1. Introduction

In recent years, air pollution such as haze has seriously affected the normal life of people. In many developing countries, many kindergartens and elementary schools have been closed, several high-speed roads have been temporarily closed, and many flights have been delayed due to the serious hazy weather in autumn and winter every year. [1–5] PM 2.5 is the most harmful one to people’s health among all the components of haze, which refers to the small particulates with a diameter of 2.5 micrometers or less.

At present, the most effective method to control PM 2.5 is to purify the air by filter material and the most popular filter material is melt-blown nonwoven. However, for common melt-blown nonwoven the filtration efficiency is usually low. [10,11] Because of the ultra-fine microporous structure composed of its own ultra-fine fibers, nanofiber filter material attracts more and more attention. [12,13] Ding et al. [14] designed and prepared a polyamide 6 (PA6) / polyacrylonitrile (PAN) / PA6 high-efficiency filter membrane with “sandwich structure” by electrospinning technology, which has an excellent filtration efficiency (99.999%) and a low filtration resistance (117.5 Pa). Yun et al. [15] prepared a polyacrylonitrile (PAN) nanofiber membrane with an average diameter of 270–400 nm and compared them with commercial polyolefin and fiberglass filters, and the former one showed a superior filtration efficiency.
performance. Ahn [16] prepared an electrospun nanofiber felt of PA6 with an average diameter of 80-200 nm and its filtration efficiency is 99.993%, which is higher than the common high-efficiency particulate air filter (HEPA).

Among many nanofiber filtration products, nanofiber window screening is a more direct, practical and effective, which can not only effectively isolate the outdoor particulate pollutants, but also maintain good air permeability and light transmission. Some researchers have done a lot of researches on this product[17]. Liu et al [18] prepared a silicon nitride elector doped polyurethane nanofiber window netting by electrostatic spinning technology. When the nanofiber membrane weighed 1.22 g/m², the filtration efficiency and filtration resistance were 79.36% and 25 Pa respectively, and this material can also keep a good light transmittance (about 60%). Khalid et al [19] have developed a blow-spinning method for fabricating nanofiber window screens on a large scale. The product achieved a transparent air filter with an optical transparency of 80% and a standard removal efficiency level of over 99% for PM 2.5. However, as a window screening product, one of the biggest challenges is the problem of aging materials. Whether they can resist the ultraviolet rays from the sunshine and the oxidation in the air environment for a long time, determines the feasibility of the application for window screening. Nevertheless, there is little research in this area[20,21].

In this study, a combined anti-aging agent (UV1/AN-1135) modified polyurethane nanofiber membrane was prepared by electrospinning, and then this membrane was used to fabricate window screens with a sandwich structure by ultrasonic compounding with glass fiber and polyester mesh. The effects of anti-aging agents on the morphology, filtration properties, and mechanical properties of nanofibers were systematically studied, and the optimal process scheme was found. This research will help improve the durability of the nanofiber window screening and promote the commercialization of the product.

2. Experimental

2.1 Laboratory equipment and raw materials

Polymer: TPU (marked as PU), MW=1000-6000, BASF 1190A10, Germany; Solvent: N, N-dimethylformamide (DMF), analysis pure, Xilong science; tetrahydrofuran (THF), analysis pure, Komeio chemical reagent. Lithium chloride (LiCl), analytical purity, Chinese medicine chemical reagent; compound anti-aging agent: anti-ultraviolet agent UV1 (molecular weight: 292.34), antioxidant AN-1135 (molecular weight: 390.6), Shandong Dedazhi. The chemical structure of UV1 and AN-1135 are shown in Fig. 1.

MYP12-2-100 W electric agitator, Guangzhou Huruiming instrument; DF-101 s collector constant temperature heating oil bath pot, Lichen science, and technology; DSA 100-GL 1- 2.8 L ultrasonic cleaning machine, Zhengzhou Hengya machinery; DDS- 307 conductivity meter, Shanghai instrument electrical science instrument; RAVV- 1 digital viscometer, Shanghai Yueping scientific instrument; Handy series electrospinning machine, Yongkangle industry; Phenom Pure desktop scanning electron microscope (SEM), compound scientific instrument (Shanghai); quv UV accelerated aging testing machine, US QL-Labs; YG 461 E-III automatic air permeability tester, Ningbo Textile instrument Factory; CARY 5000 UV visible near-infrared spectrophotometer, Agilent science and technology; INSTRON 3365 universal power machine, Instron (Shanghai); 8130 A automatic filter material detector, TSI, USA.

2.2 Preparation of the spinning solution

Dissolve a certain amount of LiCl into the mixed solvent of DMF/THF, configure LiCl solution with LiCl content of 0.3 wt%, heat oil bath at 40 °C, stir for 3 h, add PU particles to LiCl solution (PU concentration is 14%), stir mechanically at room temperature for 24 h, then add appropriate amount of UV1/AN-1135 (UV1 to AN-1135 mass ratio 1:1) in the solution, stir mechanically for 24 h at room
temperature. The spinning solution with UV1/AN-1135 content of 0, 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt% was prepared.

2.3 Preparation of the nanofiber membrane

The nanofibers were prepared by electrospinning. The prepared spinning solution is injected into the syringe, and the positive pole and the negative pole of the high voltage generator are connected with the needle and the collecting device of the syringe, respectively. The nylon screen was attached to the drum to receive nanofibers, and the gram weight of the nanofiber membrane was controlled by spinning time. The spinning conditions were as follows: the receiving distance was 18 cm, the spinning voltage was 20 kV, the spinning flow rate was 0.2 ml/h and the winding speed was 100 mm/min; indoor temperature 26 ̊C; indoor humidity 30%. The schematic diagram of the spinning principle is shown in the Fig. 2.

![Fig. 2 Schematic diagram of preparation principle of nanofibers.](image)

2.4 Conductivity and viscosity tests/measurements of the spinning liquid

The viscosity and conductivity of the above spinning solution were measured by RVAV-1 digital viscometer (Shanghai Yueping Scientific instrument Co., Ltd) and DDS-307 conductivity instrument (Shanghai Yiping Scientific instrument Co., Ltd). The average value of viscosity and conductivity was obtained by 5 measurements.

2.5 Characterization and test of the nanofibers

The surface morphology of the fiber was observed by Phenom scanning electron microscope (SEM). The prepared nanofiber membrane was pasted on the sample table with double-sided conductive adhesive. The test conditions were as follows: the gold spraying time was 60 s, the current was 10 mA, and the scanning voltage was 10 kV. About 100 nanofibers were randomly selected in electron microscope photos to test the average fiber diameter.

2.6 Ultraviolet-visible spectrum test of the nanofiber membrane

Agilent technology CARY 5000 UV-visible near-infrared spectrophotometer was used to test the nanofiber membrane before and after adding the aging agent, and the scanning wavelength range was 200-800 nm.

2.7 Air permeability tests of nanofiber membrane

YG461E-III automatic breathability meter was used to test the air permeability of the nanofiber membrane. Test the pressure difference of 100 Pa, test the area of 200 cm², select the automatic mode, cut 20 cm² nanofiber membrane as the sample, and test the air permeability of the screen window.

2.8 Mechanical properties test of the nanofiber membrane

The nanofiber membrane spun with the same gram weight was cut into a 5 mm × 100 mm square sample. The strength and elongation of the sample were tested on the all-purpose strength machine of INSTRON, and the stress-strain curve was obtained. Each sample was tested 20 times and the average value was calculated. The clamping length was 30 mm and the tensile rate was 5.00 mm/min.

2.9 Filtration performance test of the nanofiber membrane

The nanofiber membrane spun with the same gram weight was cut into a 15 cm × 15 cm square, and the filter resistance and filter efficiency were tested by using the 8130A filter resistance test machine. Test air volume: 26 L/min, aerosol particles: NaCl (particle size: 0.3 microns). Each sample was tested 20 times and the average result was calculated.

3. Results and discussion

3.1 Morphology analysis of the nanofibers

The morphology of the nanofiber membrane was analyzed. Table 1 shows the conductivity, viscosity, and the average diameter of the spinning solution.

| UV1/AN-1135 content (wt%) | Conductivity (µs · cm⁻¹) | Viscosity (mPa·s) | Average fiber diameter (nm) |
|---------------------------|--------------------------|------------------|-----------------------------|
| 0                         | 100.96                   | 1473             | 151.99                      |
| 0.5                       | 110.21                   | 1480             | 142.66                      |
| 1                         | 112.85                   | 1485             | 135.97                      |
| 1.5                       | 117.52                   | 1489             | 148.17                      |
| 2                         | 118.35                   | 1521             | 162.73                      |
with different UV1/AN-1135 contents. Fig. 3 shows the electron microscope photos of nanofibers with different UV1/AN-1135 contents.

As shown in Fig. 3, the morphology of fiber kept almost unchanged after adding UV1/AN-1135. As shown in Table 1, along with the increase of the content of UV1/AN-1135, the fiber diameter of 151.99 nm (UV1 / content of the AN-1135 0) is reduced to 135.97 nm (UV1 / content of the AN-1135-1 wt%), and with the further increase of UV1/AN-1135 content, the fiber diameter increases from 135.97 nm to 162.73 nm (UV1 / content of the AN-1135 2 wt%). The reason is that along with the increase of the content of UV1/ the AN-1135, the spinning fluid conductivity and viscosity increase, while the spinning fluid flow speed and the surface tension increase at the same time, which leads to an insufficient drafting of PU polymer under electric field force.

3.2 Ultraviolet-visible spectrum analysis of the nanofiber membrane

The UV-vis spectra of the nanofiber membrane was analyzed. Fig. 4 shows the UV transmittance curves of the nanofiber membrane with different UV1/AN-1135 contents.

It can be seen from Fig. 4 that before UV1/AN-1135 was added, the UV transmittance of the nanofiber membrane was lower and the UV absorption rate was higher; after the addition of UV1/AN-1135, the near-ultraviolet (UVA) transmittance with wavelength of 315-400 nm was significantly reduced, while the near-ultraviolet transmittance gradually decreased with the increase of UV1/AN-1135 content. When the UV1/ content is 0.5 wt%, the AN-1135 near UV transmittance drops rapidly, when the UV1/AN-1135 content is 1 wt%, 1.5 wt%, and 2 wt%, the nanometer fiber membrane UV transmittance curves are relatively close, and the near-ultraviolet transmittance drops while the amplitude become smaller. Thus, UV1/AN-1135 of near-ultraviolet ray has a strong absorption, when the UV1 content reaches to 1 wt% and the AN-1135 nanometer fiber membrane has a strong anti-aging performance. In addition, the curve shows that after adding UV1/AN-1135, the absorption of the nanofiber membrane to the far-ultraviolet ray (UVB) is more obvious. Based on the above analysis, the addition of UV1/AN-1135 results in a low transmittance to both UVA and UVB and a good ultraviolet absorption performance, especially when the content of UV1/AN-1135 reaches 1 wt%.

Further analysis of the nanofiber screens pervious to light, can be seen from the Fig. 4. Also, with different contents of UV1/AN-1135, the 380-780 nm nanofiber membrane in band of visible light transmittance are relatively high, not add UV1/AN-
1135 nanofiber membrane in the AN-1135 380-780 nm band transmission rate above 80%, and with the increase of the content of UV1/AN-1135, the light transmittance of the nanometer fiber membrane decreases. On the one hand, it is because that the UV1/AN-1135 absorbs some wavelengths in 380-400 nm UV light; on the other hand, UV1/AN-1135 makes the surface of the nanofibers have a structure more adhesive, and the fiber structure is more complex, which interferes with the diffraction of the visible light in the fiber membrane, so the penetration rate is reduced.

3.3 Analysis of the air permeability of nanofiber membrane

Air permeability is an important performance of the filter materials. To verify the air permeability of the nanofiber membrane, this work analyzes the air permeability of the nanofiber membrane. Table 2 shows the experimental results of the air permeability of the nanofiber membrane with different UV1/AN-1135.

Table 2 Experimental air permeability results of the nanofiber membrane.

| Compound anti-aging agent content (wt%) | Before the aging Air permeability test results (mm/s) | After aging Air permeability test results (mm/s) |
|----------------------------------------|-----------------------------------------------------|--------------------------------------------------|
| 0                                      | 840                                                 | 847                                              |
| 0.5                                    | 839                                                 | 845                                              |
| 1                                      | 835                                                 | 840                                              |
| 1.5                                    | 840                                                 | 844                                              |
| 2                                      | 845                                                 | 848                                              |

It can be seen from Table 2 that the nanofiber membranes with different compound anti-aging agent contents have a good permeability, and the permeability test results are all above 800 mm/s. The data show that the addition of the compound anti-aging agent has little effect on the permeability of the fiber membrane.

3.4 Mechanical properties analysis of the nanofiber membrane

The mechanical properties of the nanofiber membrane were analyzed. Fig. 5a shows the stress-strain curve of the nanofiber membrane before ultraviolet aging. Fig. 5b shows the stress-strain curve of the nanofiber membrane after ultraviolet aging. The addition of small organic molecules into the polymer will damage the mechanical properties of the polymer material, as shown in Fig. 5c and Fig. 5d. Before aging, the breaking strength and elongation of the PU fiber film continuously decrease with the increase of the anti-aging agent content. However, after the aging test, the mechanical properties (breaking strength and elongation at break) of PU fiber film decreased sharply. After aging, the PU molecular chain inside the fiber will break, so the fiber film became brittle. In the UV1/AN-1135 content range of 0-1%, the mechanical properties of PU nanofiber film after aging treatment was improved with the increase of UV1/AN-1135 content. When the content of anti-aging agent is 1%, the breaking strength of nanofiber film reaches the maximum and the anti-aging performance is the best. However, as the anti-aging agent content continues to increase, the mechanical properties begins to degrade due to the plasticizing effect of the aging agent. By comparing the mechanical properties of PU fiber film before and after aging at the same content, it can be found that the reduction of the mechanical properties was the smallest when the UV1/AN-1135 content was 1%.

3.5 Filtration performance analysis of the nanofiber membrane

Fig. 6a-d are the actual picture, structure, and local enlarged picture of the nanofilament window screening. It can be seen from Fig. 6e that the addition of UV1/AN-1135 has a certain influence on the filtration performance of the nanofiber membrane before the UV aging treatment. With the increase of UV1/AN-1135 content, both of the filtration efficiency and filtration resistance of the nanofiber membrane show a trend of increasing initially and then decreasing. When the UV1/AN-1135 content is 1%,
The filtration efficiency of the nanofiber membrane is maximized (filtration efficiency: 97.195%, filtration resistance: 30.86 Pa). It can be seen from Fig. 6f and Fig. 6g that when the UV1/AN-1135 content is 1%, the nanofiber membrane filtration efficiency before and after UV aging treatment are 97.195% and 96.925% respectively; the filtration resistance are 30.86 Pa and 30.66 Pa respectively. After the UV aging treatment, the filtration efficiency and filtration resistance of the nanofiber membrane with the UV1/AN-1135 content of 0 decrease greatly. With the increase of the UV1/AN-1135 content, the effect of the ultraviolet aging treatment on the quality factors of nanofiber membrane become smaller.

The content of UV1/AN-1135 has a certain influence on the filtration performance of the nanofiber membrane before and after the aging. Adding the UV1/AN-1135 itself can influence the fiber morphology. When the UV1/AN-1135 content is 1 wt%, the fiber diameter is the finest and the morphology is the most uniform, so the nanofiber membrane has the highest filtration efficiency and the maximum filtration resistance. After the UV aging treatment, the internal structure of the nanofiber membrane is damaged to some extent, and the filtration performance is lower than that before the aging treatment. With the increase of the UV1/AN-1135 content, the anti-aging performance of the fiber gradually increases, and the UV aging treatment is applied to the nanometer. The effect of the fiber membrane filtration performance is reduced.

4. Conclusion

In this work, electrostatic spinning technology was used to prepare the PU nanofiber film doped with an anti-UV agent and anti-aging agent, and the nanofiber composite film was successfully applied in the anti-haze window screening of the nanofiber, and the results showed as followed:

When the content of UV1/AN-1135 was 1 wt%, the obtained nanofiber showed a uniform morphology, and the diameter of the nanofiber was the smallest, 135.97 nm. Before and after the anti-aging treatment, at that time, the tensile strength of the nanofiber membrane was the highest, 21.61 MPa. More importantly, with the addition of UV1/AN-1135, the UV resistance of the nanofiber membrane was significantly improved. When the content of UV1/AN-1135 was 1 wt%, the nanofiber membrane had a better filtration resistance and filtration efficiency before and after aging (before aging, the filtration efficiency and filtration resistance were 97.195% and 30.86 Pa respectively; after aging, the filtration efficiency and filtration resistance were 96.925% and 30.66 Pa respectively). Furthermore, the PU/UV-1/AN-1135 nanofiber membrane prepared by us has better mechanical properties, UV resistance, and filtration performance. Therefore, the anti-haze window screening prepared by us will have a great application prospect.
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