Morphological evolution from porous nanofibers to rice like nanobeans

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ABSTRACT

Polycaprolactone/Polyethylene oxide (PCL/PEO) blends with different morphologies are prepared by electrospinning, and the porous PCL structures are obtained by selective removal of the PEO phase through water treatment. Morphology of the electrospun products evolves from the nanofiber to the rice like nanobeans by controlling the concentration of the blend polymer solution. Nanofiber is obtained at a high solution concentration, and the porosity and diameter of the nanofibers could be tuned by adjusting the PCL content in the blend solution. The needle like materials are present with decreasing solution concentration, and rice like nanobeans are observed with further decrease of the concentration. The decreased macromolecular entanglement is responsible for such morphology evolution.

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1. Introduction

Biodegradable and biocompatible nanofibers with porous structures have found many applications in drug release, tissue engineering, cellular infiltration, etc., because of their large specific surface area as well as low density [1–5]. Poly(L-lactic acid) nanofibers with nanopores on their surfaces were fabricated by electrospinning of the polymer using volatile dichloromethane as the solvent, and the pore formation was mainly attributed to the phase separation between polymer rich and solvent rich regions [6]. However, this approach strongly depends on the volatile solvent and only applicable for the specific polymer–solvent pairs. Furthermore, the pores usually sit on the nanofiber surface rather than extend into the whole electrospun nanofibers, which severely limited the permeability. In fact, nanofibers with a tunable porosity can be harvested by electrospinning polymer blend solution followed by selective removal of one phase, and the porous structure could be easily controlled by adjusting the weight ratio between the two incompatible phases [7–11]. In addition, some polymers, for example chitosan, cannot be electrospun to form fibers because of lack of sufficient macromolecular entanglements, and some electrospinnable polymers such as Polyethylene oxide (PEO) are often incorporated to the solution to improve its electrospinnability [12–16]. PEO could also be mixed with PCL for fabrication of PCL/PEO blend nanofiber membrane for the application of medical patch [17]. Previous work was mainly focused on the fabrication of porous nanofibers, while other morphologies of the electrospun products have seldom been reported in the open literatures. In fact, it is of high importance to understand the morphology evolution of the electrospun products, by which both the construction and the microstructure of materials can be well designed. Herein, PCL with various nanostructures was fabricated by controlling the concentration of the blend polymer solution used for electrospinning. Interestingly, the blend nanofiber gradually turned to rice-like nanobeans by decreasing the PEO concentration, and the morphology evolution might originate from the decreased electrospinnability. The corresponding porous PCL microstructures were obtained by selective removal of the PEO through water treatment.

2. Experimental section

Materials: Polycaprolactone (PCL) and Polyethylene oxide (PEO) were obtained from Sigma-Aldrich Corporation, with molecular weight of 80,000 and 400,000, respectively. N,N-dimethylformamide (DMF) and dichloromethane (DCM) were also provided by Sigma-Aldrich.

Preparation of electrospun products: PCL and PEO with different weight ratios were dissolved in a mixture of DMF and DCM with the volume ratio of 1:1. The prepared solution was loaded in a plastic syringe and fed through a metallic nozzle at a feed rate of 1 mL/h. The applied voltage was 12.5 kV and the distance between the metallic needle and the collecting drum was 12.5 cm. The nanofibers were collected on an aluminum foil. The porous PCL products were obtained as follows: the electrospun PCL/PEO mat was immersed in deionized water at room temperature for 24 h, and then washed out with deionized water for several times. Finally, the mat was dried at 50 °C in an oven for 24 h.

Characterization: The surface morphology of the gold-sputtered electrospun products was examined by scanning electron microscopy

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(SEM, FEG JSM6335) with an accelerating voltage of 5.0 kV. The diameters of electrospun products were determined by using an image analyzer (Adobe PhotoShop). Electrospun blend nanofibers were directly deposited onto a copper grid for a few seconds, and then experienced water treatment to obtain porous nanofibers for transmission electron microscopy (TEM, Philips FEG CM200) observation.

3. Results and discussion

Fig. S1 shows morphologies of electrospun PEO/PCL blend nanofibers. The concentration of PEO was kept at 2.5 wt%, while PCL content varied from 5 wt% to 1.25 wt%. (Here, the weight ratio between PEO and PCL is defined as WR.) It was observed that smooth and uniform fibers were generated for all the three concentrations. Fig. S1d describes the dependence of the diameter of the electrospun fibers on the polymer concentration. When the blend concentration was 7.5 wt% (WR=1:2), the average diameter of the blend fiber was about 1048 nm, and significantly decreased to 455 nm and 248 nm with decreasing blend concentration to 5 wt % (WR=1:1) and 3.75 wt% (WR=2:1). The decrease of the diameter might originate from the decreased viscosity of the blend solution, which facilitated the elongation of the taylor cone during electrospinning. The water soluble PEO could be completely removed after water treatment (WT), which was verified from the FTIR (Fig. S2). There were many peaks in the spectra corresponding to various functional groups in their polymer chains. Apparently, the PEO/PCL blend fiber possessed characteristic peaks of both PEO and PCL. However, two absorbance peaks at 1282 and 1342 cm^{-1} corresponding to the CH_2 twisting and CH_2 wagging motion of PEO polymer chain [18] disappeared after the blend fiber experienced the WT; however, they were visible for both PEO and blend fiber, and the porous PCL fiber almost shared the same characteristic peaks with the pure PCL fiber, indicating the complete removal of the PEO phase. Fig. 1 shows the SEM and TEM images of the electrospun PEO/PCL fibers with different WR after

the WT. Obviously, the porous PCL fibers were obtained after the selective removal of the water soluble PEO, and the pore size had a wide distribution ranging from a few tens to several hundred nanometers, depending on the WR. When the WR is 1:2, PCL fibers exhibit wrinkled surface after the WT, and the pores or the microgaps are distributed through the wrinkled region, which could be observed in Fig. 1a. In addition, the porous nanofibers are capable of keeping their integrity. This is because PCL formed a continuous phase in the blend nanofibers, and the continuity of the porous nanofiber was thus well maintained after the phase separated PEO was selectively removed. Continuously porous structure of the nanofiber could also be observed from the TEM image (the inset of Fig. 1a). The dark region refers to the solid material, namely PCL, while the light part represents the pores. It was worth noting that the diameter of the porous PCL fibers dramatically decreases to 615 nm, compared to about 1 μm for the blend nanofiber (see Fig. S1a). It might be caused by the partial collapse or shrinkage of the PCL during the WT. As the blend concentration decreases to 5 wt% (WR=1:1), the porous PCL fibers (Fig. 1b) seem looser than those in Fig. 1a, and some of them even break down. The diameter of the porous PCL nanofiber slightly decreases to about 356 nm. In addition, the continuity of the PCL decreases, due to the decreased PCL content in the blend fiber, and some thin necks appear in the nanofiber as shown in the inset of Fig. 1b. With further decreasing the concentration of the blend solution to 3.75 wt% (WR=2:1), the porous PCL nanofiber becomes much looser, compared with that in Fig. 1b. Many porous nanofibers break down into several short sections (Fig. 1c), which is attributed to the removal of the continuous PEO skeleton in the blend fibers. The porous structure could be further revealed from the TEM image in the inset of Fig. 1c. It was more evident than that in Fig. 1a and b, and many large pores destroy the integrity of the nanofiber, resulting in the generation of the discontinuous segments. It is also found that the standard deviations of the diameter for the porous nanofiber are much larger than those of the blend nanofiber (see Figs. 1d and S1d), which is probably caused by the increased surface roughness.
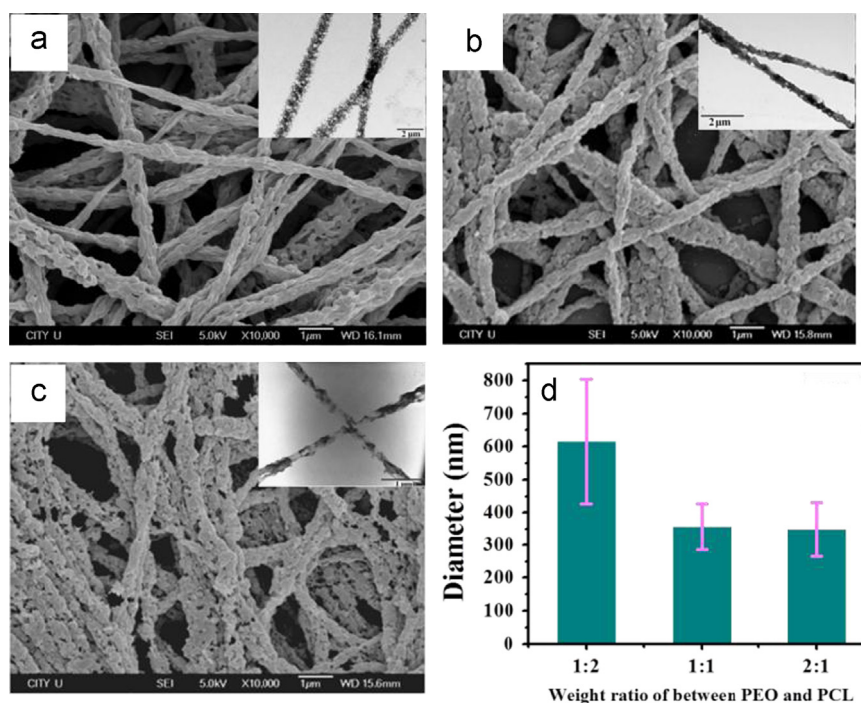

Fig. 1. SEM images of the electrospun blend fibers after the WT. The weight ratio between PEO and PCL was (a) 1:2 (b) 1:1 and (c) 2:1, and the PEO concentration was fixed at 2.5 wt %. The insets show the corresponding TEM images. (d) Diameters of the porous PCL nanofiber as a function of the weight ratio.