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Mathematical Analysis of the Diameter Distribution of Electrospun Nanofibres

Abstract

In the electrospinning process a web of nanofibres is formed on various surfaces, the web usually consisting of nanofibres of different diameters. There is no one opinion about the reasons for such phenomena as the distribution of the nanofibre diameter is also very sophisticated. The goal of this article is to analyse the distribution of the nanofibre diameter using mathematical statistics and to compare the results with well-known statistical distributions. Analysis of various distributions shows that they are similar to a log normal distribution, but on the other hand the electrospinning process does not depend on the time. For estimation of the nanofibre diameter distribution, the compound distribution from several normal distributions is proposed. This hypothesis was checked by empirical investigation of a web from PVA nanofibres. A high correlation between empirical and calculated values using a compound distribution has been established ($R^2=0.804$). The method presented was checked with other kinds of web from PVA nanofibre, and positive results were obtained.

Key words: electrospinning, PVA nanofibre, diameter distribution.

Introduction

Electrospinning is a process where, by using electrostatic forces, nanofibres from polymer solution or melt is produced. The diameter of the nanofibres usually varies from 50 to 500 nm [1]. The structure of a nonwoven web made from nanofibres depends on the polymer type, its molecular weight, concentration and other characteristics, as well as on technological parameters such as the applied voltage and the distance between electrodes; electrospinning ambient parameters – temperature, humidity and pressure are also significant. All these characteristics have a lesser or higher influence on the diameter of nanofibres and, hence, on the properties of the web [2-7].

An analysis of various works shows that the distributions of the nanofibre diameter are always different and not close to a normal distribution. Thus it is very difficult to compare average values when the dispersions of diameters are different. The main problem is that the measurements of the diameter are distributed in an unclear distribution.

Comparing parameters with different kinds of distributions is not clear from a mathematical statistical point of view. Hence, it is very difficult to analyse how various parameters or chemicals influence the nanofibre diameter and structure of the web. Changes in the average values do not mean the same changes in mode values and other characteristics of value dispersion – wide of the value distribution, left or right skew of the distribution etc. Therefore it means that only

the average value of the nanofibre diameter cannot be used for nanofibre characterisation, and new methods of nanofibre characterisation are needed.

From the classical theory it is known that values of the fibre diameter of various textile materials are usually distributed by normal distribution [8]. But the shape of the distribution of the nanofibre diameter is far from a normal distribution. Some authors state that measurements of the nanofibre diameter have a lognormal-like distribution [9]. It is well known that a lognormal distribution is very often found for parameters dependent on the time; however, the electrospinning process does not depend on the time as all nanofibres in the web are manufactured at the same moment. Hence, describing results using a lognormal distribution does not have a theoretical basis. An analysis and comparison of the empirical distribution of the nanofibre diameter with well known distributions of measurements of textile characteristics shows a high similarity with a compound distribution, which is very characteristic for blended spun yarns from several kinds of fibres. Any other known distribution does not have a similar view [8, 10].

To calculate a compound distribution from several normal distributions is very easy, but a problem arises of how to divide the compound distribution into several normal distributions. The goal of the present article is to establish a method of dividing the compound distribution into several normal distributions and to present a new method of nanofibre diameter characterisation which also evaluates the shape of the distribution obtained.

Materials and methods

An aqueous solution of PVA was diluted using distilled water in order to get an 8% concentration of the solution. A web of nanofibres was formed by the electrospinning method using “Nanospider™” equipment (Elmarco, Czech Republic). On this equipment the spinning head is a rotating roller (*Figure 1*). The rotating roller is submerged halfway into the polymer solution. By increasing electrostatic forces, Taylor cones are created from the polymer solution on the roller, which is transported up to the support material, which is covered by a layer of nanofibres.

During all the experiments carried out, the temperature of the environment was $T = 20 \pm 2^\circ\text{C}$ and the humidity $\varphi = 50 \pm 2\%$. The distance between electrodes was 13 cm and the applied voltage – 65 kV for the main part of experiment and 45 kV for the second part (for method checking).

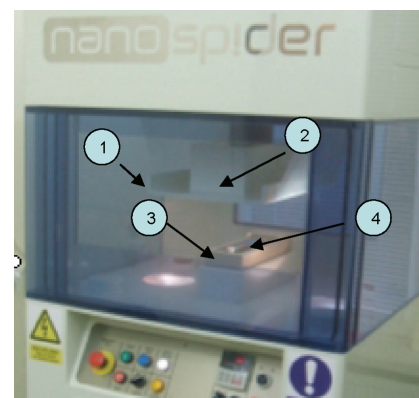


Figure 1. Technique of electrospinning using a “Nanospider™”: 1 – support material, 2 – upper electrode, 3 – bath with polymer solution, 4 – rotating roller.

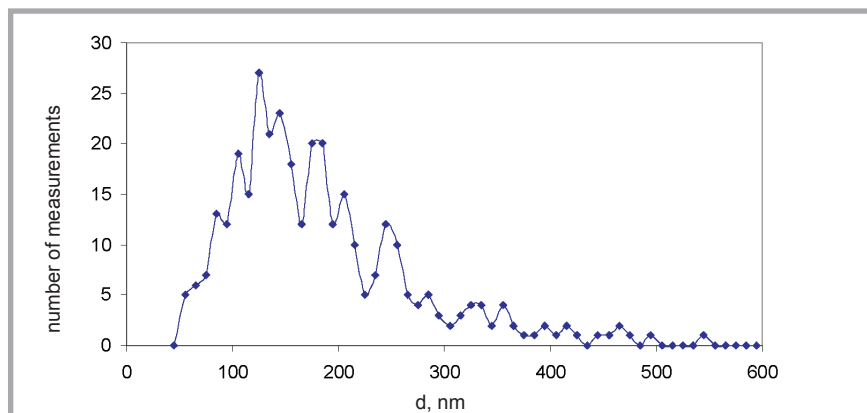


Figure 2. Empirical distribution of the nanofibre diameter.

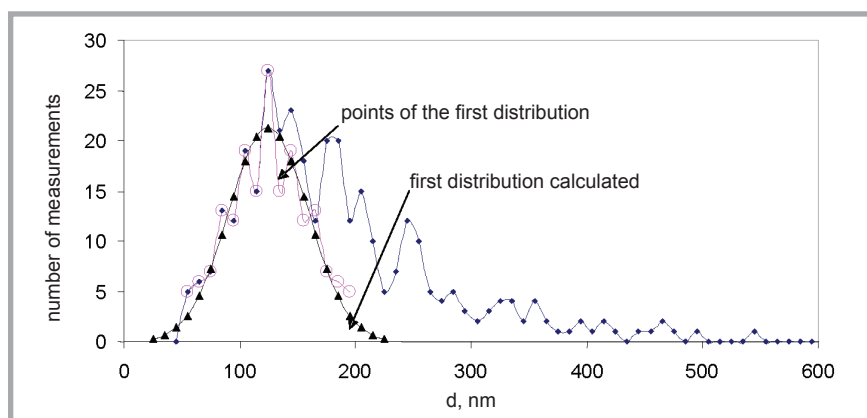


Figure 3. Calculation of the first distribution.

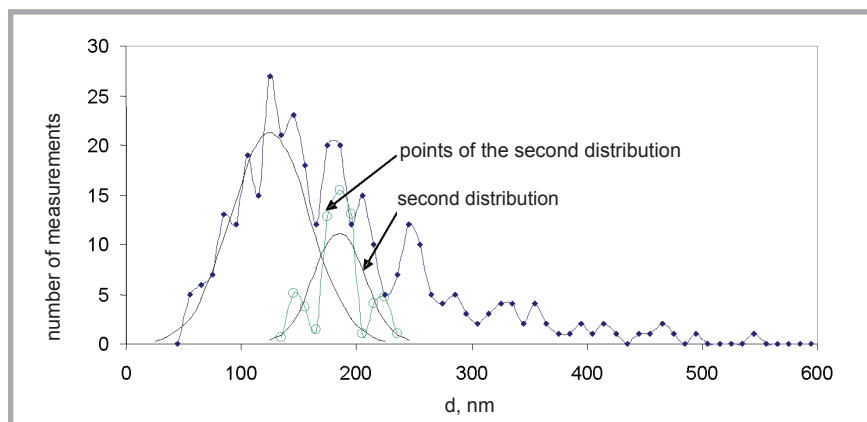


Figure 4. Calculation of the second distribution.

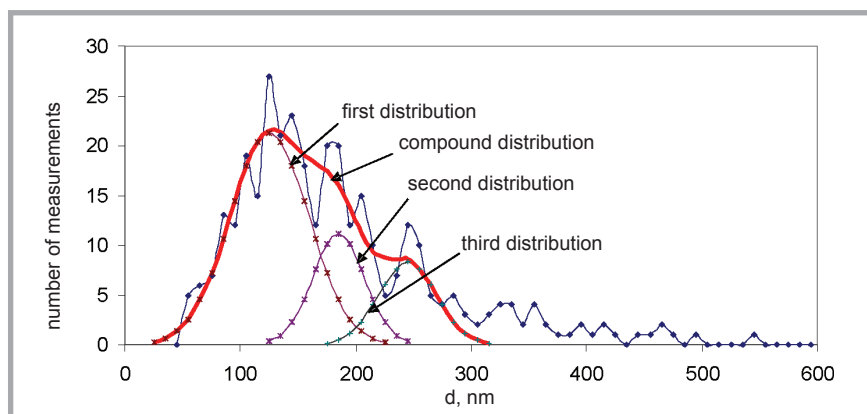


Figure 5. Calculation of the compound distribution.

Fiber morphology was observed by Scanning Electron Microscopy (SEM) SEM-FEI Quanta 200 (Netherlands). The diameter of nanofibres was measured from SEM images taken by a LUCIA Image 5.0 program, with an accuracy of ± 0.01 nm. Measurement of all nanofibres in each image from 5 different images (from different places but for the same width of the web) was made for both variants.

Results

The first series of experiments were conducted when the distance between electrodes was 13 cm and the applied voltage – 65 kV. In this experiment 5 SEM images were made and 342 diameters of nanofibres measured from all the SEM images. The distribution of empirical measurements of the diameters is shown in Figure 2 (the interval of the nanofibre diameter is distributed by 10 nm).

From Figure 2 we can see that the distribution of the nanofibre diameter is not normal. In the curve presented in Figure 2, we can observe three peaks. The first peak is the diameter of PVA nanofibres around 125 nm; the second peak is for a diameter of nanofibres of around 175-185 nm, and the third peak is for a diameter of nanofibres of around 245 nm. Thus the following assumption can be made: the compound distribution presented consists of three normal distributions (three peaks are clearly visible).

In this study, we propose a way of dividing the compound distribution presented into three normal distributions. First of all, we need to describe the first normal distribution, hence it is necessary to find the empirical points of this distribution. From the level of the empirical values to the modal value of the total distribution we called the points of left part of the first normal distribution. Considering that the diameter of nanofibres has a normal distribution, on the other side of the modal value we can mark points of a symmetrical character. Now, according to probability density function (1), the first normal distribution is calculated (Figure 3).

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x_i - x)^2}{2\sigma^2}} \quad (1)$$

The second step of the method presented is to establish the left part of the second normal distribution. The difference between the empirical measurements n_e and

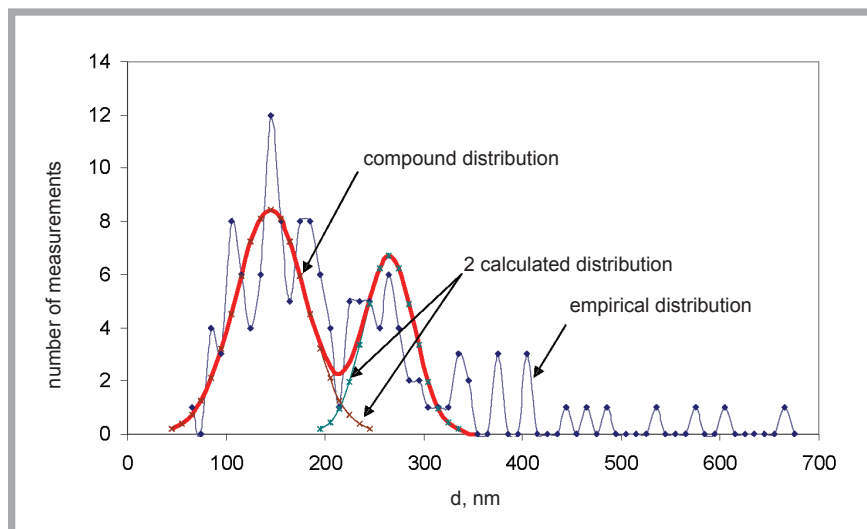


Figure 6. Compound distribution of the second part of experiments.

those calculated by the first normal distribution n_{e1} is attributed to the left part of the second normal distribution n_{e2} , i.e. $n_{e2} = n_e - n_{e1}$. The right part of the empirical values is found as in the previous case, i.e. it is the symmetrical points to the mode value of the second distribution. The second distribution can now be calculated by the probability density function (Figure 4).

The third distribution was established using the same method as for the second distribution. However, there are too few empirical measurements to calculate the fourth distribution in the case presented. Thus we can state that our distribution until the diameter of nanofibres is 310 nm is a compound one from three normal distributions. Lastly by summarising the values of all three distributions established, a compound distribution can be calculated (Figure 5).

From Figure 5 we can observe that the compound distribution calculated corresponds to the empirical distribution very well. In this case when the number of empirical points is great (27 points), the coefficient of determination of the curve calculated is high ($R^2 = 0.804$), meaning that the correlation between the curve of the compound distribution obtained and empirical results is very strong; hence the method presented can be used for dividing a compound distribution into several normal distributions. Now we can use the mode value of the first distribution (it is the same as the mode value of all distributions) and the percentage quantity of the measurement of the first distribution as the criterion of

the nanofibre diameter and estimation of the measurement dispersion. These values can be used for comparing various nanofibre webs because these two values characterise not only the mode value of all nanofibre measurements but also the quantity of measurements distributed by a normal distribution with an average value the same as the mode value of the total distribution. Increasing the percentage quantity means a less wide dispersion of measurements and a more unique structure of the web, while the mode value characterises the diameter of nanofibres.

The method presented was checked by a second series of experiments carried out when the distance between electrodes was 13 cm and applied voltage – 45 kV. The temperature of the electrospinning environment and the humidity were the same: $T = 20 \pm 2^\circ\text{C}$ and humidity $\varphi = 50 \pm 2\%$. The same was used for the PVA solution.

The compound distribution was calculated using the same method. In this part of the experiment, a distribution with only two peaks was identified, and a compound distribution was calculated from two normal distributions. As is seen from Figure 6, the compound distribution also correlated with empirical values; however, in this case the coefficient of determination is smaller – $R^2 = 0.515$. It is necessary to note that in the second part of the experiment, in 5 SEM images only 138 nanofibres were found, while in the first part there were even 342 nanofibres, meaning that the accuracy of the method presented very strongly depends on

the number of measurements. However, even in the case of nanofibres with a not high density in the web, this method can be used for nanofibre diameter and web structure estimation.

In our cases the diameter of nanofibres is 125 nm when the applied voltage was 65 kV, and 145 nm when the applied voltage was 45 kV (difference is 16%). The percentage quantity of nanofibres of the first kind (distributed by a first distribution) is 53% and 55%, respectively (the difference is 4%), meaning that the applied voltage does not have a significant influence on the diameter of nanofibres, the only effect being on the process of electrospinning and on the density of fibres in the web.

In the next step of the investigations, the reasons for such phenomena (a web consisting of several kinds of nanofibres) was investigated. As is seen from Figure 5, the peaks of the total distribution are very close to those of the normal distributions calculated. Of course, the question arises as to what happened to the fibres that they were formed in one process but with different diameters. The hypothesis states that it happens when two or three nanofibres stick together and do not separate before reaching the second (upper) electrode. In this way (especially in the first case), the diameter of nanofibres must be a discrete value. At this stage of our investigations we checked this hypothesis. If the mode (also average) value of the diameter of a single fibre is $d_1 = 125$ nm (see Figure 6), in this case the diameter of a double fibre will be $d_2 = 177$ nm and that of a triple fibre $d_3 = 217$ nm. The surface area of a cross section of a stick fibre can be calculated using formula $S_n = nS_1$, from which it is very easy to calculate the diameter of the stick fibre – $d_n = d_1\sqrt{n}$ (here n is the number of stick fibres). As is seen from Figure 6, the second peak is when the diameter of nanofibres is $d_{2emp} = 185$ nm and the third peak – when $d_{3emp} = 245$ nm. In this case, the relative errors calculated are $\delta_2 = 4.3\%$ and $\delta_3 = 11.4\%$, respectively. Thus it is possible to state that the differences are not high. Verification of the hypothesis presented concerning the sticking (or the non-disappearance) of nanofibres with a deeper statistical analysis of several kinds of polymers will be the subject of further investigations.

■ Conclusions

The distribution of the nanofibres diameter is not normal or log normal but a compound one from several normal distributions.

The compound distribution can be divided into several normal distributions by the method presented, which is based on the mode value of the total distribution and the assumption that the right part of empirical normal distribution is symmetrical to left part.

For nanofibre diameters comparison is necessary to describe new methods, one of which can be the mode value and the percentage quantity of measurements of the first distribution.

The preliminary investigations confirm the possibility of sticking several nanofibres together to make one thicker fibre.

References

1. Ioannis S., Chronakis. *Journal of Materials Processing Technology*, Vol. 167 (2005) pp. 283-293.
2. Mo X.M., Xu C.Y., Kotaki M., Ramakrishna S.; *Biomaterials*, Vol. 25 (2004) pp. 1883-1890.
3. Heikkilä P., Harlin A., Soderlund L., Uusimäki J., Kettunen L. *AUTEX 2007 Conference proceedings CD, 2007, Tampere, Finland*.
4. Adomavičiūtė E., Milašius R., Levinskas R. *Materials Science (Medžiagotyra)*, Vol 13(2007) No.2 pp.152-155.
5. Adomavičiūtė E., Milašius R. *Fibre & Textiles in Eastern Europe*, Vol. 15 (2007) No.5-6 pp. 69-71.
6. Adomavičiūtė E., Milašius R., Žemaitaitis A., Bendoraitienė J., Leskovšek M., Demšar A. *Fibres & Textiles in Eastern Europe*, Vol. 17 No.3 (2009) pp. 29-33.
7. Danelevičiūtė-Vaišnienė A., Katunskis J., Buika G. *Fibre & Textiles in Eastern Europe*, Vol 17(2009) No 6 pp.40-43.
8. Leaf G.A.V. *Practical Statistics for the Textile Industry: Part I, The Textile Institute, Manchester, 1984*.
9. Tsimliaraki A., Zuburtikudis I., Marras S.I., Panayiotou C. *Latest Advances in High Tech Textiles and Textile-Based Materials, Book of Proceedings, Ghent, Belgium, 2009 pp.128-133*.
10. Malašauskienė J., Adomavičiūtė E., Milašius R. *Mathematical Analysis of Web from Nanofibres, Book of Abstracts of 41st International Symposium on Novelty in Textiles, Ljubljana, Slovenia, 2010, p.7*.

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