

Effects of solvent sort on casting solution and morphology of poly(ether sulfones) filtration membrane

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Abstract

Four kinds of solvent were chosen to prepare poly(ether sulfones) (PES) filtration membranes by the nonsolvent induced phase separation (NIPS) method. Ternary phase diagram and shear viscosity measurement were conducted to analyse the formation of prepared membrane from thermodynamic and kinetic perspectives. The micro-structure of the membranes with different solvents were analysed, and the result showed a high relevance to the thermodynamics and dynamics of the casting solutions, and promoted the proposal of a reasonable membrane formation mechanism.

Key words: membrane, membrane formation mechanism, PES, solvent, structure

Highlights

- Thermodynamic stability of casting solution with different solvents based on ternary phase diagrams.
- Detailed influence of solvent sorts on the membrane structure.
- Membrane formation mechanism based on thermodynamic and kinetic properties of casting solution.

INTRODUCTION

At present, the most widely used method to prepare polymer membrane materials is nonsolvent induced phase separation (NIPS), which was developed by Loeb and Sourirajan in 1962 (Xin *et al.* 2012; Zhu & Zhang 2014; He *et al.* 2018; Liu *et al.* 2018). By immersing the homogeneous polymer casting solution into a nonsolvent bath, phase separation takes place spontaneously, forming a porous membrane (Peinemann *et al.* 2007; Susanto & Ulbricht 2009). With more extensive and in-depth research, this method of membrane preparation has gained considerable development and attention in recent decades due to its merits such as room temperature operation, various solvent selection, rapid membrane forming and low costs (Zhou *et al.* 2010; Guillen *et al.* 2011; Fan *et al.* 2017, 2018).

To fabricate membranes with high performance through this method, the whole process of membrane preparation, including the selection of polymer materials, environmental conditions, additives, solvent selection and concentration of casting solution etc., on the effects of polymer properties has been studied (Rabiller *et al.* 2008; Sun *et al.* 2009; Madaeni & Rahimpour 2010; Arthanareeswaran & Starov 2011). Among them, solvent sort of the casting solution is of great importance to the formation process of the membrane (Li & Jiang 2001). As early as 1990, Jeong Rim

Hwang *et al.* examined the effects of the combination of two solvents, dichloromethane (DCM) and N-methyl-2-pyrrolidone (NMP), on membrane performance, realizing that the addition of DCM affected the thermodynamic stability of the casting solution (Hwang *et al.* 1996).

As a common membrane material, polyethersulfone (PES) has excellent chemical, thermal and mechanical properties (Zhao *et al.* 2013). However, PES membrane prepared by the NIPS method has strong rigidity and insufficient flexibility, which easily leads to flat membrane rupture and hollow fiber membrane breakage under high pressure in the water treatment process (Xu & Qusay 2015). Whether this phenomenon is related to the selection of solvent in the process of membrane preparation is worth studying. In addition, it is widely accepted that, as an organic solvent, PES membranes prepared by NMP have better permeability and filtration performance in commonly used organic solvents, such as dimethyl acetamide (DMAc), dimethyl sulphoxide (DMSO), and dimethyl formamide (DMF) etc., which has different interaction parameters (Flory-Huggins parameters) with PES (Fan *et al.* 2020). Is it related to the thermodynamic stability and viscosity properties of the casting solution, and their effect on the rationalized mechanism of membrane formation have not been carried out yet.

Therefore, the aim of this study is to provide a more comprehensive understanding on the role of solvent sort during PES membrane formation, and compares the effects of different solvents on the microstructure of the membranes.

EXPERIMENTAL

Materials

Polyethersulfone (PES) from Shandong Caihong Advanced Material Company, China, was dried in an oven at 70 °C for at least 20 h before use. Polyvinyl pyrrolidone (PVP, K30), polyethylene glycol with 20 kDa molecular weight (PEG 20,000), dimethyl acetamide (DMAc, AR), 1-methyl-2-pyrrolidone (NMP, AR), dimethyl sulphoxide (DMSO, AR), and dimethyl formamide (DMF, AR) were purchased from Sinopham Chemical Reagent Company (China) and used as received. All experimental water is deionized water treated by Millipore-Q system.

Methods

Cloud point titration

Generally, the cloud point titration method is used to draw the ternary phase diagram of membrane casting solution (Wu *et al.* 2006). In the case without adding PVP, PES solutions with different mass fractions (0.1, 0.5, 1, 2 and 3 wt. %) and solvents were dissolved together to form a homogeneous solution of 50 ml and prepared for titration. In the case of adding PVP, the mass ratio of PVP to PES was kept at 1:3; considering that this ratio can be used in the actual membrane fabrication, a membrane with potent permeability and retention rate can be obtained (Fan *et al.* 2020), and the total mass fraction was still set at 0.1, 0.5, 1, 2 and 3 wt. %. Under stirring condition, an accurate 0.05 ml of deionized water was continuously dropped into the homogeneous PES solution. A water bath heated on a magnetic stirrer was used to maintain the temperature at 25 °C. The whole titration process needed to be operated slowly. When the homogeneous solution begins to appear of stable turbidity, the titration should be stopped immediately. Then it should wait for 30 minutes under stirring condition to check whether the turbid solution could return to clarification. If the solution becomes clear, continue titration. If not, the data is recorded as a cloud point for the composition of the solution, and used to draw the final ternary phase diagram.

Casting solution preparation

Referring to our previous research results (Fan *et al.* 2020), in order to accurately reflect the effect of different solvents on the viscosity properties of the casting solution, for casting solutions with PVP additive, 18 g PES and 6 g PVP were dissolved with 76 g organic solvent in a flask. For casting solutions without PVP additive, the mass ratio of PES to the organic solvent is 18:82, with a total mass of 100 g. Then the polymer solution was stirred at 70 °C for 48 h to obtain homogeneous solutions and kept in an oven at 70 °C for 24 h to remove the gas bubbles. The shear viscosity of the casting solutions was measured by a rotational viscometer (NDJ-79A, Geological Instrument Co. Ltd, Shanghai). The temperature was stabilized at 25 °C during the whole experiment. Prior to the start of the test, the casting solution needed to be placed in the testing cylinder for at least 15 minutes to reach thermal equilibrium. Then the instrument automatically recorded the shear viscosity of the casting solutions at different shear rates during the test.

Membrane fabrication

The casting solution was scraped evenly on the glass plate with a cast blade, and the original membrane thickness was controlled at 0.2 mm by the distance between the blade and glass plate. Controlling the room temperature at 24 °C, the nascent membrane was evaporated for 15s in air and then immersed in a coagulation bath at 19 °C for complete precipitation. All these membranes separated from the glass plate were transferred into a water bath and stored there for 2 days to remove the possible existence of organic solvents in the membrane matrix before characterization. The membrane was first cut into pieces of different sizes and the surface was dried with filter paper. Liquid nitrogen was used to rapidly freeze these pieces for 20–30s, which were then taken out and brittle fractured immediately, and then kept in a desiccator. In order to enhance the electric conductivity of the membrane cross section, the dry samples should be sputtered with gold before testing. The cross-section images of membranes were examined by a scanning electron microscope (SEM) (LEO1530vp, Germany).

RESULTS AND DISCUSSION

Ternary phase diagram

The thermodynamic stability of the casting system can be reflected by its ternary phase diagram (Neelakandan & Kyu 2011). We can deem that the thermodynamic stability is high if the cloud point curve is far away from the Polymer-Solvent axis in the diagrams, which means more non-solvent is needed for the precipitation of polymers from the casting solution. As shown in Figure 1(a), the cloud point curve of the PES/NMP/H₂O system is the farthest from the PES-solvent axis. Thus, the PES/NMP/H₂O system has the highest thermodynamic stability among these four systems, followed by the PES/DMAC/H₂O, PES/DMF/H₂O, and PES/DMSO/H₂O systems in sequence.

As expected, the thermodynamic stability of the casting solution changes with the addition of PVP additives. Figure 1(b) shows that all four curves of the PES + PVP/solvent/water systems follow the same order. It means that the order of thermodynamic stability of the four solutions with addition of PVP does not change.

The thermodynamic stability of the casting solution affects the phase separation rate during the formation of the porous membrane. The thermodynamically unstable system usually leads to rapid phase separation, which means the duration for microcrystal formation will be shorter and possibly results

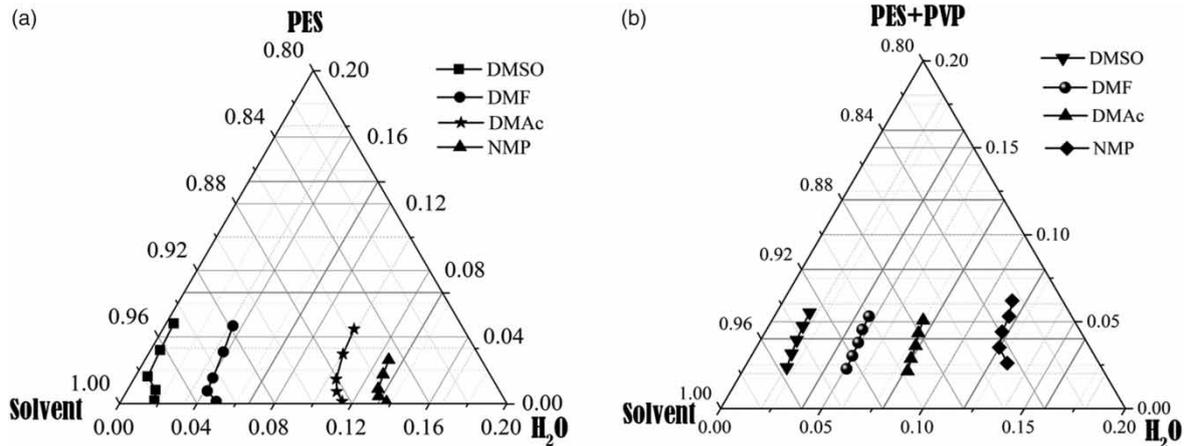


Figure 1 | Ternary phase diagram for (a) PES/solvent/water systems and (b) PES + PVP/solvent/water system.

in larger pores. Thus, these experimental results will help to have a profound understanding of the morphology and permeability performance of membranes fabricated by the NIPS method.

Compared with non-polar PES, PVP has stronger polarity and different interaction parameters with organic solvent. Some studies have also proved that the addition of PVP can reduce the thermodynamic stability of the casting solution and induce phase separation behavior in the NIPS process (Mbareck *et al.* 2009). Maybe this is the reason why PVP is used as the pore forming agent during membrane fabrication.

Viscosity of casting solutions

Another important factor in membrane fabrication is the viscosity of the membrane casting solution, which is considered an important factor during the solvent/nonsolvent exchange (Zhang *et al.* 2010). Casting solutions with high viscosity can inhibit the exchange of solvent and non-solvent during the phase inversion process, so the precipitation kinetics and the formation of membrane morphology were therefore changed (Zhen & Xu 2004).

Figure 2(a) shows that the casting solution of PES/DMSO has the highest rotational viscosity without PVP additives, followed by the PES/NMP solution. The rotational viscosities of the PES/DMF and the PES/DMAc solution are much smaller. With the addition of PVP, the viscosity values of the four solutions increase significantly, but follow the same order as that without PVP.

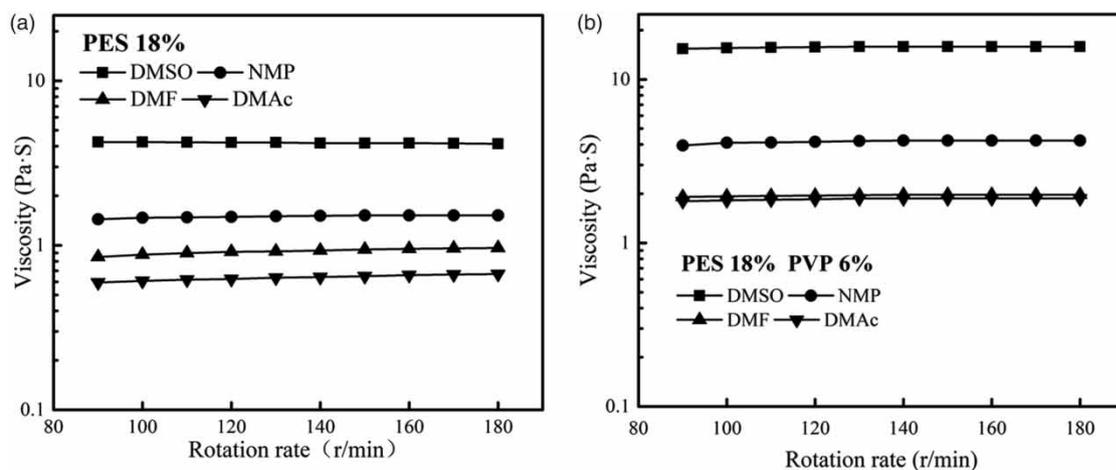


Figure 2 | Effects of different solvents on viscosity of casting solution (a) without and (b) with PVP additive.

We can also find that all the casting solutions exhibit characteristics of Newtonian fluids in the selected range of shear rates, indicating that there is no or rare chain entanglement in all kinds of solutions with or without the existence of PVP addition. It has been proved that the PES/NMP casting solutions behave as Newtonian fluids even at PES concentrations up to 38 wt.%, and the presence of PVP has no influence on the Newtonian characteristics of casting solutions using NMP as solvent (Li & Jiang 2000). Clearly, this conclusion can be extended to the casting solutions in which DMSO, DMF, and DMAc are used as solvents.

Cross-section structure of membranes

As shown in Figure 3(a), with DMSO as the solvent the cross section of the membrane shows a structure of finger-like pores with the same pore diameter and no cavities at all. The formation of this structure can be attributed to the low thermodynamic stability of the PES/DMSO/H₂O system, a little nonsolvent (i.e. H₂O) was sufficient to induce the phase inversion of the polymer solution. Therefore, fast liquid-liquid phase separation formed a skin layer rapidly, hindering the formation of macrovoids. These results would favor the formation of an impermeable finger-like structure with low membrane porosity. As shown in Figure 3(b), membranes cast with DMAc are still dominated by finger-like structures, but there are some holes in the supporting layer. When DMF was used as the solvent, the cross section of the membrane was dominated by some big holes, shown in Figure 3(c). In the case of NMP as solvent, irregular macrovoids were observed beneath the skin layer in Figure 3(d). Obviously, the cross-section structure of the membrane from different solvent systems was different, which was also the result of the interaction of the thermodynamic properties of the casting solution and the kinetic factors in the process of membrane formation.

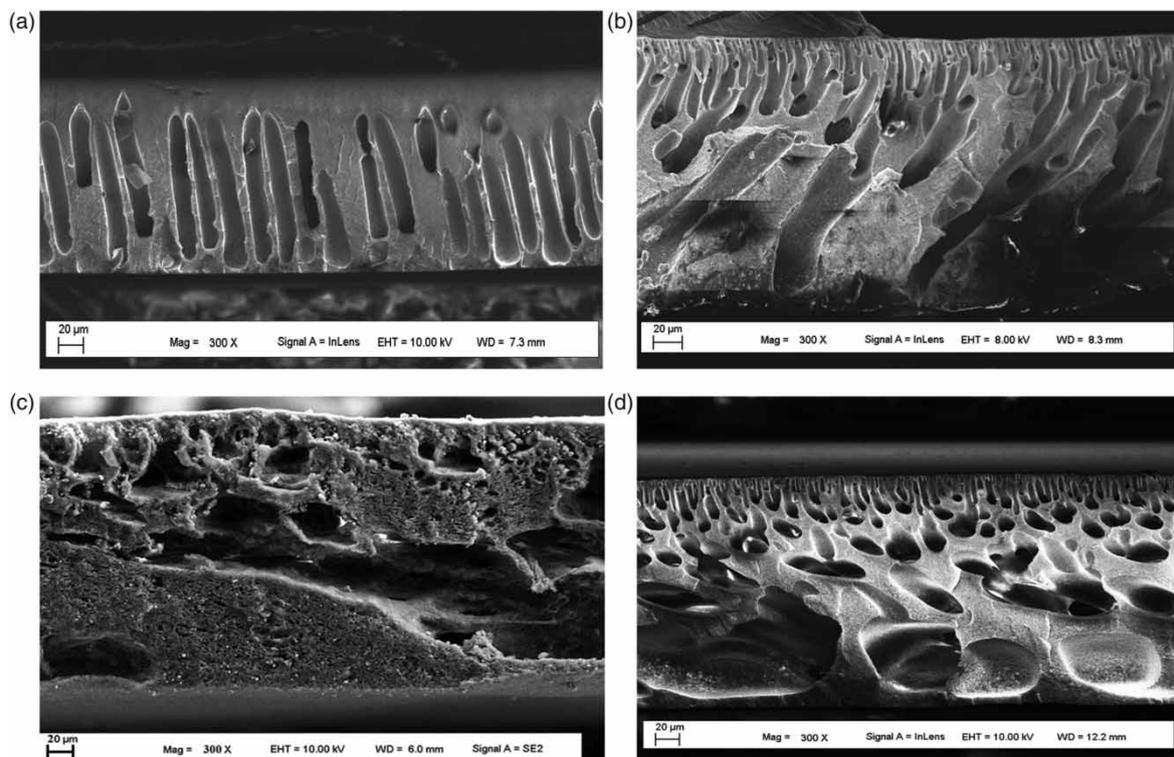


Figure 3 | Cross-section SEM image of membranes cast from (a) DMSO, (b) DMAc, (c) DMF, (d) NMP solution.

Formation mechanism of PES membrane in different casting solutions

It is generally accepted that, according to the speed of liquid-liquid phase separation, there are two different membrane-forming mechanisms, which refer to the formation of a porous membrane with an instantaneous separation, and a dense membrane with a delayed separation, as shown in Figure 4(a) and 4(b) (Hao & Wang 2010). Because the methods for preparing all these membranes were the same, all of them formed asymmetric porous membrane structures through the NIPS method (Boom *et al.* 1994). Therefore, we will discuss the influence of different solvents on the membrane structure formed by instantaneous phase separation.

Relevant research shows that the existence of a micronucleus of poor polymer phase is the main reason for the formation of big holes in a membrane; meanwhile, the solvent diffuses from the surrounding polymer solution and flows in, which makes the micronucleus grow (Chen *et al.* 2015). The critical line of phase transformation in the ternary phase diagram for casting solution with different solvents is not the same (thermodynamic properties), thus the composition change curve and membrane formation pathway are not the same (dynamic performance), as shown in Figure 4(c).

DMSO/PES system has the weakest affinity with the non-solvent phase (water), so it takes the shortest time to form a porous membrane from instantaneous phase separation. The micronucleus of poor polymer phase diffuses rapidly from casting solution to water, forming a finger-like pore structure with almost the same pore size. On the contrary, the NMP/PES system has the strongest affinity with water, and takes the longest time for phase separation, which leads to the increase of solvent

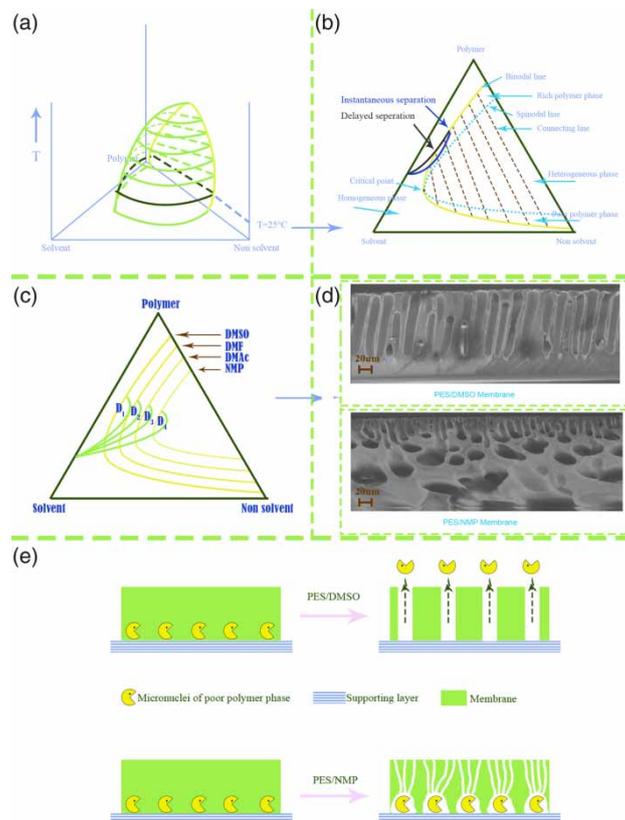


Figure 4 | Schematic illustration of different formation mechanisms of membranes. Three-dimensional phase diagram of polymer, volume and non-solvent ternary system at different temperatures (a). Ternary phase diagram with liquid-liquid phase separation at 25 °C (b). The evolution curve of the composition for different solvent casting solutions after immersion into non-solvent (c). Comparison of membranes' cross-section structure for DMSO and NMP as solvent (d). Comparison of the formation mechanism of membrane with DMSO and NMP as solvent (e).

absorption of the micronucleus, resulting in the formation of large holes and a high porosity in the membrane as shown in Figure 4(d).

However, due to the good affinity between the NMP/PES system and water, and the growing of a micronucleus, it is difficult for the poor polymer phase micronucleus to rush out from the membrane surface to form a penetrating pore like the DMSO/PES system as shown in Figure 4(e). Correspondingly, the small pore structure on the skin layer is formed by the slow precipitation of the poor polymer phase micronucleus.

In the process of PES membrane preparation through the NIPS method, the choice of different solvents will affect the interaction parameters (Flory-Huggins parameters) between solvent/nonsolvent and solvent/polymer, which will change the thermodynamic stability of the casting solution and mainly affect the 'support layer' structure of the membrane, as shown in Figure 4(d). It is well known that the mechanical properties of the membrane are primarily affected by the support layer of membrane (Mbareck *et al.* 2009). Therefore, the study on the thermodynamic and viscosity properties of the casting solution from different solvents in this paper provides an important theoretical basis for the preparation of PES membranes with different support layer structures and different mechanical properties.

CONCLUSIONS

In this paper, we focus on the effects of four different organic solvents on the cross-section structure, especially the support layer structure of the PES membrane. Due to the influence of the thermodynamic stability and the viscosity of the casting solution with different solvents, the cross-section structures of the membranes have changed from a 'figure-like' structure of PES/DMOS casting solution to a 'sponge-like' structure of PES/NMP casting solution. Finally, the mechanism of membrane formation from the casting solution with different solvents is also provided, which provides an important theoretical basis for the preparation of PES membranes with different support layer structures and different mechanical properties.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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