

Electrospun PVDF nanofibrous membranes effectively capturing PM_{2.5} and releasing negative ions

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Abstract. Polyvinylidene fluoride (PVDF) nanofibrous membranes doped with negative ion powder were fabricated by electrospinning, which were aimed to efficiently capture PM_{2.5} and robustly release negative ions. Different fiber morphologies were formed by regulating the solution concentration. The effect of solution concentration on air filtration property and negative ion release capacity of the PVDF membranes was also investigated. The results show that with the increase of PVDF concentration, bead-on-string fibers are formed firstly and then smooth fibers with larger diameters can be obtained. The filtration efficiency and the pressure drop increase initially and then decrease. The quality factor of the membrane is highest when the PVDF concentration is 17 wt%. The negative ion release amount is small due to the formation of bead-on-string structure at low solution concentration; then it reaches the highest value of 2026 ions/cm³ when the PVDF concentration is 17 wt%. However, further increase of the solution concentration intensify the covering of polymeric components on negative ion powder, therefore, the negative ion release amount reduces gradually.

1. Introduction

With rapid urbanization and industrialization, many environmental problems have emerged. Particularly the PM_{2.5}, one of the major sources of air pollution, has posed grave health threats to human extrapulmonary organs and the respiratory tract [1]. According to a report by the United States Environmental Protection Agency, more than 2 million people died worldwide because of the increasing level of PM_{2.5} [2]. Therefore, high performance filters with excellent air filtration property are in urgent need. Furthermore, air filtration materials with the function of providing healthcare have gained more and more attention. Negative ions can cure asthma, chronic bronchitis, hypertension, and boost the immune system [3]. Herein, artificial generation of negative ions in air is a very useful approach for protecting human health. Electrospinning has gained more and more appeal as an efficient and versatile technique that manufactures sub-micron to nanoscale fibers through an electrically charged jet of polymer solution [4]. Electrospun nanofibrous membranes exhibit attractive features such as ultrathin fiber diameter, high porosity and the ease of functionalization, making them suitable candidate for advanced filtration material production [5].

For the reasons above, electrospun polyvinylidene fluoride (PVDF) nanofibrous membranes doped with negative ion powder, which were capable of releasing negative ions for healthcare and efficiently capturing PM_{2.5}, were introduced in this study. Fiber morphologies were subtly controlled by tuning the solution concentration. The effect of solution concentration on filtration efficiency, pressure drop and negative ion release amount of the PVDF membranes was systematically analyzed.

2. Experimental



2.1. Materials

Industrial-grade polyvinylidene fluoride (PVDF, $M_w=660000$) was supplied by Wuxi united Hengzhou chemical Co., Ltd., China. Negative ion powder (with an average particle size of 50 nm) was supplied by Zhengzhou Shengyu chemical products Co., Ltd., China. N,N-Dimethylformamide (DMF, analytical pure) was supplied by Jinan Hengrui chemical Co., Ltd., China. The polypropylene nonwoven substrate (with negligible filtration efficiency of 3% and pressure drop of 2 Pa under the airflow velocity of 32 L/min) was provided by Hebei Hongrun new fabrics Co., Ltd., China.

2.2. Preparation of polymer solutions

Negative ion powder was dissolved in DMF solvent by keeping the negative ion powder concentration of 9 wt%; then PVDF was added to the mixture with vigorous stirring for 16 h at 80 °C. The resultant PVDF concentrations were 15, 17, 19 and 21 wt%, respectively.

2.3. Electrospinning of PVDF nanofibrous membranes

The nanofibrous membranes were fabricated on the DT-1003 electrospinning equipment (Dingtong science and technology Co., Ltd., China). The polymer solution was loaded into a syringe and ejected through the metal needle with a feed rate of 1 mL/h. A direct voltage of 20 kV was applied at the tip of the needle. The nanofibrous membranes deposited on the tumbling barrel covered by the nonwoven substrate, which rotated at a velocity of 60 r/min. The tip-to-collector distance was 15 cm. The temperature and the relative humidity during electrospinning were maintained at 25 °C and 45%.

2.4. Characterization

The morphology of the PVDF membranes was studied by the scanning electron microscope (SEM, TM3000, Hitachi Ltd., Japan). The fiber diameter was measured by image processing software (Image J 1.40G). The negative ion release amount was analyzed by a negative ion detector (KEC-900+, Shanghai IBS instrument equipment Co., Ltd., China). The TSI8530 automated filter tester (TSI, Inc., MN, USA) was used to test the filtration efficiency and the pressure drop of the membranes. Neutralized NaCl aerosol particles of 300 nm mass median diameter were delivered from TSI8530 with a fixed airflow velocity of 32 L/min. To comprehensively evaluate the filtration property of the nanofibrous membranes, the quality factor (QF) [6] was calculated according to equation (1).

$$QF = -(\Delta p)^{-1} \ln(1 - \eta) \quad (1)$$

Where η and Δp were the filtration efficiency and the pressure drop across the filter, respectively. A large quality factor value indicated good filtration performance.

3. Results and discussion

3.1. Effect of solution concentration on morphology of the PVDF membranes

The SEM images of the PVDF membranes obtained by varying the PVDF concentration were shown in figure 1, and the average fiber diameters of the corresponding PVDF membranes were displayed in figure 2. It can be seen in figure 1 that all the nanofibrous membranes had randomly oriented three-dimensional structures. Figure 1 (a) showed that bead-on-string fibers were electrospun from the 15 wt% PVDF solution. The fibers were composed of thin fibers with an average diameter of 163 nm and micro-sized spindle-shaped beads along the fiber axis. This could both be ascribed to the low solution viscosity at low solution concentration. When the PVDF concentration was 17 wt%, the bead-on-string structure disappeared and the average fiber diameter increased slightly to 197 nm. Further increasing the PVDF concentrations to 19 and 21 wt%, no beads could be observed in figure 1 (c)-(d), and the average fiber diameters were 406 and 623 nm, respectively. These changes in fiber morphology could be attributed to the increase of the solution viscosity caused by the increased solution concentration. A higher viscoelastic force helped suppress the surface tension of the polymer solution and prevent the jet from collapsing into droplets before the solvent evaporated, thus bead-free fibers with larger diameters occurred [7].

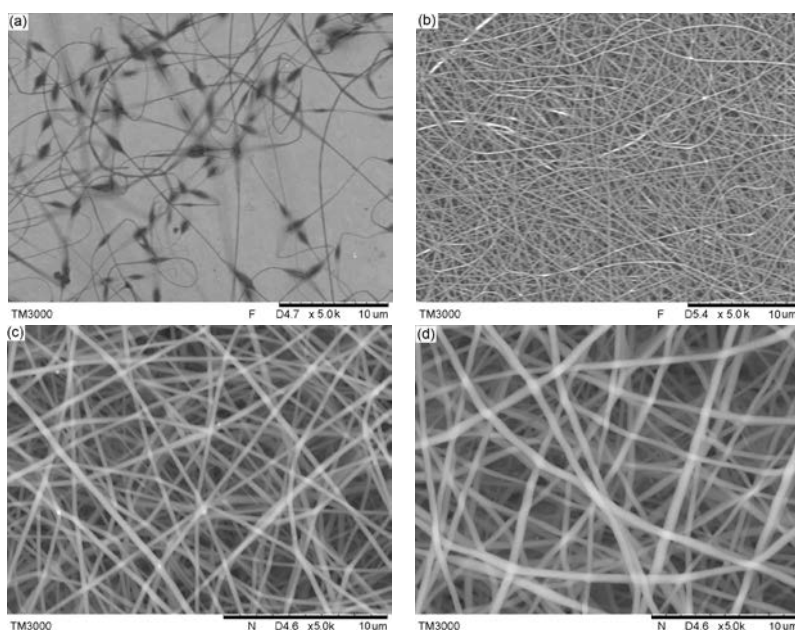


Figure 1. SEM images of the PVDF membranes formed at different solution concentrations of (a) 15 wt%, (b) 17 wt%, (c) 19 wt% and (d) 21 wt%.

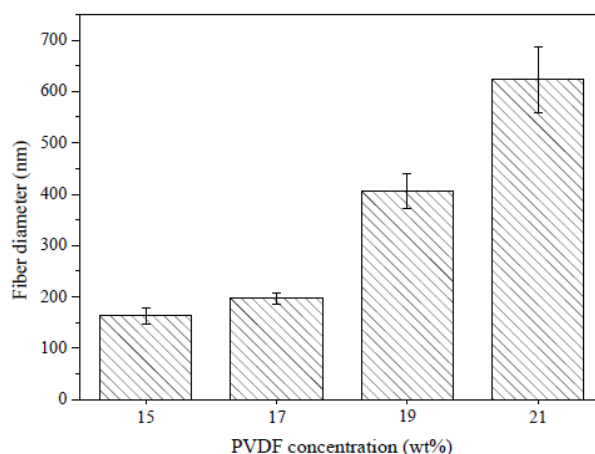


Figure 2. Average fiber diameters of the PVDF membranes fabricated at different PVDF concentrations.

3.2. Effect of solution concentration on air filtration property of the PVDF membranes

The filtration efficiencies of the PVDF membranes (basis weight of $\sim 1.5 \text{ g/m}^2$) fabricated from 15, 17, 19 and 21 wt% solutions were 67.7%, 97.5%, 92.9% and 83.5%, and their pressure drops were 76, 108, 101 and 90 Pa, respectively, as presented in figure 3. Both the lowest filtration efficiency and the pressure drop of the membrane from 15 wt% PVDF solution could be attributed to the wide distribution of beads, which was in favour of air permeability but hindered the fine airborne particles capture. With the aid of continuous and thin fibers, the membrane from 17 wt% PVDF solution had the highest filtration efficiency and relatively low pressure drop. Further increasing the PVDF concentrations to 19 and 21 wt%, the filtration efficiencies dropped rapidly with the increased fiber diameter, meanwhile, the pressure drops decreased rapidly owing to the thicker fibers without beads. The quality factor values of the PVDF membranes were 0.0149, 0.0342, 0.0262 and 0.0200 Pa^{-1} when the solution concentrations were 15, 17, 19 and 21 wt%, respectively, as shown in figure 4. It could be seen that the membrane from 17 wt% PVDF solution possessed the highest quality factor, further

implying the important role of fine fiber diameter and continuous fiber morphology in the construction of nanofiber filter materials.

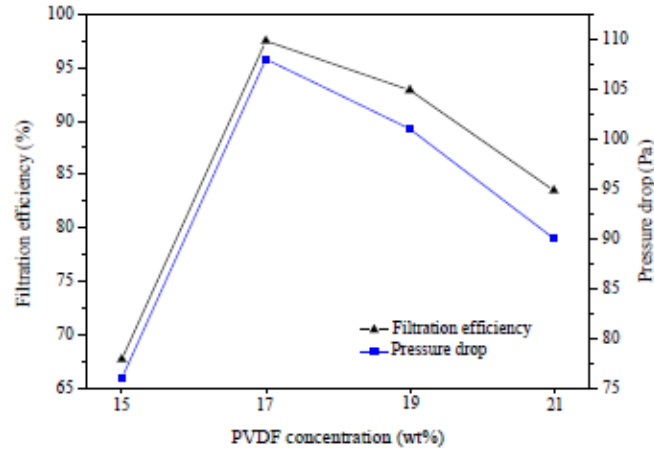


Figure 3. Filtration efficiency and pressure drop of the membranes fabricated at different PVDF concentrations.

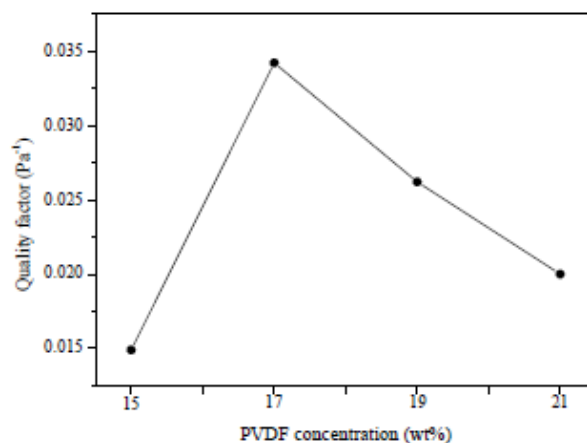


Figure 4. Quality factor of the membranes fabricated at different PVDF concentrations.

3.3. Effect of solution concentration on negative ion release amount of the PVDF membranes

Figure 5 presented the curve between PVDF solution concentration and the negative ion release amount of the relevant membrane. It can be found that the negative ion release amount decreased constantly from 2026 to 1329 ions/cm³ as the PVDF concentration increased from 17 to 21 wt%. Since less negative ion powder could be naked on the surface of the fibers to aggravate the shielding effect of polymeric components from the electric potential difference between the particles of the negative ion powder, as a result, the negative ion release amount showed a decreasing trend. However, further decrease of the PVDF concentration to 15 wt% led to a significant reduction of the negative ion release amount to 1072 ions/cm³. This was mainly because the formation of the bead-on-string structure, which stored a lot of negative ion powder in the beads.

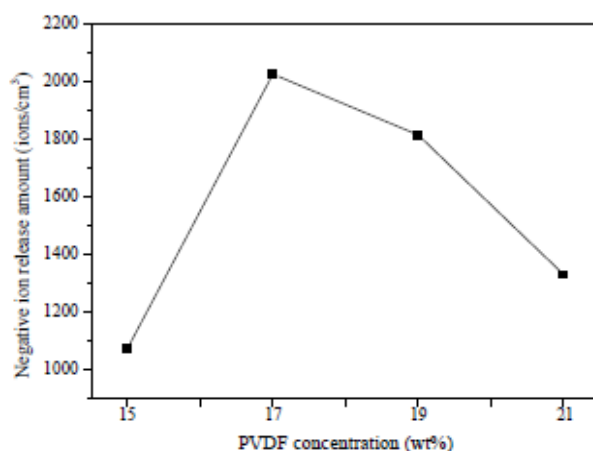


Figure 5. Negative ion release amount of the membranes fabricated at different PVDF concentrations.

4. Conclusion

PVDF nanofibrous membranes capable of releasing negative ions and effectively capturing PM_{2.5} have been successfully prepared. The morphologies of the PVDF nanofibers are controllable by regulating the solution concentration, which are highly important to air filtration and negative ion release. Results indicate that bead-on-string fibers are formed when the PVDF concentration is 15 wt%, and then smooth fibers with larger diameters are obtained as the solution concentration increases. The filtration efficiency and the pressure drop increase initially and decrease gradually. When the PVDF concentration is 17 wt%, the quality factor of the membrane reaches its highest value. Thin fiber diameter is conducive to the improvement of negative ion release amount. On the contrary, thick fiber intensifies the covering of polymeric components on negative ion powder, leading to the reduction of the negative ion release amount. Ultimately, the nanofibrous membrane possesses a high PM_{2.5} purification efficiency of 97.5%, low pressure drop of 108 Pa and good negative ion release amount of 2026 ions/cm³ when the PVDF concentration is 17 wt%.

5. References

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Acknowledgments

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