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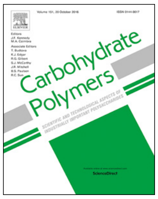

Antibacterial and environmentally friendly chitosan/polyvinyl alcohol blend membranes for air filtration

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ABSTRACT

An antibacterial and environmentally friendly chitosan (CS) /polyvinyl alcohol (PVA) blend membrane for air filtration was prepared via nonsolvent induced phase separation (NIPS) method. The chemical structure, thermal behavior, morphology, mechanical property and surface charge of the resultant CS/PVA membranes were characterized. Results showed that CS and PVA were miscible due to the intermolecular hydrogen bond between them. The blend membrane obtained from over 20 wt.% CS concentration exhibited a gradient interconnected porous structure without skin layer. The air filtration efficiency and pressure drop obtained from CS/PVA membrane with 30 wt.% CS concentration and the thickness of 37 μm under a face velocity of 5.3 cm s^{-1} were 95.59% and 633.5 Pa, respectively. The performance of air filtration obtained is mainly attributed to the direct interception of membrane surface. Further, the antibacterial rate of the blend membrane was up to 94.8% for *E. coli* and 91.3% for *S. aureus*.

1. Introduction

Air pollution, especially particulate matter (PM), has been considered as one of the most serious health threats to the public health, atmosphere visibility, production efficiency, global climate and ecosystems (Apte, Marshall, Cohen, & Brauer, 2015; Huang et al., 2014; Zhang, He, & Huo, 2012). Depending on the particulate size, PM can be classified into PM10 (aerodynamic diameter ≤ 10 μm) and PM2.5 (aerodynamic diameter ≤ 2.5 μm). Herein, PM2.5 has a long lifetime for spreading over thousands of kilometers. It can adsorb toxic pollutants and bacteria in the air due to larger surface areas, and penetrate into the respiratory system and even the blood (Shen et al., 2011; Turner et al., 2011). Therefore, the development of versatile air filters to prevent PM2.5 from invading environment and human body is of great importance (Barhate & Ramakrishna, 2007).

Nowadays, the nanofibers based filter has been verified to be an effective strategy for the removal of sub-micron aerosol (Leung & Hung, 2012). Consequently, many technologies, especially electrospinning have been developed to fabricate nanofibers in recent years (Zhu et al., 2017). This is because the electrospun nanofibers based filter can be prepared by various materials and exhibit controllable morphology and distinctive 3D structures (Jing et al., 2016; Wang & Pan, 2015; Zhang, Tang, et al., 2016). In particular, to further improve the filtration performance or tackle the trade-off between the filtration efficiency and pressure drop, the electrospun nanofibers incorporated with carbon nanotubes (CNT), metal-organic framework (MOF) or polytetrafluoroethylene nanoparticles (PTFE NPs) have been fabricated and show enhanced filtration performance due to the "slip effect" and electrostatic adsorption (Li, Wang, Zhang, & Wei, 2014; Wang, Zhao, Yin, Yu, & Ding, 2016; Zhang, Yuan, et al., 2016). However, unclear biological toxicity of nanoparticles and the dissipation of charges are unavoidable issues (Xiong, Yang, Zhu, Chen, & Dong, 2017). More importantly, the electrospun nanofibers usually suffer from low production rate and instability owning to their weak mechanical property (Singh, Ravi, Sun, & Tan, 2017). Consequently, other innovative approaches have been proposed to prepare the filter media.

For instance, Liu et al. (2015) prepared poly(vinyl alcohol-*co*-ethylene) /TiO_2 (PVA-*co*-PE/TiO_2) hybrid nanofibrous filters via melt phase separation and suspension coating technique. The prepared nanofibers with diameters in a range of 50 nm–300 nm displayed a filtration efficiency of 95.3% owning to the decrease of pore size and the electrostatic absorption of TiO_2 nanoparticles. Further, a different approach

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was described by using organic molecules self-assembly to design nanofibers. The self-assembled nanofibers based air filter reached a filtration efficiency of 89.69% for PM2.5 and 93.08% for PM10 particles (Singh et al., 2017). Very recently, an asymmetric polyvinylidene fluoride-polyethylene glycol (PVDF-PEG) hollow fibers were developed by a dry-jet wet spinning technique and firstly applied to air filtration, which exhibited excellent filtration efficiency of 99.999% against poly-dispersed NaCl particles in both dead-end filtration and cross-flow filtration (Wang, Yong, Yu, & Chung, 2017). However, the pressure drop of the hollow fibers was too high and up to 5000 Pa.

In addition to the preparation methods mentioned above, recent studies have found that nanofibers made from higher polar polymer materials can be used as high-efficient filters (Xu et al., 2018). For instance, Zhang, Zhang et al. (2017) reported that the direct e-spinning chitosan (CS) nanofibers exhibited more timesaving than other polymers in removing PM2.5, which was attributed to the strong polarity, positively charged $NH3^+$ group and smaller diameter. Besides, CS is the second most abundant natural cationic polysaccharide with good membrane forming, biocompatibility and antibacterial ability. However, the mechanical brittleness of CS materials limits the practical applications. It is well-known that polymer blend with flexible-chain polymers is the most common method to improve the brittleness (Sionkowska, 2011). Polyvinyl alcohol (PVA) as a common synthetic polymer possesses good mechanical property and membrane forming, which is able to interact with CS through aggregation, ether-bridge connection and intermolecular hydrogen bond. Moreover, both CS and PVA have biodegradable ability so as to avoid the secondary environment pollution. Up to now, CS/PVA blend membranes have been extensively applied to reverse osmosis desalination, heavy metal adsorption, and wound dressing (Morgado, Miguel, Correia, & Aguiar, 2017; Salehi & Madaeni, 2014; Shafiq et al., 2017).

The aim of this study is to explore a new avenue to tailor an antibacterial and environmentally friendly CS/PVA blend membrane for air filtration. A series of CS/PVA blend membranes with various mass ratios and thicknesses were prepared via NIPS. Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) were adopted in order to explore the miscibility between CS and PVA. Subsequently, the morphology, structure, mechanical property and surface charge were characterized. The filtration performance for NaCl aerosol particles removal was explored. Additionally, the antibacterial ability against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) was also evaluated.

2. Experimental

2.1. Materials

CS powder (M_w = 540 kDa, degree of deacetylation = 87.3%) was purchased from National Pharmaceutical Co., Ltd. (China) and PVA pellet (M_w = 77 kDa, degree of hydrolysis = 88%) was purchased from Tianjin Guangfu Technology Development Co., Ltd. (China). Adipic acid and other reagents were obtained from Tianjin Kermel Chemical Reagent Co. Ltd. (China). Polyethylene terephthalate (PET) nonwoven fabrics with negligible filtration efficiency (3.0%) and pressure drop (3.3 Pa) as supporting in the filtration test was kindly provided by Seattle New Material Technology Co., Ltd. (China). *E. coli* (ATCC8739) and *S. aureus* (ATCC 6538) were obtained from Tianjin Medical University (China). Phosphate buffered saline solution (PBS) (7.16 g L^{-1} $Na_2HPO_4{\cdot}12H_2O$, 1.36 g L^{-1} KH_2PO_4) was prepared in house. Beef extract, peptone, and agar powder were supplied by Tianjin Sanjiang Chemical Technology Co., Ltd. (China).

2.2. Membrane preparation

The CS/PVA membranes with various mass ratios were prepared via NIPS as demonstrated in Fig. 1(a). Firstly, CS solution was prepared by dissolving CS powder in 0.2 mol L^{-1} adipic acid aqueous solution at 30 °C under magnetic stirring for 6 h. And similarly, PVA solution was prepared after dissolving PVA pellet in 0.2 mol L^{-1} adipic acid aqueous solution at 90 °C under mechanical stirring for 3 h and cooled to room temperature. Then, the casting solution was prepared by mixing the two solutions in various mass ratio and stirred until to a homogeneous solution. After degassed, the casting solution was cast on a clean glass plate using an automated membrane applicator (Elcometer 4340, England) with a desired thickness, and then immediately immersed into the coagulation bath of saturated Na_2SO_4 aqueous solution at 20 °C for 30 min. Finally, the prepared membrane was neutralized with 0.1 mol L^{-1} NaOH aqueous solution and rinsed with deionized water to remove the residual alkali and Na_2SO_4. Before characterization, the CS/PVA blend membranes were fully lyophilized. The composition and viscosity of different casting solutions were listed in Table 1. The polymer concentration in all casting solutions was 7 wt.%. The corresponding membranes with different CS concentrations (10–50 wt.%) were named as M10, M20, M30, M40, and M50, respectively.

2.3. Membrane characterization

The chemical structure of CS/PVA blend membrane surface was characterized using ATR-FTIR spectrophotometer (Nicollet NEXUS-670, USA) at 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. The thermal behavior of CS/PVA blend membrane was evaluated by a differential scanning calorimeter (DSC) (DSC 204F1, Germany) operated from 50 °C to 250 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere protection. The crystallinity of PVA component (χ) was calculated as Eq. (1) (Bonilla, Fortunati, Atarés, Chiralt, & Kenny, 2014).

$$\chi\ (\%) = \Delta H/(\Delta H_0 \times w) \times 100\% \tag{1}$$

where ΔH is the enthalpy of melting, ΔH_0 is the enthalpy of melting for 100 wt.% crystalline PVA, which is 156 J g^{-1}, and w is PVA concentration in the membrane samples. The surface and cross-sectional morphologies of CS/PVA blend membrane was observed by scanning electron microscopy (SEM) (TM3030, Japan). The membrane was attached on an aluminum stage, and the cross section of blend membrane was fractured after frozen in liquid nitrogen. All samples were dried in a freeze dryer (FD-1A-50, Boyikang, China), and sputter-coated with gold before observation. The pore size distribution and the average pore size of CS/PVA blend membrane were obtained by a capillary flow porometer (3H-2000PB, Beishide, China). The samples were thoroughly infiltrated with the wetting liquid (Porewick) prior to measurement. Moreover, Image J analysis software was used to examine the surface porosity by analyzing the surface SEM images. Five SEM images of each sample were selected randomly to calculate the surface porosity. The membrane porosity was determined according to dry-wet weight method (Li, Cui, Zhang, He, & Li, 2016). The mechanical property of CS/PVA blend membrane was evaluated using an electronic stretching machine (INSTRON-5969, USA) with a crosshead speed of 20 mm min^{-1} and an applied force of 0.25 cN. To minimize the experimental error, each sample with a valid size of 5 mm × 25 mm was tested five times to obtain the tensile stress and elongation at break. The zeta potential of CS/PVA blend membrane surface was analyzed by an electrokinetic analyzer (Anton Paar, Austria). The samples were tested in 1 mmol L^{-1} KCl aqueous solution at 25 °C under an operating pressure of 300 mbar.

2.4. Filtration performance

The filtration performance of CS/PVA blend membrane was measured by an automatic filter tester (Model 8130, TSI Group, USA) (Gao et al., 2017). The charge neutralized mono-dispersed NaCl aerosols with mass median diameter of 260 nm and count median diameter of 75 nm were generated by an aerosol particle generator. Under the help