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Design of high efficiency PVDF-PEG hollow fibers for air filtration of ultrafine particles

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ABSTRACT

This study reveals as the first attempt to apply hollow fibers for air filtration of ultrafine particles. Different from symmetric nano-fiber filters and non-woven fabrics, asymmetric polyvinylidene fluoride – polyethylene glycol (PVDF-PEG) hollow fibers with high gas permeances have been developed by the dry-jet wet-spinning process. The addition of high molecular weight PEGs in spinning dopes facilitates the formation of loosely connected cross-section and porous outer skin, thus enhances the gas permeance for air filtration. Under the inside-out testing mode, all PVDF-PEG hollow fibers display excellent filtration efficiency of 99.999% against polydispersed NaCl particles with a geometric mean size of ~30 nm. Since permeance increases with an increase in PEG molecular weight in spinning dope, the PVDF-PEG hollow fiber with a PEG molecular weight (MW) of 12,000 Da possesses the highest quality factor because it has the highest permeance and lowest transmembrane pressure. However, the PVDF-PEG hollow fiber with a PEG MW of 8000 Da has the best mechanical properties. Under the dead-end filtration, the filtration efficiency increases with an increase in air flow rate. This trend is contrary to the findings observed in the flat and symmetric fibrous filtration. The asymmetric structure in the cross-section of the newly developed hollow fibers may enhance aerosol deposition via direct impaction and Brownian motion at high flow rates. The dead-end filtration results also show that the quality factor is higher at a lower flow rate. Similarly, the cross-flow filtration results show that the hollow fiber modules operated at low cross-flow ratios have high quality factors. Therefore, it is preferred to operate the newly developed PVDF-PEG hollow fiber at a low flow rate or low cross-flow ratio. This study may provide useful insights for developing hollow fibers for air filtration with the optimal operation conditions.

1. Introduction

Air pollution has become a global issue in the last few decades. Particulate matter (PM) is one of the major air pollutants. $PM_{2.5}$, which refers to particles with an aerodynamic diameter less than 2.5 μm, is particularly harmful to human being [1,2]. Toxicology studies indicate that $PM_{2.5}$ is closely associated with cardiovascular diseases, lung cancers and the increase of mortality, even when exposure to a low concentration of $PM_{2.5}$ (6 $\mu g/m^3$) [3,4]. Recently, the ultrafine particles ($PM_{0.1}$) with an aerodynamic diameter less than 0.1 μm have attracted extensive attention since they are the dominant particles in urban PMs [5]. The sources of $PM_{0.1}$ are from the emissions of power plants, vehicles, and cooking [6]. Comparing to $PM_{2.5}$, $PM_{0.1}$ has a higher deposition efficiency in human body and could cause severe damages to neuronal cells [7]. Therefore, it is essential to eliminate PMs from the atmosphere, specifically the $PM_{0.1}$ particles.

A lot of techniques have been developed to remove or filter PMs from polluted air, such as cyclones, electrostatic precipitators (ESPs) and fibrous filters including high efficiency particulate air (HEPA) filters and nanofiber filters [8,9]. Among them, nanofiber filters for air filtration have been extensively studied in recent years. The nanofiber membranes are usually made of organic or inorganic polymers with fiber diameters ranging between 100–500 nm and pore sizes between 0.2–5 μm [10,11]. It is worth to note that sieving is not the most important mechanism in air filtration [12]. Thus, the porous size of fibrous filters could be larger than the aerosol particles. The most well-known air filtration mechanisms are Brownian diffusion, direct interception, inertial impaction, and gravity settling [12–14]. For particles smaller than 0.3 μm, the filtration is governed by the Brownian diffusion [14,15]. Considering the adverse health effects and the large population, it is crucial to filtrate $PM_{0.1}$. However, most air filtration studies focused on the filtration of particles with a size about 0.3 μm [16–18]. The filtration results for $PM_{0.1}$ are seldom reported [15,19].

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Table 1
Spinning conditions for PVDF hollow fibers.

Hollow fiber ID	PVDF	PVDF-P400	PVDF-P4k	PVDF-P8k	PVDF-P12k
PEG additives (M.W.)	–	400	4000	8000	12,000
Dope composition (%)	PVDF/NMP: 15/85		PVDF/PEG/NMP:15/10/75		
Dope viscosity (mPa s)	3.48 ± 0.06	3.49 ± 0.20	3.54 ± 0.10	3.77 ± 0.10	3.71 ± 0.11
Bore fluid composition (%)			NMP/Water: 60/40		
Spinneret size (ID/OD/L)			1.05/1.6/6.5		
External coagulant composition (%)			IPA/Water 40/60		
Dope flow rate (mL/min)			4		
Bore fluid flow rate (mL/min)			2		
Air gap (cm)			3		
Take up rate (m/min)			Free fall		

Different from most commercially available nanofiber filters that require a supporting media [20], hollow fibers are self-supported. They have been applied to various separations including microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) because of their tunable pore size during membrane fabrication [20–23]. For flat nanofiber filters, the flow of particles is usually perpendicular to the filter surface, while a cross-flow configuration is often adopted in hollow fiber filtration where the particles flow through the hollow fiber in its longitudinal direction [18,24]. As a result, the former tends to form a cake layer on the filter surface with a pressure drop across the filter increasing with time, while the latter possesses the unique feature of cross-flow filtration that reduces the cake formation by tangential flow [25].

Until now, only few studies work on particle-laden gas filtration using the cross-flow configuration [26–28]. Ferrer et al. demonstrated the possibility of cross-flow filtration under high temperatures using ceramic filters [26]. They found that a higher tangential flow limited the cake formation on filter surfaces. In a similar work, Sibanda et al. used polycarbonate filters with a downstream collection device to filtrate limestone dust particles from air [27]. They showed that the deposited particles could be detached by the swept flow over the filters and subsequently removed by a downstream device. By manipulating the cross-flow conditions, the segregation of particles might occur and the trajectories of particles across the filters could be calculated [28]. However, the inner diameter of the filters used in their studies was in the centimeter range which was much larger than hollow fibers. Besides, the size of their aerosol particles was ~5 μm which was also larger than the majority of PMs in air. Furthermore, the aforementioned studies only focused on the cake formation and how the particles pass through the fibers. The particle concentration in the permeate side was not studied.

Polyvinylidene fluoride (PVDF) is a semi-crystalline polymer with characteristics of good mechanical properties, high thermal stability, and excellent chemical resistance [29]. PVDF hollow fibers have been successfully fabricated for various applications including UF and MF because of their excellent intrinsic properties [22,29]. Recently, PVDF nanofiber membranes have been applied to air filtration, showing a high filtration efficiency [30,31]. However, PVDF hollow fibers have not been applied to air filtration. Therefore, we aim to explore the possibility of designing PVDF hollow fibers as membrane for air filtration in this study. The objectives are to (1) develop PVDF-PEG hollow fibers with high gas permeability for air filtration of ultrafine particles; (2) evaluate the filtration performance of the fabricated PVDF and PVDF-PEG hollow fibers, and (3) optimize the filtration conditions, including the filtration flow rate and cross-flow ratio. The results obtained in this study may provide useful insights to develop hollow fibers membranes with suitable operation conditions for air filtration.

2. Experimental

2.1. Materials

The polyvinylidene fluoride (PVDF) polymer (Kynar HSV900) was kindly supplied by Arkema Inc. N-methyl-2-pyrrolidone (NMP, > 99.5) and isopropanol (IPA, HPLC) were purchased from Merck and VWR, respectively and used as a solvent and external coagulant, correspondently. Polyethylene glycols (PEGs) with various molecular weights (MWs) were used as additives in the dope solutions. PEGs with MWs of 400 Da and 4000 Da were obtained from Merck while PEGs with MWs of 8000 Da and 12,000 Da were acquired from Sigma-Aldrich. Sodium chloride (NaCl, 99.5%) was bought from Merck and used in filtration experiments. Deionized (DI) water with the resistivity of 18 MΩ cm was produced by a Milli-Q (MilliPore) system and was used in all experiments.

2.2. Fabrication of PVDF-PEG hollow fiber membranes

The dope solution was prepared by dissolving the PVDF polymer into the solvent, NMP, at 60 °C and stirred for one day. Then, PEG with a certain MW was added into the dope and stirred for another day. The weight percentage of PEG in the final PVDF/PEG/NMP solution was 10%. Prior to spinning, the dope was degassed overnight, and subsequently loaded into an ISCO syringe pump. The PVDF hollow fiber membranes were fabricated via a dry-jet wet spinning technique [32]. The spinning conditions such as bore fluid composition, external coagulant, bore or dope fluid flow rate, and take up speed were the same for all dopes, as listed in Table 1. The hollow fibers were spun at 60 °C. The as-spun PVDF-PEG hollow fibers were immersed in water for 3 days to remove the residual NMP and PEG. Thereafter, the fibers were frozen at −20 °C for 5 h, and then dried in a freeze dryer (S61-Modulyo-D, Thermo Electron Corp.). The PVDF-PEG hollow fibers were named as PVDF-P400, PVDF-P4k, PVDF-P8k, and PVDF-P12k corresponding to the dopes containing PEG additives with MWs of 400, 4000, 8000, and 12,000 Da respectively. For comparison, the PVDF hollow fibers without the PEG additive were also prepared and were named as PVDF.

2.3. Membrane characterizations

The viscosity of PVDF/NMP and PVDF/PEG/NMP dopes was determined using a viscometer (B-one touch, Lamy Rheology). The polymer dopes were heated at 60 °C before the testing. Each measurement was conducted at 50 rpm for 30 s and the average value of five measurements was reported.

The outer and inner diameters (OD and ID) of PVDF and PVDF-PEG hollow fibers were observed by an optical microscope (SZX2-ILLT, Olympus Corp.). The inner and outer surfaces as well as the cross-sectional morphology of the freeze-dried hollow fiber membranes were examined by a field-emission scanning electron microscope (FESEM