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Formation, morphology and control of high-performance biomedical polyurethane porous membranes by water micro-droplet induced phase inversion

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ABSTRACT

Biomedical polyurethane (BPU) porous membranes with controlled morphology and excellent permeability and mechanical properties were prepared via a method involving a phase inversion induced by water micro-droplets, which were generated by an ultrasonic atomizer. The cross-section morphology, air permeability and mechanical properties of the porous membranes were investigated. The SEM images demonstrated that the adjacent pores were connected by a micro-hole, serving as a "backdoor" for the pore. An interconnected porous structure was obtained, improving the air permeability of the BPU membrane relative to the membrane produced by immersion precipitation. Our studies indicated that the diameter of the pores in the membrane depended on the solution viscosity, allowing porous membranes with a desired morphology to be obtained by adjusting the polymer concentration and solution viscosity. The application of micro-droplets of water during membrane preparation reduced the exchange rate between the solvent and nonsolvent, resulting in the microphase separation of polymer molecules and the formation of a uniform porous structure in the membrane, which improved the air permeability and mechanical properties of the BPU porous membranes. This is a simple and effective preparation method for high-performance porous membranes with potential applications in tissue engineering scaffolds, controlled-release drug delivery and vascular grafts.

1. Introduction

Biomedical polyurethane (BPU) has been widely used in tissue engineering scaffolds and blood vessel prostheses for decades because of its excellent biocompatibility and mechanical properties [1–9]. The BPU membranes with interconnected pores have been fabricated and used as scaffolds to improve biocompatibility. The morphology and uniformity of the pores determine the physical properties of the BPU membrane, including surface wettability, mechanical properties and air permeability, which further in turn influence its biocompatibility and application performance. Therefore, it is essential to control the pore structure of the membrane. Many methods have been developed in recent years to prepare BPU porous membranes [10–16]. In Refs. [16], we used a phase inversion method to prepare the porous membrane and discussed the pore formation mechanism. However, in that work, the pore size could not be controlled very precisely in the phase separation process. We modified the preparation method in this work. Liu et al. [17] used a freezing process to fabricate porous polyurethane (PU) vascular prostheses with variable compliance. How et al. [18] produced porous PU vascular prostheses by an electrostatic spinning method to improve the biocompatibility. Khorasani et al. [19,20] employed a phase inversion method to fabricate PU porous membranes. Three-dimensional porous scaffolds of PU with a highly interconnected porous structure were fabricated using a particulate leaching technique by Grenier et al. [21].

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The method of phase separation induced by water is a simple way to fabricate porous PU membranes because water is an excellent nonsolvent for PU solutions. This phase inversion process is induced by distilled water when a homogeneous PU solution is immersed into water. The exchange of the solvent and water across the interface results in a very rapid phase separation into a polymer-rich phase and a polymer-poor phase. With the exchange between water and solvent, phase separation continued until the polymer-rich phase was solidified. The final morphology of the PU membrane was strongly influenced by the solidification process of the polymer-rich phase. In traditional wet-phase inversion methods, the exchange rate between the water and solvent and the pores structure (involving size, figure-like or honeycomb-like) are mostly determined by concentration of DMF in solidification bath and concentration of PU solution at a certain temperature. In common, higher concentration of PU solution results in a thick dense skin layer and honeycomb pores with small size, while lower concentration of DMF in solidification bath results in thin dense skin layer and figure-like structure pores with large size. When the PU solution was first placed in contact with water, rapid exchange between water and solvent happened immediately, which led to the fast precipitation of the PU molecules and the formation of a dense layer [22]. The dense top layer decreased the exchange rate between the water and solvent, which provided sufficient time for the growth of nuclei into droplets of the polymer-poor phase in the polymer solution. A porous structure was formed after the water in the polymer-poor phase was removed from the PU membrane during drying [23]. The application of the PU membrane for tissue engineering scaffolds and drug controlled release was limited due to the complex structure formed in the phase inversion process. The dense top layer blocked air penetration and the transport of nutrients through the membrane. On the other hand, the pore formation was uncontrollable during the fast phase inversion process, making it difficult to fabricate a uniform porous structure. Therefore, innovative methods were needed to prepare an improved PU membrane with a uniform porous structure as well as excellent air permeability and mechanical properties.

Vapor has been used to induce the phase inversion of polymer solutions when preparing porous films [24–30]. This approach is useful for controlling the structure of microporous membranes, especially honeycomb structures. Honeycomb films with thicknesses of 10–30 μm were prepared by evaporating the solutions of star-shaped polystyrene or polystyrene-polyparaphenylene (PS-PPP) block copolymer in carbon disulfide under a flow of moist gas by Gilles Widawski et al. [31]. Porous polysulfone (PSF) membranes with a thickness of 10–100 μm were prepared using water vapor as the coagulant by Park et al. [30]. These studies have shown that the relative humidity and polymer solution concentration have obvious effects on the pore morphology. The pore size increased as relative humidity and polymer concentration decreased. Numerous reports have indicated that membranes prepared via phase inversion induced by vapor are thin (10–100 μm) and unable to provide good mechanical properties in application. In the preparation using high relative humidity, it is hard to control water droplets size due to asynchronism of moisture condensability. The variation on water droplets size could decrease the uniform of micropores. It is therefore necessary to develop a new approach to the fabrication of porous polymer membranes with the desired thickness and mechanical properties via phase inversion induced by vapor.

As we know, it was difficult to control the exchange velocity between solvent and nonsolvent when liquid was used as coagulant during preparation process of polyurethane membrane. The adjusting on exchange rate can be realized by choosing desired liquid which have different diffusion coefficient with polymer solvent. But, the variation of exchange rate was limited, and it was difficult to characterize. In order to study the effect of exchange rate on porous morphology and physical properties of porous membrane on macroscale, a novel method, ultrasonic atomization, was used firstly to supply continuously nonsolvent at low speed in preparation. The exchange rate between solvent and nonsolvent was controlled accurately by varying supply velocity of water droplets. The relationship between porous morphology, air permeability and mechanical properties and preparation parameter has been built based on experiment data in our paper. Therefore, the porous BPU membrane with excellent physical properties or air permeability could be conducted according to the relationship. We believed that the conclusion have great value for studying of phase inversion behavior of synthesis molecules and preparing of advanced porous membrane in the future. The porous membrane with excellent mechanical properties and air permeability was prepared using water droplets as nonsolvent. Comparison with traditional method using water and N,N-Dimethylformamide composition as nonsolvent, only water was used as nonsolvent, which reduced the producing cost and environment pollution.

In the present work, the BPU membranes with uniform pores and excellent air/vapor permeability were fabricated via a phase inversion process induced by water droplets generated from an ultrasonic atomizer. The cross-section morphology of the BPU porous membranes was characterized by scanning electron microscopy. The effect of BPU concentration on the pore morphology was studied. The differences between the mechanical properties of the porous membranes prepared with distilled water and water droplets were also investigated.

2. Experimental

2.1. Materials

Biomedical polyurethane (BPU, Pellethane® 2363-80AE) was purchased from Dow Chemical Corporation. N,N-Dimethylformamide (DMF) was purchased from Sigma–Aldrich and used without further purification. The ultrasonic atomizer (frequency: 20 kHz, atomization volume >300 mL/h) used in this study was provided by Shanghai Qiuse Electronic Technology Co. Ltd.

2.2. Preparation of BPU porous membranes

Homogeneous BPU solutions with different weight concentrations (10%, 15%, 20% and 25%) were prepared by dissolving BPU pellets in DMF at room temperature. The BPU solutions were placed in a container under a vacuum of −0.1 MPa for 4 h to remove all air bubbles. The BPU porous membranes were formed by casting the solutions onto clean glass substrates with a 1-mm depth at ambient temperature, which were then placed into a chamber filled with water droplets generated by an ultrasonic atomizer. The temperature within the chamber was controlled at 30 °C. As shown in Fig. 1, the water droplets in the chamber were continuously supplied through a silicon tube connected to a vessel containing the ultrasonic atomizer and distilled water. The BPU membranes were taken out of the chamber after 8 h and immersed into distilled water for 2 h to remove residual DMF. The prepared BPU membranes were dried at 30 °C for 48 h and peeled off the glass plates. Before characterization, the BPU porous membranes were preconditioned in a conditioning room at 25 ± 2 °C with a relative humidity of 65 ± 2% for 24 h. In this study, the BPU porous membranes prepared by phase inversion induced by distilled water at 30 °C according to reference [19] and those prepared with water droplets as the coagulant were denoted as M_o (original membrane) and M_h (high-performance porous membrane), respectively.