Electrospun openwork structures for applications in environmental engineering

Maciej Borowczak[1), *)] (ORCID ID:0000-0002-7172-1791), **Karolina Sobczyk**[1)] (0000-0002-8911-7840), **Karol Leluk**[1)] (0000-0002-1992-7477)

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Abstract: The article presents the possibilities of producing fibrous structures using electrospinning from polymer solutions based on PBS and a binary solvent system. The main component of the system was chloroform. Dimethyl sulfoxide (DMSO) or *N,N*-dimethylformamide (DMF) was used as an additional solvent to increase the boiling point of the system. The influence of process parameters on the structure of the obtained fibers was described. The results were compared with those obtained using the extrusion blow molding method. The developed fibers will be used in air filtration processes.

Keywords: openwork structures, electrospinning, air filtration, fibrous structures.

Elektroprzędzone struktury ażurowe do zastosowań w inżynierii środowiska

Streszczenie: W artykule przedstawiono możliwości wytwarzania struktur włóknistych techniką elektroprzędzenia z roztworów polimerowych na bazie PBS i binarnego układu rozpuszczalników. Głównym składnikiem układu był chloroform. Sulfotlenek dimetylu (DMSO) lub *N,N*-dimetyloformamid (DMF) stosowano jako dodatkowy rozpuszczalnik w celu zwiększenia temperatury wrzenia układu. Opisano wpływ parametrów procesu na strukturę otrzymanych włókien. Wyniki porównano z wynikami uzyskanymi metodą wytłaczania z rozdmuchiwaniem. Opracowane włókna znajdą zastosowanie w procesach filtracji powietrza.

Słowa kluczowe: struktury ażurowe, elektroprzędzenie, filtracja powietrza, struktury włókniste.

Deteriorating air quality is becoming an increasing problem and challenge for both societies and the environment. It particularly affects areas with a high degree of urbanization and intensified industrial production, which is associated with emissions of pollutants that arise in this type of areas [1]. Pollutants emitted into the air consist of suspended dust and volatile organic compounds [2]. The COVID-19 pandemic has shown that microbiological contamination in the form of viruses and other pathogenic organisms can also dangerous, the containment of which is particularly important in medical facilities or areas with high population density [3].

The $PM_{2.5}$ fraction (<2.5 μm) is dangerous for the human body because it can penetrate directly into the lung alveoli, which may lead to serious health consequences [4]. According to research and analyses, air pollution is becoming an increasing problem and leads to a significant increase in the number of illnesses and complications, most often involving the respiratory and cardiovascular systems [5, 6]. For this reason, it is particularly important for modern filter materials to be able to retain contaminants with the smallest possible particle diameter while maintaining low flow resistance of the filtered air [7, 8]. One of the most frequently used methods for producing fibrous filter materials is the melt blown method and its modifications [9]. In this method, the polymer melt is extruded through a slot nozzle and blown by an air stream of appropriate pressure and temperature, which causes the extraction of separate fibers, which are then deposited on the collector in the form of a nonwoven fabric [10].

The disadvantage of this method is the broad range of diameters of the produced fibers, which reflects in material's free volume to fiber ratio, reducing in turn filtration efficiency of the obtained system [11]. The second limitation of this method is requirement of a sufficiently high viscosity of the melt, enabling the fibers to be pulled out. In the electrospinning method, the above limitations do not occur, which allows the processing of a wide range of materials and their modifications to conduct the most effective process. Additionally, structures produced using this method are characterized by much smaller fiber sizes, reaching tens of nanometers [12]. The process of electrospinning fibrous structures is widely developed

1) Faculty of Environmental Engineering, Wroclaw University of Science and Technology, Wybrzeże Stanisława Wyspiańskiego 27, 50-370 Wroclaw, Poland.

*) Author for correspondence: maciej.borowczak@pwr.edu.pl

for the filtration of various media, in particular air [1, 13, 14]. This is confirmed by the fact that using this method, already in 1984, filters made of smooth polyamide (PA) fibers were produced, the filtration efficiency of which is higher than HEPA filters [15].

The electrospinning process has an additional advantage compared to classical methods of producing filter materials, which is the possibility of modifying structures in many ways. The first is the use of additives of various types at the stage of solution preparation, such as: metal nanoparticles, carbon materials or plant extracts. The use of this type of admixtures leads to many benefits, starting from modifying the way the air stream flows through the membrane through the possibility of adsorption of volatile chemical pollutants, or giving the nonwovens biostatic properties [16–18].

Modification can also take place during the process using the appropriate selection of process parameters or adaptation of the manufacturing element. The main goal of these treatments is to increase the specific surface area by reducing the average diameter and modification the surface morphology of the fibers from smooth to porous [19].

An example of the commercial use of electrospun structures as personal protective equipment are FD 92 class masks produced by Bioinicia, Spain. In addition to high filtration capacity, they have an additional advantage of being biodegradable. Research has shown that the material from which they were made biodegraded within 22 days, leaving behind only metal reinforcing elements, which significantly reduces the amount of waste generated [20]. During the COVID-19 pandemic, the amount of plastic waste generated significantly increased, disposable gloves and protective masks, which limited the transmission of the virus. The use of biodegradable materials allows us to reduce the stream of plastic waste and its negative impact on the natural environment.

Only in 2021, global plastic production reached over 391 million tons [21]. Assuming that trend is maintained, the expected production of polymer materials by 2050 will amount to approximately 33 billion tons [22]. It should also be noted that despite the regulations and directives being introduced, the average level of plastic recycling in the European Union in 2022 was only 26.9% [23]. It is therefore necessary to look for alternative solutions that allow to reduce the use of plastics by replacing them with biodegradable equivalents.

The aim of the work was to obtain biodegradable fibers from solutions of poly(butylene succinate) (PBS) in selected solvents by electrospinning methods and to examine the process parameters on the structure of the obtained fibers. PBS was used due to its wide application potential, starting from disposable products (tableware, bags), through geotextiles, ending with tissue scaffolds and drug delivery systems [24, 25]. An additional advantage of this polymer is the short biodegradation time of about 10 months in the soil. The results were compared with those obtained using the melt blowing method.

EXPERIMENTAL PART

Materials

Poly(butylene succinate) (PBS) with the trade name BioPBS FD 92 (Mitsubishi Chemical Corporation, Thailand) was used to prepare polymer solutions for the electrospinning process. PBS was characterized by the following properties: density – 1.24 g/cm^3, melt flow rate (190°C, 2.16 kg) – 4 g/10 min, melting point – 84°C, impact strength – 47 kJ/m^2. The polymer was dissolved in mixtures of two solvents, the main component of which was chloroform (Chempur, Poland) and dimethyl sulfoxide (DMSO) (EUROCHEM BGD, Poland) or *N*,*N*-dimethylformamide (DMF) (Chempur, Poland) as an additional solvent. The second solvent was used to raise the boiling point of the system. All reagents were of analytical grade.

Solution preparation

PBS was dissolved in chloroform (45 cm^3) using a magnetic stirrer at ambient temperature, and finally DMSO or DMF (5 cm^3) was added. Addition of the second solvent in the amount of 10% vol. was enough to stably carry out the electrospinning process and obtain a fibrous structure.

Characterization of solutions and electrospinning process

The dynamic viscosity and surface tension of the solutions were determined using a Rotavisco SBS viscometer (IKA, Staufen, Germany) and a Sigma 701 tensiometer (KSV Instrument Ltd., Helsinki, Finland). The fibers were then electrospun from solutions using an LE-10 device (Bioinicia, Valecia, Spain). The morphology of the obtained fibers was characterized using a Vega 3 scanning electron microscope (Tescan, Brno, Czech Republic). The ImageJ program was used to process the obtained photos. Prior to analysis, samples were coated with a silver layer using a Cressington 108 sputtering device (Watford, England). The sputtering process time was 60 seconds at a current of 40 mA.

RESULTS AND DISCUSSION

As a result of electrospinning, fibrous structures with various morphologies were obtained, resulting from both the mixture of solvents (addition of DMF or DMSO to chloroform) and the selection of process parameters. The dynamic viscosity and surface tension of the prepared solutions are presented in Table 1. The values of these parameters for both solvent solutions are similar. However, the solution containing DMSO had slightly higher values, but the difference did not exceed 5%. The lack of significant differences in the measured parameters allows us to assume that the main reason for the differences between the obtained structures will result from the selected process parameters and the interactions between the solvent particles and polymer chains.

T a b l e 1. Dynamic viscosity and surface tension for prepared solutions

Parameter	Chloroform/DMSO	Chloroform/DMF
Viscosity, Pa·s	1236±89	1179±65
Surface tension, N/m^2	32.9±0.1	32.3±0.1

Openwork structures obtained using solutions containing a mixture of chloroform and DMF at a flow of 2.5 mL/h, an electric potential of 10.0 kV and a distance from the collector of 24.5 cm are shown in Figures 1 and 2.

The material presented in Fig. 1 is fibrous, but deformations in the form of spindles are clearly visible. Therefore, it was necessary to modify the electrospinning process parameters, which resulted in obtaining significantly different morphological structures from the same solution. The structures shown in Figure 1 belong to the spindle-shaped or coral-on-filament morphology, while the sample in Figure 2 shows a typical fibrous morphology. The difference between the obtained structures results directly from the change in the process parameters at which they were made. In the case of the first material, the presented spindle-shaped structure is caused by too intense electric field affecting the polymer solution stream, resulting in the formation of a network of thin fibers and spindles. The analysis of the structure shown in Figure 2 allows us to conclude that the process parameters used: flow rate – 3 mL/h, applied electric potential – 11 kV and distance from the collector – 26 cm. These conditions allowed to obtain a fibrous morphology without defects in the form of spindles or spheres. This is caused by the balance between the viscoelastic forces of the polymer solution and the forces of the electric field. It should be noted, that despite the different morphology of both materials, their surface remains smooth.

The use of different process parameters also resulted in significant differences in the sizes of the obtained structures. Conducting the process at lower flow rates (Fig. 1) resulted in a much lower the average fiber diameter than for nonwoven fabric produced using higher flow rates (Fig. 2), despite the use of a longer path between the injector needle and the collector. This is also confirmed by the histographic analysis presented in Figure 3.

a) b) c)

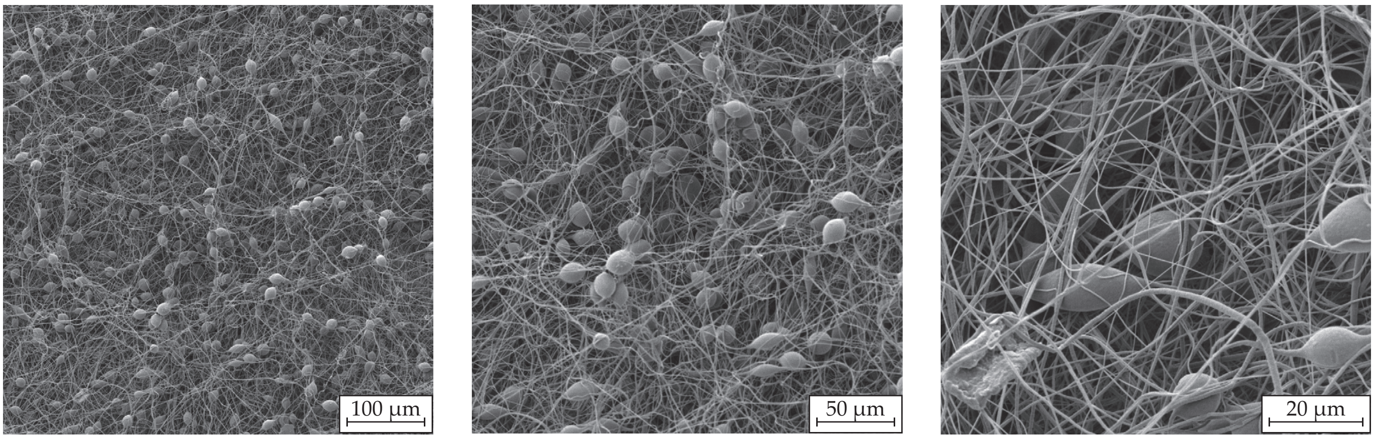

Fig. 1. SEM images of electrospun fibrous structures obtained from chloroform/DMF solution at a flow of 2.5 mL/h, an electric potential of 10 kV, and the collector distance of 24.5 cm: a) 500× , b) 1000× , and c) 3000× magnification

a) b) c)

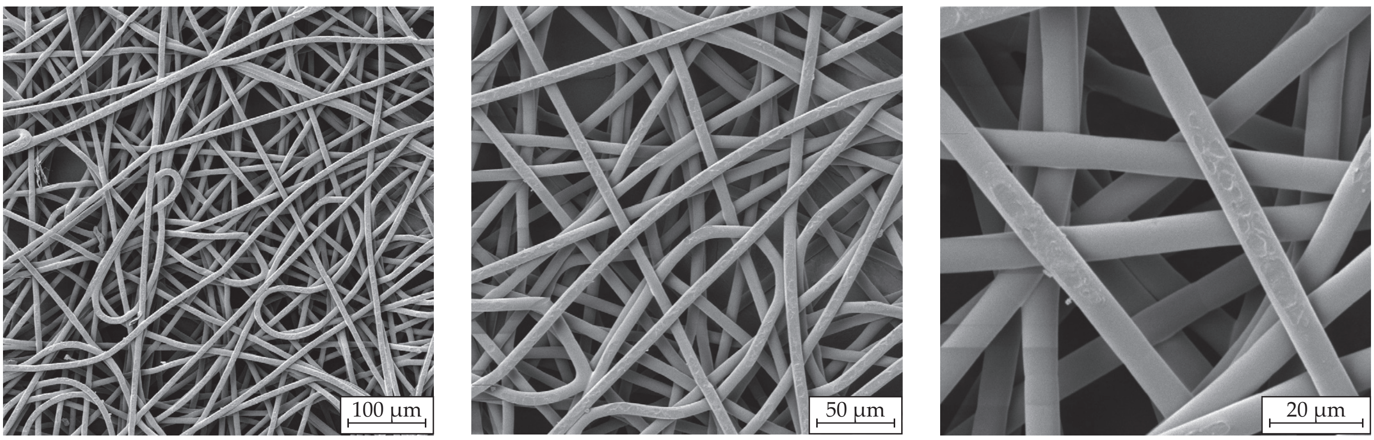

Fig. 2. SEM images of electrospun fibrous structures obtained from a chloroform/DMF solution at a flow of 3 mL/h, an electric potential of 11 kV and the collector distance of 26 cm: a) 500× , b) 1000× and c) 3000× magnification

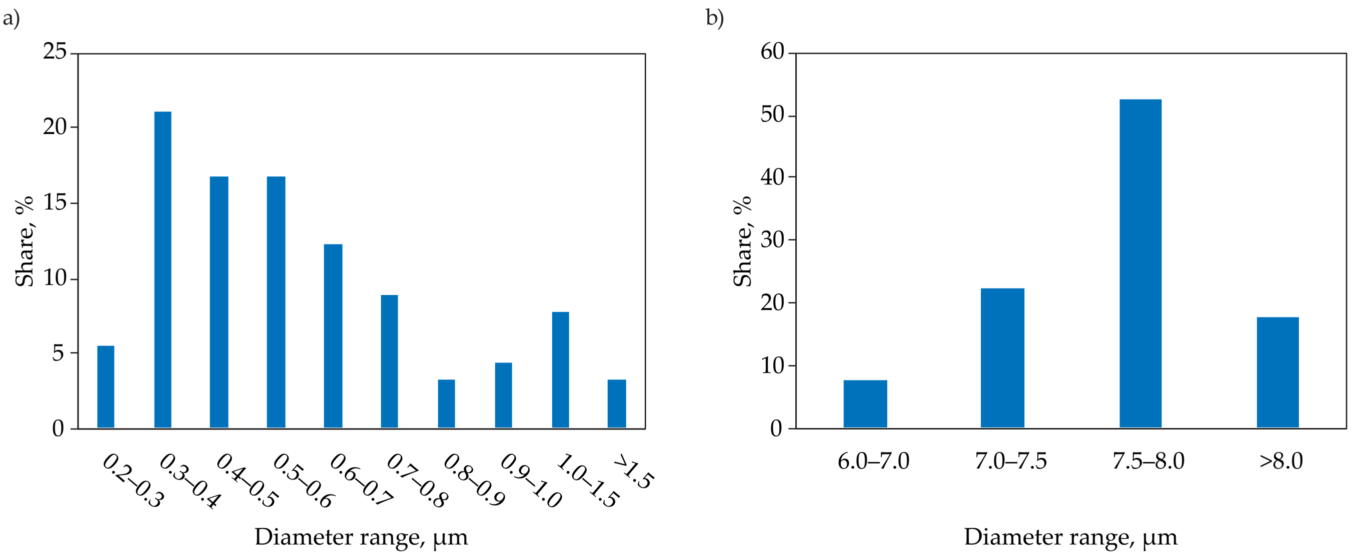

Fig. 3. Distribution of fiber diameters obtained from the chloroform/DMF solution at various electrospinning parameters: a) flow rate 2.5 mL/h, electric potential 10 kV, and the collector distance of 24.5 cm, b) flow rate 3 mL/h, electric potential 11 kV, and the collector distance of 26 cm

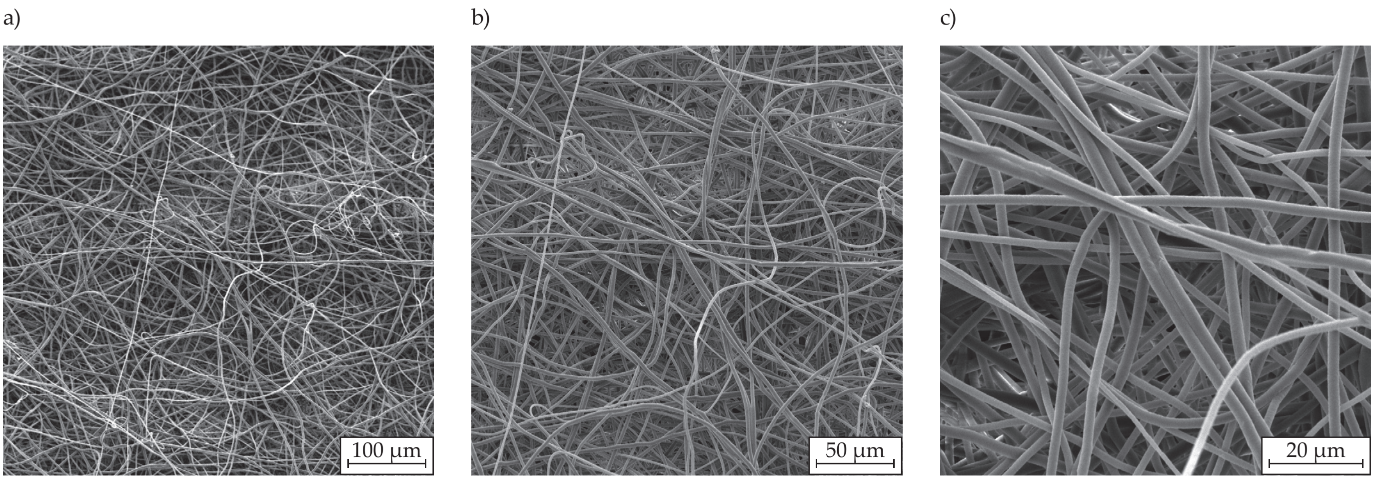

Fig. 4. SEM images of electrospun fibrous structures obtained from chloroform/DMSO solution at a flow of 2.5 mL/h, an electric potential of 8 kV, and the collector distance of 24.5 cm: a) 500x, b) 1000x and c) 3000x magnification

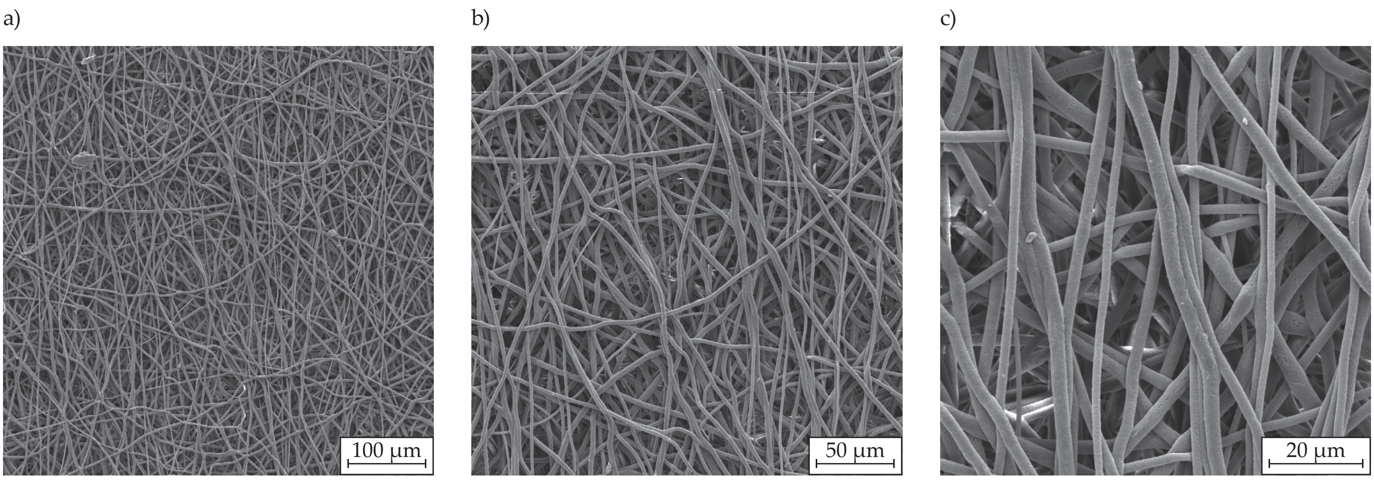

Fig. 5. SEM images of electrospun fibrous structures obtained from chloroform/DMSO solution at a flow of 2.5 mL/h, an electric potential of 8 kV, and the collector distance of 22 cm: a) 500x, b) 1000x and c) 3000x magnification

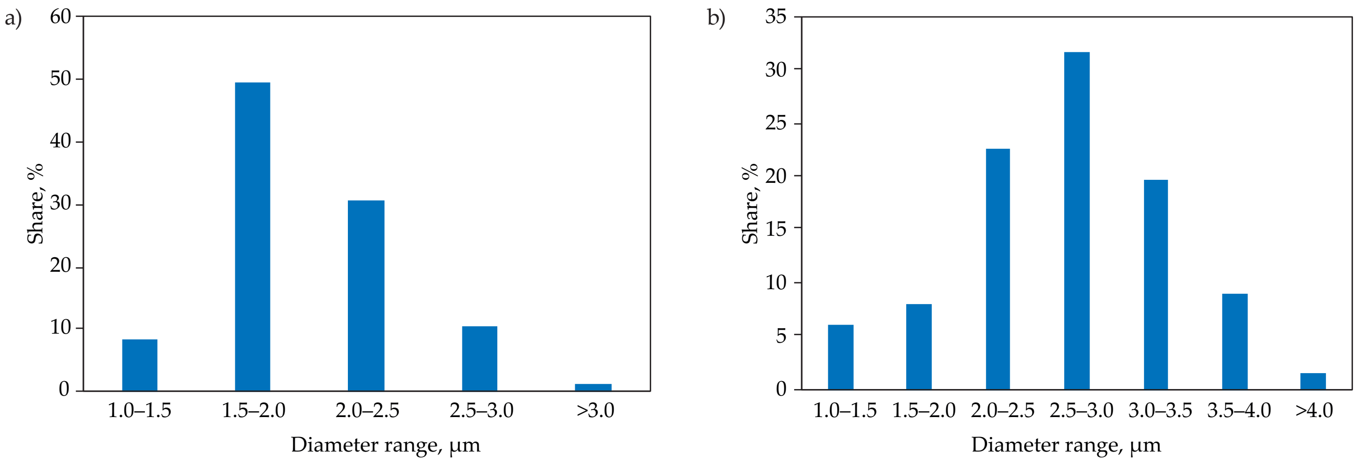

Fig. 6. Distribution of fiber diameters obtained from the chloroform/DMSO solution: a) flow rate 2.5 mL/h, electric potential of 8 kV, and the collector distance of 24.5 cm, b) flow rate 2.5 mL/h, electric potential of 8 kV, and the collector distance of 22 cm

The analysis of the diameter distribution of the sample presented in Figure 3a allows us to conclude that it contains fibers on the nanometer scale in the range from 0.28 to 1.79 μm. There is also a significant distribution of diameters, but more than half of the results obtained (54.4%) are in the range from 0.3 to 0.5 μm. Spindle-shaped structures that are visible in SEM images (Fig. 1) were not included in the histographic analysis due to the significant difference in their sizes. Their diameters were much above the values measured for fibers and varied in the range from 8.7 to 18 μm.

The change in diameter distribution presented in Figure 3b is caused by an increase in electric potential, distance from the collector and flow rate of the polymer solution, which resulted in the removal of the spindle-shaped structure in favor of obtaining homogeneous fibers. At the same time, an increase in the average fiber diameter was also noted, which is visible in the histogram (Fig. 3b). The obtained structure was characterized by a diameter range from 6.4 to 8.5 μm. These values are close to the lower range in which the spindles appeared in Fig. 1. Depending on the selection of process parameters, a very wide modification of the obtained structures is possible for a specific application.

The structures obtained from the chloroform/DMSO solution with various process parameters are fibrous, without any defects in the form of spindles or balls, but there are some differences between them, as can be seen in Figures 4 and 5. Reducing the distance between the needles and the collector from 24.5 to 22 cm caused the fibers to bind together and create porosity on their surface.

The binding is caused by incomplete evaporation of the solvent along the intended path, which means that the fibers reaching the collector still contain it in trace amounts and have the possibility of "sticking together". This phenomenon may be desirable in some applications, such as the production of tissue scaffolds or filtration materials by increasing the integrity of the material due to the formation of a network of interpenetrating fibers or reducing the volume of capillaries between them. Porosity may also be caused by shortening the distance. This treatment can increase the intensity with which the electric field acts on the resulting polymer fiber, causing a change in the dynamics of solvent evaporation in some areas. Additionally, reducing the distance had a direct impact on the size and distribution of the obtained fiber diameters, which can be observed in Figure 6. In the case of the structure created at 24.5 cm from the collector (Fig. 4), the uni-

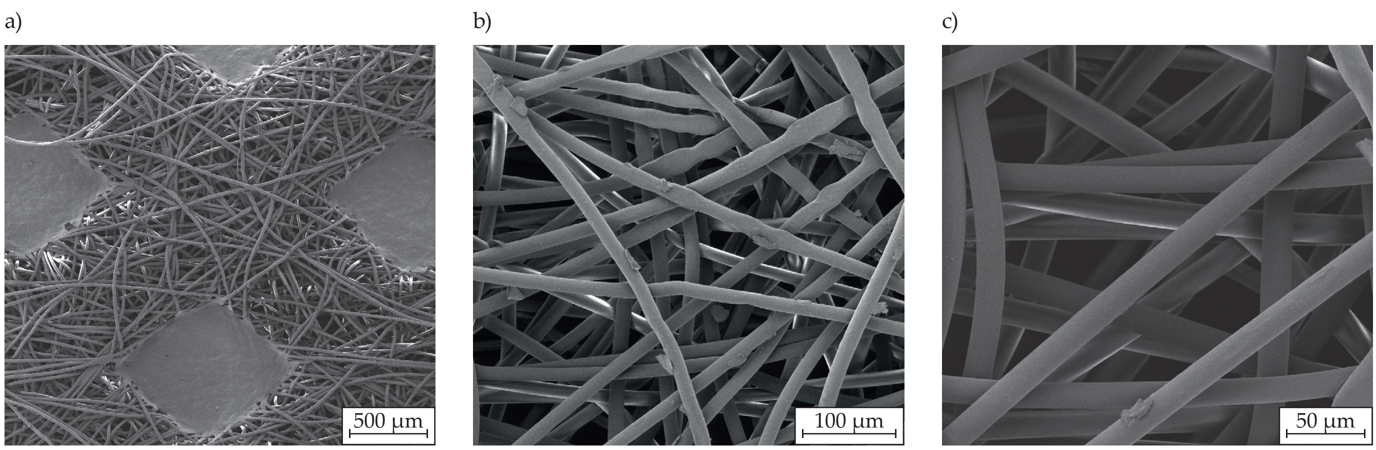

Fig. 7. SEM images of a commercially available filter fabric made using the melt blown method: a) 100x, b) 500x and c) 1000x magnification

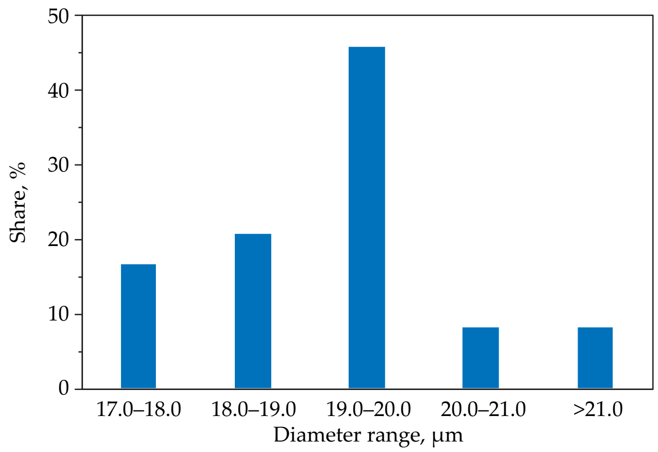

Fig. 8. Distribution of fiber diameters of commercially available filter nonwoven fabric made using the melt blown method

formity of the fibers was much greater, and their diameters ranged from 1.3 to 3.1 μm. Reducing the collector distance to 22 cm (Fig. 5) resulted in a greater spread of diameters ranging from 1.2 to 4.1 μm. Differences in diameter distribution seem to confirm that the cause of this effect may be an increase in the intensity of the impact of the electric field on the forming fiber, which directly affects the uneven stretching of the polymer solution stream.

The obtained materials were compared with commercially available polypropylene filter nonwoven fabric made using the melt blown method. The main difference between this method and the electrospinning technique is the much larger diameter of the obtained fibers, which is confirmed by SEM analysis (Fig. 7).

The morphology analysis shows that nonwoven fabrics produced by melt blowing are characterized by a much larger fiber diameter compared to the obtained electrospun structures. This is also confirmed by histographic analysis showing that the diameter distribution for commercial material ranges from 17.2 to 21.4 μm (Fig. 6), and the largest share in the studied population are fibers with sizes ranging from 19 to 20 μm (approximately 46 %). This means that, depending on the solvent system used, fibers produced by electrospinning have diameters that are up to 20 times smaller (DMF-based system) compared to nonwoven fabrics available on the market.

CONCLUSIONS

The paper discusses the preparation of fibrous structures with a large specific surface and the influence of electrospinning parameters of the obtained openwork structures morphology. Three types of morphology were obtained: smooth, porous, and spindle-shaped fibers. This was possible by selecting and correlating appropriate process parameters, but also by using various solvents. Structures made from solutions with the addition of DMF were characterized by a smooth fiber surface, and DMSO promoted the formation of pores. The morphological structure of filter materials may have a significant impact on filtration efficiency. Increasing the porosity of the filter material can reduce the resistance to air flow through the filter membrane.

The results were compared with commercially available material used in the air filtration process. The produced materials have great potential for use in the filtration process due to their developed specific surface. This is the result of a smaller fiber diameter compared to the product available on the market. An additional advantage of the solutions discussed is the fact that they are made of biodegradable materials, which reduces their carbon footprint and eliminates the problem of managing the waste generated. This means that the proposed solution comprehensively affects several areas of environmental engineering, such as atmosphere protection and air purification by creating a high-efficiency filtering material, but also waste management by limiting the stream of waste generated. The next stage of testing of the manufactured materials will be to determine their filtration capacity and flow resistance to optimize the manufactured openwork structures for their use as filtration materials.

Authors contribution

M.B. – conception, data analysis, investigation, writing-original draft, material preparation; K.S. – edition, SEM microscopy, writing-original draft; K.L – super-vision, edition. All authors have read and agreed to the published version if the manuscript.

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Conflict of interest

The authors declare no conflict of interest.

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