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Investigation of the Possibility of Forming Nanofibres with Potato Starch

Abstract
In this paper nanofibres were formed from PVA solution with potato starch and a small amount of ethanol. Due to the previous study, it was determined that with the addition of ethanol (30 wt.%) in the solution, it is possible to form bicomponent PVA/cationic starch (75/25 wt.%) nanofibres. Preparation of a procedure using cationic starch was quite difficult, and therefore a high quantity of ethanol was also not desirable. In this study the influence of simple potato starch (which is used in the food industry) and a low quantity of ethanol on the formation of nanofibres was analysed. The results showed that with a 5 wt.% amount of potato starch it is impossible to form nanofibres by the electrospinning process. However, when a 5 wt.% amount of ethanol is added to the PVA solution, it was possible to form nonwoven material from nanofibres. It was confirmed that even a small amount of ethanol has a significant positive influence on the electrospinning process but not a positive influence on the nanofibres and web structure.

Key words: *electrospinning, nanofibre, PVA, potato starch.*

Introduction

Electrospinning has become a widely used fibre formation technique in the last decade. It employs a strong electric potential on a polymer solution or polymer melt to produce nanoscale fibres from a few nanometres to several micrometers, usually in the range of 100 - 500 nm [1, 2].

Most varieties of functional polymers, such as polysaccharides, have been spun into various nanofibres with seemingly almost unlimited functionalities and applications [3 - 5]. Due to their enhanced conductivity and high aspect ratio, nanofibres have found use in unconventional energy sources and storage cells, as well as in the synthetic and rubber industry due to their mechanical properties as fillers in composites [2, 3, 5, 6]. Polymers from quaternised chitosan and poly(vinyl alcohol) have intrinsic antimicrobial activities, hence they are used for the fabrication of materials in medical applications, including wound-healing dressings, drug delivery and filters [7].

Additionally, some nanofibres have been found to exhibit catalytic activities and can possess interesting surface properties, giving them great potential for use as catalytic substrates [3]. Nanofibres are also used in the aerospace and semiconductor industries. Furthermore, nanowebs show great potential for use in filtration processes and protective clothing [3, 8].

Due to its easy, cost-effective fabrication and its readiness to upscale to commercial production, many studies have been performed on the electrospinning technique for nanofibre production over recent years [8, 9].

Chitosan is used for the formation of functional nanofibres with excellent biocompatibility, biodegradability, as well as anti-microbial and non-toxic properties, showing great potential for medical use [4]. Starch as a bicomponent can also be used for the formation of nanofibres. This component has good characteristics applicable in paper making and textile finishing areas. Moreover, due to its biodegradability and excellent iodine absorption, starch can be used for medical purposes [10]. One of the main advantages of starch, in comparison with chitosan, is cost reduction and, at the same time, good medical properties.

Poly(vinyl alcohol) (PVA) is a commonly used polymer due to its many useful properties, such as chemical and thermal stability, non-toxicity and good water absorption [11, 12]; therefore it has been extensively studied as an electrospun precursor polymer [9 - 17]. Some studies have been performed to investigate various parameters, such as solution properties and various process conditions, which were tested to assess their affect on the morphology and diameter of electrospun PVA nanofibres. It was reported that it was possible to form nanofibres from polymer solutions containing cationic starch and a high amount of ethanol (30 wt.%); however, it was noticed that adding cationically modified starch to PVA solution had a negative influence on the electrospinning process [10, 13, 16].

The goal of this paper is to find a possibility of forming nanofibres using spinning solutions prepared from simple inexpensive potato starch, PVA and a small amount of ethanol. The morphology, diameter and structure of the nanofibres and nonwoven webs were investigated.

Materials and methods

Preparation of polymer solutions

PVA solutions were prepared by dissolving a weighed amount of PVA powder (ROTH - Germany, M = 72000 g/mol) in deionized water at 85 °C under constant stirring for 2 h to attain solutions with concentrations of 7 wt.% and 8 wt.% of PVA.

Several types of PVA polymer solutions were prepared. To test the effect of ethanol on PVA nanofibre formation, an 8 wt.% concentration of PVA solution was prepared with an addition of ethanol ranging from 0, 1, 3 and 5 wt.% in relation to the final solution. Potato starch consists of amylose 20 - 25% and amylopectin 75 - 80%. To test the effect of potato starch (Alvo and Ko - Lithuania) on nanofibre formation, 7 wt.% PVA and water solutions were prepared with the addition of potato starch powder (without any additional preparation procedure) ranging from 0, 1, 3 and 5 wt.% in relation to the final solution. To test the effect of ethanol on nanofibre formation using starch as an electrospinning component, 7 wt.% PVA, water and 5 wt.% ethanol were prepared with the addition of starch ranging from 0, 1, 3 and 5 % in the final solution.

A VZ – 246 funnel form viscometer was used to measure the viscosity of the PVA spinning solution at 21 ± 0.1 °C. The

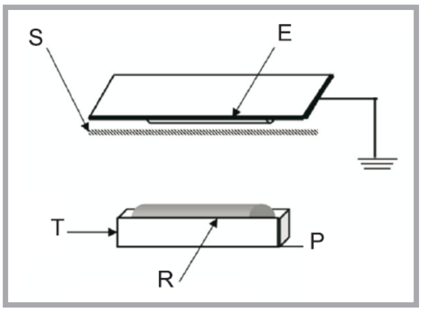

Figure 1. Principal scheme of the electrospinning setup – "NanospiderTM": S - substratum material, E - electrode, T - tray with polymer solution, R - rotating drum, P - power supply polarity 0 - 75 kV.

principle of this method was to measure the time in which 50 ml of the spinning solution flowed down through the 6 mm size hole of the funnel. This time represents a quantity related to viscosity.

Electrospinning technique

A nonwoven web was formed from nanofibres using NanospiderTM electrospinning equipment (Elmarco, Czech Republic). In this equipment, while rotating, the drum is 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 are formed on the rotating drum. A further increase in the voltage applied causes the formation of Taylor cones from the hemispherical drops. Only when the electrostatic force overcomes the surface tension of the polymer solution, is a jet of polymer solution ejected from the Taylor cone. The jet moves towards the upper electrode and sets down on the substratum material – spunbond from polypropylene filaments (thickness of spunbond - 0.125 ± 0.015 mm, surface mass - 21.1 ± 3 g/m^2). Meanwhile the nanofibre becomes thinner, the solvent evaporates and then the fibres solidify.

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

Characterisation of nanofibre morphology

The structure of the electrospun nonwoven material from nanofibres was observed by Scanning Electron Microscopy (SEM) - SEM-FEI Quanta 200 (Netherlands). The Lucia 6 computer program was used to measure the diameter of nanofibres from every SEM image and to calculate the average diameter of nanofibres (all nanofibres were measured from 3 SEM images for each variant).

Results

The effect of ethanol on PVA nanofibre formation

The main objective of the experimental part was to analyse how a small amount of ethanol influences electrospinning and to find out what ethanol concentration in the electrospinning solution is preferable for the procedure. Ethanol concentrations in the solutions were the following: 0% (native solution), 1%, 3%, and 5 wt.% ethanol in relation to the final solution.

Average values and dispersions of the diameters of nanofibres from 8 wt.% PVA and various ethanol concentrations at 55 kV voltage are shown in ***Figure 2***. From the data presented it can be noticed that the addition of ethanol to the spinning solution had no significant influence on the diameter of PVA nanofibres. Differences in the average values of nanofibre diameters are within the margin of error.

Figure 4 (see page 26) shows SEM images of PVA nanofibres formed from the initial 8 wt.% PVA solutions containing 0, 1 and 5 wt.% ethanol at 55 kV voltage. From the SEM images it can be seen that increasing the amount of ethanol in the spinning solution formed more spots (near 2D forms of solidified spinning solution visible on the SEM images) on electrospun nonwoven material (***Figure 4.B, D, F***), but it does not have a significant influence on the diameter of nanofibres (***Figure 4.A, C, E***). In the experimental part it was also noticed that ethanol has a significant influence on the electrospinning process. Nanofibres without ethanol were possible to form only at 45 kV, while with the PVA solution with 5 wt.% of ethanol it was possible to form nanofibres even at 35 kV voltage.

The effect of potato starch on PVA nanofibre formation

The main objective of the experimental part was to analyse how potato starch influences electrospinning and to find out if it is possible to form bicomponent nanofibres with simple potato starch. The starch amounts in the solutions were the following: 0% (native solution), 1%, 3% and 5 wt.% starch in the final solution.

Average values of the diameters of nanofibres from 7 wt.% PVA and various starch amounts at 65 kV voltage are shown in ***Figure 3***. From the data presented it can be observed that increas-

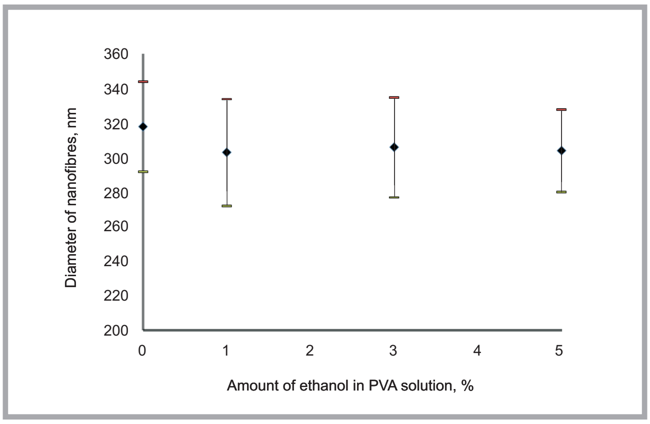

Figure 2. Average values and dispersions of diameters of nanofibres spun from 8 wt.% PVA solutions with different amounts of ethanol at 55 kV voltage.

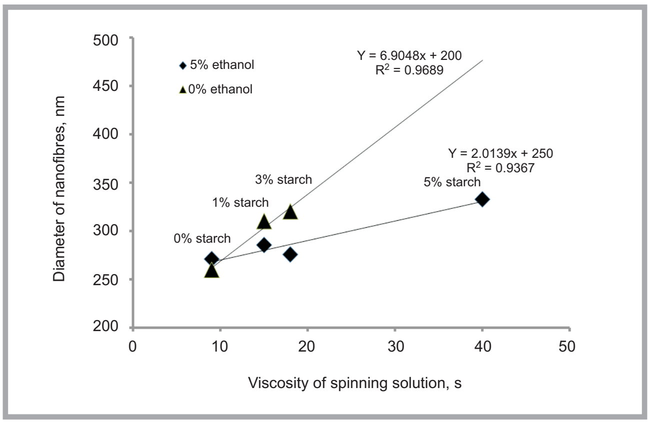

Figure 3. Dependence between the average diameters of nanofibres from 7 wt.% PVA solution and the viscosity of the spinning solution with various starch amounts at 65 kV voltage.

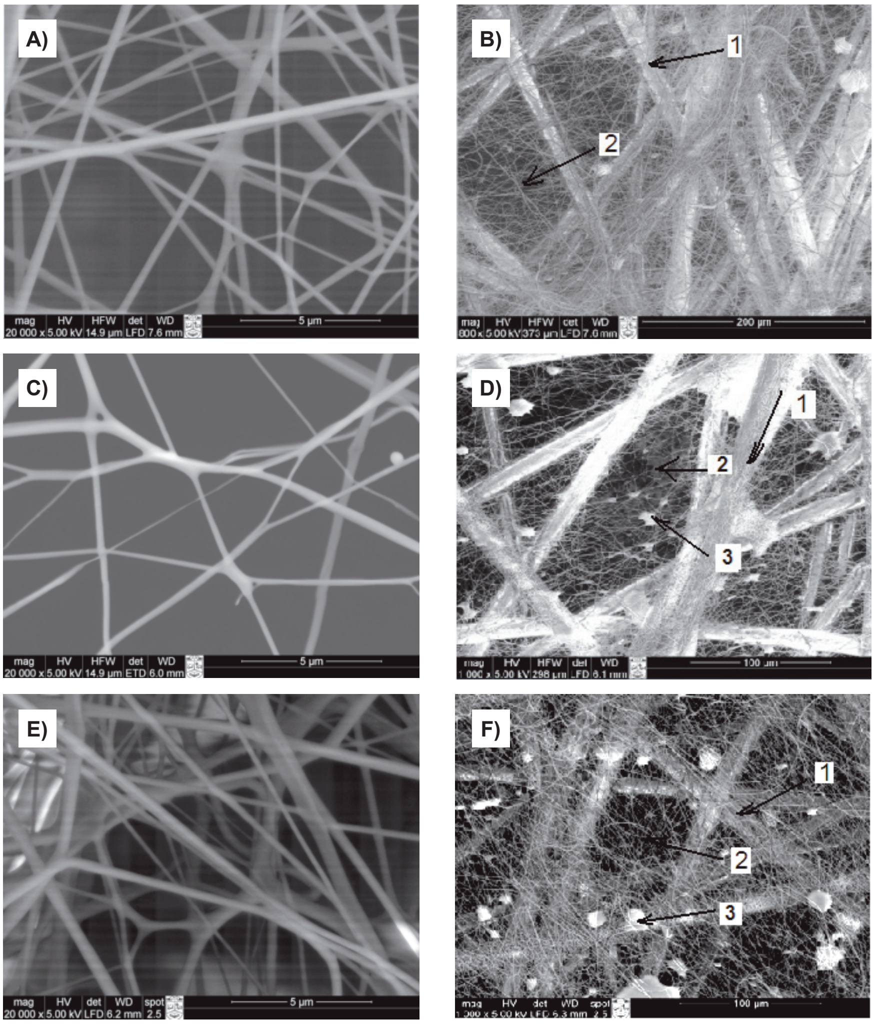

Figure 4. SEM images of nonwoven webs formed from 8 wt.% PVA solutions containing various amounts of ethanol at 55 kV voltage. A – 0% ethanol (scale 5 µm), B – 0% ethanol (scale 200 µm), C – 1% ethanol (scale 5 µm), D – 1% ethanol (scale 200 µm), E – 5% ethanol (scale 5 µm), F – 5% ethanol (scale 200 µm), (1 – fibres of support material, 2 – nanofibres, 3 – spots of polymer solution).

ing the amount of starch, the viscosity of the PVA solution also increased - potato starch is a thickener of PVA solution. It was observed that increasing the viscosity of the PVA solution, the density of nanofibres also increased linearly (R^2 = 0.9689, ***Figure 3***). Herewith it is important to note that it was impossible to spin nanofibres with 5 wt.% of starch because it was proved unsuitable for electrospinning due to its high viscosity in comparison with other solutions.

The effect of ethanol on PVA nanofibre formation using starch as an electrospinning component

In the previous study [10] it was estimated that after an addition of 30 wt.% ethanol in the solution, bicomponent nanofibres with an amount of cationic starch of 25 wt.% were formed. The main objective of the experimental part was to analyse how a small quantity of ethanol (5 wt.%) influences the electrospinning process of nanofibres with potato starch. Starch concentrations in the solutions were the following: 0% (native solution), 1%, 3% and 5 wt.% starch in the final solution.

Spinning solutions with 5 wt.% ethanol and 0, 1, and 3 wt.% starch showed no observable differences in viscosity in comparison with an analogous solution without ethanol (***Figure 3***). Increasing the starch amount added in this range also did not significantly affect the average diameter of nanofibres formed. On the contrary, the spinning solution with 5 wt.% ethanol and 5 wt.% starch showed an increase in viscosity and also a significant increase in the diameter of electrospun nanofibres (***Figure 3***).

Figure 5 shows SEM images of webs from 7 wt.% PVA solutions containing various starch amounts at 65 kV voltage. Samples with two SEM images in different scales (5 and 200 µm) were selected to analyse not only the morphology of nanofibres but also the structure of the nonwoven web. Analysis of SEM images showed that by increasing the amount of starch added to the spinning solution, it was possible to form nonwoven material without spots but at the same time with a lower density of the number of nanofibres. While in the case of decreasing the amount of starch in the PVA spinning solution, the spots on the web are very visible (***Figure 5***), meaning that decreasing the starch does not have a positive influence on the structure of a nonwoven web from nanofibres.

The spinning solution with 5 wt.% ethanol and 5 wt.% starch was shown to be inappropriate for electrospinning at an electric potential of 55 kV due to its high viscosity and the fact that electrospinning equipment is automatically discharged.

Conclusions

- Increasing the amount of ethanol in the spinning solution formed more spots on electrospun nonwoven material, but it was noticed that ethanol has a significant influence on the electrospinning process. Nanofibres without ethanol were possible to form at 45 kV, while those from a PVA solution with 5% of ethanol were formed at 35 kV.
- Potato starch is a thickener of PVA solution; with an increase in the amount of starch, the viscosity of the solution increased.
- A small amount of starch (till 5%) in the spinning solution does not have an influence on nanofibre diameter but has a significant influence on the electrospinning process. It was difficult to form nonwoven material from nanofibres. The addition of starch into the spinning solution caused the formation of thin nonwoven material with a lower density of the number of nanofibres and amount of spots.
- The maximum possible amount of potato starch (without ethanol) to form nanofibres was 3 %, but with the addition of 5% ethanol into the PVA spinning solution, it was possible to form nanofibres with 5% of starch.

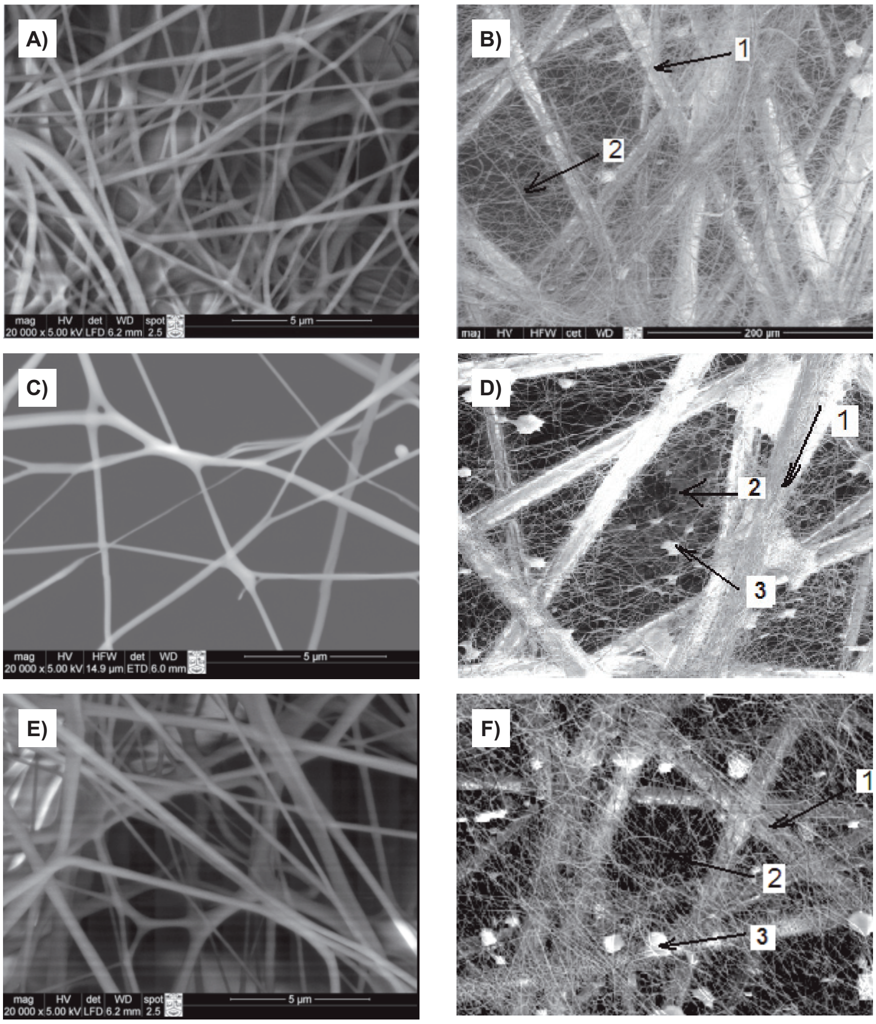

Figure 5. SEM images of nonwoven webs formed from 7 wt.% PVA solutions and 5 % ethanol containing various starch amounts at 65 kV applied voltage. A – 1% starch (scale 5 μm), B – 1% starch (scale 200 μm), C – 3% starch (scale 5 μm), D – 3% starch (scale 200 μm), E – 5% starch (scale 5 μm), F – 5% starch (scale 200 μm) in the polymer solution, (1 – fibres of support material, 2 – nanofibres, 3 – spots of polymer solution).

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