

Research Article

Investigation and Estimation of Structure of Web from Electrospun Nanofibres

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During the electrospinning process the web of nanofibres is manufactured by means of electrostatic forces between two electrodes. The diameters of nanofibres usually differ and they depend on various parameters. The different fineness of fibres influences the structure of the web and herewith the end-use properties of such kind of nanomaterial. Analysis of nanofibres diameters distribution also shows big differences; even more, the distributions are not spread along the normal distribution. Understanding the influence of electrospinning parameters and the reason why the shapes of distributions are so sophisticated is very important. The goal of this paper is to analyse the distribution of diameter and to propose the new criterion for nanofibres diameter comparison and web of nanofibres estimation. In this paper the influence of covering time of support material on structure of PA6.6 nanofibre web has been investigated. It was estimated that this parameter does not have a significant influence on the average diameter of nanofibres, and only the structure of web has been influenced by the changes in covering time. According to the results provided the phenomena of nanofibres sticking on the support material at the time of electrospinning can be proved and explained.

1. Introduction

Electrospinning is one of the most common processes used for nonwovens production. The diameters of electrospun fibres diameter may range from 10 nm to 1500 nm [1]. It has been discovered that the diameter of nanofibres and the final properties of the produced nonwovens depend on type of polymer, solution properties (viscosity, conductivity, surface tension, etc.), applied voltage, distance between electrodes, coating time of support material, air humidity, and temperature [2–5]. The diameter of the fibre is arguably the most important factor for determining the quality of nonwoven structure. So, it is very important to understand how the diameter of fibre and its distribution is affected by various parameters [6].

There are a lot of studies analyzing the influence of various parameters on nonwoven structure. The analysis of such studies shows that in some cases the different researches, analyzing the influence of the same factor on the structure of nanofibres, obtain different results. The reasons of different conclusions can be explained in several ways. According to

one of them, in some cases the authors do not analyze the dispersions of nanofibres diameter. The other reason—quite often the authors skip the description of the main parameters which may have a significant influence on nonwoven structure. It is possible that the mismatches of the results occur because of the lack of common methodology for nanofiber diameter characterization.

While analyzing the literature sources we noticed that the measurements of nanofibres diameter are distributed in unclear distribution and the shapes of all distributions always differ. Ellison et al., Tsimpliaraki et al., and Gu et al. [7–9] state that the measurements of nanofibres diameter are distributed by log normal distribution. Dosunmu et al. [10] states that distribution of electrospun nanofibres could be well fitted as normal distribution in log normal scale. But log normal distribution does not have the theoretical background in electrospinning process, because this process does not depend on the time and all nanofibers in the web are being manufactured simultaneously. Usually the values of fibres diameter of various textile materials are distributed by normal distribution [11]. But sometimes the

shapes of the distributions of nanofibres diameter are not similar to this one.

It is impossible to compare the average values when dispersions of diameter are different, so it is absolutely wrong way to estimate the web of nanofibres, in order to compare parameters having different kinds of distribution. According to mathematical statistic point the average value of nanofibres diameter (if they are distributed in not normal distribution) cannot characterize the nanofibres precisely, because changes in average values do not suppose changes in modal value and other characteristics. It means that in order to compare the diameter of nanofibres with an average value it is necessary to use the other characteristics too.

In our previous study [12] the similarity of empirical distribution of nanofibres diameters to the compound distribution, consisting of several normal distributions, has been noticed. The compound distribution is a characteristic of blended spun yarns, received from several kinds of fibres. It means that the web of nanofibres consists from nanofibres of different diameter. There is no single opinion about the reasons of this phenomenon. It is possible that the web of nanofibres forms when nanofibres in the distance from Taylor cone to the other electrode do not separate completely. Although the possibility also exists that the web of several kinds of fibres forms depending on the sticking of nanofibres at the time when they are moved to other electrode. The goal of this paper is to analyse the dispersion of nanofibres diameter and to check the hypothesis about the possibility of the sticking of several nanofibres.

2. Method of Distribution Calculation

In our previous study [12] the method of dividing the compound distribution into several normal distributions had been presented. The first normal distribution was calculated using the following method: empirical values up to the modal value of the total distribution were set as the points of the left part of the first normal distribution. It has been considered that the diameter of nanofibres had been distributed in normal distribution, so the right part of the first normal distribution was marked as symmetrical points of the left side. The first normal distribution has been calculated according to the probability density. The left part of the second normal distribution has been calculated as a difference between empirical measurements and measurements calculated by the first normal distribution. The right part of empirical values and the second normal distribution have been calculated similarly as in the previous case. All normal distributions have been calculated using this method. Finally the compound distribution has been calculating by summarising the values of all normal distributions. The coefficient of determination confirmed the correlation of empirical curve with the compound distribution. This method can be used for dividing a compound distribution into several normal distributions.

The main disadvantage of this method is sophistication of compound distribution calculation. For this reason the short-cut method of the quality of nonwoven structure

estimation has been presented [13]. The short-cut method is more straightforward and is based on the modal value of empirical values. The points of the modal value of the empirical distribution are called the points of left part of the first normal distribution. It has been considered that diameter of nanofibres is distributed by normal distribution, and in the other side of modal value the symmetrical points were marked. The results calculated by both methods were identical.

The obtaining of compound distribution confirms that the web of nanofibres at the electrospinning process consists of different kinds of nanofibres.

3. Material and Methods

An 8% solution of PA6.6 in 85% formic acid was gently stirred at ambient temperature for 12 hours until the polymer granules dissolved completely. The nonwoven web from PA6.6 nanofibres had been formed using the electrospinning equipment "Nanospider" (Figure 1). The principle of this equipment includes the rotating roller which is submerged in a bath filled with polymer solution. The Taylor cones with increasing electrostatic forces are formed on the rotating roller. When electrostatic forces overcome the surface tension, a jet of polymer solution is ejected from the Taylor cone and it is directed up to the support material [14]. During this experiment the electrode with narrower tines has been selected as it is easier to form PA6.6 nanofibres. The sufficiently powerful electric field is not formed by means of the cylindrical electrode; consequently the continuous flow of Taylor cones cannot be formed. According to the electric field theory, the major supply of electric charge has been collected on the top of tines, where the surface curvature is greater and the surface electric field density in these places is higher. As a result, the continuous flow of Taylor cones can be formed on the tines [15].

During all experiments, the ambient temperature was $T = 24 \pm 2^\circ\text{C}$, the humidity was $\phi = 50 \pm 2\%$. The distance between electrodes was 13 cm. The applied voltage was 70 kV. Experiment has been carried out by changing the duration of support material covering. The speed of support material was $v = 0.010$ m/s, the time of covering $t = 25$ s (indicate I); $v = 0.006$ m/s, $t = 41$ s (II); $v = 0.002$ m/s, $t = 125$ s (III).

The structure of received nanofibres web has been analyzed by Scanning Electron Microscopy (SEM)—SEM-FEI Quanta 200 (Netherlands). The value of diameter of PA6.6 nanofibres was measured from SEM images by LUCIA Image 5.0 programme, with an accuracy ± 0.01 nm. Nanofibres have been measured using the 5 different SEM images.

4. Results

Nanofibres have been manufactured from PA6.6 solution of 8% concentration. The first series of experiments were carried out at the speed of support material 0.010 m/s, the second 0.006 m/s, and the third 0.002 m/s. With decreasing in speed the covering time of support material increased from 25 s to 125 s. The influence of the speed (and herewith the

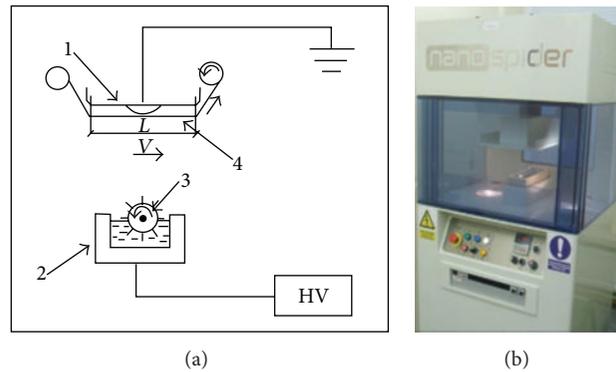


FIGURE 1: Principal scheme and photo of electrospinning technique “Nanospider”: 1: upper electrode, 2: bath with polymer solution, 3: rotating roller with tines, 4: support material, L : the distance of support material, which is covered with a layer of nanofibres (250 mm).

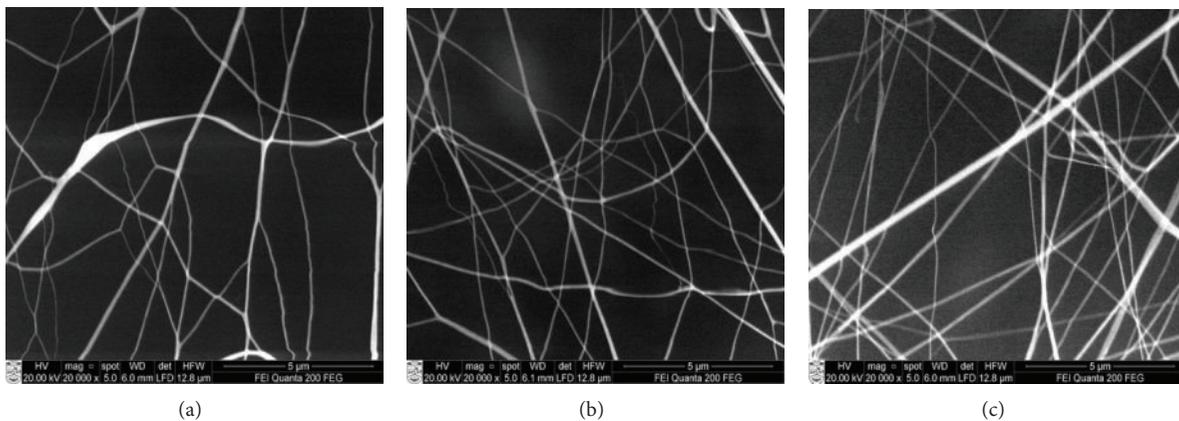


FIGURE 2: SEM images of electrospun PA6.6 mats when the speed of support material was (a) $v = 0.010$ m/s, $t = 25$ s (I); (b) $v = 0.006$ m/s, $t = 42$ s (II); (c) $v = 0.002$ m/s, $t = 125$ s (III).

covering time) of support material on PA6.6 nanofibres web morphology is presented in Figure 2.

As is seen from Figure 2, at the higher speed of support material fewer nanofibres cover it. During the tests the 5 SEM images for each variant of speed have been analysed. The 165 diameters of PA6.6 nanofibres for the I variant, 200 diameters of nanofibres for II variant, and 288 nanofibres for III variant were found and measured. The density of nanofibres was calculated by number of nanofibres in SEM images. The following density has been established—23 nanofibres for I variant, 29 nanofibres for II variant, and 42 nanofibres for III variant in $100 \mu\text{m}^2$. The results showed that the speed (also the covering time) of support material does not have significant influence on the average value of PA6.6 nanofibres diameter, as the difference is less than $\pm 3.5\%$ ($d_{\text{average}} = 357$ nm; II $d_{\text{average}} = 373$ nm; III $d_{\text{average}} = 382$ nm), while the density of fibres depends on the speed. That means that the structure of web needs a deeper analysis. In the next step of investigations the dispersions of PA6.6 nanofibres have been studied. The frequency distributions of all series of experiment are presented in Figure 3.

First of all Figure 3 demonstrates that the diameter of nanofibres in all cases is distributed in different distributions.

In histogram which is presented in Figure 3(c) only one peak of distribution when the diameter of nanofibres is around 350 nm is observed. It is evident that this value is the modal value of this distribution too. Therefore we can make the assumption that this distribution is very close to normal distribution, because the average value is 382 nm. In the histogram presented in Figure 3(a) two peaks are observed: the first peak is around 200 nm, while the second peak is around 300 nm. A similar view, the distribution with several peaks, may be observed in Figure 3(b): first peak is around 200 nm, the second around 300 nm, and the third 400 nm. In Figure 4 more comprehensive analysis of measurements dispersion of I variant is presented—the interval of nanofibre diameter is distributed not by 50 nm as in Figure 3, but by 25 nm. As is seen from Figure 4 it is evident that the histogram really has not one peak—the first peak is around 212.5 nm, the second—around 312.5 nm. So, values are distributed not by normal but by compound distribution from several normal distributions.

According to the results it is possible to assume that at the lowest speed of support material, the thicker nanofibres were formed and at the higher speed the thinner nanofibres were formed.

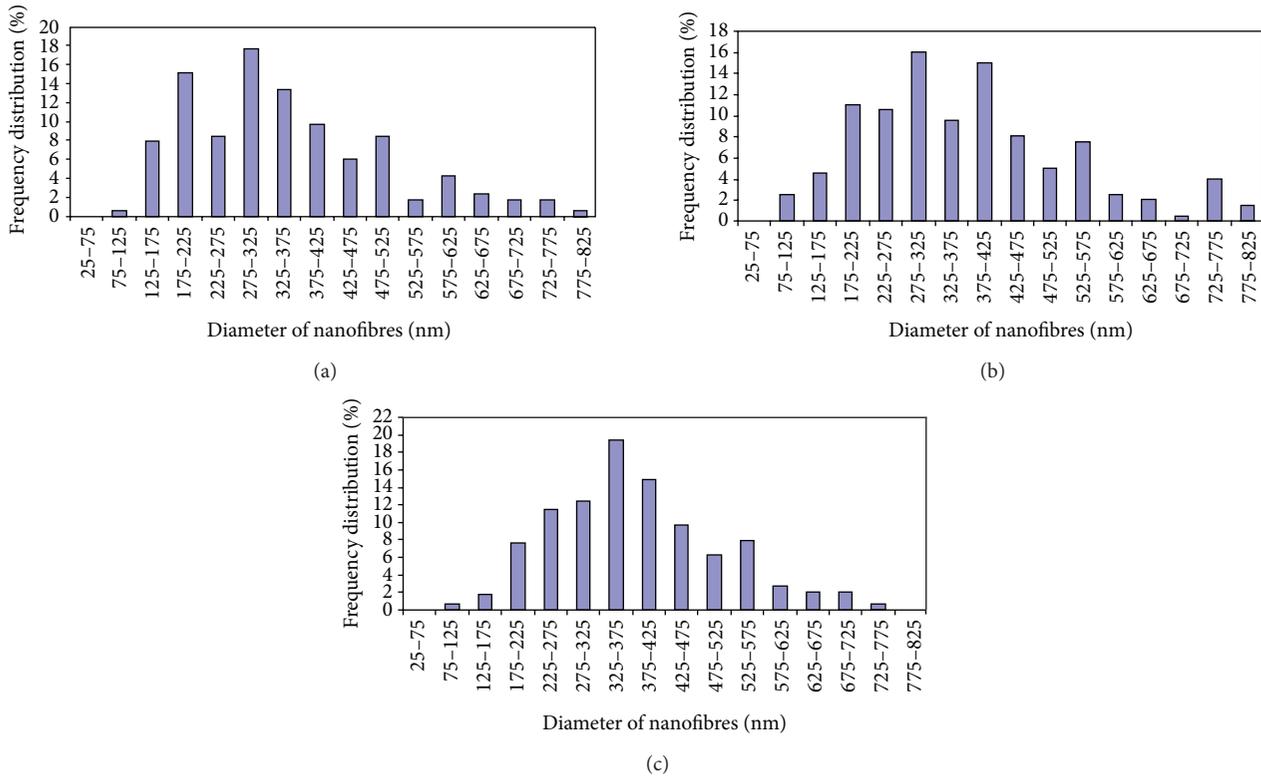


FIGURE 3: Distributions of PA6.6 nanofibres during the experiment: (a) $v = 0.010$ m/s, $t = 25$ s (I); (b) $v = 0.006$ m/s, $t = 42$ s (II); (c) $v = 0.002$ m/s, $t = 125$ s (III).

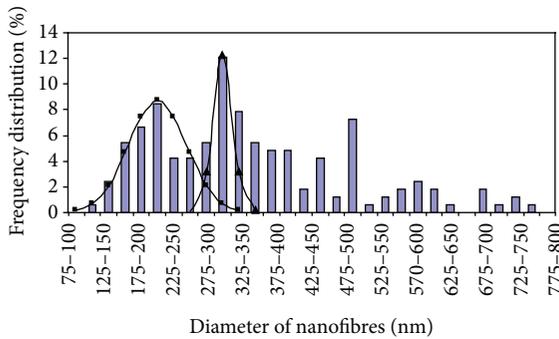


FIGURE 4: Detailed distributions of the results of the I variant.

In previous work [12] it was proved that in the case when the diameter of nanofibres is distributed in compound distribution from several normal distributions, the modal value of the first distribution and the percentage quantity of measurements of the first distribution can be used as a criterion of nanofibres diameter and measurement dispersion estimation. The more the percentage increases, the more unique the structure of the web obtained as well. Using this method we can determine the influence of covering speed (the covering time too) on the structure of manufactured web.

The following results have been received using the histograms presented in Figure 3. As is seen, in the variant I mostly single and no stucked nanofibres had been formed. The percentage quantity of nanofibres distributed in the first

distribution is 32.2%. As in the II variant the quantity of nanofibres distributed in the first distribution has been just 24.04%. It means that in this case less single nanofibres were formed. The modal value of the first distribution in both cases is 200 nm. In this work the new criterion is proposed for estimation of web structure. This criterion may conclude the average of two values—modal values and value of the second highest peak, and it can be calculated using the formula: $d' = (d_{\text{modal}} + d_{2\text{modal}})/2$ (where d_{modal} is the modal value of all distribution; $d_{2\text{modal}}$ is the second value, close to modal value of this distribution). During the analysis of the results, we noticed that the diameter d' decreased along with a speed of support material increase. Using the histograms in Figure 3 the following data has been calculated: (III) $d' = 375$ nm; (II) $d' = 350$ nm; (I) $d' = 250$ nm. It means that thinner fibres are formed at a higher speed (lower time).

The next stage of our investigation has been aimed to check the hypothesis that the web from different diameter of nanofibres forms from single nanofibres which stick together on the support material. It is known that the surface area of cross-section of single nanofibre may be calculated using formula: $S_1 = (\pi d_1^2)/4$. A surface area of cross-section of stucked nanofibres makes $S_n = nS_1$. As a result, the diameter of stucked nanofibres is calculated using $d_n = d_1 \sqrt{n}$. So, if the modal value of the diameter of a single fibre is $d_{\text{modal}} = 200$ nm (see Figures 3(a) and 3(b)), the diameter of a double fibre would be about $d_2 = 283$ nm. As is seen from Figure 3(a), the second peak is when diameter of nanofibres is about $d_{2\text{emp}} = 300$ nm. The relative error in both

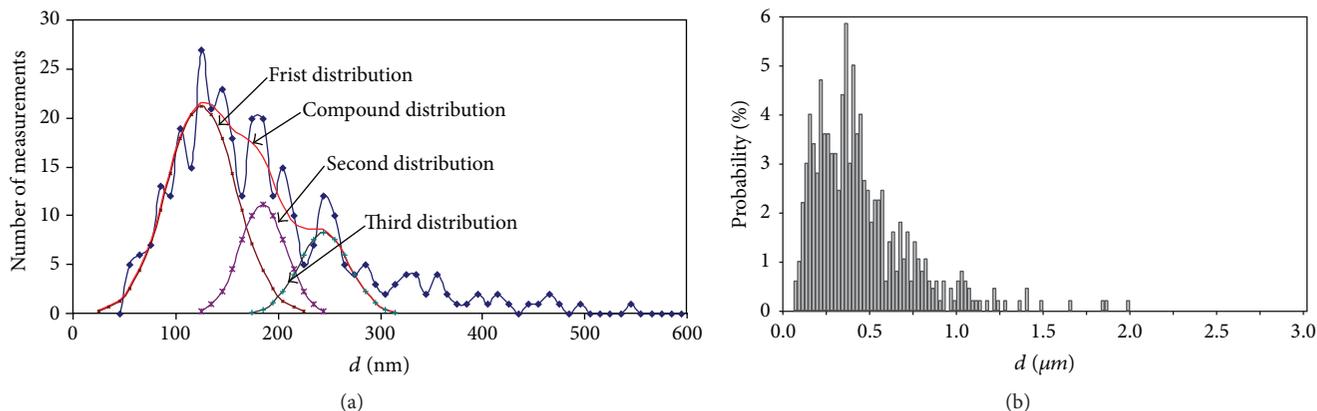


FIGURE 5: Fibre diameter distributions (a) from PVA [12]; (b) from PP [10].

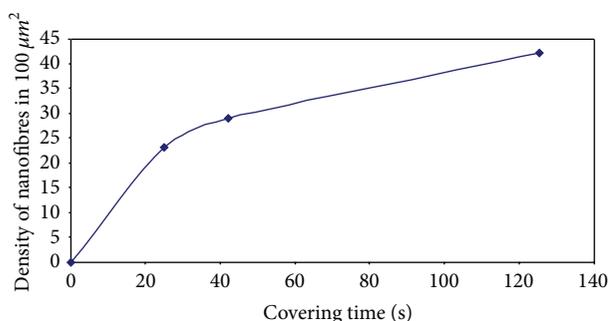


FIGURE 6: Dependence of the density of nanofibres (in $100 \mu\text{m}^2$) on the covering time.

cases is $\delta = 6\%$. The recurrent values of nanofibres diameter confirm the hypothesis about the sticking of nanofibres on the web. The similar conclusions about the sticking were approved in our previous work, when the structure of PVA web was analysed [12]. The histograms of this article (especially of Figures 3(a) and 3(b)) can be compared with histogram from literature sources as well [10] (Figure 5).

In this figure few peaks can be noticed as well. According to this data one can guess that these peaks appeared for the sticking of PP nanofibres on the web. It means that this problem is typical for the whole electrospinning process regardless of the type of polymer—the similar results can be observed with PA6.6, PVA, and PP nanofibres.

At the last step of this study, the dependence of the density of nanofibres (in $100 \mu\text{m}^2$) on the covering time is presented in Figure 6.

During the analysis of the data presented in Figure 6, it has been stated that during 1 second of the electrospinning process the support material is covered approximately by 1 nanofibre. According to this, we can state that as the covering time increases, the density of nanofibres should increase linearly. At the same time it is obvious that the curve in Figure 6 is not linear. It is very well visible that at the highest covering time there were not 120 nanofibres, just 42. That also confirms the phenomenon of fibres sticking on the support material. Such data make us sure that the covering time is a

very important parameter for the structure of nanofibre web, and, using the higher covering time, more stucked fibres are forming.

5. Conclusions

- (i) The distributions of electrospun nanofibres diameter are always different and the shapes of such distributions usually do not differ from the compound distribution, which consists of several normal distributions.
- (ii) The speed of support material from 0.002 m/s till 0.010 m/s does not have a significant influence on the average value of PA6.6 nanofibres diameter. It only influences the structure of nanofibre web; that is, as the speed of the support material decreases, the more stucked nanofibres are formed.
- (iii) For the web structure estimation the modal value of the first distribution, the percentage quantity of the first distribution, and the average diameter of two peaks of distribution—modal value and the value of the second highest peak—may be used.
- (iv) The results of the tests confirm that the web of nanofibres consists of various nanofibres due to the sticking of several nanofibres during the process of their manufacturing.

Conflict of Interests

The authors declare no possible conflict of interests.

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