

STRUCTURE AND PERFORMANCE OF POLYAMIDE-6 MEMBRANES PREPARED BY THERMALLY INDUCED PHASE SEPARATION*

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Abstract The asymmetric polyamide-6 (PA6) membranes were prepared by thermally induced phase separation. From the scanning electron microscopy (SEM) images, it is observed that with the increase of silicon dioxide (SiO₂) content the structure of obtained membranes gradually varied from cellular structure to large ball-shaped cluster aggregates. Subsequently, with the addition of SiO₂, pure water flux increased first and then decreased, while rejection showed the opposite trend. Besides, raising the coagulation bath temperature was favorable to increase pure water flux. Consequently, different membrane morphologies and performance were obtained by changing SiO₂ content and coagulation bath temperature.

Keywords: Thermally induced phase separation; Membrane; Polyamide-6.

INTRODUCTION

Membrane separation processes have been studied extensively as promising energy-saving separation techniques^[1]. Owing to its good chemical stability, good biocompatibility, excellent hydrophilicity and outstanding strength, PA6 was considered as a promising membrane material. Some literatures indicated that PA6 membrane was an ideal choice for nanofiltration (NF) and osmosis reversal (OR) process^[2], others investigated gas permeation properties of PA6 membranes^[3]. In the work of Ma *et al.*^[4], PA6/chitosan blend membranes were prepared by combining solvent evaporation and a phase inversion technique, and their anti-bacterial properties were studied. In the study of Nie *et al.*^[5], covalent coupling of chitosan (CS) to activated nylon membrane was performed after the reaction of the microporous nylon membrane with formaldehyde. Porous PA6 membranes have been commercialized for many years and nowadays widely used in fine separation processes such as beverages and alcohol sterilization, pharmaceutical filtration, *etc.* However, commercial PA6 membranes are often manufactured by a 'phase inversion' process. To date, few scientific papers have reported the use of thermally induced phase separation (TIPS) method for PA6 membranes. Since the 1980s, by Castro, TIPS method has been studied extensively for the preparation of porous membranes. This process gains much interest because of its advantages over other conventional membrane preparation methods such as solvent casting, stretching and track etching. The TIPS process, which is applicable to a wide range of polymers including crystalline polymers, requires few parameters in determining the micro-pore structure compared with other processes. A mixture of a polymer with diluents that does not form a single phase around room

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temperature often forms a homogeneous mixture at an elevated temperature caused by the upper critical solution temperature (UCST)-type phase behavior^[6]. PA6 has strong intermolecular hydrogen bonding and no suitable solvent at room temperature. Therefore, *N*-ethyl-2/4-methylbenzenesulfonamide was chosen as diluent. This paper aims to offer an attractive way to prepare PA6 membrane in which PA6 is dissolved in diluents, then the homogeneous solution undergoes phase separation during cooling process and finally the diluent is extracted out, leaving micro-pores.

In this paper, PA6 membranes were prepared by thermally induced phase separation from ternary system (diluents/PA6/additive), and the performance of membranes was evaluated by the testing of water flux, rejection and porosity. The fine morphology of membranes was visualized by scanning electron microscopy (SEM). In addition, the membrane and its casting solution's crystalline properties were determined using differential scanning calorimetry (DSC). The structures of the membranes were also studied in detail through FTIR spectra.

EXPERIMENTAL

Materials

Commercial PA6 (Tian He Chemical Fiber Co., Ltd., Tianjin, China) of fiber-grade was received in pellet form. *N*-ethyl-2/4-methylbenzenesulfonamide used as diluent was purchased from Jin Li Chem. Co., Ltd. Jiaxing, China. Microsized silicon dioxide (SiO₂) was obtained from Institute of Chemical Planning Tianjin, China. Antioxidant 1076 was supplied by Li Sheng Chemical Plant, Tianjin, China. All the other reagents were obtained from Keruishi Fine Chemical Co., Ltd., Tianjin, China, which were of analytical grade and used without further purification.

Preparation of Membrane and Characterization of Solution

The mixed diluents (MD) were prepared by adding polyethylene glycol 20000 (PEG20000) and Tween-80 into *N*-ethyl-2/4-methylbenzenesulfonamide in weight proportion of 1:1:8. Here, Tween-80 not only serves as a composition of MD but also benefits the extraction of MD. The weight ratio of PA6 in PA6/MD is 50%, while SiO₂ (additive) accounts for 0%, 5%, 10%, 15% of the weight of PA6, respectively, and named as S1, S2, S3, S4, correspondingly. PA6/MD/additive (SiO₂, extremely little antioxidant 1076) mixtures were stirred in a vessel heated to 200°C in a temperature-regulating heater. After stabilizing for about half an hour, the homogeneous solution was poured onto a preheated stainless steel plate, and with the help of a drawknife it became a membrane. The membrane accompanying with the stainless steel plate was rapidly exposed into a specific temperature water bath. The default is 20°C.

After peeling off the plates, the membranes were immersed into absolute alcohol to extract diluents out. Then, the membrane samples were submerged in glycerin for 48 h and dried at room temperature for performance testing.

Differential scanning calorimetry (NETZSCH, DSC200F3) was used for characterizing the thermodynamic properties of S1, S2, S3 and S4 solutions at a changing temperature rate of 10 K/min.

Characterization of the Membranes

Morphology and crystallization

For scanning electron microscopy (SEM, Quanta, 200, Netherlands FEI) observation, the samples were fractured in liquid nitrogen, and then attached to the sample supports and coated with a gold layer. DSC analysis was carried out with a heating/cooling rate of 10 K/min in a temperature interval 25–300°C. Crystallization heat ΔH_c was determined from the crystallization peak area. Crystallinity was evaluated by:

$$\phi_{\text{DSC}} = \frac{\Delta H_c}{\Delta H_{100} \times V_m} \quad (1)$$

$\Delta H_{100} = 230 \text{ J/g}$ is the crystallization heat for a 100% crystalline sample of PA6. V_m is the mass fraction of PA6^[7]. The membranes were characterized by FTIR spectroscopy (BRUKER VECTOR22, Germany) in film forms.

Pure water flux

Pure water flux was measured with a self-made water flux test device at 0.4 MPa pressure. The flux was equilibrated for the passage of the first 15 min permeate whilst the following 15 min permeate was collected. Pure water flux was evaluated by:

$$J = \frac{V}{At} \quad (2)$$

where J is pure water flux (L/(m²·h)), V the volume of penetrated water (L), A the effective area of the membrane (m²) and t is the recorded time (h). All the experiments have been conducted thrice to obtain the results presented in this study which were an average value.

Rejection

Rejection was determined by UV spectrophotometer with the filtered solution. It's the solution of 2 g egg white albumin dispersed in 0.3 g/L aqueous solution of sodium hydroxide that was used as the original solution. Then, the filtered solution was obtained in the same way as water flux testing. The membrane rejection (R) was defined as:

$$R = \left(1 - \frac{c_2}{c_1}\right) \times 100\% \quad (3)$$

where c_1 and c_2 represent the feed and permeate concentrations, respectively.

Porosity

The membrane porosity (ε) was defined as the pore volume divided by the total volume of the porous membrane. It can be determined by gravimetric method:

$$\varepsilon = \frac{m_0 - m_3}{m_1 - (m_2 - m_0)} \times 100\% \quad (4)$$

where m_3 is the dry membrane weight, m_0 is the wet membrane weight, m_1 is the weight of pycnometer full of water and m_2 is the weight of pycnometer after putting wet membrane into pycnometer full of water.

Bubble point pore diameter

The pore size of the membrane was investigated by the bubble-point with gas permeation method, similar to that described by Piatkiewicz *et al*^[8]. While the maximum pore size of membranes can also be obtained by calculating^[9]. The measurement was conducted by capillary flow porosimetry (Laurel, CFP-1100-A*, USA). During the variation of transmembrane pressure drop from 0 MPa to 0.60 MPa, the pressure at which nitrogen flux began to increase was considered as the bubble point pressure. The relationship between pore size and pressure drop is given by Laplace equation:

$$r = \frac{\sigma \cos \theta}{\Delta p} \quad (5)$$

where σ , θ and Δp represent surface tension of wetting liquid, contact angle between wetting liquid and the membrane, and pressure drop respectively.

RESULTS AND DISCUSSION*Thermodynamic Property of the Casting Solutions*

Thermodynamic property plays a very important role in the membrane morphology formation, especially in TIPS process, because it determines the mechanism of phase separation. So melting and crystallization properties of the casting solutions are shown in Fig. 1.

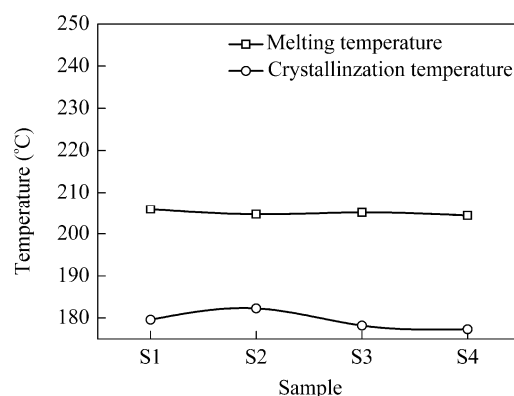


Fig. 1 Melting and crystallization properties of the casting solution

As is illustrated in Fig. 1, on the melting temperature curve all samples exhibit a melting endothermic peak at around 205°C which is observed at 225°C in pure PA6 curve^[4]. MD greatly reduced the processing temperature of PA6, while SiO₂ content had little impact on the melting of casting solutions. On the crystallization temperature curve, crystallization peaks occur at around 180°C which is slightly lower than that of pure PA6. Because the MD lowers the chemical potential of the blends and depresses the equilibrium melting point of the polymer, the crystallization temperature decreases with the addition of diluents^[10]. It shows that the crystallization temperature of S2 is higher than that of others. A possible explanation for this could be certain amount of SiO₂ plays a role of heterogeneous nucleation^[11].

Thermal Analysis of the Membranes

As is shown in Fig. 2, all kinds of membranes feature a similar crystallization peak at around 180°C. The addition of SiO₂ changed the crystalline morphology of PA6. However, the crystallinity calculated from the crystallization heat varies with the content of SiO₂ as shown in Fig. 3. It's obvious that the crystallinity of S2 membrane is higher than that of the others. This indicates that an appropriate content of SiO₂ is favorable to PA6 crystallization. When the value is 5%, the crystallinity of PA6 reaches a maximum. This phenomenon is likely attributed to heterogeneous nucleation of SiO₂, which is confirmed by DSC of the casting solution. The relationship between absorption bands at 1199 and 1180 cm⁻¹ in the FTIR spectra demonstrates the similar conclusion.

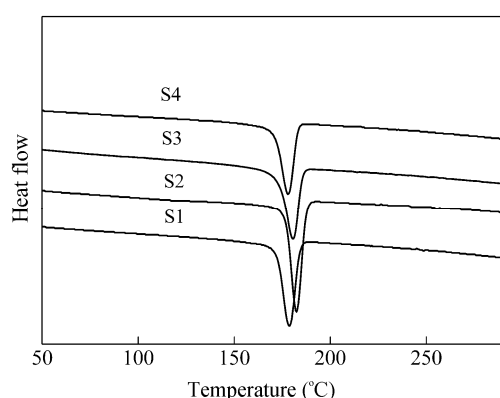


Fig. 2 The crystallization curves of membranes

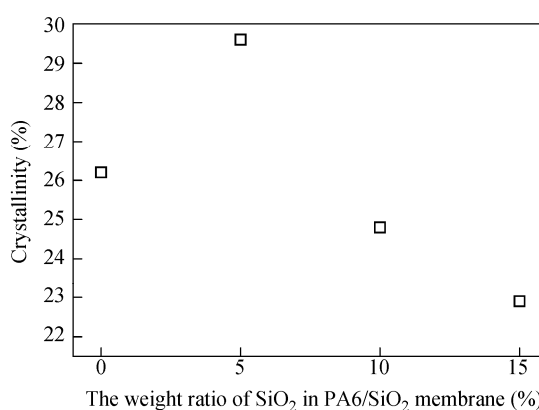


Fig. 3 Effect of SiO₂ content on the crystallinity of membranes

Fourier Transform Infrared Spectroscopy

In order to study the extraction effect of MD and explore the internal structure of the membranes, FTIR spectra

were taken (see Fig. 4), which revealed the bands that are ascribable to PA6 and SiO₂. This indicates that MD was almost extracted completely. From the spectra, it can also be inferred that there is no strong interaction between PA6 and SiO₂. FTIR assignments of the membranes are shown in Table 1.

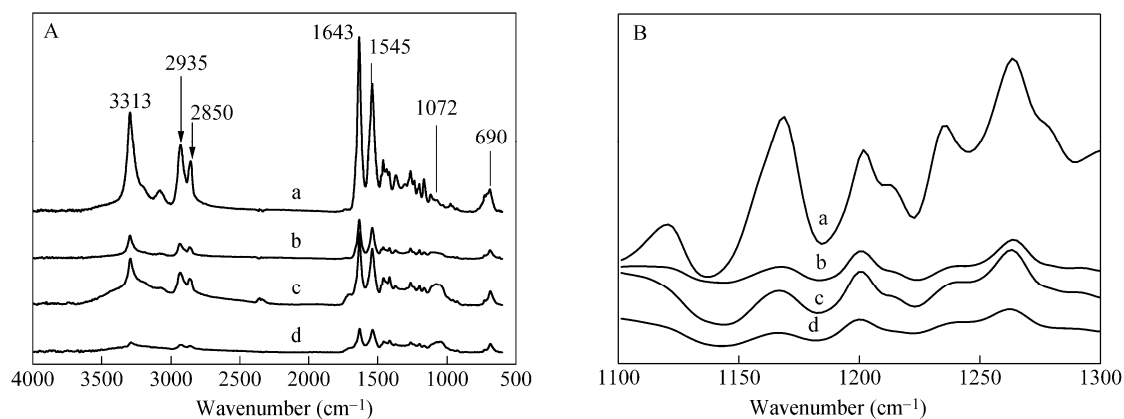


Fig. 4 FTIR spectra of membranes (a) 0% SiO₂, (b) 5% SiO₂, (c) 10% SiO₂, (d) 15% SiO₂
A) Whole wavenumber; B) Part wavenumber

Table 1. FTIR spectral assignments for membranes

Spectral assignments		Wavenumber (cm ⁻¹)
NH	stretching	3313
CH ₂	stretching	2935
CH	stretching	2850
CO	stretching	1643
NH	bending	1545
CN	stretching	1260
SiO	stretching	1072
NH	swing	690

The IR absorption spectra of the membranes were also used to determine the relative levels of crystalline and amorphous phases in the membranes. For α -type PA6 crystals bands at 1199 and 1180 cm⁻¹ represent the crystalline and amorphous components, respectively. The ratio $R = A_{1199}/A_{1180}$ has been used by a number of authors^[12, 13]. From Fig. 4(B) we calculated the ratio and the result was shown in Fig. 5. At high temperatures or molding under pressure, PA6 tends to form α -type crystals^[7]. Therefore, Fig. 5 can reflect the crystallization of membranes. The results are consistent with DSC tests.

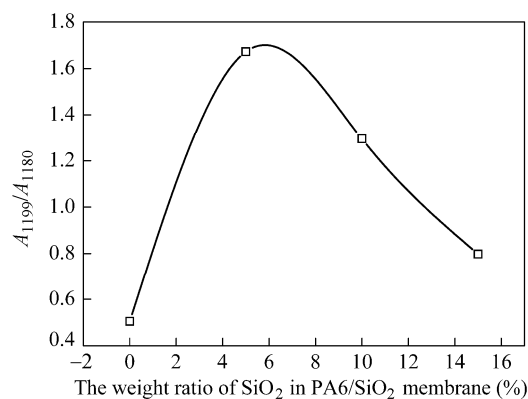


Fig. 5 The curve between A_{1199}/A_{1180} and weight ratio of SiO₂

Surface Morphology of the Membranes

Figures 6 and 7 show the morphology of the top surface and the bottom surface, respectively.

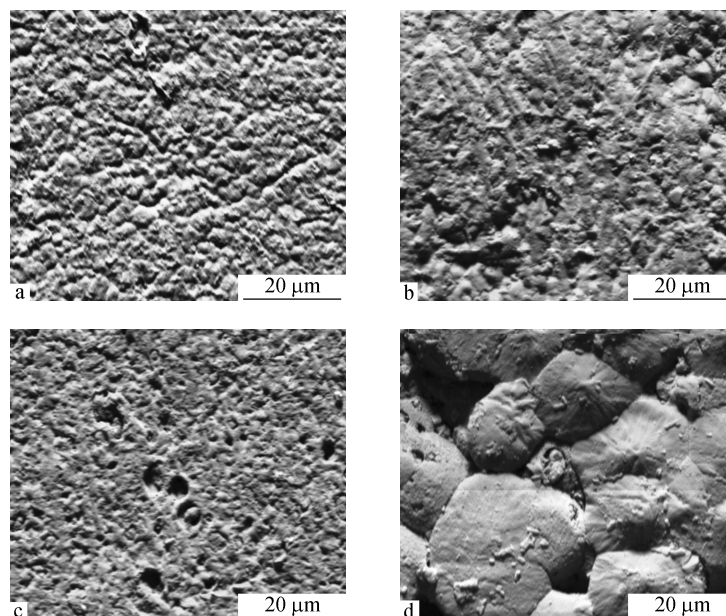


Fig. 6 Scanning electron micrographs (SEM) from top surfaces of the membranes a) 0% SiO₂; b) 5% SiO₂; c) 10% SiO₂; d) 15% SiO₂

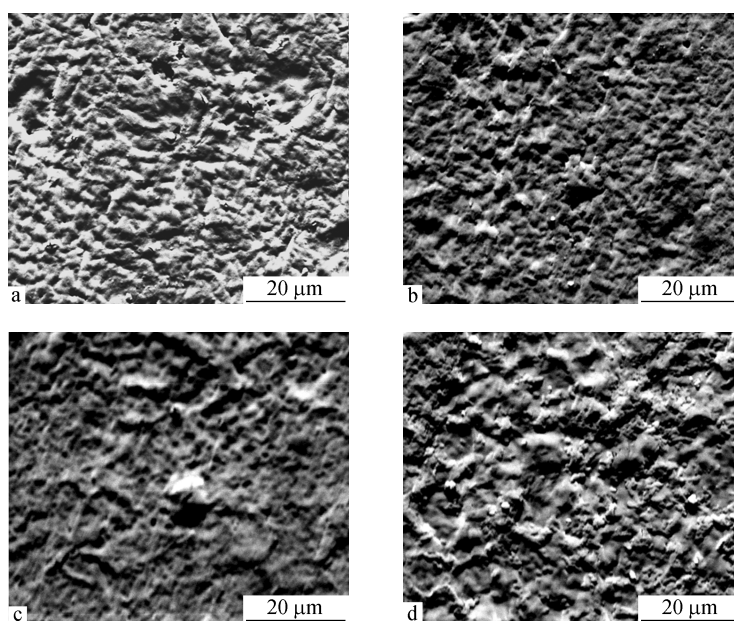


Fig. 7 Scanning electron micrographs (SEM) from the bottom surfaces of the membranes a) 0% SiO₂; b) 5% SiO₂; c) 10% SiO₂; d) 15% SiO₂

Figures 6 and 7 indicate that the membranes have an asymmetric structure, which can be clearly seen in Figs. 8(a'–c'). The top surface consists of polyamide spherulites which have grown together to form polygonal plates. With the adding of SiO₂, large ball-shaped cluster aggregates structure has become more and more

evident, especially in Fig. 6(d). MD is excluded between the spherules, leaving micro-pores. While the bottom surface exhibits a highly porous structure, which is probably due to the longer phase separation time for the bottom surface area (see Fig. 7). But excessive content of SiO_2 is prone to reunite, thus covering part of the surface micro-pores (see Fig. 7d). Besides, big hole defects appeared in Fig. 8(d) and 8(d'). The cross sections near the bottom surfaces show cellular structure while the cross sections near the top surfaces are composed by many small spherulites. In other words, the cross sections represent the morphology of asymmetric 'cellular structure' which is found inside the membrane. The structure is clearly visible in Figs. 8(a–c). According to surfaces and cross-section scanning electron micrographs (SEM), it is not difficult to predict that with the increase of SiO_2 content the membrane morphology varied correspondingly from typical cellular structure to large ball-shaped cluster aggregates^[14].

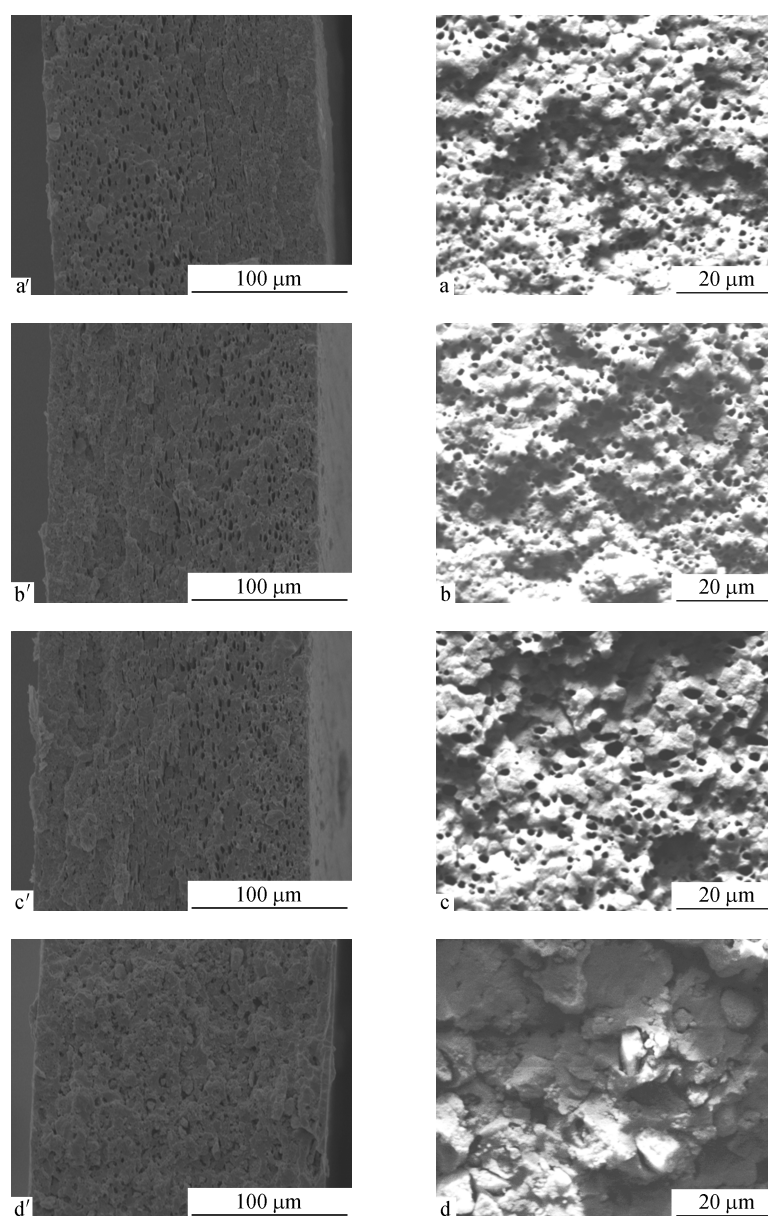


Fig. 8 Scanning electron micrographs (SEM) from cross-sections of the membranes a) 0% SiO_2 , b) 5% SiO_2 , c) 10% SiO_2 , d) 15% SiO_2 ; a'–d') Overview, a–d) Detail

Penetration and Separation Performance

The pure water flux and rejection of the membranes are, respectively, shown in Fig. 9. It clearly illustrated that with the addition of SiO_2 , pure water flux was increased first and then decreased, while rejection showed the opposite trend. This result has been observed in many literatures^[15, 16]. It depends on the properties of membrane micro-pores, which could be speculated by SEM images of the membranes.

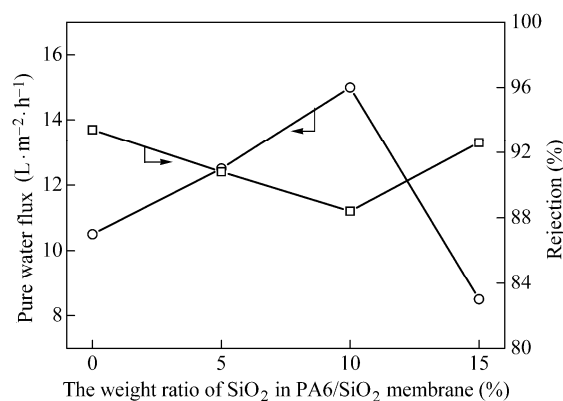


Fig. 9 Pure water flux and rejection of the membranes

Figures 10 and 11 show porosity, bubble point pressure and bubble point pore diameter of the prepared membranes, respectively. As shown in the figures, it is clearly observed that the addition of SiO_2 increased porosity and bubble point pore diameter and decreased bubble point pressure of the membranes, which may be attributed to interface micro-pores between PA6 and SiO_2 due to poor compatibility between inorganic particles and polymer. Whereas, when the content of SiO_2 exceeded 10%, the membrane morphology varied correspondingly from cellular structure to large ball-shaped cluster aggregates, and accordingly penetration properties including porosity and bubble point pore diameter declined. This result is in good agreement with the result of pure water flux. As is illustrated in Fig. 7(d), this may be due to the excessive content of SiO_2 which plugged some micro-pores and reduced penetration properties of the membrane.

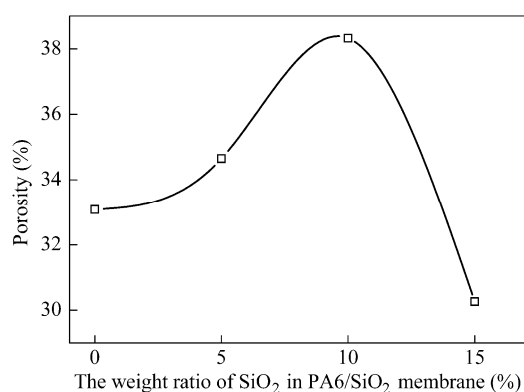


Fig. 10 Porosity of the membranes

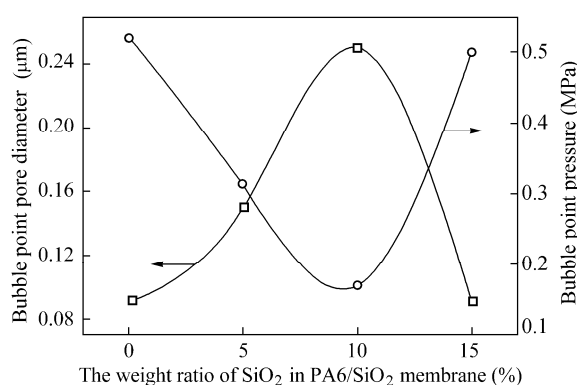


Fig. 11 Bubble point pressure and bubble point pore diameter

The effect of cooling rate on pure water flux is presented in Fig. 12. With the cooling rate decreasing, pure water flux is improved significantly. This result has been observed in many literatures^[17, 18]. This is attributed to the different phase separation time caused by cooling rate. During the slow cooling process, diluents had longer time to gather and larger pores formed after extraction. While in the case of quenching, the degree of super-

cooling is so great that polymer crystallization and diluents precipitation complete in a very short period of time. But more crystal nuclei are produced and the number of spherules increases, which is unfavorable to pure water flux.

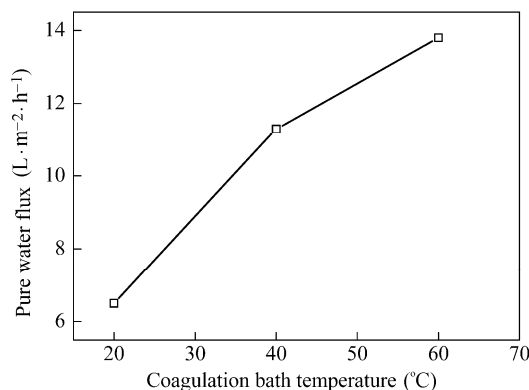


Fig. 12 Effect of coagulation bath temperature on pure water flux of the membranes (5% SiO₂ membranes)

CONCLUSIONS

Asymmetric PA6 membranes can be manufactured by thermally induced phase separation. The membranes have good penetration and excellent separation performance. Coagulation bath temperature and SiO₂ content have an appreciable effect on membrane properties. With the increase of SiO₂ content, the membrane morphology varied correspondingly from typical cellular structure to large ball-shaped cluster aggregates. Therefore, the membrane morphology and performance could be controlled by additive content and coagulation bath temperature. In addition, polymer concentration is another important factor, which is to be studied further.

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