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Nanofibres from polyaniline/polyhydroxybutyrate blends

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ABSTRACT

Three-dimensional nanofibres nonwoven webs were obtained from solution of poly(3-hydroxybutyric acid) (PHB) and dodecylbenzene sulfonic acid (DBSA) doped polyaniline in chlorophorm/trifluoroethanol mixture, using electrospinning method. The morphology, electro-active properties and supermolecular structure of nanofibres webs have been analyzed and discussed. Obtained nanofibres are potentially applicable as scaffolds for tissue engineering.

1. Introduction

The electrospinning technique has been known since the last century. This method seems to be the most suitable one in order to obtain polymer fibres of submicron diameters, which can be applied anytime when the high surface area to volume ratio is needed as for instance in case of highly efficient filtering materials or scaffolds for tissue engineering, etc. [1,2].

Among the natural and fully biodegradable polymers, the polyester such as poly(3-hydroxybutyric acid) is an important due to its biocompatibility. Being produced by microorganisms this natural, thermoplastic polymer is an attractive material for scaffold production, as it is totally bioresorbable. Moreover, the biocompatibility of PHB was confirmed in case of variable cells and tissues [3,4].

In some cases of tissue engineering the electrical stimulation of the tissue growing process is advantageous. So that it would be desirable to obtain the conductive scaffolds enabling the control over the electrical stimulation of the tissue growing process [5,6]. Polyaniline seems to be one of the attractive conductive polymers, which can be potentially used in biomedical applications, as it is chemically and thermally stable in a wide range of parameters [7]. Moreover the biocompatibility of PANI was also confirmed in some cases.

This paper presents our recent and preliminary results on obtaining PHB/PANI (DBSA doped) blended electrospun nanofibres. The main aim of this study was to analyze the possibilities of formation of conductive scaffolds.

2. Experimental

2.1. Materials

Due to the excellent biocompatibility poly[(R)-3-hydroxybutyric acid] from Aldrich was used as a matrix polymer. Polyaniline from Aldrich (aver. Mw ~50,000) in form of emeraldine base was doped with dodecylbenzene sulfonic acid (DBSA, Acros). Both polymers were mixed in solutions of chloroform (POCh, PL) and/or 2,2,2-trifluoroethanol (Alfa Aesar) in order do obtain the spinning dope.

2.2. Electrospinning

A custom-made high voltage power supply based on a DC to DC converter (EMCO 4330) was the core of the experimental setup, enabling remote voltage adjustment in the range 0–33 kV, with a maximum current output of 0.3 mA. A separate sensitive (nanoampere range) amplifier was used in order to measure electric current carried by an electrospun nanofibre. A constant volume flow rate of the polymer solution was maintained using a syringe pump (AP12, Ascor S.A., PL). The following optimal parameters of spinning process were established: capacity: 0.2 cm^3/h, voltage: 10 kV; nozzle to target distance: 15 cm. All of electrospinning trials were done at ambient conditions.

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2.3. Scanning electron microscopy

The observations of fibres morphology were carried using the JSM-5500 LV JEOL scanning electron microscope. Samples were sputtered with gold prior to observations, using JFC 1200 JOEL sputtering device. Images were obtained using a secondary electrons detector. In order to estimate diameters of nanofibres image analysis was performed.

2.4. UV–vis analysis

UV–vis spectra of electrospun nanofibres were collected using the Perkin-Elmer Lambda 35 spectrophotometer. Samples of nanofibres thin layers deposited on quarts were analyzed.

2.5. X-ray diffraction studies

The measurements were carried out with a compact Kratky camera, equipped with the SWAXS optical system of Hecus-MBraun (Austria). The Cu target X-ray tube, operated at 30 kV and 10 mA (PW1830 Philips generator), was used as the radiation source ($k = 1.542$ Å). The primary beam was monochromatized by Ni filter and the scattered radiation was detected by a linear position sensitive detector.

3. Results and discussion

Series of experimental trials were done in order to optimize the composition of spinning solution. The most important criterion was spinnability allowing obtaining well separated three-dimensional electrospun fibrous nets. As a result of optimization the following composition of spinning dope was established—PHB: 4.3% (w/w); PANI: 0.15% (w/w); PANI:DBSA ratio: 0.84. The optimal solutions were obtained using the mixture of chloroform and 2,2,2-trifluoroethanol (3:1).

Fibres were conditioned in vacuum container for 1 week at temp. 20 °C. Fibres obtained in optimized conditions were subjected to further morphological and structural studies.

Morphology of obtained fibres was analyzed by means of SEM. Typical microphotographs of nanofibres nets are presented in Fig. 1. Observed electrospun nonwoven structure is composed of joined, three-dimensional irregularly distributed nanofibres. The length of fibrous elements is higher than thousands nanometers, however the diameters are in the range of dozens or hundreds of nanometers (Fig. 1). It is probable that observed bimodal distribution of fibres diameter is a result of spinning solution instability and inhomogeneity, leading to formation of fibres of two dominant groups of diameters, as a result of phase separation. This hypothesis may be substantiated with SAXS result indicating bimodal inhomogeneous structure of polymer blend (Fig. 2). The character of SAXS patterns of analyzed blends indicates formation of two different types of supermolecular structure as also observed in case of phase separation.

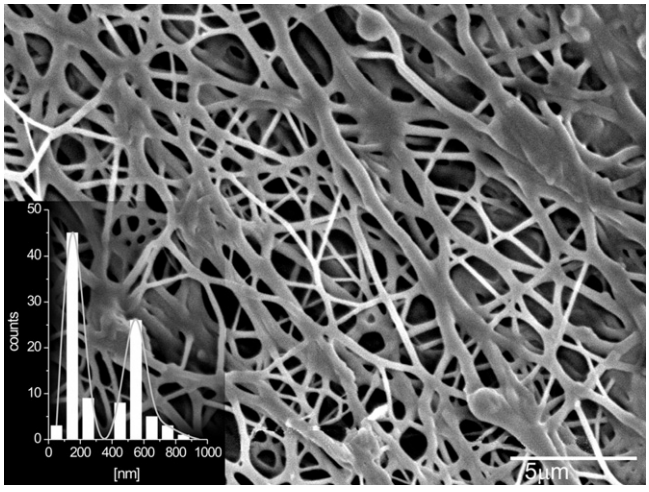

Fig. 1. Microphotograph of nanofibre net electrospun from PHB/PANI blends with plot presenting the distribution of fibres diameters.

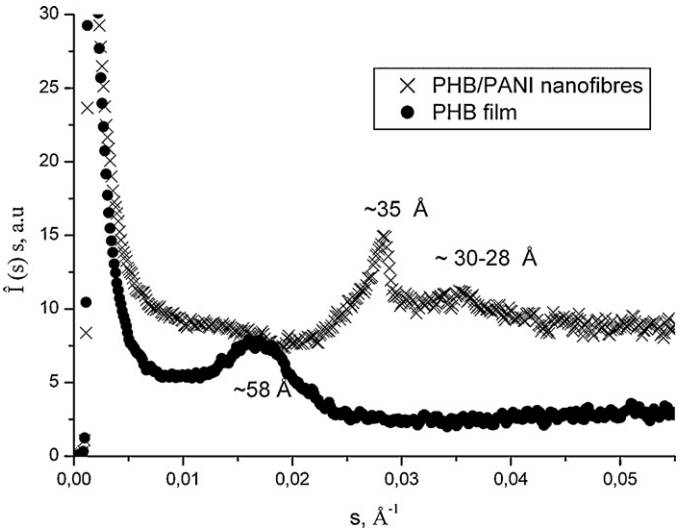

Fig. 2. Smeared Lorenz corrected SAXS patterns of PHB/PANI nanofibres and pure PHB.

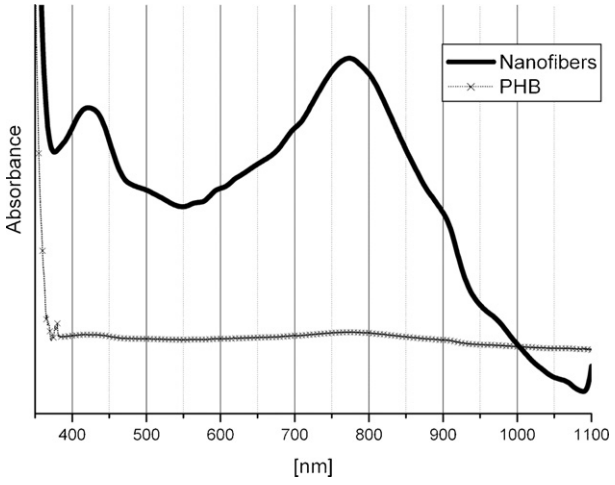

Fig. 3. UV–vis spectra of PHB/PANI blended nanofibres and pure PHB.

UV–vis spectrum of thin layer of nanofibres was compared with the spectrum of pure PHB (Fig. 3). Both the absorption band at 400 and 780 nm are typical for conducting form of polyaniline. The shift of polaron band up to 780 nm indicate the conformation of polyaniline described as the amorphous compact coil, with delocalization of electrons in macromolecule on tetramer [8,9]. The position of polaron band indicate comparatively good conductivity of PANI is such blended composition, which was confirmed by measurements of resistance giving result on the level of 10^{-6} ohm.

4. Conclusions

As the result of conducted experiments it can be stated, that it is possible to obtain conductive nanofibres nonwoven nets composed

of PHB and doped PANI, potentially applicable as the scaffolds for tissue engineering. There are limitations in composition of blended system and the PHB:PANI:solvent ratio must be optimized in order to obtain reasonable spinnability of compositions. The special attention should be given to the solvent in order to obtain the uniform spinning solution. Even small amount of PANI causes changes in super molecular structure of PHB/PANI nanofibres. The nanofibres nets will be used in future trials with cell cultures growing on the PHB/PANI nanofibres webs.

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