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Formation of Poly(Vinyl Alcohol)/Cationic Starch Blend Nanofibres via the Electrospinning Technique: The Influence of Different Factors

Abstract

This paper describes the formation of bicomponent nanofibres from poly(vinyl alcohol) (PVA) and modified cationic starch (CS) mixed solutions (PVA/CS mass ratio 3/1) with different total concentrations of solids in water (8, 10 and 12 wt.%) via the electrospinning technique using two types of rotating electrodes (a plain cylindrical electrode and an electrode with tines). The best results were obtained using a PVA/CS solution with a solid concentration of 8 wt.%. The viscosity of 12 wt.% spinning solution was significantly higher compared to that with a concentration of 8 wt.%. These differences in viscosity had a significant influence on the process of electrospinning, as thinner nanofibres were produced from the less viscous solution. In comparison with the cylindrical electrode, the electrode with tines showed a better performance, where the diameter distribution of nanofibres and the electrospinning process were improved. The purpose of the second part of the experiment was to investigate the influence of different amounts of ethanol in the 8 wt.% PVA/CS solution on the electrospinning process and the properties of nanofibres. The results showed that 3 wt.% of ethanol in the spinning solution influenced the diameter of nanofibres in comparison with 9 wt.% of ethanol (the diameter of nanofibres significantly increased in this case).

Key words: electrospinning, nanofibre, PVA, cationic starch.

Introduction

Electrospinning techniques enable the production of continuous fibres with dimensions on the scale of nanometers from a wide range of natural and synthetic polymers. One major attractive feature of electrospinning is the simplicity and inexpensive nature of the setup. This nanofibre formation method, based on natural polymers, has recently emerged as having enormous possibilities for better utilisation of bio-based materials. Also, electrospinning has recently gained popularity with the tissue engineering community as a potential means of producing scaffolds [1 - 6].

From the previous description of the theory, it is clear that the electrospinning process can be manipulated by a number of variables. Solution parameters include the viscosity, electrical conductivity, surface tension, polymer molecular weight, dipole moment, and dielectric constant. Controlled variables include the flow rate, electric field strength, distance between the electrode and collector, needle electrode design, and collector composition and geometry. Ambient parameters include temperature, humidity, and air velocity [2, 7].

Solution viscosity (as controlled by changing the polymer concentration) has been found to be one of the biggest determiners of fibre size and morphology

when spinning polymeric fibres. It has also been found that increasing the solution electrical conductivity or charge density can be used to produce more uniform fibres with fewer beads present [8, 9].

Many publications have reported the fabrication of PVA and natural polymer blend fibres using the electrospinning technique. Because of the hydrophilic nature of PVA, allowing for good compatibility, blending it with natural polymers enables to form blends that have good characteristics such as a fibre-forming capability, as well as the high strength, modulus, and flexibility of products. [10 - 13].

Wide varieties of polysaccharides are studied with respect to the possibility of forming fibres using electrospinning. Polysaccharides are homopolymers or copolymers of monosaccharides. Such biopolymers can be obtained from different natural sources, namely algae (e.g., alginate), plants (e.g. pectin, guar gum), microorganisms (e.g. bacteria, fungi such as dextran, xanthan gum, and pullulan), and animals (e.g., chitin, chondroitin) [8,13 - 17]. Biopolymers produced from renewable resources are an elegant and innovative answer to replace conventional petroleum-based products and comprise a real sustainable development approach [15].

Native starch is one of the most abundant biopolymers on earth and is present in

living plants as energy storage material. Starch has good characteristics applicable in paper making and textile finishing areas. Due to its biodegradability and excellent iodine absorption, starch can be used for medical purposes. One of the main advantages of starch, in comparison with chitosan, is cost reduction and, at the same time, good medical properties [18]. Fabrication of nanofibres containing starch has recently attracted considerable attention from researchers due to the excellent biocompatibility and physicochemical properties of this biopolymer [11 - 13].

The properties of starch can be improved by various modifications. Oxidized starch (OS) has been widely used in many industries to provide surface sizing and coating property. To improve the mechanical properties of starch or oxidised starch, blending them with other polymers such as methylcellulose, low-density polyethylene and poly(vinyl alcohol) (PVA) is regarded as an effective way [9, 19].

PVA/OS fibres may be used in wound dressing, drug delivery, tissue engineering, as a new potential material because of its non-toxic features, solubility and biodegradability [9].

In previous studies [19] blended nanofibres were produced by electrospinning a mixture of PVA and cationic starch solution. The effect of the starch derivative solution preparation procedure and the weight ratio of PVA to cationic starch on the morphology of nanofibres was investigated. It was found that the homogenisation procedure for cationic starch improves the spinability of the bicomponent solution. The use of ethanol in the solution allows to form nanofibres, even from one consisting of 25 wt.% homogenised cationic starch. It was estimated that for the conditions tested a solution composition of PVA/hCS (85/15w/w) in a mixture of ethanol/water is optimal to produce nanofibres by electrospinning. The use of ethanol in the spinning solution causes the formation of thicker nanofibres.

The main goal of this work was to form nanofibres from a mixture of poly(vinyl alcohol) (PVA) and modified cationic starch (CS) solutions (constant mass ratio of PVA/CS = 3/1) diluted with water at different levels, i.e. to find the most preferable concentration of the spinning solution for the electrospinning procedure,

using two types of rotating electrodes: a plain cylindrical electrode and an electrode with tines [21]. The influence of the amount of ethanol added to the spinning solution on the process of electrospinning and the structure of nanofibre web was analysed.

It should be emphasised that our research was not directed towards a total optimisation of the technological process applied, but only in order to determine the conditions mentioned above. Therefore all other parameters e.g. the geometrical dimensions of the stand, environmental conditions, voltage supply etc. were kept constant. Only one exception was made in order to better recognise the influence of ethanol at a content of 99%: the supply voltage was decreased, with satisfactory results.

Materials and methods

Preparation of polymer solutions

Cationic starch with a degree of substitution of 0.66 was prepared from potato starch by a method previously described [19]. 15 wt.% CS aqueous solution (with a dynamic viscosity of 20 mPa·s at 25 °C) was mixed with 13 wt.% PVA aqueous solution at a PVA/CS mass ratio of 3/1. The mixture of polymer solutions was then diluted with different amounts of distilled water in order to obtain spinning solutions with a final solid concentration of 8, 10 and 12 wt.%. PVA/CS spinning solutions containing 3, 6 and 9 wt.% of ethanol were prepared by adding the required amount of ethanol during the dilution process.

Electrospinning technique

Nanofibre webs were formed by Nanospider™ (Elmarco, Czech Republic) electrospinning equipment using two types of rotational electrodes (the plain cylindrical electrode and the electrode with tines). On this equipment the rotating electrode was covered by a film of the polymer solution (*Figure 1*). By increasing the applied voltage between the electrodes, i.e. increasing electrostatic forces, hemispherical drops were formed on the

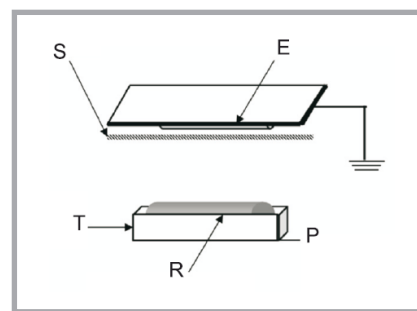


Figure 1. Principal scheme of electrospinning setup – “Nanospider™” S – substratum material, E – electrode, T – tray with polymer solution, R – rotating cylindrical electrode, P – power supply polarity 0 - 75 kV.

rotating electrode. A further increase in the applied voltage caused the formation of Taylor cones from the hemispherical drops. Only when the electrostatic force overcame the surface tension of the polymer solution was a charged jet of polymer solution ejected from the Taylor cone. The jet then moved towards the upper electrode and set down on substratum material spunbond from polypropylene (PP) (surface density $Q = 21,5 \pm 3 \text{ g/m}^2$) in accordance with our previous experiments [18].

Meanwhile the solvent evaporated and finally the jet solidified into a fibre [19]. The distance between electrodes was constant for all experiments (13 cm). All electrospinning processes were carried out at a relative humidity of $(40 \pm 2\%)$ at room temperature $(20 \pm 2^\circ\text{C})$.

Characterization technique

The dynamic viscosity was measured using a rotational viscometer - Rheotec RC02-R (Germany) equipped with a small-sample thermostated adapter - spindle TR8 at $25 \pm 0.1^\circ\text{C}$, while electrical conductivity measurements of the spinning solutions were performed with a Radelkis OK-102 conductometer (Hungary). The surface tension of the solutions were measured using Dataphysics DCAT21 (Germany) apparatus with a willhelmy plate.

The structure of the nanofibre webs obtained was determined using a scanning

Table 1. Diameter of nanofibres spun from PVA/CS solution with concentrations (8, 10, and 12 wt.%).

Type of electrode	Diameter of nanofibres, nm		
	8 wt.%	10 wt.%	12 wt.%
Cylindrical	270 ± 17	260 ± 18	310 ± 17
Electrode with tines	215 ± 16	230 ± 15	280 ± 17

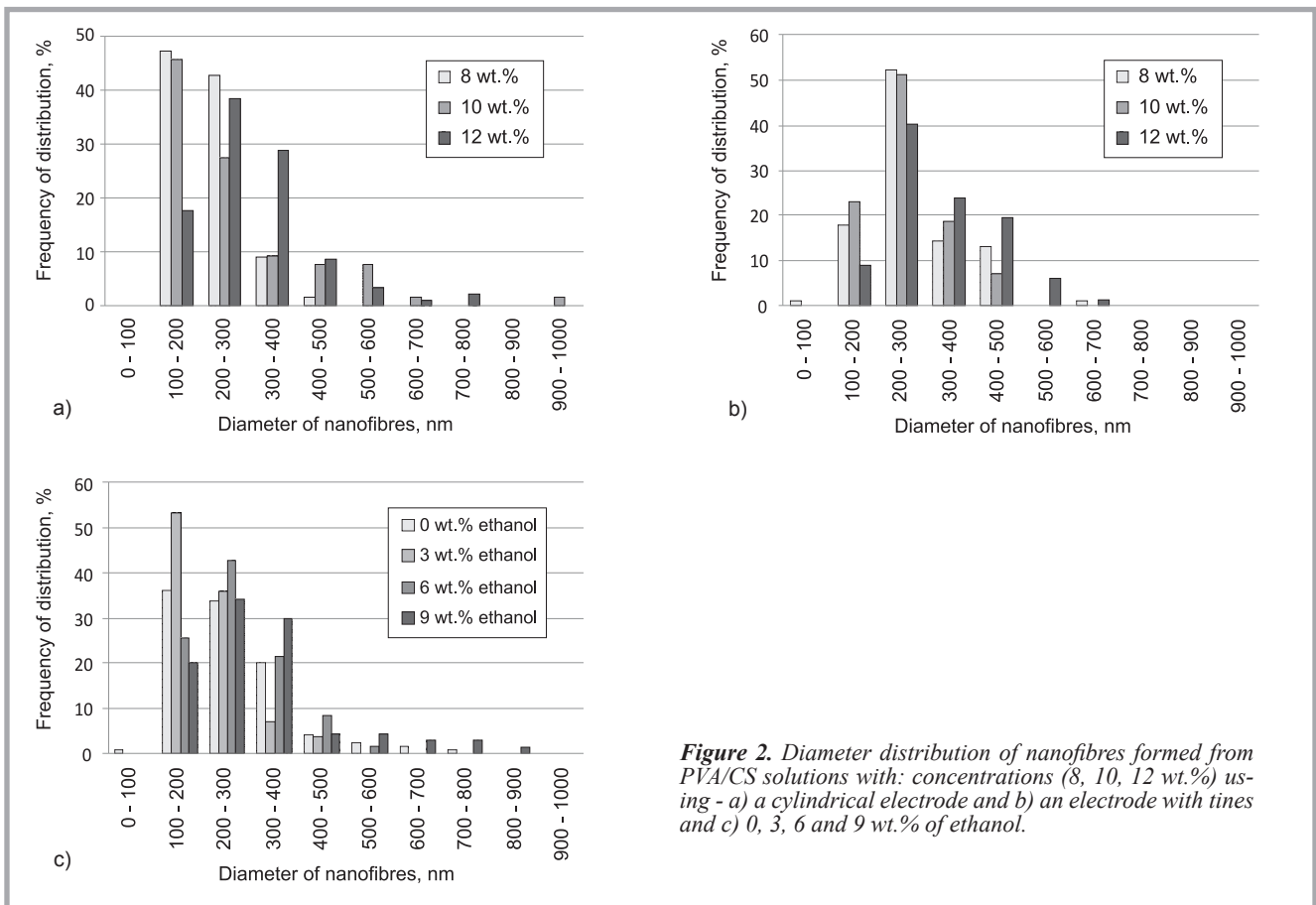


Figure 2. Diameter distribution of nanofibres formed from PVA/CS solutions with: concentrations (8, 10, 12 wt.%) using - a) a cylindrical electrode and b) an electrode with tines and c) 0, 3, 6 and 9 wt.% of ethanol.

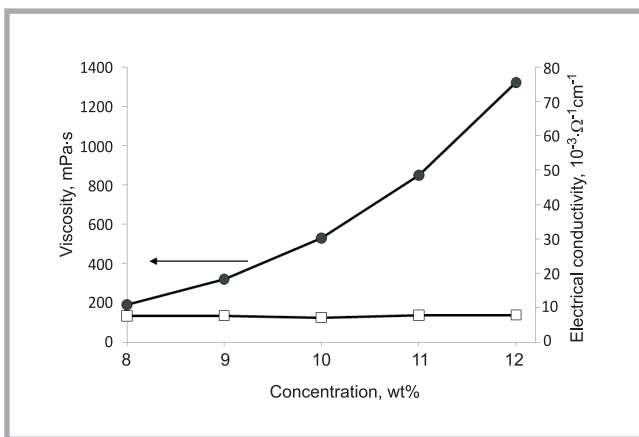


Figure 3. Viscosity and electrical conductivity of PVA/CS solutions with various concentrations.

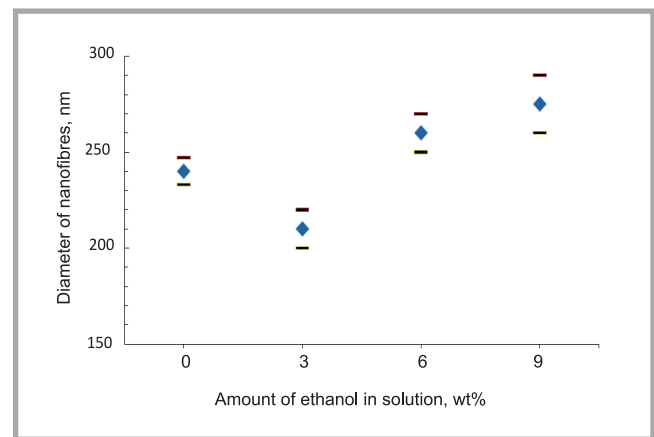


Figure 4. Average values of the diameter of nanofibres spun from 8 wt.% PVA/CS solutions with 0, 3, 6 and 9 wt.% of ethanol at 65 kV voltage.

electron microscope - (SEM) Quanta 200 FEG (FEI, Netherlands). The analysis system LUCIA 5.0 was utilised to measure the diameter of nanofibres from every SEM image.

Results

In the first experimental part nanofibres were formed from the mixtures of PVA and CS solutions (PVA/CS mass ratio 3/1) using both kinds of rotating elec-

trodes (the plain cylindrical and the electrode with tines). Spinning solutions with solid concentrations of 8, 10 and 12 wt.% were prepared. The objective of this part of the experiment was to find the more preferable rotating electrode for the formation of nanofibres. The diameters of nanofibres electrospun from PVA/CS solutions with various concentrations (8, 10 and 12 wt.%) using both rotating electrodes at 65 kV are shown in **Table 1** (see page 17). From data presented, it

can be noticed that by using the electrode with tines instead of the plain cylindrical electrode, the diameter of nanofibres was decreased significantly. The histograms (**Figures 2.a** and **2.b**) show the diameter distribution of nanofibres formed from the spinning solutions with various concentrations (8, 10, 12 wt.%) by using both rotating electrodes. From the data presented, it can be observed that by using the cylindrical electrode, the majority of PVA/CS nanofibres formed from solu-

tions with concentrations of 8 wt.% and 10 wt.% are 100 - 200 nm in diameter. However, the majority of fibres formed from the solution with 12 wt.% concentration appear to be 200 - 300 nm in diameter. In the case of the electrode with tines, the majority of nanofibres formed are 200-300 nm in diameter for all concentrations (8, 10 and 12 wt.%). Also it was noticed that by using the cylindrical electrode more nanofibres were formed with the diameter higher than 500 nm. From this part it can be concluded that the electrode with tines is more appropriate for the electrospinning of PVA/CS fibres and that the best concentration of the spinning solution for the conditions accepted is 8 wt.%

Table 2 shows the results of surface tension measurements of PVA/CS mass ratio 3/1 solution with different concentrations (8, 9, 10, 11 and 12 wt.%). From the data presented, it can be noticed that surface tension values vary insignificantly (from 45,11 to 47,08 mN/m) at all solution concentrations and should not have influenced the experiment. **Figure 3** shows the results of viscosity and electrical conductivity tests of PVA/CS solutions (8, 9, 10, 11 and 12 wt.%). It can be noticed that the viscosity of the solution with the highest concentration (12 wt.%) was, as could be foreseen, significantly higher (1320 mPas) compared with that of the 8 wt.% solution (190 mPas). These differences in viscosity were found in the formation of thinner nanofibres from 8 wt.% solution. As is clear from **Figure 3**, the electrical conductivity values of the PVA/CS solution at different concentrations almost coincide. SEM images of nanofibres webs formed from 8 wt.% PVA/CS solution using a different type of rotating electrode (cylindrical electrodes and electrodes with tines) are shown in **Figure 5**. It can be clearly observed that by using the electrode with tines, a nanofibre web with a higher density of nanofibres was formed over a similar time of spinning. Hence, for the next experiments the electrode with tines was chosen because of the successful results obtained using it (improved electrospinning process and diameter distribution of nanofibres).

In the second part of this experiment, nanofibres were produced from 8 wt.% PVA/CS (PVA/CS mass ratio 3/1) solution and different amounts of ethanol added. The results from a previous study [18] indicated that a small amount (5 wt.%) of ethanol strongly influenced

Table 2. Surface tension values of PVA/CS solutions with various concentrations.

Concentration of spinning solution, wt.%	Surface tension, mN/m
8	47.08
9	46.50
10	46.68
11	45.11
12	46.78

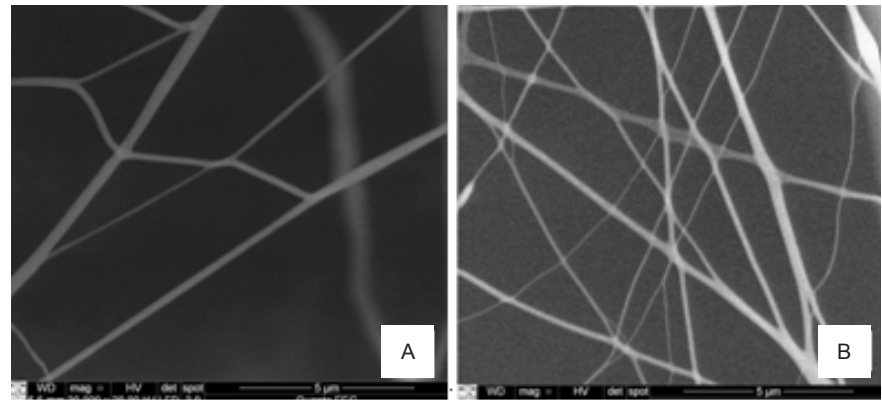


Figure 5. SEM images of webs with nanofibres formed from 8 wt.% PVA/CS solution at 65 kV voltage. A – cylindrical electrode, B – electrode with tines.

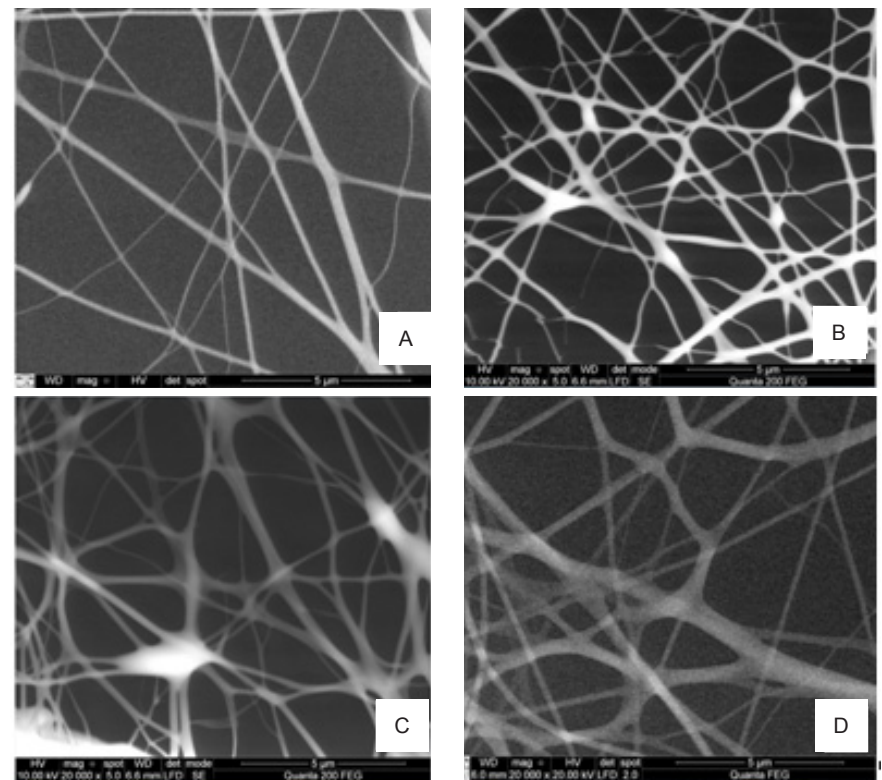


Figure 6. SEM images of webs with nanofibres formed from 8 wt.% PVA/CS solutions containing various amounts: A – 0 wt.%, B – 3 wt.%, C – 6 wt.%, D – 9 wt.% of ethanol at 65 kV voltage.

the electrospinning process of PVA nanofibres. For this reason another aim was to analyse the role of ethanol in the formation of PVA/CS and to determine the optimal amount of ethanol in the spinning solutions for the spinning conditions

used in our experiment. The influence of 3, 6 and 9 wt.% of ethanol in 8 wt.% PVA/CS solutions was tested. Average values of the diameter of nanofibres spun from these solutions at 65 kV voltage are presented in **Figure 6**. It can be noticed

that the diameter of nanofibres significantly increased with an increase in the amount of ethanol in the spinning solution drops of between 0 and 3%, with the next highest being at 9% of ethanol. Considering the criterion of the smallest fibre diameter, the most preferable amount of ethanol in PVA/CS solution was found to be 3 wt.% (**Figure 5**). **Figure 2.c** (see page 18) shows that the majority of PVA/CS nanofibres formed from a solution containing 3% of ethanol are 100 - 200 nm in diameter. From this figure it can be concluded that a relatively high amount of ethanol (9 wt.%) in the spinning solution resulted in the formation of nanofibres with a higher diameter. However, it was additionally noted that by adding 6 wt.% of ethanol to the spinning solution, the formation of nanofibres was possible to perform starting from 35 kV voltage, and in the case of 9 wt.% of ethanol, even at 30 kV voltage, which would certainly be advantageous; however, the choice of conditions depends on the criterion accepted. SEM images (**Figure 6**) (see page 19) shows that by using a small amount of ethanol in PVA/CS solution, a nanofibre web with a higher density of nanofibres is formed over a similar period of time.

Conclusions

- Nanofibres from PVA/CS solutions (PVA/CS mass ratio 3/1) with different concentrations were successfully electrospun. By comparing the performance of two types of electrodes, it can be concluded that better results were obtained with the electrode with tines, as nanofibre webs with a higher density of nanofibres can be formed with this electrode.
- The diameter of nanofibres can be changed by using PVA/CS spinning solutions with different concentrations of solids. An 8 wt.% concentration is the best for the spinning conditions under consideration, as webs with a higher nanofibre density are formed over similar periods of time in this case. The viscosity of spinning solutions increases with an increase in PVA/CS concentration, leading to the formation of thicker fibres.
- The addition of ethanol to 8 wt.% PVA/CS spinning solutions improved the electrospinning process. By using 9 wt.% of ethanol in the spinning solution, it was possible to form nanofibres at lower voltages (30 kV). 3 wt.% of ethanol in the spinning solution

influenced the diameter of nanofibres in comparison with that containing 9 wt.% of ethanol (the diameter of nanofibres increased significantly in this case).



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