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Electrospun preparation of polylactic acid nanoporous fiber membranes via thermal-nonsolvent induced phase separation

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ABSTRACT

A novel polylactic acid (PLLA) fiber membrane with nanoporous structures has been successfully developed via thermal-nonsolvent induced a phase separation technique by electrospinning a single solvent system of PLLA/dichloromethane. A water bath receiver was necessary for preparing the nanoporous fiber membranes in this paper. The results showed that the nanoporous fiber membranes could be obtained within a wide range of humidity. Compared with non-porous PLLA fiber membranes, the nanoporous fiber membranes displayed significantly improved specific surface area (improved about 20%) and rejection ratio (about 3 times) toward methylene blue. Besides, the PLLA nanoporous fiber membranes showed a water flux up to 4836.6 L m^{-2} h^{-1}, increased by 25% than that of the non-porous fiber membranes. In addition, the oil adsorption capacity of the PLLA nanoporous fiber membranes could reach 26.8 g g^{-1}. The new developed PLLA nanoporous fiber membranes via thermal-nonsolvent induced phase separation technique would demonstrate an impressive prospect for oil adsorption and organic dye filtration.

1. Introduction

Electrospinning is a straightforward way to prepare micro-/nanometer scale and high porosity fibers [1,2]. Since the electrospun fibers have many advantages, such as good repeatability, various morphological modifications, and three-dimensional porous structures [3,4], electrospinning progress has attracted a great deal of attention. Therefore, these nanofibers/nanowebs are quite applicable in many areas including filtration [5], biotechnology [6], *etc.*

Some interesting structures, such as core/shell structure [7], porous structure [8] and hollow structure [9], have emerged in recent years, and attracted widely attention due to the unique properties and functionalities. A lot of applications may be favored if the fibers are endowed with rough or porous structures [10]. In fact, widespread attention has been paid to the electrospinning technique in increasing the specific surface area and porosity of the fiber membranes [11,12]. Up to now, there were four methods to prepare the porous fiber membranes in literature: (1) using high/low boiling point solvent mixtures [13], (2) using solvent/nonsovent mixtures [14,15], (3) post-processing electrospun composite nanofibers by selectively removing one of the components [16,17], (4) electrospinning of polymers in a high humid environment [18]. Currently, porous fiber membranes have been used for various fields including tissue engineering [19], carriers in drug delivery system [20], and electrode application [21].

In recent years, a lot of methods have been published to prepare electrospun porous fibers. Cao and his coworkers [22] have prepared polylactic acid ultrafine fibers with mesopores of 30–150 nm by electrospinning. The fiber diameters and morphologies could be controlled by adjusting the composition ratio of the dichloromethane/dimethyformamide solvent mixtures. A facile method to fabricate porous fiber membranes by electrospinning a ternary system of nonsolvent/solvent/poly(L-lactic acid) was presented by Qi and his coworkers [23]. Nanoporous polyacrylonitrile ultrafine fibers were prepared by Li and his workers [17]. Post-processing electrospun polyacrylonitrile composite nanofibers by selectively removing polyvinylpyrrolidone was the main method to prepare porous fibers. The specific surface area of the porous polyacrylonitrile ultrafine fiber membranes was more than 70 m^2 g^{-1}. The porosity of electrospinning porous fibers obtained from polystyrene/dimethyformamide solution at 60% relative humidity was characterized by H.Fashandi et al. [24]. It was obvious that the high humid environment was the main factor to prepare polystyrene porous fibers. Kim et al. [25] fabricated the electrospun polymer nonwoven mats with porous surface morphologies by varying the collector temperature. Though these fore-mentioned methods have been used widely, there are a few factors to be considered in the process of preparation, such as dispersion of binary polymers in the same solvent, compatibility between binary solvents, and the control of the relative humidity.

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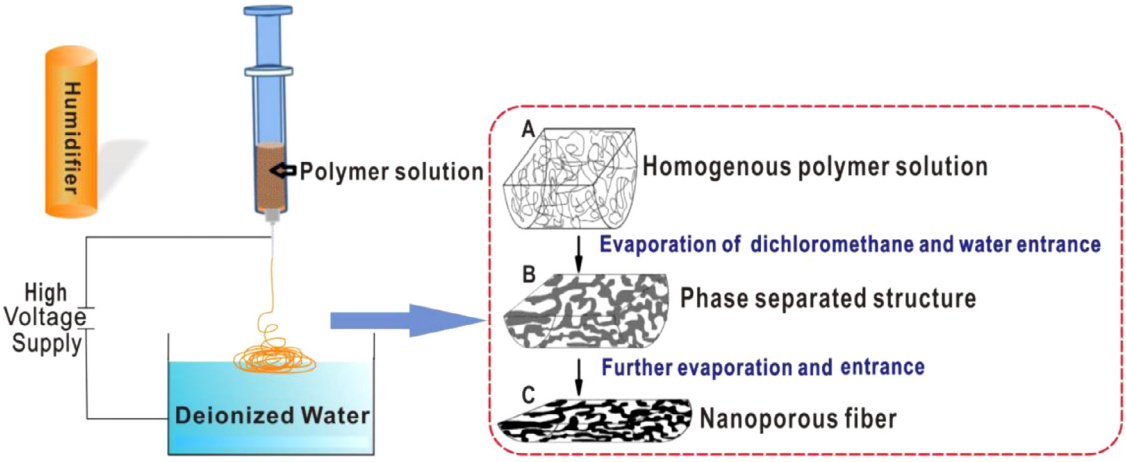

Fig. 1. The process of electrospinning and the principle of nanopore formation.

Table 1
The contrast of preparation methods.

Solvent	Humidity or temperature	Receiver	Mainly application	Ref.
Double solvent	Not mentioned	Roller	Drug carrier	[26]
Double solvent	49%, room temperature	Roller	Tissue engineering	[27]
Double solvent	40%, room temperature	Roller	Tissue engineering	[23]
Single solvent	25%, 40°C	Roller	Tissue engineering	[25]
Single solvent	20–70%, room temperature	Water bath	Filtration and oil adsorption	This work

In this study, without regard to complicate factors in the process of preparation, polylactic acid fibers with nanoporous structures were obtained by electrospinning a single solvent system of PLLA/dichloromethane. Based on the mechanism of thermal-nonsolvent induced phase separation, a water bath was used to obtain the nanoporous fiber membranes within a wide range of humidity. The resulting membranes were subject to characterizations including scanning electron microscope (SEM), nanopore sizes and interconnected pore size distributions, specific surface area measurements, contact angle tests, oil adsorption tests, permeation flux and rejection measurements. The influence of humidity during electrospinning on the morphologies and properties of membranes was investigated.

2. Experiment

2.1. Materials

Polylactic acid (PLLA, $M_w = 110{,}000$) was purchased from Ningbo global biological material Co.Ltd. Dichloromethane (CH_2Cl_2, AR, 99.5%) was supplied by Tianjin Fuyu Chemical Co. Ltd. All the chemicals were analytical grade.

2.2. Preparation of electrospun PLLA nanoporous fiber membranes

The PLLA granules were dissolved in dichloromethane solvent and the concentration was 9 wt%, and then the PLLA solution was mixed uniformly by magnetic stirring for 6 h.

The setup of electrospinning process was composed of a high voltage power supply, an injector, a water bath (receiver) and a humidifier. The obtained PLLA spinning solution was placed in the injector with a capillary tip (inner diameter=0.67 mm). The anode of the high voltage power supply was clamped to an injector needle tip, and the cathode was connected to a water bath. The electrospun fibers were collected in the water bath. The applied voltage was 20 kV, the tip-to-collector distance was 15 cm, and the flow rate of the spinning solution was 2 ml h^{-1}. All of the electrospinning operations were performed under room temperature. After electrospinning, the resulting membranes were subject to characterizations without any treatments except for drying for 24 h.

Fig. 1 showed the process of electrospinning and the principle of nanopore formation. It was obvious that the change of ambient humidity was due to the cooperation between humidifier and water bath. And the variation of humidity was read by hygrometer. In this paper, the influence of humidity during electrospinning on the morphologies and properties of membranes was investigated. Hence, according to the reading of hygrometer, the change of ambient humidity was achieved by adjusting the humidifier. In order to identify all various kinds of membranes easily, the membranes which were prepared at the humidity of 30%, 40%, 50% and 60% were named as membrane-30, membrane-40, membrane-50 and membrane-60 correspondingly. In addition, the non-porous fiber membranes were obtained at the same electrospinning conditions except for a roller receiver. Compared with other preparation methods, the advantages of our work were shown in Table 1.

2.3. Morphology analysis

The surface morphologies of electrospun PLLA nanoporous fiber membranes were investigated using SEM (Quanta 200,Holland) instruments. Prior to the observation, all the samples were coated with gold. After SEM tests, the nanopore sizes on the single fiber were measured by Image-Pro Plus software on the images of SEM. And each final nanopore diameter was obtained by averaging over more than fifty nanopores of different fibers.

The interconnected pore size distributions of the membranes were obtained by capillary flow porometry measurements [28], based on the wet/dry flow method. The membranes were immersed in wetting liquid (Porefil, provided by PMI) with a surface tension of 16 dyn/cm for 24 h at room temperature. A wet gas was performed using a solvent filled sample that was followed by a dry gas (sample without wetting liquid) for obtaining flow rate curves as a function of applied pressures. The differential pressure of the gas at which flow through a pore occurs yields the throat (most constricted) diameter