



Study of the dual role mechanism of water-soluble additive in low temperature thermally-induced phase separation



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ABSTRACT

In the NIPS method, polyethylene glycol-400 (PEG400) was a common water-soluble additive and usually played the role of a pore-forming agent due to NIPS double-diffusion. In this paper, the new role of non-solvent PEG400 in the low temperature thermally-induced phase separation (L-TIPS) was analyzed. PEG400 were used to regulate the phase separation mechanism of the dope solution, and then to improve the membrane structure and performance. The membrane structure was regulated by gradually increasing the PEG400 content, the role evolution of water-soluble non-solvent PEG400 on the phase transformation mechanism and the effect on tensile strength of the polyvinylidene fluoride (PVDF) membrane were studied. The results show that the increase of PEG400 content can increase the cloud point temperature of dope solution, accelerate the thermally induced phase separation (TIPS) effect and inhibit the negative effect of the non-solvent induced phase separation (NIPS) effect on membrane structure. Meanwhile, the increase of PEG400 content can shift the TIPS effect of the dope solution system from solid-liquid phase separation to liquid-liquid phase separation and inhibit the growth of PVDF spherulites during the TIPS process. The dual role mechanism of PEG400 together eliminates the NIPS finger-like voids and the TIPS sphere-packed aggregation structure, which have the negative impact on tensile strength of the PVDF membrane. The PVDF membrane shows excellent mechanical properties; the tensile strength of the membrane reaches 3.12 MPa (more than 3–6 times higher than the membranes reported), pure water flux reaches 391 L m⁻² h⁻¹, and the rejection rate of carbon ink is 100%.

1. Introduction

The preparation of high-performance polyvinylidene fluoride (PVDF) membranes is a focus of the water treatment field [1–5]. Traditional membrane preparation methods primarily include non-solvent induced phase separation (NIPS) [6–10] and thermally induced phase separation (TIPS) methods [11–15]. The NIPS method, although simple, usually forms a large number of finger-like voids in the membrane due to double-diffusion, resulting in insufficient membrane mechanical properties [6–10]. 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 is 172 °C) with the high temperature diluent. Therefore, problems such as high energy consumption and stringent requirements of membrane preparation equipment [11–15] arise. In addition, the PVDF membrane prepared via TIPS method is easy to form sphere-packed aggregation

structure due to solid-liquid phase separation, the tensile strength of the membrane is also not satisfactory. Owing to most water-soluble diluents having lower relative heat stabilities, they can hardly be used in TIPS. Therefore, the choice of diluent to regulate the membrane structure is usually water-insoluble. 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 [16–18].

To solve the problems in the NIPS and TIPS methods, Japanese scholars Akihiro and Hideki [19] 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). They put forward the concept of water-soluble latent solvent in their 2007 patent, i.e., the water-soluble solvent had a poor ability to

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dissolve the polymer at room temperature; however, with increasing temperature, it can form a homogeneous solution with a high concentration of polymer. They analyzed the water-soluble latent solvents of PVDF such as γ -butyrolactone, propylene carbonate, and triethyl phosphate. Based on the water-soluble latent solvent, they prepared PVDF membranes with excellent comprehensive performance at 140–160 °C. Although they did not provide the specific preparation method, the progress from water-insoluble diluent to water-soluble latent solvent was a breakthrough in the TIPS formation method. Lu [20] 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.

A few studies on PVDF membrane prepared via L-TIPS method have been reported [21,22]. However, when the coagulation bath is water, the membrane will still form sphere-packed aggregation structure due to solid-liquid phase separation, which has a negative impact on the tensile strength of the membrane. The attempt to eliminate the sphere-packed aggregation structure by altering the coagulating condition and the cooling rate entails complicated post-treatment and environmental pollution but also resulted in a mediocre tensile strength. Therefore, it is worth researching how to start from diluent, using water-soluble diluent to regulate the phase separation mode of the membrane formation system, which in turn helps eliminate the sphere-packed aggregation structure in the membrane and improve the tensile strength. yet, so far no report on this has been found in the literature. Through this simple and effective method, water can be directly used as the coagulation bath to extract diluent in the post-treatment process. Meanwhile, it can provide convenience and possibility for the hydrophilic modification of the membrane, which is useful in the application of the membrane.

In this paper, the PVDF flat membrane was prepared via L-TIPS method with water-soluble solvent triethyl phosphate (TEP) and conventional water-soluble non-solvent PEG400 as mixed diluent. Among them, TEP was suitable for the L-TIPS method due to the low compatibility with PVDF at low temperature and the good compatibility with L-TIPS at high temperature. PEG400 was used to regulate the membrane structure. The method of covering both sides of the dope solution with polyimide film was used to prevent dissolution of PEG400 out from the dope solution due to NIPS double diffusion during the membrane formation process. The occurrence mechanisms of TIPS and NIPS processes in L-TIPS membrane formation were regulated by changing the PEG400 content. The role evolution of PEG400 on the phase transformation mechanism and the effect on tensile strength of the PVDF membrane are studied. The effect of the role evolution on the structure and performance of the membranes is also discussed.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF): industrial grade, Solvay Specialty Polymers, Solvay Solexis Company in France. Polyethylene glycol (PEG400): analytical pure grade, Tianjin Kermel Chemical Reagent Co., Ltd. Triethyl phosphate (TEP): analytical pure grade, Tianjin Guangfu Fine Chemical Research Institute. Polydimethylsiloxane: analytical pure grade, Tianjin Fengchuan Chemical Reagent Co., Ltd. Carbon ink: Tianjin Ostrich-Ink Company.

Table 1
The mass ratio of dope solution system containing PVDF/PEG400/TEP.

	Dope solution sample	PEG400(g)	TEP(g)
1	D25-0	–	75.0
2	D25-10%	7.5	67.5
3	D25-20%	15.0	60.0
4	D25-33%	25.0	50.0
5	D25-38%	28.5	46.5
6	D25-42%	31.5	43.5
7	D25-46%	34.5	40.5
8	D25-50%	37.5	37.5
9	D25-54%	40.5	34.5

Note: the PVDF content of the four dope solutions is 25.0 g.

2.2. Preparation of dope solution system containing PVDF/PEG400/TEP

Dope solutions of PVDF/PEG400/TEP system were prepared and the composition of each dope is listed in Table 1. In this study, the content of PVDF relative to the total dope solution was 25%. At 160 °C, the maximum content of water-soluble non-solvent PEG400 at which the dope solution can be formed in the mixed diluent is 54%. Before being allowed to stand for defoaming (oil bath was polydimethylsiloxane), the dope solutions (Table 1) were stirred for 3 h at 160 °C. At this time, the dope solutions had a transparent and uniform state which proved that PVDF had been fully dissolved. After that, the prepared solutions were introduced into test tubes (preheated at 160 °C). The test tubes containing the solutions were cooled in liquid nitrogen and sampled. The dope solution systems were named D25-0, D25-10%, and so on based on the content of PVDF in the total solution and the content of non-solvent additive PEG400 in the mixed diluent.

2.3. Preparation of PVDF membranes

D25-0, D25-10%, D25-33%, and D25-54% samples were placed at the center of two polyimide films and pressed into a mold preheated beforehand at 160 °C. The membrane formation pressure was 4 MPa and the thickness of the membrane was 0.30 mm. The products were then immediately put into 10 °C water coagulation bath. After 20 s, the polyimide film on the upper side of the sample was removed, and the sample was directly contacted with the coagulation bath to solidify into a membrane. The membranes were named M25-0, M25-10%, M25-33%, and M25-54%, respectively. The schematic diagram of membrane formation equipment is illustrated in Fig. 1.

2.4. Scanning electron microscopy

The membranes were freeze-fractured in liquid nitrogen, plated with gold, and observed under a S-4800 field emission scanning electron microscopy (FE-SEM) (Hitachi, Japan).

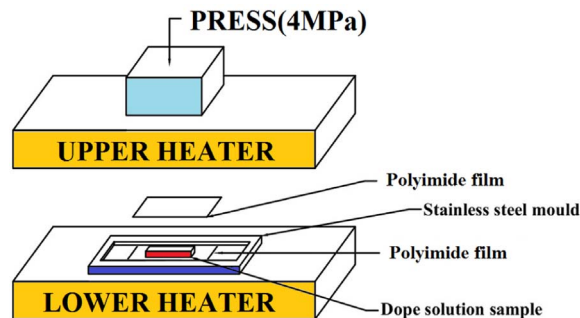


Fig. 1. The schematic diagram of membrane formation equipment.

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