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Multilevel porous structured polyvinylidene fluoride/polyurethane fibrous membranes for ultrahigh waterproof and breathable application

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ABSTRACT

Porous membranes that can resist water droplet and transmit water vapor simultaneously have aroused wide attention due to their promising application in individual protection. However, the fabrication of such materials remains a challenge. Here we fabricated electrospun fibrous membranes exhibiting ultrahigh waterproofness and excellent breathable performance simultaneously by constructing a multilevel porous structure. The careful control over the concentration of polyvinylidene fluoride (PVDF) generated improved hydrostatic pressure and water vapor transmitting rate (WVTR). More importantly, by coupling polyurethane/fluorinated (PU/FPU) membrane with PVDF membrane layer by layer, the resultant composite PVDF/PU membrane presented ultrahigh hydrostatic pressure (140 kPa) and WVTR (11.3 kg m^{-2} d^{-1}). We unveiled that this excellent waterproof/breathable performance was achieved benefitting from the differentiated pore size and porosity of the two membranes. The creation of such an encouraging membrane could establish a new optimization methodology for waterproof/breathable membranes.

1. Introduction

Waterproof/breathable membranes have been acknowledged as indispensable materials for winter jacket, ski suit, and army boots due to its function of resisting water droplet but transmitting water vapor simultaneously [1]. This unique function can supply both protective performance and wearing comfort under extreme climatic conditions, such as rain, wind, and snow [2]. The mainstream technologies for fabricating this functional membrane include biaxial stretching, phase separation, and template-based strategy, resulting in representative hydrophilic thermoplastic polyurethane (TPU) membranes and polytetrafluoroethylene (PTFE) membranes [3]. Hydrophilic TPU membranes can achieve ultrahigh hydrostatic pressure (140 kPa) due to their imporous compact structure, however, which unfortunately gives rise to a low water vapor transmittance rate (2 kg m^{-2} d^{-1}). In terms of PTFE membranes, which are capable of transmitting water vapor at a relative high rate (6.3 kg m^{-2} d^{-1}) due to its countless tiny porous channels and their waterproofness performance can achieve modest level (110 kPa). Unfortunately, PTFE membranes will be banned gradually due to their long fluorocarbon chain ($-C_nF_{2n+1}$, $n \geq 8$), which is bioaccumulative and nondegradable [4]. Therefore, it has become increasingly significant to find a new strategy to obtain high performance waterproof/breathable membranes.

The existing researches have proved that electrospun fibrous membranes are able to be an alternative to the existing waterproof/breathable membranes owing to its easily controllable porous structure and cost-efficient process [5]. Up to now, the polymers used for preparing electrospun waterproof/breathable membranes are represented by polyurethane (PU) and polyacrylonitrile (PAN). However, limited by the hydrophilic property of PU and PAN, hydrophobic modifiers have to be introduced to ensure the waterproofness [6,7]. Unfortunately, the typical polydimethylsiloxane (PDMS) modifier suffered from the uneven distribution within membranes due to the complicated post-coating procedure. Additionally, another commonly used fluorinated polyurethane (FPU) modifier also suffer from its long fluorocarbon chain currently [8,9].

Recently, we successfully fabricated environmentally friendly PVDF/LiCl fibrous membranes by taking advantage of the hydrophobic property of PVDF. The resultant PVDF/LiCl fibrous membrane exhibited modest hydrostatic pressure (110 kPa) and high WVTR (11.5 kg m^{-2} d^{-1}). Nevertheless, limited by the relative high porosity 76.2 and maximum pore size of 1.2 μm, the hydrostatic pressure

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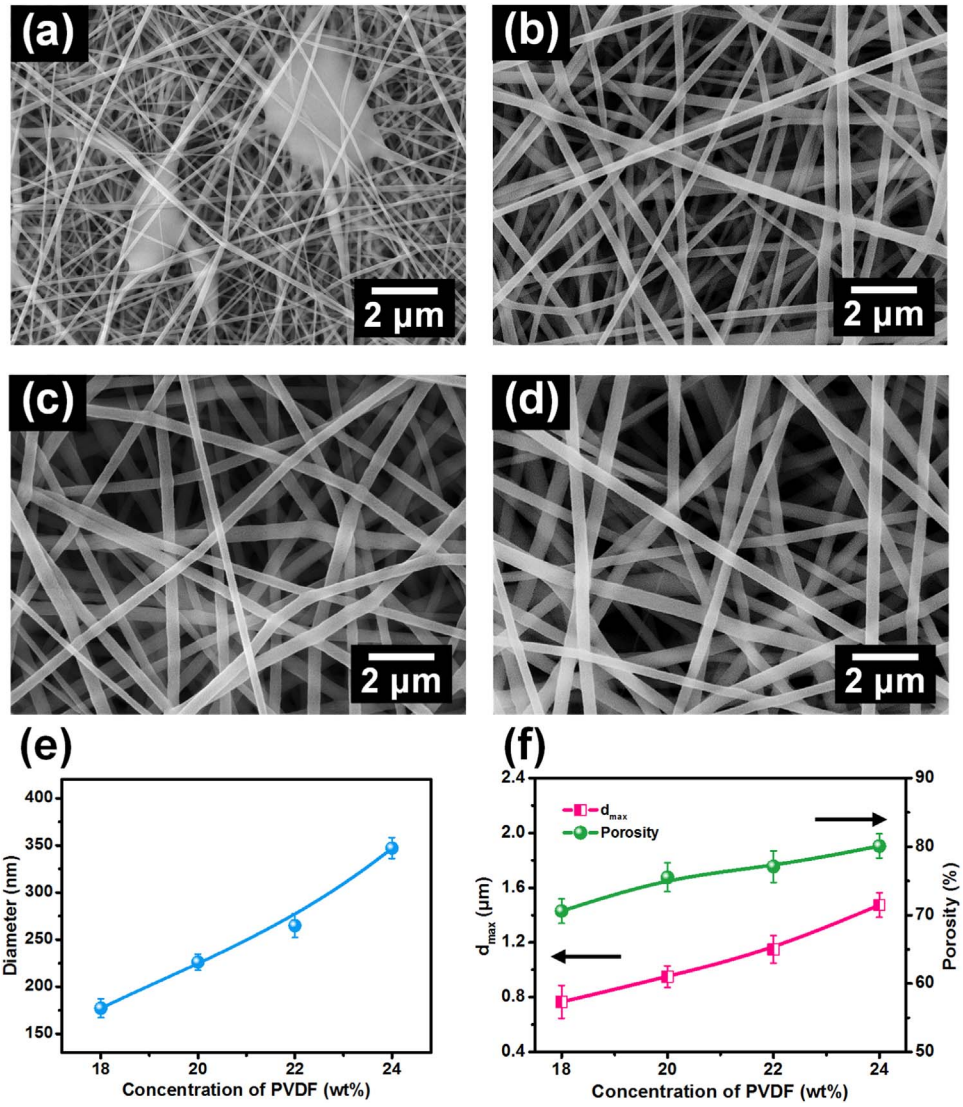

Fig. 1. Morphology of PVDF fibrous membranes. SEM images of PVDF membranes resulted from different solution concentration of (a) 18, (b) 20, (c) 22, and (d) 24 wt%. (e) Average fiber diameter, (f) d_{max} and porosity of PVDF fibrous membranes obtained from different solution concentrations.

couldn't be elevated further [10]. Therefore, we combined PU/FPU membrane with compact structure and designed multilayered PVDF/PU structure with the aim of elevating hydrostatic pressure while keeping a stable WVTR.

2. Experimental section

2.1. Materials

PU with the density of 1.1 g cm^{-3} was bought from Bayer, Germany. PVDF (M_w = 320,000, density = 1.78 g cm^{-3}) was bought from Solvey, America. LiCl (> 99.5%) was supplied by Sinopharm Group Co. Ltd., China. N,N-dimethyl acetamide (DMAc, 99%, Aladdin) and acetone (≥99.9%, Sigma-Aldrich) were used without any purification process. PFU with short perfluorohexyl (-C_6F_{13}) was self-synthesized, the process for preparing which was presented in our recent study [11].

2.2. Preparation of solutions

PVDF solutions with various concentrations (18, 20, 22, and 24 wt %) were prepared via three steps: firstly, 0.1 g LiCl was dissolved in 9.9 g mixture of DMAc/acetone (with the ratio of 7/3) and was subjected to vigorous stirring. Then, 40.703, 39.703, 38.703, and 37.703 g mixture of DMAc/acetone (with the ratio of 7/3) was added into four clean bottles and 0.3 g LiCl solution was dropped. Finally, 9, 10, 11, and 12 g PVDF was added and sufficient stirring for 12 h was imposed until PVDF solutions became transparent pseudosolution. In addition, PU/FPU solutions were obtained by dissolving 6 g PU and 0.75 g FPU in 43.25 g DMAc and being stirred for 8 h.

2.3. Preparation of membranes

PVDF flat films were prepared by pouring the polymer solutions on a polypropylene plate little by little to ensure the smoothness of flat films. Then, a heating process was carried out in a vacuum oven for 5 h with the temperature of 80 °C. The prepared PVDF flat films with various concentrations were named as PVDF-F18, PVDF-F20, PVDF-F22, and PVDF-F24. PVDF and PU/FPU nanofibrous membranes were fabricated by using a DXES-3 electrospinning machine (SOF Nanotechnology Co., Ltd., China). The parameters were set as follows: a feed rate of 2 mL/h, a tip-to-collector distance of 18 cm, an applied voltage of 30 kV, and a roller speed of 100 r/min. The temperature and relative humidity (RH) were regulated and kept at 25 ± 2 °C and 80 ± 2%, respectively. The obtained PVDF fibrous membranes with various concentrations were named as PVDF-M18, PVDF-M20, PVDF-M22, and PVDF-M24. Multilayer composite membranes were acquired via electrospinning PVDF solution and PU/FPU solution alternatively. Defining the combination of one layer PVDF fibrous membrane and one