

SOLVENT EVAPORATION IN A BINARY SOLVENT SYSTEM FOR CONTROLLABLE FABRICATION OF POROUS FIBERS BY ELECTROSPINNING

by

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Solvent evaporation is used for fabrication of nanoporous fibers by electrospinning, where multiple solvents are used. Pore size and distribution can be controlled by the fractions of the spun solution. An experiment was carefully designed, where polysulfone and poly(lactic acid) were dissolved in a binary solvent of dichloromethane and dimethylacetamide, to reveal the controllable process for fabrication of nanoporous fibers.

Key words: porous fiber, electrospinning, controlled pore size

Introduction

Because of ultra high specific surface and unique adsorption properties, electrospun porous polymer fibers have been caught much attention in removing organic matters from water, such as oil, dyes, bilirubin, and so on [1-3]. The electrospun nanoporous polymer fibers can be prepared by using solvents with high vapor pressure and adjusting spinning parameters without any post-treatment [4, 5]. It has been recognized as the simplest and most efficient method to prepare porous superfine polymer fibers without the use of multiple synthetic steps, or post-processing surface treatment [6, 7].

It is well known that the pore size and porosity of porous materials have great effluence on efficiently removing different sizes of adsorbates in water. According to the sizes of adsorbates in water, pore structure of fibers has to be optimized by controlling solvent evaporation.

In this paper, electrospun polysulfone (PSF)/poly(lactic acid) (PLA) porous fibers were prepared by controlling weight ratio of PSF and PLA. The PSF and PLA were dissolved in a binary solvent of dichloromethane (DCM) with high vapor pressure and dimethyl acetamide (DMAC) with low vapor pressure. The fiber diameter and pore size of electrospun PSF/PLA porous fibers with different ratio were investigated.

Experimental

The porous fibers were fabricated by an electrospinning method under an optimal condition. Briefly, PSF (M_w 75000) and PLA (M_w 100000) with different weight ratios of 9:1,

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7:3, 6:4, 4:6, 3:7, 1:9, and 0:10, respectively, were dissolved in a binary solvent of DCM/DMAC (weight ratio of 10:1) at room temperature for 4 hours stirring to obtain 8 wt.% solutions. Each solution was loaded into a 5 ml syringe and discharged at a collector with a rotation speed of 6.2 m per minute. The PLA/PSF porous fibers were electrospun on the drum located 10 cm below the needle tip (0.6 mm inner diameter) with 1 ml per hour flow rate and a 13 kV voltage were provided. All the experiments were carried out at 20 °C and $45 \pm 5\%$ relative humidity. The morphology of the electrospun fibers were examined by a field emission scanning electron microscope (SEM). Image processing software (Image-pro plus 6.0) was used to measure the fiber diameter, porous length, and width.

Results and discussions

Figures 1 and 2 illustrated SEM images of electrospun PSF/PLA porous fibers with different weight ratio of PSF/PLA. It could be seen that the pore shape was changed from approximate circle to long oval, and the fiber diameter, pore length and pore width increased

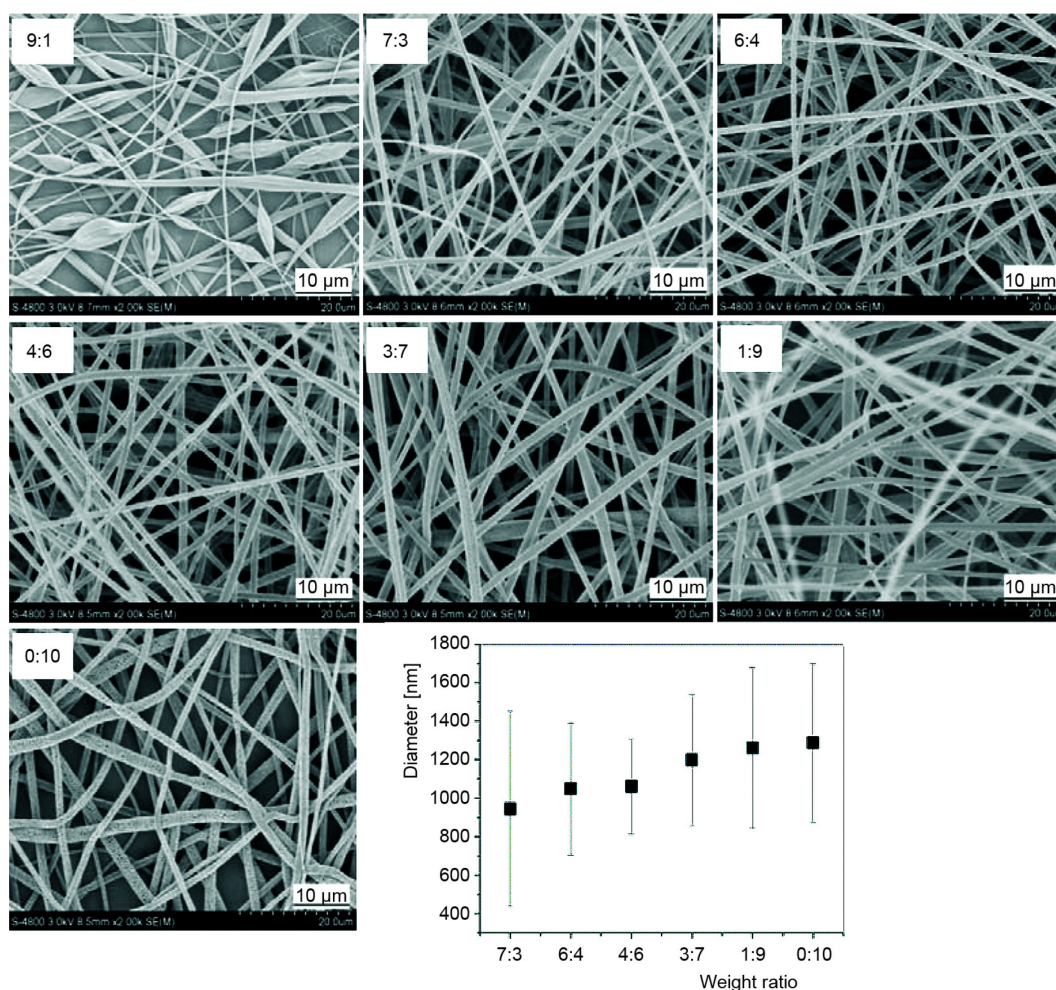


Figure 1. Morphology and diameter of electrospun PSF/PLA with different weight ratios

with increasing the ratio of PLA. All pores oriented along with the fiber axis, and the pore walls between each other changed to interconnect with increasing of the ratio of PLA. Phase separation due to solvent evaporation is the main factor affecting the fibers morphology.

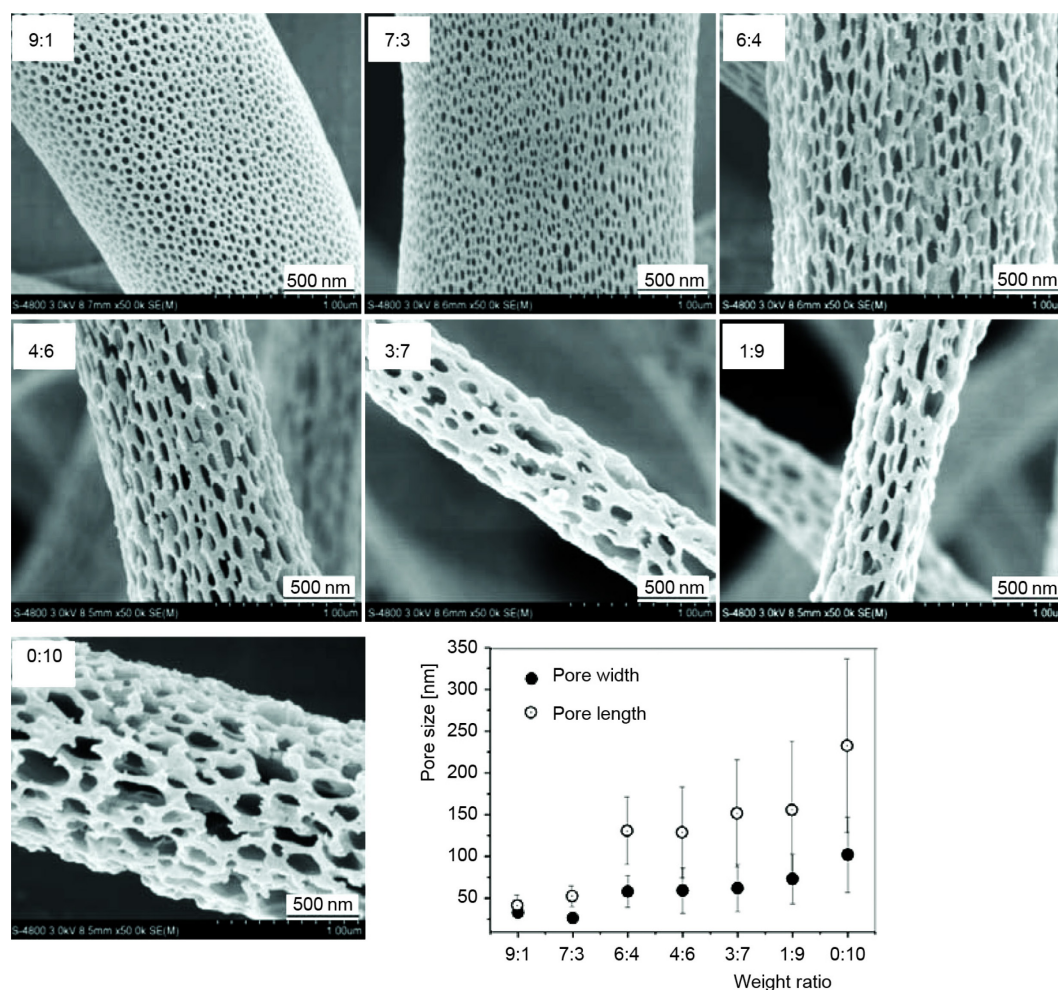


Figure 2. Morphology and pore size of electrospun PSF/PLA with different weight ratios

Phase separation due to solvent evaporation occurs when the polymer solution is ejected into a solvent-free air environment, the solvent at the surface of the jet evaporated rapidly, whereas that within the jet diffused outward simultaneously. The temperature of the jet decreases dramatically due to the rapid vaporization of solvent, which results in a thermodynamically unstable jet, inducing phase separation to form polymer-rich and polymer-lean phases [8, 9]. In addition, the cooling of the jet due to the rapid solvent evaporation condensed the water vapor in the air to form water droplets on the surface of the jet, which is called the breath figure [10, 11]. As the solvent and water droplets were removed from the jets, the concentrated polymer-rich phase solidified to form the matrix, whereas the polymer-lean phase and water droplets left imprints that formed the pores.

For whipping motion of the jet, based on theoretical model for electrospinning dilation [12-14].

Conservation of mass gives:

$$\pi r^2 \rho u = Q \quad (1)$$

where Q is the volume flow rate, ρ – the liquid density, u – the velocity, and r – the radius of the jet. The radius of the jet decreases with the increase of the velocity of the incompressible charged jet.

When the electrospinning velocity reaches a maximum in a very short time before it becomes unstable, macromolecules of the polymers are compacted together tighter and tighter during the electrospinning process. There must exist a critical minimal radius, r_{cr} , for all electrospun jet $r \leq r_{cr}$ for continuous ultrafine fibers, and the critical maximal velocity is:

$$u_{cr} = \frac{Q}{\pi \rho r_{cr}^2} \quad (2)$$

However, the velocity can exceed this critical value if a higher voltage is applied. In cases when the radius of the jet reaches the value of the critical value, and the jet speed exceeds its density, leading to porosity of the electrospun fibers. This phenomenon was called *electrospinning-dilation*.

Based on eq. (1), the ultrafine fiber diameter is:

$$r = \sqrt{\frac{Q}{\pi \rho u}} \quad (3)$$

When the applied voltage and volume flow rate, Q , are constant, the initial velocity of electrospun jet was decreased with increasing the viscosity of electrospun jet. That will result in fiber diameter increasing and the pore size increasing too.

The PSF can dissolve in DCM and DMAC to form homogeneous solution. While PLA can dissolve in DCM, but can not dissolve in DMAC. The DMAC was used as non-solvent, and DCM as solvent in PSF and PLA blending solution. The PSF and PLA were not compatible in DCM/DMAC. So, the phase separation also occurred between the PSF and PLA, and resulting in connected pores with increasing the weight ratio of PLA, as show in fig. 2. In addition, the viscosity of PSF/PLA solution in DCM and DMAC binary solvent increased as the weight ratio of PLA increased. So, based on eq. (3), the PSF/PLA diameter increased, as shown in fig. 1.

Conclusion

Highly oriented pore structure of porous fibers were prepared by electrospinning PSF/PLA with different weight ratio dissolved in a binary solvent DCM/DMAC (weight ratio of 10:1). Experimental results demonstrate that, pore size of electrospun PSF/PLA porous fibers can be easily achieved by adjusting the weight ratio of PSF and PLA. The large surface area and controlled pore structure make these porous fibers to be ideal candidates for adsorbed organic matters in water.

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