



Macromolecular Nanotechnology

Structure and morphology of electrospun polycaprolactone/gelatine nanofibres

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ABSTRACT

Blends of polycaprolactone (PCL) and gelatine (Ge), being effective materials for tissue engineering strategies, were electrospun at various conditions and polymer weight ratios. The morphology, the supermolecular structure as well as the mechanical properties of resulting submicron sized fibres have been analyzed in relation to electrospinning conditions and PCL/Ge weight ratio. Compared to pure PCL, Ge addition leads to large reduction of fibre diameter and finally to changes of fibre morphology. For parallelised fibres collected on a rotating drum, preferred molecular orientation of PCL crystals is found. With increasing Ge content a general reduction of molecular orientation is observed. In addition, there is peculiar dependence of polycaprolactone crystallinity on the content of Ge, showing maximum at low Ge concentration (20%) as determined by differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS). Such a trend can be explained by hydrophobic interactions in the system containing PCL, gelatine and water, being additional driving forces for crystallization of nonpolar PCL molecules. The presence of water within investigated blend systems has been evidenced experimentally using thermal gravimetric analysis (TGA). Young's modulus of nonwovens, as determined by uniaxial tensile testing, indicates the effect of additivity of the stiffness of both polymers as well as the influence of preferred molecular orientation. Additional experiments were performed using collagen (Col) as a biopolymeric alternative to Ge. WAXS results show evidently amorphous structure of Col within the blended fibres, indicating strong tendency for denaturation of collagen into gelatine under the influence of hexafluoroisopropanol as a solvent.

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1. Introduction

Electrospinning is one of the most common methods to produce fibrous substrates for tissue engineering applications by use of natural and synthetic polymers. Ideally, a substrate should mimic both the form and functionality of the native extracellular matrix (ECM) [1]. It is known

that morphology, architecture and surface properties have strong influence on cells growth, spreading, activity and functions [2]. Thereby, scaffolds formed by electrospinning are gaining increasing interest due to their tunable properties to provide ideal microenvironments for various kinds of cell types.

Naturally occurring polymers such as collagen (Col) and gelatine (Ge) do not cause foreign body response [3,4]. PCL does elicit such a response, though minimal. As major drawbacks the poor mechanical properties and their variable physical properties have been identified [5]. In contrast, synthetic biopolymers have predictable and

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reproducible mechanical and physical properties (e.g. tensile strength, elastic moduli and degradation rate) and they can be synthesised with high reproducibility. Most synthetic polymers incorporate strong hydrophobic surface properties which present poor cell adhesion sites and thus promote a low level of cell attachment. Thereby, different approaches have been realised to adjust surface wettability properties e.g. by chemical and coating routes. A timely fashioned way is the use of hydrophilic and water soluble native extracellular matrix materials such as Col or Ge to form a hybrid of natural and synthetic polymers. In that way, scaffolds are generated which combine the advantages of both types of material and mainly alter materials surface properties.

Up to now, various research works describe influencing parameters such as morphology and architecture of electrospun patches with respect to cell growth and proliferation (e.g. [5–13]). Focusing on blend nanofibers, Col/elastin [14,15], polyurethane/polycaprolactone (PCL) [16], and PCL/Ge [17], PCL/Col [18,19] have been described. However most of them concentrate on morphological topics, chemical structure and biological investigations (cell morphology, cytotoxicity and proliferation). For instance, Chong et al. showed reasonable growth of human dermal fibroblast on polyurethane – PCL/Ge sandwiched structures being promising candidates for wound healing applications [19]. Zhang et al. prepared PCL/Ge 1:1 electrospun nanofibers and found improved bone marrow stromal cell attachment compared to pure synthetic PCL nanofiber scaffolds. Cellular infiltration was demonstrated on the blend fibres of up to 114 μm in-depth [20]. PCL/Col electrospun fibres were investigated by Lee et al. [18]. Compared to pure PCL, the Col-added nanofibers showed better cell responses (adhesion and growth) *in vitro* and penetration *in vivo*.

However, there are only few papers describing molecular structure of the two polymers for electrospun blend fibres, which influences surface properties and mechanical properties of the materials. It is known that crystallinity and molecular orientation are important parameters on physical properties and cell-scaffold adhesion and interaction [21].

The aim of this work is to investigate mutual effect of gelatine introduction into PCL electrospun fibres on non-woven architecture, fibre molecular structure and mechanical properties. Analytical tools such as scanning electron microscopy (SEM), wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) were used to investigate fibre morphology, molecular structure and surface properties. Young's modulus was evaluated from stress-strain measurements. In comparison, results from Col addition on molecular structure of the blend fibres are presented.

2. Materials and methodology

2.1. Materials

PCL having a molecular weight of $M_w = 80,000$ g/mol (Sigma–Aldrich, Switzerland) and gelatine (Ge) from por-

cine skin Type A, having average molecular weight of 50,000–100,000 g/mol (Sigma–Aldrich, Switzerland), were used. Collagen (Col) from tail tendons of young rats, characterised in [22–25] was used. The polymers were dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Fluka, Switzerland).

2.2. Electrospinning process

The electrospinning equipment was operated in horizontal mode and consisted of a medical infusion pump, a static plate or a rotating drum collector and two high voltage generators. The positive voltage was connected to stainless steel needle (0.6 mm inner diameter \times 26 mm length) and the negative one to the collector. A voltage of ± 10 kV and flow rate of 7 $\mu\text{l}/\text{min}$ was applied. Solutions were prepared at a total polymer concentration of 5 wt.% with following weight ratios for PCL/Ge: 80:20 (PG4:1), 50:50 (PG1:1), 20:80 (PG1:4) and PCL/Col 80:20 (PC4:1). Fibres were collected on static plate and on a rotating drum (approximately 1000 min^{-1}).

The temperature and relative humidity were recorded during electrospinning process, being in the range of 22–25 $^{\circ}\text{C}$, and 35–45%, respectively.

2.3. Characterisation

A rheometer (Anton Paar Physica MCR 300, Austria) equipped with a plate – cone system was applied in controlled shear rate mode to assess the shear viscosities in function of the shear rate. Flow curves with shear rates varying from 0.01–500 $1/\text{s}$ were recorded at 20 $^{\circ}\text{C}$.

Electrical conductivity of solutions was measured using a Metrohm 660, (Switzerland), conductometer. The calibration of conductivity measurement was performed using 0.001, 0.01 and 0.1 mol/l potassium chloride solutions (KCl, Sigma–Aldrich, puriss). Before use KCl was dried for 24 h at 100 $^{\circ}\text{C}$.

Morphology of fibres was determined by scanning electron microscopy (SEM) (Hitachi S-4800, Japan) using 2 kV accelerating voltage at 10 mA flow current. Small pieces of fibre patches were coated with gold for 2 min before SEM imaging. Mean fibre diameter was calculated from SEM micrographs by averaging 30 measurements.

Supermolecular structure in terms of crystallinity and molecular orientation was analysed by wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) supported by thermal gravimetric analysis (TGA).

In the case of DSC, a Mettler T 28E (Switzerland) apparatus was used. Samples (ca. 5 mg) were heated from 10 $^{\circ}\text{C}$ to 190 $^{\circ}\text{C}$ at a rate of 10 K/min. Crystallinity of PCL was evaluated while specific heat of fusion of 100% crystalline PCL was taken as 142.9 J/g [26]. Temperature and heat calibration was performed using indium as reference material. Melting temperature and crystallinity were taken usually as an average value from three measurements. Results are presented as mean \pm standard deviation. The thermograms were fitted by use of Pearson functions to separate the signals for PCL and Ge.

WAXS (Oxford Diffraction, United Kingdom) was performed using X-ray diffractometry using Mo $K\alpha_1$ radiation

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