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Influence of Glycerin Adding on the Electrospun Nanofibers Diameter

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Abstract. The aim of this work was to determine the effect of adding glycerin to an aqueous solution of polyvinyl alcohol on the diameter of electrospun nanofibers. Glycerin is chosen as functional additive for webs producing for medical and cosmetic purposes. The influence of the glycerol content on the properties of spinning solutions was determined. It was found that most of the fibers in the webs obtained from solutions containing glycerin have a core-shell structure. In these fibers the core layer is formed from PVA and the outer layer is from glycerin. The fiber diameter in electroformed materials depends on the components content. A formula has been proposed that describes the diameter depending on the consumption of the spinning solution without the addition of glycerin and with glycerin content of up to 7%.

INTRODUCTION

Electrospinning is a versatile and efficient method to produce continuous nanofibers from submicron diameters down to nanometer diameters by using a high potential electric field. It has been a process of great scientific and industrial interest due to its versatility, cost efficiency and potential to be used in a wide range of applications, resulting in an outstanding potential for nanotechnology research [1].

Currently, a huge amount of research is being carried out on the creation of micro- and nanofibers for various applications, including for the needs of biomedicine and cosmetology [2].

Electrospinning can be used to obtain vascular grafts. The clinical need for vascular grafts is associated with cardiovascular diseases frequently leading to fatal outcomes. Artificial electrospun vessels based on bioresorbable polymers can replace the damaged vascular tissue or create a bypass path for blood flow while stimulating regeneration of a blood vessel in situ [3]. Nonfunctionalized nanofiber films from natural or synthetic polymers are extensively used, electrospun materials combined with peptides are gaining more interest. In fact, the selection of specific peptides improves the performance of the material for biological applications and mainly for tissue engineering, mostly by maintaining similar mechanical properties with respect to the simple polymer [4].

There is an increasing interest for works dedicated to the creation drug delivery systems. Nanofibers based transdermal drug delivery is a promising platform, and it effectively delivers the drug to tumor sites. For example, the paper [5] describes the fabrication of stimuli-responsive polymeric nanofibers encapsulated with an active targeting micellar system for in situ drug delivery. Stimuli-responsive core–shell nanofibers release the drug at target sites with minimum side effects to the other organs, decrease the drug administration concentration.

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Electrospun bioactive nanofibers have great potential as promising reinforcement fillers for next generation bone tissue engineering application. Electrospun nanofibrous membrane can be prepared from blend of poly(vinyl) alcohol, nanohydroxyapatite using fish bone, collagen type I from fish bone, and graphene oxide by electrospinning for their prospective application in bone regeneration [6]. Fibrous polymeric scaffold which comprise capabilities of biomimicry to the native tissue architecture are promising for achieving functional tissue-engineered products with minimal surgical implantation. Fibrous electrospun scaffolds can be obtained of biodegradable microbial poly(-hydroxybutyrate) produced from a mutant Azotobacter vinelandii strain. Such scaffolds are also suitable for bone tissue engineering supporting adhesion and proliferation of normal human osteoblast cells and cab be used in bone tissue repair involving bone defects and guided bone regeneration [7].

Tissue engineering is an interdisciplinary field that integrates medical, biological, and engineering expertise to restore or regenerate the functionality of healthy tissues and organs. The three fundamental pillars of tissue engineering are scaffolds, cells, and biomolecules. Electrospun nanofibers have been successfully used as scaffolds for a variety of tissue engineering applications because they are biomimetic of the natural, fibrous extracellular matrix and contain a three-dimensional network of interconnected pores [8].

In order to overcome the shortcoming associated with traditional administration routes such as including injection, oral and nasal route, many researchers have been focusing their attention on long-acting biomedical implants, which have gained great interest within the scientific community in the last decade. These are usually intended to replace the functions of a specific organ by slowly releasing the medication, to replace the organ itself, or simply monitor body functions. In this regard, the availability of new manufacturing approaches and novel biocompatible materials have positively contributed to design innovative personalised and targeted drug delivery systems [9, 10, 11].

Biomedicine needs materials with precisely designed characteristics that will meet the specified qualities, give the necessary therapeutic effect and reduce the toxic load on the patient's body. This will be possible when the understanding of the interaction of the fiber-forming polymer with the active component is complete, and the characteristics and quality of the material are controlled. In this regard, studies devoted to an in-depth study of both the processes of electrospinning and the fibers obtained by this method (including their properties, morphology, structure, etc.) are of great relevance.

Among biomedical materials, heterogeneous electrospun materials are of particular interest to researchers. The structure of an inhomogeneous material produced with active substances allows slow and gradual release of them, which ensures good absorption and allows you to accurately calculate the dosage of the substances used. Currently, researchers are looking for such therapeutic agents that will allow using the targeted delivery mechanism to reduce the number of side effects for organs, as well as make therapy intensive and more effective due to the direct delivery of the drug to the organ. All target systems, materials, substances and coatings aimed at drug delivery consist of excipients and target particles - micro- or nanoparticles or fibers responsible for the direct transfer of the drug. When creating a material with a drug delivery system, it is necessary to pay great attention to its structure, which largely determines the duration and / or sequence of exposure to various active substances included in it. It is urgent to solve the problem of obtaining an electrospun inhomogeneous material with a pre-predicted structure.

For biomedicine, the design of the properties of a nanofiber material is a major issue. This is due to the fact that the material must meet strict requirements for the composition, time and type of biodegradation, its conditions, etc., which depend on the morphology and structure of its nanofibers. Since the diameter of a nanofiber is a random variable, an important issue is to estimate the law of its distribution, both for comprehensive statistical processing of experimental data and for analyzing the electrospinning process.

One of the prospective areas of electrospinning method application is the development of new materials for cosmetology and regenerative medicine. For this purpose as an additive to the spinning solution can be chosen hyaluronic acid (HA) which has many benefits and is one of the most significant ingredients in skin care [12]. HA is proven to be beneficial in the wound healing process.

Thus, the choice of the additive to the spinning solution is based on the purpose of the manufacturing material taking into account its compatibility with the fiber-forming polymer and the absence of difficulties when using such solutions in the electrospinning process.

The aim of this work was to determine the effect of adding glycerin to an aqueous solution of polyvinyl alcohol on the diameter of electrospun nanofibers.

MATERIAL AND METHODS

One of the most common polymers used for producing biomedical materials by electrospinning technology is polyvinyl alcohol (PVA). Its widespread use is due to its relatively low cost and unique properties [13]. With the use of PVA it is possible to create concentrated solutions with various medicinal substances to obtain effective therapeutic agents for internal and external use. Due to its non-toxicity, polyvinyl alcohol is used in medicine as adhesives, plasters, sterile napkins, surgical threads, pharmaceuticals and for the manufacture of plasma replacement solutions. Therefore, in this work, it was decided to use polyvinyl alcohol as a fiber-forming polymer during the research. In particular PVA grade Arkofil PPL gr (Archroma, Switzerland) was selected because this modification showed good results in previous experiments.

As a substance that can be added to the spinning solution to obtain materials for medical or cosmetic use was chosen glycerin. Glycerin is one of the important components in cosmetology and medicine. It is part of many creams, ointments, soaps. Glycerin has a protective function of the skin as it retains moisture in the skin cells. In medicine, it is used as an antiseptic in the complex treatment of many diseases, especially skin diseases (it promotes wound healing, prevents infection and suppuration). The water-absorbing effect leads to dehydration and death of pathogenic bacteria.

For research combinations of two solutions were used:

- 14 % PVA + 86 % water;
- 85 % glycerin + 15 % water.

For the shortening in the paper text instead of a glycerin solution glycerin will be indicated.

The experiments were carried out on the machine Fluidnatek LE-50 (Bionicia, Spain) [14]. Electrospinning is carried out at room temperature with atmosphere condition. A high voltage is applied to create an electrically charged jet of polymer solution or melt. The jet undergoes stretching before it reaches the collector and it solidifies on the collector in the form of nanofibers by the evaporation of the solvent. The process principle involves subjecting a polymer solution held at its own surface tension at the end of a spinning head's needle to an electric field. As the intensity of the electric field is increased, the hemispherical surface of the solution at the tip of the needle elongates and forms a conical shape known as the Taylor cone. The electric field reaches a critical value where the repulsive electric force overcomes the surface tension force. At this critical value, a charged jet of the solution is ejected from the tip of the Taylor cone. The solvent evaporates as the jet travels in air. In the case of the melt, the discharged jet solidifies when it travels in the air. The charged polymer fiber is randomly deposited on a collector [1].

When developing new electrospun materials, researchers put forward a number of requirements for its quality. The following general requirements are imposed on electrospun nanofibers [1]:

a) the diameters of the fibers must be consistent and controllable;
b) the fiber surface must be defect-free or defect-controllable;
c) continuous single nanofibers must be collectable.

To assess the influence of glycerin adding on the electrospun nanofibers diameter scanning electron microscope LEO 1420 (Carl Zeiss, Germany) was used.

RESULTS AND DISCUSSION

On the first stage of research it is necessary to determine influence of glycerin percentage on the spinning solution properties. The most important technological properties of investigated spinning solutions are presented in Table 1. It can be noted that the dynamic viscosity of the solutions is characterized by strong correlation with their surface tension ($r = 0.962$) and electrical conductivity ($r = -0.987$).

The publications state [8, 15] that polymer solutions with a concentration of up to 20% with a dynamic viscosity of 0.05 to 1 Pa·s are usually used in the process of electrospinning. However, for some low molecular weight polymers, higher concentrations and viscosities are possible. Table 1 shows that 14% PVA solution and its combinations with glycerin solution in terms of viscosity, are outside the upper limit of the theoretically recommended range, and with an rise in the content of glycerin, the viscosity of the spinning solution of the polymer increases and the dependence is not linear character.

TABLE 1. Properties of spinning solutions

Solution number	Composition	Dynamic viscosity, Pa·s	Surface tension, N / m	Electrical conductivity, mS/m	Evaporation rate in 30 min, g/m^2
1	PVA solution (14 %)	2,603	0,0626	0,497	0,0060
2	96 % PVA solution (14 %) + 4 % glycerin solution (85 %)	2,639	0,0618	0,483	0,0040
3	96 % PVA solution (14 %) + 7 % glycerin solution (85 %)	3,002	0,0621	0,475	0,0035
4	96 % PVA solution (14 %) + 10 % glycerin solution (85 %)	4,345	0,0676	0,424	0,0020

As a result of statistical processing of experimental data the following dependence of the dynamic viscosity (Pa·s) on the percentage of the glycerin (β) in the spinning solution was obtained ($R^2 = 0.999$):

$$\eta = 2,6 + \left(\frac{\beta}{8.7}\right)^4. \quad (1)$$

Analyzing the obtained dependence, it can be noted that a significant increase in the dynamic viscosity of the solution occurs when the content of the glycerol solution in it exceeds 8.7%. Due to the high correlation between the viscosity of solutions and their other properties the effect of the glycerol content on them is similar.

Figure 1 shows SEM images of samples of electrospun webs manufactured from different spinning solution with consumption 1,3 ml/h. Analyzing presented image of samples of electrospun web obtained from solutions containing 10% glycerin it can be noted that glycerin does not actually form individual fibers but envelops the fibers formed from PVA. This is especially evident in those areas where individual fibers intersect. Some sections of PVA fibers are not covered with glycerin as evidenced by the fact that in diameter and appearance they correspond to the fibers of the sample produced from a pure PVA solution. Thus, it can be argued that the resulting fibrous webs consist of fibers, most of which have a core-shell structure. In such fibers the core layer is obtained from PVA and the outer layer is from glycerin. It can also be noted that with a high content of glycerin in the solution, a significant proportion of this component is located between the fibers.

In webs from solutions containing 4 % and 7 % glycerin this component is found in the fiber structure. The revealed qualitative difference in the structure of materials can be explained by the fact that, according to formula (1) when the glycerin content is exceeded 8.7 %, the properties of solutions significantly change which is reflected in the nature of the electrospinning process.

So, the next research will be carried out for spinning solutions with glycerin contend not exceeding 7 % (solutions 1, 2, 3 in the Table 1).

The next stage of research was to establish the effect of the glycerin content in the spinning solution and the consumption of this solution on the characteristics of the electrospun fibers.

Samples of webs were obtained from each studied solution at different flow rates (1.0, 1.3, 1.6 mL/h). For each manufactured sample the diameters of 100 fibers were measured. Figure 2 presents several histograms of the fiber diameter distribution which were obtained on the basis of the experimental data. Data analysis shows lognormal distribution of the fibers diameters for all the electrospun web samples.

According to the theory developed by Kolmogorov, when crushing materials at a constant speed, a lognormal distribution of the resulting particles is achieved [16]. With regard to the electrospinning process, it can be argued that the splitting of the spinning dope jets can be considered stable if the lognormal distribution of the fiber diameters in the materials obtained is proved.

Table 2 shows the mean values of the fiber diameters in the web samples and the coefficients of their variation.

Taking into account that the average fiber diameter in the obtained samples is 160 - 200 nm the question arises whether these materials can be attributed to nanostructured objects. According to ISO/TS 80004-1:2015 “Nanotechnologies — Vocabulary — Part 1: Core terms” nanoscale is length range approximately from 1 nm to 100 nm. However, the length range of nano-objects might fall outside the precise boundaries normally associated with the concept of scale, by indicating that the upper and lower boundaries are approximate. It is more important that the region is defined by a boundary representing a discontinuity in properties.

The literature also notes that nanofibers can be considered fibers with a diameter of <500 nm, meaning the practical application of any scientific developments [15]. Consequently, nano-objects in some cases can be considered as objects, the sizes of which go beyond the established limits of the nano-range, if the materials from them have nanoscale effects or properties.

TABLE 2. Parameters of fibers in electrospun webs

Glycerin content in spinning solution, %	Spinning solution consumption , mL/h	Fiber diameter, nm	Coefficient of fiber diameter variation, %
0	1,0	161,78	29,12
0	1,3	170,18	21,86
0	1,6	178,29	23,18
4	1,0	202,41	16,90
4	1,3	186,63	24,09
4	1,6	187,30	28,15
7	1,0	194,71	24,92
7	1,3	183,32	23,32
7	1,6	180,79	24,47

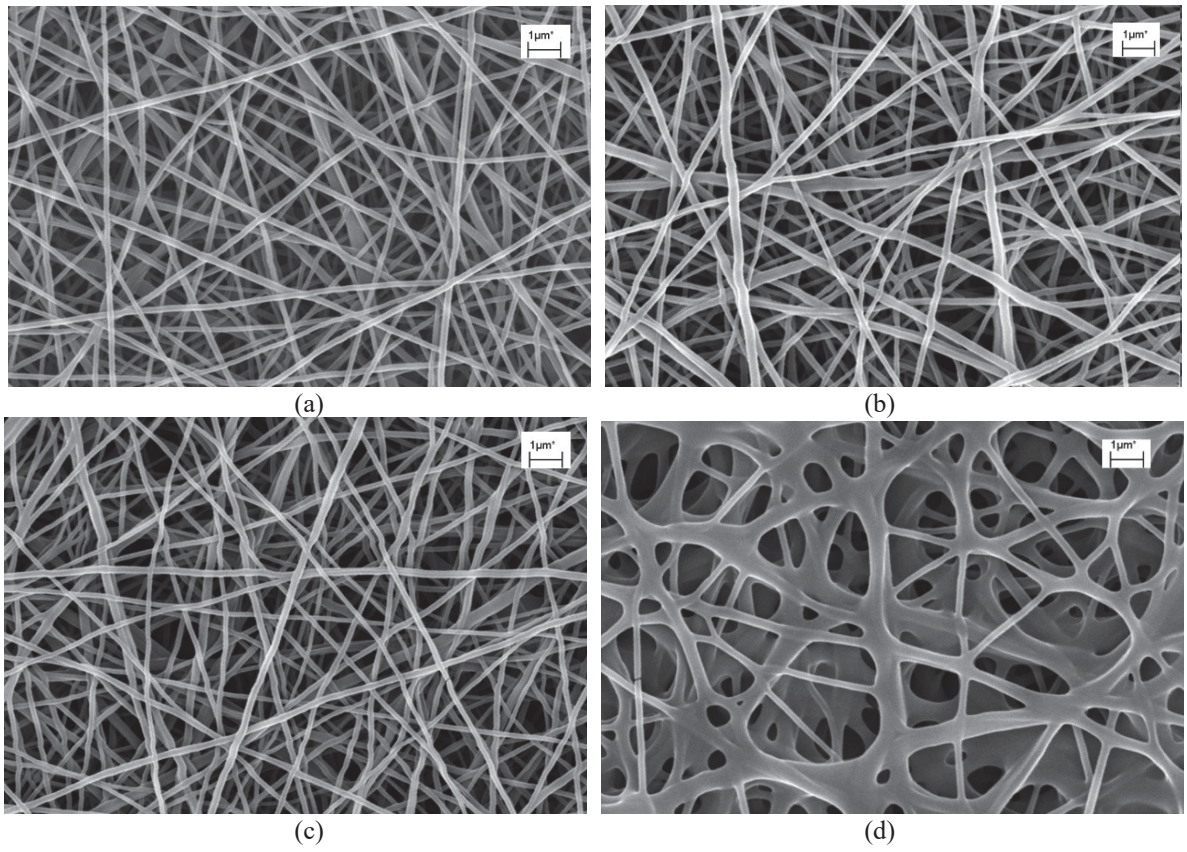

FIGURE 1. SEM Images (15 000x) of electrospun webs obtained from different solutions:
(a) without glycerin, (b) 4 % glycerin, (c) 7 % glycerin, (d) 10 % glycerin

Electrospun webs obtained from PVA differ significantly in properties from materials of a similar composition, the sizes of which are within the micro and macro ranges. The main nanoscale effect, achieved by reducing the thickness of the fibers is the significant increasing the materials solubility in comparison with the original granulate. The datasheet states that Arkofil PPL granulate is only sparingly soluble in water at room temperature. The product slowly dissolves in warm water to form a slightly yellowish, opaque, cloudy solution. Analysis of the granulate showed that the size of the granules varied from 0.5 to 1.6 mm and averaged 1 mm.

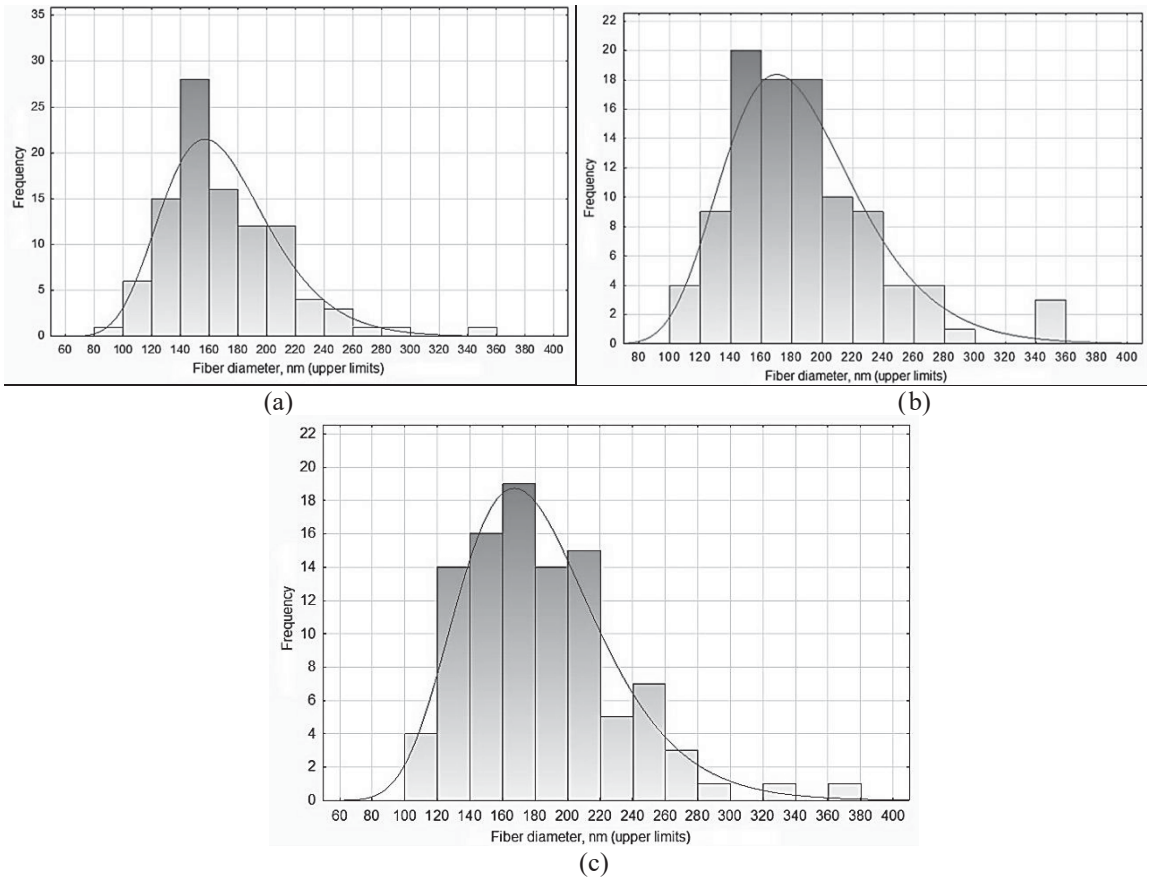

FIGURE 2. Distribution of fibers diameters in webs obtained with solution consumption 1,3 mL/h from different solutions: (a) without glycerin, (b) 4 % glycerin, (c) 7 % glycerin

At the same time, it has been experimentally determined that electrospun webs from this granulate dissolve in water at room temperature almost instantly, which ensures the effectiveness of their use in various fields, for example, in cosmetology. Thus, the resulting materials can be characterized as nanostructured or consisting of nanofibers. Figure 3 illustrated influence of solution consumption on mean value of fibers diameter.

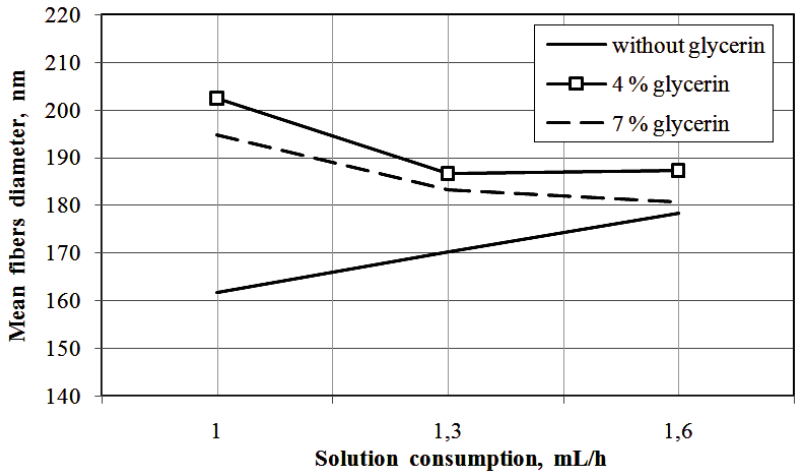

FIGURE 3. Influence of solution consumption on mean value of fibers diameter

Analyzing the obtained dependences it can be noted that, for solutions of different compositions, the effect of the electrospinning modes on the fiber diameter is significantly different.

Thus, with an increase of the consumption of PVA solution without glycerin the fiber diameter rises linearly. The opposite trend is observed for solutions containing glycerin. Obtained results can be explained as follows. Obviously, a greater consumption of the spinning solutions of constant composition is achieved by increasing the voltage of the electrostatic field in the electrospinning zone.

The effect of the voltage on the electrospun PVA web morphology and fibers diameter distribution have been extensively studied. It has been found that at higher voltages increases the volumetric flow of the polymer that provides the formation of a larger diameter fiber [17]. The same pattern was found in the study described in this paper. However, the addition of glycerin leads to the fact that with an increase in the consumption of the solution, the fiber diameter reduces. A hypothesis is proposed that since the increase in flow rate is caused by the voltage rise the electrostatic forces acting on the solution jet also increase. As a result, the glycerin component of the jet is thinned in the space between the emitter and collector to a greater extent than at the minimum solution flow rate.

To predict the heterogeneous fiber diameter is necessary to find the analytical model describing the dependence of the diameter on the flow rate and composition of the spinning solution containing PVA and glycerin.

Based on the statistical processing of the experimental data, the following model was obtained fiber diameter calculation depending on the consumption of the spinning solution of PVA without the glycerin adding:

$$d = 138 + 24 \cdot Q \tag{2}$$

were, Q – consumption of spinning solution, mL/h.

The addition of glycerin to the spinning solution increases the fiber diameter by an amount that also depends on the flow rate. The rise of diameter Δd can be calculated using the following formula:

$$\Delta d = 1\frac{270}{Q^3} \cdot \frac{\beta}{12 + \beta^2} \tag{3}$$

were, β – glycerin contain in spinning solution, %.

Thus, the model describing the influence of the consumption of the spinning solution and the glycerin content on the fibers diameter will look like this:

$$D = d + \Delta d = 138 + 24 \cdot Q + \frac{270}{Q^3} \cdot \frac{\beta}{12 + \beta^2}. \tag{4}$$

The Figure 4 shows that for experimental samples of nanofibrous webs observed and predicted values of fiber diameter are practically identical. The deviation of the calculated values of the diameter of nanofibers from the actual ones does not exceed 2.5%.

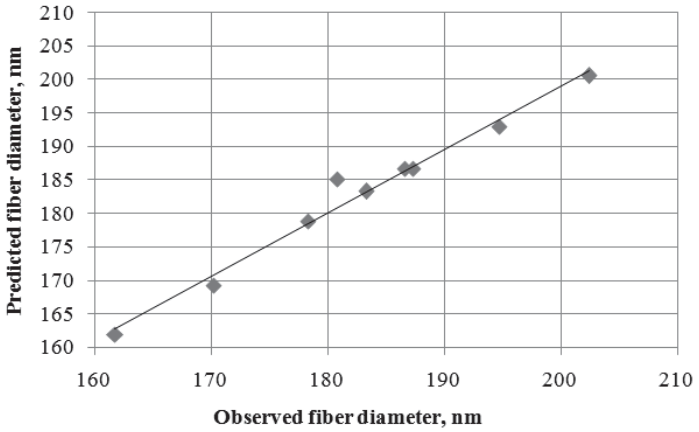

FIGURE 4. Comparison of results of fiber diameter measuring and calculation using formula (4)

The coincidence of the calculated and experimental data confirms that the obtained formula can be used to predict the nanofibers diameter from solutions of PVA with glycerin in the studied range of their percentage.

CONCLUSIONS

To produce materials for medical and cosmetic purposes from polyvinyl alcohol it is proposed to apply glycerin into the solution as a functional additive.

With an increase of the glycerin content in the solution of more than 8.7% its properties change significantly which leads to in the electrospun web structure modification.

Most of the fibers in the webs obtained from solutions containing glycerin have a core-shell structure. In these fibers the core layer is formed from PVA and the outer layer is from glycerin. The fiber diameter in electroformed materials depends on the components content.

Data analysis shows lognormal distribution of the fibers diameters for all the electrospun web samples obtained from different spinning solutions and with varied their consumption.

For solutions of different compositions the effect of electrospinning process modes on the fibers diameter is significantly different. In this regard a formula has been proposed that describes the diameter depending on the consumption of the spinning solution without the addition of glycerin and with glycerin content of up to 7%.

The coincidence of the calculated and experimental data confirms that the obtained formula can be used to predict the nanofibers diameter from solutions of PVA with glycerin in the studied range of their percentage.

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