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VIRGINIJA KLEIVAITĖ

THE METHOD OF HIGHEST PORE ESTIMATION OF ELECTROSPUN THIN FIBROUS WEBS

SUMMARY OF DOCTORAL DISSERTATION

TECHNOLOGICAL SCIENCES, MATERIALS ENGINEERING (T 008)

Kaunas
2021

KAUNAS UNIVERSITY OF TECHNOLOGY

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The dissertation was carried out in 2016–2020 at Kaunas University of Technology, Faculty of Mechanical Engineering and Design, Department of Production Engineering. The research was supported by the Lithuanian Science Council.

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

VIRGINIJA KLEIVAITĖ

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INTRODUCTION

The nanofibers obtained from different materials are used in textiles, electronics, environment, medicine and many other areas. However, most of the work has been done to adapt nanofibers to health. Dense and ultra-low pores fabrics are fine air filters that catch even the smallest particles in the air. The cleaned air of such filters would further improve the lives of sensitive groups of people. Another area of great interest to scientists is biomedicine. Woven fibers from biodegradable and harmless materials can potentially become the basis for artificially cultivating human tissues, subsequently used for reconstructing damaged organs or even replacing, for example, clogged blood vessels or striking heart valves [1–5].

Porosity is one of the factors that influences the physical interactions and chemical reactivity of solids with gases and liquids for many industrial applications. The examples of industrially important porous materials include catalysts, construction materials, ceramics, pharmaceutical products, pigments, sorbents, membranes, electrodes, sensors, active components in batteries and fuel cells as well as oil and gas bearing strata and rocks. The most common characteristics of porous solids are specific surface area, average pore size and pore size distribution [6].

The electrospun nanofibers incorporated with antimicrobial agents have been produced with the antimicrobial capability against the wide range of microorganisms. The morphologies and performance of antimicrobial electrospun nanofibers are emphasized, and a specific attention is given to the future application of electrospun nanofibers with antimicrobial capability. The porosity of the structure of nanofibers has not been evaluated, although it can be considered as a structural imbalance. Many people may ask for materials containing barrier properties such as to prevent any harmful effects to the human body, and because of this, there are many additional substances that can have an antibacterial effect and can easily get into the structure, but there are many people who are allergic to such substances as silver or zinc. Therefore, it is necessary to block the path to bacteria without additional added substances [7–11].

In electrospinning, a web of nanofibers usually consists of different pores and nanofibers of different diameters. There is no single opinion about the reasons for such phenomena, as the distribution of the nanofiber diameter is very sophisticated as well. Many applications of electrospun nanofibers could be greatly improved by increasing the surface area and porosity of the fibers. The analysis of various works shows that the distributions of the nanofiber diameter are always different and usually far from 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, and it is not easy to characterise webs mathematically and evaluate the shape of the obtained distribution. The different fineness of fibers influences the structure of the web and herewith the end-use properties of such kind of nanomaterial [12–17].

The aim of the doctoral dissertation is to develop a method for estimating the maximum possible pore of thin filamentary coatings formed by electrospinning based on the mathematical statistical criteria and the laws of probability theory.

Objectives of the dissertation:

1. To analyse the existing methods for determining the porosity of nanofiber coating and evaluate their shortcomings for predicting the maximum possible probability of the pore.
2. To analyse and determine the regularities of the value distribution of the maximum pore diameter of PA6 nanofiber coating and their differences with the usual Gaussian distribution.
3. To determine that the value of the xS rule that can be used to predict the probability of the largest pore of PA6 nanofiber coating with 99.9% probability instead of the usual 4S rule at normal Gaussian distribution and the dependence of x value on the number of maximum pore measurements.
4. To determine the correlations of the distribution asymmetry coefficient A and xS of the maximum web diameter values and the relative value between the largest web diameter and the average maximum web diameter value Δd and xS and evaluate the probability of occurrence of the largest mesh accordingly.
5. To determine the validity of Δd and xS correlation for different types of polymeric nanofiber coatings and compare this correlation with the corresponding correlation of PA6 nanofiber coating.
6. To develop a new method for estimating and predicting the maximum pore size of a nanofiber coating based on the correlation regularities of Δd and xS.

Novelty and practical value of the dissertation. There are many works in which the authors analyse the influence of various parameters on the process of electrospinning or nanofiltration, but most of them do not analyse the structural uniformity of the structure using mathematical statistical criteria. The authors rarely indicate the method of measuring, i.e., how many measurements were made on the surface of the formed webs. The structures of the electrospun webs are very often not uniform in the whole area. The analysis of papers has shown that the authors sometimes evaluate the structure of the formed web on the basis of data only from one or two SEM images. This means that only one or two sites of a certain area are analysed, but this is not an objective method of structure evaluation, since such analysis does not take into account the unevenness of the entire structure of the resulting web. However, in any case, it is necessary to evaluate the coverage of the entire area with the unevenness; therefore, the structure must be evaluated on the basis of different surface web measurements, and more precisely, the influence of the parameters on the structure and the diameter of the nanosized webs [24–26].

In this dissertation, all measurements and their results are presented by surface analysis of nanofiber coating, and the experiments are applicable only to very thin (less than 1 μm) coatings. The obtained research results have an important practical significance, because the method of nanofiber coating evaluation proposed in the work allows to evaluate and compare any thin filament structure formed by the electric spinning. The dissertation proposes a new structure estimation method that does not require many calculations, based on the relative value between the largest pore and the value Δd. The developed method was tested with nanofiber structures of different polymers at different results. It has been shown that the developed method can be applied to various polymeric nanofiber coatings.

RESULTS ANALYSIS

Analysis and evaluation of coatings formed from PA6 nanofibers

The nanofibers structures formed by electrospinning are influenced by many factors. Analysing various literature sources about the process of electrospinning, the opinions of the authors often differ due to the influence of various parameters on the porosity of nanofibers. Analysing the nanofiber coatings formed during the research and their SEM images, it has been observed that the structure consists of pores of different sizes. Porosity is one of the factors that influences the physical interactions and chemical reactivity of solids with gases and liquids for many industrial applications. The examples of industrially important porous materials include catalysts, construction materials, ceramics, pharmaceutical products, pigments, sorbents, membranes, electrodes, sensors, active components in batteries and fuel cells as well as oil and gas bearing strata and rocks. The most common characteristics of porous solids are specific surface area, average pore size and pore size distribution [6].

The electrospun nanofibers incorporated with antimicrobial agents have been produced with the antimicrobial capability against a wide range of microorganisms. The morphologies and performance of antimicrobial electrospun nanofibers are emphasized, and a specific attention is given to the future application of electrospun nanofibers with antimicrobial capability. The porosity of the structure of nanofibers is not evaluated, although it can be considered as a structural imbalance. Many people may ask for materials containing barrier properties such as to prevent any harmful effects to the human body, and because of this, there are many additional substances that can have an antibacterial effect and can easily get into the structure, but there are many people who are allergic to such substances as silver or zinc. Therefore, it is necessary to block the path to the bacteria without additionally added substances.

SEM images were measured at 30 kV and 50,000x magnification scale. The measurements of nanofiber diameters were performed using the computer program Image.J. A computer program was used to measure the maximum pores. When a maximum pore is found in the sample, the circle is drawn in the middle, and its diameter is measured. All samples were measured in this way. In each sample, the pore with highest diameter was measured, and in such a way, 4 series with 100 measurements (in total 400 measurements) were obtained.

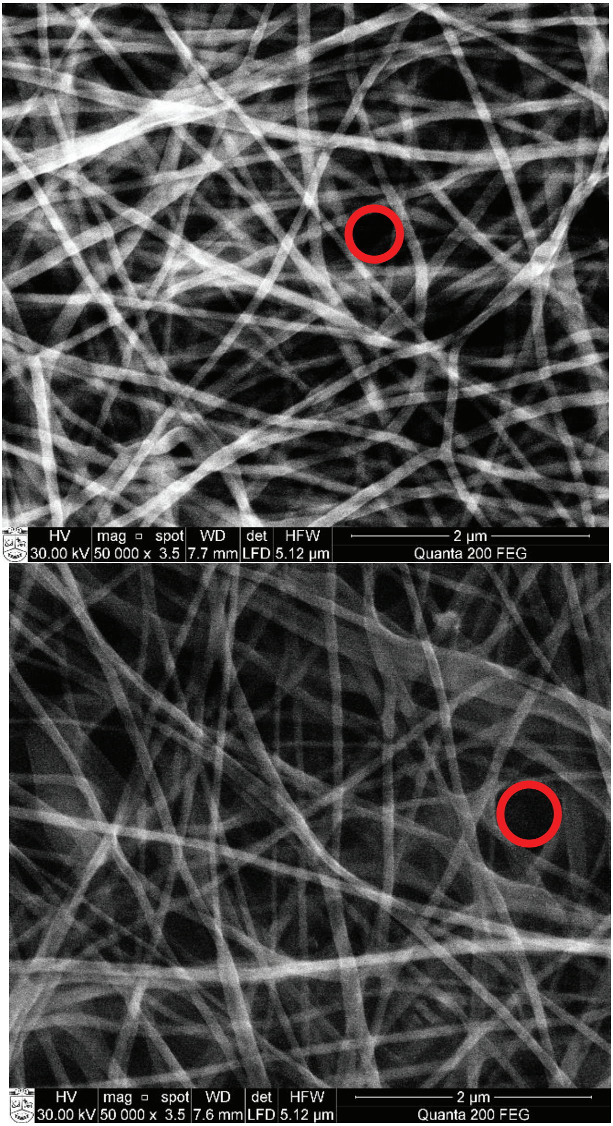


Fig. 1. SEM images describing the porosity of the surface

Table 1. Percentage of porosity

Range of results, nm	Number of results, units	Percentage of porosity, %
0–50	8	2
50–100	59	14.75
100–150	60	15
150–200	112	28
200–250	91	22.75
250–300	15	3.75
300–350	14	3.5
350–400	26	6.5
400–450	2	0.5
450–500	7	1.75
500–550	1	0.25
550–600	4	1
600–650	0	0
650–700	1	0.25

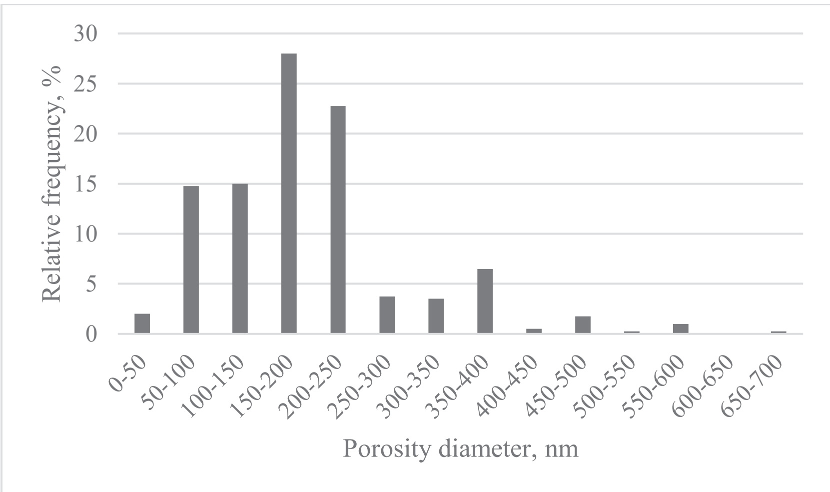


Fig. 2. Porosity distribution

The analysis of 4 series of measurements shows that the character of distribution in all cases was very similar: the average value in all cases was obtained in the column of modal value of distribution, i.e., at 100–200 nm. All distributions have similar positive skew, and the coefficient of asymmetry A, which evaluates the skewness of distribution, was obtained in the range of 1.4. Such relatively high skew shows an important difference from the classical normal Gaussian distribution [29]. It means that the classical statistical evaluation of obtained distributions cannot be used, and the highest value of possible pore size cannot be predicted without additional analysis of distribution.

Table 2. Percentage of porosity

Range of results, nm	Percentage of porosity, %
0–100	13
100–200	44
200–300	29
300–400	8
400–500	3
500–600	2
600–700	1

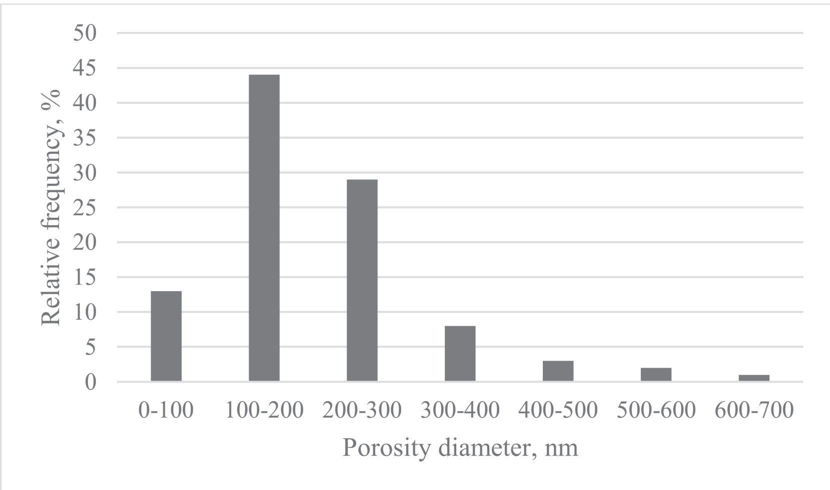


Fig. 3. Porosity distribution of the first series

Table 3. Percentage of porosity

Range of results, nm	Percentage of porosity, %
0–100	11
100–200	46
200–300	29
300–400	11
400–500	2
500–600	1
600–700	0

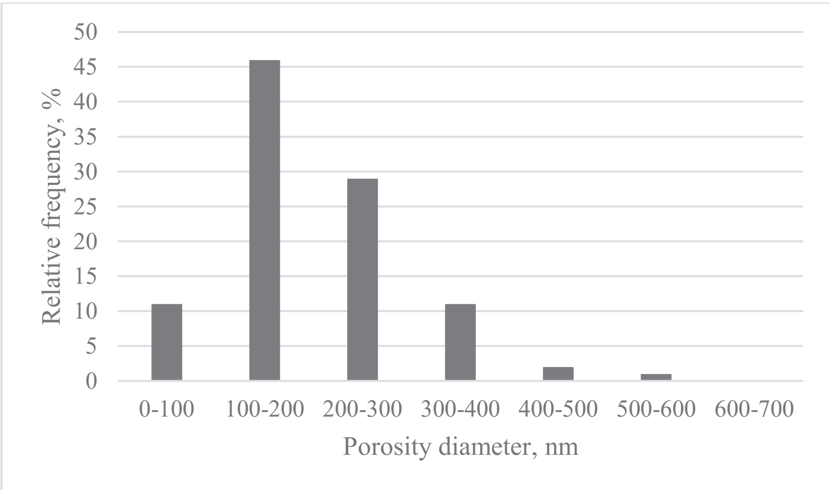


Fig. 4. Porosity distribution of the second series

Table 4. Percentage of porosity

Range of results, nm	Percentage of porosity, %
0–100	15
100–200	41
200–300	28

300–400	13
400–500	3
500–600	0
600–700	0

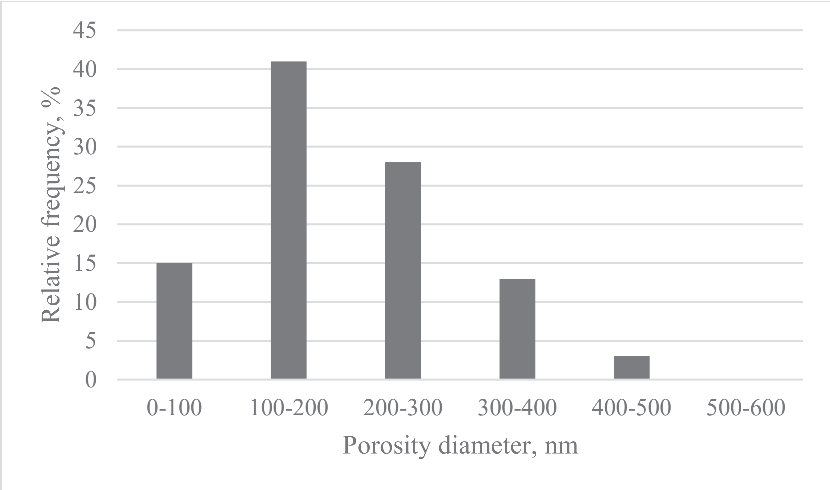


Fig. 5. Porosity distribution of the third series

Table 5. Percentage of porosity

Range of results, nm	**Percentage of porosity, %**
0–100	28
100–200	41
200–300	20
300–400	8
400–500	1
500–600	2
600–700	0

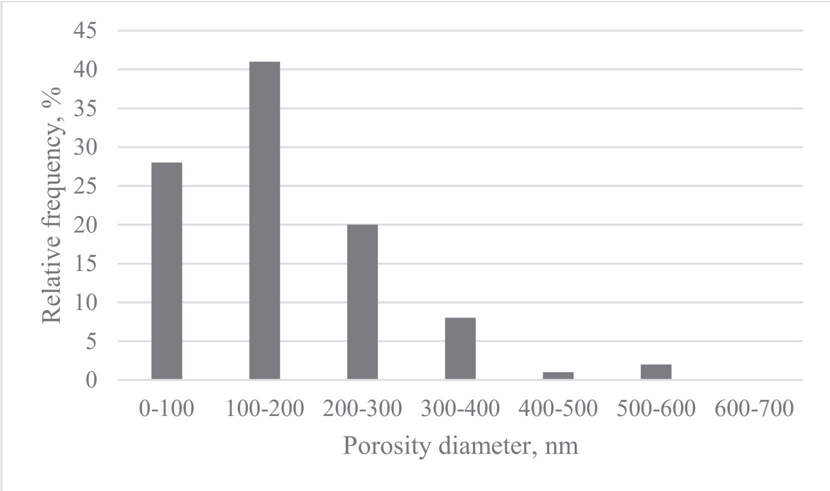


Fig. 6. Porosity distribution of the fourth series

The highest differences were obtained in the maximum pore of all measurements of 4 series: it was obtained twice that the maximum pore is in the range of 500–600 nm, once in the range of 400–500 nm and once in the range of 600–700 nm. It means that sometimes in an electrospun web, there can be found a pore whose range is not similar to the other series of measurements. This phenomenon creates a big difficulty for the maximum porosity of all web evaluation. However, it was found only once that a pore of web is much higher than in the other series: only one pore had the diameter higher than 600 nm, i.e., it had 667 nm, and the next one after the maximum pore was similar to the cases of maximum pore of series No. 2 and No. 4, i.e., the diameters were in the range of 580 nm. The difference between the maximum pore and the second one is not very high, only 13% in all series of measurements.

Four series with 100 photos in each were measured for comparing the distribution similarity. All four graphs show a similar distribution of pores, i.e., about 45 percent of the distribution of all pores is between 100 and 200 nanometers. The results show that similar distribution is seen in pores at different locations.

Mathematical statistical evaluation of nanofiber coating according to 3S rule

Based on the studies, it is not appropriate to evaluate the porosity of the nanofiber coating based on one or two SEM photographs (by measuring one or two filament coating sites). The process results in a very different structure, and this needs to be taken into account when assessing the total coating that was formed. Although the number of pores measured at each measurement site affects the number of measurement sites required for the evaluation, the test showed that in order to obtain reliable evaluation results, the structure of the nanofiber coating should be analysed in at least 5 coating sites.

At the next step of this investigation, the author of the dissertation has checked how big is the difference between the average value of the maximum pore and the maximum pore in each series. From the theory of mathematical statistics, it is known that if the maximum value of all the measurements is not higher than the average value plus 3S (3 standard deviations), the highest possible value of reliability that is obtained is 99%, in the case 4S, the reliability is 99.9%, and in the case 5S, 99.99%. While in these cases of all 4 series, there has been obtained higher inequality: the distance between average values and maximum values in some cases were higher. The calculation of relation of the distance between the maximum pore and the average pore l and square deviation S showed that this distance is in the range of 2.83–4.34. It means that the influence of distribution skewness is significant, and in this analysed case, it is not absolutely Gaussian normal distribution, as in Gaussian normal distribution for 100 measurements, the 4S rule need to work, and no measurements could be obtained whose value would be higher than the average value plus 4S.

Thus, it could be stated that for the maximum porosity evaluation, not 3S or 4S rule, but much higher reserve needs to be used, as in two cases, the obtained value is higher than 4.

Table 6. Statistical parameters of 4 series with 100 measurements of porosity

	1	2	3	4
Pore average, d (nm)	200	198	189	171
Standart deviation S	108	91	94	107
Max pore, dmax (nm)	667	576	455	576
Pore averaged + 3S	200+324=524	198+273=471	189+282=471	171+321=492
The distance between the largest pore and the average value, l (nm)	467	378	266	405
Value x / S	4.34	4.15	2.83	3.79

Thus, it means, that if there are 100 measurements for the maximum pore size prediction with reliability of 99.9%, not 4S rule as in normal Gaussian distribution, but the 5S rule needs to be used, as the 4S rule did not work for two of the analysed series.

However, 100 photos is a huge amount for practical usage: to make such a high number of SEM images would take a lot of time, and for researchers, it would be not very acceptable. Thus, at the next step of this investigation, the author of the dissertation checked what xS rule needs to be used if the number of measurements is lower. For this purpose, the 3rd series of measurements (the series was chosen as the closest to the Gaussian normal distribution) was randomly divided into 5 series with 20 measurements in each, and the results were compared with the maximum pore size of all 400 measurements. In such a way, the author of the dissertation compared the most drastic case of the investigations: the most unique distribution (series 3) was taken and compared with the highest pore of all measurements, which appeared not in the 3rd series, but in the 1st series. The statistical parameters of all series are presented in Table 7.

Table 7. Statistical parameters of 5 series with 20 measurements

	3.1	3.2	3.3	3.4	3.5
Pore average, d (nm)	238	179	171	150	208
Standart deviation, S	89	98	92	85	87
Max pore, dmax (nm)	424	394	455	273	364
Pore average d + 3S	238+267= 505	179+294= 473	171+276= 447	150+255= 405	208+261= 469
Distance between the largest of all 400 measurement pores (667 nm) and the average of the current series, l (nm)	667-238=429	667-179=488	667-171=496	667-150=517	667-208=459
Value x / S	4.82	4.98	5.39	6.08	5.28

The results show that in 20 photo cases, even 6S rule cannot be used, as it does not work for one of the series. When the measurements of the 3rd series were divided into ten series with 10 photos, the results were even worse: the maximum value l/S was calculated as 6.08. It means that for the maximum pore prediction with 99.9% reliability, 7S rule needs to be used.

At the next step of this investigation, 3.4 series (the reason for choosing 3.4 series is the same as in the previous case) were randomly divided into two series by 20 measurements. The statistical results are presented in Table 8

Table 8. Statistical parameters of 2 series with 10 measurements

	3.1.1	3.2.2
Pore average, d (nm)	142	158
Standart deviation, S	72	101
Max pore, dmax (nm)	242	364
Pore average d + 3S	142+216=358	158+303=461
Distance between the largest of all 400 measurement pores (667 nm) and the average of the current series, l (nm)	667-142=525	667-158=509
Value x / S	7.29	5.04

It is evident that for the maximum pore size prediction with reliability 99.9% in 10 photos cases, 8S rule needs to be used, as the maximum value l/S was obtained higher than 7.

Thus, it has been found that in the case of 100 measurements for the maximum pore prediction with reliability of 99.9%, it is necessary to use the 5S rule, for 20 measurements, 7S rule and for 10 measurements, 8S rule.

The results were compared with other kinds of electrospun webs from: polyester, polyvinyl alcohol, cellulose acetate, and in all cases, similar results were obtained: in the case of 10 images for maximum pore size evaluation with reliability 99.9%, the rule of 4S does not work, and for the evaluation, it is necessary to use the 8S rule at least.

It was stated that the distribution of maximum pore size in various places of the web is close to the Gaussian normal distribution with some positive skew, and the coefficient of asymmetry of skewness is in the range of 1.4. This skewness affects the results of the maximum pore size evaluation. It was stated that for the maximum pore size evaluation with reliability 99.9%, it is not possible to use 4S (4 standard deviation) rule. In the case of 100 measurements, it is necessary to use the 5S rule, and in the case 20 or 10 measurements, even 7S and 8S rule, respectively. Thus, the results show that for the maximum possible pore size evaluation, it is necessary to have much more than 10 or 20 measurements (photos), and with the standard deviation, it is necessary to use higher coefficient as in the classical statistical case for obtaining the same reliability. The obtained results show good correlation with the results of the other electrospun webs from other kinds of polymers. Nevertheless, for an objective method development, many more various kinds of electrospun webs need to be used. This paper shows only the problem of an objective maximum pore size evaluation of electrospun web, and the way in which this problem could be solved.

Possibilities of asymmetry coefficient estimation of nanofiber diameter dispersion

In the next stage of the research, the author checked the possibility to predict the largest pore and its probability using the distribution asymmetry coefficient A. The asymmetry coefficient was chosen because it is relatively easy to calculate and is calculated in almost all statistical analysis software packages, e.g., ANOVA etc. All the results for individual 20 series of 20 photos are shown in Table 9.

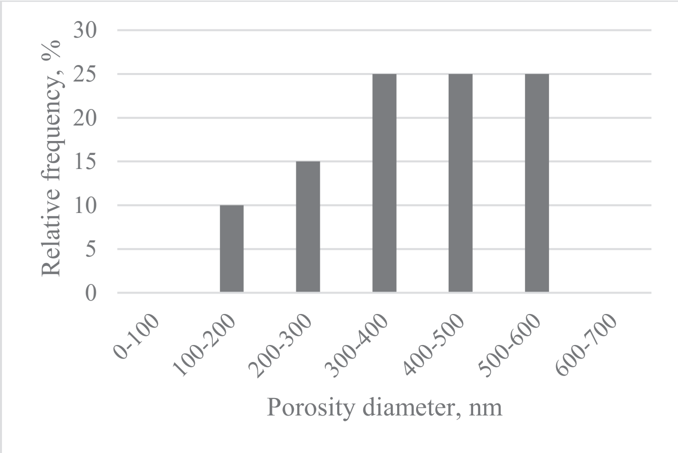
Table 9. Statistical parameters of 20 series with 20 measurements of mesh porosity

Serial No.	Δd, %	Average, nm	|A|	S	3S	Max pore, nm	l, nm	xS
1	46.19	394	0.216	139	418	576	182	1.31
2	66.82	220	0.499	61	182	367	147	2.43
3	191.27	229	2.25	132	397	667	438	3.31
4	190.42	167	2.15	95	285	485	318	3.35
5	129.07	172	1.242	75	225	394	222	2.96
6	106.12	147	036	68	205	303	156	2.28
7	152.56	156	1.636	90	269	394	238	2.65
8	66.48	182	0.833	55	164	303	121	2.21
9	147.28	184	1.58	89	267	455	271	3.04
10	175.12	209	1.71	113	339	575	366	3.24
11	147.62	147	1.284	90	269	364	217	2.42
12	102.22	180	0.517	86	258	364	184	2.14
13	96.4	139	0.517	71	214	273	134	1.88
14	61.33	150	0.314	51	152	242	92	1.82
15	281.13	159	2.497	126	378	606	447	3.55
16	114.12	170	0.164	92	277	364	194	2.1
17	61.17	188	0.76	54	163	303	115	2.11
18	121.95	205	0.423	100	299	455	250	2.51
19	67.34	199	0.187	73	218	333	134	1.85
20	116.52	224	0.306	114	342	485	261	2.29

The data that is presented in Table 9, which was obtained by randomly dividing all the results into twenty parts, gave 20 equal parts after 20 measurements out of 400 results. In the next stage, further calculations of these measurements were made: the average of the maximum pore diameter of each series, the variance of these maximum pores, the distance from the maximum pore of each series to the average maximum pore diameter of the same series and the relative value to the average value of this distance as well as the asymmetry coefficient of the maximum pores of each series.

At the next step of the research, the author of the dissertation checked how big is the difference between the average value of the maximum pore and the maximum pore in each series. From the theory of mathematical statistics, it is known that if the maximum value of all measurements is not higher than the average value plus 3S (3 standard deviations), the reliability that a higher value is never obtained is 99.5%, in the case of 4S, the reliability is 99.9% and in the case 5S, 99.99%.

However, 400 photos is a huge amount for the practical usage, to make such a high number of SEM images would take a lot of time, and for the researchers, it would not be very acceptable. Thus, at the next step of this research, the author of the dissertation checked what xS rule needs to be used if the number of measurements is lower. For this purpose, a series of measurements were randomly divided into 20 series with 20 measurements in each, and the results were compared with the maximum pore size of all 400 measurements. If the data point is within a few standard deviations from the average of the model under study, it is a strong enough evidence that the resulting value is incompatible with that model. Often in science, the five-sigma limit is considered a strong confirmation that the result is in line with the theory: only one measurement per million is random.


30
25
20
15
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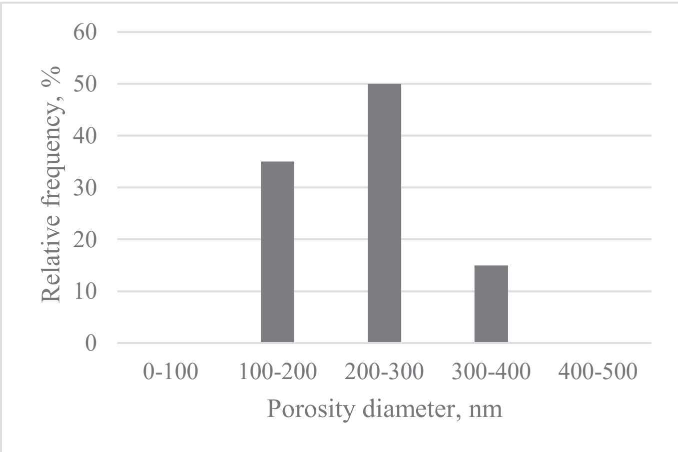
0
Relative frequency, %
0-100
100-200
200-300
300-400
400-500
500-600
600-700
Porosity diameter, nm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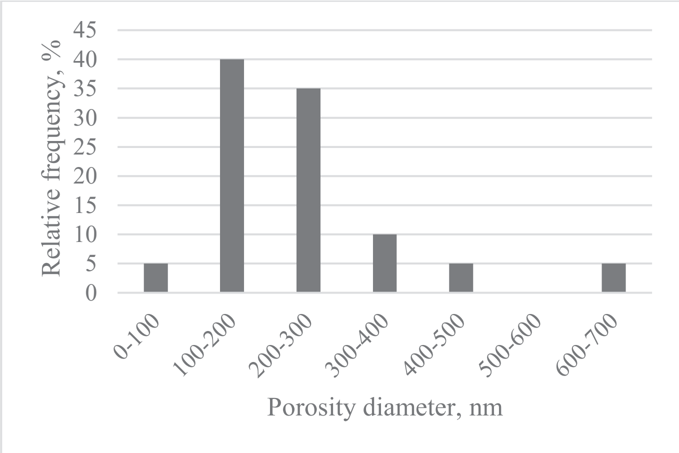
Porosity diameter, nm


Relative frequency, %
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200-300
300-400
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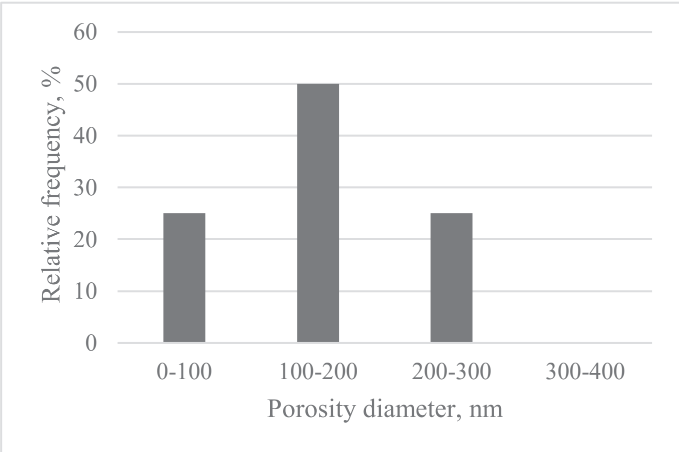
500-600
600-700
Porosity diameter, nm


Relative frequency, %
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0
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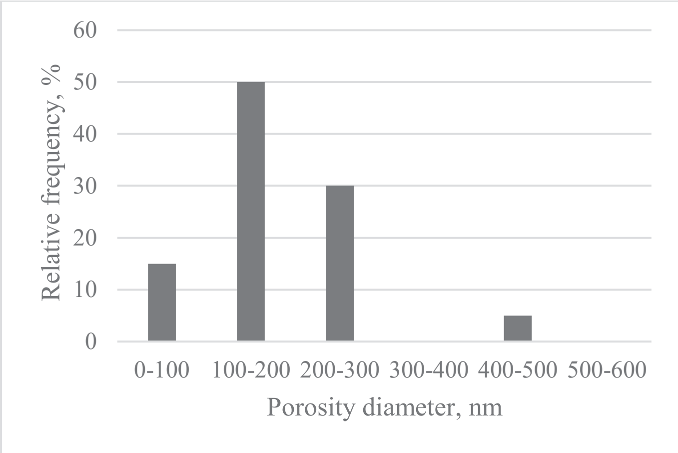
Porosity diameter, nm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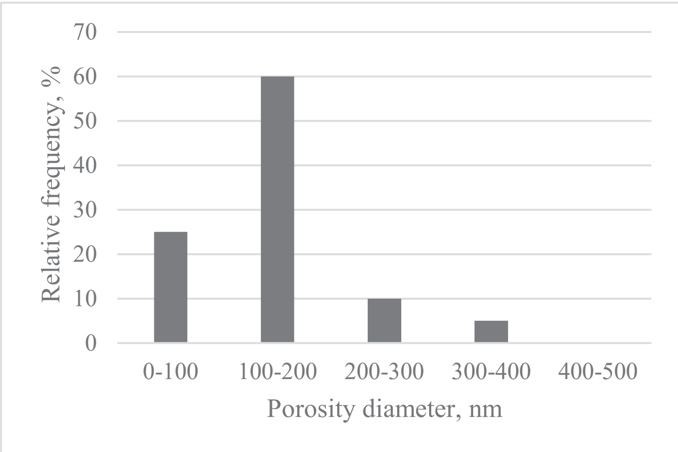
Porosity diameter, nm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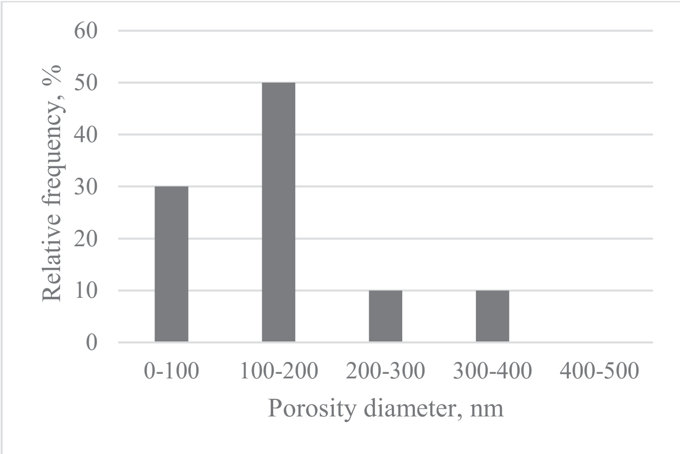
Porosity diameter, nm



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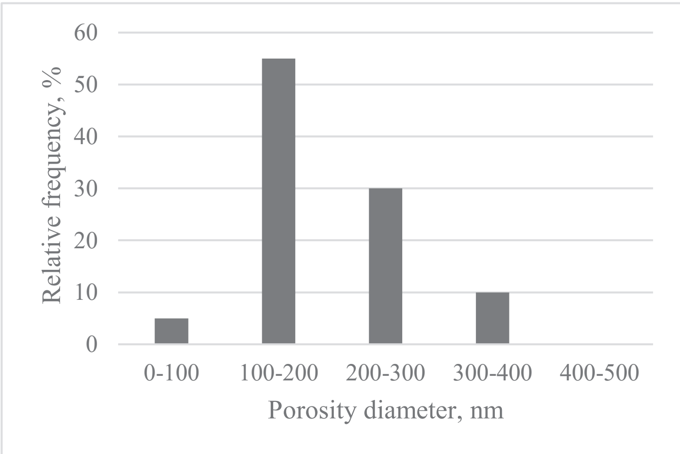

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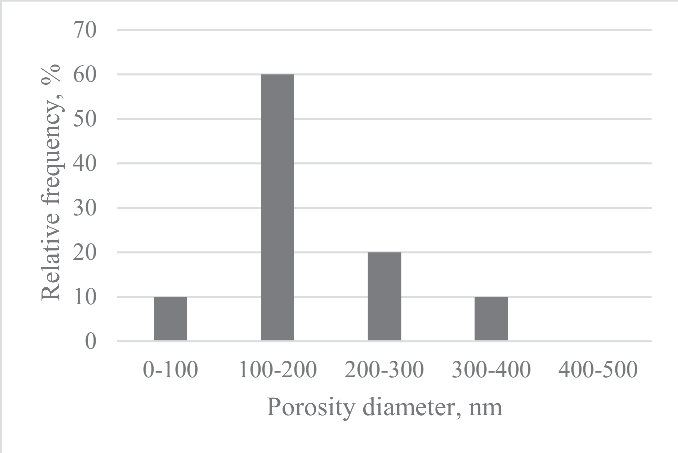
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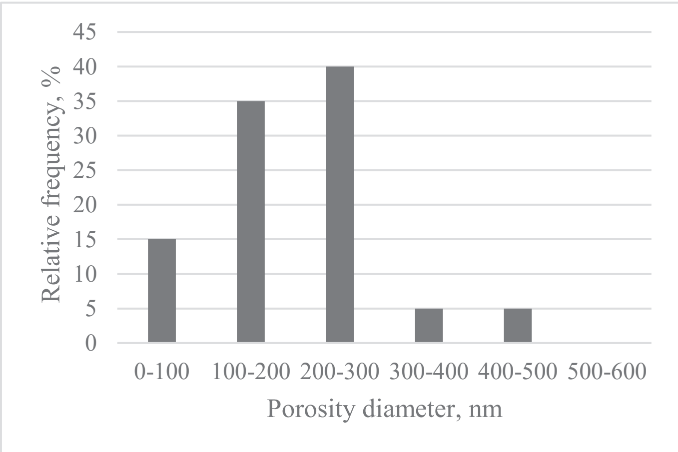
Porosity diameter, nm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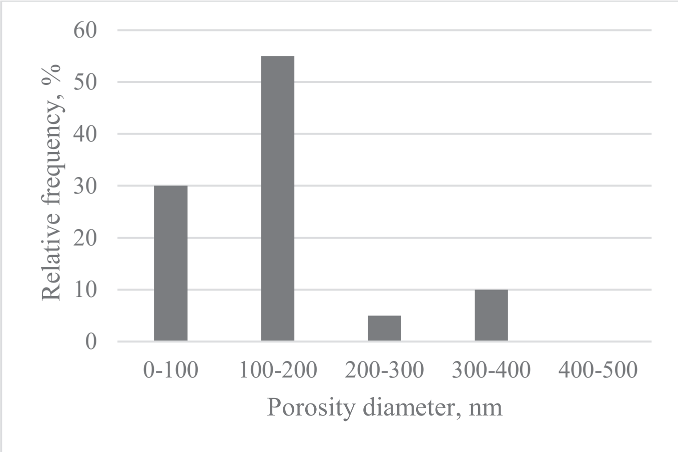
Porosity diameter, nm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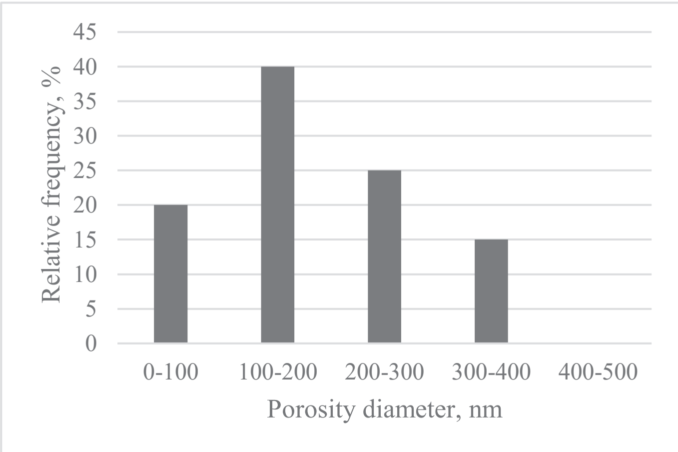
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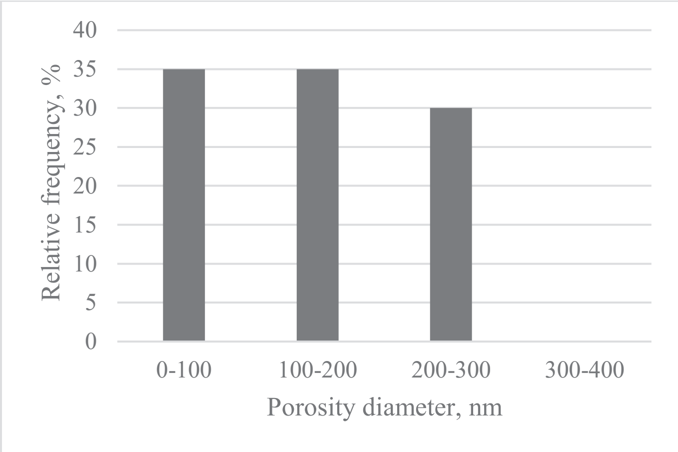
Porosity diameter, nm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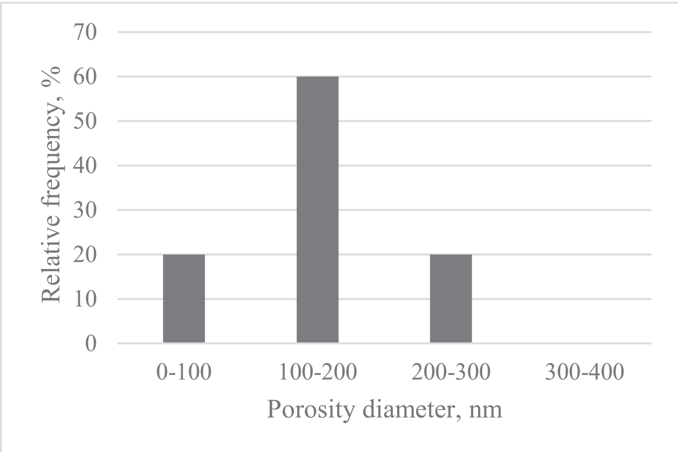
Porosity diameter, nm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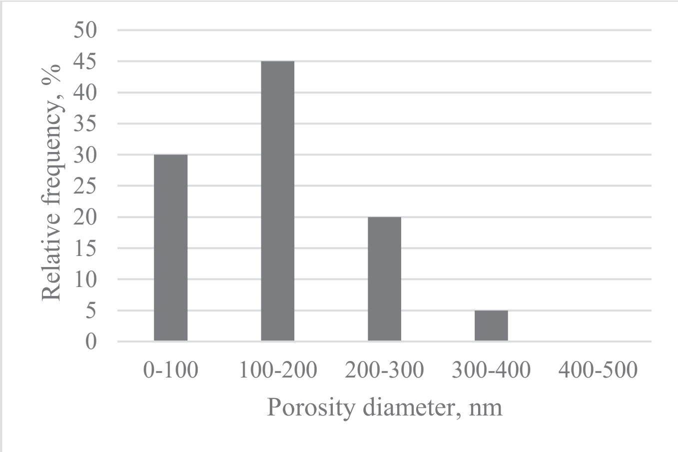
Porosity diameter, nm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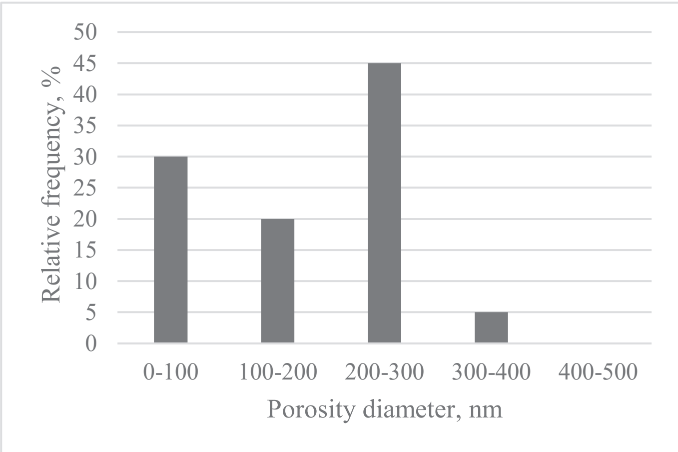
400-500
Porosity diameter, nm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Relative frequency, %
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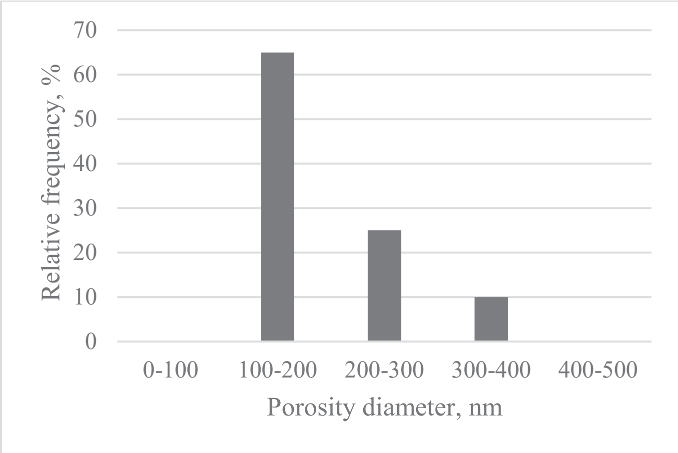
400-500
Porosity diameter, nm



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Relative frequency, %
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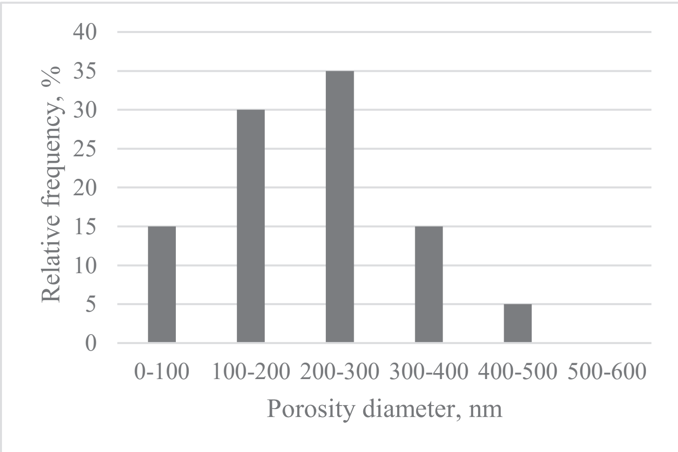
Porosity diameter, nm



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20
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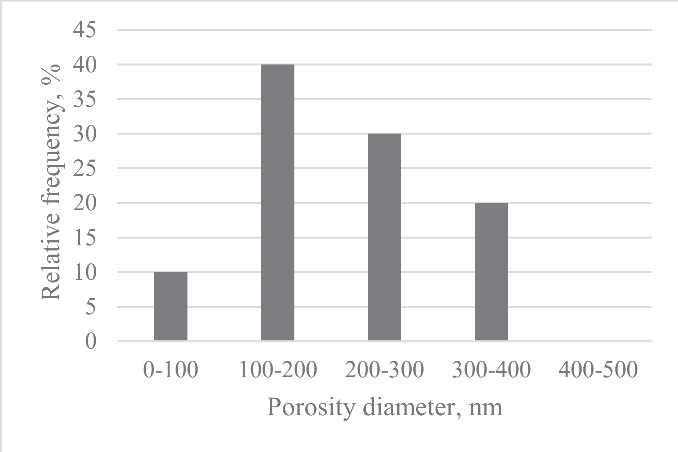
Relative frequency, %
0-100
100-200
200-300
300-400
400-500
500-600
Porosity diameter, nm



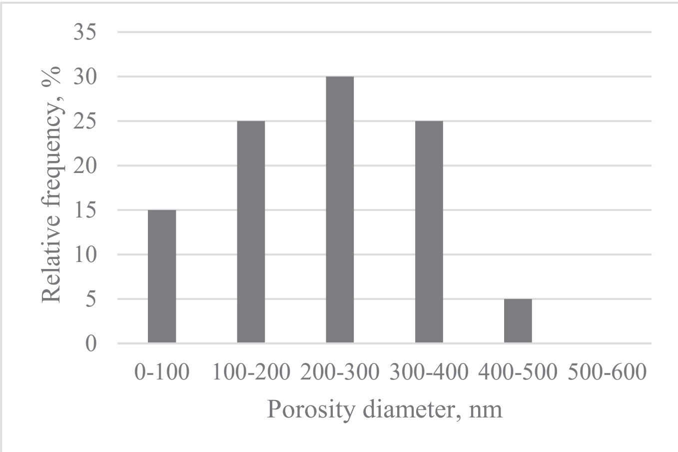


Fig. 7. Pore diameter distribution

In the next step of this investigation, it was decided to check the correlation between skewness coefficient A and xS. Most results (see Fig. 4) are obtained when the skewness coefficient does not exceed 0.6, while the maximum asymmetry ratio of all the measured series reaches 2.55. In this case, xS is obtained well above 3, which means that 3S is not applicable for the reliability prediction. As a result, with the skewness coefficient above 1.5, for the same reliability as in the classical case, it is impossible to use 3S law, and it is necessary to use 4S. Such a way of reliability prediction could be used; however, it requires a lot of various calculations and is not very good for the practical use.

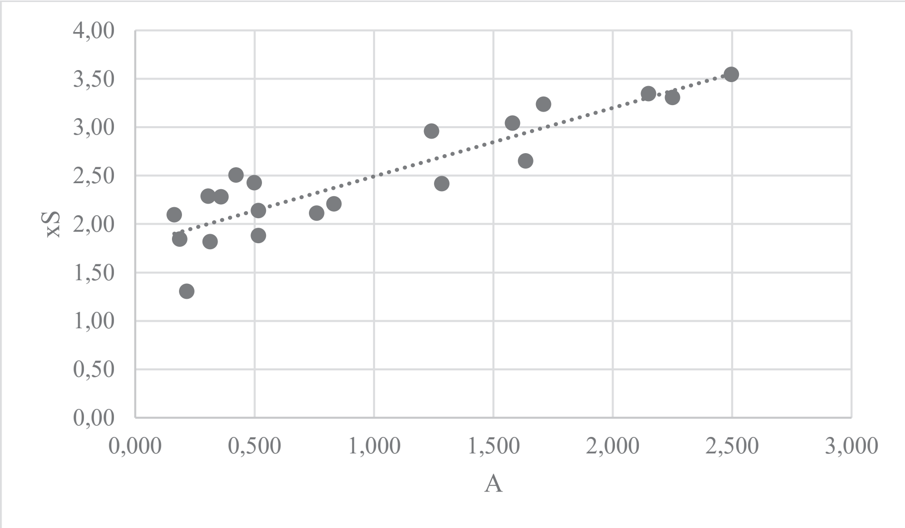


Fig. 8. Correlation between asymmetry factor and xS

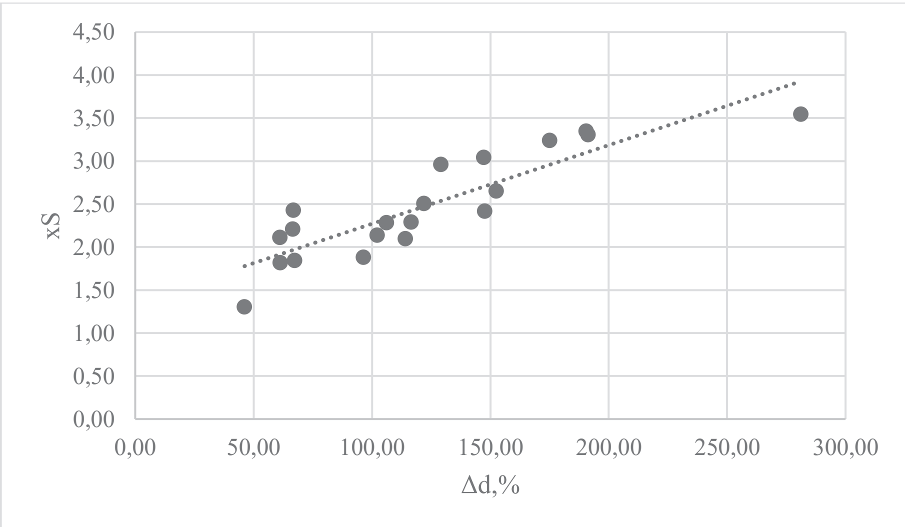


Fig. 9. Correlation between Δd (%) and Xs

In the next step of the study, the simplest way of computing was analysed, which would not require many results, but would, of course, remain reliable. This was followed by the calculation of the Δd values obtained by subtracting the maximum pore of each series from the average of pores and dividing it by the average.

The figure shows a very similar distribution of points as in the previous section. The results show that only one point is at the maximum distance of 90% since the last score, and its xS value is 3.55. It is clear that this does not satisfy the 3S law. At Δd about 150%, it could be observed that one point is 3.04, which as well dissatisfies 3S. However, there is one result that exceeds 150%, but it is satisfying the 3S law. According to the obtained results, it can be stated that at a ratio of up to 150%, the 3S rule could be used, but for higher safety, the 3S rule can be used only up to the distance 120%. In the case when Δd is higher than 120%, for obtaining the same 99.5% reliability, it is necessary to use the 4S rule.

In the following stages of the research, the above-mentioned mathematical statistical method of web evaluation was tested in the presence of different polymer solutions. The preliminary tests give positive results, and the developed method can be used as a starting point for further investigations.

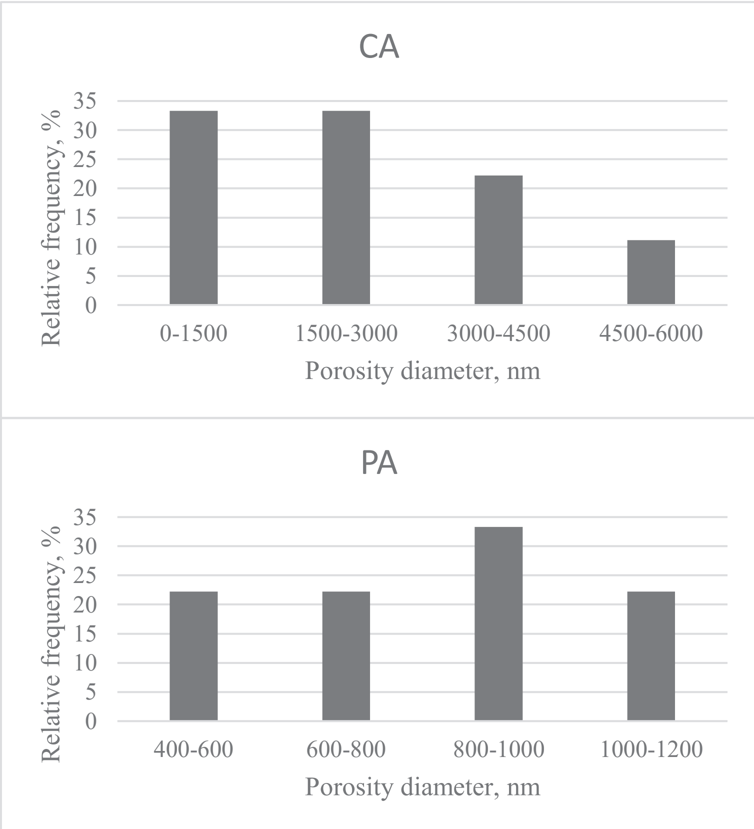
Possibilities of nano- and microgeny mesh dispersion assessment in different polymer solutions

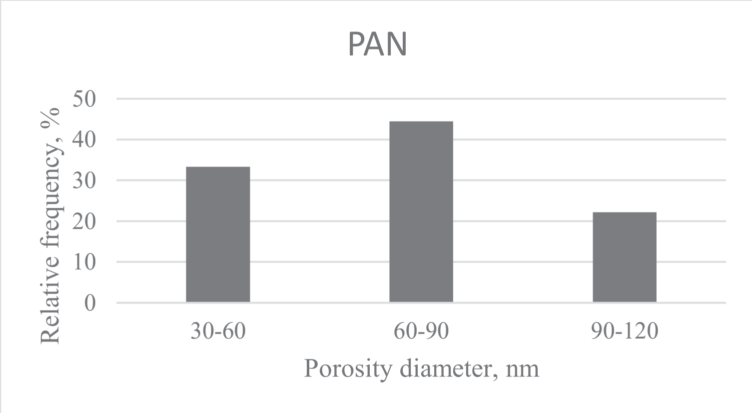
At this stage of the research, it was decided to test the above-mentioned mathematical statistical methods for coating evaluation in the presence of different polymer solutions. All of these specimens were found in various literature sources by randomly selecting SEM photographs based on the polymer blend that was used. In this way, 10 different polymers and different SEM images of each polymer were selected. These calculations are intended to verify whether the mathematical calculations obtained for nanofiber coatings of different materials are affected. The results of the mathematical calculations for all 10 polymers are presented in Table 10.

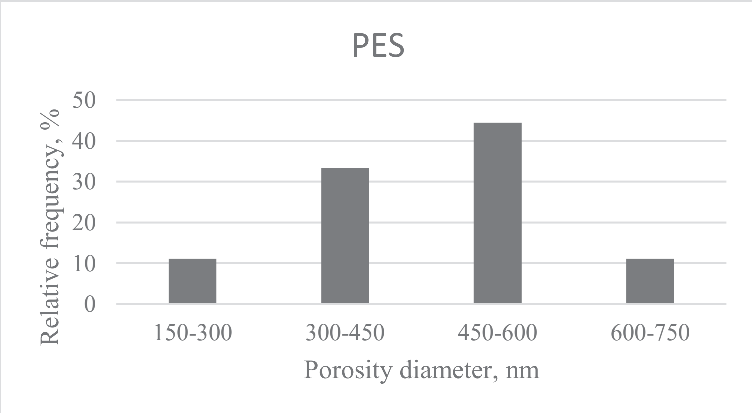
Table 10. Statistical parameters of mesh porosity of 10 polymer measurements [181–190]

	CA	PA	PAN	PES	PEN	PC	PU	PVA	PVC	PVP
Average, nm	2325	828	80	525	587	2444	6825	1296	530	197
Δd, %	111.74	31.64	50.00	168.95	46.00	22.75	56.92	71.45	76.89	182.23
S	1531	205	27	270	132	583	2022	555	202	114
3S	4593	615	81	810	396	1749	6066	1665	606	342
Max pore	4923	1090	120	1412	857	3000	10710	2222	938	556
l, nm	2598	262	40	887	270	556	3885	926	408	359
xS	1.70	1.28	1.48	3.29	2.05	0.95	1.92	1.67	2.02	3.15

The mathematical distributions of these samples are given below. All distributions were obtained uneven with both positive and negative slopes, and the asymmetry coefficient A, which estimates the slope of the distribution, differed radically. The figure (Figure 10) shows contrasting examples of the distributions of the obtained results. The results showed that all 10 distributions were asymmetric, as mentioned earlier, sometimes, with strong positive and negative asymmetries. The range of all distributions was chosen differently, adapting it to the measured results; this is due to the fact that all samples differ in polymer solution and its concentration (this was not determined), the obtained wells differed significantly; it can be seen that not all wells were measured. All of these distributions do not show the exact pattern of random selection of the material used for testing, which again shows the surface roughness of the resulting nanofilament structure and how it differs under different test conditions.




PAN
Relative frequency, %
50
40
30
20
10
0
30-60
60-90
90-120
Porosity diameter, nm


PES
Relative frequency, %
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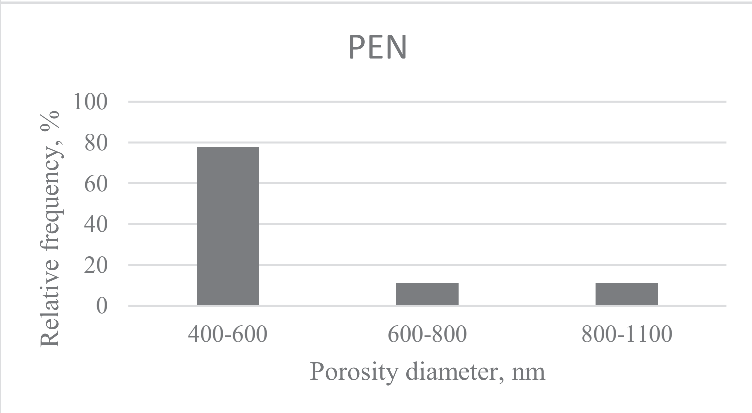
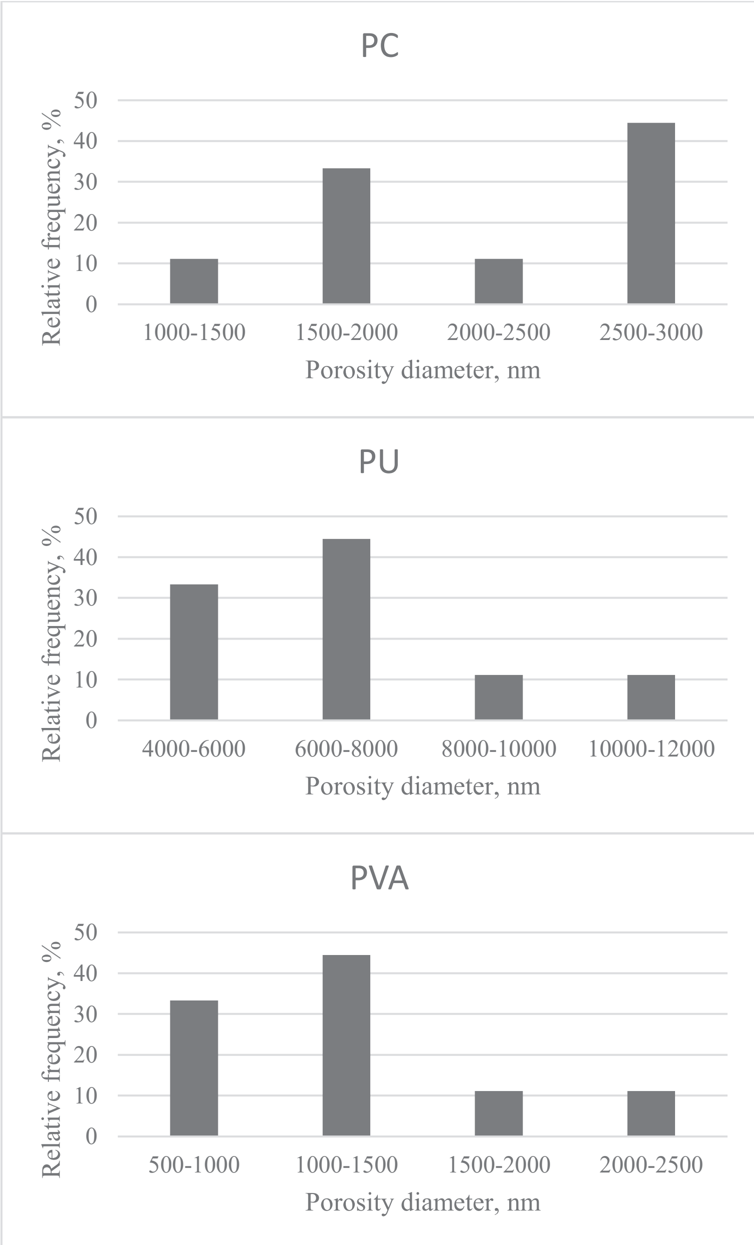
40
30
20
10
0
150-300
300-450
450-600
600-750
Porosity diameter, nm


PEN
Relative frequency, %
100
80
60
40
20
0
400-600
600-800
800-1100
Porosity diameter, nm


PC
Relative frequency, %
0
10
20
30
40
50
1000-1500
1500-2000
2000-2500
2500-3000
Porosity diameter, nm
PU
Relative frequency, %
0
10
20
30
40
50
4000-6000
6000-8000
8000-10000
10000-12000
Porosity diameter, nm
PVA
Relative frequency, %
0
10
20
30
40
50
500-1000
1000-1500
1500-2000
2000-2500
Porosity diameter, nm

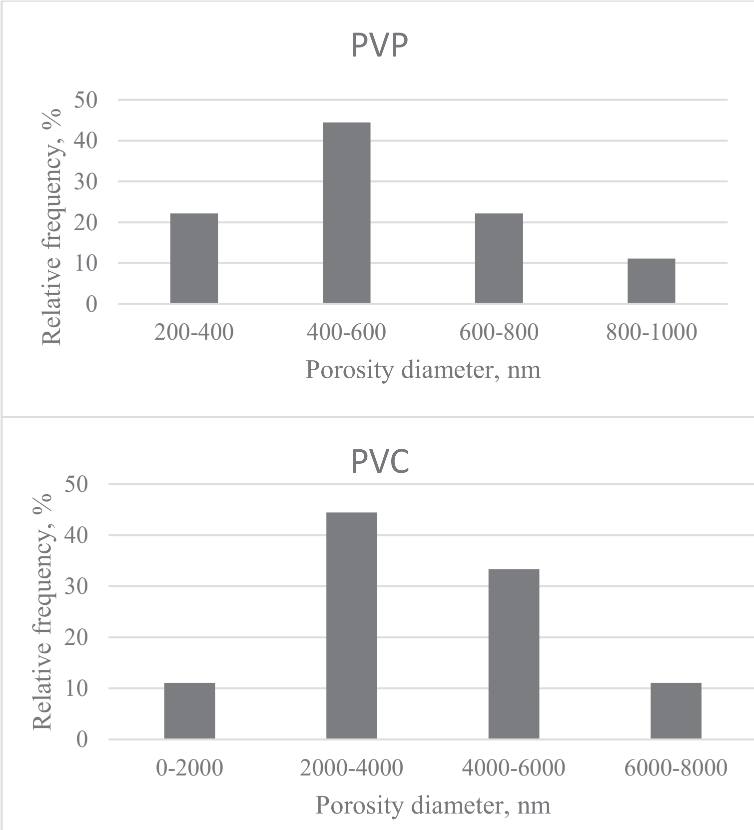


Fig. 10. Pore diameter distribution [181–190]

After analysing the obtained results and forming their graphic images, it was decided to check the correlation of the obtained results between xS and Δd (%). As in the section before, this is the simplest method of calculation that does not require a lot of different and difficult mathematical operations, but it is reliable. The graph obtained in the figure (see Figure 11) shows that not all results satisfy the 3S rule. From the 10 analysed polymers, it can be seen that 2 of them fail the 3S rule, and their Δd (%) exceeds 160%. Based on the results obtained, it can be stated that at a ratio of up to 120%, the 3S rule can be used.

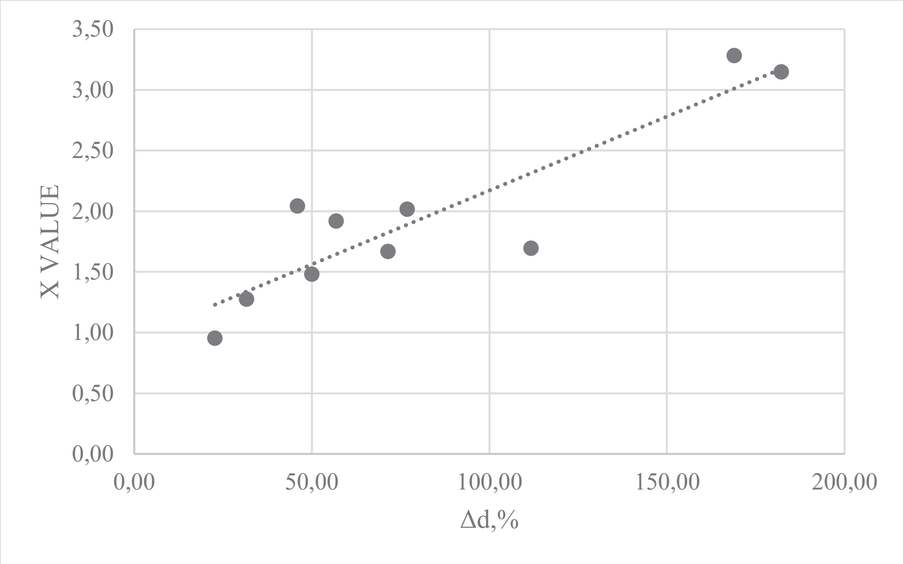


Fig. 11. Correlation between Δd (%) and xS

It has been determined that 400 measurements divided into random parts give contrasting distributions of maximum pores. It was stated that in order to estimate the maximum pore size with a confidence level of 99.5%, it is not possible to use the standard 3S (3 standard deviations) rule. Additional calculations are required to verify that the results meet the rule 3S. For deeper analysis and real reliability prediction, it is possible to use skewness coefficient A; if skewness is up to 1.5, the 3S rule could be used, in other cases, the 4S rule needs to be used for the same 99.5% reliability prediction. However, skewness determination required a lot of various calculations. For a faster distribution checking, it is possible to use the relative distance between the maximum pore and the average pore value Δd. It was found that if this relative distance is up to 120%, the 3S rule could be used, while in other cases, the 4S rule needs be used for the same 99.5% reliability prediction.

The presented investigation shows that for the maximum pore prediction with the same reliability as in standard Gaussian distributions, researchers need to carry out additional statistical analysis and only then present data with a note what level of xS is necessary to use for obtaining the standard 99.5% reliability.

The method presented in the paper could be a starting point for the evaluation of other kind of web and prediction of their maximum pore size. However, the empirical investigations and checking of method need to be provided at first. However, the developed method is a possible way to analyse structures of various kinds of webs and how to predict their maximum pore size.

The presented study shows that in order to achieve the highest hole prediction with the same reliability as in the standard Gaussian distributions, the researchers need to perform additional statistical analysis and only then provide data on what xS level should be used to obtain standard 99.5% confidence.

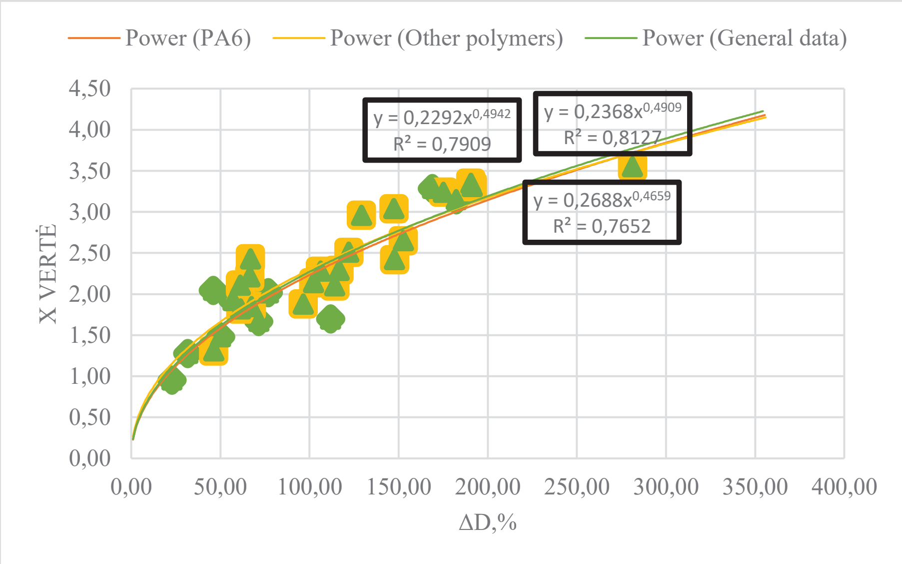


Fig. 12. X value dependence on Δd (%)

Based on the obtained results, the difference between the dependencies of the x value of polyamide and the other polymers on Δd were examined. In Fig. 12, 3 degree equations are shown: the first results for polyamide, the second for the other polymers studied in the work, and the third for the total sum of all data. Their equations and their definition coefficients R2 have been determined. It can be seen from the graph that all three equations are very similar, but their empirical equations and R2 are slightly different. With such similar results, it can be argued that the polyamide results can be used to predict the largest mesh of any coating (or thin layer).

Method for predicting the maximum pore of thin nanofiber coatings

Summarizing the method of nanofiber coating evaluation proposed in this work, it is necessary to mention that this method allows to evaluate any structure as well as to compare different porosity scattering and various structural coatings formed by electrospinning. It is likely that the practical application of this method in the field of assessment of nanofiber structures would reduce discrepancies in the obtained results and increase the accuracy of the results as well as allow for an objective comparison of the work of different researchers and use their results. In order to analyse the obtained results and objectively examine the porosity of the nanofiber coating, and in comparison with the works of other authors, a new method of nanofibers structure assessment is required. The analysis of current literature sources showed that such method does not exist, and there is no consensus on how to purposefully evaluate the obtained results. For this reason, a mathematical method for assessing the porosity of a structure was presented and analysed in the dissertation. This section presents how the porosity of nanofiber coatings should be assessed in practice:

1. During the experiment, nanofiber structures are formed from the obtained samples, and their SEM photographs are measured. The method is based on the estimation of the largest pore; thus, the diameter of the largest pore is measured from the obtained photos.
2. Draw a distribution from the measured maximum pore diameter values. The distribution should be at least 4 peaks.
3. After compiling the distribution, the possibility of comparing the scatter of the pore measurements with the normal (Gaussian) distribution known in mathematical statistics is evaluated. For this purpose, the asymmetry factor is calculated, which determines the asymmetry of the distribution.
4. Calculate the difference between the values of the largest pore and the average pore l, and the ratio of the standard deviation S. Determine which xS rule satisfies the obtained results.
5. It was found that if there is less than 20 photos, the method of estimating the structure according to the ratio of the largest pore to the average pore is not appropriate, because the obtained results satisfied only the 7S rule. As the number of test results decreases, the value of the xS rule increases accordingly.
6. The author has checked the possibility to predict the maximum pore and its probability using the distribution asymmetry coefficient A. For the asymmetry coefficient obtained up to 1.5, the 3S rule is satisfied, and the reliability is 99.5%, if the asymmetry coefficient limit is above 1.5, it requires the use of the 4S rule.
7. For a simpler data analysis than the calculation of the Δd value from the asymmetry factor, the Δd values are obtained by subtracting the average of the pores from the value of the largest pore diameter of each row and dividing it by the average. This method is valid even with little data. If Δd is up to 120%, it satisfies the 3S rule, if Δd exceeds 120%, 4S must be used.

CONCLUSIONS

1. The nanofiber structure tha was formed during electrospinning usually consists of nanofibers with different pores and different diameters. Analysing the literature, it was found that the authors sometimes misjudge the filamentary structure by assuming that the values of the structural elements (filament diameter or pore) are distributed according to the Gaussian normal distribution. It was found that there is no developed method to estimate the diameter of the largest possible pore in the nanofibers structure, which mainly determines the barrier properties of the coating, and the probability of its occurrence using known criteria of mathematical statistics and probability theory.
2. After experiments and analysis of 400 photographs of polyamide 6 thin nanofiber coating, it was found that the obtained structure is uneven, and the usual rules of mathematical statistics cannot be used to estimate the probability of its barrier properties. The distribution of the maximum pore diameter value at different locations in the nanofiltration was found to be close to the Gaussian normal distribution, but with a certain positive slope of 1.4 asymmetry, which means that the distribution of values has a strong asymmetry, and the normal rules of mathematical statistics cannot be used.
3. By randomly dividing all images into 4 series of 100 images in each, the asymmetry was found in all series, and all four distributions show a similar distribution of the largest pore diameter, i.e., about 45% of all cells distributed between 100 and 200 nm; the mean was obtained in all cases in the modal value column of the distribution, i.e., at 100–200 nm, and all distributions have pores that are several times larger than average.
4. After checking the difference between the average maximum pore value and the largest pore in each series and calculating the difference between the largest pore and the average pore (size l) and the ratio of the standard deviation S, this ratio is found to be between 2.83–4.34. This means that the usual 4S (4 standard deviations) rule cannot be used for the maximum pore size estimation with a probability of 99.9%. It has been found that for 100 measurements, there should be used 5S and even 7S and 8S rules for 20 or 10 measurements, respectively, to obtain the same 99.9% probability as the conventional 4S rule for the classical Gaussian normal distribution. As the difference is quite large, it means that the classical mathematical statistical methods cannot be used to estimate the reliability of the occurrence of the largest pore, and a new estimation method is required.

5. It has been established that a distribution asymmetry factor can be used to estimate the probability of occurrence of the maximum pore diameter, i.e., with an asymmetry factor up to 1.5, the 3S rule is met, and the reliability is 99.5%, but when the asymmetry factor is higher than 1.5, to obtain the same reliability, it is necessary to use the 4S rule.
6. It has been established that the probability of the appearance of the maximum pore diameter can be estimated by a method based on the relative value between the maximum pore value and the mean pore value Δd, at a ratio of Δd to 120%, rule 3S can be used, and rule 4S should be applied at a higher value to achieve the same probability of 99.5%.
7. The proposed method was tested with threaded coatings of 10 different polymers. The relative distance between the maximum pore value and the mean pore value Δd up to 120% has been established, and the reliability of the results is maintained at 99.5% for these coatings. The nature of the correlations between x and Δd in the case of polyamide coatings and all other studied polymeric materials has been very similar; therefore, it can be said that detailed studies on coatings formed from polyamide 6 can as well be applied to nano or micro fibers coatings that are as well made of other polymers.
8. The presented study shows that in order to obtain the maximum reliability of thin nanofibers web coatings with the same reliability as a normal distribution of the Gaussian measurements, the researchers need to perform additional statistical analysis before providing the xS level to obtain a standard 99.5% or 99.9% confidence. The proposed method can be used to calculate the value of x and assess the reliability.

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A LIST OF PUBLICATIONS, PARTICIPATION AT CONFERENCES

Thomson Reuters Web of Science in the publications of the main list

1. Kleivaitė V., & Milašius R. Electrospinning – 100 Years of Investigations and Still Open Questions of Web Structure Estimination. *Autex Research Journal*. 2018, 18(4), 398-404. doi: https://doi.org/10.1515/aut-2018-0021

2. Kleivaitė V., & Milašius R. Investigation of Electrospun Web Porosity and its Statistical Evaluation. *The Journal of the Textile Institute*. 2019, No. JOTI.4991R2 https://doi.org/10.1080/00405000.2019.1645534

3. Kleivaitė V., & Milašius R. Prediction of Electrospun Web Maximum Pore Diameter Reliability. *The Journal of the Textile Institute*. 2020. https://doi.org/10.1080/00405000.2020.1865506

Participation at conferences

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REZIUMĖ

Tiriamos problemos pagrindimas ir darbo aktualumas. Nanotechnologijos, kaip tyrimų objektas, stiprina mokslą ir pramonės konkurencingumą. Norint visiškai suprasti didžiulį nanotechnologijų panaudojimą, vis dar reikia išspręsti kai kuriuos klausimus ir apribojimus, tokius kaip didelio masto gamybos platformų poreikis, mažas cheminis ir biologinis lankstumas, ekonominiai ir aplinkos veiksniai, t. y. nanomedžiagų toksiškumo aspektai. Įvairių medžiagų savybės pasikeičia, kai jų dydis sumažėja iki nanometrų. Nanogijas galima suformuoti iš įvairių medžiagų, taip pat ir iš polisacharidų, kitų gamtinių ar sintetinių polimerų. Atsižvelgiant į naudojamų polimerų fizikines ir chemines savybes, nanogijų gamyboje dažnai naudojamas sintezės būdas – elektrinis verpimas. Be to, nanogijų modifikavimui gali būti naudojamos įvairios organinės ir neorganinės medžiagos. Šiandien tekstilės moksle vis plačiau taikomos aukštosios technologijos. Dėl jų yra sukurtos įvairios daugiafunkcinės medžiagos, kurios apsaugo nuo lietaus, vėjo ir ultravioletinių saulės spindulių, naikina blogą kvapą, yra lengvai prižiūrimos, sintetinės, hidrofilinės, laidžios drėgmei. Pasitelkiant nanotechnologijas sukurtos eksploatacijai ypač atsparios, nesiglamžančios, hidrofilinės apdailos, mažai susėdančios ir net savaime apsivalančios medžiagos.

Su nanotechnologijų atsiradimu vis daugiau mokslininkų pradėjo tyrinėti unikalias nano- ir mikrogijų savybes. Pirmasis dirbtinį siūlą iš polimerinio tirpalo, panaudodamas elektrinį krūvį, pagamino Formhalds‘as [1]. Elektrinis verpimo būdas pastaraisiais metais sulaukė nemažo susidomėjimo dėl šios technologijos universalumo ir panaudojimo daugiapusiškumo. Gijinė danga iš nano-mikrogijų atlieka svarbų vaidmenį audinių inžinerijoje, biojutiklių ir filtrų gamyboje, tvarsčių ir vaistų pramonėje, fermentų imobilizacijoje. Nanogijinės medžiagos gaminamos veikiant elektriniam laukui ir naudojant polimerinius tirpalus [2].

Šiuo metu išskiriamos pagrindinės technologijos nanogijinėms dangoms pagaminti: savitvarkos principas, fazių atskyrimo, tempimo, sintezės būdai, cheminis ir mechaninis poveikis bei elektrinio verpimo būdas. Paskutinis metodas yra populiariausias ne tik dėl paties metodo paprastumo, bet ir dėl šiam procesui reikalingos nebrangios įrangos. Gijos, pagamintos elektrinio verpimo būdu, pasižymi ypatingomis savybėmis, tokiomis kaip didelis paviršiaus ploto ir tūrio santykis, mažas svoris, akyta nanostruktūra, palyginti vienodas gijų skersmuo. Dėl šių savybių nanogijinės medžiagos, pagamintos elektrinio verpimo būdu, naudojamos filtrų gamyboje, medicinoje, audinių inžinerijoje (implantai, tvarstomoji medžiaga ar kaip barjeras, apsaugantis nuo biologinių bei cheminių pavojų) bei apsauginių rūbų gamyboje [3–7].

Nanogijinės medžiagos iš nano-, mikrogijų elektrinio verpimo būdu dažniausiai formuojamos naudojant polimerinius tirpalus. Populiariausi tokių neaustinių medžiagų gamyboje naudojami polimerai: polivinilalkoholis,

polietilenoksidas, poli(glikolio rūgštis), celiuliozės acetatas, chitinas, kolagenas, poliamidas ir kt.

Elektrinio verpimo metu, naudojant antimikrobines medžiagas, gautos nanogijos, gaminamos kaip antimikrobiniai pluoštai, kurie apsaugo žmogų nuo mikroorganizmų patekimo. Nanogijinių struktūrų akytumas itin dažnai nėra vertinamas, nors tai labai svarbu, kadangi struktūra dažnai būna labai nevienoda. Šiuo metu labai svarbu ir populiaru naudoti medžiagas, turinčias barjerinių savybių, kurios apsaugotų nuo žalingo poveikio žmogaus organizmui. Dėl to naudojama daug papildomų medžiagų (antibakterinių savybių turinčių elementų), kurios gali turėti antibakterinį poveikį ir lengvai prisijungti prie nanogijinės struktūros, tačiau yra žmonių, kurie yra alergiški tokioms medžiagoms kaip sidabras ar cinkas. Todėl reikalingos medžiagos, galinčios užkirsti kelią bakterijoms be papildomų cheminių medžiagų [8–11]. Dėl didelio nanogijinių medžiagų panaudojimo potencialo ir perspektyvų elektrinio verpimo procesas yra plačiai analizuojamas ir aprašomas įvairiuose literatūros šaltiniuose. Remiantis įvairiais tyrimais, galima teigti, kad elektrinio verpimo procesas yra labai jautrus procesas, kuriam įtakos turi polimero tirpalo savybės, technologiniai ir aplinkos parametrai. Išanalizavus priežastis, kodėl skirtingų tyrimų rezultatai skiriasi, daroma išvada, kad pagrindinė neatitikimų priežastis yra ta, kad nėra sukurta bendra nanogijų įvertinimo metodika. Susidariusios nanogijinės dangos struktūra ir jos vienodumas plote literatūroje analizuojami retai, o išvados apie vieno ar kito parametro įtaką dangos morfologijai pateikiamos remiantis vien tik vidutine gijų ar modalinio skersmens verte, kai kada akytumu. Literatūroje randama, kad autoriai dažnai subjektyviai įvertina nanogijinės dangos struktūrą remdamiesi vidutiniu skersmeniu ir ne visada nurodo, iš kokių pirminių duomenų buvo apskaičiuoti rezultatai, matematiškai neįvertina gautos struktūros, neanalizuoja duomenų sklaidos. Šaltinių analizė parodė, kad nanogijinių struktūrų vertinimui reikalingas naujas metodas, kuris įvertintų akytumo pasiskirstymą, kaip tai buvo padaryta anksčiau nanogijų skersmens pasiskirstymo atveju [12]. Toks metodas turėtų būti grindžiamas matematinės statistikos kriterijais, o ne subjektyviu tyrėjų vertinimu.

Pagrindinis disertacijos objektas – nanogijinės struktūros akytumas. Šaltiniuose dažnai sutinkama pavyzdžių, kai vertinamas gijos akytumas, tačiau autoriai nemini nanogijinės struktūros paviršiaus akytumo arba vertina tik vidutinį medžiagos akytumą. Toks akytumo vertinimas yra labai svarbus, jei elektrinio verpimo metu suformuota nanogijinė medžiaga naudojama ląstelių augimui ar barjerinėms savybėms, kurioms svarbus tam tikras debitas per medžiagą. Tačiau jei tyrėją domina ne debitas per medžiagą, o kokio dydžio dalelės negalės prasiskverbti, tai vidutinis akytumas neturi prasmės. Tokiu atveju svarbiausias parametras yra didžiausia akutė. Daug autorių savo darbuose nagrinėja struktūros akytumą, tačiau straipsniuose nėra rasta pateiktų didžiausios akutės vertinimo metodų [2, 13–16].

Darbo tikslas – sukurti matematiniais statistikos kriterijais ir tikimybių teorijos dėsniais pagrįstą elektrinio verpimo būdu suformuotų plonų gijinių dangų didžiausios galimos akutės įvertinimo metodą.

Darbo uždaviniai:

1. Išanalizuoti esamus nanogijinės dangos akytumo nustatymo metodus ir įvertinti jų trūkumus didžiausios galimos akutės tikimybės prognozavimui.
2. Nustatyti didžiausios akutės skersmens vertės pasiskirstymo dėsningumus elektrinio verpimo būdu suformuotoje poliamido 6 nanogijinėje dangoje.
3. Nustatyti, kokios vertės xS taisyklę galima naudoti prognozuojant poliamido 6 nanogijinės dangos didžiausios akutės atsiradimo galimybę su 99,9 % tikimybe vietoje įprastinės 4S taisyklės, esant normaliam Gauso skirstiniui, bei x vertės priklausomybę nuo didžiausios akutės matavimų skaičiaus.
4. Nustatyti didžiausios akutės skersmens verčių skirstinio asimetrijos koeficiento A ir xS bei santykinės vertės tarp didžiausios akutės skersmens ir vidutinės didžiausios akutės skersmens vertės Δd ir xS koreliacijas ir galimybes pagal juos įvertinti didžiausios akutės atsiradimo tikimybę.
5. Nustatyti Δd ir xS koreliacijos galiojimą įvairių rūšių polimerinėms nanogijinėms dangoms bei palyginti šią koreliaciją su atitinkama poliamido 6 nanogijinės dangos koreliacija.
6. Sukurti naują nanogijinės dangos didžiausios akutės vertinimo ir prognozavimo metodą, paremtą Δd ir xS koreliacijos dėsningumais.

Darbo naujumas ir jo reikšmė. Yra daug darbų, kuriuose autoriai analizuoja įvairių parametrų įtaką elektrinio verpimo procesui ar nanogijinei struktūrai, tačiau dauguma jų neanalizuoja struktūros sandaros vienodumo, naudodamiesi matematiniais statistiniais kriterijais. Tokia situacija lemia skirtingas išvadas ir neįmanoma palyginti įvairių autorių darbų. Nepaisant daugybės elektrinio verpimo tyrimų, nanogijinės struktūros įvertinimo metodų trūksta. Iki šiol nebuvo sukurtas pluošto skersmens ir dangos akytumo matavimo bei įvertinimo metodas. Tokio metodo būtinybė yra akivaizdi, o jo nebuvimas gali turėti neigiamos įtakos elektrinio verpimo būdu gauto gaminio praktiniam naudojimui. Šioje disertacijoje visi bandymai ir jų rezultatai yra pateikiami nanogijinės dangos paviršiaus analizavimu ir eksperimentai taikytini tik labai plonoms (mažiau nei 1μm) dangoms. Gauti tyrimų rezultatai turi svarbią praktinę reikšmę, nes darbe pasiūlytas nanogijinės dangos vertinimo metodas leidžia įvertinti ir palyginti bet kokią elektrinio verpimo būdu suformuotą ploną gijinę struktūrą. Disertacijoje pasiūlytas naujas struktūros vertinimo metodas, nereikalaujantis daug skaičiavimų, paremtas santykine verte tarp didžiausios akutės ir vidutinės akučių vertės Δd. Sukurtas metodas patikrintas su įvairių polimerų nanogijinėmis struktūromis, esant skirtingiems rezultatų kiekiams. Įrodyta, kad sukurtą metodą galima taikyti įvairioms polimerinėms nanogijinėms dangoms.

Išvados:

1. Elektrinio verpimo metu suformuotą nanogijinę struktūrą paprastai sudaro skirtingos akutės ir skirtingo skersmens nanogijos. Analizuojant literatūros šaltinius, buvo nustatyta, kad autoriai kartais neteisingai vertina gijinę struktūrą laikydami, kad sandaros elementų (gijų skersmens ar akučių) vertės pasiskirsčiusios pagal Gauso normalųjį skirstinį. Nustatyta, kad nėra sukurto metodo, kaip vertinti gijinės struktūros didžiausios galimos akutės skersmenį, kuris iš esmės lemia dangos barjerines savybes, ir jos atsiradimo tikimybę naudojantis žinomais matematinės statistikos ir tikimybių teorijos kriterijais.

2. Atlikus eksperimentinius bandymus ir išanalizavus poliamido 6 plonos nanogijinės dangos 400 nuotraukų, nustatyta, kad gauta struktūra yra nevienoda, o jos barjerinių savybių tikimybės įvertinimui negalima naudoti įprastų matematinės statistikos taisyklių. Nustatyta, kad didžiausios akutės skersmens vertės pasiskirstymas įvairiose nanogijinės struktūros vietose yra artimas Gauso normaliajam pasiskirstymui, tačiau turi tam tikrą teigiamą pakrypimą –asimetrijos koeficientas yra 1,4. Tai reiškia, kad verčių skirstinys turi stiprų asimetriškumą ir didžiausios akutės atsiradimo tikimybės įvertinimui negalima naudoti įprastų matematinės statistikos taisyklių.

3. Atsitiktiniu būdu sudalinus visas nuotraukas į 4 serijas po 100 nuotraukų kiekvienoje, nustatyta, kad asimetriškumas būdingas visoms serijoms, o visi keturi skirstiniai rodo panašų didžiausios akutės skersmens pasiskirstymą, t. y., apie 45 % visų akučių yra pasiskirsčiusios nuo 100 iki 200 nm, vidutinė vertė visais atvejais buvo gauta pasiskirstymo modalinės vertės stulpelyje, t. y. esant 100–200 nm ir visuose skirstiniuose yra akučių, kurios kelis kartus didesnės už vidutinę.

4. Patikrinus, koks yra skirtumas tarp vidutinės didžiausios akutės vertės ir didžiausios akutės kiekvienoje serijoje, bei apskaičiavus skirtumą tarp didžiausios akutės ir vidutinės akutės (dydis l), taip pat standartinio nuokrypio S santykį, nustatyta, kad šis santykis yra tarp 2,83–4,34. Tai reiškia, kad didžiausiam akučių dydžio įvertinimui, su tikimybe 99,9 %, negalima naudoti įprastinės 4S (4 standartiniai nuokrypiai) taisyklės. Nustatyta, kad atliekant 100 matavimų, reikia naudoti 5S taisyklę, o 20 ar 10 matavimų atveju – atitinkamai net 7S ir 8S taisyklę, norint gauti tą pačią 99,9 % tikimybę, kaip įprastinės 4S taisyklės klasikinio Gauso normalaus skirstinio atveju. Skirtumas yra gana didelis, vadinasi, didžiausios akutės atsiradimo patikimumo įvertinimui negalima naudoti klasikinių matematinės statistikos metodų ir reikalingas naujas vertinimo metodas.

5. Nustatyta, kad didžiausios akutės skersmens atsiradimo tikimybės įvertinimui galima naudoti skirstinio asimetrijos koeficientą, t. y., esant asimetrijos koeficinetui iki 1,5 yra tenkinama 3S taisyklė ir patikimumas yra 99,5 %, tačiau kai asimetrijos koeficientas yra didesnis nei 1,5, siekiant gauti tokį patį patikimumą, būtina naudoti 4S taisyklę.

6. Nustatyta, kad didžiausios akutės skersmens atsiradimo tikimybę galima įvertinti metodu, paremtu santykine verte tarp didžiausios akutės ir vidutinės akučių vertės Δd. Esant santykiui Δd iki 120 % galima naudoti 3S taisyklę, o esant didesnei vertei reikia taikyti 4S taisyklę tai pačiai 99,5 % tikimybei pasiekti.

7. Pasiūlytas metodas patikrintas su 10 skirtingų polimerų gijinėmis dangomis. Nustatyta, kad esant santykiniam atstumui tarp didžiausios akutės ir vidutinės akučių vertės Δd iki 120 %, ir šioms dangoms yra tenkinama 3S taisyklė ir rezultatų patikimumas išlaikomas 99,5 %. Koreliacijų tarp x ir Δd pobūdis poliamidinės dangos atveju ir visų kitų tirtų polimerinių medžiagų atveju gautas labai panašus, todėl galima teigti, kad iš poliamido 6 suformuotų dangų išsamius tyrimus galima taikyti ir nano- ar mikrogijinėms dangoms, pagamintoms ir iš kitų polimerų.

8. Pateiktas tyrimas rodo, kad siekiant plonų nanogijinių dangų didžiausių akučių prognozės tokiu pat patikimumu kaip ir esant

įprastiniam normaliam Gauso matavimų pasiskirstymui, tyrėjams reikia atlikti papildomą statistinę analizę ir tik tada pateikti duomenis, kokį xS lygį reikia naudoti norint gauti standartinį 99,5 % ar 99,9 % patikimumą. Pasiūlytas metodas gali būti naudojamas x vertės apskaičiavimui ir patikimumo įvertinimui.

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