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Methods of Forming Nanofibres from Bicomponent PVA/Cationic Starch Solution

Abstract
In this study nanofibres were manufactured from bicomponent PVA/cationic starch (CS) polymers solutions using the electrospinning method. The effect of the starch derivative solution preparation procedure and weight ratio of bicomponent polymer solution on the morphology of nanofibres was investigated. Three types of polymer solutions were prepared: PVA/CS and PVA/homogenizated (hCS), both in water, and PVA/hCS in a mixture of ethanol/water. It was found that the homogenisation procedure for CS improves the spinability of the bicomponent solution. The use of ethanol in the solution allows to form nanofibres, even from one consisting of 25% hCS. It was estimated that a solution composition of PVA/hCS (85/15w/w) in a mixture of ethanol/water is optimal to produce nanofibers by electrospinning. Analysing the morphology of webs formed, it was estimated that more stick nanofibres were formed from the PVA/hCS solution than from the PVA/CS one. The use of a ethanol/water mixture in PVA/hCS causes the formation of thicker nanofibres.

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

Introduction

Many methods have been used for manufacturing polymer nanofibres, such as drawing, phase separation, self assembly and electrospinning. Among these methods electrospinning is very attractive because of its simplicity, flexibility and low cost of producing nanofibres [1].The main, unique properties of nanofibres are the high specific surface area and small diameter of the fibers. Due to these characteristics, nanofibres are excellent candidates for medical applications, filtration, composites, protective clothing manufacture etc.

Poly(vinyl alcohol) (PVA) is a semicrystalline, hydrophilic, non-toxic polymer with good chemical and thermal stability. PVA absorbs water and swells easily. The solubility of PVA manufactured from poly(vinylacetate) in water increases greatly as the degree of hydrolysis of the poly(vinylacetate) increases. PVA is used in various contemporary technologies, such as the production of hydrogels, optics and biomaterials including soft contact lenses, implants and artificial organs [2, 3]. Due to the many advantages of PVA, much attention has been focused on the electrospinning of PVA. The effects of the molecular weight of PVA and the concentration of PVA solution on the nanofibre structure have already been analysed [3 - 5]. The effect of the applied voltage on the diameter of PVA nanofibres formed [6-8] have also been described, as well as the effect of pH on the morphology and diameter of electrospun PVA nanofibres [9]. There are a lot of investigations concerning the electrospinning of bicomponent solutions, in which one of components is PVA. Electrospun nanofibres from PVA/cellulose acetate [10], Zn:Cu/PVA [11], PVA/ZnO [12], PVA/multi-walled carbon nanotubes [13], and PVA/LiCl [14], PVA/poly(phenylene vinylene) were successfully obtained [15].

Nanofibers obtained from ionogenic polymers are of great interest because of the peculiarities of polyelectrolytes and also because of the possibility of modifying the nanofibre at a later stage. The preparation of polyelectrolyte containing electrospun nanofibers has already been achieved from mixed PVA/chitosan [16], from PVA/N-carboxyethylchitosan [17] and from PVA/quaternised chitozan [18] solutions.

Highly cationic derivatives of starch obtained from cheap, renewable and biodegradable natural polysaccharide by easy modification [19] have recently attracted interest as potential sources for nanofibers, which may be used for medical purposes. Potato starch used as a raw material for cationisation is a mixture of linear amylose (appr. 20 - 30%) and highly branched amylopectin (appr. 70 - 80%). No literature data were found about the electrospinning of water soluble starch derivatives. Therefore, the question is still open: does highly cationic starch possess a fibre forming ability and could it replace the linear macromolecules of quaternised chitosan in a mixed solution in electrospinning.

The aim of this work was to form nanofibres from polymer solutions, with (if possible at a high level of concentration) cationic starch being one of the components.
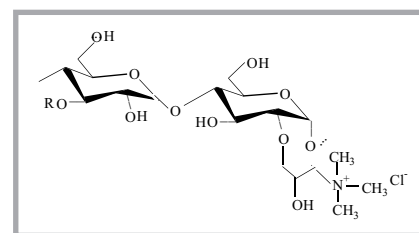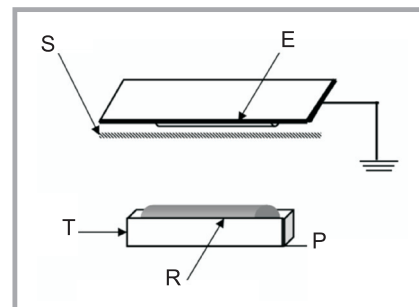

Figure 1. *Cationic starch.*

Figure 2. *Principal scheme of electrospinning setup - "Nanospider"TM; S - substratum material, E - electrode, T - tray with polymer solution, R - rotating drum, P - power supply positive polarity 0 - 75 kV.*

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Experimental

Materials

Hydroxyethylated starch, Kollotex 1250 ($[\eta] = 0.136 \times 10^3$ ml/g), was purchased from Avebe (Netherlands). Poly(vinyl alcohol) (PVA), JP-24 (dynamic viscosity of 4% solution was 45 mPa×s at 20 °C) (degree of hydrolysis of 88%), was supplied by Japan Vam α Paval Co.Ltd (Japan).

Nanofibres were collected on support material – spunbond from polypropylene (surface density $Q = 21.5 \pm 3$ g/m²).

Methods

Preparation of polymers solutions
PVA solution was prepared by dissolving PVA granules in distilled water of 70 ºC. CS solution was obtained by dissolving CS microgranules in distilled water.

Water soluble cationically modified starch (CS) (*Figure 1*) was prepared by the reaction of hydroxyethylated starch with 2.3-epoxypropyltrimethylammonium chloride in the presence of sodium hydroxide (molar ratio of the starch : epoxy compound : NaOH was 1 : 0.35 : 0.04) at 45 °C for 24 h [19]. After the reaction, the CS was washed (5 times) with isopropanol and dried at 50 °C. The degree of substitution (DS = 0.3) was calculated from the nitrogen content. The nitrogen content in the CS was estimated by the Kjeldahl method after purification using Soxhlet extract with methanol for 16 h.

Three types of PVA/CS solution were prepared for electrospinning:
1. The electrospinning solutions were prepared by mixing 8 wt.% aqueous solution of PVA with 8 wt.% solution of CS at weight ratios of PVA/CS = 95/5 and 90/10.
2. In order to increase the homogeneity of the mixed solutions, the 8 wt.% aqueous solution of CS was initially homogenised for 5 min using a dispersing instrument (IKA Ultra-Turrax) at a rate of 10000 r.p.m. and then mixed with the 8 wt.% aqueous PVA solution. The final polymer mixture was homogenised once more for 10 min at 16000 r.p.m. Homogenous aqueous polymer solutions at weight ratios of PVA/CS = 95/5, 90/10 and 85/15 were obtained.
3. In order to improve the spinability of the compositions, 30 wt.% of the water in the solutions was re-placed with ethyl alcohol. In this way homogenous water-ethanol polymer solutions at weight ratios of PVA/CS = 95/5, 90/10, 85/15 and 75/25 were obtained.

The total polymer concentration in all the electrospinning solutions was 8 wt.%.

Electrospinning equipment
The substratum material was covered by a layer of PVA/CS nanofibres using electrospinning equipment - "Nanospider TM" (Elmarco, Czech Republic). While rotating, the drum is covered by a film of the polymer solution. 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 applied voltage 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. Meanwhile the nanofibre becomes thinner, the solvent evaporates and then solidifies (*Figure 2*) [5].

During all the experiments carried out, the distance (*d*) between electrodes was 11 cm and 14 cm, applied voltage (*U*) was varied between 40 kV and 70 kV, the temperature of the electrospinning environment was $t = 20 \pm 2$ °C and the humidity $\gamma = 42 \pm 2\%$.

Characterisation techniques
The dynamic viscosity of the solutions was measured using a RheoTec RC01/02 viscometer (Germany) at 25 ± 0.1 °C. Conductivity measurements of the spinning solutions were performed on a Radelkis OK-102 conductometer (Hungary). The structure of the nanofibre webs obtained was determined using a scanning electron microscope - (SEM) JSM-6060 LV (JOEL). The diameter of bicomponent nanofibres was measured using the image analysis system LUCIA 5.0. In this study the structure of the web prepared from nanofibres was analysed, in which all derivatives of the nanofibres (single, stick) from every SEM image were evaluated.

Results and dicsussion

Starch is one of the most widespread polysaccharides in nature. Due to its unique technological characteristics and biodegradability, it is widely used in paper making, textile finishing and medical areas. As was mentioned above, there is currently no information about nanofibres from starch or starch derivatives. Hence the aim of this work was to form nanofibres by the electrospinning method in which one of the components was modified starch. An attempt to electrospin pure starch was not successful, therefore it was decided to try and make nanofibres from the bicomponent PVA/CS polymer solution.

The conductivity of PVA/CS solution with a weight ratio of 90/10 is about 30 % higher than that of a solution with a weight ratio of 95/5 (*Table 1*). Due to existing quaternary ammonium groups, pure CS solution is very conductive,
$$\sigma_{CS} = 8.8 \cdot 10^{-3} \ \Omega^{-1}\text{cm}^{-1},$$
compared with pure PVA solution,
$$\sigma_{PVA} = 0.6 \cdot 10^{-3} \ \Omega^{-1}\text{cm}^{-1}.$$
With an increase in the CS content of the solution, the conductivity of bicomponent PVA/CS solution increases too. It should be noted that the viscosity of PVA/CS solution almost does not change with an increase in the CS content of the solution.

All the sets of experiments are presented in *Table 2*. It was possible to form nanofibres from PVA/CS only at the high-

Table 1. *Viscosity and conductivity of the polymer solutions.*

Polymer	Composition of polymer solution, wt%/wt%	Viscosity, mPa·s	Conductivity, $10^{-3} \cdot \Omega^{-1}\text{cm}^{-1}$
PVA/CS in water	95/5	655	0.81
	90/10	660	1.20
PVA/ hCS in water	95/5	640	0.89
	90/10	560	1.23
	85/15	620	1.40
PVA / hCS in the ethanol/water mixture	95/5	1230	0.38
	90/10	990	0.54
	85/15	860	0.66
	75/25	610	0.84

Table 2. *Settings of experiments, *--- it was not possible to form any nanofibres, even at the highest (70 kV) applied voltage.*

Polymer	Composition of polymer solution, wt%/wt%	The distance between electrodes, cm	Ranges of applied voltage, kV
PVA/ CS in water	95/5	11	70
	95/5	14	---*
	90/10	11	70
	90/10	14	---
PVA/ hCS in water	95/5	11	40, 50, 60, 70
	95/5	14	---
	90/10	11	50, 60, 70
	90/10	14	---
	85/15	11	---
	85/15	14	---
PVA / hCS in the ethano/water mixture	95/5	11	30, 35, 40, 45
	95/5	14	35, 40, 45, 50, 55, 60
	90/10	11	25, 30, 35, 40, 45
	90/10	14	35, 40, 45, 50, 55, 60
	85/15	11	30, 35, 40
	85/15	14	35, 40, 45, 50, 55
	75/25	11	40, 45, 50
	75/25	14	40, 45, 55, 60

est strength of the electrical field, i.e., when the distance between electrodes was 11 cm and the maximal applied voltage-70 kV. All the width of the moving substratum material was covered by a web of nanofibres from the PVA/CS polymer solution with a weight ratio of 95/5. In the second case (PVA/CS = 90/10) only the edges of the substratum material were covered by a smooth layer of web from nanofibres. Taylor cones (initiators of nanofibres) were not formed throughout the whole length of the electrode but only on its corns , where the strength of the electrical field is the biggest (both electrodes (in Nanospider™) are in the form of a cylinder, both of whose tips taper). Such experimental results may be possible to explain by analysing the structure of CS macromolecules. The macromolecule of PVA is linear, but a number of CS macromolecules are very branchy. It may be that due the effect of the polielectrolytical swell of branchy CS macromolecules; this polymer is not easy to spin. Consequently, an increase in the

CS content in the polymer solution worsens the electrospinning process, although the conductivity of the solution increases.

From the dates presented in **Table 2**, it is possible to see that it was not possible to form any nanofibres from the PVA/CS solution when the distance between electrodes was 14 cm, due to an insufficient electric field in the electrospinning chamber.

In **Figure 3** SEM images of PVA/CS nanofibre webs with a weight ratio of 95/5 (a) and 90/10 (b) are presented. The nanofibre web from the PVA/CS solution with a weight ratio of 90/10 is sparser, with fewer defects (spots of polymer solution) than a web from a solution with a weight ratio of 95/5, because fewer Taylors cones were formed from the PVA/CS solution 90/10 during the electrospinning process.

The average nanofibre diameter of the PVA/CS with a weight ratio of 95/5 and

90/10 are $\overline{d}$ =320 nm and $\overline{d}$ = 340 nm, respectively. The viscosity of PVA/CS solution almost does not change with an increase in the CS content of the solution (**Table 1**), which is why the content of CS in the bicomponent solution does not have an influence on the average nanofibre diameter. Analysing the distribution of nanofibre diameters (**Figure 4**), it was noticed that in both cases the majority of nanofibres formed are 200 - 300 nm in diameter. Hence a percentage part of CS in the solution does not have an influence on the diameter of nanofibres formed but has a great influence on the electrospinning process.

Influence of CS homogenisation on the electrospinability of bicomponent polymer solution

In order to form nanofibres from bicomponent solution with a weight ratio of more than 5% of the CS, it was decided to use homogenised CS. During the homogenisation of CS, a number of microgels of modified starch (probably from less modified starch microparticles) are destroyed.

All the width of the substratum material was covered by a layer of nanofibres, then the weight ratio of the PVA/homogenous CS (hCS) polymer solution was 95/5 and 90/10. The distance between electrodes was 11 cm, and the applied voltage was 40 - 70 kV. As is seen from **Table 1**, the homogenisation procedure does not have a significant influence on the conductivity and viscosity of the bicomponent polymer solution. The conductivity of the solution with hCS is 2 - 8% higher, the the viscosity is 2 - 15% lower nor conductivity and viscosity of solution with CS. Therefore it is easier to form nanofibres from homogenised CS than from raw CS due to better distribution of hCS macromolecules (**Table 2**) in the solution. In this case it was possible to form nanofibres even at a small (40 kV) applied voltage, i.e. an electrical field of smaller strength is needed.
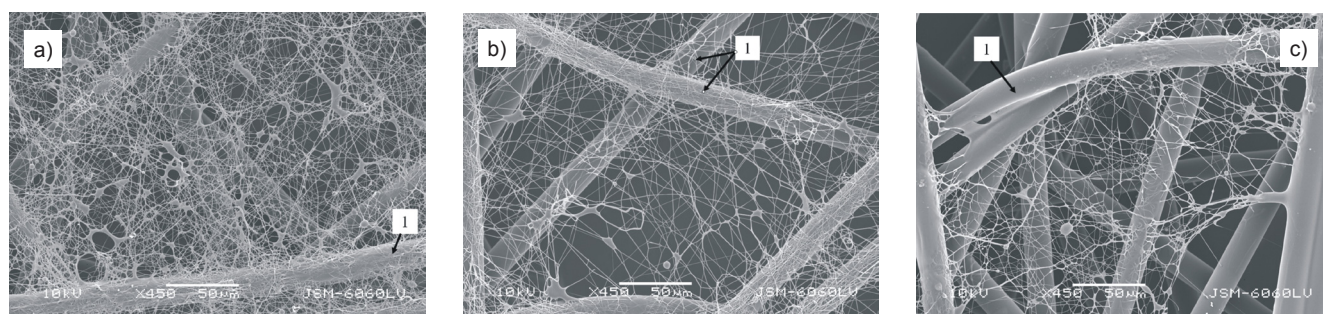

Figure 3. *SEM images of webs from PVA/CS nanofibres with a weight ratio of a) 95/5 and b) 90/10. c) SEM image of web from PVA/hCS (90/10) nanofibres; the distance between electrodes l=11 cm, applied voltage U=70 kV (number 1 indicates a filament of the support material).*
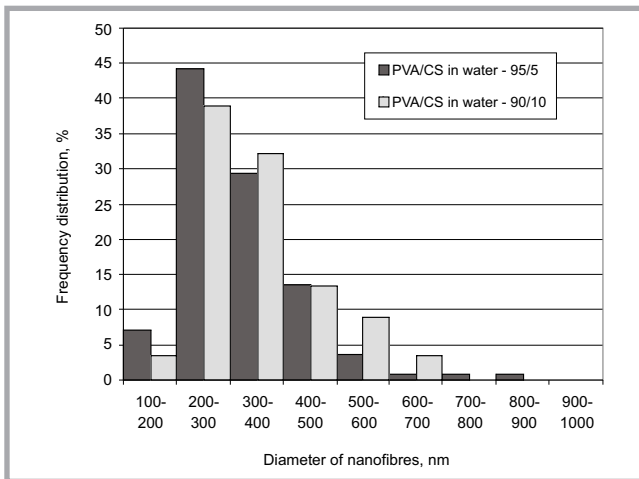
Figure 4. *Distribution of the diameter of PVA/CS nanofibres with a weight ratio of 95/5 and 90/10.*
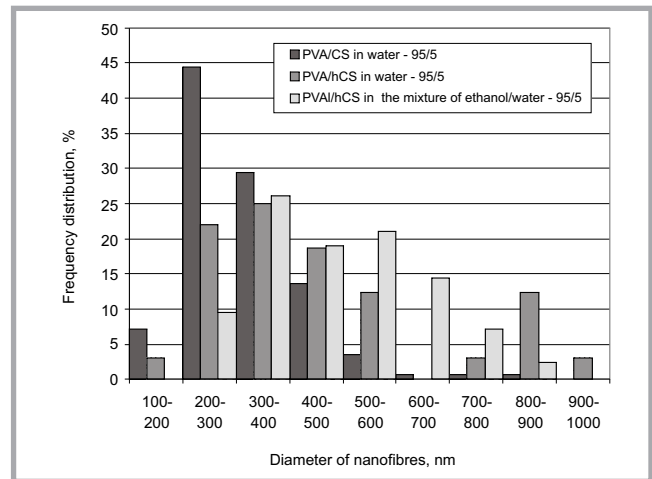

Figure 5. *Distribution of the diameter of nanofibres from PVA/CS, PVA/hCS in water and PVA /hCS in a mixture of ethanol/water with a weight ratio of 95/5.*

The attempt to form nanofibres from PVA/hCS polymer solution with a weight ratio of 85/15 was not successful; also it was not possible to form nanofibres at a larger distance between electrodes (14 cm).

The average nanofibre diameter from PVA/CS and PVA/hCS with a weight ratio of 95/5 are $\bar{d}$ = 320 nm and $\bar{d}$ = 440 nm, respectively. From *Figure 5* it is possible to see that almost 45 % of all measured nanofibres formed from PVA/CS solution are 200-300 nm in diameter. In the case of PVA/hCS (95/5), only 22% of nanofibres are 200 - 300 nm in diameter. The difference between the viscosities of the polymer solutions analysed is not significant. Therefore, to propose that thicker nanofibres are formed from PVA/hCS solution would not be correct. Such experimental results are possible to explain in this way: it is easier to form nanofibres from PVA/hCS solution due to better distribution of hCS macromolecules in the solution. Many more Taylors cones are created on the rotating drum from PVA/hCS solution than from PVA/CS. Consequently, far more nanofibres are formed, and as they move to the upper electrode, more nanofibres stick to each other due the small distance between electrodes. In this study all derivatives of nanofibres (single, stick) from every SEM image were evaluated. There are more stick nanofibres in the web from PVA/hCS solution, although the average PVA/hCS nanofibre diameter is bigger.

There is no difference between the average nanofibre diameter for PVA/CS ($\bar{d}$ =340 nm) and PVA/hCS ($\bar{d}$ =336 nm) solutions with a weight ratio of 90/10. To compare this case is difficult because of the bad spinability of PVA/CS solution

(in this case it was possible to form a thin layer of nanofibres only on the edges of the substratum material). However, analysing the SEM images (*Figure 6.b* and *6.c*), it is possible to see that there are also more stick nanofibres in the web from PVA/hCS solution.

Influence of ethanol on the electrospinability of bicomponent polymer solution

It is well known that when a nanofibre moves to the collector it elongates, the solvent evaporates, and a stiff nanofibre appears on the substratum material. In order to get a web of uniform, non- stick nanofibres, it was decided to used ethanol, due its very quick evaporation. Using ethanol, it was possible to form nanofibres even when the content of hCS in the solutions was 15% & 25% and the distance between electrodes was 14 cm, which was not possible to achieve during other experiments (*Table 2*).

All the width of the substratum material was covered by a layer of nanofibres when the weight ratio of PVA/hCS in the water/ethanol mixture was 95/5, 90/10 and 85/15. In the case of the electrospun solution with a weight ratio of 75/25, only the edges of the substratum material were covered by nanofibres.

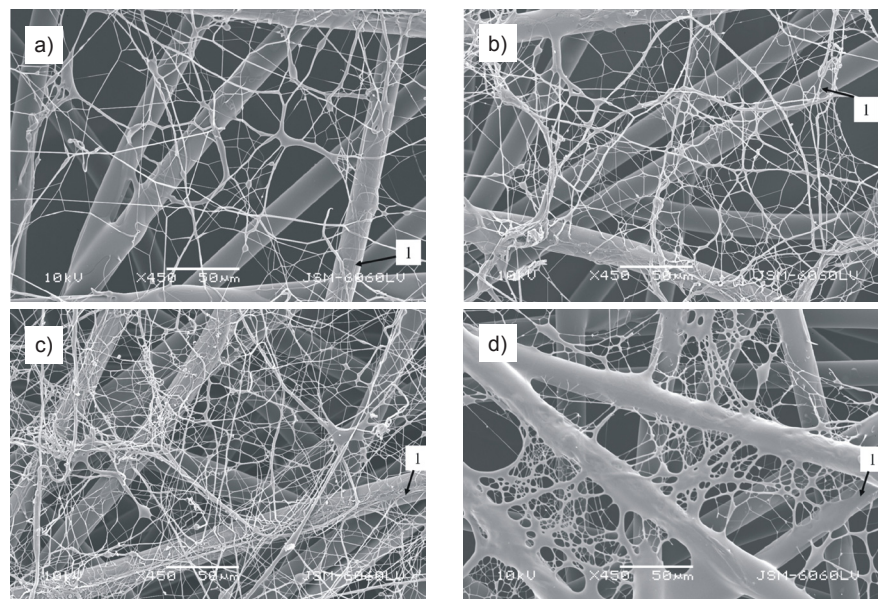From the dates presented in *Table 1*, it is possible to see that the conductivity of

Figure 6. *SEM images of webs of nanofibres from PVA/hCS in a mixture of ethanol/water with a weight ratio of a) 95/5 b)90/10 c) 85/15, d) 75/25. The distance between electrodes is l=11 cm, and the applied voltage U =50 kV (number 1 indicates a filament of the support material).*
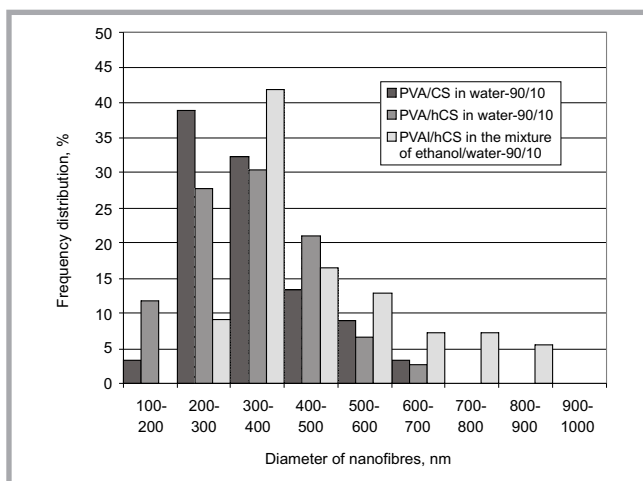
solutions with ethanol is 60 % lower and the viscosity 40-50 % higher than those of PVA/hCS solutions with the same content of hCS. Analyzing the SEM images (***Figure 3, 6***) of nanofibre webs from PVA/hCS and PVA/hCS in the water/ethanol mixture solutions, it is possible to notice that the structure of webs formed is very similar; in both cases there are a lot of nanofibres stuck together. The average nanofibre diameter for PVA/hCS from water solution and PVA/hCS from ethanol/water solution with a weight ratio of 95/5 are $\overline{d} = 440$ nm and $\overline{d} = 532$ nm, respectively. In both cases 25% of all nanofibres measured are 300 - 400 nm in diameter (***Figure 7***). The average diameter of nanofibres from PVA/hCS with a weight ratio of 90/10 from water and ethanol/water mixture solutions are $\overline{d} = 336$ nm and $\overline{d} = 476$ nm, respectively. In this case the majority of nanofibres are 300-400 nm in diameter. Hence it is possible to make nanofibres with a bigger content of hCS in the solution using ethanol. Due to the higher viscosity of the PVA/hCS water/ethanol solution, thicker nanofibres were formed; consequently, the average nanofibre diameter is higher.

■ Conclusions

■ CS has branchy polyelectrolytical swellable macromolecules, and it may be the main reason why to form nanofibres by electrospinning process from CS solution is not possible.

■ Analysing the electrospinability and morphology of nanofibres from PVA/CS solution, it was noted that the content of CS in the solution is 10%, which worsens the elecrospinning process. In this case nanofibres

are formed only on the edges of the lower electrode, i.e. it is not possible to cover all the width of the substratum material by a web of nanofibres. The content of CS in the solution does not have an influence on the diameter of nanofibres formed.

■ During the homogenisation procedure for the solutions, CS microgels were destroyed. Due to this, it was possible to cover all the width of the substratum material with a layer of PVA/hCS nanofibres, where CS composes 10% of the homogenised solution. Comparing the morphology of nanofibres from PVA/CS and PVA/hCS solutions with a weight ratio 95/5, it was noted that fewer nanofibres appear stuck together in webs formed from PVA/CS solution. Because many more nanofibres are formed during the electrospinning of PVA/hCS solutions, they stick to each other as they move towards the upper electrode. Homogenised CS solution improves the electrospinning process but worsens the structure of webs formed.

■ The use of ethanol in polymer solution improves the electrospinning process. From PVA/hCS in a water/ethanol mixture, it was possible to form nanofibres even when 25% of the fibre material was composed of CS. However, due to the higher viscosity of this polymer solution, much thicker nanofibres were formed.

■ The optimum solution of those analysed is PVA /hCS (weight ratio 85/15) in a water/ethanol mixture. With this solution it is possible to form a smooth layer of nanofibres throughout the width of the support material, with starch, i.e. 15%, being the biggest in-

gredient in the polymer mixture. The possibilities of eliminating stick nanofibres in a web of nanofibres from this polymer solution will be analysed in further works. □

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