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The unidirectional regulatory role of coagulation bath temperature on cross-section radius of the PVDF hollow-fiber membrane

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ABSTRACT

In this paper, the low-temperature thermally induced phase separation (L-TIPS) method was adopted to prepare a high-performance polyvinylidene fluoride (PVDF) hydrophobic membrane for membrane distillation (MD) with non-solvent polyethylene glycol-400 (PEG400) and solvent triethyl phosphate as a fully water-soluble mixed diluent. In the process of L-TIPS membrane formation, the unidirectional regulatory role of coagulation bath temperature on cross-section radius of the PVDF hollow-fiber membrane was analyzed. The results show that the tensile strength of the membrane increases with the increase of the external coagulation bath water temperature, which is the opposite of the general rule. PEG400 is employed to regulate the membrane structure, and more specifically to increase the cellular structure (a positive impact on tensile strength) and reduce the sphere-packed aggregation structure (a negative impact on tensile strength). When the coagulation bath temperature is 60 °C, the tensile strength of the membrane reaches 6.21 MPa (more than 2–4 times higher than the hydrophobic membranes reported). Meanwhile, the PVDF hollow-fiber hydrophobic membrane also has a high flux, the vacuum membrane distillation flux reaches 30.6 kg m^{-2} h^{-1}, which is 14.6 times higher than that at the coagulation bath temperature of 15 °C.

1. Introduction

Membrane distillation (MD) technique is a kind of membrane separation technology combined with traditional distillation process, in which only vapor molecules are able to pass through the porous hydrophobic membrane. The driving force in the MD process is the vapor pressure difference between two sides of the membrane. Compared to other separation techniques, MD has the following advantages: higher rejection, higher concentrating multiple and lower operating temperature. Therefore, MD technique is widely used in desalination, pure water preparation, solution concentration, among many others. Polyvinylidene fluoride (PVDF) is a focus in the field of MD due to its good mechanical stability, chemical resistance, tolerance to most solvents and commercial availability [1–6].

According to the different methods of condensing the water vapor on the cooling side of the membrane, MD processes can be divided in different categories: direct contact membrane distillation (DCMD); sweeping gas membrane distillation (SGMD); air gap membrane distillation (AGMD); osmotic membrane distillation (OMD); and vacuum membrane distillation (VMD) [7]. Among them, VMD is a focus due to its higher evaporation efficiency and permeation flux.

Despite its great potential, MD has not been industrialized. One important reason for this is that the comprehensive performance of the membrane is not excellent. Although some reports focus on improving the permeability of MD membranes, the lower tensile properties will seriously affect the service life of the membranes during membrane distillation [8–10]. Traditional MD membrane preparation methods primarily include non-solvent-induced phase separation (NIPS) method [8–13] and thermally induced phase separation (TIPS) method [14]. The NIPS method, although simple, usually forms a large number of finger-like voids in the membrane due to double-diffusion [15–18], resulting in insufficient membrane mechanical properties. The TIPS method is able to prepare high mechanical strength membranes; however, the formation temperature is generally above the fusion point of the polymer, the homogeneous dope solution is formed by mixing the molten polymer (for PVDF, the melting point of is 172 °C) with the high temperature diluent. Therefore, problems such as high energy consumption and stringent requirements of membrane preparation

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equipment [19–23] arise. In addition, owing to most water-soluble diluents of PVDF having lower relative heat stabilities, they can hardly be applied to the high temperature conditions of TIPS process. Therefore, the choice of diluent to regulate the TIPS membrane structure is usually water-insoluble (under the melting point of PVDF, they almost incompatible with PVDF). The post-treatment process needs to use a two-step method, i.e., extracting the diluent via a non-water coagulating bath (the coagulation bath is usually ethanol), then further post-treatment via water. The process is cumbersome, and is also not conducive to environmental protection.

To solve the problems in the NIPS and TIPS methods, Japanese scholars Akihiro and Hideki [24] found a method that can prepare the TIPS membrane with high mechanical strength at a lower formation temperature (the formation temperature is lower than the melting point of the polymer, melting polymer is unnecessary, it is enough to prepare homogeneous dope solution only through dissolving polymer with diluent). Due to the decrease of the formation temperature, it is possible to use more environmentally friendly water-soluble diluents in TIPS process. The water-soluble diluent has a poor ability to dissolve the polymer at room temperature; however, with increasing temperature, it can form a homogeneous solution with a high concentration of polymer. Lu [25,26] named this method the low-temperature thermally induced phase separation (L-TIPS) and gave a more specific definition: the polymer and the diluent in a homogeneous solution at a temperature below the fusion point of the polymer. During phase inversion membrane formation, the dope solution is kept at a temperature below this fusion point but above the cloud point of the dope solution. Additionally, the coagulating bath temperature is significantly below the cloud point of the dope solution. Thus, both TIPS and NIPS phase separation mechanisms will operate when the dope solution enters the water coagulating bath [27].

A few studies on PVDF membrane prepared via L-TIPS method have been reported [28,29]. However, the research focuses on the hydrophilic membrane field. In the process of PVDF hydrophilic membrane formation, water-soluble additives such as large-molecular-weight polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP) play the role of pore-forming agents to prepare the membrane with high flux and high tensile strength. However, for a PVDF hydrophobic membrane, because large-molecular-weight water-soluble agents cannot be completely dissolved in the process of membrane formation, the application of the agents to membrane formation will severely diminish the hydrophobicity of the membrane. Therefore, only small-molecular-weight pore-forming agents are suitable for PVDF hydrophobic membrane formation. To prepare high-performance PVDF hydrophobic membranes, it is of significant importance to regulate the membrane structure and performance according to the mechanisms of membrane formation.

For the formation process in the L-TIPS method, TIPS and NIPS processes are simultaneous. Under the melting point temperature of PVDF, the dope solution system with higher PVDF concentration can be prepared by accelerating the TIPS process. At this time, the tensile strength of the membrane can be improved. Under the condition of adding small-molecular-weight additives, more and larger voids can be formed by accelerating the NIPS process. At this time, the permeability of the membrane can be improved. However, since the heat transfer rate is much faster than the mass transfer rate [27], in the process of membrane formation, there is a competition mechanism between the TIPS and NIPS processes. Compared to the phase separation process caused by double-diffusion (NIPS mass transfer process) in the process of solidification, the phase separation process caused by the temperature difference (TIPS heat transfer process) is dominant.

Fig. 1 shows a schematic diagram of the effect of the coagulation bath temperature on the competing mechanisms of TIPS and NIPS. During the competition process between TIPS and NIPS, when the coagulation bath temperature is very low, the temperature difference between the cloud point of the dope solution and the coagulation bath temperature is significant. At this time, the dominant advantage of the TIPS process will be excessively manifested, which completely suppresses the double-diffusion effect caused by NIPS and adversely affects the permeability of membranes. Therefore, the competing mechanisms of the TIPS and NIPS processes should be regulated by changing the coagulation bath temperature.

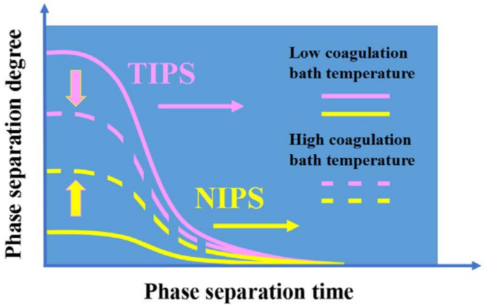

Fig. 1. Effect of coagulation bath temperature on competing mechanisms of TIPS and NIPS.

By changing the coagulation bath temperature, a balance between the competing mechanisms can be achieved. A PVDF membrane for MD with high flux and high tensile strength owing to the TIPS structure in the bulk and the NIPS porous skin structure on the outer surface can be prepared via the L-TIPS method with small-molecular-weight water-soluble diluent. However, so far, no report on this has been found in literature. Using this economical, simple, and environmentally friendly method to develop high-performance PVDF hollow-fiber membranes for MD is useful in the application of the membrane.

In this study, under the melting point of the polymer, a dope solution with a high polymer concentration was prepared with conventional non-solvent polyethylene glycol-400 (PEG400) and solvent triethyl phosphate as a fully water-soluble mixed diluent. The PVDF hollow-fiber membrane for MD was prepared via L-TIPS method. The unidirectional regulatory role of coagulation bath temperature on cross-section radius of the PVDF hollow-fiber membrane was investigated. Among them, triethyl phosphate was suitable for the L-TIPS method owing to its low compatibility with PVDF at low temperatures and its good compatibility with L-TIPS at high temperatures. PEG400 played the role of a NIPS pore-forming agent to regulate the membrane structure and improve the permeability and mechanical properties of the membrane.

2. Experiments

2.1. Materials

Polyvinylidene fluoride (PVDF): Solef 6010, Solvay Specialty Polymers, Solvay Solexis Company in France. Triethyl phosphate: analytical pure grade, Tianjin Guangfu Fine Chemical Research Institute. Polyethylene glycol (PEG400): analytical pure grade, Tianjin Kermel Chemical Reagent Co., Ltd. Triethylene glycol: analytical pure grade, Tianjin Guangfu Fine Chemical Research Institute.

2.2. Preparation of PVDF hollow-fiber hydrophobic membrane

Polymer dopes including PVDF, TEP and PEG400 were stirred for 4 h at 160 °C in the stirred tank reactor. After keeping at 160 °C for 2 h for removing the bubbles, the homogeneous PVDF solutions were fed into a spinneret under the nitrogen pressure. In this study, triethylene glycol (boiling point is 285 °C) was employed as bore liquid for a special purpose. The hollow-fibers were extruded from the spinneret and wounded on a take-up winder after entering into the water coagulant bath to induce the phase separation and solidify the membranes. The residual diluent in the hollow-fibers was extracted by immersing the