % poly(vinyl alcohol) solution without starch, the average diameter of nanofibres is 260 nm, while with 1 % of starch – 310 nm, i.e., an increase of 16 %.
2. The increasing amount of ethanol in the poly(vinyl alcohol) spinning solution formed more spots on electrospun nonwoven material with fibres, but it was noticed that ethanol has a positive influence on the electrospinning process. The fibres without ethanol were possible to form at the lowest 45 kV voltage, while poly(vinyl alcohol) solution with 5 % of ethanol could form fibres at the lowest 35 kV voltage of electrospinning process.
3. It was found that even a small amount of starch in the poly(vinyl alcohol) solution had a positive influence on the structure of fibres, formed fibres with lower number of spots on the nonwoven material.

4. It was noticed that the most suitable concentration of poly(vinyl alcohol) and cationic starch spinning solution with mass weight ratio 75/25 using rotating electrode with the tines was 8 %. At concentration of 12 % poly(vinyl alcohol) and cationic starch with mass weight ratio 75/25, the average diameter of fibre increased by 23 % compared with the 8 % concentration.
5. It was found out that the type of rotating electrode of the electrospinning process influences the diameter of fibres of poly(vinyl alcohol) and cationic starch solution with mass weight ratio 75/25. The average diameter of fibres formed from 12 % concentration poly(vinyl alcohol), and cationic starch solutions with a plain rotating electrode was 310 nm, while the same concentration and polymer composition using rotating electrode with tines - 280 nm, i.e., 10 % thinner.
6. Rotating electrode with tines had an effect on the electrospinning process, but it was insignificant. It was possible to form nanofibres at a lower voltage 35 KV of electrospinning process, which could not be achieved with the plain rotating electrode. Using rotating electrode, the biggest number of nanofibres were formed at 10 % concentration poly(vinyl alcohol) and cationic starch solution, i.e., 119 fibres, while electrode with tines formed a bigger number of fibres at 12 % concentration of spinning solution, i.e., 91 fibres.
7. It was found out that by increasing the amount of ethanol in 8 % poly(vinyl alcohol) and cationic starch spinning solution with mass weight ratio 75/25, it was possible to form nano-microfibres at lower voltage 30 kV of electrospinning process. The density of nano-microfibres web increased (128 fibres), when the amount of ethanol was 3%, but by increasing the amount of ethanol to 9 % in the spinning solution, the density of forming nano-microfibres decreased (63 fibres).
8. It has been proved that fibres with 12 % poly(vinyl alcohol) and cationic starch at mass ratios of 50/50 and 35/65 were successfully electrospun. The results have shown that the most suitable amount of cationic starch of the poly(vinyl alcohol) solution was 50 %, as smaller diameter fibres were formed on the nonwoven web. The diameter distributions have shown that there are no fibres with larger diameter than 500 nm. SEM images showed that by increasing the cationic starch to 65 % of PVA solution, more fibres formed stuck together, which is a negative occurrence for further use of the filament structure.

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REZIUMĖ

Tiriamos problemos pagrindimas ir darbo aktualumas.

Nanotechnologijos šių dienų kontekste jau nėra naujovė. Šios technologijos naudojamos buityje, medicinoje, tekstilės, automobilių ir daugelyje kitų pramonės sričių. Nanotechnologijos yra labai įvairios, pradedant nuo naujų galimybių taikymo įprastiems gaminiams iki visiškai naujų medžiagų kūrimo, kurių dydis būtų nanoskalėje. Tačiau šios technologijos taip pat kelia daug klausimų: kaip diegiant naujas technologijas išspręsti nanomedžiagų toksiškumo problemas, koks poveikis aplinkai ir pasaulio ekonomikai.

Elektrinis verpimas yra universalus ir efektyvus gijų formavimo būdas, kurio suformuotos gijos pasižymi puikiomis mechaninėmis savybėmis, dideliu paviršiaus plotu bei dideliu akytumu, ir tai šį audimo būdą padaro plačiai taikomą daugelyje sričių. Elektrinio verpimo procesu galima formuoti gijas iš didelės įvairovės biopolimerų, taip pat iš skirtingų polimerinių mišinių ar netgi mažos molekulinės masės, nelakių medžiagų (Mendes, Stephansen ir Chronakis, 2017).

Polisacharidai kelia didelį mokslininkų ir įvairių pramonės sričių specialistų susidomėjimą dėl galimybės sintetinius polimerus pakeisti gamtiniais polimerais. Šį susidomėjimą lemia polisacharidų teigiamos savybės, tokios kaip: biologinis skaidumas, biologinis suderinamumas, netoksiškumas bei maža polimerų kaina. Suformuotos gijos su gamtiniais polimerais yra perspektyvios ir dėl plataus pritaikymo spektro, ypač biomedicinos srityje.

Galima teigti, kad iš visų polisacharidų krakmolas yra vienas iš labiausiai paplitusių gamtoje ir yra gana pigus. Gijų formavimui su gamtiniais polimerais elektrinio verpimo būdu didelę įtaką turi jų cheminė struktūra, koncentracija bei klampa (Mendes, Stephansen ir Chronakis, 2017).

2010 m. pradėjus analizuoti ir tirti krakmolo formavimo galimybes naudojant elektrinio verpimo būdą buvo dar labai mažai tyrėjų, atliekančių bandymus su krakmolu ar jo dariniais. Pirmieji žingsniai elektrinio verpimo būdu formuojant gijinį pluoštą iš modifikuoto krakmolo buvo pradėti 2009 m. KTU prof. dr. A. Žemaitaičio ir prof. dr. R. Milašiaus vadovaujamų tyrėjų grupės, tiriant poli(vinilo alkoholio) (PVA) ir katijoninio krakmolo (KOEK) formavimo galimybes (Adomavičiūtė ir kt., 2009). Rezultatai parodė, kad naudojant PVA/KOEK tirpalą, kai masės santykis 75/25, elektrinio verpimo būdu pavyko suformuoti gijinę neaustinę dangą. Toliau buvo tęsiamas tyrimas šia tema ir analizuojamos formuojamos dangos galimybės.

Elektrinio verpimo būdu suformuoti gijinį pluoštą iš gamtinio krakmolo yra sudėtinga. Keletas mokslininkų yra aprašę bandymus, kurių metu buvo formuojamas gijinis pluoštas iš gamtinio krakmolo elektrinio verpimo būdu. Šiam bandymui atlikti reikėjo modifikuoti patį elektrinio verpimo procesą į vadinamąjį šlapiąjį elektrinį verpimą, kurio metu kolektorius yra panardinamas į skystį. Verpimo tirpalas paruošiamas tirpinant 15 % kukurūzų krakmolą 95 % vandeniniame dimetilsulfoksido (DMSO) tirpale. Šis modifikavimas atliekamas siekiant pašalinti tirpiklį ir gauti mikrometro dydžio vienalytį pluoštą (Kong ir Ziegler, 2012; 2013; 2014). Tai buvo pirmieji žingsniai bandant elektrinio verpimo būdu suformuoti gijinę dangą iš gamtinio krakmolo, tačiau gijinės dangos formavimas iš šio polisacharido yra gana sudėtingas.

Siekiant pagerinti krakmolo verpimo galimybes, šis gali būti modifikuojamas, t. y. pakeičiama jo cheminė struktūra, kuri leidžia suformuoti gijinę dangą iš šio polisacharido. Gamtinis krakmolas gali būti modifikuojamas cheminiais ir fizikiniais metodais. Be to, šis polisacharidas gali būti maišomas kartu su sintetiniais polimerais, pagerinančiais gamtinio krakmolo ar jo darinių verplumo galimybes.

Darbo naujumas ir jo reikšmė.

Remiantis įvairiais tyrimų rezultatais, pateiktais literatūros šaltiniuose, pastebėta, kad suformuoti gijas nanodydžio ribose elektrinio verpimo būdu iš gamtinio krakmolo yra labai sudėtinga. Dėl šios priežasties biopolimerai yra modifikuojami ar maišomi su sintetiniais polimerais, dėl kurių pavyksta suformuoti gijinę pluoštinę dangą.

Polimerinių baktericidų, kuriuose molekulinis jodas gali būti prijungiamas prie polimero makromolekulių nekovalentiniais ryšiais, žaliava gali būti sintetiniai ir gamtiniai polimerai. Juose jodas įjungiamas į polimerinę matricą ją apdorojant jodo garais, tirpalais organiniuose tirpikliuose arba vienvalenčio jodo darinių anijonų vandeniniais tirpalais (Bendoraitienė ir kt., 2012). Jodas yra puikus antiseptikas, turintis antimikrobinių savybių ir yra plačiai taikomas gydant žaizdas. Iš krakmolo ar katijoninio krakmolo/jodo mišinių suformuotas gijinis pluoštas gali būti pritaikytas ir naudojamas gydant žaizdas ir tvarsčiuose. Chitozanas (CS), kuris taip pat turi antimikrobinių savybių ir yra naudojamas gydant žaizdas, gali būti pakeičiamas krakmolo/jodo mišiniu, toks sprendimas būtų itin ekonomiškai patrauklus, nes CS yra gana brangus polisacharidas. Tačiau gamtinio krakmolo cheminė struktūra yra nepalanki taikant elektrinio verpimo procesą. Siekiant pagerinti šio polisacharido verplumą, jis gali būti maišomas su sintetiniais polimerais, kurie taip pat pasižymi puikiomis savybėmis. PVA yra vienas iš plačiausiai naudojamų sintetinių polimerų, dėl savo teigiamų savybių plačiai taikomas farmacijos, biomedicinos srityse. Bet vienas iš svarbiausių šio sintetinio polimero privalumų yra gana žema kaina. Ekonomiškai palanki kaina yra vienas pagrindinių privalumų taikant PVA/krakmolo ar PVA/katijoninio krakmolo mišinius.

Disertacijos tyrimų objektu, kaip vienas iš mišinio komponentų, buvo pasirinktas krakmolas – gamtinis polisacharidas. Šis gamtinis polimeras buvo modifikuotas, gautas vandenyje tirpus polimeras ir taip pagerintos jo formavimo galimybės taikant elektrinio verpimo būdą. Literatūros šaltiniuose nėra duomenų, kad elektrinio verpimo būdu būtų bandyta formuoti gijinę dangą iš PVA tirpalo su daugiau nei 25 % KOEK. Šioje disertacijoje įrodoma, kad galima suformuoti gijas iš PVA tirpalo su 50 % ir 65 % KOEK. Analizuojant literatūros šaltinius nebuvo rasta tyrimų, kurių metu gijos būtų formuojamos iš PVA tirpalų su daugiau nei 25 % krakmolo ar jo darinių naudojant elektrinio verpimo įrenginį su besisukančiu elektrodu. Visi bandymai formuoti gijinį pluoštą su krakmolu ar jo dariniu buvo atlikti naudojant purkštukinį elektrinio verpimo metodą ar šį metodą modifikuojant į vadinamąjį šlapiąjį elektrinį verpimą. Šiame darbe gijos buvo formuojamos su besisukančiu elektrodu, taip pat analizuojama ir skirtingų sukamųjų elektrodų įtaka formuojamai gijinei dangai.

IŠVADOS

1. Elektrinio verpimo būdu pavyko suformuoti gijas iš 7 % poli(vinilo alkoholio) ir bulvių krakmolo mišinių. Krakmolas poli(vinilo alkoholio) tirpale neigiamai veikia elektrinio verpimo procesą. Dėl per didelės tirpalo klampos elektrinio verpimo procesas, kai buvo 5 % krakmolo poli(vinilo alkoholio) tirpale, nebuvo įmanomas. Tačiau 7 % poli(vinilo alkoholio) tirpalas su 5 % krakmolo ir 5 % etanolio buvo tinkamas suformuoti gijas elektrinio verpimo būdu. Krakmolas turėjo įtakos didesniam gijų vidutiniam skersmeniui – naudojant 7 % poli(vinilo alkoholio) tirpalą be krakmolo, gijų vidutinis skersmuo buvo 260 nm, o su 1 % krakmolo – 310 nm, t. y. padidėjo 16 %.
2. Etanolis turėjo neigiamos įtakos iš 8 % poli(vinilo alkoholio) tirpalo formuojamų gijų morfologijai ir struktūrai – didinant etanolio kiekį, gautas didesnis verpimo tirpalo dėmių kiekis ant gijinės dangos.

3. Nustatyta, kad gijinė danga susiformavo su mažesniu kiekiu verpimo tirpalo dėmių, esant net ir mažam krakmolo kiekiui poli(vinilo alkoholio) tirpale. Be verpimo tirpalo dėmių gijinė danga susiformavo, kai poli(vinilo alkoholio) tirpale buvo 5 % krakmolo ir 5 % etanolio, tačiau buvo gauta retesnės gijinė danga ant pagrindo medžiagos.

4. Nustatyta, kad tinkamiausia poli(vinilo alkoholio) ir katijoninio krakmolo tirpalo koncentracija, kai masės santykis 75/25, yra 8 %. Nustatyta, kad didėjant koncentracijai, vidutinis gijų skersmuo didėjo. Su 12 % koncentracijos verpimo tirpalu suformuotų gijų vidutinis skersmuo padidėjo 23 %.

5. Nustatyta, kad elektrinio verpimo sukamojo elektrodo tipas turėjo įtakos iš poli(vinilo alkoholio) ir katijoninio krakmolo tirpalo suformuotų gijų skersmeniui, kai masės santykis buvo 75/25. Nustatyta, kad 12 % poli(vinilo alkoholio) ir katijoninio krakmolo tirpalo su lygiuoju elektrodu suformuotų gijų vidutinis skersmuo – 310 nm, o tokios pačios koncentracijos ir kompozicijos tirpalo, panaudojus elektrodą su adatėlėmis, vidutinis gijų skersmuo buvo 280 nm, t. y. 10 % plonesnės.

6. Elektrodas su adatėlėmis turėjo įtakos elektrinio verpimo procesui, tačiau ji buvo nereikšminga. Su šiuo elektrodu buvo galima suformuoti gijinę dangą esant žemesnei (35 kV) elektrinio verpimo įtampai. Rezultatai parodė, kad elektrinio verpimo sukamojo elektrodo tipas neturėjo įtakos suformuotų gijų skaičiui. Naudojant lygųjį elektrodą daugiausia gijų susiformavo, kai poli(vinilo alkoholio) ir katijoninio krakmolo tirpalo koncentracija buvo 10 % (119 gijų), o su elektrodu, turinčiu adatėles, daugiausia gijų suformuota, kai poli(vinilo alkoholio) ir katijoninio krakmolo tirpalo koncentracija buvo 12 % (91 gija).

7. Nustatyta, kad didėjant etanolio kiekiui 8 % poli(vinilo alkoholio) ir katijoninio krakmolo tirpale, kai masės santykis 75/25, elektrinio verpimo būdu pavyko suformuoti gijas esant žemesnei elektrinei įtampai (30 kV). Gijinė danga susiformavo tankesnė (128 gijos), kai etanolio kiekis poli(vinilo alkoholio) ir katijoninio krakmolo tirpale siekė 3 %, tačiau didėjant etanolio kiekiui iki 9 %, suformuotų gijų skaičius mažėjo (63 gijos). Taip pat pastebėta, kad didėjant etanolio kiekiui poli(vinilo alkoholio) ir katijoninio krakmolo tirpale pasitaiko daugiau gijų, sulipusių tarpusavyje.

8. Įrodyta, kad elektrinio verpimo būdu pavyko suformuoti gijas iš 12 % poli(vinilo alkoholio) ir katijoninio krakmolo mišinių, kai masės santykis buvo 50/50 ir 35/65. Rezultatai parodė, kad tinkamiausias katijoninio krakmolo kiekis poli(vinilo alkoholio) tirpale yra 50/50, nes ant neaustinės medžiagos susiformavo mažesnio skersmens gijos. Skersmens skirstiniai įrodė, kad nėra didesnių skersmens gijų nei 500 nm. SEM nuotraukos patvirtino, kad, esant katijoninio krakmolo kiekiui 65 % poli(vinilo alkoholio) tirpale, nemažai gijų susiformavo sulipusios tarpusavyje, o tai vertinama kaip tolesniam gijinės struktūros panaudojimui kenkiantis reiškinys.

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