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Fabrication of polysulfone membrane via thermally induced phase separation process

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ABSTRACT

Polysulfone (PSF) membranes were successfully prepared by thermally induced phase separation (TIPS) using dipropylene glycol dibenzoate (DPGDB) as the diluent for the first time. Interestingly, the typically liquid-liquid (L-L) phase separation with coarsening process was not observed and the gelation occurred for the system during the cooling process. Moreover, the cross-section morphologies of all the membranes showed the network structure for the PSF concentration is in the range of 17wt%–21wt%. The membrane formation mechanism concerning the phase separation-gelation was proposed. The rejection of bovine serum albumin (BSA) of the membrane increased from 83.5% to 95.9% with the increase of PSF concentration. Additionally, the maximum break strength the membrane was as high as 7.3 MPa. The present study may open a new method to fabricate PSF membrane and control membrane structure.

1. Introduction

Membrane separation technique has been widely used in water treatment, food process and protein purification [1,2]. Among the polymers, polysulfone (PSF) is a common material to prepare membrane due to its better acid and alkali resistance, good thermal and chemical properties. So far, all the PSF membranes were prepared by non-solvent phase separation (NIPS) technique [3]. The mass transference for this method suggests the so many parameters during the membrane formation process, which in turn leads to the difficulty in controlling the membrane structure [4]. Thermally induced phase separation (TIPS) technique, based on heat transfer, was first introduced by Castro in 1980 [5]. In this method, a polymer solution is formed at high temperature and cooled to induce phase separation and polymer solidification. The porous membranes were obtained after the extraction of diluent. Compared with NIPS, TIPS technique is more reliable for controlling the membrane structure because the parameters of influencing membrane structure are fewer. Presently, the TIPS method is mainly used to prepare crystalline polymer membranes and few researches were carried out to investigate the preparation of amorphous polymer, especially for PSF.

In this work, PSF membranes were successfully prepared via the TIPS process by using dipropylene glycol dibenzoate (DPGDB) as diluent. In contrast to the previous reports [6], the cross-section morphologies of all the membranes showed the network structure within the experimental scope. The membrane formation mechanism concerning the phase separation-gelation was proposed and the influence of PSF concentration on the membrane performance was investigated. To our knowledge, this is the first investigation on the preparation and discussion of PSF membrane by TIPS process.

2. Experimental

PSF ($\eta = 0.60$) was purchased from Dalian polysulfone Plastic Co. Ltd., P. R. China. DPGDB, provided by Shanghai Chemical Reagent Co, Ltd., was used as diluent. Ethanol (purity > 99%) was used as the extractant. They were used without further purification.

Measured PSF and DPGDB, listed in Table 1, were mixed in a glass flask at 150 °C for 4 h under nitrogen atmosphere. After deaerated under reduced pressure, the casting solution was uniformly spread onto a 100 °C clean stainless plate using a casting bar with a gap of 200 μm and immediately chilled into 25 °C deionized water bath(the interval time is controlled within 5 s).Then, the membrane was transferred to ethanol for 48 h to remove diluent. The final membranes were vacuum freeze-dried for 10 h.

The cloud temperature (T_{cloud}) of phase diagram was determined according to Sharma [7]. It should be noted that the cloud points are represented by the microgel resulting from phase sepa-

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Table 1
The code and composition of PSF/DPGDB casting solutions.

Code	Composition of the casting solution (wt%)	
	PSF	DPGDB
M1	17	83
M2	19	81
M3	21	79

ration of the polymer solution [8]. T_{cloud} was also determined visually by the appearance of turbidity under an optical microscope (Nikon Eclipse E600POL). The gelation temperature (T_{gel}) of phase diagram was determined by HAAKE MARS. The temperature scanning from 150 °C to 25 °C was carried out and the cooling rate was 10 °C min^{-1} [9].

The cross-section and top-surface morphologies of the membranes were observed by a field-emitting scanning electron microscope (FE-SEM, S-4800, Hitachi) after sputter-coated with gold. The cross-sections of the membranes were obtained by freeze-fractured in liquid nitrogen.

Water permeability and rejection of BSA were used to characterize the permeability. The mean pore size and porosity were measured to characterize the pore structure of the membrane. Details are shown in Supporting Information.

The mechanical properties of the membranes were measured on a tensile apparatus (AG-1 pull equipment, Japan) at room temperature. The membrane was fixed between two pairs of tweezers with a length of 50 mm and then extended at a constant elongation rate of 25 mm min^{-1} until it was broken.

3. Results and discussion

Fig. 1(a) shows the phase diagram of PSF/DPGDB system. There existed the cloud line and the gelation line. Moreover, with the decrease of temperature, the coarsening process of liquid droplets, the typical behavior of liquid-liquid (L-L) phase separation for amorphous polymer cannot be observed under the optical microscope, which is contradicted with those reported in documents [5,6,10]. However, phase separation of the PSF/DPGDB system indeed occurred because turbidity can be observed when the temperature decreased to 71 °C and the turbidity became more and more obvious with further lower temperature, as shown in the optical microscope on the right.

The above phenomenon can be ascribed to that the PSF/DPGDB system had formed microgel domains resulting from selective interactions between the PSF and parts of the diluent molecule during the temperature decreased to T_{cloud}. That is, in the proper conformation of DPGDB, small domains of PSF could form gels while the rest remains solvated, presumably by the benzoate groups. As shown in Fig. 1(b), both PSF and DPGDB contained the benzene ring and ether bond, which will lead to the selective interactions between PSF and DPGDB). These microgels can lead to turbidity but not coarsen with decreasing temperature, even the temperature reached the gel temperature, which suggested the interconnection between microgels and forming gel.

Fig. 2(a) shows the cross-section morphologies of PSF membranes. It can be seen that the cross-section morphologies are all the network structure. The cellular pore structure, the typical structure formed via L-L phase separation, was not found. This can be ascribed to the formation of the gel, which will restrict the movement of polymer chains and thus suppress the formation of the cellular structure [11].

Based on the phase diagram and membrane morphologies, the membrane formation mechanism, the phase separation-gelation, was proposed in Fig. 2(b). In detail, as the temperature decreased to T_{cloud}, phase separation caused by the formation of microgel domains, that is the individual loose ensemble formed with the interconnection of PSF molecular chain. These microgels grew and the number of microgels increased until the temperature decreased to the gelation temperature. The gel (the solidified PSF/DPGDB system) of the three-dimensional network, composed of the interconnected ensembles and the diluent filling other space, was formed. Finally, the membrane with uniform and interconnected network structure was formed after the extraction of the diluent.

Fig. 3 showed the pore structure and performance of PSF membrane. It can be seen that as PSF concentration increased from 17 wt% to 21 wt%, PWF and the mean pore size decreased from 297.1 L h^{-1} m^{-2} to 18.4 L h^{-1} m^{-2} and from 59 nm to 17 nm, while the break strength and the retention of BSA for the membrane increased from 4.7 MPa to 7.3 MPa and from 83.5% to 95.9%,

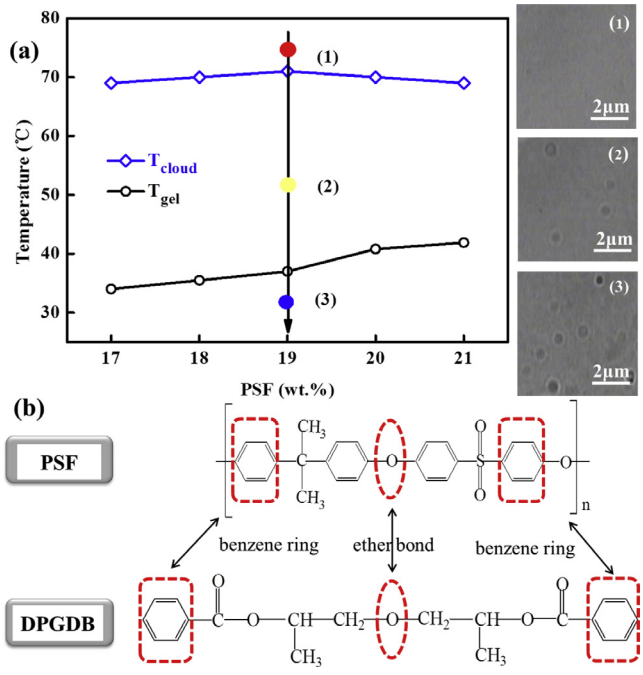

Fig. 1. (a) Phase diagram and the optical images of PSF/PGDB system (b) The schematic diagram of molecular interaction between PSF and DPGDB.

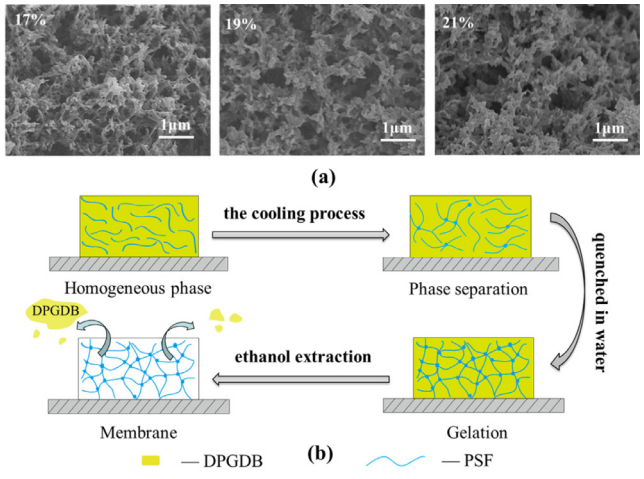

Fig. 2. (a) Cross-section SEM micrographs (b) Schematic diagram of membrane formation mechanism.