

Erika Adomavičiūtė,
Rimvydas Milašius

The Influence of Applied Voltage on Poly(vinyl alcohol) (PVA) Nanofibre Diameter

Kaunas University of Technology,
Faculty of Design and Technologies,
Department of Textile Technology,
Studentu 56, LT-51424 Kaunas, Lithuania
E-mail: erika.adomaviciute@stud.ktu.lt
rimvydas.milasius@ktu.lt

Abstract

Nowadays the electrospinning process is being widely investigated due to huge interest in nanotechnology science, but this process still has not been fully explained. So far there has been no general agreement amongst researchers about the influence of the main technological parameter – the influence of voltage applied on the diameter of manufactured nanofibres. In this study nanofibres were manufactured using the electrospinning method for a 12% concentration solution of poly(vinyl alcohol) (PVA) water solution. Two sets of experiments were performed in order to evaluate the influence of the voltage applied on the PVA nanofibre diameters. In the first case nanofibres were collected on a PES substratum, in the second – on a PP substratum. Next, the average nanofibre diameter was calculated from all derivatives of the nanofibres and only from the thinnest nanofibres. It was estimated, that the voltage applied does not have a noticeable influence on the diameter of the manufactured nanofibres. Only the structure consisting of nanofibre mats was influenced by the change in voltage.

Key words: electrospinning, nanofibre, applied voltage.

Introduction

Electrospinning is one of the most popular techniques for manufacturing nanofibres. In this process a high voltage is used to create an electrically charged jet of polymer solution or melt. In the space between the capillarity tip and collector, the jet becomes unstable and a rapid whipping of the jet follows. This leads to evaporation of the solvent, leaving a polymer behind. The polymer undergoes stretching and at the same time thinning as a result of whipping, and finally fibres are collected on a grounded collector as a randomly oriented web of micro- or nanofibres [1 - 4]. Current research mostly focuses on the structure and morphology of nanofibres manufactured by electrospinning. Generally, the dependences of nanofibres structure on polymer solutions parameters, such as concentration, molecular weight, surface tension, viscosity, conductivity, governing parameters, such as applied voltage, and the distance between electrodes are being analysed [5 - 17].

It is important to have control over the fibre diameter which is a function of material and process parameters. Despite the relatively early introduction of the electrospinning process, the effect of the process and material parameters on fibre formation is still under theoretical and experimental investigation [12]. There is no common agreement on the effect of applied voltage on the diameter of nanofibres [8, 13 - 17]. There are a lot of works published in which the influence of applied voltage on the electrospinning

process and nanofibre diameter is analysed. But conclusions in these studies are different. Gu et al. [8] reported that fibre diameter did not significantly change by altering the voltage applied. Mo et al. [13] and Heikkilä et al. [14] concluded that nanofibre diameter tends to decrease with an increase in the voltage applied. Contrary to this, from the results obtained by Zhang et al. [11] he himself noticed that there was a slight increase in the average diameter of PVA nanofibres with an increase of the electric field applied. Yördem et al. [16] reported that voltage influences fibre diameter, but at a different level of significance depending on the polymer solution concentration and on the distance between the electrode and the collector. According to Gu et al. [8] such inconsistency may be caused by the difference in experimental conditions. So, electrospinning equipment, type of polymer solution, experimental conditions, all these rates have a significant influence on the nanofibre forming process and the final product.

The aim of this study is to show that the method of calculating nanofibre diameter has a significant effect on conclusions made after analysing the influence of applied voltage on the diameter of PVA nanofibres.

It should be emphasized that the dependencies identified are valid firstly for the equipment used and the conditions applied

Experimental

Preparation of polymer solution

A 16 wt% PVA (molecular weight - 70.000 g/mol, degree of hydrolysis 88%) solution was diluted with distilled water in order to prepare a 12 wt% PVA solution. To improve the conductivity of the PVA solution prepared, 0.5 % of phosphoric acid was added.

Electrospinning equipment

The substratum material was covered by a layer of PVA nanofibres using “Nanospider™” equipment (Elmarco, Czech Republic) [18]. This method of nanofibre production was developed at Technical University of Liberec and patented [19]. As opposed to other electrospinning equipment, in “Nanospider™” a rotating drum, partially immersed in a polymer solution, is used instead of a set of needles having capillaries (Figure 1). The main advantage of this electrospinning technology is the significant increase in the production capacity of nanofibres.

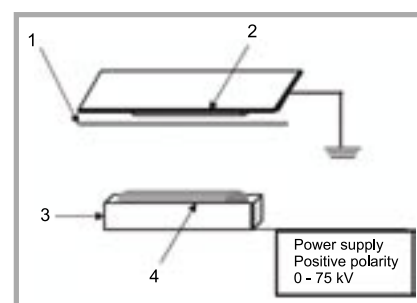


Figure 1. Principal schema of “Nanospider™”; 1) substratum material, 2) electrode, 3) tray with polymer solution, 4) rotating drum.

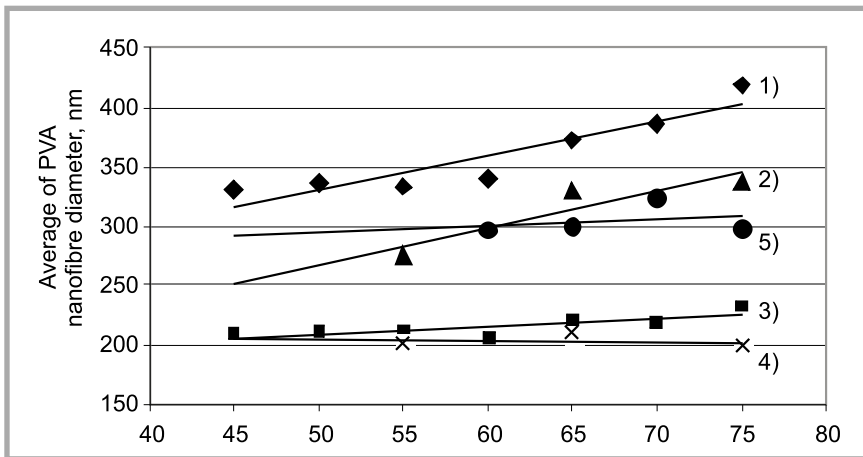


Figure 2. The dependence of the average value of PVA nanofibre diameter upon applied voltage. The nanofibres were collected on substratum materials from PES and PP, at different distances between the electrodes and using two different measuring methods. To the PES substratum are related the dependencies 1, 2, 3 and 4, to the PP substratum the dependency 5. The distance of 11 cm concerns the runs 1 and 3, the distance of 13 cm concerns the runs 2, 4 and 5. Only the thinnest 20 nanofibres collected were measured for the dependencies 3 and 4, whereas all monofibres collected were measured for the dependencies, as well as, for 5 (but here any sticked fibres were identified).

The rotating drum was covered by a film of polymer solution. Increasing the applied voltage between the electrodes, i.e. increasing the electrostatic forces, we cause, that first of all, the hemispherical drops are formed on the rotating drum. A further increase in the applied voltage caused the formation of Taylor cones from the hemispherical drops. Only when the electrostatic force overcame the polymer's surface tension, a jet of polymer solution was ejected from the Taylor cone. The jet moved toward the upper electrode and was deposited on the substratum material. Meanwhile, nanofibre became thinner, the solvent evaporated and then solidified.

In all the experiments such equipment parameters as the drum rotary speed, the speed of feed support material were the same, except applied voltage, distance between electrodes and support material. During all the experiments carried out the temperature of the electrospinning environment was $t = 21 \pm 2 \text{ }^\circ\text{C}$ and humidity $\gamma = 42 \pm 2\%$.

Characterisation techniques

The structure of PVA nanofibres mats was determined using a JOEL 5600 scanning electron microscope (SEM). The diameter of PVA nanofibres was measured using an image analysis system LUCIA 5.0.

Results and discussion

In our previous study [17] we analysed the effect of applied voltage on the di-

ameter of nanofibres spun from 12 wt% PVA polymer solution. The nanofibres were collected on PES spunbonded nonwoven. In order to calculate an average value of PVA nanofibres diameter in the usual way, the diameter of all nanofibres from every SEM image was measured. Analysing the results, we estimated that the average value of nanofibre diameter increased with an increase in voltage. The main part of the experiment was done when the distance between the electrodes was 11 cm, the applied voltage was changed every 5 kV from 45 kV to 75 kV (Figure 2, curve 1). With an increase in the voltage applied, the average value of nanofibre diameter increased by 25% (average relative error $\delta = 12\%$, at confidence level $t_{\alpha} = 95\%$). When the distance between the electrodes was 13 cm, the voltage applied was increased from 55 kV to 75 kV (Figure 2, curve 2), and the average value of nanofibre diameter increased by 18% ($\delta = 10\%$). However, while analysing the structure of PVA nanofibre mats on the PES substratum, we observed that the increase in applied voltage caused an increase in the amount of stick nanofibres (Figure 3.1), which subsequently causes an increase in the average value of the diameter of PVA nanofibres (all derivatives of nanofibres secondary formed were measured). We assumed that if the aim of the research was to define the distribution of nanofibre diameter on substratum, then all derivatives of nanofibre – single and stick nanofibres – should be measured (Figure 3). But

if one is interested in the technological process of nanofibre manufacture, such a method is not informative. The reason is that in such a case it is possible to know what the diameters of nanofibres layered on a substratum material are, but not what the diameter of nanofibres formed via electrospinning process directly from rotating drum is. When there are a lot of stick nanofibres on substratum material, and a researcher is not interested in the structure of the mat, but in the characteristics of manufactured nanofibres, it is better not to measure all nanofibres, but only their ones, i.e., eliminate all stick nanofibres which are much thicker than most nanofibres.

In Figure 2 dependences of nanofibre diameter upon applied voltage are presented. We can identify two characteristic groups of dependencies. The first group of runs with moderate slopes includes the dependencies 1 and 2 obtained for the PES substratum (at 11 mm and 13 mm distance between the electrodes) when the diameter of all fibres and sticked fibre derivatives was measured.

The second group of that dependencies includes the runs 3 and 4 taken at similar

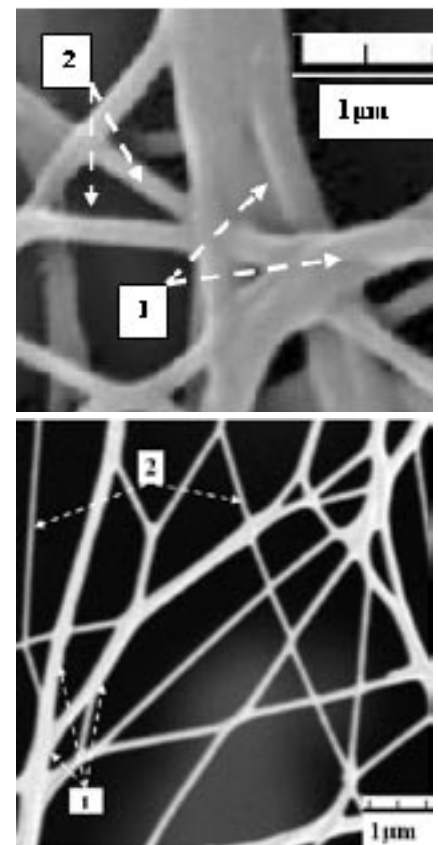


Figure 3. SEM images of mat from nanofibres, number 1 indicate stick nanofibres, 2 indicate single nanofibre.

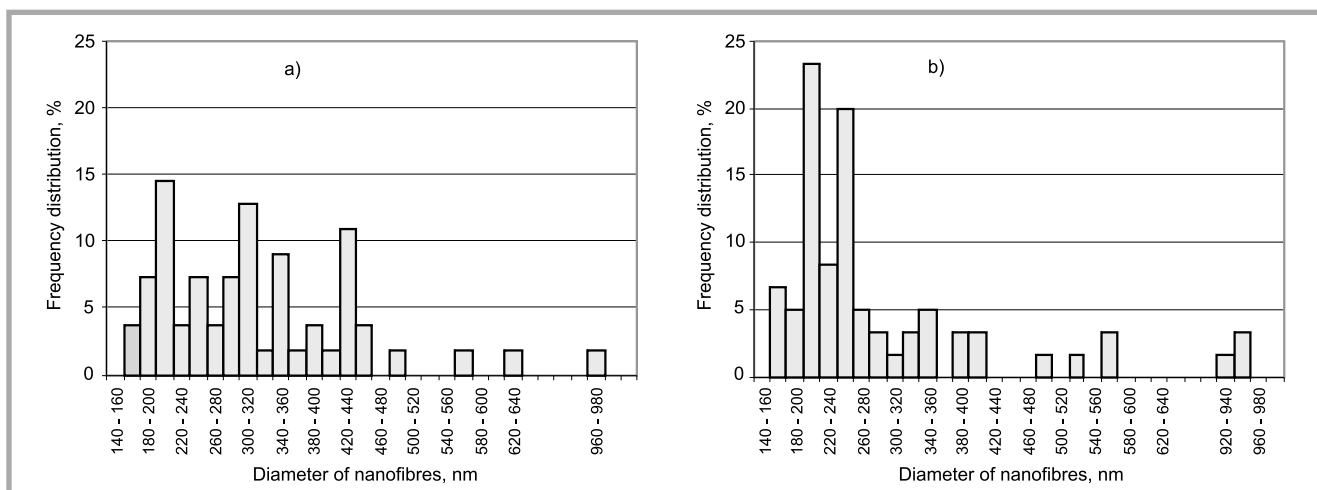


Figure 4. PVA nanofibres collected on: a) PES substratum and b) PP substratum diameter distribution.

conditions as dependencies 1 and 2 but while the diameter of only the 20 thinnest fibres was measured, as well as the dependency 5 obtained while measuring the diameter of all fibres, but collected on a PP substratum when no stuck fibres were observed.

The above-mentioned dependencies allow to state that the increase in applied voltage causes an increase in the amount of stick nanofibres. But an increase in the applied voltage does not have an influence on the diameter of thinnest PVA nanofibres. Thus it is possible to conclude that an increase in applied voltage does not significantly influence nanofibre diameter at the moment when they are formed, but has an influence on the structure of nanofibre mat i.e., on the amount of stick nanofibres.

It is obvious that stick nanofibres are considered as a defect of the electrospinning process. There might be several reasons that cause the formation of stick nanofibres: a too high concentration of polymer solution, too small distance between electrodes (the solvent does not have time to evaporate and, consequently, nanofibres that cover substratum material stick to each other), not suitable substratum material for electrospinning, etc.

For further research we have chosen substratum material – a spunbond web of PP filaments. The thickness and area density of the spunbonds of PES and PP filaments were the same. From curve 5 Figure 2, we can see that the increase in applied voltage (from 60 kV to 75 kV) does not influence the PVA nanofibre diameter, even when all nanofibres from every SEM image were measured. When analysing the structure of PVA nanofibre

mat, it was noticed that there are much more single nanofibres collected on the PP spunbond web and that is why the diameter of nanofibres almost does not change while changing the applied voltage.

In Figure 4 the distribution of the nanofibre diameters of fibres collected on two different substratums is presented; in both cases the diameters of all nanofibres from every SEM image were measured. There are few peaks in the histogram (Figure 4.a) of PVA nanofibres collected on the PES substratum, when the interval of nanofibre diameters varies between (i) 200 - 220 nm, frequency distribution $w=14.55\%$, (ii) 300 - 320 nm, $w=12.73\%$, (iii) 420 - 440 nm, $w = 10.91\%$. Such a type of mathematical statistical distribution of the results is not known. Therefore it is possible to assumed that thicker nanofibres are formed due to the influence of some additional factors, i.e., much thicker nanofibres are formed not directly from the rotating drum, but later, when they are moving to the upper electrode. From the histogram presented in Figure 4.b, we can see that there are two peaks: (i) when the interval of PVA nanofibres diameter 200 - 220 nm, $w = 23.33\%$, and (ii) 240 - 260 nm, $w = 20\%$. Values of these peak diameters are very close and can be treated as one peak. Such a distribution of results is very close to the well known χ^2 or log normal distribution. It means that nanofibres of such diameters can be directly formed on the rotating drum. In this case there are no stick nanofibres collected on PP spunbond, consequently there are not so many peaks in the histogram. From all these results, we can say that at 13 cm distance between electrodes with an applied voltage of 75 kV, from 12% concentration of PVA solution, mostly nanofibres

whose diameters vary within the range of 200 - 260 nm are formed. If it is possible to create such experimental conditions, which do not let nanofibres stick, the substratum material will be covered by nanofibres of near similar diameter, even when the applied voltage is high.

Hence this study can partially explain why different researchers analysing the influence of the same factor on nanofibrous structure present quite different conclusions. The electrospinning process is very sensitive and may depend on insignificant change in experimental conditions. The influence of the substratum material on the character of nanofibres spun by electrospinning from a rotating drum observed by us, should be the subject of further investigations.

Conclusions

1. According to the aim of the research work carried out, the measurement of nanofibre diameter methodology should be chosen. If the electrospinning process is being investigated, stick nanofibres should be eliminated from the measurements. Whereas if the structure of the final product is being investigated, all, both single and stick nanofibres, should be taken into account.
2. Applied voltage does not have a significant influence on the diameter of PVA nanofibres formed directly from a rotating drum. It only influences the structure of nanofibre mat, i.e., an increase in the applied voltage causes an increase in the amount of nanofibres. After the elimination of stick nanofibres on the PES substratum, it was indicated that voltage applied does not have a significant influence on

the nanofibre formation process. The same was stated when analysing the diameter of nanofibres collected on the PP substratum; in this case all nanofibres were measured, because any stick nanofibres were visible on the substratum. Thus the elimination of stick nanofibres is a proper method for analysing the nanofibre formation process. It is possible to reduce the proclivity of nanofibres to stick via the exchange of substratum material.

3. When the applied voltage is 75 kV and the distance between electrodes is 13 cm, from a 12% wt PVA solution, mostly nanofibres of 200-260 nm diameters are formed.



References

1. Lu C., Chen P., Li J., Zhang Y.; *Polymer* Vol. 47(2006) pp. 915-921.
2. Smit E., Büttner U., Sanderson R. D.; *Polymer* Vol. 46(2005) pp. 2419-2433.
3. Tomaszewski W., Szadkowski M.; *Fibres & Textiles in Eastern Europe*, Vol. 13(2005) No. 4(52), pp. 22-26.
4. Blasińska A., Krucińska I., Chrzanowski M.; *Fibres & Textiles in Eastern Europe*, Vol. 12(2004) No. 4(48) pp. 51-55.
5. Shenoy S. L., Bates W. D., Frisch H. L., Wnek G. E.; *Polymer* Vol. 46(2005) pp. 3372-3384.
6. Theron S. A., Zussmann E., Yarin A. L.; *Polymer* Vol. 45(2004) pp. 2017-2030.
7. Deitzel J. M., Kleinmeyer J., Harris D., Beck Tan N. C.; *Polymer* Vol. 42(2001) pp. 261-272.
8. Gu S. Y., Ren J., Vancso G. J.; *Eur. Polym. J.*, Vol. 41(2005) pp. 2559-2569.
9. Tao J., Shivkumar S.; *Materials Letters*, 2006. doi:10.1016/j.matlet.2006.09.04
10. Koski A., Yim S., Shivkumar S.; *Materials Letters*, 2004, 58, pp. 493-497.
11. Zhang C., Yuan X., Wu L., Han Y., Sheng J.; *Eur. Polym. J.* Vol. 41(2005) pp. 423-432.
12. Zhang W., Yan E., Huang Z., Wang C., Xin Y., Zhao Q., Tong Y.; *Eur. Polym. J.*, 2007, doi:10.1016/j.eurpolymj.2006.11.015.
13. Mo, X.M., Xu, C.Y., Kotaki, M., Ramakrishna, S.; *Biomaterials*, Vol. 25(2004) pp. 1883-1890.
14. Heikkilä P., Harlin A., Söderlund L., Uusimäki J., Kettunen L. Autex 2007 From Emerging Innovations to Global Business 7th Annual Textile Conference by Autex, PROCEEDINGS, 26-28 June 2007, Tampere, Finland.
15. Demir, M.M., Yilgor, I., Yilgor, E., Erman, B.; *Polymer*, Vol. 43(2002) pp. 3303-3309.
16. Yördem O.S., Papila M., Menciloğlu, Y.Z. *Materials and Design*, 2006, doi:10.1016/j.matdes.2006.12.013.
17. Adomavičiūtė E., Milašius R., Levinskas R.; *Materials Science (Medžiagotyra)*, Vol. 13(2007) pp.152-155.
18. <http://www.elmarco.com>
19. Jirsak O.: CZ Patent, 2003-2414 (294274).

Received 15.11.2007 Reviewed 15.01.2008

**INVESTING YOUR
CAPITAL IN ŁÓDŹ
INDUSTRY YOU
NOT ONLY HAVE
ACCESS TO
THE LARGE POLISH
MARKET; YOU ALSO
ENTER THE TEXTILE
AND CLOTHING
BASE OF EUROPE
AND YOU CAN
EASILY ADVANCE
TO THE EASTERN
MARKET**

FIBRES & TEXTILES in Eastern Europe



reaches all corners of the world !
It pays to advertise your products
and services in our magazine !
We'll gladly assist you in placing
your ads.