Desalination and Water Treatment
www.deswater.com

27 (2011) 76–80
March

1944-3994/1944-3986 © 2011 Desalination Publications. All rights reserved
doi: 10/5004/dwt.2011.2055

Polyamide 66 membranes with PVP addition prepared by phase inversion

Patrícia Poletto[a], Jocelei Duarte[a], Mônica B. Thürmer[a], Mára Zeni[a,b,*]

[a]*Center of Science and Technology, University of Caxias do Sul, 95070-560 Caxias do Sul, RS, Brazil*
Tel. +55 54 32182100; email: mzandrad@ucs.br
[b]*Caxias do Sul University, Box 1130, CED 95070-560, Caxias do Sul, RS, Brazil*

Received 31 May 2010; Accepted 22 July 2010

ABSTRACT

The membranes prepared from synthetic polymer are used worldwide in separation processes. Polymeric membranes from polyamide 66 (PA 66) in hydrochloric acid (HCl) at the concentrations of 10 and 15 wt.% were prepared by phase inversion method. Poly(vinyl pyrrolidone) (PVP) was used as the polymeric additive in the casting solution to improve the morphology and properties of the PA 66 membranes prepared. The membranes analyzed by Fourier transform infrared (FTIR), maintaining the same chemical structure of pure PA 66 membranes, indicating that the PVP was eliminated in nonsolvent bath. The determination of cloud point showed that PVP addition promotes a thermodynamic instability in the casting solution, reducing the time precipitation and influencing in the dense layer formation of the membrane. The scanning electron microscopy (SEM) showed that the PVP addition promoted a decrease in the thickness of dense layer and an increase in the percentage of the porous sublayer, greater uniformity of pores membrane. The pure water flux membranes with PVP addition was higher than in membranes of pure PA 66. The pure water flux increases from 1365 to 2590 l m^{-2} h^{-1} and from 66 to 362 l m^{-2} h^{-1} at the concentration of 10 and 15 wt.% of PA 66, respectively.

Keywords: Polyamide 66 membranes; Poly(vinyl pyrrolidone); Phase inversion

1. Introduction

In 1953, Reid and Breton obtained integral membranes which presented good saline rejection. In the 1960s Loeb and Sourirajan developed the first cellulose acetate (CA) asymmetric membrane [1]. The membrane separation process achieved great advances with the development of these membranes. These CA membranes were characterized by the unique structure, a thin skin layer supported by a porous sublayer which yielded comparable salt rejection and higher fluxes than the structures that existed at the time [2].

For several years most asymmetric membranes were prepared from cellulose acetate. Nowadays, the membranes used in separation process are prepared from synthetic polymers like polyamide, polysulfone, poly(vinylidene fluoride), poly(methyl methacrylate) and others.

The preparation of membranes by the phase inversion method was reported by many researchers [3–6]. In this method, two types of demixing process occurred in phase separation resulting in two different types of membrane morphology: instantaneous liquid–liquid demixing and delayed onset of liquid–liquid demixing. When liquid–liquid demixing occurs instantaneously, membranes with a relatively porous top layer are obtained. This demixing mechanism results in the formation of a porous membrane (microfiltration/ultrafiltration type). However, when liquid–liquid demixing sets in after a finite period of time, membranes with a

---

*Corresponding author.

Presented at the VII Ibero-American Conference on Membrane Science and Technology (CITEM 2010), April 11–14, 2010, Sintra, Portugal

relatively dense top layer are obtained. This demixing process results in the formation of dense membranes (gas separation/pervaporation). In both cases the thickness of the top layer depends on all kinds of membrane formation parameters (i.e., polymer concentration, coagulation procedure, additives) [2].

In our recent research [7], the polyamide 66 (PA 66) membranes were prepared and presented a dense layer and a porous sublayer. According to many authors [8–11], the addition of a high molecular weight polymer additive in a casting solution induces the enlargement of macrovoids in the membrane as well a significant increase in membrane permeability.

Wienk et al. [12] observed that the addition of a high molecular weight component to the polymer solution changes the structure of the membranes drastically, the porosity is higher and pores are well interconnected. Ochoa et al. [13] and Susanto and Ulbricht [14] studied the effect of poly(vinyl pyrrolidone) (PVP) on porosity the poly(ether sulfone) (PES) membranes and observed that the addition of small quantities of PVP of different molecular weights resulted in an increase of permeability.

Hence, adding hydrophilic additives, such as PEG, to the casting solution increases viscosity of the cast film due to the higher molecular weight. Viscosity increase of the cast film slows down the diffusional exchange rate of solvent and nonsolvent during solidification process and consequently prevents instantaneous demixing. This leads to suppression of macrovoids and formation of denser structure [15].

In the present work, PA 66 membranes were prepared by phase inversion. The PVP was used as additive and the morphology and the permeation characteristics of the prepared membrane were investigated and compared with pure PA 66 membranes.

2. Experimental

2.1. Materials

Commercial PA 66 from Alfa Chem. Co., Mw 161,000 g mol^{-1}, was received in pellet form. The pure chloride acid (HCl) (Merck, 37%) was used as the solvent and used as received. PVP K360 (Sigma) (molecular weight 360 kDa) was used as pore forming additive in the casting solution. Distilled-deionized water was used as the nonsolvent for PA 66.

2.2. Membrane preparation

Flat sheet PA 66 membranes were prepared by phase inversion method. Homogeneous polymer solutions of 10 and 15 wt.% of PA 66 in HCl with and without 1 wt.% of PVP were cast on glass plates in film form. After casting, the solvent was evaporated and the glass plates were immersed in a coagulation bath containing distilled water at 25°C. After coagulation was completed the solidified flat-sheet membranes were dried by placing them between sheets of filter paper.

2.3. Determination of cloud point curve

Cloud point were obtained by a simple titration method. The PA 66 solutions at different concentrations were titrated with the nonsolvent. The cloud points were determined in a previously weighed polymer solution under agitation and adding small amounts of water by an adjustable volume micropipette with 5 ml accuracy. The cloud point was given by the water concentration in the polymer solution when it remained turbid for more than 24 h, indicating that phase separation had occurred. The cloud point composition was then determined by the amount of nonsolvent, solvent, and polymer present in the bottle.

2.4. Fourier transform infrared (FTIR)

The membranes in film form had been characterized in the FTIR (Nicolet spectrophotometer Impact 400) to evaluate the effect the PVP addition in the membrane structure.

2.5. Scanning electron microscopy (SEM)

The samples were initially fractured in liquid nitrogen and gold-coated. The cross-section morphology of the membranes was obtained by scanning electron microscopy Shimadzu SSX 550 operated at 10 kV. The pores number of the membrane cross-section was calculated with the help of software Image Tools 3.0, using an area of 5 mm^2 and the data processed in the software Origin 7.5.

2.6. Pure water flux (J_w)

Pure water permeation fluxes of the membranes prepared were measured with a parallel flux type cell (area 16 cm^2) at 2 bar and J_w values were calculated using Eq. (1).

$$J_w = \frac{V}{A\Delta t} \tag{1}$$

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

3. Results and discussion

3.1. Cloud point results

PVP as an additive can induce a dual effect in a polymer solution, depending on the molecular weight. One is a reduction of the miscibility of the casting solution with water, which causes the thermodynamic enhancement of the phase separation (thermodynamic factor). At the same time, they may increase the viscosity of the casting solution to a certain extent which causes kinetic hindrance against phase separation (rheological factor) [16]. As shown in Table 1, the cloud point data measurement induced a decrease in the miscibility of casting solutions, in reaction with the precipitating nonsolvent. The original solution of 10 wt.% PA 66 is phase separated as the water added into the solution reached 35.3 wt.%. With the PVP addition, the solution shows the increase in thermodynamic instability, as indicated by the lower amount of water (33 wt.%) at a demixing point. The same trend was observed to 15 wt.% of PA 66, where the amount of water decreased with the PVP addition.

3.2. Fourier transform infrared (FTIR)

The FTIR analysis showed that the membrane chemical structure with the PVP addition has remained the same as the pure PA 66 (Fig. 1), indicating the removal of PVP in the phase inversion bath. The PVP additive is leached out of cast solution film, due to its high molecular weight, while the rearrangement of the polyamide structure occurs. The spectra shows the region around 3300 cm^{-1}, which corresponds to the stretching of the N–H bond. The region around 2930 and 2860 cm^{-1} corresponds to stretching of the CH_2 group, the 1365 cm^{-1} region corresponds to the C=O grouping, which is characteristic of the amide group, and in 1416 cm^{-1}, the C–N group stretching.

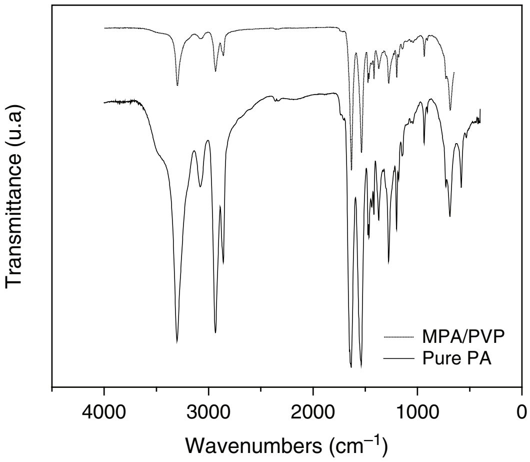

Fig. 1. FTIR spectra of the PA 66 membranes prepared from inversion phase (PA66/PVP/HCl/water).

3.3. SEM analysis

Fig. 2 shows the SEM image of the membrane cross-section prepared in 10 and 15 wt.% of PA 66 with and without PVP addition. It can be seen that all the membranes formed have an asymmetric structure consisting of a dense layer and a porous sublayer. The introduction of an evaporation step before immersion in a nonsolvent bath (dry-wet phase inversion) resulted in a dense layer. During evaporation the film becomes turbid indicating the onset of phase separation, which will be completed when the film is submitted in a bath of non-solvent (water).

Table 1
Cloud point data of PA 66 casting solution

Membranes	Solution composition (wt.%)		Water content at cloud point
	PA 66	PVP	(g/wt.%)
PA10/PVP	10	1	63.7/33
PA10	10	0	71/35.5
PA15/PVP	15	1	74.5/35.8
PA15	15	0	82.3/38

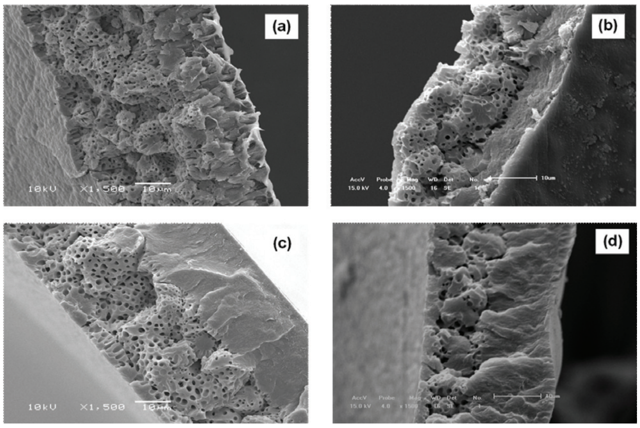

Fig. 2. Micrographs (MEV) of membrane cross-sections prepared by the phase inversion method (1500×) (a) PA10/PVP, (b) PA10, (c) PA15/PVP and (d) PA15.

The PVP addition resulted in significantly differences the asymmetric structure of the membranes decreasing the dense layer and increasing the porous sublayer, which presented a uniform distribution of spherical pores. The PVP concentration (1 wt.%) used was sufficient to result in morphological changes in the membranes structure. The membranes presented a reduction of the dense layer about 6% to PA10/PVP and 23% to PA15/PVP compared to pure PA 66 membranes, as seen in Table 2. These results confirm the data

Table 2
Morphological and permeability parameters of polyamide 66 membranes

Membrane	Thickness (μm)	Dense layer (%)	Water flux ($l\ m^{-2} h^{-1}$)
PA10/PVP	33	24	2590
PA10	24	30	1365
PA15/PVP	35	37	362
PA15	26	60	66

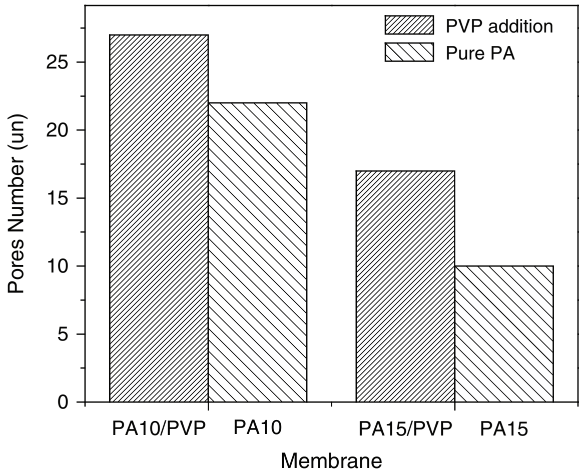

Fig. 3. Effect of PVP addition in pores number of PA 66 membranes.

obtained in cloud point measurements, where the percentage of water added to casting solution was lower with the PVP addition, reducing the time precipitation and decreasing the thickness of dense layer.

The pores number in the cross-section with diameters between 1 and 2 μm, were counted. Fig. 3 shows that the PVP addition for both concentrations of polymeric solution increased the pores number for the same area of membrane (5 mm^2). Between the membranes with PVP addition, the smallest amount of pores in the membranes PA15/PVP may be related to the increase of polymeric concentration.

3.4. Pure water flux

The effect of additive on pure water flux of PA 66 membranes was investigated, as shown in Fig. 4.

The pure water flux increased for the PA 66 membranes with PVP (PA10/PVP and PA15/PVP), which may be attributed to the increased in number and interconnectivity pores, and the reduction in the thickness of dense layer, as discussed previously. The addition of high molecular weight PVP (e.g., PVP 360 kDa in the present case) increased the viscosity of the casting solution, which according to the theory proposed by Lee [8], results in more porous membranes. Another parameter influencing the pure water flux is the polymer concentration. When the wt.% of PA 66 increased from 10 to 15 wt.%, the pure water flux decreased significantly for membranes with and without PVP addition. According to Mulder [2], increasing the polymer concentration, a lower porosity membrane is obtained and consequently a lower flux. In low polymer concentrations (12–15%) typical ultrafiltration membranes are obtained, but with increasing the polymer concentration the resulting water flux can be reduced to zero. Table 2 presents the water flux values for the pure polyamide and with the PVP addition membranes after 60 min of permeation. When the PVP addition was used, the pure water flux increased from 1365 to 2590 l m^{-2} h^{-1} at 10 wt.% of PA 66 and increased from 66 to 362 l m^{-2} h^{-1} at 15 wt.% of PA 66. The membranes with and without PVP addition showed a stable behavior with small variations in pure water flux.

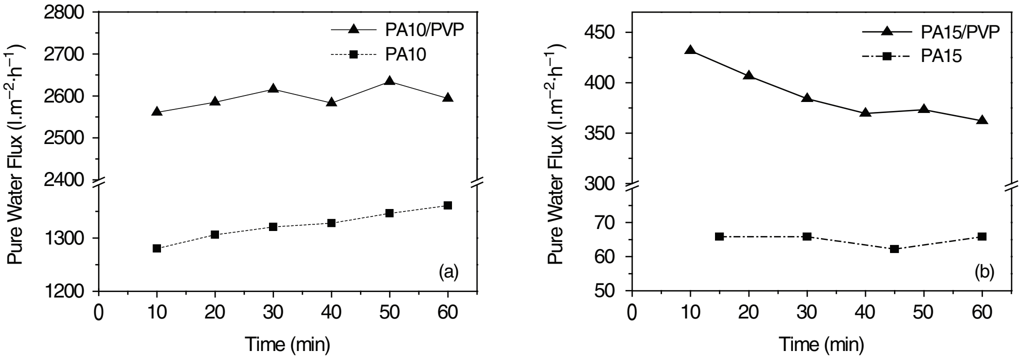

Fig. 4. Pure water flux membranes with and without PVP addition (a) membranes prepared at 10 wt.% of PA 66 and (b) 15 wt.% of PA 66.

4. Conclusion

According to the analysis performed for the characterization of PA 66 membranes prepared at concentrations of 10 and 15 wt.% with the PVP addition, some changes in membrane structure were observed.

The PVP addition did not change the chemical structure of PA 66 membranes (FTIR). A decreased of thickness dense layer and increase the porous number in the sublayer and possibly improved the pores interconnectivity, which significantly increased the pure water flux. Due to the lower concentration of casting solution, the pores number and the pure water flux were higher for the membranes prepared at a concentration of 10 wt.% of PA 66.

The use of additive such as PVP, played an important role in the morphological and permeability changes in the PA 66 membranes in accordance with the purpose of the work.

Acknowledgement

The authors would like to acknowledge University of Caxias do Sul, CNPq, Capes and HidroFiltros do Brasil Co. for financial support.

References

[1] S. Loeb and S. Sourirajan, Seawater demineralization by means of a semi-permeable membrane, UCLA Dept. of Engineering Report, No. 60−60, 1960.
[2] M. Mulder, Basic Principles of Membrane Technology, 2nd ed., Dordrecht, NL: Kluwer Academic Publishers, USA, 1996.
[3] D.J. Lin, C.L. Chang, C.K. Lee and L.P. Cheng, Eur. Polym. J., 42 (2006) 356–367.
[4] C.H. Shih, C.C. Gryte and L.P. Cheng, J. Appl. Polym. Sci., 96 (2005) 944–960.
[5] J.L. Thomas, M. Olzog, C. Drake, C.H. Shih and C.C. Gryte, Polymer, 43 (2002) 4153–4157.
[6] D.J. Lin , L.P. Cheng and S.P. Lin, Desalination, 145 (2002) 31–37.
[7] M. Zeni, R. Riveros, J.F. Souza, K. Mello, C. Meireles and G.F. Rodrigues, Desalination, 221 (2008) 294–297.
[8] K.W. Lee, B.K. Seo, S.T. Nam and M.J. Han, Desalination, 159 (2003) 289–296.
[9] B. Chakrabarty, A.K. Ghoshal and M.K. Purkait, J. Membrane Sci., 309 (2008) 209–221.
[10] G. Arthanareeswaran, P. Thanikaivelan, K. Srinivasn, D. Mohan and M. Rajendran, Eur. Polym. J., 40 (2004) 2153–2159.
[11] G. Arthanareeswaran, T.K. Sriyamuna Devi and D. Mohan, Sep. Purif. Technol., 67 (2009) 271–281.
[12] I.M. Wienk, R.M. Boom, M.A.M. Beerlage and A.M.W. Bulte, J. Membrane Sci., 113 (1996) 361–371.
[13] N.A. Ochoa, P. Prádanos, L. Palacio, C. Pagliero, J. Marchese and A. Hernández, J. Membrane Sci., 187 (2001) 227–237.
[14] H. Susanto and M. Ulbricht, J. Membrane Sci., 327 (2009) 125–135.
[15] E. Saljoughi, M. Sadrzadeh and T. Mohammadi, J. Membrane Sci., 326 (2009) 627–634.
[16] B. Chakrabarty, A.K. Ghoshal and M.K. Purkait, J. Membrane Sci., 315 (2008) 36–47.