Fabrication and formation mechanism of poly(L-lactic acid) ultrafine multi-porous hollow fiber by electrospinning

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Received 16 June 2012; accepted in revised form 22 August 2012

Abstract. Poly(L-lactic acid) (PLLA) ultrafine multi-porous hollow fibers are fabricated by electrospinning with methylene dichloride as solvent. The Kirkendall effect has been widely applied for the fabrication of hollow structure in metals and inorganic materials. In this study, a conceptual extension is proposed for the formation mechanism: the development of porous hollow fiber undergoes three stages. The initial stage is the generation of small voids or pits on the surface of the fiber via surface diffusion and phase separation; the second stage is the formation of multi-pores penetrating the core of the fiber through the interaction of Kirkendall effect, surface diffusion and phase separation; the third stage is dominated by surface diffusion of the core material along the pore surface. To explore the formation conditions, the factors including ambient temperature, relative humidity (R. H.), molecular weight and fiber diameter are studied. The longitudinal and cross sectional morphologies of these fibers are examined by scanning electron micrograph (SEM). The results show that the prerequisite for the formation of uniform porous hollow PLLA fibers include moderate ambient temperature (10~20°C) and appropriate molecular weight for the PLLA, as well as the diameter of the fiber in the range of several micrometers to about 100 nanometers.

Keywords: biodegradable polymers, electrospinning, multi-porous hollow fiber, microstructure, mechanism

1. Introduction

Many of the applications of electrospun fibers could be greatly enhanced by increasing the surface area and porosity of the fibers. To this purpose, reliable production of porous nanofibers in a simple and inexpensive way has been attempted by a number of groups. Previous methods of producing porous polymer fibers relied on either the electrospinning of blends followed by selective removal of one of the phases or phase separation based on the evaporation of solvent or in the presence of vapor.

PLLA nonwoven fibrous matrices have been widely used in various tissue regenerative therapies because of their excellent mechanical properties and biocompatibility [1–3]. Many researchers have engaged

in fabricating multi-porous PLLA fiber membrane with various methods. Lee and his coworker [4] fabricated dual-porosity structure PLLA/MMT fibers by combining electrospinning with salt leaching method. Qi *et al.* [5] fabricated PLLA fibers with micro- and nano-porous structure by electrospinning a ternary system of nonsolvent/solvent/PLLA. It is reported by Zhang *et al.* [6] when PLLA was dissolved in dimethylformamide (DMF) and methylene chloride (CH₂Cl₂) mixed solvent with different ratios, semi-hollow fiber with porous inner structure and compact shell wall was formed by controlling the content of DMF in the mixed solvents. But there is little report that the micro- and nano-porous outer structures of PLLA ultrafine hollow fibers were

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fabricated only by electrospinning with only one solvent. Although Bognitzki *et al.* [7] reported the use of dichloromethane yielded PLLA fibers with a regular pore structure by electrospinning and considered the regular phase morphology is generated by rapid phase separation during the electrospinning process. There has been no report about the fabrication of PLLA ultrafine hollow fibers with multi-porous outer structure by electrospinning and detailed analysis about the formation mechanism of this structure.

The Kirkendall effect is a classical phenomenon in metallurgy [8–9]. It basically refers to a non-equilibrium mutual diffusion process through an interface of two metals so that vacancy diffusion occurs to compensate for the unequal material flow. Atomic diffusion occurs through vacancy exchange and not by the direct interchange of atoms. The net directional flow of matter is balanced by an opposite flow of vacancies, which can condense into pores or annihilate at dislocations. In a spherical material system where the fast-diffusion phase is enclosed by the slower one, the Kirkendall effect can also apply and manifest itself by forming hollow crystals composed of a compound shell. Coming to the nanoscale, due to the structural perfection and wide availability of single crystal metal nanoparticles, the Kirkendall effect can result in smooth and uniform-sized hollow compound nanocrystals [10–12]. An extension to cylindrical nanotubes has recently been reported via either a solid – solution, solid – gas, or solid – solid reaction [13–16].

In this paper, PLLA ultrafine hollow fibers with multi-porous outer structure were prepared only by electrospinning with only one solvent. The exact growth mechanism for the formation of this structure is still under investigation, but on the basis of experimental observations, a mechanism based on the ‘Kirkendall effect + surface diffusion’ model [8] was proposed.

2. Experimental section

2.1. Materials

PLLA (M_w : 100 000~70 000, M_w/M_n : 1.40) chips were purchased from Jiaying Haobang Science and Technology Development Co., Jiaying, China. Methylene dichloride, A. R., was supplied from Guoyao Chemical Company, Shanghai, China. Hexafluoroisopropanol (HFIP), A. R., was purchased from

Huaweiruike Chemical Limited Company, Beijing, China. Pyrrole monomer was distilled under reduced pressure and stored below 0°C. All the other reagents were analytical grade, and were used without further purification.

2.2. Preparation

2.2.1. Preparation of PLLA fibers

10 or 12 wt% PLLA in methylene dichloride or HFIP was prepared by dissolving PLLA chips in methylene dichloride or HFIP under magnetic stirring for at least 5 hrs, the solution was held in a syringe for electrospinning. A voltage of 12 kV was applied to the solution and the fibers were collected on the flat aluminum plate. The distance from the tip of the nozzle to the collector was 15 cm.

2.2.2. Preparation of PLLA/polypyrrole(PPy) composite fibers

PPy was introduced by the *in situ* polymerization on the surface of the obtained PLLA fibers mentioned above section. Typically, 0.25 g of pyrrole was dissolved in 20 mL of 1 M H_2SO_4 solution with stirring. Some PLLA fibers with a length of 200 mm immersed into the above solution followed by ultrasonication for 30 min to allow the fibers to be saturated with the pyrrole solution. 0.61 g of ammonium persulfate (APS) in 20 mL of 1 M H_2SO_4 solution was added dropwise to the above mixture with the ultrasonic aided dispersing. Then the polymerization proceeded for 5 h without any dispersing. The fibers were then washed 3 times with 40 mL of deionized water and acetone in sequence. Finally, the fibers were dried under vacuum and stored for usage.

2.3. Characterization

The morphologies of electrospun PLLA fibers fabricated under different conditions were observed using Hitachi JSM-5510 SEM. The specimen used for imaging the cross-section of the electrospun fiber was prepared by dropping a drop of collodion on the sample, followed by cutting with a sharp knife.

3. Results and discussion

Fixing the PLLA weight percent [wt%] in methylene dichloride at 12 wt%, the SEM images of fibers fabricated at 15°C and different R. H. are shown in

Figure 1. SEM images of the fibers fabricated at 15°C and different R. H. (a) 28%, with higher molecular weight (M_W : 100 000, M_W/M_n : 1.40) PLLA; (b) 49%, the inset is the corresponding higher-magnification image of a nanofiber, with higher molecular weight (M_W : 100 000, M_W/M_n : 1.40) PLLA; (c) 49%, with lower molecular weight (M_W : 70 000, M_W/M_n : 1.40) PLLA; (d) cross section of (a); (e) cross section of (b).

Figure 1. Figure 1a–1c is the longitudinal morphologies of these fibers and Figure 1d–1e is the corresponding cross-sectional one. From Figure 1, it can be found that most fibers are multi-porous fibers with diameters ranging from 3 to 7.2 μm , but the fibers fabricated at 15°C, 28% R. H. are more uniform in diameter and pore size than those fabricated at 15°C, 49% R. H. The most interesting thing is that, from Figure 1d–1e, we noticed that some fibers with diameters range from 3 to 7.2 μm not only have multi-porous outer structure, but also have visible holes in the inner region of the fibers. That is, these fibers are hollow fibers with multi-porous outer structure; although the holes of some fibers are closed because of becoming too soft to maintain the shape when they were cut and at the action of the solidification of collodion.

To further confirm the hollow structure, these PLLA fibers were used as matrix to fabricate PLLA/PPy composite fibers by *in situ* polymerization. The obtained PLLA/PPy composite fibers have obvious core-shell structure and smooth fractured surface of the core, as shown in Figure 2 [17]. This fact demonstrates these PLLA fibers are really hollow fibers.

Figure 2. SEM image of the cross section of PLLA/PPy micro fibers [17]

Some reports [7] considered the formation of pores or pits in the electrospinning fibers controlled by a rapid phase separation induced by the evaporation of the solvent and a subsequent rapid solidification. The exact mechanism of porous hollow fiber fabricated by electrospinning with only one solvent is not fully understood. Here, we propose a formation mechanism based on the void formation in ‘Kirk-

Figure 3. Simplified schematic representation of the formation of porous hollow structure (cross section) (a) the initial stage, (b) the second stage, (c) the third stage

endall effect + surface diffusion' model [16]. Figure 3 shows schematically this generalized model. In the initial stage (Figure 3a), due to the rapid volatilization of the methylene dichloride through surface diffusion result in the dropping of the surface temperature, the phase separation occur and form the voids or pits on the surface of the fiber [16]. In the second stage (Figure 3b), driven by concentration gradient, the methylene dichloride molecules diffuse outward continuously and the PLLA molecular chains condense inward. The mutual diffusion rates of the methylene dichloride and PLLA molecular differ by a considerable amount. For the diffusion flux, $J_a > J_b$ (a index methylene dichloride and b index PLLA). A large quantity of vacancies diffusion occur to compensate for the unequal material flow between methylene dichloride molecules and PLLA molecular chains, the voids are enclosed by the slower PLLA molecular chains. In a sub-micro

system, due to the finite volume and spatial confinement, a high vacancy supersaturation can readily be reached [10]. Thus, the voids have a high chance to touch the outer layer of the fiber, resulting in the multi-pores penetrating the core of the fiber. The voids coalesce into bigger ones and touch the compound layer ab, on one hand breaking the connection between PLLA molecular chains and on the other hand establishing new bridges as fast transport paths for the methylene dichloride molecules. At this stage (Figure 3c), diffusion of molecules of the remaining methylene dichloride along the bridges, i.e. the pore surface, to the reaction front becomes the dominant material transport process. The methylene dichloride can redistribute itself at the open surface of the methylene dichloride and PLLA mixture via fast surface diffusion. While within the methylene dichloride and PLLA mixture, the material exchange mechanism remains the

Figure 4. SEM images of the fibers fabricated at (a) and (b) 26°C, 50% R. H.; (c) and (d) 26°C, 80% R. H.; (e) cross section of (a). PLLA weight percent in methylene dichloride was 12 wt%.

Figure 5. (a) SEM images of the fibers fabricated at 34°C, 60% R. H. (b), (c) and (d) the corresponding high magnification of (a) in different sections; (e) cross section of (a). PLLA weight percent in methylene dichloride at 12 wt%.

same, viz. bulk interdiffusion associated with Kirkendall effect. Therefore vacancies are continuously generated and flow inward. The hollow multi-porous fiber is formed.

To further explore the formation conditions, we fabricated some fibers above 20°C. When the ambient temperature was above 20°C, the obtained fibers with diameters of several micrometers are not uniform in both the morphologies and diameters, as shown in Figures 4–5. Some sections of the fibers only have some pits on the surface; while some sections have no visible pores. Moreover, the pore size and distribution of the pores in the sections with multi-pores are also not uniform; while some sections also have multi-pores penetrating the core of the fiber (Figures 4a, 4e and Figures 4c–4e).

These indicate that under too high ambient temperature (above 20°C), the electrospinning jet is unstable due to the rapid volatilization of the solvent through surface diffusion. It can be confirmed by observing the shapes of the jets.

Appropriate ambient temperature is the prerequisite to fabricate uniform porous hollow PLLA fibers by electrospinning. As we know, the boiling temperature of methylene dichloride is 39.8°C. The closer the ambient temperature to the methylene dichloride boiling temperature is, the higher its volatilization rate is.

In addition, the collapsed wrinkled skins are also found on some sections of the fibers (Figure 4d and Figure 5d). One of the explanations is that at high ambient temperature, especially when it is near its boiling temperature, the solvent evaporation rate is very high through fast surface diffusion, and this might induce the formation of fibers with sheath-core structure due to the different solidification speed between the outer layer and the inner layer. The further solidification and shrinkage of the core would result in local collapse of outer layer [18, 19]. The surface diffusion and phase separation resulted in pits on the surface of nanofibers with a diameter smaller than about 50 nm, as shown in the inset of Figure 1b. Surface diffusion becomes the dominant solvent transport process due to the very higher surface area in the nanofibers. The rapid evaporation of methylene dichloride on the surface of the fibers and fast solidification induce the formation of fibers with sheath-core structure. The further solidification and shrinkage of the core result in pits occurred on the surface of the fibers. If the fibers with a diameter larger than several micrometers, due to the large space, a high vacancy supersaturation will be difficult to be reached. Thus, the voids have a low chance to touch the outer layer of the fiber, resulting in some pits not penetrating the core of the fiber.

Figure 6. SEM images of the fibers fabricated at 8°C, 45% R. H. with different PLLA concentrations (a) 10 wt%; (b) 8 wt%, PLLA M_W was 100 000 and M_W/M_n was 1.40

As weight percent of PLLA is fixed at 12 wt%, using the lower molecular weight PLLA (M_W : 70 000, M_W/M_n : 1.40) to electrospin the PLLA fibers, the obtained fibers only have pits on their surface, as shown in Figure 1c. The low molecular weight PLLA has high molar percent of polymer molecular, which upon methylene dichloride evaporation contributes to retain less methylene dichloride to form porous surface [20]. In addition, the low molecular weight PLLA has more molecules with relatively lower molecular weight and shorter molecular chains, the diffuse rate of these PLLA molecules are higher than those PLLA molecules with higher molecular weight, and result in less quantity of vacancies diffusion resulting from Kirkendall effect occur to compensate for the unequal material flow between methylene dichloride molecules and PLLA molecular chain. Thus, it will become difficult to reach a high vacancy supersaturation and reduce the chance of voids to touch the outer layer of the fiber, resulting in some pits not penetrating the core of the fiber.

We also observed the PLLA fibers fabricated by electrospinning at 8°C have only pits on the surface, as shown in Figure 6. Moreover, the pits enlarged with the PLLA concentration decreased. This is because of the low temperature result in slow evaporation rate and diffusion rate of methylene dichloride, forming fewer vacancies and low gas pressure within the fibers. Thus it is difficult to form enough large pores.

This can be confirmed by using HFIP, which has lower volatilization rate than that of CH_2Cl_2 at the

same ambient temperature, as the solvent for PLLA solution. Figures 7a, 7c, 7e and Figures 7b, 7d, 7f are the SEM images of the samples fabricated by using CH_2Cl_2 or HFIP as solvent, respectively. It can be seen that the obtained fibers all have beads due to the low viscosity, but it can be obviously seen that the fibers fabricated by using CH_2Cl_2 as solvent are multi-porous fibers while the fibers fabricated by using HFIP as solvent are not (Figure 7f), only some pits can be found even in the bigger beads (Figure 7d).

4. Conclusions

PLLA hollow fiber with multi-porous outer structure can be fabricated by electrospinning with only one solvent. But it must be fabricated at moderate ambient temperature (10~20°C), using appropriate molecular weight (M_W : about 100 000, M_W/M_n : about 1.40) PLLA to electrospin and has a diameter in the range of several micrometers to 100 nanometers.

The formation of multi-porous hollow fiber is a complex process. We propose a formation mechanism of the result of mutual action of ‘Kirkendall effect, surface diffusion and phase separation’.

We believe the technique described here can be extended to many other materials for the fabrication of such kind of fibrous scaffolds with potential applications not only in tissue engineering, but also in catalysis, sensing, encapsulation, drug delivery and filtration.

Figure 7. SEM images of the fibers fabricated by different solvent (a) CH_2Cl_2 , (c) and (e) the corresponding high magnification of (a) in different sections; (b) HFIP, (d) and (f) the corresponding high magnification of (b) in different sections. The ambient temperature was 28°C, and R. H. was 25%. PLLA weight percent in solvent was 10 wt%. PLLA M_w was 100 000 and M_w/M_n was 1.40.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 51073072), the Zhejiang Provincial Natural Science Foundation of China (No. Y4100745), the Key Laboratory Open Foundation of Advanced Textile Materials & Manufacturing Technology of Zhejiang Sci-Tech University from Ministry of Education of China (No. 2009007).

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