Waterproof and Moisture permeable Nanofibrous Membranes with Cross-Linked Structure

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Abstract. Functional flexible membranes with superior water repellency and moisture permeability, which prevent water penetration and allow rapid passage of water vapor, offer new possibilities for a wide range of applications in various fields. A new type of functional nano-fiber membrane can be prepared by a facile electrospinning method, thermal post-treatment and chemical crosslinking, which can provide excellent mechanical properties. In this study, low melting point polyvinyl-butyral (PVB) elastomers were incorporated into polyvinylidene fluoride (PVDF) to change the adhesion between the membrane bonding network structure and the fibers to impart durable and strong mechanical properties to the membrane. The effects of PVDF/PVB concentration on the waterproof and breathable properties were investigated by systematically tabulating the morphology, contact angle, water vapor transmission rate (WVTR), and fracture length of PVDF/PVB. The results showed that the prepared nanofiber membrane could maintain high hydrostatic pressure (85.15 kPa) and high water vapor transmission rate (10.28 kg m⁻²d⁻¹), and at the same time, the membrane exhibited excellent tensile stress (13.07 MPa), indicating its wide application in separation process and protective clothing.

1. Introduction
Flexible smart membranes have superior waterproofness and moisture permeability and are widely used in wearable protective clothing, aerial navigation equipment, construction materials and medical devices[1-3]. The material should have high moisture permeability, good hydrophobicity and excellent hydrostatic pressure, giving the membrane stable performance. Due to its peculiarities, how to adjust the balance between moisture permeability and hydrophobicity has become a major challenge for waterproof and water molecule permeable membranes.

With the gradually recognize of the potential application of waterproof and breathable membranes, research and preparation there of is started, various methods have been developed to prepare waterproof and moisture permeable membranes in nowadays. Mechanical fibrillation, phase separation, biaxial stretching, template-based, and melt blown methods etc [6-8], were commonly used in preparation strategies. However, these methods are severely limited due to serious environmental pollution, complicated manufacturing processes, high cost in adjusting water resistance and breathability[6-9].

This work is based on the Young-Laplace equation to fabricate a waterproof and moisture permeable nano-fiber membrane with a physically cross-linked structure through a two-step strategy by combining of electrospinning and heating treatment. As shown in Figures 1 and 2, the membrane structure can be tuned by adjusting the solvent composition of the PVDF solution. By controlling the
concentration of PVB in the polymer solution, the coarse structure was constructed on the surface of the membranes by heat treatment. Most importantly, the hydrophobicity and mechanical properties of the composite PVDF are greatly improved by adjusting the effective maximum pore size and porosity of the nanofiber membranes.

2. Experimental section

2.1 Material & Equipment

Polyvinylidene fluoride (PVDF, Kynar 741, Mw=400000 g mol⁻¹); was purchased from Arkema Co., Ltd., France. Polyvinylidene fluoride (PVB, particle size 20 micron) was purchased from DuPont Company, U.S. N, N-dimethylacetamide (DMAc, analytical pure AR), Acetone (analytical pure AC) was purchased from Chemical Reagents Co., Ltd. of China Pharmaceutical Group.

2.2 Preparation of Fibrous Membranes.

A series of PVDF/PVB blends with different concentrations were prepared. The solid content of PVDF/PVB blends was 12wt%. The mass ratios of PVDF to PVB were 10/0, 9/1, 8/2, 7/3 and 6/4, respectively. PVDF/PVB was added into the mixed solution of DMAc and AC and stirred for 6h. The mass ratio of DMAc to AC in the mixed solution was 7/3. The prepared nano-fiber membrane (NFM) was named PVDF-x/PVB-y, where x/y was the PVDF/PVB of different weight ratio. The stirred solution was put into a needle-tip injector. Connected with the anode high voltage power supply, the tin foil was evenly attached to the receiving roller. The receiving distance between the injector and the roller was 18cm, the environment temperature was 20±2℃, the relative humidity was 65±5℃ the voltage was 16kV, advance speed was 0.0015mm/s, the prepared composite membrane in the vacuum oven at 120℃ for 30min.

2.3 Characterization

The SEM images of prepared samples were observed by S-3400N scanning electron microscopy SEM (Hitachi Company, Japan.HQ), the micro-structure and morphology of the relevant composite membrane was characterized. The surface molecular structure and functional group orientation were examined by Spectrum-two Fourier transform infrared (FTIR) spectrometer (PerKin Elmer Company, USA.). The permeability was determined by the pore size, shape and porosity of the micropore in the diaphragm. The thermodynamic properties of the films were studied, the porosity of the composite membrane was determined by the following formula.

\[
\text{Porosity} = \frac{W - W_0}{\rho \times A_h} \times 100\%
\]

where \(P\) was the porosity, \(W_0\) was the mass before soaking N-butanol, \(W\) was the mass after soaking N-butanol, \(P\) was the density of N-butanol, and \(A_h\) was the geometric volume of the diaphragm.

G461E-III automatic permeability meter was used to measure the permeability of fibre mesh. The test pressure difference was 100Pa and the test area was 20mm2. The waterproof performance of fiber membranes were tested by hydrostatic testing machine (YG812C, Nantong Hongda Experimental Instrument Co., Ltd.). In order to observe the wettability of PVDF/PVB composite membranes, the water contact angle (WCA) was measured by using liquid droplets of 5µL in volume (Beijing Jinshengxin Testing Instrument Ltd, China). Breathability of the membranes was tested by YG601H moisture permeability equipment (Ningbo Textile Instruments Co., Ltd.). The Water Vapor Transmission Rate (WVTR) were obtained with the following formula:

\[
WVTR = \frac{M - M_0}{A} \times 24
\]

where \(M\) was the NFM mass before test, \(M_0\) was the NFM mass after test, was the test area, and the unit of the value was kg m⁻² d⁻¹.
Waterproof performance was indicated by hydrostatic pressure. Hydrostatic pressure measured the waterproofness of fibrous membranes through the (YG812C, Nantong Hongda Experiment Instruments Co., Ltd.). Each sample was measured at least five times, and the arithmetic average values of each parameter were analyzed. Tensile stress-strain and fracture strength are characterized. The formula for calculating fracture strength is shown below.

\[ P = \frac{F}{10 \times \sigma \times W} \]

where: 
- \( P \) is fracture strength (cN/dtex),
- \( F \) is fracture strength (cN),
- \( \sigma \) is surface density (g/m²),
- \( W \) is specimen width (mm).

3. Results and Discussions

3.1 PVDF/PVB Fibrous Membranes

Its morphology and structure were characterized by SEM. In the first stage, we added PVB to pure PVDF solution to study the effect of PVB concentration on its morphology and pore structure. As shown in Fig. 3, The original electrospun original PVDF nanofiber membranes were straight and uniformly arranged with uniform diameter, and also had no adhesive structure. After the introduction of PVB, the fiber morphology and ossification structure changed significantly. The original PVDF nanofiber membrane was too low in viscosity, and the fiber fracture in the membrane was too much, and the fracture led to a decrease in mechanical properties, which was insufficient to meet the requirements of industrial applications. With the increase of PVB content to 10 wt%, the PVDF-9/PVB-1 membranes showed a bead-like fiber structure, with most of the beads arranged along the nanofiber axis. The nanofiber molding process formation of binding points between the fiber diameters and adhesion structures due to the low viscosity of the PVDF solution, which led to insufficient stretching. With the increase of PVB concentration, the average diameter of the fiber film underwent a significant change and the adhesion structure appeared. Gradual increase. Due to the gradual increase in the average diameter of the fibers, the number of binding points increased, which facilitated the formation of inter-fiber fusion, and the three-dimensional structure of physical bonding between the fibers could be clearly seen.

3.2 Waterproof and breathable performance of PVDF/PVB fibrous membranes

The surface wettability mainly depends on the intrinsic hydrophobicity of the material and the maximum diameter (dmax) of the fiber membrane. To observe the wettability of PVDF/PVB composite membranes, the contact angle of PVB composite membranes was measured. Figure 4. depicts the water contact angle of the original PVDF with a WCA value of 132°, which increases to 138.4° as the PVB weight ratio increases to 7/3, which may be attributed to the presence of bonded nanofibers in the PVB reducing the porosity and the maximum pore size. As expected, the hydroxyl group contained in PVB is hydrophilic and affects the WCA, the consequence of which should be a slight decrease with the increase of PVB, which increases the hydrophobicity of the composite film to some extent by synergistic interaction, with a significant increase in the contact angle under synergistic reaction. However, with the further increase of PVB weight ratio, the WCA decreases to 128°, which is equal to the original membrane. This may be due to the excessive introduction of hydrophilic groups leading to an increase in fiber fracture.

Afterwards, the waterproof and breathable properties of the fiber membrane were tested. As shown in Figure 4, the Prinstine PVDF membrane exhibited a water resistance of 60.34 kPa. With increasing PVB weight ratio and heat treatment, the hydrostatic pressure increased to 85.15 kPa, due to the bonding structure that enhances water solubility. However, when the PVB w/w ratio reaches 5/5, a further increase of the w/w ratio shows a decrease in the effect of PVB on hydrophobicity, which may be due to the constant pore size. According to the air permeability analysis, the functional membranes with different water vapor permeability. PVDF-9/PVB-1 had higher water vapor permeability, 10.28kg m⁻²d⁻¹, and better windproof performance. After adding PVB, the water vapor permeability
slightly decreased, and the composite membrane has good windproof performance. The increase in the bond structure enhanced the resistance to air transformation. Although the porosity is reduced, the nanopores formed are still sufficient to allow water vapor to pass through. The change in hydrostatic pressure can be explained by the Young-Laplace model with two key factors: the maximum pore size and the size of the contact angle.

$$\text{Young-Laplace equation} = -\frac{4\gamma}{d_{\text{max}}} \cos \theta_{\text{adv}}$$

### 3.3 Mechanical Property of PVDF/PVB fibrous membranes

Figure 5 shows the typical stress-strain curves of electrospun films at different weight ratios of PVDF/PVB. The non-uniformly dispersed fibers are forced to align in the direction of stress, resulting in the first non-linear elastic behavior. With the continuation of tension and increase in stress, the curves exhibit a linear elastic behavior, which stems from the inherent properties of the fibers in the composite membrane. In the case of pure PVDF NFM, the discontinuity of fibers in the membrane makes it unable to withstand the stresses applied to the membrane. As the PVB ratio is increased from 0 to 40 wt%, the adhesion between adjacent fibers gradually increases, the nanofibers thicken, and the tensile stress increases with the increased adhesion between adjacent fibers.

The increase in fiber diameter and the formation of inter-fiber adhesion play a key role in the improvement of load-bearing capacity. The electrospun PVDF/PVB membrane exhibited robust strengths of 7.54, 9.18, 9.80, and 13.07 MPa, but when the PVB content exceeded 30 wt%, although the tensile stress was still increasing, the strain began to decrease in the opposite direction. This is due to the gradual increase of the physical bond structure, and the flexibility of the membrane deteriorated due to the interweaving and winding of the nanofibers. On the other hand, the strain of the membrane is also affected due to the increase in the thickness of the membrane. Therefore, the strain curves of the relevant membranes first increased and then decreased.

### 3.4 Effect of thermal treatment on hydrophobic properties

Considering that the composite membranes of physical bonding network was affected by temperature, which can affect the hydrophobic properties. Figure 6. depicted four groups of data before and after heat treatment were tested in the oven at 120°C for 30 minutes. Without adding PVB, because the high melting point of PVDF, heat treatment had no discernible effect on pure PVDF membrane. With the increase of PVB weight ratio of 9/1 to 6/4, the contact angle of composite membrane after heat treatment was obviously higher than that before heat treatment. This change trend can be explained as the bonding structure increased gradually and the porosity decreased with the increase of temperature. The maximum pore size distribution decreased, and the fiber changes from linear connection to three-dimensional bonding structure, which improved the hydrophobicity of the composite membrane and enlarged the contact angle.

### 4. Conclusion

In summary, a waterproof and breathable nanofibrous membranes with enhanced mechanical properties were fabricated by two-step via electrospinning and thermal treatment method. Compared with the previously reported traditional coating treatment, this approach was simple and feasible. The embedded PVB with low softening point imparted the composite membranes with physically bonded structures to decrease the pore size. Moreover, the nanofibers morphology, porous structure, surface wettability of the membranes were systematically optimized, through tuning weight ratio of PVDF/PVB and heating temperature. Therefore, the PVDF/PVB membranes exhibited a sufficient waterproof property of 85.15kPa, and the water contact angle can reach 138.4°, which was much greater than the pristine PVDF membranes, while the resultant membranes also possessed WVT rate of 10.28kg m⁻²d⁻¹. Additionally, due to the enlarged adhesion area, the membranes displayed excellent tensile strength of 13.07MPa, which was much higher than the pristine membranes and other traditional fabrication.
Acknowledgment
This work was supported by the National Natural Science Foundation of China (Grant No. 11702169), Talents Action Program of Shanghai University of Engineering Science (Grant No.2017RC522017) and Shanghai Local Capacity-Building Project (Grant No. 19030501200). This work also supported by National Natural Science Youth Fund (Grant No.21808165), Scientific Research Foundation funds of Shanghai University of Engineering Science (Grant No. 0239-E3-0507-19-05161). Research and innovation project for Postgraduates of Shanghai University of engineering science (Grant No. 0239-E3-0903-19-01399).

References
[1] N. Nawaz, O. Troynikov, C. Watson, “Thermal Comfort Properties of Knitted Fabrics Suitable for Skin Layer of Protective Clothing Worn in Extreme Hot Conditions”J. Advanced Materials Research, vol. 331. pp.184-189. Sept 2011.
[2] A. Ciszewski, J. Kunicki, I. Gancarz, Huizing R. Mérida, Walter, Ko F. “Impregnated electrospun nanofibrous membranes for water vapour transport applications”J. Journal of Membrane Science, vol. 461. pp 146-160. 2014.
[3] T. Maneerung, S. Tokura, R. Rujiravanit. “Impregnation of silver nanoparticles into bacterial cellulose for antimicrobial wound dressing”J. Carbohydrate Polymers, vol. 72. pp 43-51. 2008.
[4] X. Wang, B. Ding, G. Sun. “Electro-spinning/netting: A strategy for the fabrication of three-dimensional polymer nano-fiber nets”J Progress in Materials science, vol. 58. pp 1173-1243. 2013.
[5] G. Andreas, W.H. Joachim. “A Fascinating Method for the Preparation of Ultrathin Fibers” J. ChemInform, vol. 46. pp. 5670-5703. 2007.
[6] A. M. Joshi, V. Mishra, R. M. Patrikar. “FPGA prototyping of video watermarking for ownership verification based on H.264/AVC”J. Multimedia Tools & Applications, vol. 75. pp.3121-3144. 2016.
[7] Y. Li, Z. Zhu, J. Yu. “Carbon Nanotubes Enhanced Fluorinated Polyurethane Macroporous Membranes for Waterproof and Breathable Application” J. Acs Appl Mater Interfaces, vol. 7. pp. 13538-13546. 2015.
[8] Z. M. Huang, Y. Z. Zhang, M. Kotaki. “A review on polymer nanofibers by electrospinning and their applications in nanocomposites”J. Composites science & Technology, vol. 63. pp. 2223-2253. 2003.
[9] J. Sheng, M. Zhang, Y. Xu. “Tailoring Water-Resistant and Breathable Performance of Polyacrylonitrile Nanofibrous Membranes Modified by Polydimethylsiloxane”J. Acs Appl Mater Interfaces, vol. 8. pp. 27218-27226. 2016.
[10] B. K. Kim, K. S. Kim and K. Cho, “Retardation of the surface rearrangement of O2 plasma-treated LDPE by a two-step temperature control,” J. Adhes. Sci. Technol, vol. 15, pp. 1805-181, April 2001.

Figure 1. (a) Schematic diagram of electrospinning for preparation of composite nanofiber membranes;
(b) SEM images of before and after treatment.

Figure 2. (a) Demonstration of the excellent breathable and waterproof properties of the PVDF/PVB. And (b) The mechanism of vapor transmitting across the nanofibrous membranes. (c) Waterproof mechanism based on Young-Laplace equation

Figure 3. SEM images of PVDF/PVB fibrous membranes at different weight ratio (a) 10/0, (b) 9/1, (c) 8/2, (d) 7/3 and (e) 6/4, respectively. (f) Porosity of PVDF/PVB at different weight ratio

Figure 4. (a) Water contact angle (WCA), (b) hydrostatic pressure, (c) air permeability and (d) water vapor transport rate (WVTR) obtained from different weight ratios of PVDF/PVB
Figure 5. Stress-strain curves of PVDF/PVB electrospun membranes at different weight ratios

Figure 6. Water contact angles before and after heat treatment with different PVDF/PVB mass ratios