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Analysis of the influence of electro-spinning process parameters on the morphology of poly(lactic acid) fibres

W. Matysiak *, A. Kapica, T. Tański, A. Dubiel
Institute of Engineering Materials and Biomaterials, Silesian University of Technology, ul. Konarskiego 18A, 44-100 Gliwice, Poland
* Corresponding e-mail address: Wiktor.Matysiak@polsl.pl

ABSTRACT

Purpose: The article focuses on the production of polymer nanofibres from poly(lactic acid) using the electro-spinning method, i.e. the technique of forming fibres in an electrostatic field. The main aim of the publication was to analyse the influence of the distance between electrodes on the morphology of one-dimensional polymeric materials obtained.

Design/methodology/approach: In the practical part of the study solutions of polylactide in acetone and a mixture of chloroform/dimethylformamide (DMF) were produced. After 72 hours of mixing, no homogeneous solutions were obtained, therefore a solution consisting of a polylactide dissolved in chloroform was prepared, to which dimethylformamide was added in order to dilute the mixture. The morphology of the nanostructures obtained was analysed by means of a scanning electron microscope (SEM) equipped with an X-ray energy dispersion spectrometer (EDS), which allowed to analyse the chemical composition of the nanofibres produced. The electro-spinning method used to obtain fibres is characterized by high versatility - it gives the possibility to produce fibres from a wide range of polymers. Electro-spinning is also an economic method, and spinned fibres have a wide application potential.

Findings: Nanofibres obtained by electro-spinning from the previously produced solution, regardless of the distance between the nozzle and the collector (10 or 20 cm) did not show any significant discrepancies in the values of measured diameters. Fibres obtained at increased distance between electrodes (20 cm) are characterized by a smaller average diameter value, but the difference is small, fluctuating between 48-49 nm. In the case of the sample formed during electro-spinning at the distance of the nozzle - collector equal to 10 cm and the sample produced at the distance doubled, no defects in the structure of the obtained nanofibres were observed. The analysis of topographic images of surfaces produced in the course of nanostructures' work did not show any significant influence of the distance between the nozzle and collector on the diameter of fibres. No defects in the structure of one-dimensional polymer materials obtained allowed to state that the distance between the nozzle and the collector in the range of 10-20 cm is the optimal parameter of the electro-spinning process allowing to obtain smooth, untangled fibres.

Practical implications: The fibrous polymer mats obtained during the electro-spinning process of polylactide can be used as protective clothing materials, as drug delivery systems, as tissue scaffolding and as filtration membranes.

Originality/value: At present, there are few articles in the literature on the electro-spinning process, due to the fact that it is a constantly developing matte for the production of nanofibres. Moreover, most of the research focuses on fibres obtained from non-biodegradable polymers, which do not have the advantages of fibres obtained from polylactide.

Keywords: Nanofibres, Poly(lactic acid), Polylactide, PLA, Electro-spinning

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

In recent years, the role of nanotechnology in the modern world has grown significantly; its use in various areas of life, from medicine to construction, transport or telecommunications, makes it an extremely attractive research area worthy of interest and exploration. The scientific field of nanotechnology focuses on the analysis of materials at the molecular level, which allows a better understanding of the material, as well as the modification of the molecular structure of known engineering materials. Modification of the internal structure of the material directly affects its mechanical properties. This paper focuses on the topic of creating one-dimensional synthetic structures, called nanofibres, from poly (lactic acid). These structures created with the use of the electro-jointing method are used in various areas of life. There are various techniques for producing polymeric fibres. The most popular of these are drawing, phase separation, molecular self-organization, template synthesis, electro-spinning. Electro-spinning is a process that is becoming more and more popular due to the possibility of obtaining submicron fibres. The technique involves producing fibres from polymers or their solutions in an electrostatic field. Fibres obtained by this method are characterized by a wide application potential – sensors, drug carriers, tissue scaffolding or filtration membranes. Poly (lactic acid) (PLA) is a biopolymer with very good mechanical properties (especially high tensile strength, flexural strength and high Young's modulus) exceeding thermoplastic polymers such as polystyrene, polyethylene or polypropylene. Comparing PLA to classical synthetic polymers, it can be concluded that it is characterized by increased brittleness. This polymer is an extremely valuable material due to its high biodegradability, biocompatibility and shape memory capacity. The aim of this paper is to produce and examine the morphology of PLA nanofibres obtained with variable parameters of the electrostatic spinning process. The project involves the production of biodegradable, biocompatible fibres, and then examination of their morphology by scanning electron microscopy (SEM) and microanalysis of their chemical composition by X-ray energy dispersion spectrometer (EDX, EDS), which is part of the electron microscope.

2. Materials and test methods

The solution used to produce nanofibres was a 10% mixture of polylactide, chloroform and dimethylformamide. The reagents used came from a company supplying materials and laboratory products POCH. In the first stage a solution consisting of 2.5 g PLA and 22 ml chloroform was prepared. The prepared material was stirred using a magnetic stirrer. After 24 hours it was decided to add 4 ml of dimethylformamide to dilute the previously formed very dense and sticky liquid. After addition of the reagent, the solution was stirred again using a magnetic stirrer for another 15 minutes. After a certain period of time, a homogeneous mixture of appropriate density was obtained.

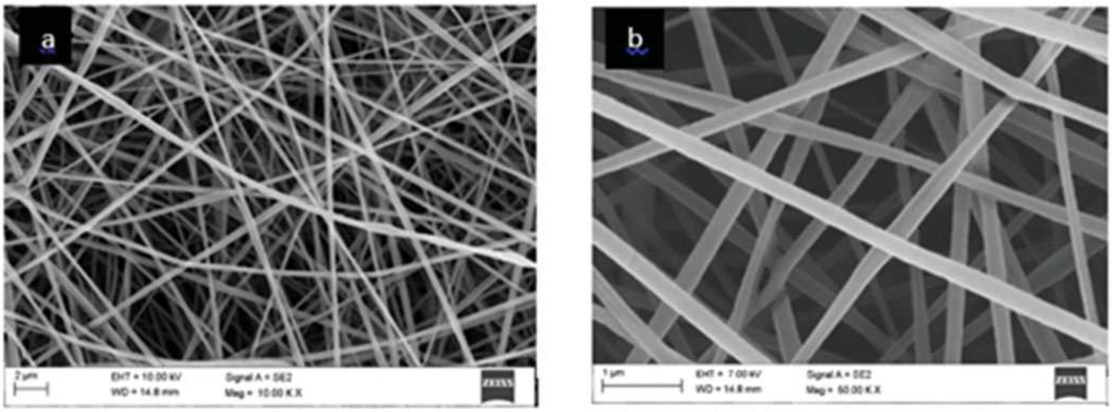
The process of electro-spinning of nanofibres was carried out on a stand equipped with the equipment for manufacturing FLOW nanofibres – Nanotechnology Solutions Electrospinner 2.2.0-500. Two samples were produced from the solution obtained using different process parameters. For both samples, the application rate through the nozzle was 2.5 ml/h and the potential difference between the upper and lower electrode (nozzle and collector) was 15 kV. The nanofibres were formed at room temperature of approximately 22°C and air humidity of 30-40% in about 15 minutes. The only variable parameter was the distance between the nozzle and the collector, which in the case of the first sample was 10 cm, while in the case of the second sample the distance was doubled. The nanofibres were deposited on a flat collector covered with aluminium foil.

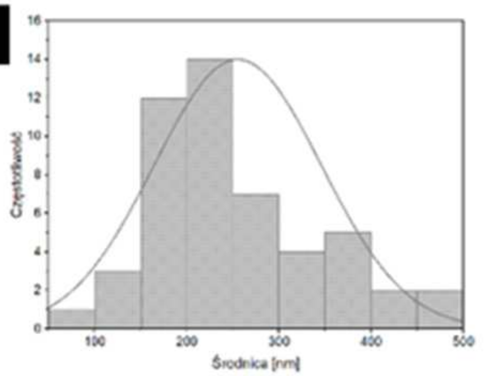
In the next part of the study, the surface and chemical composition were analysed with the use of Zeiss Supra 35 scanning electron microscope (SEM) equipped with TRIDENT XM4 spectrometer (EDAX). Scanning of the surface was carried out in the mode of detection of signals coming from retrograde dispersion electrons, the analysis of chemical composition was created as a result of receiving by the EDX detector signals of X-ray energy dispersion. Before analysis, the fibres were subjected to a sputtering process (vacuum PVD method). The sprayed coating consisted of Au-Pd conductive elements. The sputtering process was carried out at 18°C at 40 mA and 520V in 70s.

3. Description of achieved results of own researches

In order to examine the structure and morphology of PLA nanofibres, produced during electro-spinning from the solution, the surface of the obtained material was observed by scanning electron microscope SEM (Figs. 1a,b-2a,b). The following parameters of the electro-spinning process were used to obtain nanofibres from polylactide: distance between needle and collector equal to 10 cm in the case of the first sample and 20 cm in the case of the second one, potential difference between electrodes equal to 15 kV and the rate of application of the polymer solution to the nozzle of 2.5 ml/h. The distance between the needle and collector is equal to 10 cm in the case of the first sample produced and 20 cm in the case of the second one.

On the basis of the topographic images of poly(lactic acid) nanofibre surfaces made on a scanning electron microscope at a magnification of 50000 times (Fig. 1b, 2b), 50 measurements of the diameter of nanofibre produced were made. The results were collected and presented in the form of histograms (Fig. 1c, 2c) and tables showing the average diameter, standard deviation and the value of the smallest and largest diameter of the measured nanofibres (Fig. 1d, 2d).

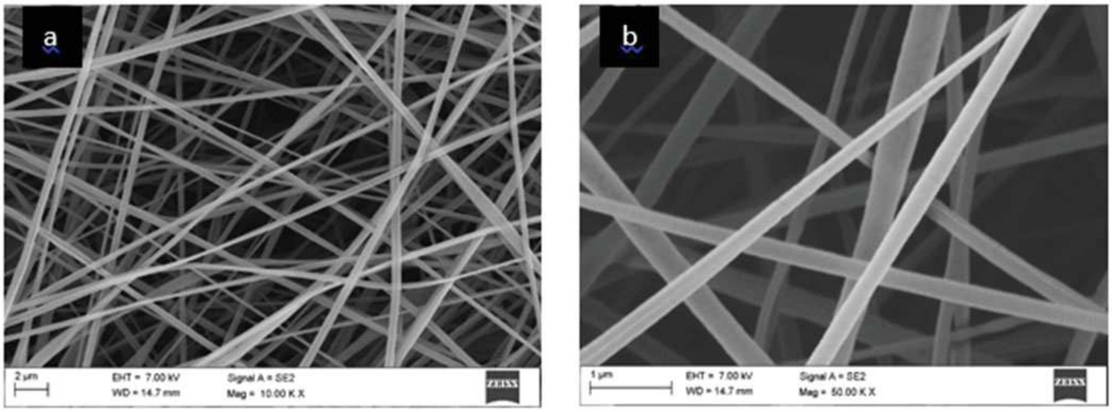


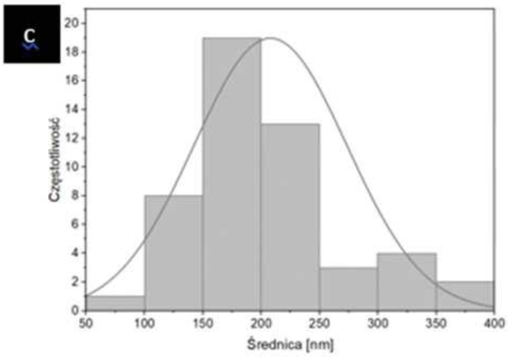


d

Average	255,033 nm
Standard deviation	90,981
Minimum value	91,660 nm
Maximal value	473,849 nm

Fig. 1. SEM images of the first test sample: a) magnification 10 000x, b) magnification 50 000x, c) histogram of distribution of fibre diameters, d) selected values of measured diameters





d

Average	207,883 nm
Standard deviation	65,648
Minimum value	90,314 nm
Maximal value	393,712 nm

Fig. 2. SEM images of the second test sample: a) magnification 10 000x, b) magnification 50 000x, c) histogram of distribution of fibre diameters, d) selected values of measured diameters

In order to examine the chemical composition of the obtained polylactide nanofibres, microanalysis of the X-ray area, which is an image of the topography of the fibre surface, was performed (Fig. 3).

Fibres made during the electro-spinning process using a distance between the nozzle and the collector of 10 cm are smooth, homogeneous, free of defects in structure. The diameters of nanofibres, obtained at a distance between the nozzle and collector of 10 cm, were in the range 91 nm to 473 nm. The average diameter of the fibres obtained oscillates between 255 nm. The most numerous group were nanofibres with diameters between 200-250 nm.

The second sample, obtained by increasing the distance between the electrodes to 20 cm, consists of directed layered fibres without defects. In the case of fibres obtained at a greater distance between the nozzle and the collector, a smaller discrepancy between the largest and smallest diameter value can be observed than in the case of the diameter values of the first sample. Fibres obtained at increased distance between electrodes are characterized by a smaller average value of diameters, but the difference is small, fluctuating in the range of 48-49 nm. The most numerous group of nanofibres obtained at the distance between the nozzle and the collector equal to 20 cm were nanofibres with diameters of 150-200 nm.

However, the difference between the diameters obtained at a variable distance between the nozzle and the collector (10 and 20 cm) is so small that it may result from the complexity of interaction of various parameters and their influence on the morphology of the fibres obtained.

Quantitative analysis of the chemical composition for nanostructured materials may be slightly disturbed due to the high interaction of the substrate in the form of carbon tape, however, the qualitative analysis of the chemical composition is very accurate. As can be seen from the graph of X-ray dispersion spectra of EDX radiation, the material consisted of carbon and oxygen, which makes it possible to state that the material studied was a pure polymer (the spectra is not able to identify the phase coming from hydrogen, due to its small atomic number – less than 5). The graph shows two peaks from the elements in the sputtered coating (gold, palladium) near the oxygen phase peak.

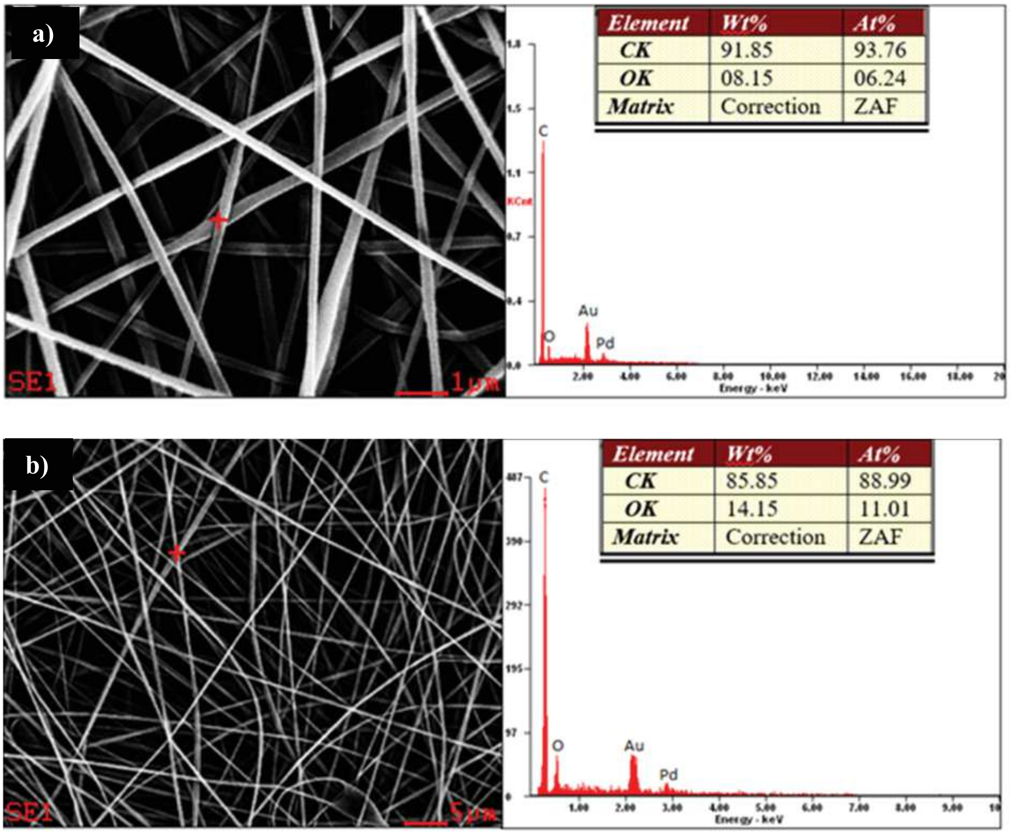


Fig. 3. Results of the chemical composition of nanofibres obtained, successively: measurement point and graph of EDX analysis with a list of percentages of identified elements: a) first sample, b) second sample

4. Conclusions

Based on the analysis of topographic images of the surface of PLA nanofibres produced, the following conclusions were drawn: the fibres produced were smooth and showed no structural defects, the fibres produced in the electro-spinning process at an increased distance between the collector and the nozzle showed a greater tendency to order, the distance between electrodes during the electro-spinning process, despite doubling, did not significantly affect the diameter of the nanofibres produced. Lack of defects in the structure of the obtained polymer nanofibres allows to state that the distance between the nozzle and the collector in the range of 10-20 cm is an optimal parameter of the electro-spinning process allowing to obtain smooth, untangled fibres. The fibrous polymer mats obtained during the process of electro-spinning of polylactide can be used as protective clothing materials, as drug delivery systems, as tissue scaffolding and as filtration membranes.

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