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Journal of Membrane Science 279 (2006) 601–607

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Influence of solvent on the structure and performance of cellulose acetate membranes

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Received 29 April 2005; received in revised form 2 December 2005; accepted 24 December 2005

Abstract

The liquid–liquid demixing process of cellulose acetate (CA) in two nonvolatile solvents *N*-methyl-2-pyrrolidone (NMP) and γ-butyrolactone (GBL) coagulating in water was investigated. Due to the relatively "poor" solvency of GBL for cellulose acetate and the higher interaction parameter between GBL and water, the CA/GBL/H_2O system exhibits a delayed liquid–liquid demixing, while the CA/NMP/H_2O has an instantaneous one. The solvent quality and the interaction parameter between nonsolvent and solvent determine the different liquid–liquid demixing behavior and the distinct membrane structures. By adjusting the GBL content in the solvent mixture, the effect of solvent on the membrane structure and performance was systematically studied. The membrane structure was tunable by changing the ratio of NMP/GBL. A critical ratio of NMP/GBL appears to exist that denotes the transition of membrane structure from macrovoids to sponge-like.

Keywords: Cellulose acetate; Membrane; Immersion precipitation; Liquid–liquid demixing process

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1. Introduction

Immersion precipitation is the most common method for the preparation of a range of membranes [1–3]. A homogenous polymer solution is cast as a thin film or spun as a hollow fiber and then immersed into a nonsolvent coagulation bath. Due to the exchange of solvent and nonsolvent between polymer solution and coagulation bath, phase separation of polymer solution is induced to form polymer-rich phase and polymer-lean phase. Then a vitrification or gelation process takes place to fix the membrane structure. The membrane structure is governed by the thermodynamics and kinetic aspects of the system. Though the membrane formation process is an interplay of different phenomena, it has been widely accepted that liquid–liquid demixing plays an important role in this process. Generally, a delayed phase separation usually results in membrane with a dense thick top layer and a sublayer with sponge-like structure, while an instantaneous phase separation usually results in a membrane with a thin porous top layer and a sublayer with macrovoids.

One of the simplest and most efficient ways to investigate the role of liquid–liquid demixing during membrane formation by immersion precipitation is to use a binary solvent mixture that can give rise to large morphological changes as a function of the ratio between the two solvents [4–6]. Kools [4] systemically studied the different morphologies obtained from polysulfone/*N*-methyl-2-pyrrolidone (NMP)/tetrahydrofuran (THF) solutions with various NMP/THF ratios coagulating in water. The polysulfone/NMP/water systems give rise to instantaneous demixing, and the obtained membranes contain large macrovoids, while polysulfone/THF/water systems give rise to delayed demixing, and the entire film is almost a dense film with closed cell structure. Intermediate morphologies are expected for solvent mixtures. By increasing THF content in the solvent mixture, not only the number of the macrovoids diminishes but macrovoids also broaden. Shieh and Chung [5] investigated the effect of liquid–liquid demixing on membrane morphology and performance of cellulose acetate (CA) hollow fibers by adjusting the ratio of NMP and THF in a binary solvent mixture. The CA/NMP/H_2O system exhibits an instantaneous liquid–liquid demixing, while CA/THF/H_2O system a delayed one. With an increase in THF content, the onset time of liquid–liquid phase separation increased, and the teardrop type

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doi:10.1016/j.memsci.2005.12.054

macrovoids became smaller. A combination of a volatile and a nonvolatile solvent was used in these studies. However, the highly volatile tetrahydrofuran would not be a favorable solvent for membrane preparation due to the complicated handling of the harmful or inflammable agents. Moreover, the superposition of evaporation of the volatile solvent would make the investigation of liquid–liquid demixing more complicated. Albrecht et al. [6] investigated the mechanism of macrovoids formation by changing the dope solvent composition. It was shown that by a systematic variation of the solvent composition, the morphology of the membrane could be varied from macrovoids to sponge-like structure under instantaneous demixing conditions. Two types of macrovoids that started at different locations in the cross-section of membranes were observed, which were induced by the thermodynamic state of the dope and the kinetics of the phase inversion, respectively. However, it is well known that the process of hollow fiber spinning is very different from that for flat-sheet membrane preparation [5]. In comparison with the complicated hollow fiber formation process, the flat-sheet membrane formation is to some extent more suitable for the investigation of the mechanism of the liquid–liquid demixing process.

On the other hand, according to the work by Peinemann et al. [7], γ-butyrolactone (GBL) is found to be an excellent membrane structure modifier that usually gives rise to sponge-like membrane structures [7,8]. For cellulose acetate, γ-butyrolactone is an interesting solvent since it combines non-volatility, water miscibility and polymer dissolving properties. However, cellulose acetate membrane formation using the GBL system was seldom discussed in the literature. By spinning the CA/NMP/GBL/triethylene glycol solution at 170 °C into a water bath consisting of NMP, GBL and triethylene glycol, Noriyuki et al. [9] prepared cellulose acetate hollow fiber membranes for hemodialysis. They also pointed out that the coagulation rate was rapid in the case of NMP as a solvent, while the coagulation rate was slow in the case of GBL as a solvent.

In this study, cellulose acetate was chosen as the polymer due to its extensive use as membrane material covering from gas separation to microfiltration. Furthermore, the inherent fouling-resistant property due to its neutral surface and hydrophilicity make cellulose acetate a popular membrane material for water and wastewater treatment [2]. The liquid–liquid demixing behavior of the binary CA/NMP and CA/GBL solutions coagulating in a water bath was investigated. Thereafter, by a systematic variation of the ratio of the two nonvolatile solvents NMP and GBL, the influence of solvent on the structure and performance of cellulose acetate membranes was studied.

2. Experimental

2.1. Materials

Cellulose acetate used in this study was CA-398-30 with averaged acetyl content 39.8 wt% supplied by Eastman Chemical Company. The polymer was dried in a vacuum oven at 110 °C over night. *N*-Methyl-2-pyrrolidone (NMP, 99.0%) and γ-butyrolactone (GBL, >99%) were purchased from Merck and Aldrich, respectively. Both the solvents were used as received.

2.2. Cloud point

The cloud point measurements on CA/NMP/H_2O and CA/GBL/H_2O were carried out at 25 ± 0.1 °C as described elsewhere [10].

2.3. Intrinsic viscosity

The viscosities of dilute CA solutions and solvent were measured using an Ubbelohde viscometer (Schott AVS360, GmbH, Germany) at 25 ± 0.01 °C. The concentration of the dilute CA solution was about 0.5 g/dl. The intrinsic viscosity $[\eta]$ was determined by the one-point method [11],

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} \tag{1}$$

where c η_r and η_{sp} are the concentrations of polymer, the relative viscosity and the specific viscosity, respectively.

2.4. Polymer solution preparation and viscosity measurements

The homogenous CA/NMP/GBL solutions with various NMP/GBL ratios were prepared (see Table 1). The viscosities of the polymer solutions were measured using a RheoStress 300 rheometer (HAAKE Instruments Inc., Germany) with a 25 mm cone-plate sensor at 25 ± 0.1 °C.

Table 1
The composition and viscosity of polymer solutions

ID	CA (wt%)	GBL concentration in solvent mixture (wt%)	NMP concentration in solvent mixture (wt%)	Viscosity (mPa s)
CA-1	11	0	100	4335
CA-2	11	50	50	5690
CA-3	11	60	40	6028
CA-4	11	67	33	6047
CA-5	11	75	25	6285
CA-6	11	80	20	6911
CA-7	11	100	0	7875