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Preparation and interface structure study on dual-layer polyvinyl chloride matrix reinforced hollow fiber membranes

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ABSTRACT

Polyvinyl chloride (PVC) matrix reinforced hollow fiber membranes including separation layer and porous supported matrix were fabricated via dry–wet spinning process. The mixtures of PVC or polyvinylidene fluoride (PVDF) polymer solutions were uniformly coated on the homogeneous PVC matrix membrane which was prepared by a melt-spinning method. The influences of pre-wetting solutions and polymer concentration on structure and performance of homogenous-reinforced (HMR) PVC hollow fiber membranes were investigated. Furthermore, the interfacial bonding state of HMR PVC hollow fiber membranes was characterized by an indirect method and comparative analysis. The results showed that a dense interface formed in the HMR PVC hollow fiber membrane between these two layers without pre-wetting process. Compared with the matrix membrane which had a rougher outer surface with obvious big pores, the prepared HMR PVC hollow fiber membrane possessed a dense and smooth outer surface with no obvious big pores. Due to the filling of the pre-wet solutions into the pores in the outer edge of the matrix membrane, the HMR PVC hollow fiber membranes formed porous interface in the coating process which improved its permeability. The HMR PVC hollow fiber membranes had a more favorable interfacial bonding than the heterogeneous-reinforced (HTR) PVDF hollow fiber membranes. The tensile strength of prepared PVC matrix reinforced hollow fiber membranes was higher than 12 MPa but lower than the original PVC hollow fiber matrix membrane.

1. Introduction

As the key part of the membrane separation technology, hollow fiber membranes which possessed excellent mechanical self-supporting and high permeability per installation area had become the main form of microfiltration and ultrafiltration compared with the flat sheet membrane and tubular membrane [1]. In the membrane separation process, the hollow fiber membranes which subjected to high pressure water flow pulsation or disturbance for a long time were easily damaged and broken by the high-pressure hydraulic cleaning process or disturbance of high velocity water and even air flow pulsation [2]. This defect that would affect the effluent quality and increase the maintenance cost, had become one of the main restricting factors for the development of the membrane technology, especially in Membrane Bioreactor (MBR) system. As the combination of membrane separation technology and biological treatment technology, MBR system had been widely used in the municipal and industrial wastewater treatment for its excellent and stable effluent quality, compact structure, simple operation and self-cleaning capacity by the oscillating friction [3–5]. The hollow fiber membranes that were used in the MBR system needed the excellent separation performance, antifouling property and high mechanical strength. However, the most popularly used hollow fiber membranes were prepared by a nonsolvent induced phase separation (NIPS) method which endowed the membrane with excellent separation performance and antifouling property, but low tensile strength [6,7]. Thus, the preparation of hollow fiber membranes with high tensile strength had important significance to the development of MBR technology.

The method to solve these problems was to prepare a kind of reinforced hollow fiber membranes which were usually fabricated by compositing the separation layer with the porous supported matrix. The separation layer provided the excellent separation performance, while the porous supported matrix provided the high tensile strength. The conventional reinforced hollow fiber membranes were the heterogeneous-reinforced (HTR) hollow fiber membranes, in which the materials were different in the two layers, such as polyester (PET) thread or tubular braid reinforced hollow fiber membranes [8–10]. The casting solutions would infiltrate in the porous supported matrix without adverse effects, such as swelling and dissolving. The incompatible thermodynamics of these two polymers might result in the obvious change of gradient in the chemical composition and structure of

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the interface between the separation layer and the porous supported matrix. The infiltration of casting solutions to the porous supported matrix could provide limited interfacial bonding strength which might result in the peeling off of the separation layer from the porous supported matrix by the high-pressure hydraulic cleaning process or disturbance of the aerated airflow in the MBR filtration process. The damage of the HTR hollow fiber membranes would shorten the service life due to the peeling off of the separation layer. Moreover, when the HTR hollow fiber membrane was subjected to the stretching or pressing effect, the deformation rate was different between the separation layer and the porous supported matrix. The interface would be damaged by the interlaminar shear between these two phases before reaching the tensile strength of the HTR hollow fiber membrane. Therefore, the interfacial bonding state of the HTR hollow fiber membrane has become the key factor of restricting its application area.

Based on the analysis of the conventional reinforced hollow fiber membranes mentioned above, the homogenous-reinforced (HMR) hollow fiber membranes which contained the same polymer in the separation layer and the porous supported layer could avoid these defects of HTR hollow fiber membranes [11]. Owing to the same polymer in the two layers of HMR membranes, the adhesion of the separation layer to the porous supported matrix was better than that of the different polymers. The condition of the HMR method contained following two points: the membrane materials could be dissolved in solvents and the porous supported matrix that is obtained from this material should have an excellent tensile strength. In the preparation process of HMR membranes, the casting solutions would infiltrate in the porous supported matrix with some adverse effects, such as swelling and dissolving mentioned above. However, the swelling and dissolving of the porous supported matrix could provide the excellent interfacial bonding strength after the solidification of the HMR membranes. In our past studies, we found that these effects would reduce the permeability of the HMR membranes [2,12]. Therefore, the pre-wetting process was used to improve the permeability of the HMR membranes. Pre-wetting could temporarily put the pre-wet solution into the pores of the external layer of the matrix which facilitated the formation of polymer poor regions and formed the porous interface during the coating process [13,14]. Also, the use of pre-wet solution could dilute the solvent concentration of the casting solution and reduce the dissolving of the porous supported matrix membrane.

The interfacial bonding strength between the separation layer and the porous supported matrix played an important role in the composite materials, such as HMR hollow fiber membranes. Good interfacial bonding state that ensured the load transfer from the matrix to the reinforcement was a primary requirement for the effective use of reinforcement properties [15]. The transverse and longitudinal strengths of the composite materials were closely related to the interfacial bonding strength. Currently, the characterization of the interfacial bonding strength for the composite materials could be divided into large specimen macromechanical tests and single fiber micromechanical test, such as interlaminar shear strength (ILSS) [16] and single fiber pull-out test [17], respectively. However, there were many difficulties to test the interfacial bonding strength of the HMR hollow fiber membranes by the above described methods. Because the separation layer of the HMR hollow fiber membranes was thin. Thus, it was necessary to characterize the interfacial bonding strength of the HMR hollow fiber membranes by the indirect method and comparative analysis. For the reinforced hollow fiber membrane, the permeability and separation properties were associated with the separation layer and the interface to a large extent. The damage of the interface might bring about the changes of the pure water flux (PWF) and rejection. Therefore, the variation of the PWF and rejection after stretching could reflect the change of the interfacial bonding state of the reinforced hollow fiber membranes indirectly.

In this study, PVC matrix reinforced hollow fiber membranes that contained HMR PVC hollow fiber membranes and HTR PVDF hollow fiber membranes were prepared by coating the PVC or PVDF casting solutions on the PVC hollow fiber matrix membrane. The PVC hollow fiber matrix membranes were fabricated by the melt-spinning method. The influences of pre-wetting solutions and polymer concentration on structure and performance of HMR PVC hollow fiber membranes were investigated by morphology, permeability and mechanical property measurements. Furthermore, the interfacial bonding state of HMR PVC hollow fiber membranes was characterized by the indirect method for the changes of PWF after stretching and comparative analysis with HTR PVDF hollow fiber membranes.

2. Experimental

2.1. Materials

Polyvinyl chloride (PVC, fiber grade, DG-1000k, the average degree of polymerization is 1030 ± 50) resin was purchased from Tianjin Dagu Chemical Plant (Tianjin, China). Polyvinylidene fluoride (PVDF, W no. 1300 powders, $T_m = 170$ °C) was purchased from Kureha Chemical Industrial Co., Ltd. (Tokyo, Japan). Dioctyl phthalate (DOP, $>99.5\%$) was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Calcium/zinc compound thermal stabilizer was supplied by Shenzhenshi AIMSEA Industrial Co., Ltd. The composite powder (a mixture of nanosized KCl and SiO_2) was provided by Tianjin Motian Membrane Engineering & Technology Co., Ltd. N,N-dimethylacetamide (DMAc, Analytical Reagent), Ethanol (EtOH, Analytical Reagent), poly(ethylene glycol) (PEG, Analytical Reagent, Mw=2000) and Polyvinylpyrrolidone (PVP, Analytical Reagent, K30, Mw=10,000) were bought from Tianjin Guangfu Fine Chemical Research Institute. Bovine serum albumin (BSA, Analytical Reagent, Mw=68,000) was supplied from Beijing Aoboxing Universeen Bio-tech Co., Ltd.

2.2. Preparation of hollow fiber matrix membrane

The PVC, calcium/zinc compound thermal stabilizer and DOP in a special weight ratio were mixed in high speed mixer. Then, the mixture was fed into a twin-screw extruder machine and the particles of the mixture were obtained through a cutter. Finally, the particles and composite powder in a special weight ratio were mixed again under a high speed agitation and were spun into hollow fibers via the melt-spinning method by a twin-screw spinning machine [18]. The composition and spinning conditions are shown in Table 1.

After that, the prepared PVC hollow fiber membranes were post-stretched under a uniform speed at different draw ratios

Table 1
Composition and spinning parameters of melt-spun hollow fiber membranes.

Spinning conditions	Value
Dope composition (PVC/DOP/thermal stabilizer)/wt%	28.9/16.6/4.5
Composite powder weight fraction/wt%	50.0
Extrusion machine and spinneret temperature/°C	155.0
Bore fluid	N_2
External coagulation	Water
External coagulation T/°C	20.0 ± 5.0
Air gap/cm	20.0
Extrusion speed/ m min^{-1}	4.8
Take up speed/m min^{-1}	14.0
Spinneret draw ratio	2.9