INFLUENCE OF THE SURFACE MORPHOLOGY AT SPECIFIC SURFACE AREA OF MICROFIBRES MADE FROM POLY (L-LACTIDE)

MACAJOVÁ Eva

Department of Material Science, Technical University of Liberec, Liberec, Czech Republic, EU,
eva.macajova@tul.cz

Abstract

Fibers prepared by electrospinning have a plenty of extraordinary properties. They have use for many applications across a wide range of fields in medicine and industry, which makes them a useful resource for innovations in various products and technologies. Large specific surface area is main advantage of these fibers. Usually the surface of nano/microfibers is almost smooth. Through the process parameters it is possible to obtain porous surface of individual fibres which leads to the pronounced increase in surface area. Variable technological process in producing nanofibers, which allows us to propound the shape and form of nanofiber structures upon request. Porous fibers may have a variety of uses in numerous applications because they show even larger specific surface area compared to smooth fibers. One of the possible method to evaluate the increase of the surface area is HR-SEM image analysis. The work demonstrates the usage of method enabling the assessment of porosity contribution to increase in micro/nanofiber surface area.

Keywords: Porous fibers, electrospinning, surface morphology, micro/nanofibers, structure

1. INTRODUCTION

Electrospinning is a method of preparation of ultrafine fibers from polymer solution or melt by means of electrostatic and capillary forces.

The electrospinning process is used to create an electrically charged stream of polymer solution or melt. A capillary, nozzle or spinning collector is connected to an electrode with high voltage and it polarises the polymer solution. The opposite pole in the electrostatic field is a conductive collector shaped as e.g. plate, mesh, metallic tip or cylinder which is grounded or connected to an opposite high voltage electrode. Electrospinning occurs when electrical forces at the surface of polymer solutions overcome the surface tension, and cause an electrically charged jet to be ejected. Due to a bending instability, the jet is subsequently enormously stretched to form continuous, ultrathin fibres. [1]

Nanofibers possess many extraordinary qualities, but the greatest advantage lay in their high specific surface area. Besides conventional and coaxial nanofibers, under the right conditions we can make porous nanofibers as well. Porous nanofibers can have a range of uses in various applications, since they have specific surface area many times higher than traditional fibers. Porous nano/mikrofibres have enormous potential in medicine e.g. in tissue engineering for improved cell proliferation into nanofiber structures, drug delivery systems (controlled release of drugs) filtration and similar technical areas. [2] Material considered for usage in medicine can not be toxic, carcinogenic, mutagenic and allergenic. [3]

These nanofibers can be made from natural materials like from biodegradable polymers suitable for application in medicine due to their biocompatibility. These materials include a variety of natural and synthetic polymers. Examples of the useable natural materials either pure or partially modified can be collagen and gelatin, cellulose and its derivatives, chitin and its derivatives. From the synthetic polymers dominate polylactic acid (PLA) and its copolyesters, polyglycolic acid (PGA) or polycaprolactone (PCL) and polyurethanes (PUR). [4]

Currently, some scientists are focused on the studies of the structural morphology of nanofibres. The studies are focused on the method how to characterize and optimize the spinning process and determine the best

spinning parameters. [5-6] Already a slight variation in the spinning conditions and parameters leads to changes in the fibre morphology (**Fig. 1**) which can also affect their surface area or cell adhesion.

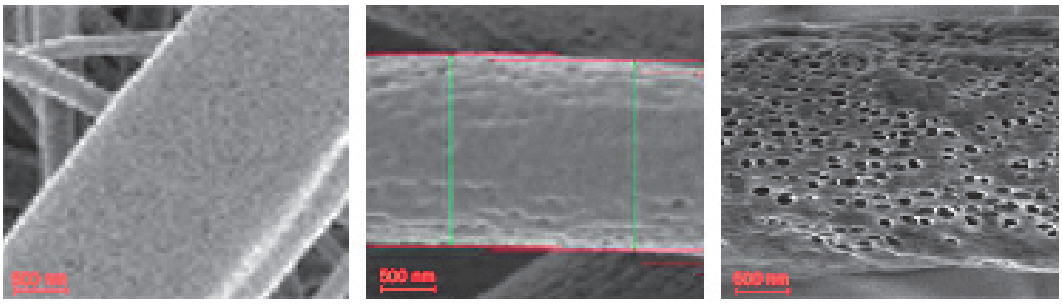

Fig. 1 Different process parameters lead to substantial changes in the fibre morphology. A) smooth surface; B) corrugated surface; C) porous surface

Electrospinning process is influenced by the properties of the polymer solution, i.e. viscosity or surface tension. Morphology and diameter of the fibers are influenced by the composition of solvent/precipitants mixture.

The surface of the fibre strongly depends on the diameter of fibers and on the fibre surface morphology. **Fig. 2** shows that the fibre surface area steeply increases with decreasing fibre diameter.

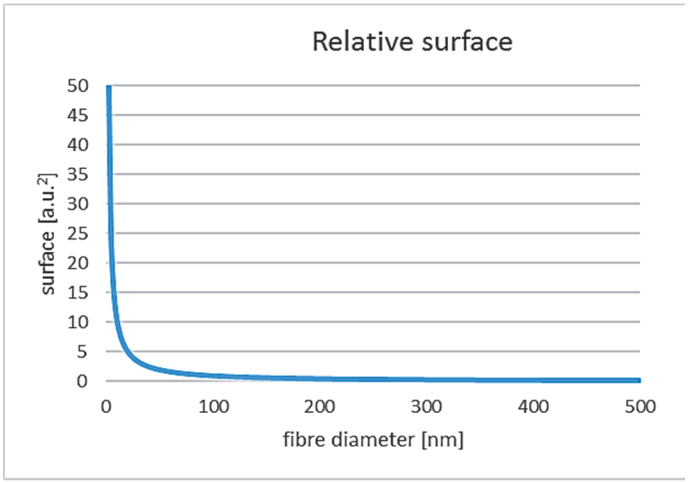

Fig. 2 Theoretical dependence of relative surface area on the fibre diameter

2. EXPERIMENTAL PART

2.1. Material

For the present experiment was selected poly(l-lactide) **-** PLLA. Poly (lactic acid) (PLA) and their copolymers are the most widely investigated und used synthetic degradable polymers for biomedical applications. [7]

2.2. Electrospinning

This work aims with creating of pores into nanofibers surface and evaluation of their efect on the increase of fibre specific surface area. Nanofibrous layers were produced by a needle electrospinning method; the schema of the apparatus used is in **Fig. 3**. The electrospinning process in described in detail in [8]. The surface porosity was achieved on the basis of combination of two solvents having different surface tension [citace]. 10% PLLA solution with molecular weight Mw = 75 000 **-** 120 000 g/mol was used for the preparation of porous nanofibers. PLLA was dissolved in the mixture of Dichlormethane **(**DCHM**)** und dimethyl sulfoxide (DMSO). Mixing ratio of solvents (DCHM/DMSO) was 9:1.

Other monitored parameters were following: spinning tension, collector distance and dosage.

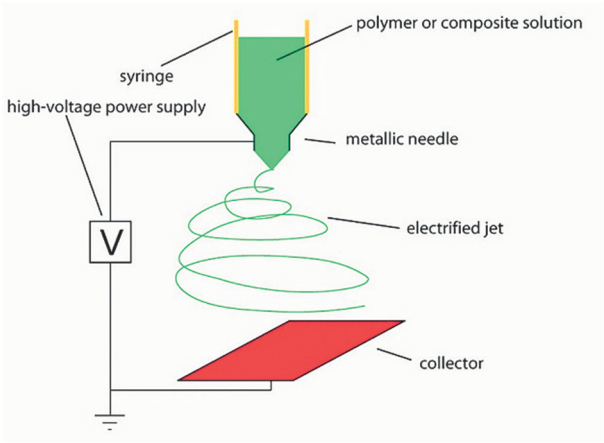

Fig. 3 Diagram of the electrospinning setup. Basic electrospinning device consits of syringe with polymer solution, needle serving as the electrode with high voltage and collector which can be grounded or connected to an opposite high voltage. The polymer solution is fed through the needle and fibers are ejected from drop of polymer in high electric field between the needle and collector. These fibers are then collected on collector

2.3. Evaluation of the structure

The morphology of the PLLA micro/nanofibers was assessed by the usage of the image analysis of HR-SEM images.

Fig. 4 shows the detail of the individual porous microfiber. The solvent ratio was 9:1, voltage of electrode 25 kV, the collector distance was 25 cm and polymer dosage of 20 ml / h. The fibre diameter ranged from 700 to 900 nm; the diameter of the particular pores ranged in the order of tens of nm.

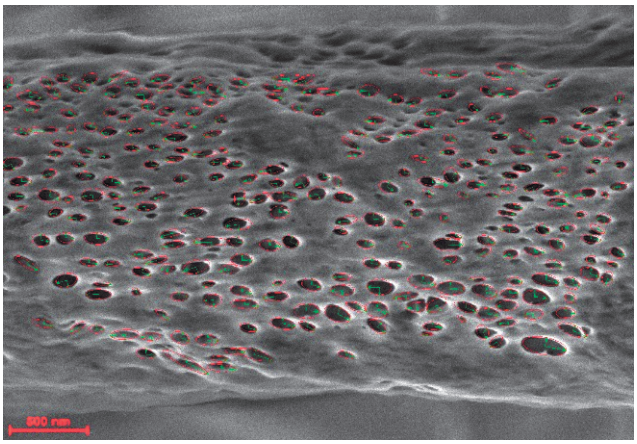

Fig. 4 HR SEM image of electrostatically electrospunn fibre of 10% PLLA. Measurement of whole pores

2.4. Specific surface area of porous fibres

For the evaluation of the effect of pores-implementation into the fiber surface, following method was suggested.

Following conditions have to be fulfiled in order to evaluate the fibrous structures:

All fibres have nearly similar diameter.
The shape of pores is ellipsoidal.
All produced fibres are porous.

Using the HR-SEM images in NIS - Elements SW enables to evaluate the porous microfiberes. On the selected representative part of porous fibre were measured: diameter of fiber,lenght and diameters of individual pores.

Smooth fibre:

The surface area (S_{sf}) of smooth fibre can be calculated using the equation (1), its volume corresponds to (2).

$$S_{sf} = \pi \cdot D.l \quad (1)$$

$$V_{sf} = \frac{\pi \cdot D^2.l}{4} \quad (2)$$

Then the specific surface (K_{SF}) could be calculated as (3).

$$K_{SF} = \frac{S_{sf}}{V_{sf}} = \frac{4}{D} \quad (3)$$

S_{sf}	*surface area of the smooth fibre*
S_{pf}	*surface area of the porous fibre*
V_{sf}	*volume in smooth fibre*
V_{pf}	*volume in porous fibre*
D	*diameter of the fibre*
d_i	*diameter of individual pores*
n	*quantity of pores on the measured length of the fibre*
l	*measured length of the fibre*

Porous fibre:

The surface area of porous fibres (S_{pf}) can be calculated as (4).

S_{pf} = surface of smooth fibre - projected area of pores + surface of ellipsoids

$$S_{pf} = \pi \cdot D.l - \sum_{i=1}^{n} S_i + \sum_{i=1}^{n} \frac{P_i}{2} \quad (4)$$

The volume of porous fibre is equal to (5).

$$V_{pf} = \pi \cdot \frac{d^2}{4} \cdot l - \sum_{i=1}^{n} \frac{4}{3} \cdot \pi \cdot \frac{ab^2}{2} - \sum_{i=1}^{n} \frac{1}{4} \cdot \frac{4}{3} \cdot \pi ab^2 \quad (5)$$

a, *b* are semi-axes of oval pores.

Finally, the specific surface of porous fibre can be calculated as (6).

$$K_{PF} = \frac{S_{pf}}{V_{pf}} \quad (6)$$

Then, the relative area increase (RAI) due to porosity could be calculated as (7).

$$RAI = \frac{S_{pf}}{V_{pf}} . \frac{V_{sf}}{S_{sf}} \quad (7)$$

For the example shown in **Fig. 2**, the relative area increase RAI due to fibre porosity:

$RAI = \frac{32314202,14}{3,1396184 \cdot 10^{10}} . \frac{3,14 \cdot 10^{10}}{30813281,26} = 1,05 \Rightarrow$ The increase in surface area due to pores presence is approximately 5 %.

3. CONCLUSIONS

This article deals with the usage of method enabling the assessment of porosity contribution to increase surface area in micro/nanofibers.

The first part of the experiment focuses on samples preparation with a respect to various parameters of the electrospinning process. The structure and porosity of micro / nanofibers is strongly influenced by a

combination of many factors. The shape of pores depends on the stage when pores are formed. If the fibre drawing by the electric forces is finished before pores forming, resulting pores will be spherical and on the other hand if pores are formed during the fibre is still drawn, pores will be oval shaped. Therefore, various configurations of spun solution, various voltage and dosage were tested. The best results with respect to the surface porosity were obtained at following conditions: the solvent ratio was 9:1, voltage of electrode 25 kV, the collector distance of 25 cm and polymer dosage of 20 ml/h. These conditions caused the oval-shape of pores in the surface of PLLA fibres. The average diameter of obtained porous fibres was ≈ 700 nm; the average pore's equivalent diameter of pores was ≈ 100 nm.

In the second experimental part the morphology of layers was evaluated by using the image analysis taken by the scanning electron microscope.

The essential measured dimensions were the fibre length and diameter and both semi-axis of pores. RAI parameter was calculated by the use of formula (1-7). This article shows that porosity of the fiber contributes to increase the specific surface area. The RAI parameter was about 5 % due to porosity.

ACKNOWLEDGEMENTS

The research was supported by the SGS project „Innovation in Material Engineering".

REFERENCES

[1] ZHUANG, Xupin, Kaifei JIA, Bowen CHENG, Ketian GUAN, Weimin KANG a Yuanlin REN. Preparation of Polyacrylonitrile Nanofibers by Solution Blowing Process. *Journal of Engineered Fibers and Fabrics* [online]. 2013, 1: 6 [cit. 2015-07-15]. Available at: http://www.jeffjournal.org/papers/Volume8/JEFF8-01-11.B.Cheng.pdf

[2] Biokompatibilní nanovlákna jako zdravotnický materiál budoucnosti. *Medicína* [online]. 2014 [cit. 2015-06-11]. Available at: http://www.technickytydenik.cz/rubriky/medicina/biokompatibilni-nanovlakna-jako-zdravotnicky-material-budoucnosti_28177.html

[3] KOŁBUKA, D., P. SAJKIEWICZA, K. MANIURA-WEBERC a G. FORTUNATOD. 2013. Structure and morphology of electrospun polycaprolactone/gelatine nanofibres [online]. : 10 [cit. 2015-07-01]. DOI: 10.1016/j.eurpolymj.2013.04.036. Available at: http://www.sciencedirect.com/science/article/pii/S0014305713002280#

[4] KUMBAR, LAURENCIN a DENG. *Natural and Synthetic Biomedical Polymers*. 1. USA: Elsevier Science, 2014. ISBN 978-0-12-396983-5.

[5] ALEXANDROS G. KATSOGIANNIS, Konstantinos, Goran T. VLADISAVLJEVIĆ a Stella GEORGIADOU. Porous electrospun polycaprolactone (PCL) fibres by phase separation. *Macromolecular Nanotechnology* [online]. 2015, 69: 284-295 [cit. 2015-07-03]. DOI: 10.1016/j.eurpolymj.2015.01.028. Available at: http://www.sciencedirect.com/science/article/pii/S0014305715000403

[6] MACAJOVÁ, E. DUFKOVÁ I., KEJZLAR P. Nanocon 2014: STRUCTURE AND MORFOLOGY OF PCL POROUS NANO/MICROFIBRES LAYERS. [online]. 2014, roč. 6, s. 5 [cit. 2015-02-15]. Available at: http://konsys-t.tanger.cz/files/proceedings/20/reports/3196.pdf

[7] SCOTT, G. a (Ed.). Degradable Polymers: Principles and Applications. 2. Kluwer Academic, 2002. ISBN 978-94-017-1217-0.

[8] [cit. 2015-06-01] Available at: http://www.fkf.mpg.de/3103472/yy1