Desalination and Water Treatment
www.deswater.com

17 (2010) 262–267
May

1944-3994/1944-3986
doi: 10.5004/dwt.2010.1727

Effect of diluents on the characteristics of cellulose diacetate membranes prepared via thermally induced phase separation method

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Received 3 August 2009; accepted 22 November 2009

A B S T R A C T

Cellulose diacetate hollow fiber membranes were fabricated via thermally induced phase separation (TIPS) method to investigate the effect of diluent on membrane characteristics. Ethylene glycol (EG), diethylene glycol, triethylene glycol and tetraethylene glycol were used as diluent. Asymmetric membrane structures with dense layers on the outer surfaces and porous structures on the inner surfaces were obtained. When EG was used as diluent, the phase separation temperature of the cellulose diacetate solution was high, resulting in the large pore on the inner surface of the fabricated membrane. This is because solution with higher phase separation temperature has the longer coarsening time for the structure. The rejection experiment elucidated that the membrane fabricated from diluent of lower phase separation temperatures showed the higher rejection. The membranes with ultrafiltration property were successfully prepared by TIPS method.

Keywords: Thermally induced phase separation; Cellulose diacetate; Phase separation temperature; Rejection; Diluent

1. Introduction

Membrane separation technology is widely applied for water treatment and receiving more attention since it is an outstanding process for the removal of particles, turbidity and microorganisms of natural and waste waters. It has also an advantage of low energy consumption compared with conventional process due to no phase change. The asymmetric structure of membrane plays an important role for ultrafiltration (UF) membrane. Thus, both of thickness of the dense layer and porosity of the support membrane should be optimized. Most of asymmetric membranes are fabricated by casting the polymer solution and immersing in a non-solvent bath to induce phase separation and gelation [1–3]. This method is called nonsolvent induced phase separation (NIPS). This technique was applied for polymers such as polymethylmethacrylate (PMMA) [4], ethylene vinyl alcohol (EVAL) [5], polysulfone (PSf) [6], and poly(vinylidine fluoride) (PVDF) [7].

Thermally induced phase separation (TIPS) process is applied to a wide range of polymers that could not be used in NIPS process due to the solubility problems. Moreover, there are many factors influencing porous structure in NIPS process although the membranes with porous structures can be obtained. Therefore, NIPS process is difficult in controlling membrane structure. Compared with NIPS process, another advantage of TIPS process is the ease of controlling membrane structure because the factors of influencing porous structure are fewer. Accordingly, a variety of

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Presented at the Fifth Conference of the Aseanian Membrane Society Aseania 2009 "Recent Progress in Membrane Science and Technology", 12–14 July 2009, Kobe, Japan.

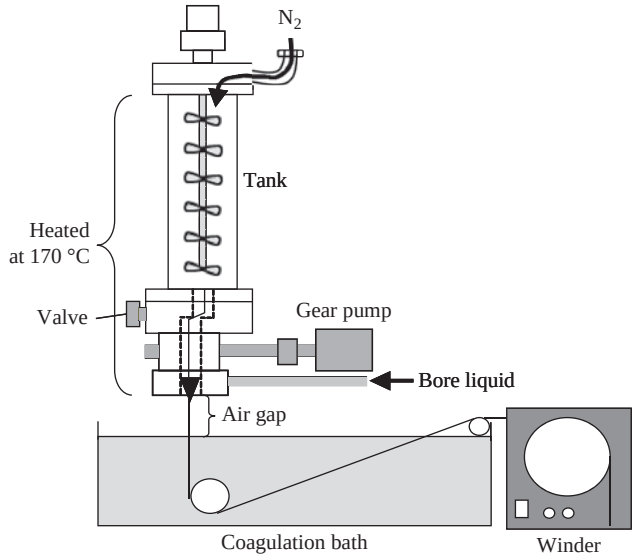

Fig. 1. Schematic diagram of the membrane fabrication apparatus.

thermally stable, chemically resistant membranes were produced by the TIPS process. To obtain membranes with more suitable characteristics such as higher hydrophilicity, strength and permeability, several studies were reported on the formation of porous membranes from a two-polymer blend and diluent system [8–10]. TIPS processes were mainly applied to fabricate the microfiltration (MF) membranes with pores larger than 0.1 μm. However, few studies were reported on the UF membrane formation by TIPS process.

The purpose of this work is to investigate the effect of diluent on the porous structure of the fabricated membranes and to vary the molecular weight cut-off of the membranes. We tried to fabricate UF membrane by TIPS process. The structure and porosity of the membranes were characterized by using a field emission scanning electron microscope (FE-SEM). The filtration performance was evaluated with solutes of various molecular weights, such as polyethylene glycol and dextran.

2. Experimental

2.1. Preparation of polymer solution

For membrane preparation, cellulose diacetate with an acetyl content of 39.8 wt% (CDA; CA-398-3, Eastman Chemical Company) was used as polymer, ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (Tet.EG) as diluent. 30 wt% homogeneous polymer solutions were prepared by stirring the polymer and a diluent in an oil bath at 170°C for 20 min.

2.2. Cloud point temperature

The prepared homogeneous solution was put between cover glasses with a lattice of 100 μm-thick Teflon® sheet. The sample was heated at 170°C for 5 min on a hot stage (HFS91, Linkam Scientific Instruments) and then cooled at a rate of 10°C min^{-1}. Cloud point temperatures during cooling were observed by microscope (BX50, OLYMPUS Co.). These measurements were repeated at least four times.

2.3. Hollow fiber membrane fabrication

Hollow fiber membranes were prepared using a batch-type extruder (BA-0, Imoto Co.) [11–12]. Fig. 1 shows the schematic diagram of the apparatus. Measured amounts of a polymer and diluent were fed into the vessel, and then mixed for 60 min at 170°C. After maintained at that temperature for 90 min, the homogeneous solution was fed to a spinneret by a gear pump under a pressure of nitrogen. The spinneret consists of outer and inner tubes, and their diameters are 1.58 and 0.83 mm, respectively. The diluent was introduced into the inner orifice to make a lumen of the hollow fiber. The hollow fiber was extruded from the spinneret and wound on a take-up winder after entering a water bath. The extrusion rate of the polymer solution and the flow rate of the diluent in the inner tube of the spinneret were fixed at 0.16 and 0.39 m s^{-1}, respectively. The diluent remaining in the hollow fiber membrane was extracted by immersing them into water.

2.4. FE-SEM observation

To obtain dry hollow fiber membranes, the prepared membranes were freeze-dried with a freeze dryer (FD-1000, Tokyo Rikakikai Co., Ltd.). The dry hollow fiber membranes were fractured in liquid nitrogen and sputtered with Pt/Pd. The cross-sections and the surfaces of the hollow fiber membranes were examined using an FE-SEM (JSM-7500F, JEOL Ltd.) with an accelerating voltage of 5 kV.

2.5. Water permeability and rejection

Water permeability through the hollow fiber membrane was measured by a method similar to that described by Iwata et al. [13]. Milli-Q water of 25°C was forced to permeate from the inside to the outside of the hollow fiber membrane. The transmembrane pressure and the flow rate of feed solution were applied to 0.15 MPa and 0.27 g s^{-1} by adjusting valves on both sides of the hollow fiber membrane. After 30 min, the

Table 1
Viscosity of the solution employed in the permeability and rejection test

Solute	Viscosity [mPa s]
Milli Q water	1.0
Sucrose	2.1
PEG 600	1.2
PEG 2000	1.0
Dextran 15,000-20,000	1.0
Dextran 35,000-50,000	1.3
Dextran 100,000-200,000	1.4
Dextran 400,000-500,000	1.2

permeated water weights were measured. The water permeability was calculated on the basis of the inner surface area of the hollow fiber membrane.

Feed solution for rejection test was prepared by dissolving 1,000 ppm of solutes and an inner standard. Sucrose, PEG600 ($M_w = 600$), PEG2000 ($M_w = 2{,}000$), four kinds of dextrans (M_w = 15,000–20,000, 35,000–50,000, 100,000–150,000, 400,000–500,000) were used as solutes, and EG as the inner standard. The viscosity of the employed solutions at 25°C, measured using a viscometer (TVB-10, Toki sangyo Co.), was listed in Table 1. One milliliters of permeate was collected by the same method as water permeability test. The solute concentration in the permeate was determined using a gel permeation chromatography (GPC) system (LC-6A, Shimadzu Co.) equipped with a refractive-index detector (RID-10V, Shimadzu Co.) and a OHpak SB – 805 HQ column at 40°C or with a SUGAR KS – 803 column at 50°C. The membrane rejection R (%) is defined as

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100, \quad (1)$$

where C_f and C_p represent the solute concentration in feed and permeate solution, respectively.

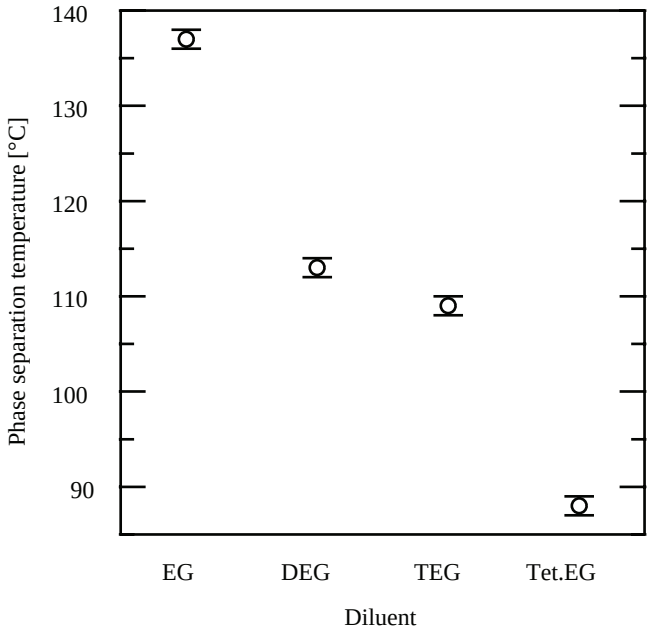

Fig. 2. Phase separation temperatures of 30 wt% CDA solutions with various diluents.

Table 2
Solubility parameters of polymer and diluents [14]

Component	Solubility parameter [$MPa^{1/2}$]
CDA	11.4
EG	32.9
DEG	29.9
TEG	27.5
Tet.EG	20.3

3. Results and discussion

3.1. Phase separation temperature

Fig. 2 shows the phase separation temperatures of 30 wt% CDA solutions with four kinds of diluents. Phase separation temperatures decreased in the order of the solutions with EG, DEG, TEG, and Tet.EG. Solubility parameters of CDA and the diluents are listed in Table 2. Generally, when the difference between the solubility parameter of polymer and that of diluents is small, it means the compatibility is high, and phase separation temperature is low. As shown in Table 2, the solubility parameters of diluents become closer to that of CDA in the order of EG, DEG, TEG, and Tet.EG. Therefore, the cloud point temperatures decrease in this order.

3.2. Membrane structure

Fig. 3 shows the cross-section and the inner and outer surface structures of the membrane fabricated from CDA (30 wt%) and TEG system. While the porous structure was obtained on the inner surface, the dense skin layer was formed on the outer surface. Thus, the clear asymmetric structure was formed. When the polymer solution is extruded from the spinneret, the polymer concentration near the outer surface of the hollow fiber membrane increases on the air gap according to the evaporation of the diluent. The concentrated polymer solution forms the dense layer on the outer surface. On the other hand, the polymer concentration

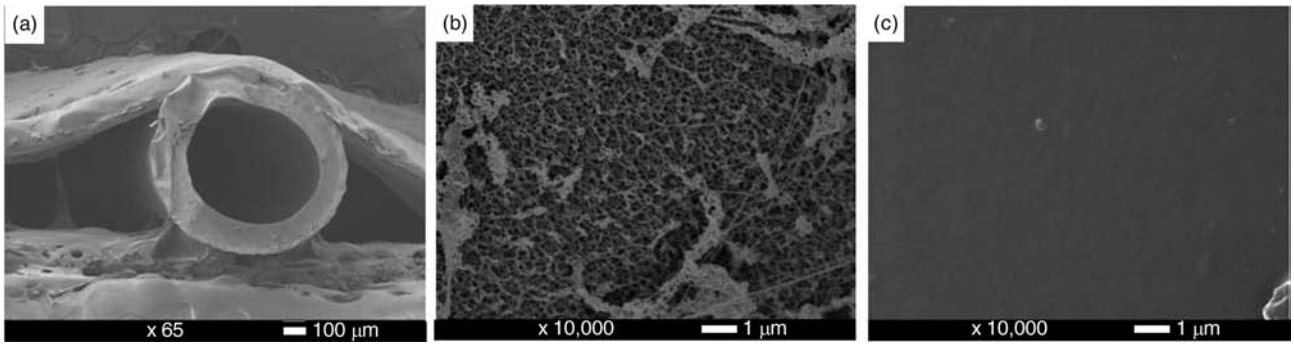

Fig. 3. FE-SEM images of fabricated membrane from CDA (30 wt%) and TEG system with air gap of 5 mm: (a) cross-section; (b) inner surface; and (c) outer surface.

is almost the same or slightly lower than the original solution on the inner surface since the diluent is introduced into the lumen of the hollow fiber as bore fluid during the extrusion. Therefore, porous structure is formed on the inner surface.

3.3. Effect of diluent on membrane structure

Using four kinds of diluents (EG, DEG, TEG, and Tet.EG), CDA hollow fiber membranes were successfully fabricated from 30 wt% CDA solutions with an air gap of 5 mm. Fig. 4 shows the FE-SEM images of the inner surfaces and the cross-sections near outer surfaces of the hollow fiber membranes. All the membranes fabricated with these diluents had asymmetric structures with submicron porous structures on the inner surfaces and dense skin layer near the outer surfaces. The membrane prepared from EG had the isolated island-like structure with the largest porous structure on the inner surface. On the other hand, the membranes prepared from the other diluents had interconnected structures. These results were due to the difference in the phase separation time. Namely, a polymer solution with higher phase separation temperatures has the longer coarsening time of the droplets generated by phase separation, and establishes the larger pores in membrane structure [15]. Thus, the largest pores were formed in the case of EG. The difference in the inner surface structures is not so clear for the membranes fabricated from DEG, TEG, and Tet.EG.

3.4. Effect of diluent on membrane performance

The solute rejection curves for fabricated membranes were shown in Fig. 5. As the polymer concentration for membrane fabrication was fixed at 30 wt%, effect of diluents on MWCO was examined. As shown in this figure, the rejections increased in the order of membranes fabricated from EG, DEG, TEG, and Tet.EG. The water permeabilities decreased as 39, 14, 4, and 0.5 L $(m^2\ h\ atm)^{-1}$ for respective membranes. This result indicated that as the phase separation temperature decreased, the denser structure was formed on the outer surface. For the membrane fabricated from Tet.EG, the rejection of dextran with molecular weight of 50,000 was about 90%. This means that the UF membrane was successfully fabricated via TIPS process. The average pore size is estimated by the following equation

$$R_p = 1.5 \times 10^{-3} \times \mathrm{MWCO} + 7.3 \quad (2)$$

where R_p is the pore radius (Å) and MWCO is the molecular weight cut-off [16]. By using this equation, R_p was found to be 13 nm for the membrane fabricated from Tet.EG. For the membrane fabricated from TEG, the rejection of smaller molecules showed minus value. This result is due to an experimental error because the rejection for such molecules is quite low.

4. Conclusions

The CDA hollow fiber membranes were prepared via TIPS process when four kinds of diluents were used. The effect of the diluents on the membrane structures and performances were investigated.

The phase separation temperatures were measured for the four solution systems. The phase separation temperatures decreased in the order of the solutions with EG, DEG, TEG, and Tet.EG. This trend could be explained based on the compatibility between CDA and the diluents.

The fabricated hollow fiber membranes had clear asymmetric structures with the dense skin layer on the outer surface and porous structure on the inner surface. The solute rejections increased in the order of membranes fabricated from EG, DEG, TEG, and Tet.EG. This result indicated that as the phase

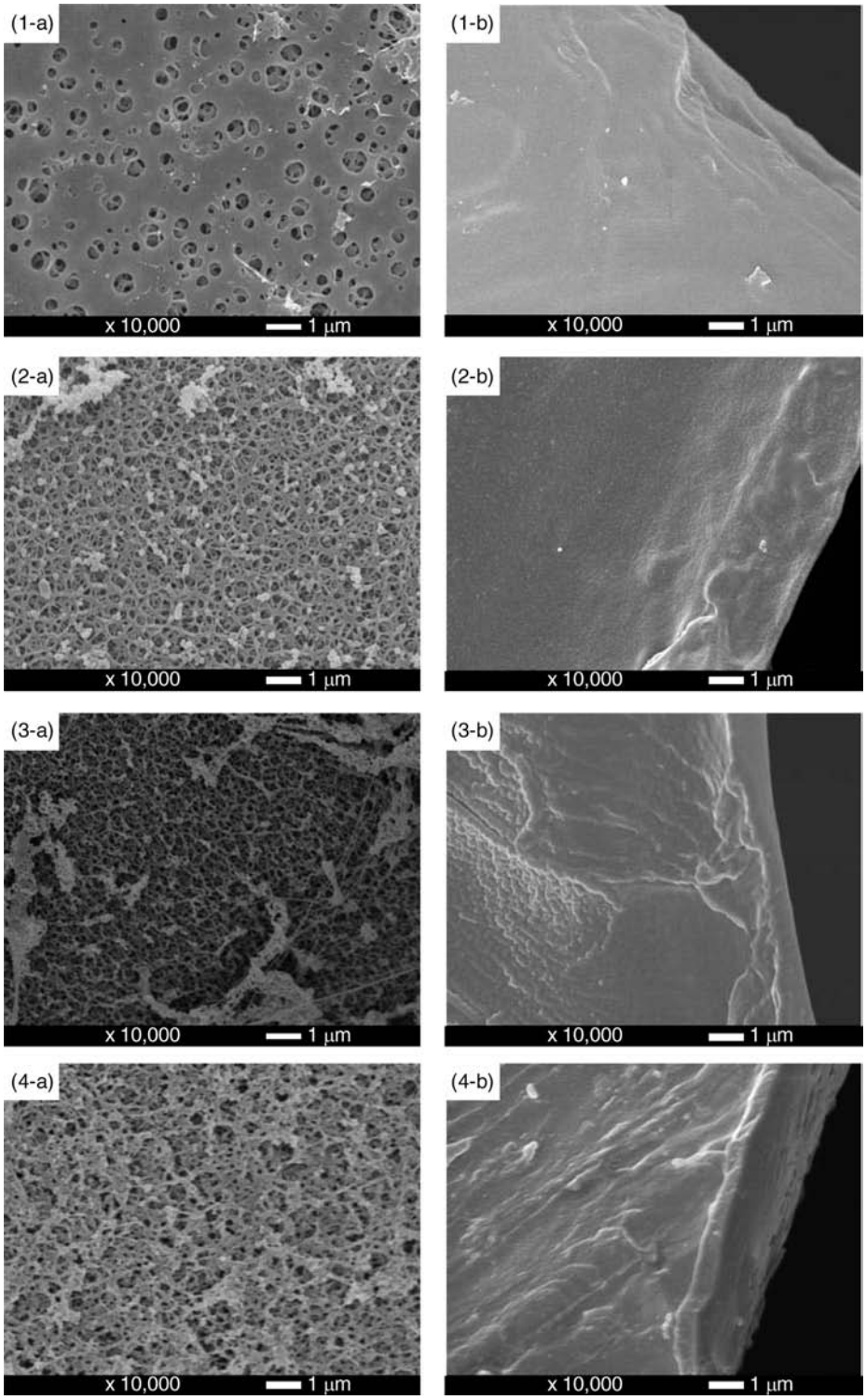

Fig. 4. FE-SEM images of fabricated membranes from CDA (30 wt%) with air gap of 5 mm: (a) inner surface and (b) cross-section near outer surface of (1) membrane fabricated from EG; (2) DEG; (3) TEG; (4) Tet.EG.

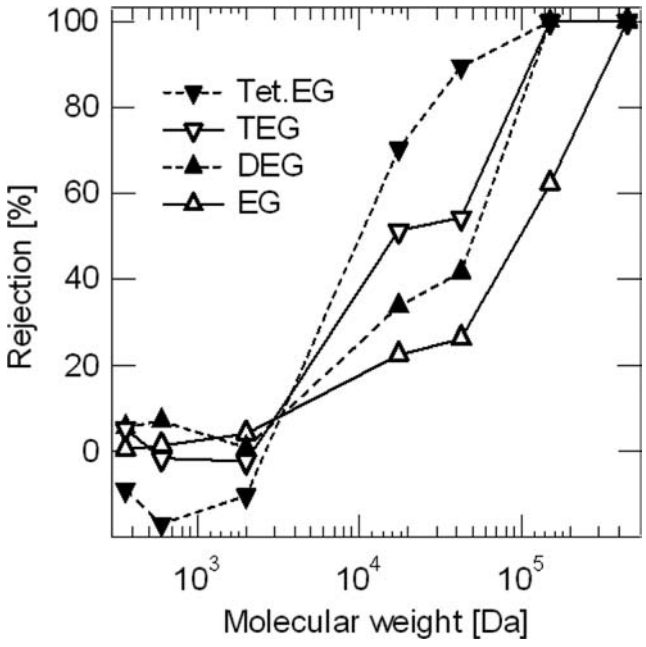

Fig. 5. Effect of diluent on the solute rejection of the membrane fabricated by CDA (30 wt%) and TEG system.

separation temperature decreased, the denser skin layer was formed on the outer surface. For the membrane fabricated from Tet.EG, the rejection of dextran with molecular weight of 50,000 was about 90%. Thus, the UF membrane was successfully fabricated via TIPS process.

Acknowledgement

This work was supported in part by the Grant-in-Aid for Scientific Research (B) (no. 20360351) from the Ministry of Education, Science, Culture and Sports of Japan.

This work was also financially supported by Special Coordination Funds for Promoting Science and Technology, Creation of Innovation Centers for Advanced Interdisciplinary Research Areas (Innovative Bioproduction Kobe), MEXT, Japan.

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