KAUNAS UNIVERSITY OF TECHNOLOGY

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STATISTICAL ESTIMATION OF STRUCTURE OF WEB FROM ELECTROSPUN NANO- MICROFIBRES

Summary of Doctoral Dissertation
Technological Sciences, Materials Engineering (08T)

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

JOLANTA MALAŠAUSKIENĖ

ELEKTRINIO VERPIMO BŪDU FORMUOJAMOS NANO- IR MIKROGIJINĖS DANGOS STRUKTŪROS STATISTINIS VERTINIMAS

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INTRODUCTION

<u>Research Problem Justification and Relevance of the Work</u>. Today, nanotechnologies are an integral part of our daily life. Although the application of various nanostructures in scientific areas and even in practice has been known for a long time, the earliest mention of the term itself dates back only to the mid-20th century. On the basis of scientific literature, the year 1959 could be considered the beginning of the era of nanotechnology, because the physicist R. Feynman, during one of his lectures, had described a process by which the ability to manipulate individual atoms and materials might be developed. Therefore, the essence of nanotechnologies lies in practical use of small particles, atoms and molecules, and their combinations. A nanometre is an extremely small unit of length. For example, a human hair has thickness of 80 000–100 000 nanometres, the diameter of a red blood cell is 7000 nm, while that of an DNA chain element reaches just 2 nm.

Electrospinning is a process, during which, with electrostatic forces acting, nano- microfibres are produced from a polymer solution or a melt. Although different literature sources introduce different definitions of nanofibres, in the present study, on the basis of the European Union recommendations, nanofibres shall be the fibres, the diameter of which ranges from 1 to 100 nm. The fibres, the diameter of which exceeds 0.1 µm, are called microfibres.

Nano- microfibres have unique properties: large area of specific surface, porosity (high porosity level, small size of pores) and small diameter. Due to these properties, nano- microfibres and nano-microfibre- based materials are especially widely used in medicine (to produce artificial organs, in tissue engineering and for medical dressing), and in production of filters, protective clothes, composites, optical and electronic devices.

Over recent years, much research has been conducted relating to electrospinning processes. Particular attention has been paid to estimate the effects of various factors on the structure of the nonwoven coating being manufactured. In the literature sources, the impact of polymer solution concentration, its surface tension and electrical conductivity on the structure of fibre coating being manufactured is widely examined. Also the effects of technological parameters, such as voltage, distance between electrodes, polymer flow velocity and ambient conditions (humidity, temperature, pressure) on the structure of coating being manufactured, alongside with morphology of fibres, are analysed. All these parameters affect the structure of the web from nano- microfibres.

On the basis of various research results provided in different literature sources, it has been noticed that quite often when analysing the impact of the same parameter on the web structure, the authors obtain different results. In other words, very often the same properties of the polymer solution, the impact of a technological or ambient parameter on fibre diameter, structure, pore size or shape are obtained different. It is likely that this is caused by the fact that authors don’t always show all data that could have decisive impact on research results. Furthermore, it has been noticed that frequently the authors subjectively estimate the structure of web manufacturing by electrospinning: on the basis of just the average or modal diameter, and they don't always indicate how the average diameter of fibres has been computed, or they infrequently present the quantity of fibres that have been used when calculating the average, and do not analyse dispersion of nanofibre diameter. Therefore, not analysing and introducing such data can determine discrepancies in the results.

The goal of the dissertation: to analyse the electrospun nano-microfibre diameter dispersion, and to propose a new method of estimation of the structure of nano-microfibre web based on mathematical statistics criteria.

The objectives of the research:

1. To analyse and to estimate the dispersion of electrospun nano- microfibre diameter through known mathematical distributions.
2. To identify criteria on the basis of which it would be possible to estimate the diameter of nano-microfibre web and its mathematical distribution.
3. To estimate the influence of selected voltage and speed of nonwoven movement, on the structure of nano-microfibre web.
4. To create a detailed description of the new method estimation of nano-microfibre web diameter.

Research novelty and practical importance. Due to wide usability and perspectives of nano- microfibres and nano-microfibre -based fabrics, the elctrospinning process is quite widely analysed and described in various pieces of literature. On the basis of this, it can be maintained that the electrospinning is an extremely sensitive process, which is affected by polymer solution properties, and technological and ambient parameters. While analysing what causes contradictory research results obtained by different authors, a conclusion has been made that essentially this phenomenon is caused by the fact that no uniform methods for nano-microfibre web estimation have been created so far. Extremely rarely in literature sources the dispersion of manufactured fibre diameter is analysed, while the findings regarding the impact of one or another parameter on web morphology are provided purely on the basis of the average diameter value or the modal diameter of fibres. The more profound analysis of results has shown that these parameters estimate the diameter only, and they do not reveal what web is manufactured during the process. There is no analysis on why during the same process fibres of different thickness are formed. As there are no common methods of estimation, it is difficult to compare the works by different authors. Therefore, the research in the nano-microfibre web field is extremely important and necessary not only in order to optimize electrospinning process, but also estimate properly the impact of different parameters on the diameter and structure of the web.

Irrespective of the fact that in the literature, the structure of fibre web most frequently is estimated just on the basis of the average diameter of fibres, one can find some works, in which the authors analyse diameter dispersion, while the diameter dispersion obtained is described through a normal (Gaussian) or lognormal distribution. Quite frequently, a distribution created in that kind of works is not similar to normal distribution; therefore, in terms of statistics, it is not correct to describe the diameter values through this distribution. Meanwhile, description of diameter values through a lognormal distribution, known in mathematics, does not have a physical sense, as the diameter values of nano- microfibresformed by electrospinning do not depend on time.

After the analysis of literature sources has been completed and their summarization finished, even during the investigation, it has been noticed that in all cases, irrespective of polymer solution being used during the investigation, the diameter of nano- microfibers formed is distributed differently, therefore, different distributions are obtained in different cases. As the character of dispersion is different, it is difficult to estimate average values; therefore, it is difficult to properly estimate how change in different parameters influences the structure of web being formed from nano-microfibres. It is not accurate to estimate the web being formed just by the average value of diameter, not taking into account diameter distribution; therefore, a new method of estimation is necessary.

The novelty of the work lies in that a new method of nano- microfibre web estimation has been created based on mathematical criteria, taking into account diameter distribution and average diameter. The results obtained have shown that frequently the change in a parameter has influence on just the electrospinning process and the structure of the web; still it does not have any decisive influence on the average diameter of the ultrafine fibres (in this work the ultrafine fibres are called fibres which are distributed by the first normal distribution). In this study, it is proposed how to estimate distributions when fibre diameter values are distributed following a pattern unknown to mathematics. The investigation results obtained have important practical implications, because the nano-microfibre web estimation method created allows estimating and comparing any structure formed by electrospinning. On the basis of this method, the results obtained by different authors can be compared.

In this study it has been established that empirical distribution of diameter that has several peaks can be compared with a compound distribution. Also, it has been established that the voltage has influence on the structure of the nonwoven coating being fabricated and on formation of various webs; still it does not have a significant influence on diameter of thin fibres. After the voltage has been increased, the web has been formed from a greater quantity of fibres that stick together, which causes increase in average diameter of all fibres. Nonwoven fabric movement speed does not have influence on the diameter of the ultrafine fibres; still, it affects web structure and density. The investigation results have shown that during the electrospinning process, due to fibre sticking together, webs of different thickness are formed. On the basis of data of experiments that have been carried out, it can be maintained that it is very important to estimate the structure formed on the basis not just one or two measurement places of web. According to the results obtained in this work, the optimal number of different measurement places, when the area of place is 160 μm^2, for estimation of web structure must be 5. To use the larger number of measurement places is inappropriate, while a lower number of places may be affected by inaccuracies.

The defence propositions:

1. During the electrospinning process, the nano-microfibre web is manufactured with very different fibre diameters, while distribution of their measurements frequently is very far from the normal (Gaussian) distribution.
2. The nano-microfibre web can be described through a normal Gaussian distribution in the case only when the skewness coefficient calculated does not exceed the limit of 0.5. If the skewness coefficient of the nano-microfibre diameter distribution is greater than 0.5, the distribution can be described through a compound distribution, consisting of several normal distributions.
3. The structure of nano-microfibre web can be analysed and estimated on the basis of no fewer than 5 different measurement places of web, when the area of place is 160 μm^2, only.
4. The selected voltage and the movement speed of nonwoven material does not have any influence on the diameter of ultrafine nano- microfibresbeing formed; still, they have impact on the structure of the web – greater quantity of stuck together fibres is produced.
5. The new method created for nano-microfibre web diameter estimation based on objective statistical parameters only, can be used to estimate and compare different coatings.

Approbation of the research results. Results of research were presented in 7 scientific publications and 17 conferences.

Structure of the dissertation. The dissertation consists of introduction, 3 chapters, conclusions, list of references (140 positions) and list of scientific publications.

CONTENT OF THE DISSERTATION

The „Introduction“ chapter there is a short description of the topicality and novelty of investigations, the aim and the tasks of the dissertation work. The defence propositions are stated at the end of „Introduction“.

The first chapter, „Literature review“, contains a short survey of literature on the theme of the dissertation. In this part, the development of electrospinning process from the 16th century, alongside with most significant achievements and patents of scientists, is analysed. Also, main polymers, biodegradable and non-biodegradable, being used in electrospinning is described. Articles concerning the influence of various parameters on the structure of web being formed from nano-microfibres are analysed. In addition, articles by different authors concerning character of dispersion of nano- microfibresformed are examined. On the basis of investigation results provided in different literature sources, it has been observed that frequently when analysing influence of the same parameter on the web structure the authors obtain different results. It is likely that discrepancies in the results are caused by the absence of uniform methods for fibre web estimation.

The second chapter, „Research methodology“, describes methodology of experimental investigations.

Experimental materials. During researches were used different types of polymer solutions.

1. To carry out the experiments, a polymer solution obtained by dissolving PVA powder (CARL ROTH, Germany) was used, agitating for 2 hours with a help of a magnetic stirrer. PVA powder was dissolved in the distilled water of 70º C temperature. This way, the 8 % concentration solution was prepared.
2. Polymer solutions were prepared also by dissolving the PA6.6 and PA6 powder (Sigma Aldrich). As a PA solvent, formic acid was chosen. To carry out the experiments, 8 % concentration PA6.6 polymer solution and 15 % concentration PA6 polymer solution were prepared.
3. PVA polymer solutions were prepared with cellulose additive, obtained from mechanically treated hemp fibre “Purini” (Latvia) and hemp shives “Bialobrziaski” (Latvia). PVA solution was prepared from PVA granules (Vam and Co. Ltd., Japan). Powder was dissolved in the distilled water of 70º C temperature.The experiments were carried out using: 8 % concentration PVA polymer solution without additives; PVA/hemp fibre solution prepared through mixing the prepared 2 % hemp fibre solution into the 8 % PVA solution; PVA/hemp shives solution prepared through mixing the prepared 2 % hemp boon solution into the 8 % PVA solution.
4. Two-component PVA polymer solutions with microcrystal cellulose (Sigma Aldrich, Ireland) were prepared through mixing 2 % cellulose nanocrystals in necessary proportion into the PVA solution; this way, the 8 % concentration solution was obtained; and another 8 % polymer solution was prepared through mixing the 3 % CNC obtained from MCC into the PVA solution in necessary proportion. PVA solution was prepared from PVA powder (Kuraray, Japan). Powder was dissolved in the distilled water of 70º C temperature.

The nano- microfibre web was manufactured using the “Nanospider™“ electrospinning equipment. Nano- microfibres being manufactured in this equipment are moving from the rotating bottom electrode, which is partially immersed into a tray with polymer solution, towards the upper electrode, which is fastened to the collection screen.

During the electrospinning process, under conditions of increasing voltage, on the rotating bottom roller, the hemispherical-shaped droplets start to form, from which, under conditions of further increase in voltage, cone-shaped droplets, called Taylor Cones, are formed. After the electrostatic forces have exceeded the surface tension, a solution jet is formed from the cone-shaped droplets (Taylor Cones). This jet, while moving towards the collection screen, stretches and splits into nano- microfibres.

To identify the structure of the nano- microfibresweb produced during the investigation, the SEM-FEI Quanta 200 scanning electron microscope (SEM) was used. Fibre diameter measurements were made applying the LUCIA Image 5.0 software.

The results of nano-microfibre diameter obtained during investigation are described through a compound distribution consisting of several normal (Gaussian) distributions. The normal distribution curve is expressed by the probability density function:

$$y = \frac{1}{s\sqrt{2\pi}} \times e^{-\frac{(x_i - x)^2}{2s^2}} ; \qquad (1)$$

where: π – the constant (3.14159…); e – the base of the natural logarithm (2.71828...); s – standard deviation; x – the arithmetic mean of fibre diameters, nm; x_i – the ith value of fibre diameter, nm.

To estimate the symmetricity of the normal distribution, the skewness coefficient |A| is used.

$$|A| = 1 - \frac{\sum_{i=1}^{n} (x_i - \bar{x})^3}{n \times s^3} ; \qquad (3)$$

where: n – number of measurements; s – standard deviation; $\bar{x}$ – the arithmetic mean of fibre diameters; x_i – the ith value of diameter.

In order to estimate compliance of the empirical equation with the experimental points, the coefficient of determination is calculated.

$$R^2 = 1 - \frac{\sum (y_e - y_t)^2}{\sum y_e^2 - \frac{\sum (y_e)^2}{N}}; \quad (4)$$

where: y_e – the number of measured nano- microfibresof a particular diameter; y_t – the number of fibres of a particular diameter calculated by the equation; N – the number of experimental points.

The third chapter, „Results of investigations“, presents theoretical and experimental investigations and their analysis.

Analysis of Nano- microfibre Diameter Dispersion. The analysis of various studies that examine the impact of different parameters on web being formed shows that frequently in these works nano- microfibre diameter values distribute following the pattern shown in Fig. 1.

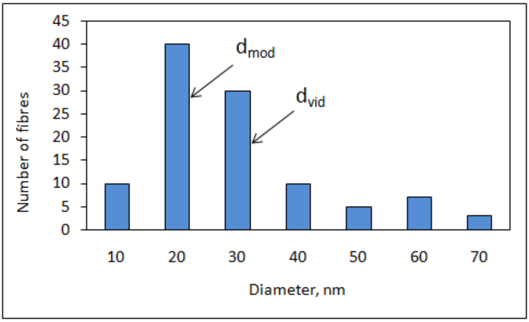
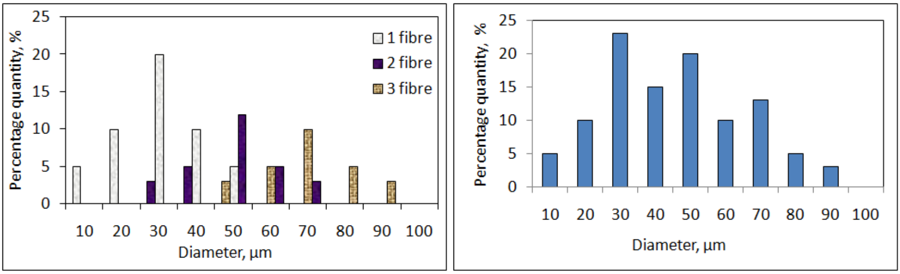


Figure 1. A typical histogram of nano- microfibres diameter distribution

On the basis of data presented, it can be seen that the average value is larger than the modal value; therefore, taking this into account, it can be maintained that nanofibre diameter values are not distributed normally.

In Fig.2 the diameter distribution histograms of blended spun fibres, made of three fibres are shown, where fibre percentage quantity in the spun is different. Fig. 2 a shows that each group of fibre that constitute the blended spun fibre has a modal value that coincides with the average value of this group. Also, it can be seen that measurements of each fibre group are distributed by normal (Gaussian) distribution.



a) b)

Figure 2. Typical histograms of distribution of blended spun fibre diameter values; a) distribution of each fibre constituting the blended spun fibre; b) the compound distribution of the blended fibre spun consisting of 3 fibres.

After the values of these fibres have been summarized, a distribution shown in Fig. 2 b is obtained. There three peaks can be clearly distinguished that concede with the modal values of each group of fibres (these values are equal to average values of each group). In this case, it can be maintained that the values of blended spun fibre are distributed following the pattern of a compound distribution, which consists of several normal distributions.

During the investigation, in order to analyse dispersion of the diameter of the electrospun PVA microfibre web, two series of experiments were carried out. After the mathematical analysis of measurements obtained during the first series of experiments had been completed (under U = 65 kV), the empirical distribution of these fibre diameter values was created and shown in Figure 3.

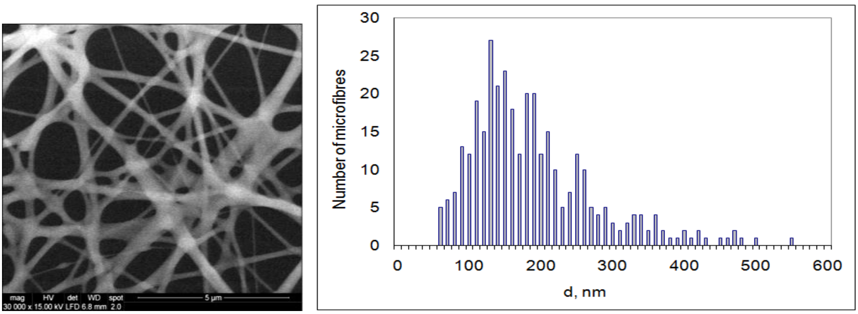


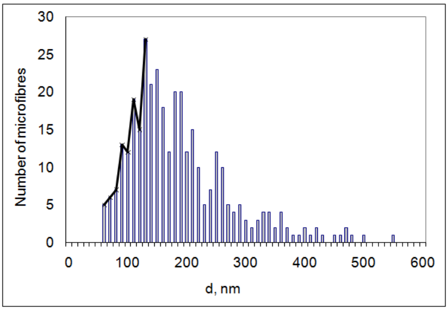
Figure 3. SEM image (scale 5 μm) and empirical distribution of the PVA microfibre diameters

The analysis of diameter distribution shows that the latter distribution is very similar to the compound distribution, following the pattern of which blended fibre yarn diameter values are distributed. Therefore an assumption is made that microfibre web consists of several microfibre groups of different thickness, when the diameter values of each group have been distributed normal distribution and constituted a compound distribution.

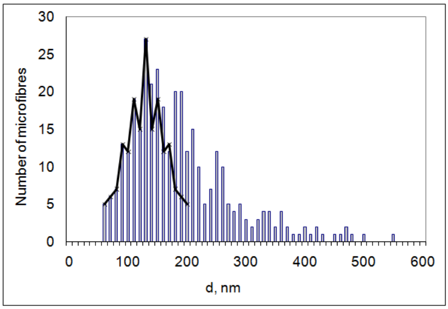
<u>Description of Nano- microfibre Diameter Dispersion through a Compound Distribution</u>. In order to confirm the assumption formulated that diameter values of different microfibre groups are distributed by normal distribution, while electrospun web diameter is distributed following the pattern of the compound distribution that consists of several normal distributions, all normal distributions must be found.

Calculation of the Compound Distribution. When calculating the first normal distribution, to the empirical values of the diameter, the points of the left-hand branch of the first empirical distribution are plotted as far as the modal value (Fig. 4, a). After the first empirical distribution right-hand branch points, symmetrical to the left-hand branch points, have been plotted away from the modal value (Fig. 4, b), in accordance with the probability density function, the first normal distribution is calculated (Fig. 4, c).

After the results have been analysed, it was noticed that not all PVA microfibres with diameter up to 220 nm belong to the first normal distribution calculated. The difference between the empirical measurements and values calculated by the first normal distribution is located as the empirical distribution left-hand branch, necessary to calculate the second normal distribution (Fig. 4, d).



a)



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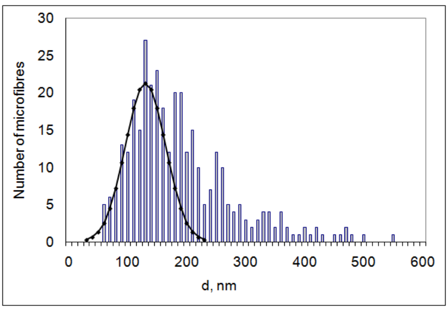

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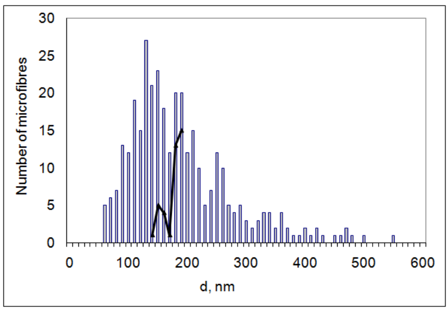

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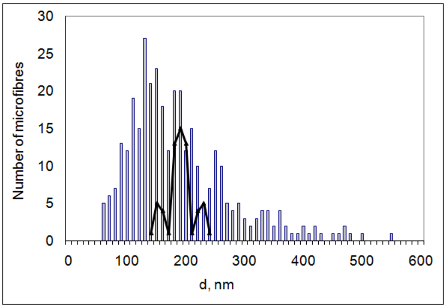

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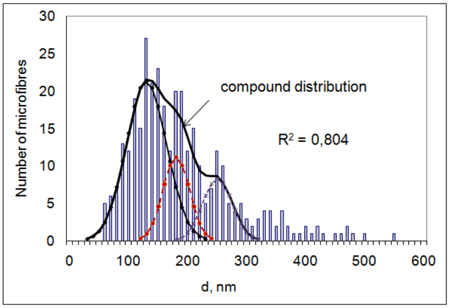

f)

Figure 4. Calculation of the first normal distribution: a) Plotting the left-hand branch points of the first empirical distribution to empirical values b) Plotting the points necessary to calculate the first normal distribution; c) Finding the first normal distribution; d) Plotting the left-hand branch points of the second empirical distribution; e) Plotting the points necessary to calculate the second normal distribution; f) Description of microfibre diameter dispersion through a compound distribution

The points of the right-hand branch are plotted applying the same principle as for the first distribution (Figure 4 e). After the points have been plotted, the second normal distribution is found using the probability density formula. The third normal distribution, the pattern of which is followed by diameter values of even thicker microfibres, is found applying the same method as for the second one. After the third distribution has been calculated, all values of the distributions calculated are summarized and the compound distribution is found (Fig. 4, f).

The average diameter of the first normal distribution calculated by formula 1 coincides with the modal value of this distribution. This value coincides with the modal value of the entire empirical distribution, D_{mod}. The average diameter of the second normal distribution calculated coincides with the modal value of the second distribution, while the average diameter of the third normal distribution calculated coincides with the modal value of the third distribution. The modal value of empirical distribution of diameter measurements is D_{mod} = 125 nm, while the average diameter of all microfibres is D_{aver} = 183 nm. As $D_{mod} \neq D_{aver}$, while $d_{1aver} = d_{1mod}$; $d_{2aver} = d_{2mod}$; $d_{3aver} = d_{3mod}$, it can be maintained that diameter of microfibres constituting the web is distributed following the pattern of the compound distribution that consists of groups of different thickness microfibres, while the diameter values of each group are distributed normally.

In order to verify the assumption formulated above, the second series of experiments has been carried out (U = 45 kV). After the analysis of results obtained was completed, distribution of diameter values was created. The diameter values measured has been described through the compound distribution following the sequence of actions presented previously (Fig.5).

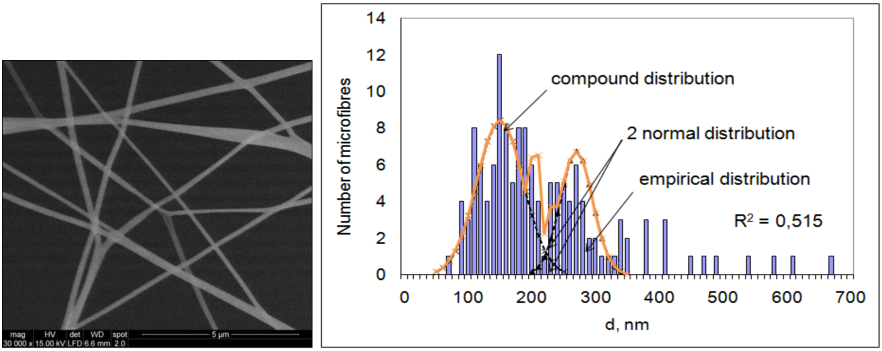

Figure 5. SEM image (scale 5 μm) and description of PVA microfibre diameter dispersion through the compound distribution, when U = 45 kV

It can be seen from Figure 5, that average diameter of the first normal distribution calculated coincides with the modal value of the first distribution, while the average diameter of the second normal distribution calculated coincides with the modal value of this distribution. The modal value of the entire empirical distribution corresponds with the modal value of the first distribution calculated. The modal value of the empirical distribution created in accordance with the microfibre diameter values measured is D_{mod} = 145 nm, while the average diameter is D_{aver} = 214 nm. Based on the results, it can be maintained that the values of different diameter groups are distributed normally, while the diameter of microfibres constituting the web are distributed following the pattern of the compound distribution.

***Estimation of Different Thickness Webs Formed by Electrospinning*.** In this phase of investigation, the assumption is verified that webs of different thickness are made due to fibre sticking together. The diameter of stuck together fibres is calculated by formula 5.

$$d_n = d_{aver} \times \sqrt{n}\,; \qquad (5)$$

where: n – the number of fibres sticking together.

Based on the empirical data (see Fig.3), it can be seen that the average diameter value of the ultrafine and non-stuck together microfibres that we have managed to form under conditions of 65 kV voltage is d_{1aver} = 125 nm. On the basis of formula 5, the average diameter of two microfibres sticking together should be d_2 = 177 nm. The diameter of three PVA microfibres that got stuck during the process of electrospinning should be d_3 = 217 nm. Based on the empirical data, d_{2aver} = 185 nm, while d_{3aver} = 245 nm.

The conformances between the calculated and measured results are estimated by relative errors. It has been obtained that deviation between the diameter values of two stuck together microfibres and second peak value of the empirical distribution is Δx_2 = 4.3 %. The relative error between the calculated and empirical values of three stuck together microfibres has been obtained Δx_3 = 11.4 %.

The average diameter value of the ultrafine and not stuck together microfibres that we managed to produce under conditions of 45 kV voltage is d_{1aver} = 145 nm. The diameter of two stuck together microfibres that has been calculated by formula 5 is d_2 = 205 nm. After the average diameters of microfibre groups calculated and measured have been found, the conformity between the calculated and measured results is assessed by the relative error Δx_2 = 22.6 %. It is likely that the larger error obtained in the second case is caused by a smaller number of measurements.

<u>Estimation of web from PVA Microfibres Applying Statistical Methods.</u> In this study, to estimate the structure of web from nano- microfibres, in addition to the average value of the entire distribution, it is proposed to use the following:

- ✓ the average diameter value of the first normal distribution ($d_{1aver;} = d_{1mod}$);
- ✓ percentage quantity of measurements (N_{meas}), which is distributed by first normal distribution.

These parameters can be used in order to compare different webs generated during electrospinning process, because by the average value of the first normal distribution (this value corresponds to the modal value of the first distribution) frequently the modal value of all diameter measurements is determined. Meanwhile the percentage quantity of measurements that belongs to the first normal distribution determines the number of fibres that belongs to the first group of non stuck together fibres. The criteria of estimation have been chosen by the data of the first normal distribution, because during the process it has been sought to form a web as even as possible and of as uniform a structure as possible from the fibres of as small diameter as possible. After the results obtained during electrospinning have been analysed, it can be seen that the average diameter of fibres of the first distribution calculated corresponds with the modal value of this distribution (this value usually corresponds with the modal value of the entire distribution D_{mod}). The percentage quantity of fibres that belongs to the first distribution is calculated by formula 6.

$$N_{meas} = \frac{n_1}{n} \times 100\ \%, \tag{6}$$

where: n – number of measured fibres; n_1 – number of fibres belonging to the first normal distribution.

In the case of U = 65 kV, the percentage quantity of measurements belonging to the first normal distribution is N_{meas} = 53 %.

After the analysis of the second experiment results has been completed, it can be seen that the average diameter of microfibres of the first calculated distribution corresponds with the modal value of this distribution. This value corresponds to the entire empirical distribution modal value D_{mod}. In the case of U = 45 kV, the percentage quantity of microfibres distributed normally following the pattern of the first normal distribution is N_{meas} = 55 %.

After the results of two experiment series have been estimated, it can be maintained that in both cases more than a half of all measurements are distributed following the pattern of the first distribution. Therefore, it can be maintained that more than a half of the PVA microfibres produced by electrospinning and constituting the nanofibre web belong to the group of single nanofibres. The remaining part consists of stuck together microfibres. The larger the percentage quantity of measurements is distributed normally following the pattern of the first normal distribution, the greater quantity of thinner microfibres is produced, which means that during the electrospinning the basic fabric is coated with more uniform microfibres.

Analysis and Estimation of the Structures of PVA Microfibre Webs Formed under the Different Voltages. The analysis of literature sources showed that the opinions of different authors about the influence of voltage on the structure of web do not always coincide. This chapter analyses how the voltage affects the structure and diameter of microfibre web being formed.

The average value of microfibre diameter of the first distribution, obtained during the first experiment, is 125 nm, the average value of microfibre diameter of the first distribution, obtained during the second experiment, is 145 nm. On the basis of formula 2, a relative error between the values of average diameter of the first distribution is calculated, Δx = 16 %. The error obtained is not significant; therefore, it can be maintained that the voltage does not have significant impact on the average diameter of microfibres.

In the first case the percentage quantity of microfibres belonging to the first distribution is 53 %, in the second - 55 %. The relative error between percentage quantity values obtained during both experiments is Δx = 4 %.

After the errors calculated have been assessed, a conclusion is made that the voltage does not have a significant impact on the diameter of the ultrafine fibres being formed; still it has a significant impact on electrospinning process and on density of nonwoven coating made from fibres.

A Short-Cut Method for Nano- microfibre Web Estimation. In the present study, a short-cut method of nano- microfibre web estimation is proposed. Through application of this method, it is not difficult to compute parameters necessary to estimate the structure of web from fibres when diameter dispersion characters are different. Based on this method, in accordance with empirical parameters (under U = 65 kV) measurement values are located as far as the modal value of microfibre diameter (125 nm). As the empirical values are considered distributed normally, the points symmetrical in respect of the left-hand branch, are located to the right from the modal value.

The average value of the distribution plotted in accordance with the empirical values is equal to the modal value of the empirical distribution, plotted in accordance with measurement results. The percentage quantity of microfibres belonging to this distribution is calculated, N_{meas} = 53 %.

The short-cut method of microfibre web estimation is verified by measurement results obtained during the experiment carried out under U = 45 kV. Measurement values are plotted as far as the modal value in accordance with the empirical parameters. From the modal value to the right, symmetrical points are plotted. In this case, the average value of the distribution that has been plotted in accordance with the empirical values is equal to the modal value of the empirical distribution as well. The percentage quantity of the microfibres belonging to this distribution is calculated, N_{meas} = 55 %.

It has been observed that the results obtained using the short-cut estimation method of web correspond with the results obtained when calculating the compound distribution.

Estimation of Structures of Web from the PA6.6 Microfibres. In the present study, to estimate the structure of fibre web, some investigation has been carried out with the PA6.6 polymer as well. Three series of experiments have been carried out for analysis of the structure of nonwoven coating produced from the PA6.6 nanofibres by electrospinning. The experiments were carried out when the movement speed of nonwoven material were different. After the mathematical analysis of the results obtained was completed, empirical distributions of diameter values of the PA6.6 microfibres have been created and shown in Fig. 6.

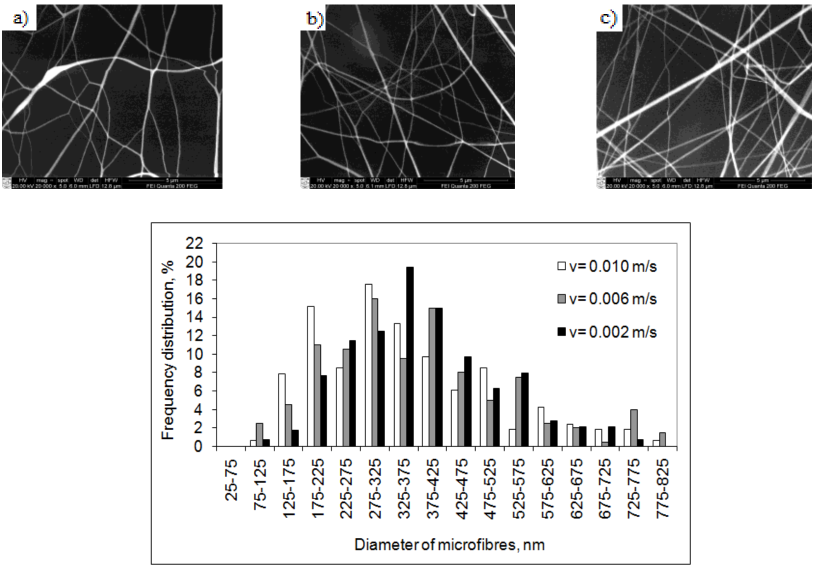

Figure 6. SEM images (scale 5 µm) of webs from PA6.6 microfibres, when the speed of movement is: a) 0.010 m/s; b) 0.006 m/s; c) 0.002 m/s and empirical distributions of diameter

Estimation of a structure made from the PA6.6 microfibres based on parameters proposed in the present work is shown in Table 1.

Table 1. Proposed criteria-based estimation of the PA6.6 micfroibre web

	v = 0.010 m/s	v = 0.006 m/s	v = 0.002 m/s
The average diameter of microfibres, nm	357	375	382
The modal value of the first distribution, nm	200	200	350
The percentage quantity of microfibres distributed by the first distribution, %	32	24	88

After the data analysis has been completed, it can be maintained that the speed of nonwoven fabric movement does not have a significante influence on the average diameter of ultrafine nanofibres, because difference between average values obtained has been just ± 3.5 %. However, the speed of movement has significante influence on web structure and density. With the decreasing movement speed during the electrospinning, fewer single and equal microfibres are generated. On the basis of data provided, it can be seen that the average diameter value d_{aver1} = 200 nm has been obtained for the ultrafine and non stuck together microfibres, which have been successfully generated at 0.010 m/s and 0.006 m/s movement speeds. The average diameter of two stuck together fibres should be d_2 = 283 nm. According to the empirical data d_{aver2} = 300 nm. A relative error Δx = 6 % obtained confirms that larger diameter webs are being formed when fibres are sticking together.

Possibilities of Estimation Nano- microfibre Diameter Dispersion through a Normal Distribution. Analysis of literature sources dealing with nano- microfibre fabrication shows that frequently authors describe fibre diameter dispersion as normally distributed (Aluigi et al., 2012; Engstrom, Hagstrom, 2009; Gu et al., 2008; Molnar et al. 2013et al.) therefore, in this part of the work, possibilities of estimating the empirical values of nano- microfibre diameter through a normal distribution.

Analysing the sources, a tricky (with several peaks) distribution of the keratin/PEO fibre web, fabricated by electrospinning, was noticed (Fig.7). The latter is similar to a compound distribution; still, the authors state that the diameter of the keratin/PEO fibres is distributed normally; therefore, a hypothesis regarding the normal distribution is verified. The skewness coefficient $|A| = 0.43$ calculated confirms that in this case diameter is distributed by normal distribution, and at the same time confirms the statement that it is not accurate to estimate distribution on the basis of just the image of this distribution. After it has been established that measurement values are distributed by normal one, the skewness coefficient, together with the average diameter value, can be used to estimate the structure of web from electrospun fibres.

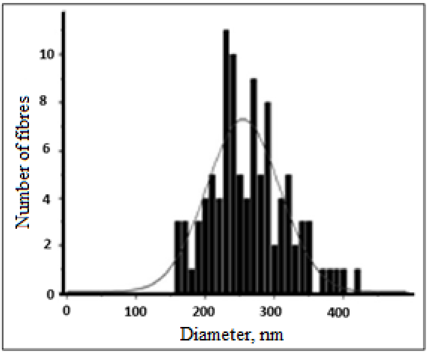

Figure 7. Distribution of the keratin /PEO fibre diameter, (Aluigi et al., 2008)

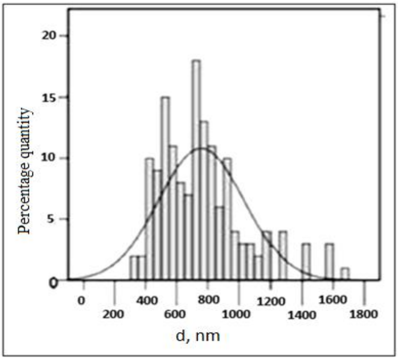

Figure 8. Empirical distribution of the PLA fibre diameter, (Cassasola et al., 2013)

In Figure 8, there is a very similar distribution provided, taken from a literature source, in which the authors state that fibre diameter is distributed by normal distribution, although it is obvious that the distribution contains several peaks. The skewness coefficient $|A| = 1.12$ being calculated denies the theory proposed by the authors regarding distribution of diameter values following the Gaussian law, because the value of the coefficient obtained is very far away from the asymmetry limit. In the case when $|A| > 0.5$, the distribution curve is considered very asymmetric in respect to the axis. This means that diameter dispersion of such character cannot be described through an asymmetric normal distribution, and measurement values must be analysed more thoroughly.

In the following phase of investigation, the distribution of the PA6 nanofibre diameter is analysed that has been obtained during the investigation (Fig. 9). The distribution of the PA6 nanofibre diameter has one peak, at the 35 nm value; therefore, the distribution has been analysed as a right-skewed normal distribution. Still, the skewness coefficient $|A| = 1.31$ obtained has shown that the distribution is extremely asymmetric and the value obtained is far away from the asymmetry limit. The assumption has been made that the PA6 nanofibre diameter is distributed following the pattern of a compound distribution. On the basis of the short-cut method of nanofibre web estimation, the empirical distribution has been described through the compound distribution that consisted of three normal distributions. The compound distribution curve corresponds to the empirical data very well ($R^2 = 0.9763$).

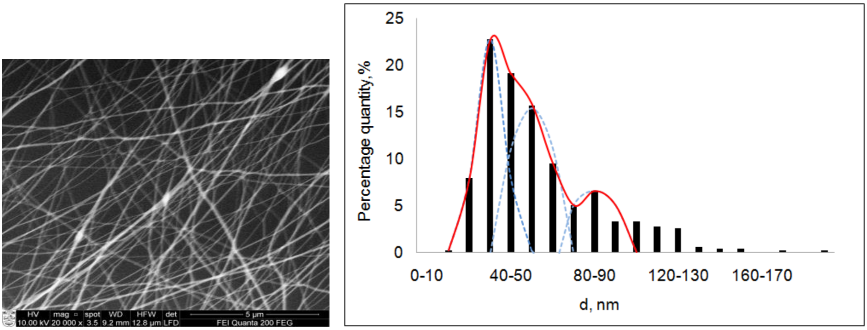

Figure 9. SEM image (scale 5 μm) and distribution of the PA6 nanofibre diameter described through a compound distribution.

In the literature sources, one can find distributions that are very difficult to assess by the curve of value distribution (Fig. 10).

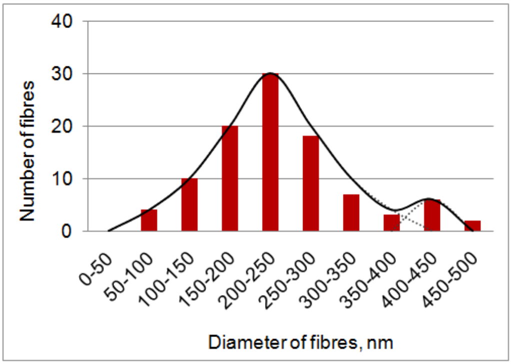

Figure 10. The empirical distribution of the PU fibre diameter described through the compound distribution (Mahadevan and Raji, 2014).

After mathematical analysis of the data has been completed, an average diameter of the PU fibres obtained has been d_{aver} = 236 nm. This value corresponds with the modal value of the entire distribution. If we consider the diameter being distributed following an assymetric distribution pattern, the skewness coefficient $|A|$ = 0.62 is calculated. Irrespective of the fact that the value obtained is very slightly away from the asymmetry limit, it can be stated that the PU fibre diameter is not distributed following the asymmetric Gaussian distribution pattern and the structure of electrospun web must be estimated through a different distribution. After the empirical values have been described through a compound distribution that consists of two normal distributions, the assumption concerning the compound distribution has been confirmed.

***Analysis of Accuracy of Fibre Web Structure Estimation*.** The PA6.6 microfibre web, manufactured from 8 % concentration solution at base movement speed v = 0.006 m/s was chosen for investigation. In total, for investigation in this study, 10 SEM images using a scanning electron microscope have been taken in different locations of nanofibre web; it means that 10 different places of web (the area of measured place 160 μm^2) have been measured. The total number of measurements of all 10 measured places images was 400. After the analysis of the data obtained has been completed, a resultant distribution of the PA6.6 microfibre diameter from all webs found in all 10 SEM images (measurement places) has been created (Fig. 11). According to the data obtained, the histogram peak can be distinguished at diameter value 200 nm. The average diameter of all micrfibres is 327.5 nm.

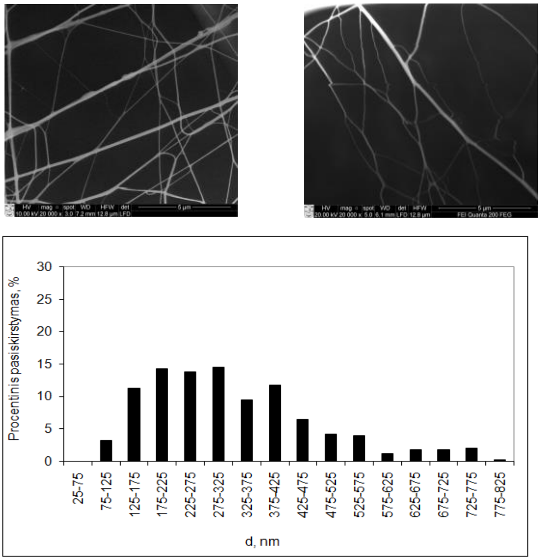

Figure 11. SEM images and resultant distribution of the PA6.6 microfibre diameters of 10 different measured places (area of measured place is 160 μm^2)

The distributions of diameter values, measured on each SEM image, are provided in Figure 12. As we can see from the distributions provided, during the electrospinning, very uneven nanofibre web is formed in different locations. The distributions created are not similar to the resultant distribution of 10 images. The modal values range from 150 nm diameter value to 300 nm value. The average values of the diameter range from diameter value 290 nm to 381 nm value. The number of measured microfibres on one image ranges from 23 microfibres to 98 microfibres. The structure cannot be estimated on the basis of data from one SEM image (one place of web).

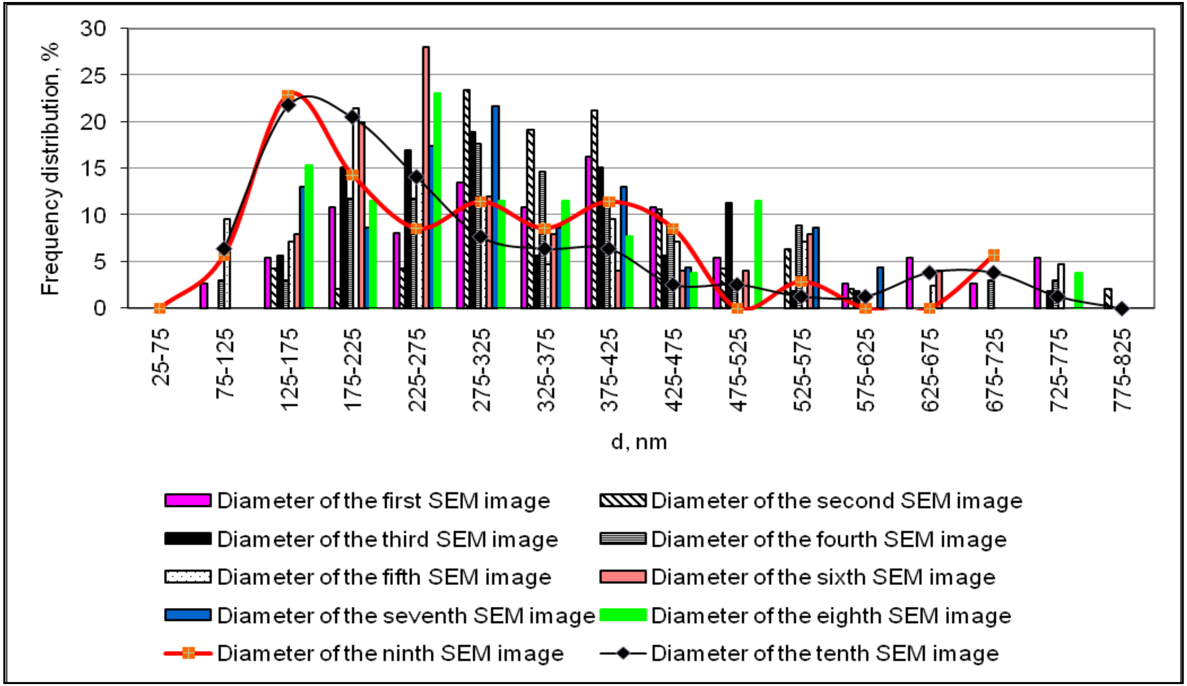

Figure 12. Microfibre diameter distributions, created on the basis of each SEM image (the area of measured place is 160 um^2)

Having created the resultant distributions from 4 and 5 first diameter values, measured in different places of electrospun web it was observed that resultant distribution of 4 images is not yet similar to the resultant distribution of 10 SEM images; still, the distribution of 5 images is quite similar to the latter.

Method of Estimation of Nano- microfibre Web Formed by Electrospinning. In this chapter, a method created in the present study is introduced in coherent sequence that describes how should be the web structure estimated in practice, taking into account the fibre diameter distribution as well (Figure 13).

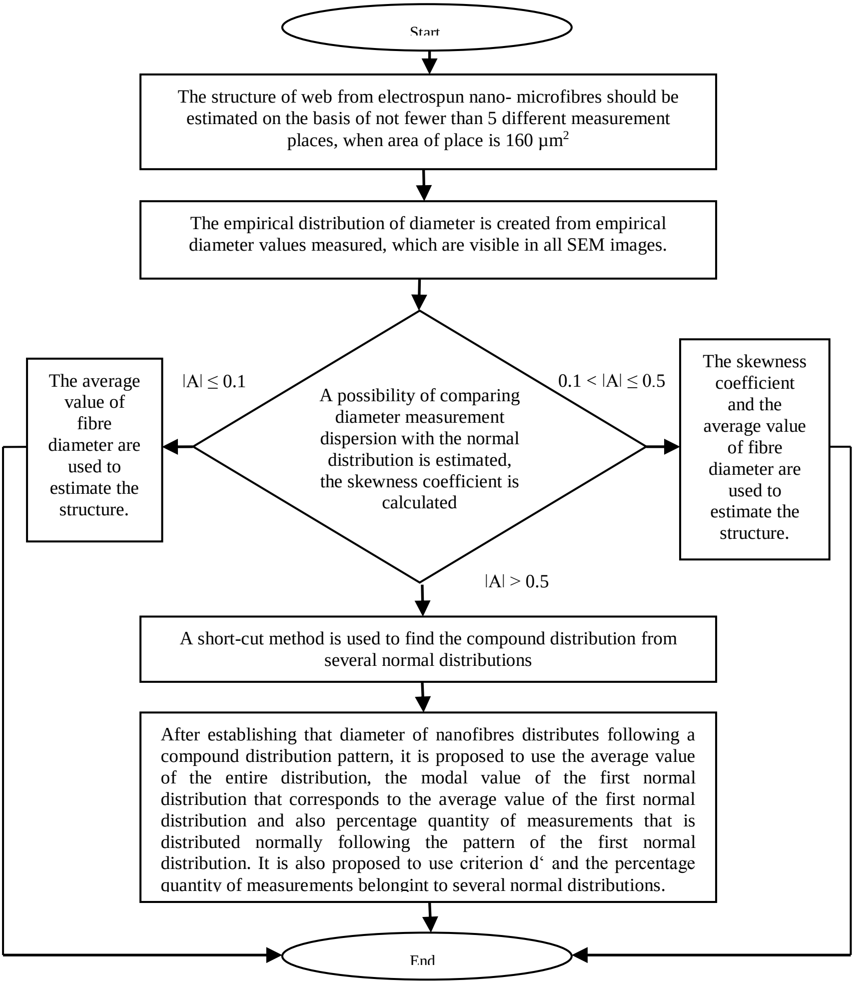

Figure 13. The algorithm of estimation of web freom electrospun nano- microfibres

1. On the basis of the method created, first of all attention is paid to the fact that the structure of nano-microfibre web must be estimated on the basis of no fewer than 5 different measurement places of web, when area of place is 160 μm^2 (SEM images). In order to evaluate the uniformity of the structure of the nanofibre web-coated covering, the SEM images applying a scanning electron microscope should be taken in different web locations.
2. During the following stage, the empirical distribution of diameter is created from empirical diameter values measured, which are visible in all 5 SEM images.
3. After the distribution has been created, a possibility of comparing diameter measurement dispersion with the normal (Gaussian) distribution is estimated. For this purpose, the skewness coefficient is calculated. If the skewness coefficient does not exceed a prescribed limit, the skewness coefficient and the average value of fibre diameter are used to estimate the structure.
4. After the skewness coefficient exceeds the prescribed limit, diameter dispersion is described through a compound distribution that consists of several normal distributions. For this purpose, a short-cut method of the compound distribution calculation is used.
5. After establishing that diameter of nano- microfibres distributes following a compound distribution pattern, to estimate the structure of web, it is proposed to use the average value of the entire distribution, the modal value of the first normal distribution that corresponds to the average value of the first normal distribution and also percentage quantity of measurements that is distributed normally following the pattern of the first normal distribution. In order to estimate the measurement values of the second normal distribution that constitutes the compound distribution, other criteria are proposed for use as well. If we need to estimate all compound distribution, not only the first normal distribution, (when a modal value is different from the first normal distribution modal value), for estimation is proposed to use criterion d’ and the percentage quantity of measurements belonging to several normal distributions.

CONCLUSIONS

1. During the electrospinning process, the web is formed from nano- microfibres with different diameter; therefore, in all cases, the results of nano-microfibre diameter dispersion are obtained differently. In the cases of different character of distribution, it is problematic to compare average values.
2. It has been established that empirical distribution of measurements that has one peak cannot be valued as lognormal distribution; still it can be valued as a normal distribution in the case when the skewness coefficient has value $|A| \leq 0.5$. In the case of normally distributed diameter values, to estimate the structure of nano-microfibre web, the average value of the diameter could be used together with the

skewness coefficient. In the case of skewness coefficient value |A| > 0.5, measurement dispersion cannot be estimated through a normal distribution.

3. The analysis of empirical distributions has shown that diameter of fibres frequently are distributed following a pattern of an incomprehensible distribution that has several peaks. During investigation, a similarity of such a distribution to a compound distribution has been identified, when through this compound distribution, the dispersion of blended spun fibre diameter values is described.

4. It has been established, that frequently the diameter of nano- microfibres is distributed following a pattern of a compound distribution, which consists of several normal distributions. In the case of larger number of measurements (342 measurements), the compound distribution describes empirical data extremely accurately (R^2=0.804). In the case of fewer measurements (138 measurements), the accuracy of the compound distribution curve conformance with empirical points is less (R^2=0.515).

5. In the case where values of nano-microfibre diameters are distributed following the pattern of the compound distribution, estimation of the structure is proposed using it together with the average value of diameter the average value of the first normal distribution, which also corresponds to the modal value and percentage quantity of measurements belonging to the first normal distribution, or criterion d' and percentage quantity of measurements belonging to several normal distributions. It has been established that the values of the proposed criteria for structure estimation (percentage quantity of fibres distributed following the pattern of the first normal distribution and the average diameter of the first normal distribution) that have been identified applying the short-cut method coincide with the values obtained through calculation of the compound. To use in practice, a short-cut method of electrospun web estimation is proposed, based just on empirical data (without calculation of normal distributions).

6. During electrospinning, the webs of different thickness are formed from several groups of different nano- microfibres, the occurrence of which during the process is determined by incomplete splitting of the solution jet into the fibres, or fibre sticking together while they are moving towards the collection screen. The peaks of the compound distribution correspond with the values of stuck together fibre diameters calculated, the relative error ranges from 4.3 % to 11. 4 %.

7. It is not accurate to estimate the structure of web by just the modal and average value of the diameter on the basis of data received from just one or two measurement places. During the process, a non-uniform structure is formed; therefore, it is proposed to create the distribution necessary for web estimation after measuring the diameter from not fewer than 5 different places of web, when area of place is 160 μm^2.

8. On the basis of structure estimation criteria proposed, it has been established that the selected voltage does not have a significant impact on the diameter of ultrafine PVA fibres being formed; still, it has some influence on the structure of

nanofibre web. With the increasing voltage, denser coating is being formed from a larger quantity of stuck together fibres; therefore, the average diameter increases. The speed of movement of nonwoven fabric does not have a significant impact on diameter of the PA6.6 fibres being formed; still, when increasing the time of movement (decreasing the speed) greater quantity of larger diameter nanofibres is formed.

9. After the analysis on different nano-microfibre webs has been completed, a new method of web structure estimation is proposed, applying which, it becomes possible to compare different webs and analyse parameters impact on diameter and quantity of fibres being formed.

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REZIUMĖ

Tiriamos problemos pagrindimas ir darbo aktualumas. Nanotechnologijos – šiandien neatskiriama mūsų kasdienybės dalis. Nanotechnologijos mus lydi buityje, kosmetikos gamyboje, medicinoje, statybų sektoriuje ir t.t. Nors įvairių nanostruktūrų taikymas mokslo srityje ir netgi praktikoje buvo žinomas nuo seno, tačiau pats terminas pirmą kartą pavartotas tik XX a. viduryje. Remiantis moksline literatūra, nanotechnologijų pradžia laikomi 1959 m., kai vienoje iš savo paskaitų mokslininkas Freyman paskelbė idėją, kad kada nors bus galima manipuliuoti medžiaga atomų lygmeniu. Nanometras – itin smulkus matas. Pavyzdžiui, žmogaus plauko skersmuo yra 80 000–100 000 nm, raudonųjų kraujo kūnelių skersmuo – 7000 nm, DNR grandinės elemento – 2 nm.

Elektrinis verpimas – procesas, kurio metu veikiant elektrostatinėms jėgoms, iš polimerinio tirpalo ar lydalo, formuojasi nano- ir mikrogijos. Nors įvairiuose literatūros šaltiniuose nanogijos apibrėžiamos skirtingai, remiantis Europos Sąjungos pateiktomis rekomendacijomis (Europos Sąjungos Rekomendacijos, 2011) šiame darbe *nanogijomis* vadinamos gijos, kurių skersmuo kinta nuo 1 iki 100 nm. Gijos, kurių skersmuo didesnis nei 0,1 µm, vadinamos *mikrogijomis*.

Nano- ir mikrogijos pasižymi unikaliomis savybėmis: dideliu savitojo paviršiaus plotu, porėtumu (didelis porėtumas ir mažas porų dydis), mažu gijų skersmeniu. Dėl šių savybių nano- ir mikrogijos bei medžiagos iš jų, itin plačiai naudojamos medicinoje (dirbtinių organų gamyboje, audinių inžinerijoje), filtrų, apsauginių drabužių, kompozitų, optinių ir elektroninių prietaisų gamyboje.

Pastaraisiais metais atlikta daugybė tyrimų, susijusių su elektrinio verpimo procesu. Ypač daug dėmesio skirta siekiant nustatyti įvairių veiksnių įtaką formuojamos nano- ir mikropluoštinės dangos sandarai. Literatūros šaltiniuose plačiai nagrinėjama polimerinio tirpalo koncentracijos, jo paviršiaus įtempio, laidumo elektros srovei įtaka, formuojamos gijinės dangos struktūrai. Taip pat nagrinėjama technologinių parametrų, tokių kaip įtampos, atstumo tarp elektrodų, polimero tekėjimo greičio ir aplinkos sąlygų (drėgmės, temperatūros, slėgio) įtaka besiformuojančios dangos struktūrai ir gijų morfologijai. Visi šie parametrai turi įtaką dangos iš nano- ir mikrogijų struktūrai.

Remiantis įvairiuose literatūros šaltiniuose pateiktais tyrimų rezultatais pastebėta, kad dažnai tirdami to paties parametro įtaką nano- ir mikrogijinės dangos sandarai, autoriai gauna skirtingus rezultatus. Kitaip tariant, labai dažnai tos pačios polimerinio tirpalo savybės, technologinio ar aplinkos parametro įtaka gijų skersmeniui, sandarai, formai, akučių dydžiui ar formai gaunama skirtinga. Tikėtina, kad taip nutinka dėl to, kad autoriai ne visuomet nurodo visus duomenis, galinčius turėti lemiamą įtaką tyrimų rezultatams. Taip pat paminėtina, kad autoriai elektrinio verpimo būdu susiformavusią dangos struktūrą dažnai vertina subjektyviai, remdamiesi tik vidutiniu ar modaliniu skersmeniu ir ne visada nurodo kaip buvo skaičiuojamas vidutinis gijų skersmuo, taip pat ne visada nurodomas gijų kiekis, kuris buvo naudojamas skaičiuojant vidurkį, neanalizuojama gijų skersmens sklaida. Galima manyti, kad rezultatų nevienodumą lemia ne visų duomenų pateikimas ir analizė.

Darbo naujumas ir jo reikšmė. Dėl didelių nano- ir mikrogijų bei medžiagų iš jų panaudojimo galimybių ir perspektyvų, elektrinio verpimo procesas yra plačiai nagrinėjamas ir aprašomas įvairioje literatūroje. Remiantis ja galima teigti, kad elektrinio verpimo procesas – labai jautrus procesas, kuriam įtaką turi polimerinio tirpalo savybės, technologiniai bei aplinkos parametrai. Analizuojant priežastis, kodėl neretai įvairių mokslininkų atliktų tyrimų rezultatai gaunami skirtingi, prieita prie išvados, kad pagrindinė neatitikimų priežastis yra ta, kad iki šiol nėra sukurtos bendros nano- ir mikrogijinės dangos vertinimo metodikos. Literatūroje itin retai analizuojama susiformavusių gijų skersmens sklaida, o išvados apie vieno ar kito parametro įtaką dangos morfologijai pateikiamos remiantis tik vidutine skersmens verte ar modaliniu gijų skersmeniu. Išsamesnė rezultatų analizė parodė, kad šie parametrai įvertina tik skersmenį, tačiau neatskleidžia, kokia danga formuojasi proceso metu. Neanalizuojamos ir priežastys, kodėl to paties proceso metu formuojasi skirtingo storio gijos. Kadangi nėra bendros vertinimo metodikos, sunku lyginti įvairių autorių darbus, todėl tyrimai nano- ir mikrogijinės dangos vertinimo srityje yra labai svarbūs ir reikalingi siekiant ne tik optimizuoti elektrinio verpimo procesą, bet ir tinkamai įvertinti parametrų įtaką skersmeniui bei struktūrai.

Nepaisant to, kad literatūroje gijinės dangos struktūra dažniausiai vertinama tik remiantis vidutiniu gijų skersmeniu, galima rasti darbų, kuriuose autoriai analizuoja skersmens sklaidą, o gautą skersmens skirstinį aprašo normaliuoju (Gauso) ar logaritminiu skirstiniu. Neretai tokiuose darbuose suformuotas skirstinys nėra panašus į normalųjį skirstinį, todėl tokiais atvejais aprašyti skersmens vertes šiuo skirstiniu nėra tikslu matematinės statistikos atžvilgiu. Paminėtina ir tai, kad skersmens verčių aprašymas logaritminiu skirstiniu neturi fizikinės prasmės, nes elektrinio verpimo metu susidariusių gijų skersmens vertės nepriklauso nuo laiko.

Išanalizavus literatūros šaltinius ir atlikus jų apibendrinimą, taip pat atliekant tyrimus nustatyta, kad visais atvejais, nepriklausomai nuo tyrimuose naudojamo polimerinio tirpalo, suformuotų gijų skersmuo pasiskirsto skirtingai, todėl įvairiais atvejais skirstiniai gaunami skirtingi. Esant skirtingiems sklaidų pobūdžiams sunku lyginti vidutines vertes, todėl sunku tinkamai įvertinti kokią įtaką daro įvairių parametrų keitimas formuojamos dangos iš nano- ir mikrogijų struktūrai. Proceso metu susiformavusią dangą vertinti tik pagal vidutinę skersmens vertę, neįvertinant skersmens skirstinio, nėra tikslu, todėl reikalingas naujas vertinimo metodas.

Darbo naujumas – sukurtas naujas nano- ir mikrogijinės dangos vertinimo metodas, pagrįstas matematiniais kriterijais, įvertinantis skersmens pasiskirstymą ir vidutinį skersmenį. Gauti rezultatai parodė, kad dažnai parametro pakeitimas turi įtaką tik elektrinio verpimo procesui ir dangos struktūrai, tačiau neturi lemiamos įtakos vidutiniam ploniausių gijų skersmeniui (šiame darbe ploniausiomis gijomis vadinamos gijos, pasiskirsčiusios pagal pirmąjį, jungtinio skirstinio normalųjį skirstinį). Darbe pasiūlyta kaip vertinti skirstinius, kai gijų skersmens vertės pasiskirsto matematikoje nežinomu skirstiniu. Gauti tyrimų rezultatai turi svarbią praktinę reikšmę, nes darbe pasiūlytas nano- ir mikrogijinės dangos vertinimo metodas leidžia įvertinti ir palyginti bet kokią elektrinio verpimo būdu suformuotą struktūrą. Remiantis šiuo vertinimo metodu galima palyginti įvairių autorių gautus rezultatus.

Darbe nustatyta, kad empirinis skersmens skirstinys, turintis kelias smailes, gali būti lyginamas su jungtiniu skirstiniu. Taip pat nustatyta, kad pasirinkta įtampa turi įtakos formuojamos gijinės dangos struktūrai ir įvairių darinių formavimuisi, tačiau neturi žymios įtakos ploniausių gijų skersmeniui. Esant didesnei įtampai susiformuoja danga iš didesnio kiekio sulipusių gijų, o tai lemia vidutinio visų gijų skersmens didėjimą. Neaustinės medžiagos judėjimo greitis taip pat neturi įtakos ploniausių gijų skersmeniui, tačiau turi įtaką dangos struktūrai bei tankumui. Tyrimų rezultatai parodė, kad elektrinio verpimo metu, dėl gijų sulipimo ar nevisiško srovelės išsiskaidymo, susiformuoja skirtingo storio dariniai. Remiantis atliktų tyrimų duomenimis galima teigti, kad struktūros vertinimo tikslumas priklauso nuo to, keliose skirtingose dangos vietose buvo atlikti matavimai. Remiantis šiame darbe gautais tyrimų rezultatais, struktūrą siūloma vertinti ir analizuoti ne mažiau kaip 5 skirtingose dangos vietose, kurių plotas yra 160 μm^2. Struktūros vertinimas remiantis matavimais, atliktais mažiau kaip 5 dangos vietose, gali būti netikslus ir sąlygoti prieš tai minėtų netikslumų atsiradimą.

IŠVADOS

1. Elektrinio verpimo metu susiformuoja danga iš įvairaus skersmens nano- ir mikrogijų darinių, dėl to visais atvejais nano- ir mikrogijų skersmens sklaidos rezultatai gaunami skirtingi. Esant skirtingiems pasiskirstymo pobūdžiams problemiška lyginti vidutines vertes.
2. Nustatyta, kad empirinis matavimų skirstinys, turintis vieną smailę, negali būti vertinamas kaip logaritminis skirstinys, tačiau gali būti vertinamas kaip normalusis asimetriškas skirstinys, kai asimetrijos koeficiento vertė $|A| \leq 0,5$. Kai

skersmens vertės pasiskirsto asimetrišku normaliuoju skirstiniu, struktūrai įvertinti galima taikyti vidutinę skersmens vertę bei asimetrijos koeficientą. Kai asimetrijos koeficientas |A| > 0,5, matavimų sklaida negali būti vertinama normaliuoju skirstiniu.

3. Empirinių skirstinių analizė parodė, kad gijų skersmuo dažnai pasiskirsto nesuprantamu skirstiniu, turinčiu kelias smailes. Tyrimų metu nustatytas tokio skirstinio panašumas į jungtinį skirstinį, kuriuo aprašoma mišriapluoščių verpalų skersmens verčių sklaida.

4. Nustatyta, kad dažnai nano- ir mikrogijų skersmuo pasiskirsto jungtiniu skirstiniu, sudarytu iš kelių normaliųjų skirstinių. Esant didesniam matavimų skaičiui (342 mikrogijiniai dariniai), jungtinis skirstinys labai tiksliai aprašo empirinius duomenis (R^2=0,804). Esant mažesniam matavimų skaičiui (138 mikrogijų skersmens dariniai), jungtinio skirstinio kreivės atitikimo empiriniams taškams tikslumas – mažesnis (R^2=0,515).

5. Kai nano- ir mikrogijų skersmens vertės pasiskirsto jungtiniu skirstiniu, struktūrai vertinti, kartu su vidutine skersmens verte, siūloma taikyti pirmojo normaliojo skirstinio vidutinę vertę, atitinkančią ir modalinę vertę bei procentinį matavimų kiekį, priklausantį pirmajam normaliajam skirstiniui arba kriterijų d' ir procentinį gijų kiekį, pasiskirsčiusį pagal kelis normaliuosius skirstinius. Nustatyta, kad struktūrai įvertinti siūlomų kriterijų (procentinio gijų skaičiaus pasiskirsčiusio pagal pirmąjį normalųjį skirstinį ir vidutinio pirmojo normaliojo skirstinio skersmens) vertės, nustatytos naudojant supaprastintą būdą sutampa su vertėmis, gautomis skaičiuojant jungtinį skirstinį. Praktiniam taikymui siūlomas supaprastintas nano- ir mikrogijinės dangos vertinimo būdas, paremtas tik empiriniais duomenimis (neskaičiuojant normaliųjų skirstinių).

6. Elektrinio verpimo metu skirtingo storio dariniai susiformuoja iš kelių skirtingų gijų grupių, kurių atsiradimą proceso metu lemia nevisiškas tirpalo srovelės išsiskaidymas į gijas arba gijų sulipimas tarpusavyje, pastarosioms judant surinkimo plokštės link. Jungtinio skirstinio smailės atitinka apskaičiuotas sulipusių gijų skersmens vertes, santykinė paklaida svyruoja tarp 4,3 % ir 11, 4 %.

7. Nano- ir mikrogijinės dangos struktūrą nėra tikslu vertinti tik modaline ir vidutine skersmens verte, remiantis vienos ar dviejų matavimo vietų duomenimis. Proceso metu susiformuoja nevienoda struktūra, todėl siekiant optimaliai įvertinti struktūrą, skirstinį siūloma sudaryti iš matavimų gautų analizuojant ne mažiau kaip 5 skirtingas dangos vietas, kurių skersmuo 160 μm^2.

8. Remiantis pasiūlytais struktūros vertinimo kriterijais nustatyta, kad pasirinkta įtampa neturi reikšmingos įtakos formuojamų, ploniausių PVA mikrogijų skersmeniui, tačiau turi įtaką gijinės dangos struktūrai. Didėjant įtampai suformuojama tankesnė danga iš didesnio kiekio sulipusių gijų, todėl didėja vidutinis skersmuo. Neaustinės medžiagos judėjimo greitis neturi reikšmingos įtakos formuojamų ploniausių PA6.6 mikrogijų skersmeniui, tačiau mažinant greitį, formuojasi daugiau storesnio skersmens mikrogijų, atsirandančių sulipus gijoms.

9. Atlikus įvairių nano- ir mikrogijinių dangų analizę pasiūlytas naujas dangos struktūros vertinimo metodas, kuriuo remiantis galima lyginti įvairias nano- ir mikrogijines dangas bei analizuoti parametrų įtaką formuojamų gijų skersmeniui bei kiekiui.

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