Polymer 55 (2014) 5017–5023

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymer communication

High definition fibrous poly(2-ethyl-2-oxazoline) scaffolds through melt electrospinning writing

Gernot Hochleitner [a, 1], Julia Franziska Hümmer [a, 1], Robert Luxenhofer [b], Jürgen Groll [a, *]

[a] Department for Functional Materials in Medicine and Dentistry, University of Würzburg, Pleicherwall 2, 97070 Würzburg, Germany
[b] Functional Polymer Materials, Chair of Chemical Technology of Materials Synthesis, University of Würzburg, Röntgenring 11, 97070 Würzburg, Germany

ARTICLE INFO

Article history:
Received 6 May 2014
Received in revised form
4 August 2014
Accepted 12 August 2014
Available online 27 August 2014

Keywords:
Polymer processing
Poly(2-oxazoline)
High temperature melt electrospinning writing

ABSTRACT

Melt electrospinning writing (MEW), a computer-aided fiber deposition process based on an electrohydrodynamic working principle, enables the rational design and fabrication of fibrous scaffolds with micrometer thin fibers. So far, MEW has mainly been applied for poly(ε-caprolactone). Here we manufactured scaffolds of poly(2-ethyl-2-oxazoline), a hydrophilic polymer with high melting temperature, by MEW for the first time. We systematically varied and investigated the crucial instrument parameters: heating temperature (200–220 °C), feeding pressure (1.0–3.0 bar), accelerating voltage (3.0–7.0 kV) and collector distance (3.0–7.0 mm) in dependence of differently sized spinnerets (23 G, 25 G, 27 G, 30 G). As criteria for homogeneous deposition, we studied the resulting fiber diameters which could be adjusted from 8 μm to 138 μm and the corresponding variances. Furthermore this letter clarifies the need of a dynamic balance between involved mass flows in order to reduce pulsing failures of the jet and thereby structural defects of the deposited structures.

1. Introduction

Research into the class of hydrophilic polymers, called poly(2-oxazoline)s (POx) has intensified over the past decade [1–7]. Synthesized via living cationic ring-opening polymerization [3], the macromolecular structure of POx is readily adjustable to produce a versatile spectrum of properties with potential for medical and pharmaceutical applications. POx is particularly interesting as a drug delivery system and is thermoresponsive with a characteristic lower critical solution temperature [8,9].POx-based polymers can have stealth-properties similar to poly(ethylene glycol), are biologically compatible and can store pharmaceutical agents, including functional proteins mimicking natural biomolecules or act as antimicrobial materials [10–12]. While the chemical and physical properties of POx are appreciated, how to process the polymer into discrete structures is still being understood. Owing to its thermoplastic and electrically non-conductive properties, POx offers the potential to be processed via melt electrospinning. When combined with a translating collector, there is also potential to 3D print POx using additive manufacturing principles, potentially allowing infinite different structures to be generated with this polymer.

Another biocompatible polymer poly(ε-caprolactone) (PCL) has already been processed into 3D printed scaffolds using this direct writing technique, termed melt electrospinning writing (MEW) [13–15]. With fiber deposition assisted by a computer-controlled axis movement of the collector, it allows the 3D stacking of fibrous structures filaments as low as 5 μm in diameter. This progress is so far focused specifically for biomedical research and TE applications [15,16]. Electrospinning is based on an electrohydrodynamic working principle, investigated heavily over the past decade [17–19]. Nevertheless, the stable electrified molten jet is not extensively investigated compared to its analogue – solution electrospinning [20]. In both cases the applied acceleration voltage reaches a critical value and thereby overcomes the surface tension of a fluid. A Taylor cone forms and an electrified polymer jet is accelerated by the electrical field to the collector system. Influencing parameters are classified as polymer-based (e.g. molar mass) and instrument based (e.g. voltage, collection distance etc.).

We show in this study, that one type of POx, poly(2-ethyl-2-oxazoline (PEtOx)), can not only be successfully melt electrospun, it is an excellent polymer for performing MEW. Several key instrument parameters to attain a stable molten jet were systematically investigated, including heating temperature, feeding

* Corresponding author. Tel.: +49 931 20173610; fax: +49 931 20173500.
E-mail address: juergen.groll@fmz.uni-wuerzburg.de (J. Groll).
[1] Tel.: +49 931 20173610; fax: +49 931 20173500.

http://dx.doi.org/10.1016/j.polymer.2014.08.024

pressure, accelerating voltage, the collector distance and spinneret diameter. Through adjustment of the parameters, quality woodpile structures of PEtOx could be produced by MEW.

2. Experimental methods

2.1. Materials

Poly(2-ethyl-2-oxazoline) (PEtOx) with $M_w \approx 50{,}000$ g/mol and PDI ≈ 3–4 was purchased from Sigma–Aldrich (372846) and used as received.

2.2. Melt electrospinning writing device

The MEW device, schematically drawn in Fig. 1, consists of a high voltage source (DX250R, EMCO, Hallein, Austria) controlled by voltage divided measurement (Digit Multimeter 2100, Keithley, Cleveland, USA), a nitrogen gas pressured assisted melt feeding system (regulator, FESTO, Berkheim, Germany) and a planar movable aluminum collector plate (XSlide, Velmex, New York, USA), triggered by G-code (MACH 3 CNC software, ARTSOFT, Livermore Falls, USA). To assure a stable heating temperature profile a proportional-integral-derivative-regulated (TR400, Delta-t, Bielefeld, Germany) electrical heating system was used.

2.3. Parameter range

Key instrument parameters were varied in five consistent steps with four different spinnerets (30 G: $d_I = 160$ μm, 27 G: $d_I = 210$ μm, 25 G: $d_I = 260$ μm, 23 G: $d_I = 337$ μm). Only a parameter was changed at a time, with the other parameters kept constant at the middle value of the parameter range, shown in Table 1. The collector velocity was adjusted (between 200 mm min^{-1} and 400 mm min^{-1}) to be just above the critical translation speed, which is the transition point between coiled and straight fibers. This ensures a straight fiber with diameters that are not stretched by the movement of the collector. To characterize the statistical significance, respectively probability p of the results, every set of parameters was investigated by the measurement of $n = 20$ fiber diameters and evaluated by analysis of variance (ANOVA).

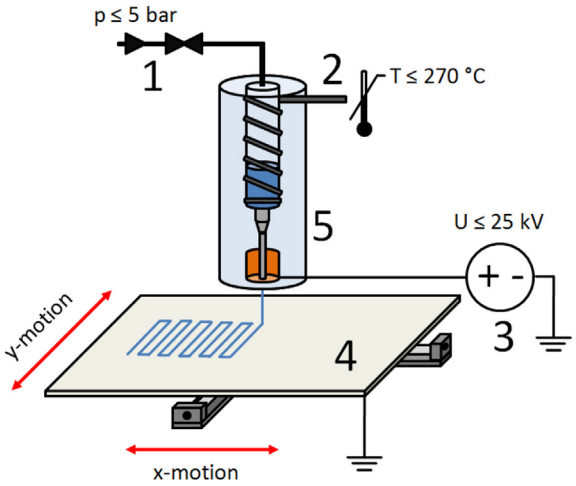

Fig. 1. Schematic drawing of the MEW device. 1) Nitrogen gas pressure assisted feeding system 2) Electrical heating system 3) High voltage source 4) Computer assisted movable collector plate 5) Syringe with molten polymer and needle tip as spinneret with electrode.

Table 1
Overview of the investigated instrument parameters.

Parameter	Parameter range	Constant value
Temperature T_h [°C]	200 to 220	210
Feeding pressure p_f [bar]	1.0 to 3.0	2.0
Acceleration voltage U_a [kV]	3.0 to 7.0	5.0
Collector distance L_c [mm]	3.0 to 7.0	5.0
Spinneret [Gauge]	23, 25, 27, 30	N/A[a]

[a] All four other instrument parameters were tested with the different spinnerets.

2.4. Scanning electron microscopy

Field emission scanning electron microscopy (SEM) images were recorded (Ultra Plus, Carl Zeiss AG, Oberkochen, Germany) using a GEMINI e-Beam column operated at 1–3 kV with an aperture size set to 10 μm to avoid excessive charging and radiation damage of the areas imaged. Gold deposition onto the samples was performed by sputtering technique using a cryo-preparation system Quorum PP2000 for 2 min at emission of 20 mA. The argon pressure in the chamber was set to $8 \bullet 10^{-2}$ mbar.

3. Results and discussion

The main focus of this work was instrument parameter combinations to optimize the fiber variability and quality and understand how best to control the fiber diameter of PEtOx. A key challenge was “pulsing” of the electrified molten jet, where fibers alternated between thick and thin, resulting in poor quality collections. As a result, many parameter combinations did not lead to desired fiber accuracies, with photographs of the defects shown in Fig. 2.

The greatest variations in fiber diameter occurred when the 23 G spinneret was used, suggesting that this spinneret diameter is too large for the polymer and conditions. Fig. 3 gives an overview on the studied parameters. It shows the relationship between fiber diameter and temperature – when the temperature is increased from 200 to 220 °C, the diameter of the deposited fibers increased significantly ($p < 0.01$) with an average value of 45 μm raising to 138 μm for the 23 G spinneret. The challenges faced with fluctuating fiber diameter are well reflected in the large error bars for the data presented in Fig. 3. The fibers were generally more homogeneous fibers at lower temperatures and pressures, as well as with higher acceleration voltages due to the approximation of the involved mass flows.

Considering that the pulsing effect was particularly significant for the largest (23 G) spinneret investigated, we looked at the mass flow of the melt, based on a dynamic balancing process. That is, the push of the melt to the spinneret versus the pull of the melt due to electrostatic attraction. Relevant here is the Hagen-Poiseuille-equation [21,22], which shows the dominating dependency of flow rates dm/dt from the spinneret diameter d_o with:

$$\frac{dm}{dt}\left[1\right] \sim d_o^4$$

Therefore, the mass flows and deposited fibers should be even smaller with smaller spinneret diameters and proper mass flow adjustment. Due to an almost constant average jet velocity (200 mm min^{-1}) and a circular fiber profile, an increase of the gas pressure assisted mass flow dm/dt by one order of magnitude could be obtained using the 23 G spinneret. This can be explained by the lowered loss and storage modulus of the melt during heating from 200 to 220 °C and seems to be more influencing as the triplication of the feeding pressure at 210 °C. Accordingly, the minimal average diameter was 58 μm at 1.0 bar and 118 μm at 3.0 bar. Thus, the mass