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# Formation of PVA Nanofibres with Iodine by Electrospinning

**Abstract**
*The area of technical textile applications is very wide, with one of the most important being medical textiles. Polymer-iodine complexes (i.e. iodophors) are widely used in antiseptic products. Nanofibers with iodine may be used to disinfect skin in medicine, and iodine is also characterised by a fungicidal effect. The aim of this research was to form an electrospun PVA mat from nanofibers with iodine and establish the influence of iodine dissolved in ethanol on the structure of electrospun mats. The results showed that it is possible to form a PVA nonwoven mat with an iodine element inserted by the electrospinning process, which has an influence on the structure of the electrospun nonwoven mat.*

**Key words:** *medical textiles, nanofibres, antiseptics, SEM.*

## Introduction

Electrospinning technology is a very effective method for producing nanofibres. Many works on experimental investigation, mathematical modelling, and instability analysis have been published in the literature of this area [1 - 5]. In the electrospinning process, a strong electrostatic field is applied to a polymer solution. A jet from the polymer solution is formed, and then an electrostatic force overcomes the surface tension (with an increase in the applied voltage) of the polymer droplet. While the polymer jet (nanofibres) is moving towards the grounded electrode, the solvent evaporates and a nonwoven mat is formed.

Electrospinning process appears to be affected by the following parameters and variables: 1) system parameters such as the molecular weight, molecular weight distribution and architecture (branched, linear, etc.) of the polymer, and polymer solution properties (viscosity, electrical conductivity, dielectric constant, and surface tension, charge carried by the spinning jet) and 2) process parameters such as the applied voltage, flow rate, the distance between two electrodes, ambient parameters (temperature, humidity and air velocity in the chamber) and finally the motion of the target screen (of the grounded electrode) [4, 6, 7]. Polymer nanofibers have a diameter in the order of a few nanometers to over 1 micrometer (more typically 50 ~ 500 nm) and possess unique characteristics, such as an extraordinarily high surface area per unit mass coupled with remarkably high porosity, excellent structural mechanical properties, high axial strength combined with extreme flexibility, low basic weight, and cost effectiveness, among others [7]. Due to these characteristics, electrospun nonwoven mats have potential applications in such areas as filters, sensor devices, electrical conductors, protective cloths, composites and for medical purposes - wound dressing, tissue engineering, vascular grafts, and drug delivery systems.

A drug-containing electrospun fiber mat is a promising controlled release formulation for future biomedical applications. The resulting mat from nanofibres containing drugs can be applied topically for skin and wound healing, or post-processed for other kinds of drug release [8, 9].

Kenaway with coauthors [10] described a method of preparing a drug delivery system of electrospun nanofibers from poly(ethylene-co-vinyl acetate) (PEVA), poly(lactic acid) (PLA) and their 50:50 blend. In this study, a tetracycline hydrochloride drug for the treatment of periodontal disease was chosen. During the study, it was stated that electrospun PEVA shows a higher release rate than mats derived from 50:50 PLA/PEVA or pure PLA. Also the release of drugs from cast films and electrospun mats were compared. In general, the total percentage released from the cast films was lower than that of the electrospun mats, due to the much lower surface area of the former [10].

The influence of the solubility and compatibility of drugs in the drug/polymer/solvent system on the encapsulation of the drug inside the poly(L-lactide) (PLLA) electrospun fibers and the release behaviour of this formulation were examined using paclitaxel, doxorubicin hydrochloride and doxorubicin base as a model drug in the study by Zeng and coauthors [8].

Gelatin/PVA bicomponent nanofibers were prepared by electrospinning, and its control release of Raspberry ketone(RK) was investigated. A significant diameter increase, tensile strength and elongation at break improvement were observed as the ratio of PVA increased. The burst release of the drug was observed in the first hour, reaching a plateau after two hours [11].

The successful incorporation and sustained release of a hydrophilic antibiotic drug (Mefoxin®, cefoxitin sodium) from electrospun poly(lactide-co-glycolide) (PLGA)-based nanofibrous scaffolds without the loss of structure and bioactivity was demonstrated in the study by Kim and coauthors [12]. The drug was successfully incorporated and released from poly(lactide-co-glycolide) (PLGA) and poly(lactide) (PLA) nanofibres. The morphology and density of the electrospun scaffolds were found to be dependent on the concentration of drug added, which could be attributed to the salt effect during electrospinning [12].

Kenawy and et. al. [13] studied the release of ketoprofen (a non-steroidal antiflammatory drug) from mats of electrospun polycaprolactone (PCL), polyurethane (PU) and their blends. It was stated that the release rates of PCL, PU and their blends are almost similar. Only the blend of PCL with PU improved the visual mechanical properties.

Using the coaxial electrospinning set up, a mat was formed from poly(vinil alcohol) (PVA) with lactate dehydrogenase (LDH) (LDH is an enzyme) [14]. A study by Moreno and et. al. [14] established the principles for posterior application in the controlled delivery of the enzyme LDH in the clinical treatment of the LDH deficience disease.

Iodine can be used for wound cleansing and debridement and for the prevention and treatment of infection [15]. In order to prepare electrospun materials suitable for wound dressing, Ignatova and

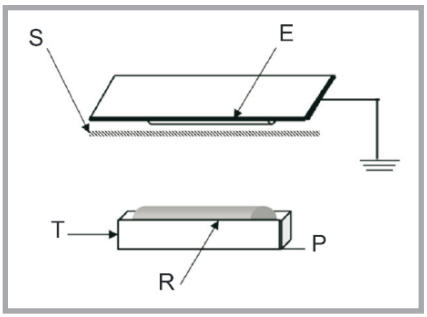


***Figure 1**. Principal scheme of the electrospinning setup – 'NanospiderTM': S - substratum material, E - electrode, T - tray with polymer solution, R – rotating drum, P - power supply polarity 0 - 75 kV.*

co-authors [16] studied the preparation of the poly(vinyl pyrroidone) (PVP)- iodine complex and poly(ethylene oxide) (PEO)/PVP –iodine containning nanofibres.

The aim of this study was to form an electrospun PVA mat from nanofibers with an iodine element and establish the influence of iodine dissolved in ethanol on the structure of electrospun mats. Such mats may be used for medical purposes and bacterial filters.

## Experimental

A PVA polymer solution of 8wt% concentration was prepared by dissolving PVA powder (Carl Roth GmbH + Co. Germany, $M$ = 72,000 g/mol) in distilled water and mixing by a magnetic stirrer for 2 hours at 70 °C temperature.

Elemental iodine (Jodum purum) was added to ethanol (Spiritus aethylicus 96%) and this solution was left for 24 hours to melt.

In the first set of experiments, a 3 wt% concentration of iodine in the ethanol solution was prepared. Before the electrospinning process, different amounts (1, 2, 3 and 4%) of ethanol, based on the 3 wt% iodine solution, were added to water based on 8 wt% PVA solution and stirred for 1 h without heating. ***Table 1*** presents compositions of the solutions prepared.

The aim of this study was also to determine the biggest amount of iodine that may be inserted into PVA solution to form nanofibres. The biggest concentration of iodine in ethanol may be 12 wt% (a bigger amount of iodine in ethanol does not dissolve). In the second set of experiments, a 1% and 2% amount of iodine based ethanol solution was added to 8 wt% PVA solution. In each of the solutions added, the concentration of iodine was increased (3 wt% (in the first set of experiments), 6, 9 and 12 wt%). ***Table 2*** presents the compositions of the solutions used with different concentrations of iodine in the ethanol.

The viscosity of the solutions was measured by a viscometer - DV II+Pro (Brookfield Engineering Laboratories, Inc., US). Nanofibers were produced using electrospinning equipment - *NanospiderTM* (Elmarco Czech Republic). 'NanospiderTM' technology is based on the discovery that it is possible to create a Taylor cone from a thin film of polymer solution on a rotating drum (***Figure 1***) [4, 17].

For visual evaluation, the nonwoven mats produced were analysed using a scanning electron microscope (SEM,) - Quanta 200 (FEI).

For evaluation of nanofibre diameters, the computer image analysis program Lucia 5.0 was used. The diameter of the electrospun nanofibres was measured from SEM images. In this study, the method of measuring the nanofibre diameter was chosen, then every SEM image with a scale of 5 μm and magnification of 20 000× was divided into squares (1000 × 1000 nm) and every fibre from every square measured, i.e the diameter of the same nanofibre may be measured several times (approximately 10 times). Therefore the diameter of the nanofibre may be mostly different across its length and this method is more suitable, than the method in which a diameter of nanofibre is measured only once in a particular SEM image

***Table 1.** Compositions of solutions prepared with different amounts of iodine (3wt%) in ethanol.*

| Samples | Amount of water based 8 wt% PVA solution, % | Amount of ethanol based 3 wt% iodine solution, % | Viscosity, mPa·s |
|---|---|---|---|
| A | 100 | 0 | 405 ± 22 |
| B | 99 | 1 | 417 ± 22 |
| C | 98 | 2 | 472 ± 18 |
| D | 97 | 3 | 485 ± 9 |
| E | 96 | 4 | 501 ± 14 |

***Table 2.** Compositions of solutions prepared with different concentrations of iodine in ethanol.*

| Samples | Amount of water based PVA solution, % | Amount of ethanol based iodine solution, % | Concentration of iodine in ethanol, % | Viscosity, mPa·s |
|---|---|---|---|---|
| B | 99 | 1 | 3 | 417 ± 22 |
| B1 | 99 | | 6 | 429 ± 11 |
| B2 | 99 | | 9 | 440 ± 10 |
| B3 | 99 | | 12 | 445 ± 26 |
| C | 98 | 2 | 3 | 472 ± 18 |
| C1 | 98 | | 6 | 480 ± 25 |
| C2 | 98 | | 9 | 486 ± 9 |
| C3 | 98 | | 12 | 493 ± 5 |

## Results

***Table 1*** presents data of the viscosity of the solutions, where the amount of iodine (3 wt%) based ethanol solution is increased (to 4%) in the PVA solution. From the data presented in ***Table 1***, we can notice that with an increase the iodine (3 wt%) in the ethanol, the solution viscosity of the biocomponent solution (PVA with iodine/ethanol) slightly increases from 405 ± 22 mPa·s (A – 100% PVA solution) to 501 ± 22 mPa·s (E solution - 96% PVA solution with a 4% amount of ethanol based 3 wt% iodine solution).

***Figure 2*** presents SEM images of electrospun mats with differ amounts of ethanol based (3 wt%) iodine solution. From the images presented it is possible to notice that increasing the amount of iodine/ethanol in the PVA solution does not have a significant influence on the structure of electrospun mats. It is only possible to notice the tendency that an increase in the amount of iodine/ethanol in the PVA solution leads to more spots formed on the electrospun mat, due to the slightly higher (to 17%) viscosity of the solution.

The forming of nanofibres from E solution (***Table 1***) by the electrospinning process was not possible. In this study, the biggest amount of iodine (3 wt%) / ethanol in the PVA solution is 3%, whereby it is possible to form nanofibres.

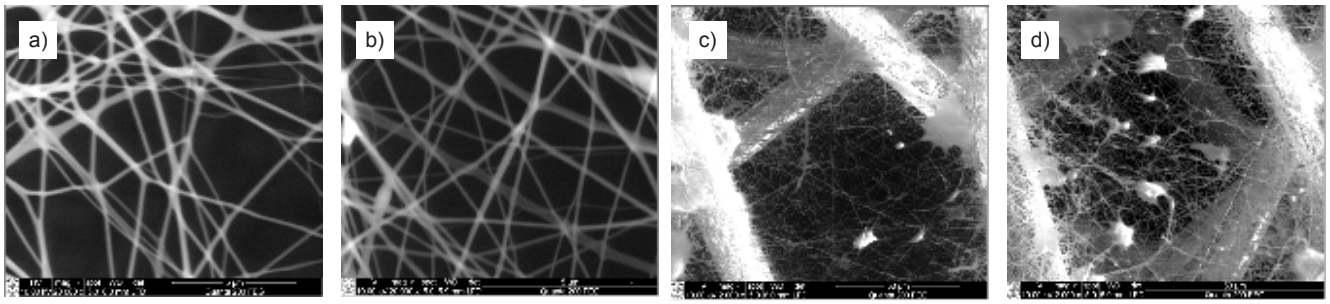


***Figure 2.*** *SEM images of electrospun nonwoven mats: a, c - from 100% PVA solution (A); b, d – 97% PVA with 3% amount of ethanol based 3wt% iodine solution (D). a, b - scale of SEM images 5 µm; c, d -50 µm.*

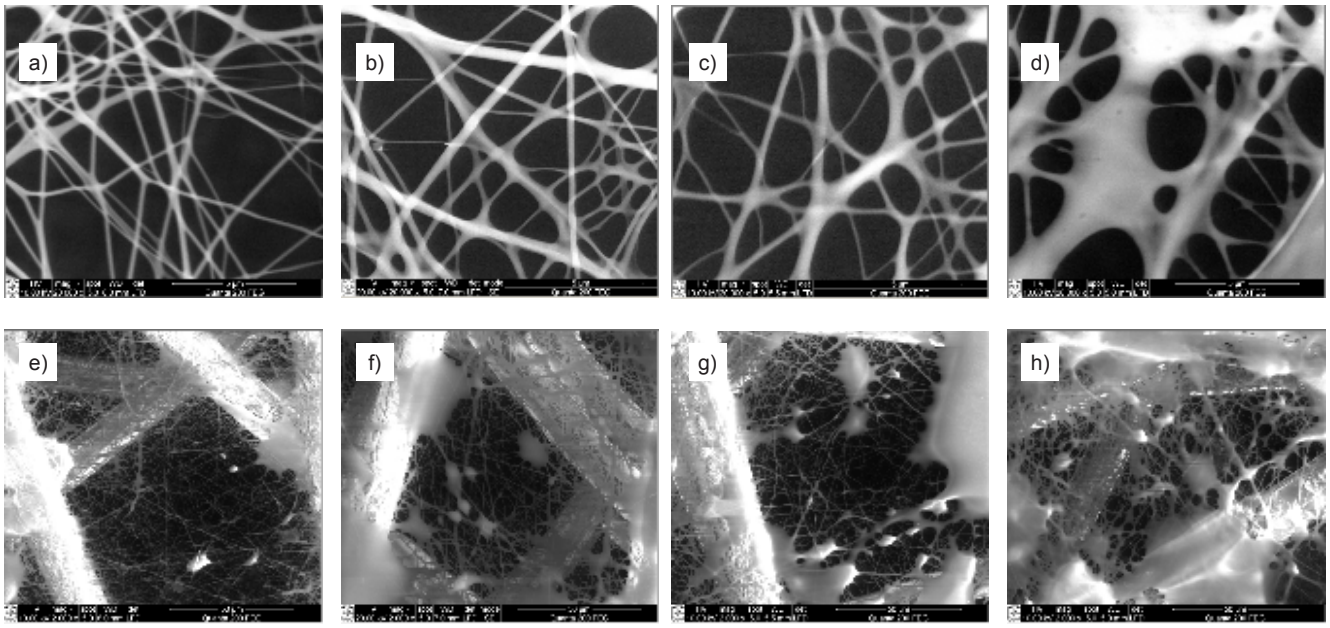


***Figure 3.*** *SEM images of electrospun nonwoven mats: a, e) A - 100% PVA solution; b, f) B - 99% PVA with 1% of amount iodine based 3 wt% solution; c, g) B2 – 99% PVA with 1% amount of iodine based 9 wt% solution; d, h) B3 - 99% PVA with 1% of amount iodine based 12 wt% solution. From solutions A, B, B1 and B2 nonwoven mats were electrospun from nanofibres, from solution B3 porous films were electrospun with a lot of spots and stick nanofibres. a - d - scale of SEM images 5 µm; e - h -50 µm.*

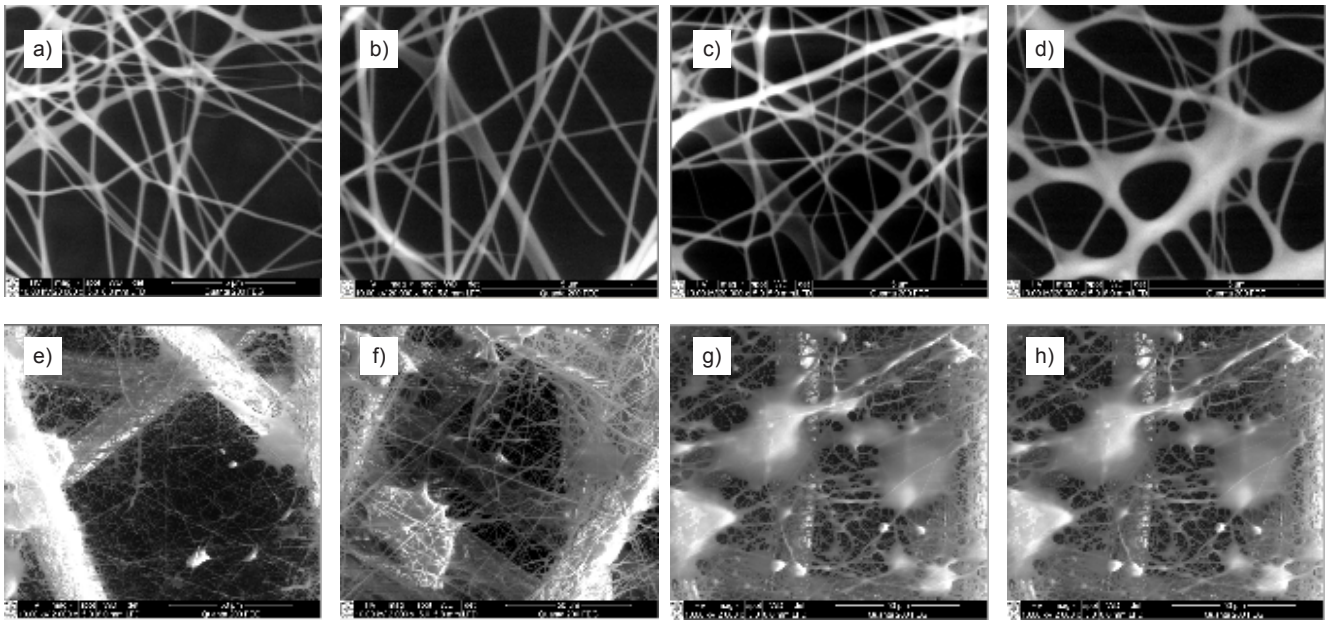


***Figure 4.*** *SEM images of electrospun nonwoven mats: a, e) A - 100% PVA solution; b, f) C - 98% PVA with 2% of amount iodine based 3 wt% solution; c, g) C1 - 98% PVA with 2% of amount iodine based 6 wt% solution; d, h) C3 - 8% PVA with 2% amount of iodine based 12 wt% solution. From solutions A, C and C1 nonwoven mats were elecrtospun from nanofibres, from solution C2 and C3 porous films were electrospun with a lot of spots and stick nanofibres. a - d - scale of SEM images 5 µm; e - h -50 µm.*

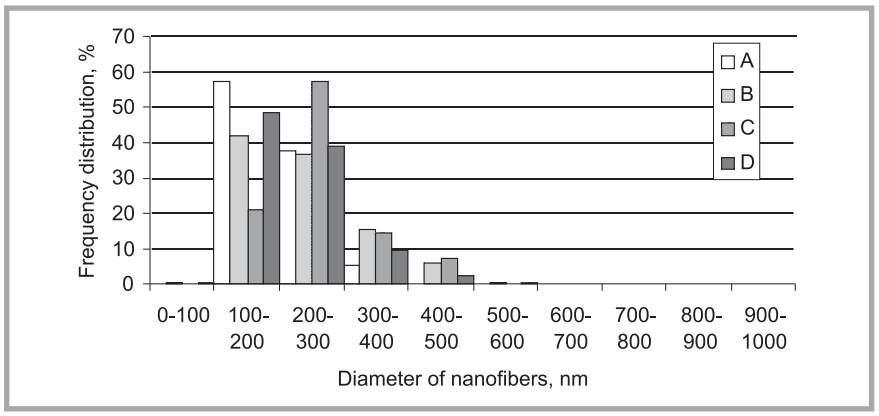


***Figure 5.*** *Frequency distribution of electrospun nanofibre diameter from solutions: A - 100% PVA solution, B - 99% PVA with 1% amount of ethanol based 3 wt% iodine solution, C - 98% PVA with 2% amount of ethanol based 3 wt% iodine solution and D - 97% PVA with 3% amount of ethanol based 3 wt% iodine solution.*

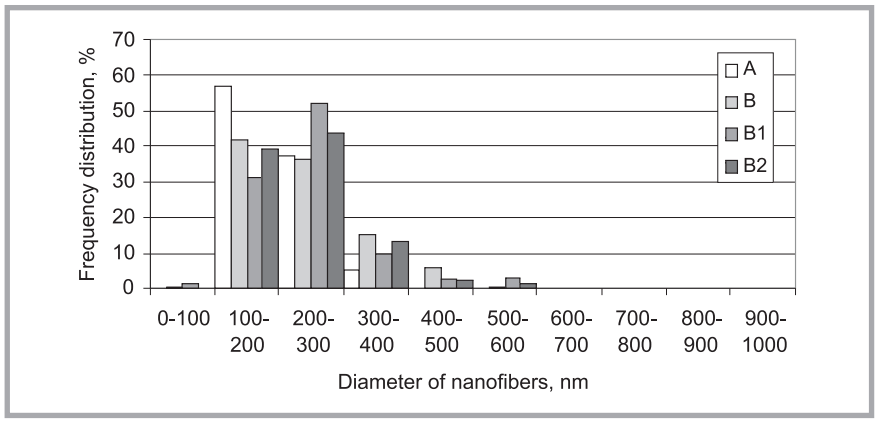


***Figure 6.*** *Frequency distribution of electrospun nanofibre diameter A - 100% PVA solution; B - 99% PVA with 1% amount of ethanol based 3 wt% iodine solution; B1 - 99% PVA with 1% amount of iodine based 6 wt% solution; B2 - 99% PVA with 1% amount of iodine based 9 wt% solution.*

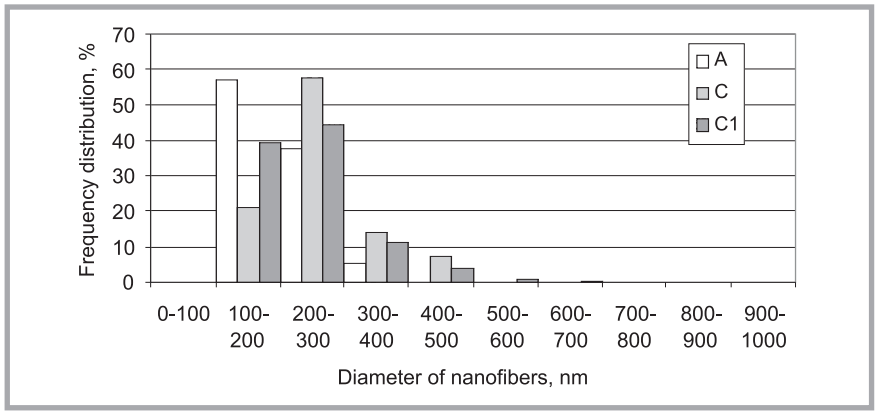


***Figure 7.*** *Frequency distribution of electrospun nanofibre diameter: A - 100% PVA solution; C - 98% PVA with 2% amount of ethanol based 3 wt% iodine solution; C1 - 98% PVA with 2% amount of iodine based 6 wt% solution.*

From the distribution of electrospun nanofibre diameters (see ***Figure 5***), it is possible to notice that slightly thicker nanofibres were formed with an increase in the amount of iodine (3 wt%) /ethanol solution in PVA. From A (pure 8 wt% PVA) solution 95% of nanofibres with a diameter of 100 - 300 nm were measured, from D solution - 87% of nanofibres were measured with a diameter in the range 100 - 300 nm. 5% of nanofibres with a diameter more than 400 nm were measured from solution A, 20% from solutions B and C and 14% from solution D. An increase in the amount of iodine (3 wt%)/ ethanol in the PVA solution causes a slight increase in the viscosity of the solution; therefore more thinner nanofibres were formed from A solution, the viscosity of which is the lowest.

The aim of the second set of experiments was to estimate the influence of the biggest concentration of iodine in the ethanol on the structure of electrospun mats. A 1% and 2% amount of iodine/ethanol solution was added to the 8 wt% PVA solution. In each of the solutions added, the concentration of iodine was increased - 3 wt% (first set of experiments), 6 wt%, 9 wt% and 12 wt% (***Table 2***, see page 22).

***Table 2*** presents data of the viscosity of PVA solution where the concentration of iodine in the ethanol increased. The results presented show that an increase in iodine concentration does not have a significant influence on the viscosity of PVA solution with iodine/ethanol, where the concentration of iodine in the ethanol increases from 3 wt% to 12 wt%, whereas the viscosity of the PVA solution increases by only 7%.

From the SEM images presented in ***Figures 3*** & ***4***, it is possible to notice that an increase in iodine concentration in the ethanol causes a change in the structure of the electrospun mat, whereas an increase in iodine concentration in the ethanol added to the PVA solution does not have a significant influence on the viscosity of the solution (***Table 2***). A porous electrospun film with many spots and stick nanofibres is formed with a 1% amount of iodine (12 wt%)/ethanol (B3) and 2% amount of iodine (9 wt%)/ethanol (C2) added to the PVA solution.

Comparing the distribution of diameters of nanofibres electrospun from PVA solution with differ concentrations of iodine (***Figure 6*** - B, B1 and B2, ***Figure 7*** - C and C1), it is possible to state that the concentration of iodine in the ethanol does not have a significant influence on electrospun nanofibre diameter. 79% of the measured nanofibres electrospun from solution B had a diameter in the range of 100 - 300 nm, and from solution B2 83% had a diameter in the range of 100 - 300 nm. A nonwoven mat with thinner nanofibres (95% of nanofibres measured had a diameter up to 300 nm) is formed from pure PVA solution (A).

## Conclusions

1. It is possible to form PVA nonwoven material with an iodine element inserted by the electrospinning process.

2. The concentration of iodine in the spinning solution has an influence on the structure of electrospun non-woven material. Porous films with a lot of spots and stick nanofibres were electrospun from PVA solutions with a high concentration of iodine (B3,C2 and C3) .
3. A mat with more thicker nanofibres was electrospun from PVA solution with iodine. The addition of iodine in the PVA solution has only a marginal influence on the electrospun nanofibre diameter.
4. In order to electrospun a PVA mat with a higher amount of iodine and fewer defects (spots, stick nanofibres), iodine should be dissolved in a higher amount of ethanol.

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