Electrospinning P(LLA-CL) Nanofiber: A Tubular Scaffold Fabrication with Circumferential Alignment

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Summary: In this paper a synthetic Poly(L-lactic-co-ε-caprolactone) [P(LLA-CL)] (75:25) copolymer has been fabricated into a nanofibrous structure by electrospinning. The polymer crystal structure has been investigated by DSC and x-ray diffraction method. During electrospinning at room temperature, a crystallization of LLA sequence in the P(LLA-CL) copolymer could not form, while a relatively regular arrangement of CL sequence was observed. In order to obtain a tubular scaffold, a rotating mandrel was designed to collect the fiber, so that the tubular scaffold can be retrieved from the mandrel with an inner diameter same as that of the outer diameter of the mandrel. An auxiliary electrode with a sharp edge and a negative charge was set under the mandrel to guide the fiber deposition on the mandrel. When the sharp edge bar was vertical to the rotating axle of the mandrel and just beneath the spinning nozzle, nanofibers with circumferential alignment were obtained. With this method it is possible to obtain a tubular scaffold with suitable fiber alignment for blood vessel tissue engineering.

Keywords: electrospinning; nanofiber; P(LLA-CL) copolymer; rotating mandrel; scaffold

Introduction

To face the new stage of tissue engineering, a biomimetic extra cellular matrix (ECM) is required, which should have a similar nanofibrous structure to that of natural collagen in native tissue. Several methods have been reported for the nanofiber fabrication, such as phase separation,[1] self-assembly[2] and electrospinning.[3] Both phase separation and self-assembly require the materials to have specific physical or chemical structures; electrospinning has the potential for making different types of polymer into nanofibers. During the electrospinning, polymer solution jet, which was charged with higher voltage, will fly towards the grounded or negative charged area. Thus, a nanofiber nonwoven membran, tube or a designed shape can be obtaine withthe special shaped collector. In this paper a fiber alignment method has been developed for tubular scaffold fabrication with the fiber aligned circumferential along the mandrel long axis direction, with the aim of constructing a small diameter biodegradable blood vessel scaffold.

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Experimental

Tubular nanofiber scaffolding: Poly(L-lactid-co-ε-caprolactone) [P(LLA-CL)] (75:25) copolymer (obtained from Japan), was dissolved in an acetone solution and electrospun into nanofiber through a nozzle under the action of 12 kV high electrostatic voltage. A rotating mandrel with a Teflon tube collector was placed under the spinning nozzle at a distance of 80 mm; below the mandrel is a parallel aluminum grid with sharp edges and negative charge of –8 kV, which guided the fiber alignment on Teflon tube. Fig. 1 shows the set-up. Tubular nanofiber scaffold was thus collected on the Teflon tube.

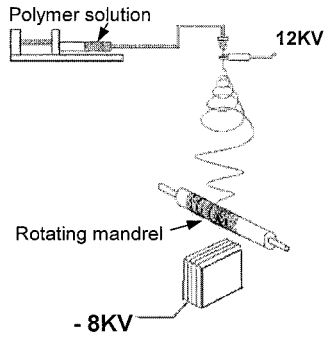

Fig. 1. Electrospinning for the fabrication of tubular scaffold.

Characterization of nanofibers: Scanning Electron Microscopy (SEM, Jeol JSM-5800LV), X-ray Diffractometer (Lab-X, XRD-6000, Shimadzu) and Differential Scanning Calorimetry (DSC, Pyris 6, Perkin Elmer) were used to investigate the morphology, crystal structure and thermal behavior of nanofiber.

Results and Discussion

Matthews et al[4] reported a tubular scaffold fabrication method by electrospinning a collagen nanofiber using a rotating mandrel under the spinning nozzle. They found that a randomly arranged nanofiber deposited on the surface of tube when the rotating speed was set at 500 rpm/s and a more or less circumferentially aligned nanofiber was obtained when the rotating speed was as high as 4500 rpm/s. Here a modified setting as in Figure 1 has been given to prepare tubular scaffold. High degree of circumferentially aligned nanofibers were obtained even though the rotating speed of the mandrel was only 830 rpm/s. Figure 2 is the SEM photo of aligned fiber. This efficient alignment was generated by the negatively charged sharp edges, which make the electron field concentrated to the edge, and guide the fiber circumferentially aligned on the Teflon tube.

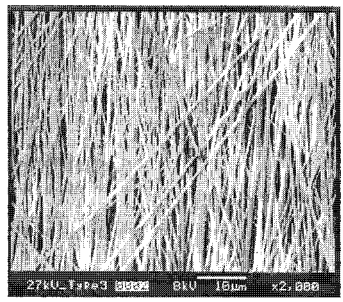

Fig. 2. Nanofibers on Teflon tube with circumferential alignment.

The nanofibers electrospun from 5 wt% P(LLA-CL) solution at an applied voltage of 12kV were used for the molecular structure investigation. Figure 3 showed the DSC curves of that nanofibers and as-received P(LLA-CL). The exothermic peak at 57.3°C given by electrospun fiber was

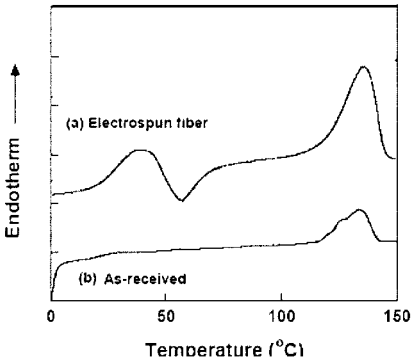

Fig. 3. DSC profile of (a) electrospun fibers, (b) as-received P(LLA-CL) copolymer.

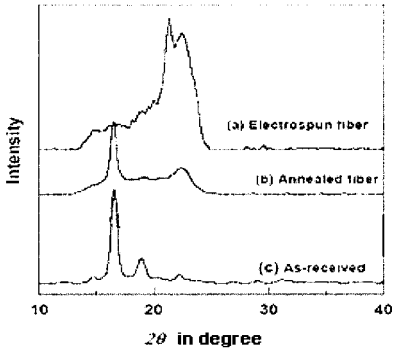

Fig. 4. XRD pattern of (a) electrospun fibers, (b) annealed electrospun fibers, (c) as-received resin of P(LLA-CL) copolymer.

recognized as the cold crystallization temperature. The as-received P(LLA-CL) showed only the melting point at 133.5°C. This means that the molecular chains in the electrospun nanofibers were not crystallized as that of as-received material. Figure 4 showed the x-ray diffraction curves of raw material (c), electrospun nanofiber (a), and annealed nanofiber at 60°C for 5 h (b). As-recieved P(LLA-CL) showed a sharp peak at about 2θ of 18° and two peaks at 19° and 21° with lower intensity. The peaks below 20° correspond to LLA sequence crystal structure and the peak higher than 20° related to CL sequence crystal structure. Electrospun nanofiber lost almost all the LLA sequence crystal structure and showed only CL sequence crystal during electrospining. But after annealed nanofiber at 60°C, LLA sequence crystal peak had singanificantly increased, since the LLA sequence crystallized freely and the CL sequence melted at 60°C.

Conclusion

During electrospinning polymer chains could not form a crystal structure especially for the LLA sequences. However, further processing, such as annealing the nanofiber at a temperature near to

the glass transition temperature of the polymer, allowed the crystal structure to form again. The negatively charged sharp edges concentrated the electron field and guided the nanofiber deposition on the Teflon tube with circumferential alignment.

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