Journal of Membrane Science 541 (2017) 271–280

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

New polyvinyl chloride/thermoplastic polyurethane membranes with potential application in nanofiltration

Zahra Maghsoud[a,*], Mojgan Pakbaz[a], Mohammad Hossein Navid Famili[b],
Seyed Siavash Madaeni[c]

[a] *Chemical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad, Iran*
[b] *Polymer Engineering Group, Faculty of Engineering, Tarbiat Modares University, Tehran, Iran*
[c] *Membrane Research Center, Chemical Engineering Department, Razi University, Kermanshah, Iran*

ARTICLE INFO

Keywords:
PVC/TPU blend membrane
Thermodynamics
Kinetics
Dye rejection
Elasticity

ABSTRACT

Due to favorable interactions between Polyvinyl chloride (PVC) and Thermoplastic Polyurethane (TPU) chain segments as revealed by viscosity measurement and differential scanning calorimetry (DSC), the ternary phase diagram of the PVC/TPU blend (for all compositions) was almost close to that of neat PVC. According to a simple diffusion model used for studying the kinetics of membrane formation, the PVC/TPU membrane structure was expected to be almost similar to that of PVC membrane which was supported by scanning electron microscope (SEM) micrographs. PVC membranes were impermeable to water up to a transmembrane pressure of 8 bar. Interestingly, adding TPU to PVC lowered the pressure at which the membrane showed permeability. Addition of 25 wt% TPU to PVC led to a substantial increase of pure water flux from 3.4 to 111.4 L/m^2 h along with no change in the separation performance (100% Coomassie Brilliant Blue (CBB) dye rejection). However, further increase of TPU content beyond 25 wt%, caused a remarkable loss in membrane performance where under a specific threshold pressure the pure water flux increased steadily with time. This phenomenon being reversible below and above the threshold pressure was ascribed to the high elasticity of TPU, justified by mechanical evaluation of membranes and their glass transition temperature.

1. Introduction

Since its introduction, membrane technology has received extensive attention both from industrial sectors and research centers. The main concern has been development of new membrane materials and processes along with improving those currently in use [1]. Among different techniques employed for preparation of polymeric membranes, immersion precipitation is very common [2]. In its simplest form, a polymer solution is cast as a thin film on a proper substrate and immersed into the nonsolvent bath. The exchange of solvent and nonsolvent leads to unstable thermodynamic conditions and finally phase separation occurs. Different morphologies could be obtained by appropriate choice of membrane forming components. However, the complicated role of thermodynamics and kinetics of phase inversion as the main governing factors of membrane formation, makes this process really difficult to understand and exploit; especially, when more than three components (polymer/solvent/nonsolvent) are utilized for fabrication of membranes. Of particular interest is using a combination of polymers, namely polymer blends, to obtain membranes with better performance than the individual components. The second polymer could merely serve as a pore former in a membrane forming system when water (nonsolvent) soluble low molecular weight polymers such as PVP or PEG are used [3]. It also could be used to modify the main membrane forming polymer. According to Boom et al. [4], in such quaternary systems, two different time scales could be distinguished during the formation step. The shorter time scale pertains to solvent-nonsolvent exchange for which the movement of polymeric molecules relative to each other is not possible. The longer time scale relates to polymer-polymer phase separation which significantly affects membrane morphology [5]. Baik et al. [6] have found that in PES/PSF system, phase separation of the polymer blend solution occurs earlier than individual polymers when the total polymer concentration goes beyond a critical value. In this case polymer-polymer phase separation precedes polymer-liquid phase separation. Similar results have been reported by Han et al. for the phase behavior of polyethersulfone, polyimide and their 50/50 blend membrane forming system [7]. According to what was reported by Panda and De for polyacrylonitrile (PAN)/polyurethane (PU) blend membranes [8], the change of cloud

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[*] Corresponding author.
E-mail address: maghsoud@um.ac.ir (Z. Maghsoud).

http://dx.doi.org/10.1016/j.memsci.2017.07.001
Received 31 March 2017; Received in revised form 29 June 2017; Accepted 1 July 2017

point trend above a critical polymer concentration was also clear. The authors explained the overall curvature of the cloud point curve with regard to the solution viscosity and the solubility parameter of mixture components.

Among different polymers available for manufacturing membranes, polyvinyl chloride (PVC) could be regarded as an appropriate one; owing to its solubility in common solvents, good mechanical and chemical performance as well as commercial availability. However, its hydrophobicity is a main hindrance for water based filtrations; hence blending PVC with some hydrophilic polymers such as chlorinated or carboxylated polyvinylchloride [9,10], Polyvinyl pyrrolidone (PVP) [11], cellulose acetate (CA) [12], polyvinyl Butyral (PVB) [13], polyethylene glycol (PEG) [14], poly(methyl methacrylate-*co*-methacrylic acid) [15] and poly acrylonitrile (PAN) [16,17] has been reported as a solution.

Blends of thermoplastic polyurethane (TPU) with PVC are of significant commercial interest. TPU is known for its high tensile strength and flexibility, excellent abrasion resistance, good chemical and thermal resistance and possible variation of segmental structure suited for many applications [18]. TPUs are biphasic materials combining the features of both a glassy or semi-crystalline thermoplastic and a soft elastomer resulting in a processable rubbery material [19].

In a recent paper by Panda and De [8], a summary of previous reports based on PU blended membranes has been reported. Although a considerable amount of research exists on PVC/TPU blends for different applications, [19–21] the use of this blend for membrane fabrication is limited to a Chinese paper by Zhu et al. [22]. They reported that the PVC/TPU hollow fiber membrane could be regarded as a promising option for sewage treatment. Moreover, no attention has been made to the effect of transmembrane pressure on the performance of the TPU containing membranes since due to their high flexibility, membrane structure deformation and subsequent deterioration of its performance is probable. Therefore, we have prepared porous membranes from PVC/TPU blend to study the effect of blend composition on pure water flux and rejection properties. Thermodynamics of the blend membrane formation was considered through cloud point measurement. In our previous paper [23] we used a simple model proposed by Fernandes et al. [24] to simulate membrane formation process. Accordingly, we took a similar approach to the kinetics of blend membrane formation. Moreover, it was the purpose of this study to investigate the changes that might be brought about in membrane performance due to the change of feed pressure. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), mechanical analysis and viscosity measurement were also used for analyzing the blend membranes.

2. Experimental

2.1. Materials

Polyvinyl chloride (PVC, S-7054, M_n = 91,000 g/mol, Density = 1.41 g/cm^3) was purchased from BIPC, Iran. Thermoplastic Polyurethane, (TPU, Poly [4,4′-Methylenebis (phenyl isocyanate)-*alt*-butanediol/di-PG/Polycaprolactone], T_g = −40 °C, M_n = 94,500, Density = 1.18 g/cm^3) was obtained from Sigma-Aldrich. The chemical structure of the applied TPU is shown in Fig. 1.

Tetrahydrofuran (THF) and Dimethylformamide (DMF) from Merck were used as solvents. Tap water was used as the coagulation media. Coomassie Brilliant Blue (CBB) G-250 dye (Mw = 854.02 g/mol) from Sigma-Aldrich was used for rejection experiments.

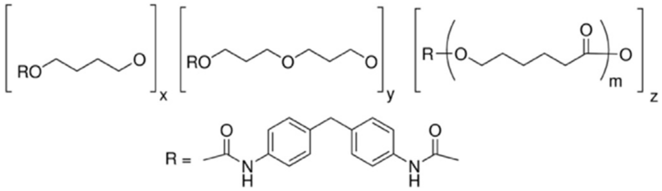

Fig. 1. The chemical structure of TPU used in this study.

2.2. Membrane preparation

PVC/TPU blend solutions with a total polymer content of 15 wt% were prepared by dissolving PVC and TPU in a mixture of DMF/THF (75/25, w/w) and stirred for 24–48 h using a magnetic stirrer. The solvent ratio was chosen according to our previous study [23]. PVC to TPU blend ratios were 0/100, 25/75, 50/50, 75/25 and 100/0 on a weight basis. For membrane preparation, solutions were degassed in an ultrasonic bath to remove air bubbles. The solutions were then cast on a glass plate using a casting knife with a thickness of 200 µm and then quickly immersed in a water containing coagulation bath and left there for about 30 min. At last, the prepared membranes were stored in fresh water for 48 h to ensure removal of the residual solvent.

2.3. Measurement of the casting solution viscosity

Measurement of the casting solution viscosity was carried out using a rheometer (Anton Paar MCR 301) at 25 °C. The viscosities of polymer solutions with different PVC/TPU ratios were measured at the shear rate of 10 s^{-1}. The total polymer concentration was 15 wt%.

2.4. Cloud point measurement

Cloud point measurement was done in a way similar to that mentioned in [25]. For cloud point measurement, the total polymer content was limited to 8 wt% due to the increased viscosity caused by high molecular weight of the two polymers. PVC/TPU and DMF/THF ratios were the same as those used for membrane preparation.

2.5. Measurement of pure water flux and rejection

Pure water flux was measured by a home-made dead-end type membrane stirred cell [23]. The following equation was used to determine the pure water flux (J_w):

$$J_w\left(\frac{L}{m^2hr}\right) = \frac{Q_w}{A \times t} \tag{1}$$

Q_w is the permeate volume passed through the effective area A of membrane at time t. Each measurement was done on at least three circular discs (with an area of ~ 16 cm^2) cut from the cast membranes.

Membrane rejection was determined using an aqueous solution of Coomassie Blue in distilled water. For preparation of feed solutions, a solution of 0.01 g/cm^3 Coomassie Blue in ethanol was prepared. This solution was used to prepare a 2l-feed solution by adding distilled water to obtain an aqueous feed with a total dye concentration of 10 ppm. Rejection was measured under a pressure of 8 bar. The following formula is often used to calculate membrane rejection (R), where C_f and C_p are dye concentration in the feed and permeate side, respectively.

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

2.6. Scanning electron microscopy (SEM)

The cross section of membranes was observed with a scanning electron microscope (SEM), (Philips XL 30). For this purpose, membranes were fractured in liquid nitrogen and then coated with a thin layer of gold.