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Cellulose acetate (CA)/polyvinylpyrrolidone (PVP) blend asymmetric membranes: Preparation, morphology and performance

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ABSTRACT

Cellulose acetate (CA) membranes are widely used for reverse osmosis (RO) and ultrafiltration (UF) applications. In this study, asymmetric CA membranes were synthesized using phase inversion method. CA with molecular weight of 52,000, polyvinylpyrrolidone (PVP) with molecular weight of 15,000 and 1-methyl-2-pyrrolidone (NMP) were used as polymer, additive and solvent, respectively. The effects of PVP concentration (at 0, 3 and 6 wt.%) and coagulation bath temperature (CBT at 0, 25 and 50 °C) on morphology, contact angle and permeability of the prepared membranes were studied and discussed. It was found out that the effects of PVP concentration and CBT depend on their values.

1. Introduction

Nowadays membrane processes are needed for the wide spectrum of separations including supply of high-quality water for domestic and industrial demands to obtain high-grade products and removal or recovery of toxic or valuable components from various industrial effluents [1–4].

The phase inversion process induced by immersion precipitation is a well-known technique to prepare asymmetric polymeric membranes [5–10]. In this technique, a cast film containing a polymer and its suitable solvent is immersed into a coagulation bath containing a non-solvent (material with high and low affinity to the solvent and the polymer, respectively). Then precipitation starts due to the low miscibility between the polymer and the non-solvent. Simultaneously, the high miscibility between the solvent and the non-solvent causes their diffusional flow (the exchange of solvent and non-solvent) in several points of the film top layer and the film sub layer which subsequently leads to formation of nucleuses of polymer-poor phase. In fact, the low affinity between CA chains and water molecules, at points that water molecules diffuse, results in repelling of the polymer chains and consequently formation of nucleuses of polymer-poor phase. Due to continuation of the diffusional flow of solvent and non-solvent, the mentioned nucleuses continue to grow until the polymer concentration at their boundaries becomes too high so that solidification occurs (demixing process completes) [2,5].

Rate of the demixing process affects morphology of the CA membranes. Instantaneous demixing often leads to macrovoids formation in the membrane structure, while slow demixing results in denser structure. In the case of slow demixing, nucleation occurs after a certain period of time and polymer concentration increases in the film top layer. Then nucleation starts in the inferior layer at short time intervals, successively. Hence, size and composition of the nucleuses in the former layer are such that new nucleuses are gradually formed in their neighborhood [5]. In other words, in slow demixing, free growth of limited nucleuses (in the film top layer) is prevented and a large number of small nucleuses are created and distributed throughout the polymer film. Consequently, contrary to instantaneous demixing, macrovoids formation is suppressed and denser membranes are synthesized [2].

A wide range of parameters have been checked concerning the membrane formation mechanism and consequently the membrane morphology and permeability such as polymer concentration in casting solution [11], type of solvent/non-solvent pair [12], cast film thickness [13], presence of certain additives [14], CBT [15] and presence of some other solvents [16]. It seems that the above parameters have significant effects on the instantaneous/delayed demixing process that takes place in the coagulation bath during the membrane formation process.

It is evident that advances in membrane technology, particularly for waste water purification, can be obtained by better understanding of the effects of the above mentioned parameters on the membrane morphology and permeability. Two major parameters seem to be the presence of additive and CBT. There are not many published literature regarding investigation of their effects, particularly effect of CBT, on membrane formation mechanism and consequently membrane

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morphology and permeability. Thus, in this study, effects of these parameters were investigated, so that different asymmetric CA membranes were prepared from the CA/PVP/NMP system via immersion precipitation in water coagulation bath. Then, effect of PVP concentration (0, 3 and 6 wt.%) and also effect of various CBTs (cold, medium and hot) on morphology and performance of the CA membranes was investigated.

2. Experimental

2.1. Materials

CA with an average molecular weight of 52,000 g/mol (Fluka) was used as the polymer forming membrane. The solvent used was 1-methyl-2-pyrrolidone (NMP) with an analytical purity of 99.5% (Merck). Distilled water was used as the non-solvent agent. PVP with an average molecular weight of 15,000 g/mol (Fluka) was used as an additive.

2.2. Preparation process

Various CA/PVP/NMP solutions with a constant concentration of CA (15.5 wt%) were prepared. Their compositions are presented in Table 1. The solution was stirred continuously so as to ensure that the polymers were dissolved. When the polymers were completely dissolved, as indicated by observing a clear solution, the solution was subsequently degassed in an ultrasonic bath for about 2 h to remove any air bubbles present and kept away from direct sunlight so as to slow down its aging process. The casting solution was poured onto a glass plate, and spread with a casting knife to be as thin as 180 μm. Then, the glass plate was immediately immersed in distilled water bath to complete the phase separation, where the solvent (NMP) and the non-solvent (water) were exchanged. Then, the formed membranes were transferred to another container containing fresh distilled water to remove their excess NMP and PVP. After 24 h, the membranes were ready to be tested.

2.3. Solution viscosity measurements

Viscosity of the prepared casting solutions was measured using POLYVISC digital rheometer (Model VISCO Star L) at a constant temperature of 25 °C.

2.4. Membrane characterization

2.4.1. Scanning electron microscopy (SEM)

The membranes were snapped under liquid nitrogen to give a generally consistent and clean break. The membranes were then sputter coated with a thin film of gold. The membranes were mounted on brass plates using a double-sided adhesion tape in lateral position. Cross-sectional images of the membranes were obtained using a CamScan SEM Model MV2300 microscope.

Table 1
Level of synthesis parameters and viscosity of the casting solutions.

Membrane code	CBT (°C)	Solution properties	
		PVP wt.%	Viscosity (Pa s)
M1	0	0	37.7
M2		3	43
M3		6	75.7
M4	25	0	37.7
M5		3	43
M6		6	75.7
M7	50	0	37.7
M8		3	43
M9		6	75.7

2.4.2. Contact angle

The contact angle between the water and the membranes was directly measured using a contact angle measuring instrument [G10, KRUSS, Germany] for evaluation of their hydrophilicity. De-ionized water was used as the probe liquid in all the measurements. To minimize the experimental errors, the contact angle was measured at three random locations for each sample and then the average value was reported.

2.4.3. Pure water flux (PWF) measurements

PWF studies were carried out using a batch mode experimental set-up. A flat sheet membrane module made from stainless steel was used in all the experiments. Effective area of the membrane in the module was 24 cm^2. Schematic representation of the module and the set-up are shown in Figs. 1 and 2, respectively. PWF experiments were run at a transmembrane pressure of 0.35 bar and their values were calculated using Eq. (1) [17].

$$PWF = \frac{Q}{A\Delta t} \tag{1}$$

where Q is quantity of permeate (L), A is membrane area (m^2) and Δt is sampling time (h).

3. Results and discussion

3.1. Effect of PVP as an additive on morphology and permeability of the prepared CA membranes

SEM images were taken in order to explain the effects of PVP concentration on the membrane morphology. Fig. 3 depicts SEM cross-sectional images of the prepared CA membranes. According to these images, it can be observed that at constant CBT (0, 25 and 50 °C), increasing PVP concentration initially from 0 to 3 wt.% causes formation of macrovoids and more porous structures. However, further increasing PVP concentration from 3 to 6 wt.% results in suppression of macrovoids and formation of denser structures. Also, a similar trend is observed in Fig. 4. According to this figure, at constant CBT (0, 25 and 50 °C), increasing PVP concentration from 0 to 3 wt.% increases PWF, however, further increasing PVP concentration from 3 to 6 wt.% reduces PWF.

It can be said that the presence of PVP, as a hydrophilic additive with non-solvent properties (additive that similar to non-solvent has high and low affinity to the solvent (NMP) and the polymer (CA), respectively) [18,19], increases thermodynamic instability of the cast film and this can consequently lead to instantaneous demixing in the coagulation bath and thus formation of macrovoids in the membrane structure [18,20].

From the other point of view, presence of PVP increases viscosity of the cast film (as seen in Table 1). Higher viscosity of the cast film slows down the diffusional exchange rate of the solvent (NMP) and non-solvent (water) during the membrane formation process in the coagulation bath and this consequently hinders instantaneous

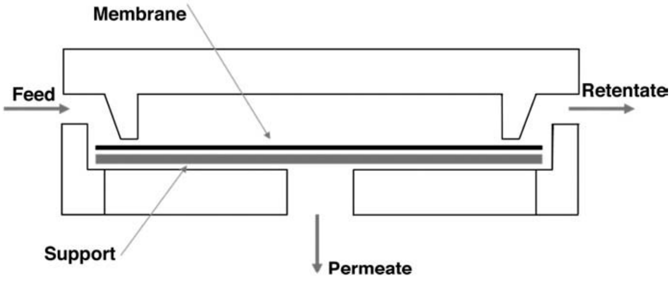

Fig. 1. Schematic view of the experimental module.