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Electrospinning poly(ε-caprolactone) under controlled environmental conditions: Influence on fiber morphology and orientation

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ABSTRACT

Reproducibility is a well-known issue in research involving electrospun materials, and, therefore, it is one of the main obstacles preventing this processing technique to prevail into the industry. Controlling environmental parameters during the electrospinning process helps in drastically reducing variability of results and, at the same time, has a strong impact on fiber characteristics. Using polycaprolactone (PCL) as a model system, in this work we investigated the influence of relative humidity and environmental temperature on the resulting mesh morphology for different PCL solutions. PCL solutions were electrospun on a rotating mandrel, for different rotational speeds and over a broad range of environmental conditions (30%–90% of relative humidity and temperature of 20 °C–40 °C) with different chloroform/tetrahydrofuran ratios in the solvent mixture. In this way we could assess the role of solvent water miscibility in determining surface features. While temperature changes have only a moderate effect on the resulting fibers, relative humidity does not only changes the surface morphology of electrospun fibers, but also the critical rotation speed of the collecting mandrel needed for obtaining alignment. Furthermore, we observed a self-assembled perpendicular monolayer-like fiber architectures when the electrospinning was performed above critical rotation speed required for aligned fibers.

1. Introduction

Due to its effectiveness and easiness in fabricating micro and nanofibers with unique properties and controllable structures, electrospinning is a widely used method for carrying out innovative research in various fields, as tissue engineering, drug delivery, textiles, filtration, and electronic devices [1–3].

To change and notably to control the final outcome of an electrospinning process, one has to tightly control the polymer solution parameters, process conditions and ambient parameters. While solution properties and processing variables are the most investigated parameters [4–6], growing attention has recently been paid to the role of climate conditions because of their strong influence on bead formation, fiber dimensions and surface textures. Megelski et al. [7] were the first to address pores formation on electrospun fibers to relative humidity. Later, many authors agreed that an increase in relative humidity during electrospinning results in an higher surface porosity [8–10], providing evidences related either to solvent volatility [11–14], polymer molecular weight and hydrophobicity [8,15], or thermodynamic phase behavior of the polymer-solvent-non solvent system [11,13,16]. Additionally, environmental conditions can affect the arrangement of macromolecular chains during solidification by changing the solvent evaporation rate, thus influencing thermal and mechanical properties of fibers [10,17,18].

Alignment and 3D structuring of fibers are highly important in tuning performances of electrospun materials [19]; but the effect of environmental conditions on fiber alignment has not been investigated yet. Existing studies about electrospinning of oriented fibers focus mainly on the design of the collecting setup, such as parallel electrodes [20], rotating discs [21–23] and drums [24–26], and the main variables addressed by authors were the linear velocity of the collector surface and the effects on the electric field of different collecting setups. Even though it has been believed that a simple rotating drum was not the best approach for collecting highly aligned fibers [27], results published by Sun et al. [28] demonstrated that electrical properties of the solvent, matched with an

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optimal choice of the uptake speed, matter far more than the collecting target design on the degree of orientation of fibers.

As meshes are commonly collected as flat layers of densely packed fibers, their application in specific fields is hindered. Hence, several studies have been published on porosity enhancement of electrospun materials, mostly for tissue engineering, where these three dimensional assemblies allow for a much better cell infiltration within the mesh [29,30]. Among all the different methods for obtaining 3D porous electrospun materials [31], self-assembling is a very promising one. Bonino et al. [32] reported cone or strands structures oriented perpendicularly to the collector, and noticed that their occurrence is strongly dependent on the relative humidity in the spinning environment. They addressed this phenomenon to the ability of high relative humidity to increase the charge on the surface of the fibers. Yan et al. [33] studied the self-assembly of polymer fibers under different environmental conditions, concluding that 3D structuring is a phenomenon that arises from electrostatic forces acting on deposition of fibers, so relative humidity can play a role in controlling it.

The overall goal of our work is to study the effect of relative humidity and temperature variations on electrospun poly(ε-caprolactone) fibers. PCL is a widely studied polymer with many applications as a biomaterial due to its biocompatibility and biodegradability [34–36]. Also in our group PCL is already used since many years as a scaffold material for tissue engineering applications [37–40]. However, in this paper we will focus on the reproducibility of producing fibers in relation with the environmental conditions and not on these applications. Fibrous mats features we addressed are fiber diameter, surface morphology and orientation. Concerning the study on surface morphology, we compared two solvents of different water miscibility but similar boiling points, in order to investigate the former parameter while minimizing the differences that can arise from solvents of different volatility. In addition, we studied how relative humidity can influence the minimum uptake speed which is necessary for obtaining oriented fibers, and we present, to our knowledge, a never reported self-assembly in which fibers are deposited on the collector as vertical monolayers, allowing porous aligned structures.

2. Materials and methods

2.1. Materials

Poly(ε-caprolactone) (PCL) was supplied by Solvay (CAPA 6800, MW ~ 80 kDa) and used as received. Chloroform ($CHCl_3$) (>99.8%, stabilized with Ethanol) was purchased from Acros Organic; Tetrahydrofuran (THF) (reagent grade, stabilized with 0.025% BHT) was purchased from Fisher Chemicals.

2.2. Solutions & electrospinning

Solutions were prepared by mixing the polymer with the solvent at room temperature and stirring overnight. The following concentrations and solvent systems were used: 15 wt% in $CHCl_3$, 15 wt% in $CHCl_3$/THF 90/10 wt, 20 wt% in $CHCl_3$/THF 50/50 wt, 20 wt % in $CHCl_3$/THF 10/90 wt and 20 wt% in THF. Electrospinning was performed on an IME Technologies EC-CLI equipment (IME Technologies, Geldrop, The Netherlands), fibers were collected on a rotating cylindrical target (diameter 20 mm) wrapped with Aluminum foil. Applied voltage was 15 kV on the electrospinning nozzle (1.0 × 0.8 mm), and −0.5 kV on the rotating collector, solution flow rate was set at 25 μL/min. A coaxial shield of chloroform rich air was used to prevent the needle exit from clogging by suppressing excessive solvent evaporation, as suggested by Larsen et al. [41]. Aside from these constant parameters, solvent system of the solution, environmental conditions, collection speed of fibers and spinning time, were varied as follows according to the specific aspect of the electrospun sample that we aimed to study.

2.2.1. Fiber diameter and surface morphology

Each sample was electrospun for 5 min, with a fiber uptake speed of 0.1 m/s (no fiber orientation occurs). Temperature was varied from 20 °C to 40 °C, increasing it by 5 °C steps for the 15 wt% in $CHCl_3$ solution, and by 10 °C steps for all the other $CHCl_3$/THF ratios. Relative humidity was varied from 30% to 90%, increasing it by 10% steps for solution 15 wt% in $CHCl_3$ and by 20% steps for the other solutions. Each condition was investigated with at least three specimens.

2.2.2. Fiber orientation

The relation between relative humidity and the minimum uptake speed for obtaining aligned fibers was studied at a constant temperature of 20 °C at four different relative humidity's (30%, 50%, 70%, and 90%). The uptake speed is defined as the tangential speed on the collector surface, expressing the speed of fibers being winded-up on the rotating collector. The spinning time was 5 min for all the samples. By changing the rpm's, the uptake speed was increased to a maximum of 2.5 m/s, with 0.1 m/s increments, in order to evaluate the critical value of collecting speed that resulted in fiber alignment. Each condition was investigated with at least three specimens.

2.2.3. Minimum uptake speed for fibers orientation

The critical uptake speed that is necessary for obtaining alignment was investigated at 20 °C for four values of relative humidity (30%, 50%, 70%, 90%). The rotation speed of the cylindrical collector was increased up to 2.5 m/s for achieving fiber alignment. Fast Fourier Transformed (FFT) was used to quantify the degree of fiber alignment present in an original Scanning Electron Microscope (SEM) micrograph according to Ayres et al. [42].

The resulting FFT output image is a distribution of intensity in arbitrary units (a.u.), which reflects the fiber orientation in the sample analyzed. The intensity was integrated radially along a circular projection between 0° and 360° (azimuthal integration). The image analysis was performed in a MatLab script (The MathWorks, Inc., Natick, Massachusetts, USA) in which all the FFT data are normalized to a baseline in order to have comparable results from different data sets. Because of symmetry of the system, the integrated intensity was plotted as a function of the angle between 0° and 180°. The width of the peak at half height (WHH) decreases with increasing fiber alignment. Critical uptake speed for obtaining aligned fiber structure was defined at the minimum WHH for each relative humidity.

2.3. Scanning Electron Microscopy (SEM)

Samples were analyzed with a FEI Quanta 600F scanning electron microscope, in high vacuum atmosphere, without any further treatment. Dimensions of fibers were measured with the software ImageJ (U. S. National Institutes of Health, Bethesda, Maryland, USA), with a minimum of at least 90 measurement points.

2.4. Statistical analysis

All data are presented as mean ± standard deviation. Statistics were performed using GraphPad Prism (GraphPad Software, La Jolla, California, USA) by mean of an unpaired *t* test. Differences were considered significant for p-values <0.05.