



Conducting electrospun polycaprolactone/polypyrrole fibers

Eliška Číková^a, Matej Mičušík^a, Alena Šišková^a, Michal Procházka^a, Pavol Fedorko^b,
Mária Omastová^{a,*}

^a Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

^b Department of Chemical Physics, Faculty of Chemical and Food Technology Slovak University of Technology in Bratislava, Radlinského 9, 812 37 Bratislava, Slovakia

ARTICLE INFO

Keywords:

Polypyrrole
Coating
Electrospinning
Conductivity
Poly(ϵ -caprolactone)

ABSTRACT

Polycaprolactone/polypyrrole (PCL/PPy) fibers were prepared using an original approach by electrospinning a mixing solution of PCL and pyrrole monomer as the first step. The presence of pyrrole monomer inside the electrospun fibers was confirmed by Time-of-Flight secondary ion mass spectrometry (ToF-SIMS) analysis. Prepared fibers were immersed into the oxidizing agent solution containing pyrrole monomer and anionic surfactant – sodium 2-naphthalenesulfonate for polypyrrole coating at room temperature. The effect of preparation conditions was studied for the production of electrically conducting fabrics using various weight ratios of PCL to pyrrole monomer for fiber production. Various analytical methods were used to characterize the fibers before and after the polymerization. The presence of the polypyrrole coating on prepared PCL substructure was verified by Fourier Transform Infrared Spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and morphology analysis. The surface properties of the prepared conducting fibers were tested by contact angle measurement. The prepared nanofibers were homogeneously coated with polypyrrole, and the samples containing at least 40 wt.% of pyrrole monomer after coating reached conductivity superior to 1 S/cm.

1. Introduction

Conducting polymers have been the focus of many research teams over past decades, with the main focus on polypyrrole (PPy), polyaniline (PANI), polythiophene and a few other polymers. PPy can be easily prepared by electrochemical or chemical oxidative polymerization of the pyrrole monomer. The electrochemically prepared PPy is in the form of thin films, while PPy synthesized by chemical oxidative polymerization is usually obtained as black powder. PPy conductivity was previously confirmed in 1968 by Dal'Olivo et al. [1]. The conductivity depends strongly on the preparation conditions and can vary from 100 to 10^{-9} S/cm [2]. PPy can be doped with reacting agents as surfactants [3] to modify its chemical, physical and even electrical properties. PPy surface properties, such as wettability and charge density, can be easily controlled [4]. Moreover, PPy is biocompatible, as shown e.g. by George et al. [5]. PPy displays some drawbacks such as processability, difficulty in dissolving the prepared black PPy powder and lack of transparency. On the other hand, the chemical synthesis of PPy allows for easy production of composites and combination with other polymers such as polystyrene, polyurethane, and polyvinylchloride [6,7].

The latest studies have shown that PPy has potential for biological and medical applications such as biosensors and in tissue engineering. The stimulation of PC12 cells (cell line derived from a

pheochromocytoma of the rat adrenal medulla), with PPy showed the accelerated growth of the cells [8] and proved the feasibility of the use of PPy as a material for neural engineering. Due to the poor mechanical properties of PPy, composites with suitable mechanical properties are prepared by combining conducting polymer and electrospun meshes using various polymers [9,10]. The biodegradable polymers, such as poly(lactic acid) (PLA), poly(lactic-co-glycolic acid) (PLGA), poly(ϵ -caprolactone) (PCL) or chitosan, are widely used for electrospinning. Cong et al. [11] electrospun PPy combined with poly(ethylene oxide) (PEO) in chloroform solutions. They found that the PEO content influenced the conductivity, with the conductivity ranging from 1.4×10^{-3} to 2.5×10^{-4} S/cm when a higher content of PEO is present. Norris et al. [12] prepared PANI/PEO fibers by electrospinning, controlling the ratio of polyaniline (PANI) to PEO. PANI provided electrical stimulation for the cells growing without reducing its conductivity. Lee et al. [13] electrospun PLGA and coated it by chemical oxidative polymerization of pyrrole at 4 °C in the presence of a surfactant. The conductivity of the samples was not sensitive to the direction of the measurements if the fibers were randomly oriented, but aligned fibers showed conductivity about one order of magnitude higher when measured along the fiber direction. The tests showed increased stability of the PLGA in the medium due to the PPy shell. The in vitro PC12 cell test showed cellular interactions and improved neurite

* Corresponding author.

E-mail address: maria.omastova@savba.sk (M. Omastová).

outgrowth compared to the non-stimulated cells. Zhou et al. [14] electrospun dissolved PLA in dichloromethane (15 wt.%) mixed with PPy nanoparticles dispersed in N,N-dimethylformamide (DMF) with various content ratios. The conductivity of the electrospun fibers increased with increasing PPy content in the fibers. The PLA/PPy meshes maintained at least 80% of their original conductivity for five days. The nanofibers provided a scaffold for the controlled orientation of cord stem cells and Schwann cells parallel to the fiber alignment. Random and aligned PLA fibers were coated with PPy by admicellar polymerization [15] using anionic surfactant dodecylbenzenesulfonic acid (DBSA) and monomer solution. The conductivity of fibers increased with increasing DBSA:pyrrole (Py) ratio, and the conductivity of the aligned fibers was higher, probably due to multiple contacts among the randomly coated fibers. The scaffolds were cytocompatible for three days, and better neural stem cells results were obtained by aligned fibers compared to the randomly oriented ones because the growth of the neural stem cells is preferred in one direction, and stimulated neural stem cells showed an increase in expression compared to the non-stimulated ones. Silk fibroin fibers [16] have been electrospun and coated in situ with PPy. The polymerization was performed in the presence of NaCl and FeCl₃ at 4 °C for 24 h.

PCL is an aliphatic biodegradable polyester known for its extremely low glass transition temperature- T_g (–60 °C) and long-term degradation properties. PCL is an attractive polymer for practical use due to its good elastomeric properties and high elongation [17]. PCL has been approved by the FDA for biomedical applications since the 1970s and can be found in many common structures and components. In the recent past, PCL has been used frequently by tissue engineers. It is a hydrophobic, semicrystalline material, but its crystallinity decreases with increasing molecular weight. It degrades by a hydrolysis of its esteric groups at a slower rate in physiological conditions than PLA [18]. The degradation kinetics and mechanical properties of PCL are tailorable. This is the main reason why we chose electrospun PCL fibers as the carrier of the conducting PPy.

Kai et al. [19] mixed doped PPy with PCL and gelatin (50:50) in hexafluoro-2-propanol for electrospinning to mimic the structure of cardiac muscles. They obtained conductivity ranging from 0.013×10^{-3} S/cm to 0.37×10^{-3} S/cm for the higher content of PPy. When a higher content of PPy was used, the cells did not grow faster, and the results of the degradation tests showed instability of the more conductive sample in the medium. Similarly, PANI/PCL/gelatin fibers were investigated and confirmed to extend neural growth for cells compared with PCL/gelatin fibers [20]. Another approach used separated oxidant and monomer phases for preparation of membranes with conducting polymers [21]. Preparation of advanced materials combining biodegradable and conducting properties is currently considered a hot topic in nanotechnology and biomedicine because of their highly promising applications as summarized in review paper by Llorens et al. [22]. Electrically conducting fibrous mats based on biodegradable polymers are of special interest for tissue engineering because they are able to stimulate specific cell functions or trigger cell responses in addition to the expected ability to physically support tissue growth.

In this study, an original approach was used for the preparation of nanofibers homogeneously coated with PPy at a laboratory temperature. A pyrrole monomer was mixed with dissolved PCL in dichloromethane/dimethylformamide for the preparation of solution for electrospinning. The presence of a pyrrole monomer inside the electrospun fibers was confirmed by ToF-SIMS analysis. In the next step, the prepared non-woven fabrics were immersed into the polymerization solution containing anionic surfactant, oxidizing agent solution and pyrrole monomer for polypyrrole coating. The effect of the preparation conditions was studied for the production of electrically conducting fibers using various weight ratios of PCL to pyrrole monomer. The polypyrrole coating on the prepared PCL substructure was verified by FTIR, XPS methods and by scanning electron microscopy analysis. The coating of the fibers is in the submicron scale, and the conductivity of prepared

fibers demonstrates the possibility of using PCL/PPy for tissue regeneration.

2. Experimental

2.1. Materials

Biodegradable poly(ϵ -caprolactone), PCL, CAPA 6800 (Solvay Interco Ltd., United Kingdom) with molecular weight (M_w) = 67.21×10^3 g/mol was used. The molar mass was measured by GPC in our laboratory using eluent chloroform (CHCl₃) for HPLC, $\geq 99.8\%$ purity, amylene stabilized from Sigma-Aldrich, Germany. Dichloromethane (DCM) and dimethylformamide (DMF) were used as solvents for PCL without further purification (CentralChem, Slovakia). Pyrrole (Acros Organics, Belgium) was purified by distillation under reduced pressure and stored in a refrigerator at approximately 4 °C prior to use. The oxidant ferric chloride (FeCl₃; Fluka, USA), and the surfactant sodium 2-naphthalenesulfonate (SNS; Sigma-Aldrich, Germany) were used as received. Methanol and acetone (CentralChem, Slovakia) were used without further purification. Distilled water was used in all procedures.

2.2. Gel permeation chromatography (GPC)

GPC was used for the determination of molecular weight of PCL. GPC system consisted of P102 pump from Watrex, Czech Republic and evaporative light scattering detector (ELSD) model ELS – 1000 from PL-Agilent Technologies, Stretton, UK. Temperature of evaporators was set at 80 °C and gas flow rate was 1.5 mL/min. GPC column was TSHgel GMH_{HR}-M, 300 × 7.5 mm, from Tosoh Corporation, Tokyo, Japan. The GPC measurements were performed at ambient temperature. The flow rate was set on 1 mL/min. Chloroform, HPLC grade > 99.7% from Fisher Scientific, UK, was used as GPC eluent. Concentration was 10 mg/mL. Molar masses are equivalent to polystyrene calibration. Data were collected and processed with help of software Clarity from DataApex, Czech Republic.

2.3. Preparation of electrospun fibers

Initially, 15 wt.% PCL solutions were prepared in the solvent system of 50/50 vol.% of DCM/DMF. The solutions in the solvents mixture were prepared by dissolving PCL granules in DCM, and DMF was added to reach the required concentrations. Then, different volumes of pyrrole were added to the mixture as blend monomer for electrospun process. The solutions were stirred intensively on a magnetic plate with intensity of 750 rpm for at least 5 h. Electrospinning was used for the preparation of the fibers. The solutions were electrospun from a 5 mL syringe with a needle at the flow rate of 0.6 mL/h at 23 °C. A high voltage of 15.6 kV was applied, and the fibers were collected on an aluminium foil collector at the distance of 15 cm from the needle tip.

2.4. Polypyrrole coating of electrospun fibers

Pyrrole was mixed with the sodium 2-naphthalenesulfonate (SNS) surfactant and dissolved in 180 mL distilled water and 60 mL methanol in a reaction vessel and stirred for 15 min, as recommended by Tada et al. [23], in order to control the polypyrrole deposition rate. Oxidizing agent FeCl₃ was dissolved in 60 mL of distilled water and mixed with pyrrole solution, and the pyrrole/SNS molar ratio of 20 was kept constant. Immediately, electrospun fibers were added into reaction solution. The mixture was stirred for 8 h, washed with distilled water and acetone, and dried in an oven for 1.5 h at 30 °C. The exact compositions of all substances in the pyrrole polymerization and sample labels are given in Table 1. A sample labeled PCL/PPy x:y was prepared first by electrospinning from the solution containing x wt.% PCL and y wt.% pyrrole and later added into the solution of surfactant, pyrrole and

Download English Version:

<https://daneshyari.com/en/article/7873674>

Download Persian Version:

<https://daneshyari.com/article/7873674>

[Daneshyari.com](https://daneshyari.com)