AIR PERMEABILITY OF NANOFIBER MEMBRANE WITH HIERARCHICAL STRUCTURE

by

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Air permeability is crucial to nanofibrous membrane applications, such as in wound dressing and membrane distillation. Herein, hierarchical structure membrane is prepared layer by layer with different fiber diameters, using electrospinning method. The results showed that with different layer arrangement results in different air permeability, and optimal condition is found.

Key words: *air permeability, hierarchical structure, layer by layer, electrospinning,*

Introduction

Due to the valuable properties including high porosity, high specific surface area, controllable fiber diameter and membrane thickness, nanofibrous membrane has drawn growing interest in both fundamental research and practical applications. Meanwhile, as the most facile method of fabricating nanofiber, electrospinning technique evokes high interest in recent decades. Electrospun nanofiber membrane is given fantastic attention and is applied in many high-tech areas such as wound dressing [1, 2] and membrane distillation [3, 4]. For both of the mentioned applications, air permeability is a key indicator for the practical applications, because good air permeability provides good micro-environment for cell proliferation in wound dressing; and for membrane distillation, better air permeability means better flux. Therefore, there is a growing urge to investigate the membrane air permeability.

Many parameters can affect the air permeability of nanofiber membrane, such as fiber diameter, membrane thickness, surface wettablity of membrane and membrane porosity [5-7]. However, to date, previous studies draw little attention to the effect of membrane configuration on membrane air permeability. Lee *et al.* [8] investigated a fabric with commercial non-woven as support layer and electrospun membrane as barrier layer. The reconstructed membrane exhibited better air permeability than commercial non-woven. Afterwards, Bagherzadeh *et al.* [9] reported a multi-layer fabric using nanofiber membrane as a middle layer. This multi-layer fabric showed better water vapor permeability. Recently, Kang *et al.* [10] constructed a double-layer membrane consisting of microfiber-layer and nanofiber-layer. The resulting membrane showed different air permeability and filtration efficiency compared to commercial non-woven. All these researches indicate that membrane configuration has important influence on air permeability of nanofiber membrane.

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In the present study, multi-layer membrane with different layer diameters was prepared by electrospinning method. Subsequently, the air permeability of different hierarchical structure membrane was investigated.

Experimental

Materials

Poly (vinylidene fluorideco-hexa-fluoropropylene) (PVDF-HFP), *Mw* 400000, was supplied by Aladdin Industrial Corporation, Shanghai, China. N,N-dimethyl formamide and acetone were purchased from Sinopharm Chemical Reagent Co., Ltd. China (Shang Hai, China). Polyacrylonitrile (PAN), *Mw* 150000, was purchased from Beijing Lark Branch Co. Ltd. All reagents were analytical grade and were used as received without further treatment.

Preparation of PVDF-HFP and PAN nanofibrous membrane

The PVDF-HFP was dissolved in a binary solvent system of N,N-dimethyl formamide/acetone (weight ratio of 5:5) at room temperature for 5 hours' stirring, obtaining 10, 13, 16, 19, and 22 wt.% transparent solutions, respectively. For the spinning process, a high electric potential of 12 kV was applied to a droplet of silk fibroin (SF) solution at the tip of a syringe needle (0.8 mm in internal diameter). The electrospun nanofibers were collected on flat aluminum foil which was placed at a distance of 15 cm from the syringe tip. A constant volume-flow rate of 1 mL/h was maintained using a syringe pump. The ambient relative humidity and temperature used in the spinning process were 45±2% and 25±2 °C, respectively, and kept constant. Then, the resulting PVDF-HFP membranes were heated 5 hours at 50 °C using lab oven.

Additionally 4 PVA solutions were prepared using N,N-dimethyl formamide as a solvent, the concentrations were 8, 10, 12, and 14 wt.%, respectively. The voltage is 17 kV. The flow rate was 0.5 mL/h. The distance between needle and collector was maintained in 17 cm.

Measurement and characterization

The morphology of electrospun PVDF-HFP and PAN nanofibers was observed using a SEM, Hitachi S-4800, Tokyo, Japan. The diameters of nanofibers were calculated by measuring at least 100 fibers at random using Image J program. The air permeability of PVDF-HFP membrane was measured by an air permeability tester (YG461E, Tianjin, China). To minimize the error, each PVDF-HFP concentration was spun with 10 minutes. Meanwhile, for air permeability test, each sample was tested for ten times, and the ultimate value is the average of the ten results. The filtration efficiency of PAN composite membranes was measured by automatic filter tester (TSI1830, USA).

Results and discussion

Figure 1 shows the morphology and diameter of electrospun PVDF-HFP nanofibers with varying PVDF-HFP concentrations. It can be clearly seen that: all the resulting PVDF-HFP nanofibers showed smooth surface and the fiber diameter increased with the increase of PVDF-HFP concentration, from 123.5±16.8 nm of 10% to 697.8±42.3 nm of 22%. The fiber diameter was relative to the pore size which affects the pore size distribution and porosity of membrane [11], and at last governs the air permeability of membrane [6, 12]. The smooth surface, uniform and wide diameter rage of resulting PVDF-HFP membrane makes it possible to reconstruct the membrane with hierarchical structure.

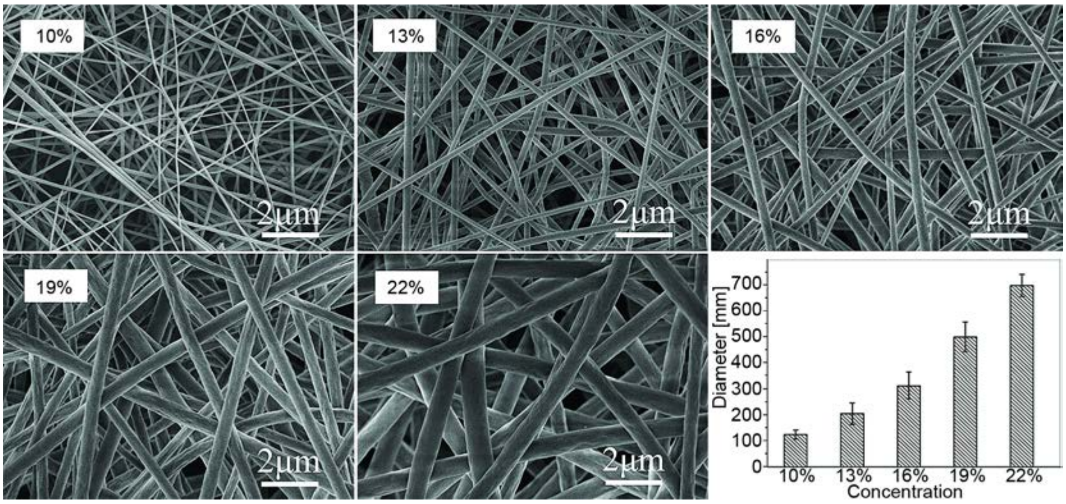

Figure 1. Morphology and diameter of electrospun PVDF-HFP with different concentrations

Inspired by the natural silkworm cocoon [13], hierarchical membrane with different diameter of single-layer was prepared by electrospinning. For the spinning process, every layer was spun with 10 minutes. For 10/13/16/19/22 hierarchical structure, fig. 2(b), 10 wt.% solution was first spun with 10 minutes, following sequentially by 13, 16, 19, and 22 wt.% solutions. After this procedure, hierarchical membrane was fabricated. As shown in fig. 2, the 10/13/16/19/22 hierarchical structure exhibited better air permeability than that for 22/19/16/13/10 hierarchical structure, tab. 1, indicating that hierarchical membrane from small pore size to large pore size is an optimized strategy. It was noting that with the increase of differential pressure the air permeability gap between 10/13/16/19/22 hierarchical structure and 22/19/16/13/10 hierarchical structure increased.

Table 1. The air permeability of different PVDF-HFP structure at different pressure

Membrane structure	50 Pa	100 Pa	150 Pa	200 Pa
10/13/16/19/22	24.71±0.25	52.16±0.26	73.16±0.28	102.96±0.27
22/19/16/13/10	20.61±0.23	44.02±0.25	59.16±0.27	81.27±0.28

The results of fig. 2 show that membrane configuration is also crucial to air permeability of membrane. Therefore, other two strategies were put forward, as shown in fig. 3.

Three single-layers with different diameters, fig. 3(a), were used and two symmetrical structures were presented in figs. 3(b) and 3(c). Interesting, the air permeability of the 22/16/10/16/22 symmetrical structure is better than the 10/16/22/16/10 symmetrical structure, see fig. 3(d) and tab. 2. Additionally, the air permeability gap between the two membranes also increased with the increase of differential pressures, conforming that membrane configuration has crucial influence on air permeability of membrane.

Figure 4 shows the morphology and diameter distribution of electrospun PAN nanofibers with different concentrations. It is obvious that the fiber diameter increases with the increase of concentration of PAN solution.

We studied the filtration efficiency filtration resistance for different structures, the fibers were spun onto a non-woven with different PAN solutions and different spinning peri-

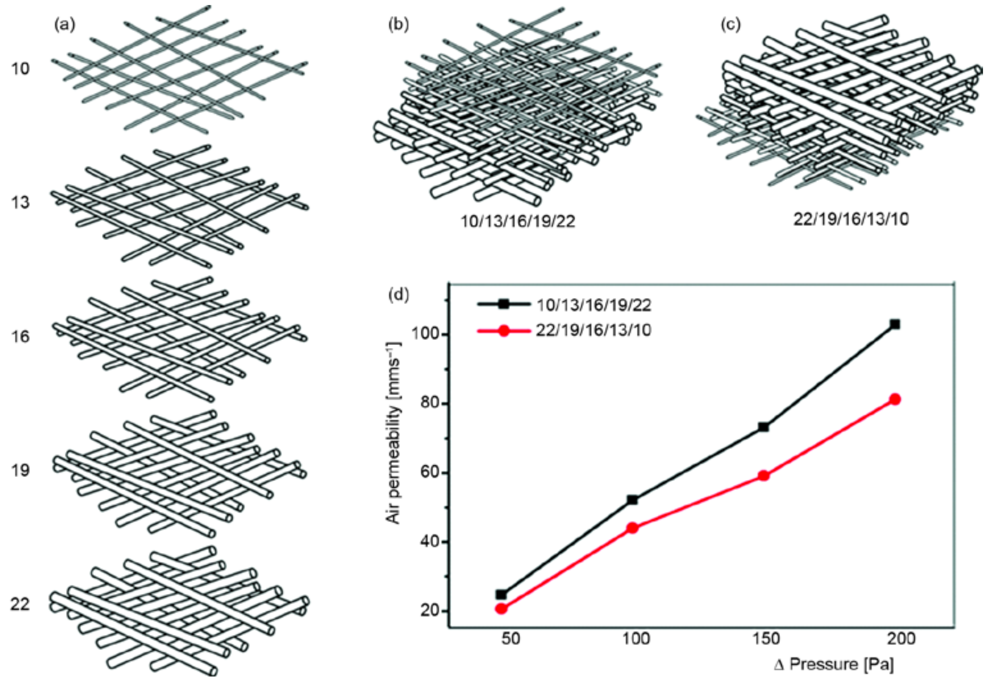

Figure 2. Schematic diagram and air permeability of reconstructed hierarchical membrane; the number implies the concentration

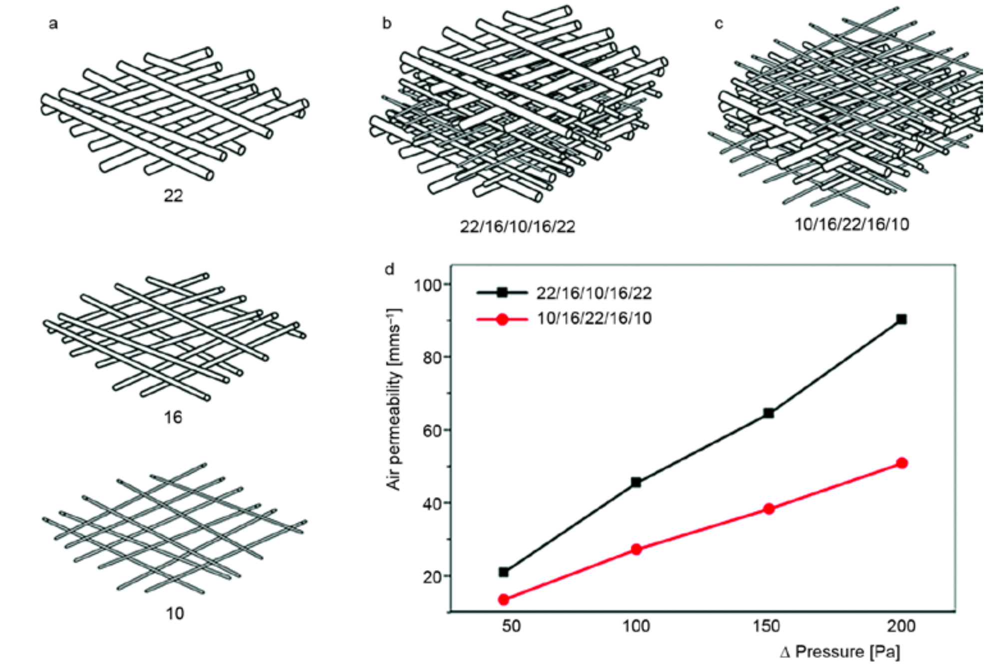

Figure 3. Schematic diagram and air permeability of reconstructed hierarchical membrane; the number implies the concentration

Table 2. The air permeability of different PVDF-HFP structure at different pressure

Membrane structure	50 Pa	100 Pa	150 Pa	200 Pa
22/16/10/16/22	20.91±0.22	45.47±0.24	64.49±0.23	90.19±0.25
10/16/22/16/10	13.46±0.18	27.2±0.19	38.32±0.21	50.86±0.23

ods, the results were given in tab. 3. It is obvious that a minimal filtration resistance of 125.5 Pa was observed for the 8/10/12/14 structure where the fiber diameters increase gradually. However, an opposite 14/12/10/8 structure saw a resistance as high as 230.0 Pa, almost twice of the 8/10/12/14 structure, while its filtration efficiency improved only 8%. The disordered 8/14/10/12 structure had the almost same filtration efficiency as for the hierarchical 8/10/12/14 structure, while its resistance increased greatly from 125.5 Pa to 153.1 Pa.

Table 3. The filtration performance of different PAN structures

Membrane structure	Spinning period [minutes]	Flow rate [L per minute]	Filtration resistance [Pa]	Filtration efficiency [%]
Non-woven	0	85.1	11.1	6.9
8/10/12/14	10/10/10/10	85.0	125.5	82.8
14/12/10/8	10/10/10/10	85.1	230	90.47
8/14/10/12	10/10/10/10	84.9	153.1	83.7
8/10/12/14	10/10/20/20	85.2	298.5	96.68
14/12/10/8	10/10/20/20	85.0	356.5	97.12

Conclusion

Different membrane configurations were prepared by electrospinning with hierarchical structure. Three strategies were used in constructing the multi-layer membrane. The results show that a membrane with hierarchical structure performs optimally with low resistance and high air permeability, which benefits the membrane application in wound dressing and membrane distillation.

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References

[1] Lowe, A., *et al.*, Electrospun Nitric Oxide Releasing Bandage with Enhanced Wound Healing, *Acta biomaterialia, 13* (2015), Feb., pp. 121-130
[2] Helary. C., *et al.*, Evaluation of Dense Collagen Matrices as Medicated Wound Dressing for the Treatment of Cutaneous Chronic Wounds, *Biomaterials Science, 3* (2015), 2, pp. 373-382
[3] Drioli, E., *et al.*, Membrane Distillation: Recent Developments and Perspectives, *Desalination, 356* (2015), Jan., pp. 56-84
[4] Wang, P., *et al.*, Recent Advances in Membrane Distillation Processes: Membrane Development, Configuration Design and Application Exploring, *Journal of Membrane Science, 474* (2015), Jan., pp. 39-56

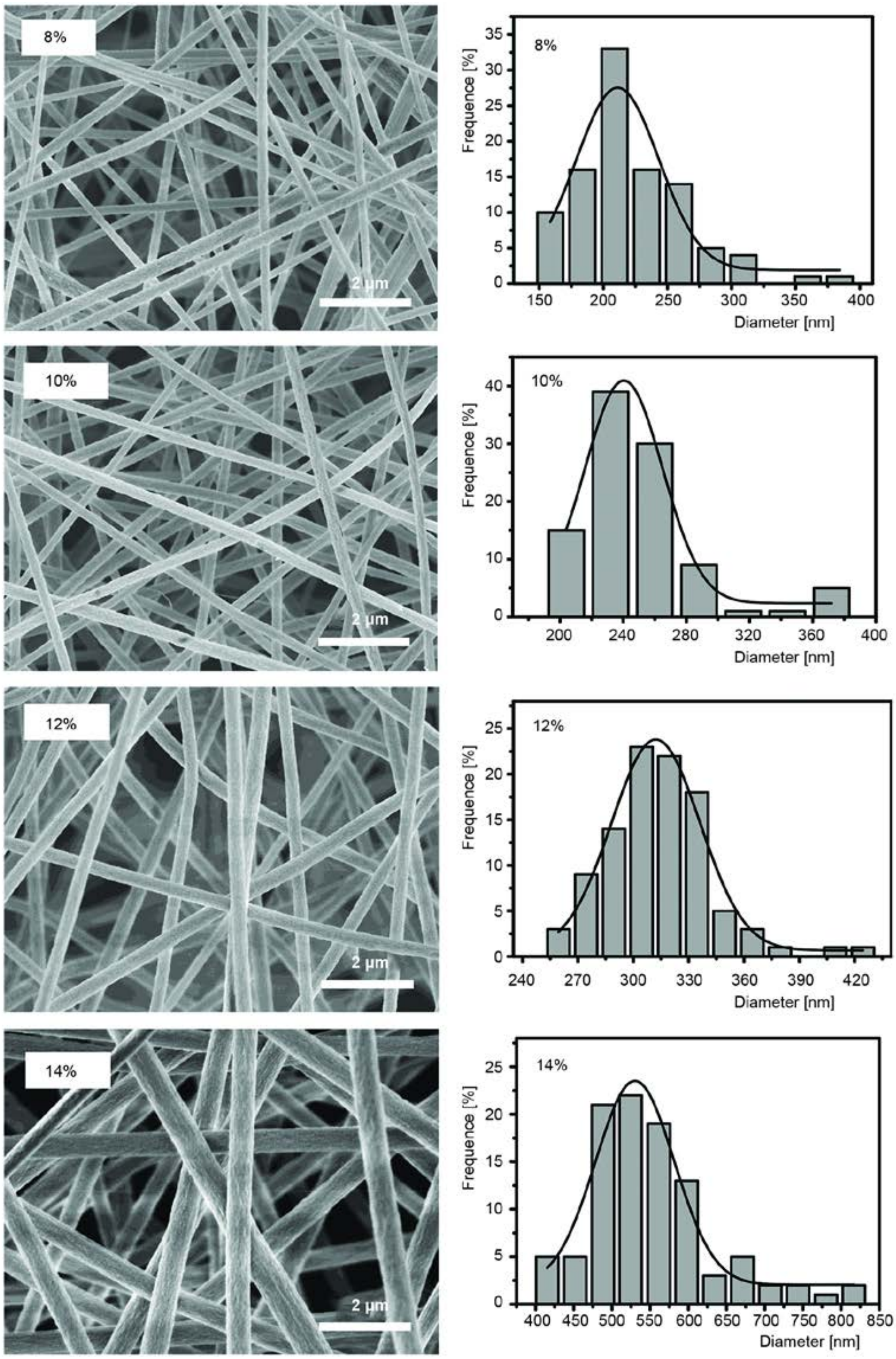

Figure 4. Morphology and diameter distribution of electrospun PAN with different concentrations

[5] Sadighzadeh, A., *et al.*, Synthesis of Polymeric Electrospun Nanofibers for Application in Waterproof-Breathable Fabrics, *Polymer Engineering & Science, 56* (2016), 2, pp. 143-149
[6] Abuzade, R. A., *et al.*, Air Permeability of Electrospun Polyacrylonitrile Nanoweb, *Journal of Applied Polymer Science, 126* (2012), 1, pp. 232-243
[7] Yang, K., *et al.*, Repeatability and Reliability of New Air and Water Permeability Tests for Assessing the Durability of High-Performance Concretes, *Journal of Materials in Civil Engineering, 27* (2015), 12, 04015057
[8] Lee, S., *et al.*, Transport Properties of Layered Fabric Systems Based on Electrospun Nanofibers, *Fibers and Polymers, 8* (2007), 5, pp. 501-506
[9] Bagherzadeh, R., *et al.*, Transport Properties of Multi-Layer Fabric Based on Electrospun Nanofiber Mats as a Breathable Barrier Textile Material, *Textile Research Journal, 82* (2012), 1, pp. 70-76
[10] Kang, Y. O., *et al.*, Morphological and Permeable Properties of Antibacterial Double-Layered Composite Non-wovens Consisting of Microfibers and Nanofibers, *Composites Part B: Engineering, 75* (2015), June, pp. 256-263
[11] Rangou, S., *et al.*, Self-Organized Isoporous Membranes with Tailored Pore Sizes, *Journal of Membrane Science*, *451* (2014), Feb., pp. 266-275
[12] Houdali, A., *et al.*, Immobilizing Hydroxyapatite Microparticles on Poly (Lactic Acid) Non-Woven Scaffolds Using Layer-by-Layer Deposition, *Textile Research Journal*, *87* (2017), 16, pp. 2028-2038
[13] Blossman-Myer, B., *et al.*, The silk Cocoon of the Silkworm, Bombyx Mori: Macro Structure and Its Influence on Transmural Diffusion of Oxygen and Water Vapor, *Comparative Biochemistry and Physiology Part A: Molecular & Integrative Physiology, 155* (2010), 2, pp. 259-263

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