



# Structure, geometrical characteristics and properties of biodegradable micro- and polycaprolactone nanofibers

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## ABSTRACT

**Purpose:** The purpose of the paper is to obtain and examine the structure and properties obtained in the electrostatic field of micro- and nanofibers PCL.

**Design/methodology/approach:** The main problem of the study is to examine the impact of properties of the polymer solutions PCL obtained from the mixture of formic acid and acetic acid in a ratio of 70:30, tetrahydrofuran and dimethylsulfoxide in a ratio of 70:30, and chloroform and methanol in a ratio of 70:30 on the structure and and surface properties of polymer micro and nanofibers PCL.

**Findings:** On the basis of outcarried researches the impact of the polymer solutions applied to researches on the diameter and the properties of obtained polymer micro- and nanofibers have been shown. It comes out that from the ourcarried researches of specific surface area of fibers the highest specific surface area BET was obtained for fibers formed from a mixture of acetic acid and formic acid and it is equalled 8.9 m<sup>2</sup>/g. Significantly smaller surface area was obtained from a mixture of tetrahydrofuran and dimethyl sulfoxide 3.1 m<sup>2</sup>/g. However, the lowest surface area for fibers obtained from a mixture of chloroform and methanol, which is 0.9 m<sup>2</sup>/g, in spite of the observation of the porous surface of fibers.

**Practical implications:** Mixture of formic acid and acetic acid may be an alternative solution for preparing nanofibers PCL.

**Originality/value:** The results confirm the possibility of receiving nanofibers PCL from a mixture of non-toxic solvents.

**Keywords:** Micro and nanofibers; Electrostatic field

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## MATERIALS

## 1. Introduction

Porous polymer materials, with their reinforcing phase being nano- and sometimes microfibers with the diameter of 50-500 nm, and the matrix function played by air, have their usage prospects resulting most of all from their geometrical characteristics. Efforts have been continued to produce a polymer-air composite featuring high porosity, air permeability, absorptivity, barrierity, bacteriocidity, biocompatibility, intoxicity, a possibility of releasing medicinal agents in a controlled way, appropriate mechanical strength and its structure supporting regeneration processes. The efforts require multiple interdisciplinary investigations, including those connected with a study into standard polymer nanofibres with a different diameter. There are many methods of fabricating polymeric composites with air acting as a matrix and with a reinforcing phase as fibres with a different diameter (standard fibres, thin fibres, microfibers). Textile technologies are most popular, i.e.: Melt-blown, needlepunching and spunlacing (hydroentanglement), Spunbond Technology, Thermal Bonding of Nonwoven Fabrics and others [1]. There are several polymer nanofiber fabrication technologies [1,2]. The one developed most intensively is electrospinning producing polymer nanofibres with an electric field from molten polymers and from solutions [3-6]. Nanofibres with a different morphology can be fabricated according to the manufacturing conditions of electrospinning, including hollow, porous, flat, directed, branched, co-axial nanofibres and ones with different composition [7-9]. The other methods are rather of laboratory than technical relevance and include: the drawing of materials with high viscosity, e.g. sodium citrate that can be subjected to a large plastic deformation without losing cohesion; phase separation where a polymer and solvent solution undergo gelling, when the solvent is removed the next time; template synthesis, i.e. a nanoporous membrane made of corundum as a template for producing nanofibres under pressure pressed by the template pores to a chamber with a solidifying solution, and molecular self-assembly where single molecules are linked into chains whose shape determines the shape of the nanofibres being formed. For the area of one-dimensional nanostructural materials, upon which this paper is concentrated, there are polymer nanofibres defined as objects with a diameter of below 1  $\mu\text{m}$ . Electrospinning [10] is a dominant nanofibres fabrication technology which enables to obtain polymer nanofibres in an electrostatic

field, including nanofibres with full and empty section, core-shell nanofibres consisting of two parts [11], porous nanofibres [12], dual- and multicomponent nanofibres, composite nanofibres [13] containing metal particles or ceramics, as well as organic materials, hybrid nanofibres being a combination of polymers of the natural and synthetic origin. It is possible to obtain polymer, carbon, metallic or ceramic nanofibres in an indirect or direct manner depending on the input material type and a combination method of materials. The paper concentrates on polycaprolactone (PCL), i.e. a semi-crystalline, linear, aliphatic and biocompatible polyester with good mechanical properties, widely used in medicine [14]. An interest in the material has been gradually growing in the recent years. It derives from its applicational possibilities, including, in particular, in: tissue engineering, regenerative medicine (e.g. for regeneration of nerves), medicine carriers, sensors and other biomedical applications. Works over the application of such materials in the medical industry, including as resorbable dressings, are impeded by popular and toxic solvents used for transformation of a polymer material into the form of a solution, such as:  $\text{CH}_2\text{Cl}_2$ , a mixture of THF:DMF, acetone, a mixture of DMF:  $\text{CHCl}_3$ , a mixture of MeOH methanol with  $\text{CHCl}_3$  chloroform, but also of tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) [15-17]. The aim of the work is to investigate and compare the properties of PCL fibres obtained from three polymer solutions as a mixture of formic acid and acetic acid at a rate of 70:30 m/m, chloroform and methanol at a rate of 70:30 m/m and tetrahydrofuran and dimethyl sulfoxide at a rate of 70:30 m/m.

## 2. Materials selection

The materials for the research were picked based on the weighted scoring method [18,19] in which, based on the criteria of attractiveness and potential (Tab. 1) and literature data, 8 polymers occurring most often in medical applications were analysed, i.e.: polylactide (PLA), polycaprolactone (PCL), chitosan, polyamide (PA6), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), polypropylene (PP) and hyaluronic acid (KH). The relevant potential and attractiveness criteria were ascribed to the above polymers, and were presented graphically after multiplying the particular criteria by weight (Fig. 1).

Table 1.  
Multicriteria analysis of attractiveness of particular polymer materials as porous scaffolds

Criteria	Values	Weight	PLA	PCL	CHITOSAN	PA6	KH	PMMA	PP	PVA
	Objective values									
K <sub>P1</sub>	Material tensile strength	0.2	1.6	1.6	2.0	1.2	1.2	1.0	1.6	1.2
K <sub>P2</sub>	Shape stability	0.1	0.7	0.9	1.0	0.6	0.8	0.4	0.7	0.8
K <sub>P3</sub>	Enzymatic or hydrolytic bioresorbability	0.3	2.4	2.7	0.9	1.5	3.0	1.8	0.0	2.4
K <sub>P4</sub>	Material transformability into the form of fibre from solution	0.2	1.6	1.6	0.4	1.6	1.0	1.6	1.8	1.0
K <sub>P5</sub>	Applicability of non-toxic solvents	0.2	0.6	1.4	1.4	0.8	2.0	0.8	0.0	1.6
		Total	6.9	8.2	5.7	5.7	8	5.6	4.1	7
	Subjective values									
K <sub>A1</sub>	Material can be used as a carrier of medicinal substances	0.25	2	2.5	2.5	0.3	2	0.5	0	2
K <sub>A2</sub>	Number of publications conc. the material (acc. to Web of Science)	0.1	0.2	0.4	0.7	0.7	0.7	0.7	0.8	0.7
K <sub>A3</sub>	Composite material manufacturing costs	0.15	1.5	1.5	1.5	1.1	1.05	1.05	1.2	0.9
K <sub>A4</sub>	Potential applicability range on industrial scale	0.25	1.8	2	2.25	0	2.25	0.25	0	2
K <sub>A5</sub>	Availability of material collection sources	0.2	1.6	2	0.6	1.4	0.8	1.2	2	1
		Total	7.05	8.4	7.55	3.4	6.8	3.7	4	6.6
		Symbol	A	B	C	D	E	F	G	H

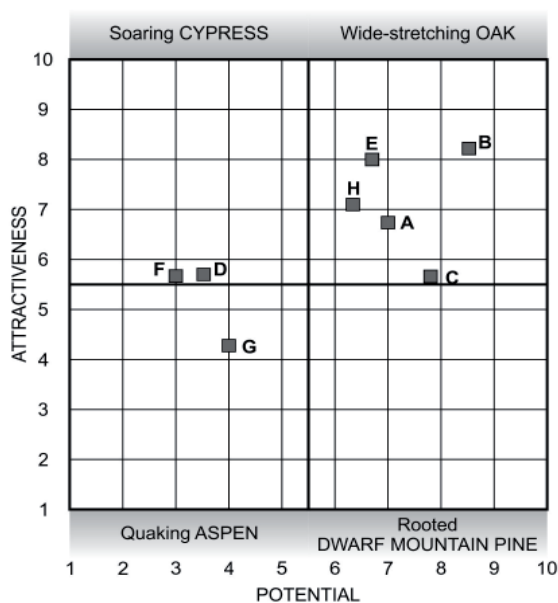


Fig. 1. Graphical representation of selected polymers' potential and attractiveness

The following polymer materials have the highest level of attractiveness and potential: polylactides (A), polycaprolactone (B), chitosan (C), hyaluronic acid (E) and polyvinyl alcohol (H) found in the most promising quarter of the matrix (wide-stretching oak). For the materials listed, polycaprolactone (B) has revealed the greatest attractiveness and potential, while chitosan (C) has proved to be another polymer with the highest potential (C). Hyaluronic acid (E) proved to be most attractive in the study and for this reason such materials (B, C and E) were selected for research as the basic materials.

Three polymer materials differing in the following properties were selected with the weighted scoring analysis method:

- polycaprolactone (PCL) being a synthetic polymer;
- chitosan being a derivative of chitin, the second most often occurring in nature natural polymer after cellulose;
- hyaluronic acid belonging to the group of biopolymers occurring in living organisms.

Polycaprolactone (PCL) was finally selected for the research. It is a semicrystalline, linear, aliphatic and biocompatible polyester with good mechanical properties.

### 3. Experimental procedure

#### 3.1. Characteristics of the materials used in the work

The following synthetic polymer materials with  $M_w = 100\,720$  g/mol by Sigma Aldrich, the chemical reagents: acetic acid 99.95% by Sigma Aldrich, formic acid 99.95% by Sigma Aldrich, N,N-dimethylformamide (DMF) 99.95% by Sigma Aldrich, dimethyl sulfoxide (DMSO) 99.95% by Sigma Aldrich, tetrahydrofuran 99.95% (THF) by Chemland, methanol 99.95% by Chemland, chloroform 99.95% by Chemland were used in the work to obtain single-component nanofibres.

#### 3.2. Preparation of solutions and fabrication conditions

The following solutions were prepared with polycaprolactone (PCL) with the molecular mass of  $M_w = 100\,720$  g/mol:

- solutions with a concentration between 2 to 10% in a mixture of acetic and formic acid solvents with a mass ratio of 70:30 m/m;
- solutions with a concentration between 2 to 10% in a mixture of chloroform and methanol with a mass ratio of 70:30 m/m;
- solutions with a concentration between 2 to 10% in a mixture of tetrahydrofuran and dimethyl sulfoxide with a mass ratio of 70:30 m/m.

A dependency (1) for calculating the necessary fraction of polymer materials with the accuracy of 0.01 g and solvents measured according to their density were used for preparing the solutions.

$$C_p = \frac{m_s}{m_r} * 100\% \quad (1)$$

where:

$C_p$  – fraction in %,

$m_s$  – mass of the dissolved substance in g,

$m_r$  – mass of the solution in g.

The solving of synthetic-origin polymers such as polycaprolactone (PCL) is a simple process as it belongs to a group of aliphatic polymers. Moreover, the dissolving of polycaprolactone is facilitated by the availability and diversity of solvents available at the market including such solvents as: tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chloroform, acetone, methanol. Although it is easy to obtain the solutions made of the aforementioned solvents and despite their availability, the aforementioned liquids are toxic or cancerogenic materials, and a risk of their penetration into an organism together with degradation of the implanted material increases the risk of a negative impact of such solutions on living organisms.

After dissolving, the solutions were placed in containers of the Electro-Hydrodynamic Atomization 2.2D – 500 device by Yflow Nanotechnology Solutions equipped with a working chamber, control panel, infusion pumps with flow adjustment for  $\mu\text{l}/\text{min}$  and  $\text{ml}/\text{h}$ , two systems maintaining solution temperature and nozzles for standard and coaxial electrospinning. Nanofibres were deposited during electrospinning onto a flat collector dimensioned 40x40 cm for 0.25 – 12 hrs. The characteristics of fabrication conditions and parameters of single-component PCL nanofibres are presented in Table 2.

Table 2.  
Fabrication conditions and parameters of single-component PCL nanofibres

Type of applied nozzle	Standard nozzle
Process type	single-stream process
Flow rate, ml/h	1.00
Type of applied collector	flat 40x40 cm collector and rotating collector with diameter of 20 cm and length of 40 cm
Collector rotational speed, rev./min.	200, 500, 600, 1400
Electrostatic voltage, kV/cm	0.95-1.00
Solution temperature, °C	25
Gas temperature in working chamber, °C	23
Gas humidity in working chamber, %	20-30

### 3.3. Research methods employed

The average molecular mass of the studied polymer materials was evaluated by means of gel permeation chromatography (GPC) in a chromatographic column filled with a porous absorbent. A solvent with a concentration of 1.000 g/l was used for the studies, dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) was used as an eluent (solvent) of polycaprolactone and the flow rate of 0/800 ml/min. was set on the column. The structure of the obtained fibres was investigated using a SEM SUPRA 35 scanning microscope by ZEISS using accelerating voltage of 3-25 kV. The observations were made with the magnification of 1000 to 100000 times in order to determine the influence of the applied solutions and fabrication conditions on the nanofibres diameter, their spatial arrangement and formation of defects. Digital Micrograph365 software was used in the research. An electrical conductivity (EC) test was undertaken for single-component solutions and double-component solutions using an MM41 multimeter by Labindex. Calibration in a water solution of Crysolyt KCl 3M with the conductivity of 1413  $\mu\text{S}/\text{cm}$  was made before a conductivity measurement. An electrical conductivity measurement according to stability over the time of 4 seconds at the temperature of 25°C was carried out. A viscosity test of single-component and double-component solutions was performed by means of an Alpha L rotational viscometer by Labindex. An APM adapter for solutions with the volume of 8-13 ml was employed in the measurements. The viscosity of solutions was measured with TL5, TL6 and TL7 spindles at room temperature and with the spindle speed of 0.3 to 100 rev./min. The specific surface area BET and porosity were assessed with the gas adsorption method by using a Gemini VII 2390t specific surface area analyser by Micrometrics. The weighed samples with the mass of 0.2 g were subject to vacuum drying for 24 hours at the temperature of 30°C to remove humidity and the adsorbed gases. The dried samples were placed in the device and measurement conditions were defined: pressure within the range of 0.01 to 0.65  $P/P_0$  was assumed for adsorption and desorption and nitrogen with the purity of 5.0 was used as measuring gas.

## 4. Results

### 4.1. Molecular mass analysis GPC

The investigation of the molecular mass of the polymers used by means of gel permeation chromatography (GPC) have shown  $M_w = 100\ 720$  g/mol.

### 4.2. Analysis of electrical conductivity and viscosity

The viscosity tests performed (Fig. 2) for the PCL solutions achieved by combining chloroform and methanol show that the highest variation in solution viscosity along with the rising polymer concentration is between 7 mPa·s for a 2% concentration to 994 mPa·s for a 10% concentration. The PCL solution obtained by combining formic acid and acetic acid has revealed the lowest increase in viscosity from 9 mPa·s for a 2% concentration to 133 mPa·s for a 10% concentration. A significant change in the viscosity of the PCL solutions obtained from a mixture of tetrahydrofuran and dimethyl sulfoxide was recorded for the value ranging from 5.1 mPa·s for a 2% concentration to 620 mPa·s for a 10% concentration. The observed differences result from the density of the applied solvents.

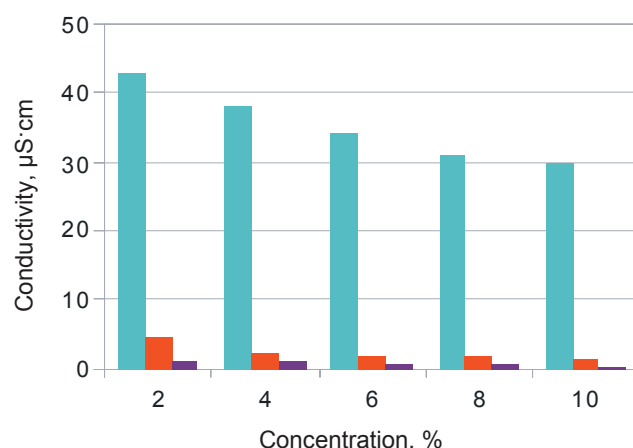


Fig. 2. Electricity conductivity variation for polycaprolactone solutions with a concentration of 2-10%; the tests pursued using the mixture of: formic acid and acetic acid of 70:30 m/m, a mixture of THF:DMSO of 70:30 m/m and chloroform and methanol of 70:30 m/m

The electrical conductivity tests carried out for the solutions (Fig. 3) have revealed a decrease in conductivity as the fraction of PLC in the solution volume rose in all the studied cases. The highest drop in electrical conductivity was observed for a mixture of chloroform and methanol, i.e. from 4.5  $\mu\text{S}/\text{cm}$  for a 2% solution to 1.5  $\mu\text{S}/\text{cm}$  for a 10% solution. The highest conductivity variation was seen for a mixture of formic acid and acetic acid, i.e. from 43  $\mu\text{S}/\text{cm}$  for a 2% solution to 30  $\mu\text{S}/\text{cm}$  for a 10% solution.



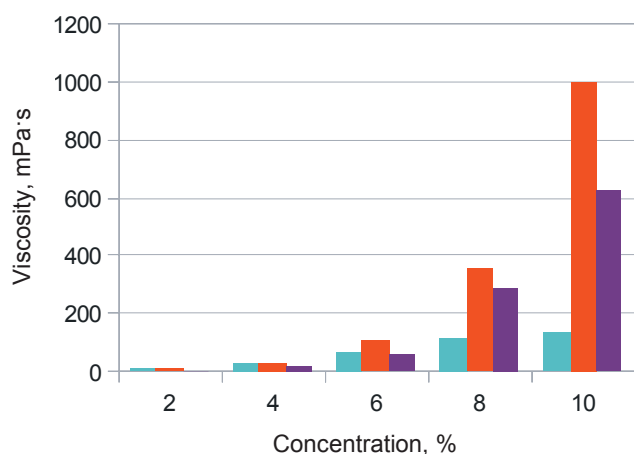


Fig. 3. Viscosity variations for polycaprolactone solutions with a concentration of 2-10%; the tests pursued using the mixture of: formic acid and acetic acid of 70:30 m/m, a mixture of THF:DMSO of 70:30 m/m and chloroform and methanol of 70:30 m/m

The investigations performed on the fibres obtained from a 10% PCL solution using a scanning electron microscope SEM confirm the significant influence of viscosity and conductivity of the solution obtained on the diameter of the achieved fibres. For the fibres obtained using a mixture of chloroform and methanol (Fig. 4), 76% of the tested sample are microfibers with the diameter of 1.0-2.1  $\mu\text{m}$ , while the remaining 24% of fibres include nanofibres. Fibbers with a high irregularity of diameters are formed by employing this mixture of solvents and numerous surface defects occur; moreover, the fibres are bonded.

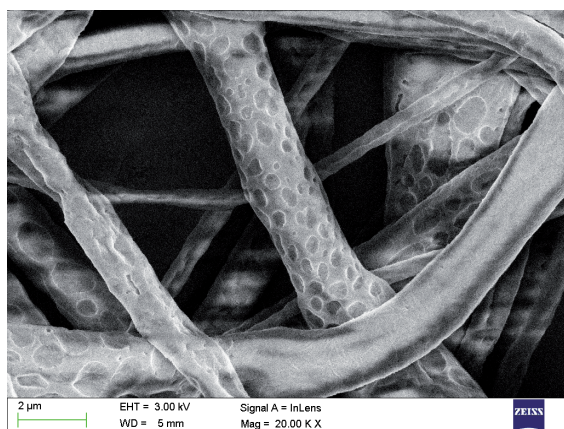


Fig. 4. Morphology of obtained polycaprolactone fibres from a 10% solution in a mixture of chloroform and methanol of 70:30 m/m, SEM

Microfibers with the diameter of 1.3 to 1.4  $\mu\text{m}$  are dominant, and the thinnest achievable fibres are nanofibres with the diameter spanning between 500 and 600 nm. In the investigated sample, fibres with the diameter up to 1000 nm account for 32% of all the obtained fibres.

The similar geometrical characteristics were observed in the fibre samples obtained from a mixture of solvents of tetrahydrofuran and dimethyl sulfoxide (Fig. 5). Microfibers with the diameter of 1.0 to 2.5  $\mu\text{m}$  exist in 68% of the tested material, with 32% being nanofibres. Fibbers obtained using tetrahydrofuran and dimethyl sulfoxide – just like fibres produced from a mixture of chloroform and methanol – are bonded and distinguished by a high surface irregularity. Microfibers with the diameter of 1.3 to 1.4  $\mu\text{m}$  are dominant in the tested sample, and the thinnest achievable fibres are nanofibres with the diameter spanning between 400 and 500 nm. Fibres with the diameter of below 1000 nm represent 24% of the sample.

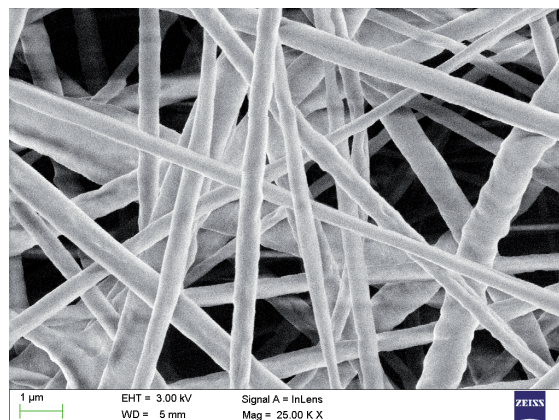


Fig. 5. Morphology of obtained polycaprolactone fibres from a 10% solution in a mixture of tetrahydrofuran and dimethyl sulfoxide of 70:30 m/m, SEM

Different geometrical characteristics were observed for the fibres achieved from a polycaprolactone solution using a mixture of formic acid and acetic acid (Fig. 6). Nanofibres within the range of 1-100 nm were only obtained in the tested sample, and the thinnest achievable fibres are nanofibres ranging 1-100 nm.

Nanofibres with the diameter of up to 200 nm constitute 84% of all those obtained from a polycaprolactone solution using a mixture of formic acid and acetic acid. Ultrathin fractions of nanofibres were observed to be created in the range of 20-30 nm in the studied samples, and no such fraction was observed in other samples. In addition, the obtained nanofibres are characterised by a smaller bonding tendency as compared to other samples.

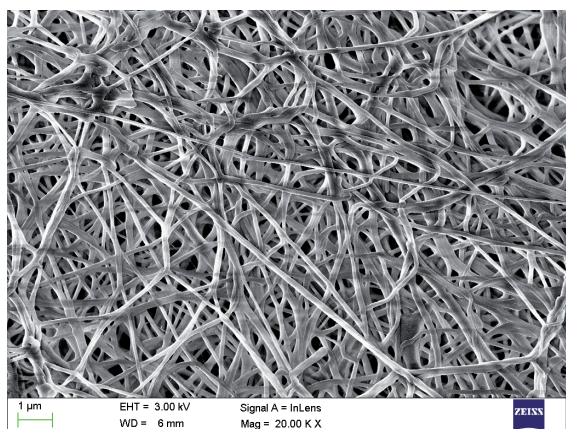


Fig. 6. Morphology of obtained polycaprolactone fibres from a 10% solution in a mixture of formic acid and acetic acid of 70:30 m/m, SEM

The studies undertaken with the gas adsorption method reveal large differences in the specific surface area BET of the samples. The observed gas adsorption isotherms show the occurrence of the 2<sup>nd</sup> isotherm type (Fig. 7) in the tested samples meaning that the tested samples are characterised by physical adsorption, i.e. the creation of a multi-molecular layer of nitrogen. The fibre surface area investigations performed provide that the highest specific surface area BET was obtained for the fibres formed from a mixture of formic acid and acetic acid and it accounts for 8.9 m<sup>2</sup>/g. A much smaller area was shown for the fibres obtained from a mixture of tetrahydrofuran and dimethyl sulfoxide, i.e. 3.1 m<sup>2</sup>/g. The smallest surface area was identified for the fibres produced from a mixture of chloroform and methanol of 0.9 m<sup>2</sup>/g, despite observing a porous surface of the fibres. Considerable differences for the particular samples are apparent when analysing the amount of the adsorbed gas (nitrogen) for the pore width range of 1.5 to 3.4 nm. 1.6 nm and 2.4 nm wide pores are dominant in the PCL fibres manufactured from the mixture of formic acid and acetic acid, as the areas adsorb most nitrogen and is, respectively, 0.00064 cm<sup>3</sup>/g and 0.00047 cm<sup>3</sup>/g (Figs. 8, 9). 1.5 nm and 1.6 nm wide pores are dominant for the fibres fabricated from a mixture of tetrahydrofuran and dimethyl sulfoxide, for which gas adsorption is revealed of, respectively, 0.00030 cm<sup>3</sup>/g and 0.00022 cm<sup>3</sup>/g. The smallest amount of the adsorbed nitrogen was determined for the PCL samples attained using a mixture of chloroform and methanol, i.e. pores with the diameter of 1.5 nm, which only adsorbed 0.00010 cm<sup>3</sup>/g of nitrogen.

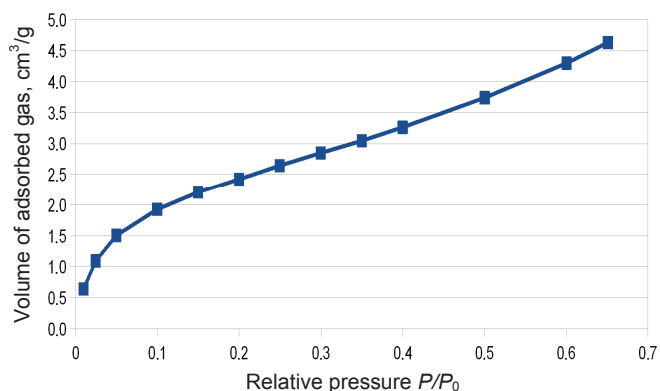


Fig. 7. Nitrogen adsorption isotherms of PCL fibres obtained from a mixture of formic acid and acetic acid at a rate of 70:30, measurements made for the relative pressure of 0.01 to 0.65  $P/P_0$

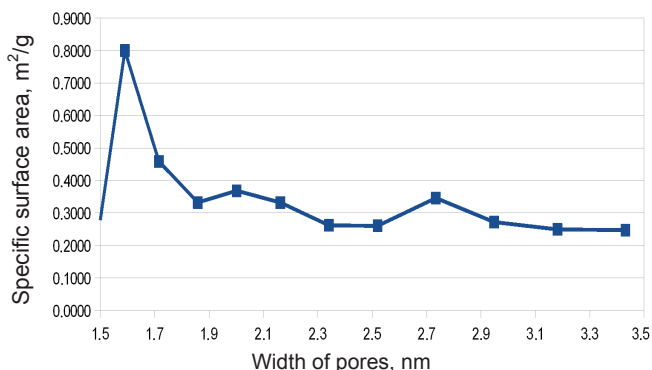


Fig. 8. Surface area change of the studied samples acc. to width of pores. A measurement made for nanofibres obtained from a mixture of formic acid and acetic acid at a rate of 70:30

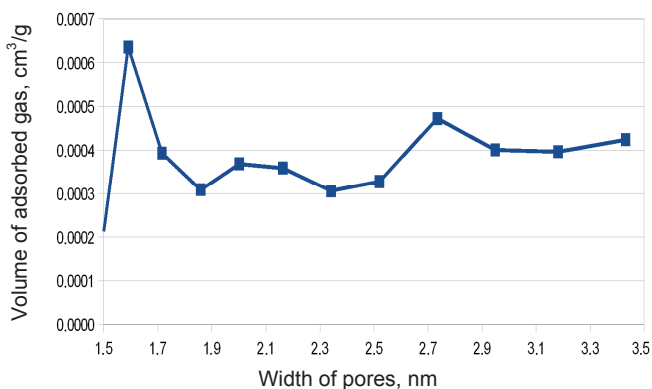


Fig. 9. A variation in the amount of the adsorbed gas depending on the width of pores. A measurement made for nanofibres obtained from a mixture of formic acid and acetic acid at a rate of 70:30

Such high differences in the surface area of fibres result from the diameter of the obtained fibres, which is highly influenced by the properties of a mixture of solvents used for producing them. Differences in the amount of the adsorbed gas by particular pores result from the properties of the solvents mixture employed, including, most of all, the evaporation rate of the solvent: the higher the solvent evaporation rate the larger diameter of fibres. The solvation of solvents is caused by adding a solvent with much lower volatility (DMSO) to a solvent with high volatility – such as THF. A solvent with longer evaporation time partially delays the evaporation process of THF, which allows to produce fibres with a smaller diameter as compared to those formed from the combination of chloroform and methanol, i.e. highly volatile solvents.

## 5. Conclusions

The developed composite material with a fraction of biodegradable nanofibres with a highly developed surface manufactured by electrospinning may find its application for tissue scaffolds, the function of which is to support the basic regeneration processes of natural tissues. This is achievable by creating structures enabling to develop tissues due to appropriate porosity, influence on the tissue environment, combating microorganisms infecting the wound environment, releasing medicinal substances in a controlled manner or supporting natural regenerative processes, such as maintaining a humid wound environment or optimum adhesive properties of the applied biomaterials. It was evidenced, as a result of the performed research that the nanocomposite nanofibres obtained with a bioactive core and antibacterial coating can be applied as tissue scaffolds. They combine both, antibacterial and bioactive properties and may represent a precious engineering material which, after performing positive *in vivo* tests, could be applied, in particular, in controlled bone tissue regeneration, where long-term resorbable scaffolds are sought which fulfil, notably, the function of a carrier of antibacterial substances, bioactive substances and, moreover, due to a long period of decomposition, the materials can act as a membrane separating two types of tissues.

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