STRUCTURE AND MORFOLOGY OF PCL POROUS NANO/MICROFIBRES LAYERS

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Abstract:

The work is mainly focused on the study of pore size, porosity, fibre diameter and also on the optimization of polymer solution composition and electrospinning parameters with respect to the structure and morphology of PCL nano/microfibres layers. Nano/microfibres were produced by electrospinning from the needle. Except spinning process parameters, the morphology of nanofibres layers can be also affected by the composition of the polymer solution and by the used solvents. In this work the new method enabling the assessment of porosity contribution to increase in micro/nanofibre surface area was demonstrated.

Keywords:

Solvent, porous nanofibres, polymer, electrospinning.

1. INTRODUCTION

In the industry, polymeric nanofibres can be produced by the use of an electrospinning method, in which electric powers affect polymeric solution or melt. Under appropriate conditions an electrically charged polymer solution will create very thin fibres by the use of the electrostatic field effect. The formation of fibre occurs between two oppositely charged electrodes, one of which is in contact with the liquid, the second electrode serves as a collector where nanofibres layer is created. The diameter of fibres made by electrospinning may vary from tens of nanometers to micrometers. The diameter of fibres is most often in the range of 100-750 nm, depending on the type of polymer and external conditions of spinning process. Nanofibres produced by electrospinning have enormous potential in many fields especially in medicine, engineering, clothing industry, aerospace, energy etc. [1-5]

1.1 POROUS NANOFIBERS

They exhibit many advantages over smooth fibers, because due to their porosity they have a significantly larger surface area. High porosity is important for the proliferation of cells into nanofibrous layers in tissue engineering and in controlled drug release [6]. For the use in medicine, material must not be toxic, carcinogenic, mutagenic, allergenic and must not contain any impurities. In addition, the large specific surface is important in filtration or in the chemical industry. [5]

Electrospinning process is influenced by the properties of the polymer solution, i.e. viscosity or surface tension. Morphology and diameter of the nanofibres are influenced by the composition of solvent/precipitants mixture. The structure and porosity of fibres can also affect the different evaporation speed of the solvent/ precipitants mixture in the polymer solution. [6]

2. SPINNINED MATERIAL

The porous nanofibres were produced from biodegradable polymers suitable for application in medicine due to their biocompatibility. For the experiment was selected polycaprolactone (PCL).

2.1 Polycaprolactone - PCL

PCL is an inner ester which is produced by catalytic polymerization with ring opening of ε - caprolactone. It is biodegradable and it can be degraded by a hydrolysis of its ester linkages in physiological conditions. It is mainly used for wound healing without subsequent scarring, healing of chronical wounds type of leg ulcers and diabetic skin defects. It is important for its biocompability with living organism and this is why this polymer is used mainly in biomedicine. [7]

3. EXPERIMENTAL PART

3.1 Preparation of porous micro / nanofiber structures

The aim of the present work is to induce and evaluate pores into nanofibres surface to futher increase their specific area. Nanofibres layers were produced by a needle-electrospinning method, the schema of the apparatus used is in Fig. 1. The electrospinning process in described in detail in [3].

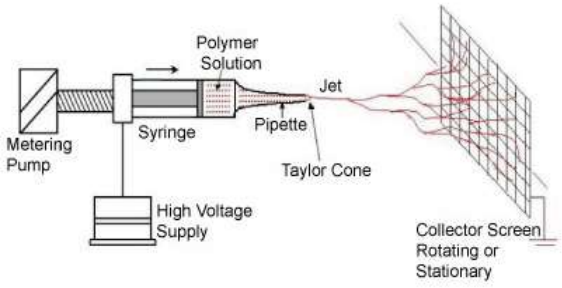

Fig. 1. Schematic diagram of electrospinning apparatus.

For the preparation of porous nanofibres was used 16 % PCL solution with molecular weight Mw = 45000 g/mol in dissolvents prepared from the mixture of ethyl acetate (HPLC) und dimethyl sulfoxide (DMSO).

Preliminary mixing ratio of solvents (HPLC/DMSO) were varied as follows: 9:1, 8:2, 7:3, 6:4. Other monitored parameters were following: spinning tension, collector distance and dosage (see Tab. 1). During the measurements, the following parameters were changed: high voltage, the distance from the collector and proportioning in [8].

Table 1. Proposed experimental parameters.

Concentration HPLC/DMSO	High voltage [kV]	Collector distance [cm]	Polymer dosing [ml/h]
9:1	15	15	3, 9, 12
8:2	20	20	3, 9, 12
7:3	25	25	3, 9, 12
6:4			

3.2 Evaluation of the structure

The morphology of the PCL micro/nanofibres layers was assessed on the basis of image analysis of HR-SEM images.

In Fig. 2. there is a detailed view on the individual porous microfiber, the solvent ratio was 8: 2, 20 kV, the collector distance of 20 cm and polymer dosage of 12 ml / h. The fiber diameter ranged from 2.70 to 4.05 μm; the diameter of the particular pores ranged in the order of hundreds of nm.

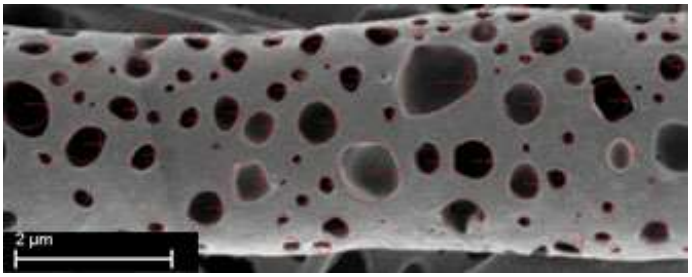

Fig. 2. HR SEM image of electrostatically spinned fiber of 16% PCL.

3. 3 Specific surface area of porous fibers

For the evaluation of the effect of pores-implementation into the fibre surface was devised following method:

Evaluated fibrous structures have to fulfil the folowing conditions:

1. All fibres have nearly same/similar diameter.
2. The shape of pores is semicular.
3. All produces fibres are porous.

Porous microfibers were evaluated on the basis of image analysis of HR-SEM images in NIS – Elements SW. On the selected representative part of porous fibre its diameter, length and diameters of individual pores were measured (see Fig. 3).

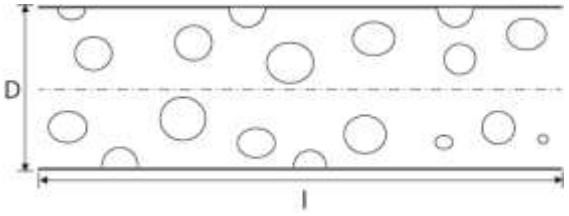

Fig. 3. A schema of porous fibre, where l is measured length and D is its diameter.

Smooth fibre:

The surface area 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}) coul be calculated as (3).

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

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

S_{pf} = surface of smooth fiber - projected area of pores + surface of a hemispheres

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

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

$$V_{pf} = \pi.D.l - \frac{\sum_{i=1}^{n} \frac{\pi.d_i^3}{6}}{2} \quad (5)$$

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

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

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*

Relative area increase due to porosity (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 due to fibre porosity

$RAI = \frac{85{,}8244}{58{,}2757} . \frac{60{,}4891}{82{,}0191} = 1{,}21 \Rightarrow$ The increase in surface area due to pores presence is approximately 21 %.

4. CONCLUSION

The experiment was focused on the production and evaluation of polycaprolactone porous nanofibres layers.

The first part dealed with the preparation of test samples with a respect to various parameters of the spinning process. The structure and porosity of micro / nanofibres is strongly influenced by a combination of many factors. Therefore various configurations of spun solution, various voltage, distance of collector and dosage were tested.

In the second part the morphology of layers was assessed using the image analysis of high resolution images taken by a scanning electron microscope. The basic measured dimensions were the length, fibre diameter and pores diameters. By the use of equations (1-7) it is possible to calculate RAI parameter which shows the contribution of fibre porosity to surface area increase. In the example shown in Fig 2. the RAI due to porosity was about 21 %.

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