

Application of Mg(OH)₂ nanoplatelets as pore former to prepare PVDF ultrafiltration membranes



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ABSTRACT

Porous polymeric membranes have been widely applied to various water treatment processes. Water flux and retention ratio, which usually counterbalance each other, are two critical factors to evaluate the separating performance of a porous membrane for filtration. In this study, Mg(OH)₂ nanoplatelets, which cannot be dissolved in both the casting solution and coagulation bath, were employed as additive to prepare PVDF ultrafiltration membrane via phase inversion method induced by immersion precipitation. After the nanoplatelets (≤ 4 wt%) were completely removed from the Mg(OH)₂/PVDF hybrid membrane by the dilute hydrochloric acid, it is exciting to find that both the water flux and retention ratio of final production membranes greatly increased, with a little decrease of mechanical strength. Compared with those membranes prepared with soluble LiCl, the membranes using Mg(OH)₂ had a reduced possibility to the formation of cracks on membrane surface. This work suggests that nonsolvent-insoluble but hydrophilic nanoparticles have greatly potential application as additive in the filtration membrane preparation.

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1. Introduction

Porous polymeric membranes have been widely applied to various water treatment processes for the removal of suspended solids, bacterial, virus and colloid. Water flux and retention ratio, which are always paradoxical to each other, are two critical factors to evaluate the separating performance of a porous membrane for filtration.

Polyvinylidene fluoride (PVDF) is an extremely attractive membrane material due to its chemically inert property, along with good physical and thermal stability [1,2]. To date, most of the commercial PVDF separating membranes including ultrafiltration (UF) are produced via phase inversion method due to the simplicity and flexible production scales of its process [3,4]. In order to prepare a UF membrane with high penetration performance, it is

convenient and efficient to introduce suitable additives as pore former into the casting solution to control membrane structure and morphology. It is noted that almost all the existing additives (e.g. PEG and LiCl) are nonsolvent-soluble, and their effects on the resulting PVDF membrane morphology and penetration performance have been reported in various publications [5–8].

Recently, some researchers attempted to use inorganic nanoparticles as pore template in the membrane preparation. For example, Kellenberger et al. [9–11] incorporated acid-soluble nanoparticles including CaCO₃ and SrCO₃ into polyethersulfone (PES) polymers, aiming to obtain the mesoporous membranes with desired structure. However, the symmetric membranes prepared by solvent evaporation process may have low porosity and flux, which will limit their applications for water filtration. In addition, Hashim et al. [12] employed SiO₂ particles to produce PVDF hollow fiber membranes by immersion precipitation method and the optimal post-treatment solution to remove the particles from the membrane precursor was found to be ~50 wt% HF acid, which requires extreme care and complex procedure in the membrane preparation process. Are there any other nanoparticles could be

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used as pore former to prepare more effective asymmetric membranes for water filtration? Do these nonsolvent-insoluble particles as additive in the casting solution have advantages compared with those nonsolvent-soluble inorganic salts? Further investigation needs to be performed in this matter.

In our previous work, the hydrophilic $\text{Mg}(\text{OH})_2$ nanoplatelets were used as inorganic fillers to prepare PVDF/ $\text{Mg}(\text{OH})_2$ hybrid membranes by phase inversion method in order to prevent flux losses caused by membrane bio-fouling [13,14]. In this study, $\text{Mg}(\text{OH})_2$ nanoplatelets were applied as pore former to enhance the separation performances of PVDF asymmetric membranes. The $\text{Mg}(\text{OH})_2$ nanoplatelets were added into the casting solution to prepare hybrid membranes via phase inversion, and then they were completely removed by the dilute hydrochloric acid. The porosity, morphology, mechanical and separation performances of production membranes were characterized and compared with those prepared by LiCl (a commonly used soluble inorganic salt).

2. Material and methods

2.1. Material

PVDF powder (FR904, $M_n = 400,000\text{--}500,000$, intrinsic viscosity = 1.6 dL/g , $T_m = 163^\circ\text{C}$, moisture content $\leq 10\%$) was purchased from 3F New Materials Co., Ltd. (Shanghai, China) and dried in a vacuum oven at 105°C for 10 h prior to be used. $\text{Mg}(\text{OH})_2$ nanoplatelets with a thickness of 20–30 nm (as shown in Fig. 1) were purchased from Damao Chemical Co. (Tianjin, China). LiCl of reagent grade was purchased from Fuchen Chemical Co. (Tianjin, China). Dimethylformamide (DMF, reagent grade) and Dimethylacetamide (DMAc, reagent grade) were obtained from Fuyu Fine Chemical Co. (Tianjin, China). Hydrochloric acid (HCl, reagent grade) was purchased from Beijing Chemical Co. (Beijing, China). Bovine serum albumin (BSA) with molecular weight of 67,000 Da was purchased from Oboxing Company (Beijing, China). Deionized water was used for preparing all solutions.

2.2. Porous membrane preparation

All the membranes were prepared by phase inversion method induced by immersion precipitation, and the preparation procedure is illustrated in Fig. 1. $\text{Mg}(\text{OH})_2$ nanoplatelets at different ratio from 0 to 5 wt% to casting suspension were ground using a mortar and dispersed into the DMF solvent by an ultrasonicator for 2 h. 18 wt% PVDF to solvent was added into the above mixture under magnetically stirring at 90°C until it dissolved completely. All the casting suspensions were used within 30 min after stirring in order

to prevent the aggregation of $\text{Mg}(\text{OH})_2$ nanoplatelets. After the air bubbles were removed with a vacuum pump, the casting suspension was cast directly upon a glass substrate at room temperature and stayed for 10 s. The casting knife setting value was $80\ \mu\text{m}$, and the coagulant bath was deionized water at 25°C . The final production membranes were obtained by dissolving the nanoplatelets through immersion into $0.2\ \text{mol L}^{-1}$ HCl solution for 24 h and followed by water rinse. For comparison, 4 wt% LiCl was also employed as an inorganic soluble additive to prepare porous membrane. All the membranes were kept in an aqueous bath for at least one day to remove residual reagents before used.

2.3. Membrane characterizations

The membrane porosity ε (%) is defined as the ratio of the volume of pores to the total volume of membrane, and in this study it was determined by wet-dry weighting method. The wet membranes to be tested were cut into small pieces ($3\ \text{cm} \times 3\ \text{cm}$) and weighted after mopping superficial water. Then these samples were put into a vacuum oven at 60°C until there was no change in weight. Therefore, ε was determined by the following equation:

$$\varepsilon = \frac{(w_W - w_D)/\rho_W}{(w_W - w_D)/\rho_W + w_D/\rho_M} \times 100\% \quad (1)$$

where w_W was the weight of wet membrane (g), w_D was the weight of dry membrane (g), ρ_W was the pure water density ($0.998\ \text{g cm}^{-3}$) and ρ_M was the density of hybrid membrane, which was a combination of the inorganic nanoplatelets ($2.36\ \text{g cm}^{-3}$) and PVDF polymer ($1.77\ \text{g cm}^{-3}$) based on their each content in the membrane matrix. For each membrane, 5 samples were tested and the porosity was the average value.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Model EQUINOX 55 FTIR spectrophotometer (Germany) in the range from 500 to $4000\ \text{cm}^{-1}$. Membrane samples were also dried at the same conditions as above (at 60°C in a vacuum oven) before the FTIR analyses. The surface morphology of membrane was viewed by a TM-3000 SEM (Hitachi, Japan) under magnifications ranging from 5000 to 20,000, and the samples were successively sputter coated with a thin gold film prior to SEM observation. Tensile strengths of the membranes were measured by a Model CMT3502 electromechanical universal testing machine (Shenzhen, China). Wet membranes were cut into the standard shape for tensile strength measurements. The strength at break and elongation were measured in ambient condition for at least 5 samples and the average value was reported.

The membrane separation properties were measured by a home-made filtration cell (effective area $33.18\ \text{cm}^2$, dead-end). The pure water flux of membrane was determined at different transmembrane pressures. For each pressure, the membrane was first compacted for 30 min to minimize compaction effects. After the flux reached steady state, the flux was calculated as:

$$F = V/(A \cdot t) \quad (2)$$

where F is the pure water flux ($\text{L m}^{-2}\ \text{h}^{-1}$), V is the permeate volume (L), A is the membrane area (m^2) and t is the time (h). The permeation performances of BSA in about $0.3\ \text{g L}^{-1}$ solution through various membranes at transmembrane pressure of $0.15\ \text{MPa}$ were measured to investigate the solute rejection capabilities of the membranes. The BSA concentrations before and after filtration were determined spectroscopically at $280\ \text{nm}$ using a UV-vis spectrophotometer (UV-7502PC, Shanghai, China). For each membrane, at least 4 samples were tested and the average value was recorded.

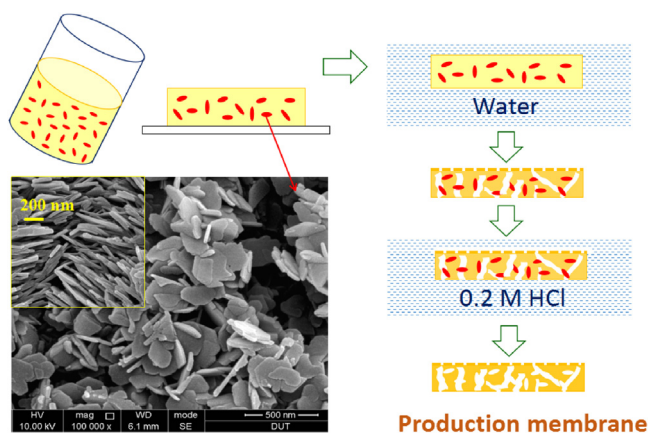


Fig. 1. SEM picture of $\text{Mg}(\text{OH})_2$ nanoplatelets and the preparation procedure of final PVDF UF membranes.

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