Electrospun Conducting and Biocompatible Uniaxial and Core-Shell Fibers Having Poly(lactic acid), Poly(ethylene glycol) and Polyaniline for Cardiac Tissue Engineering

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METHODS

Synthesis of PAni

PAni doped with DBSA, hereafter PAni/DBSA, was obtained as follows. First, 0.06 mol of aniline monomer were added to a cooled (4 °C) emulsion produced by mixing 200 mL of water with 0.10 mol of DBSA and 50 mL of toluene. After 1 h of stirring, 0.04 mol of APS (initiator) dissolved in 50 mL of water were slowly dripped into the solution over a period of 1 hour. The reaction was maintained for 18 hours. Finally, 200 mL of toluene was added to the solution to terminate the polymerization process. Although a homogeneous mixture was initially formed, after 24 hours it separates into aqueous and organic phase. PAni/DBSA remained solubilized in the organic phase while unreacted DBSA and APS were solubilized in the water phase. After extraction of the PAni/DBSA-containing phase, 100 mL aliquots of toluene were added to the water phase for subsequent extraction (after 24 h) of the polymer retained in it. For the purification, rotary drying for solvent evaporation was carried out at 70 °C for 2 hours. After this, the polymer was re-solubilized in toluene at a 20% w/v concentration.

Characterization

The morphology and texture of electrospun fibers was examined by scanning electron microscopy (SEM) using a Focus Ion Beam Zeiss Neon 40 instrument (Carl Zeiss, Germany). Carbon coating was accomplished using a Mitec K950 Sputter Coater fitted with a film thickness monitor k150x. Samples were visualized at an accelerating voltage of 5 kV. Diameters of electrospun fibers were measured with the SmartTiff software from Carl Zeiss SMT Ltd.

Atomic force microscopy (AFM) was conducted to obtain topographic and phase images of the surface of fibers using silicon TAP 150-G probes (Budget Sensors,
Bulgaria) with a frequency of 150 kHz and a force constant of 5 N/m. Images were obtained with an AFM Dimension 3100 microscope using the NanoScope IV controller under ambient conditions in tapping mode. The row scanning frequency was set at 0.8 Hz. Data were acquired using the Research NanoScope software (v. 7.30) and, afterwards, analyzed using the Nano Scope Analysis software (v. 1.20).

Roughness measurements of selected samples were carried out using a Dektak 150 stylus profilometer (Veeco, Plainview, NY).

FTIR spectra were recorded with a Fourier Transform FTIR 4100 Jasco spectrometer (Jasco Analytical Instruments, Easton, USA) in the 4000–600 cm\(^{-1}\) range. An attenuated total reflection (ATR) system with a heated Diamond ATR Top-Plate (model MKII Golden Gate\textsuperscript{TM}, Specac Ltd., Orpington, UK) was used.

All samples were characterized by micro-Raman spectroscopy using a commercial Renishaw inVia Qontor confocal Raman microscope. The Raman setup consists of a laser (at 785 nm with a nominal 100 mW output power) directed through a microscope (specially adapted Leica DM2700 M microscope) to the sample after which the scattered light is collected and directed to a spectrometer with a 1200 lines mm\(^{-1}\) grating. The exposure time was 10 s, the laser power was adjusted to 1% of its nominal output power and each spectrum was collected with 3 accumulations.

Calorimetric data were obtained by differential scanning calorimetry (DSC) with a SHIMADZU DSC-60. Experiments were conducted at a heating rate of 10 °C min\(^{-1}\) under a flow of dry nitrogen with a sample weight of approximately 5 mg.

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The electrical conductivity was determined using the four-probe method. The fibers were cut into disk samples (diameter: 25 mm). The equipment consists of a Signatone four-fixed tip holder (S-301-6 model) and a Keithley 2400 source.

Mechanical properties were determined with a Zwick Z2.5/TN1S (Zwick/Roell; Ulm, Germany) testing machine in stress-strain tests carried out at a deformation rate of 10 mm/min. Measurements were performed on rectangular samples (30 × 5 mm²) cut from the electrospun fibrous mats. The mechanical parameters were averaged from a minimum of six measurements for each sample.
**Figure S1.** FTIR spectrum of PANi/DSBA.

**Figure S2.** FTIR spectra of PLA and PLA/PEG/PANi uniaxial fibers. The most important bands for PLA, PANi and PEG are indicated in black, red and green, respectively.
Figure S3. FTIR spectra of PLA and PLA/PEG//PLA/PAni core-shell fibers. The most important bands for PLA, PAni and PEG are indicated in black, red and green, respectively.

Figure S4. (a) PLA/PEG-0.3/PAni and (b) PLA/PEG-0.3//PLA/PAni Raman spectra at the cross points in the optical images (scale bar: 50 μm).
**Figure S5.** DSC heating scan of PAni/DBSA.

**Figure S6.** DSC heating scans of uniaxial PLA/PEG/PAni-5% fibers. For comparison, the heating scan of PLA fibers is shown.
Figure S7. DSC heating scans of coaxial PLA/PEG//PLA-PAni fibers. For comparison, the heating scan of coaxial PLA//PLA/PAni fibers is shown.