

Polymeric Homogeneous Composite Membranes for Separations in Organic Solvents

Enrica Fontananova, Gianluca Di Profio, Francesco Artusa, Enrico Drioli

Institute on Membrane Technology of the National Research Council (ITM-CNR), Via Pietro BUCCI, c/o The University of Calabria, 87036 Rende CS, Italy

Correspondence to: E. Fontananova (E-mail: e.fontananova@itm.cnr.it or enrica.fontananova@cnr.it)

ABSTRACT: A new generation of organic solvent nanofiltration (NF) composite membranes was prepared combining a support layer with a selective layer made both from the same polymeric material (P84 copolyimide). These membranes, homogeneous in composition, but composite in structure, were defined as polymeric homogeneous composite (PHC) membranes. The composite membranes have the advantage over the asymmetric ones that each layer can be optimized independently. Moreover, the use of the same material for the preparation of both, the selective and the support layer, ensures a high affinity between the two layers and increases the long-term stability of the composite membranes, reducing the possibility of delamination phenomena. In the design of the PHC membranes, a great attention was devoted to the support layer development. The effects of the composition of the casting solutions on the structure of porous P84 copolyimide membranes were investigated allowing to identify the conditions for the preparation of highly permeable, chemically, and mechanically stable P84 sponge like porous membranes. PHC membranes were prepared by coating and controlled solvent evaporation of a P84 solution on the optimized support crosslinked by reaction with a diamine (1,5-diamino-2-methylpentane). Pure solvent permeation test and rejection experiments were carried out on the P84 supports and the corresponding PHC membranes in aggressive organic solvents like *N*-methyl-2-pyrrolidone and *N,N*-dimethylformamide, in which the original polymer was soluble. The PHC membrane resulted completely stable over long times (>96 h). © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 1653–1659, 2013

KEYWORDS: coatings; composites; crosslinking; membranes; morphology

Received 25 June 2012; accepted 19 September 2012; published online 17 October 2012

DOI: 10.1002/app.38612

INTRODUCTION

Organic solvent nanofiltration (OSN) is an emerging membrane separation technique able to retain species with molecular weight in the range from 200 to 1000 g mol⁻¹ in organic solvents.^{1,2} The most popular polymers used as membrane material for OSN applications are the polyimides (PIs), including co-polyimide (co-PIs), polyamide-imide, and polyetherimide.^{3,4}

PIs combine an easy processability in the form of membranes, with a high chemical and thermal stability over a wide range of operative conditions. Moreover, the crosslinking by thermal treatment, UV irradiation, or chemical reaction confers to the PI membranes high resistance in various organic solvents in which the original polymers are not stable.^{3,5} Asymmetric PI membranes, that is, membranes in which the structure varies over the cross-section, are usually prepared by nonsolvent-induced phase separation (NIPS).^{6,7}

For the preparation of PI membranes, the polymers are usually solubilized in polar aprotic solvents like *N,N*-dimethylformamide (DMF), *N,N'*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), in some cases, in the presence of a nonpolar volatile cosolvent like 1,4-dioxane (dioxane) and tetrahydrofuran (THF); the nonsolvent used is typically water.^{1,4,8} Moreover, PI membranes have been used in the form of composite membranes prepared in a two-step process in which a barrier layer is deposited or formed on a porous substructure.⁹ In a composite membrane, the sublayer has usually only a mechanical support function and a lower influence on the transport phenomena respect to the upper layer. The composite membranes have the advantage over the asymmetric ones that each layer can be optimized independently. Usually, the barrier and the support structures are made from different materials. An example of polymeric composite membrane realized using the same polymer for the two layers can be found in a US patent published in the 2003 describing the process of forming multilayered membranes

Table I. Composition of the Dope Solutions Used to Prepare Porous Membranes and Their Solvent Permeance

Membrane code	P84 (wt %)	NMP (wt %)	H ₂ O (wt %)	EtOH (wt %)	Permeance (L h ⁻¹ m ⁻² bar ⁻¹)				
					CH ₃ CN	DMF	H ₂ O	EtOH	NMP
P84-0	21	79	0	0	675		218	176	
P84-W1	21	78	1	0	438		106	80.2	
P84-W2	21	77	2	0	361		94	132	
P84-W4	21	75	4	0	357	62.6	126	122	33.2
P84-Et1	21	78	0	1	391		95	108	
P84-Et2	21	77	0	2	471		67	128	
P84-Et4	21	75	0	4	445		45	112	
P84-Et10	21	69	0	10	398		154	124	

by cocasting of two polyvinylidene fluoride solutions.¹⁰ However, the cocasting process limits the possibility to optimize the two layers independently because of the simultaneous casting of the two liquid films, which, obviously, solidified under the same conditions (e.g., temperature and composition of the coagulation bath). More numerous are the examples of composite membranes in which the selective layers is formed or deposited on an already formed support by interfacial polymerization, coating, or plasma techniques.⁶

Thin-film composites (TFC) membranes have been realized by interfacial polymerization of polyamide (PA) on a PI support.¹¹ In addition, TFC membranes have also been prepared by casting of a thin selective layer of polydimethylsiloxane on a PI support layer.¹² In this work, a new generation of OSN composite membranes was realized combining a support layer with a selective layer made both from the same polymeric material, a co-PI known under the trade name of P84. These membranes, homogeneous in composition, but composite in structure, will be defined in the following text, polymeric homogeneous composite (PHC) membranes. P84 is a co-PI characterized by an high-glass transition temperature (T_g of 315°C), but not a melting point.¹³ Moreover, it provides good stability in organic solvents including toluene, hydrocarbons, alcohols, and ketones, but it is soluble at room temperature in polar aprotic solvent like DMF, DMA, and NMP. However, it is possible to render the P84 insoluble in the previous polar aprotic solvents by a simple crosslinking reaction with diamines.^{3,4} Thanks to the peculiar chemistry of the PIs, it was possible to use the crosslinked P84-based porous membrane as support layer of a composite membrane in which the selective layer is made of the same material of the support. At the best of our knowledge, this is the first example of polymeric composite membrane in which the two layers are realized in a two-step casting process using the same polymeric material.

EXPERIMENTAL

Materials

P84 co-PI, synthesized by the condensation reaction of 3,3',4,4'-benzophenone tetracarboxylic dianhydride with 80 mol % 2-methyl-*m*-phenylene diisocyanate (TDI) and 20 mol % 4,4'-methylenebis (phenyl isocyanate),⁴ was purchased from HP

polymer GmbH, Austria. NMP, DMF, THF, ethanol (EtOH), and glycerol were purchased from Carlo Erba (Italy). 1,5-Diamino-2-methylpentane (DAMP) and Solvent blue 35 (MW 350 g/mol) from Sigma-Aldrich.

Membranes Preparation

Porous P84-based membranes were prepared from a homogeneous solution of the polymer (21 wt %) in NMP or in a mixture of NMP/water or NMP/ethanol under stirring at room temperature (the composition of the dope solutions are reported in Table I).

After the complete removal of air bubbles, the solutions were cast at 250 μm thickness onto a glass plate by using a casting knife (Elcometer 3700) and an automatic film applicator (Elcometer 4340 Applicator, Elcometer, UK) at the speed 2 cm/s. The liquid film was immediately immersed into a water coagulation bath at 25°C \pm 3°C for at least 24 h. The membrane surface not in contact with the glass support was indicated as "up surface"; that in contact was indicated as "down surface". The membranes were then crosslinked by immersion in a 10 wt % DAMP/ethanol solution for 24 h at 25°C \pm 3°C. The chemically modified membranes were washed with fresh ethanol for 24 h and then with water for additional 24 h to wash away any residual crosslinker unreacted. Then the crosslinked membranes were stored in water until their use.

A selected membrane (P84-W4) was used as support for the preparation of a PHC membrane. The P84-W4 membrane was immersed in a glycerol solution (40 wt %) in ethanol at room temperature for 24 h, then it was mounted on a tilted glass plate to remove the excess of solution, and the membrane was dried at room temperature. A 5 wt % solution of P84 in NMP/THF (50 : 50 wt %) was coated using a manual bar coater with an initial thickness of 250 μm on the up surface of the support membrane, positioned in horizontal position inside an lab-made climatic chamber working at 40°C \pm 1°C and 30% \pm 1% of relative humidity. After being left to evaporate for about 24 h, the composite membrane was immersed in water in order to remove eventual residual traces of solvent and finally crosslinked with DAMP using the same procedure used for the support

membrane. The obtained composite membrane was indicated as PHC-5 membrane.

Membranes Characterization

The cross-section and surface structure of the membranes were examined by scanning electron microscopy (SEM) using a FEI Quanta 200 Philips SEM or a Cambridge Instruments Stereoscan 360. Cross-sections were prepared by fracturing the membrane in liquid nitrogen.

Fourier transform infrared analysis in attenuated total reflectance method was performed using a Perkin Elmer Spectrum One on the up surface of each membrane.

Surfaces morphology was assessed by Nanoscope III atomic force microscope (AFM; Digital Instruments, VEECO Metrology Group) in a tapping mode AFM imaging, as the average among three different measurements across $10 \times 10 \mu\text{m}^2$ squares of the sample surfaces. Roughness analysis of surfaces was performed by SPIP 6.0 software (Image Metrology), by calculating average roughness (R_a), root-mean-square roughness (R_q), and maximum height (R_{max}).

Membrane Permeation and Retention Experiments

Filtration experiments were performed in a dead-end mode with a Sterlitech™ HP4750 stirred cell, pressurized by nitrogen and operating at $25^\circ\text{C} \pm 3^\circ\text{C}$. The active membrane area was 14.6 cm^2 . The transmembrane pressure (TMP) applied varied from 0.5 to 30 bar, depending from the experiment. Permeate samples were collected over time in order to determine the flux, calculated as:

$$\text{Flux} = \frac{V_p}{t \cdot A} \quad (1)$$

where V_p (L) is the permeate volume, t (h) is the permeation time, and A (m^2) is the active membrane area.

The permeance was calculated from the slope of the flux versus the TMP (bar) plot [eq. (2)]

$$\text{Permeance} = \frac{J}{\text{TMP}} \quad (2)$$

Before the tests, each membrane was first soaked in the target solvent for 24 h (if not otherwise indicated) and then loaded in the cell. The membrane was stabilized at each operating pressure until the permeation flux reached a steady state. In the experiments, in which the flux was measured as a function of the TMP, the pressure was varied from the higher to the lower value of TMP in order to ensure the same compaction during the entire experiment.

In the rejection test, 100 mL of a Solvent Blue 35 solution in NMP or DMF (100 mg/L; 0.29 mM) was used as feed; 50 mL of permeate was collected under TMP of 2 bar for the support and 30 bar for the PHC-5 membrane. The concentration of the solute in the feed, retentate, and permeate was analyzed by a UV spectrometer (Lambda 650S UV-vis spectrometer, PerkinElmer). During the experiment, the feed solution was stirred using a magnetic stirrer at high speed to prevent concentration polarization. The membrane rejection (R) was calculated using the eq. (3).

$$R (\%) = \left(1 - \frac{C_p}{C_r}\right) \times 100 \quad (3)$$

where C_p and C_r represent feed and permeate concentrations, respectively. In all rejections, a mass balance [eq. (4)] was used to check any loss during the experiment.

$$\text{Mass balance} (\%) = \left(\frac{V_p \cdot C_p + V_r \cdot C_r}{V_f \cdot C_f}\right) \times 100 \quad (4)$$

where C_f , C_p , and C_r represent concentrations of feed, permeate, and retentate, and V_f , V_p , and V_r are volumes of feed, permeate, and retentate, respectively.

RESULTS AND DISCUSSION

In the design of the PHC membranes, a great attention was devoted to the support layer development. The ideal structure for the support corresponds to a porous sponge-like membrane, in order to combine a low mass transport resistance with a high-mechanical resistance under elevated pressure. The effects of the composition of the dope solution on the structure of porous P84 co-PI membranes were investigated. The membrane prepared from a NMP solution was characterized by finger-like macrovoids (Figure 1) caused by the rapid liquid-liquid demixing during the phase separation process because of the high affinity between the coagulation bath (water) and the NMP (partition coefficient octanol/water $\log P_{o/w} -0.46$). The presence of macrovoids is undesired in pressure driven membrane process, because they reduce the mechanical stability of the membranes, facilitating the collapse of this structures under high TMP. It is possible to suppress macrovoids formation by reducing the rate of the demixing during the NIPS process.⁷ This delay can be induced using a more soft coagulation bath (e.g., adding some solvent in the coagulation bath or using, as nonsolvent, an organic liquid having lower affinity for the solvent of the dope solution). However, this strategy has evident economical and environmental drawbacks because of the larger quantity of organic solvents used. Another possibility is the increase of the dope solution viscosity for example by increasing the polymer concentration.¹⁴ However, the increase of concentration usually increases significantly the mass transport resistance of the resulting membrane. Alternative chemical additives such as LiCl,¹⁵ TiO₂¹⁶ and γ -butyrolactone,¹⁷ have been used. In this work, a more environmentally friendly strategy was used to delay the demixing rate adding small quantity of water or ethanol in the dope solution.

The solutions containing water or ethanol (Table I) were more close to the miscibility gap in the ternary phase diagram of the system polymer/solvent/nonsolvent (thermodynamic effect). However, these liquids increased the solution viscosity of the solutions and induced the delay of the demixing process (kinetic effect).

As a consequence, the macrovoids present in the membrane P84-0 were suppressed as the nonsolvent content increased. In the case of the use of water in the dope solution, the threshold of the transition from finger-like to sponge-like morphology

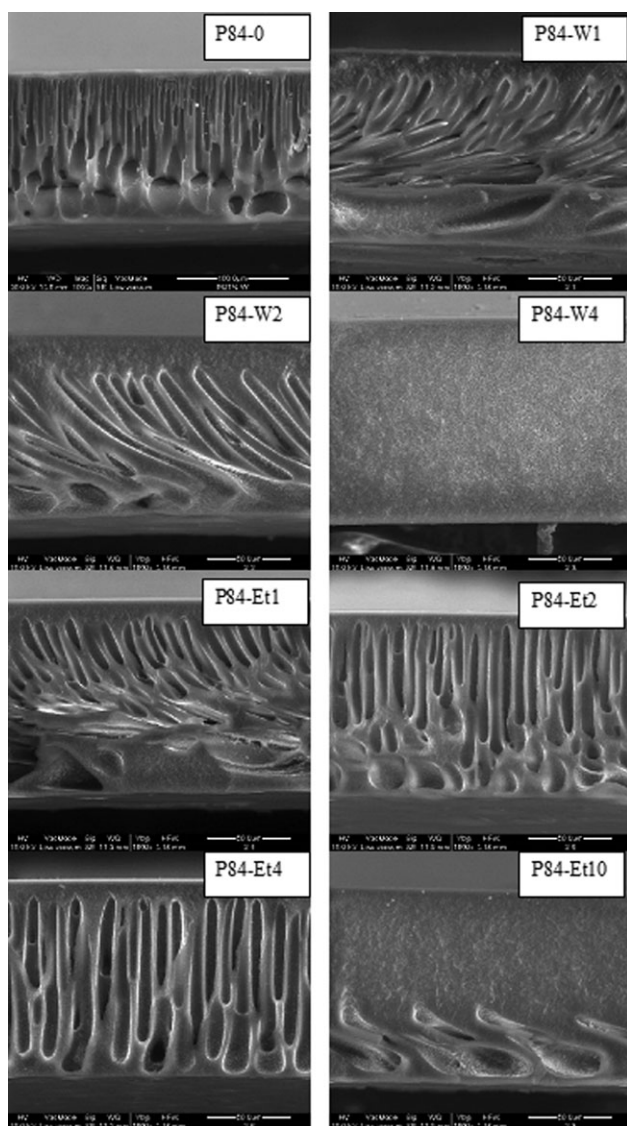


Figure 1. Cross section of the membranes prepared from different solutions (see Table I for the codes used and the compositions of the corresponding dope solutions).

was found to be 4 wt %; in the case of ethanol, having a less nonsolvent power for the polymer than water, the macrovoids did not completely disappear at 10% of concentration (Figure 1). As a consequence, the morphology and permeance of the P84 membranes depended from a combination of the thermodynamic and kinetic effect of the nonsolvent additives on the phase-separation process.¹⁵

Membranes were screened in pure solvent filtration, including polar aprotic solvents in which the original polymer was soluble (DMF and NMP). All the membrane prepared resulted completely stable after immersion in these solvent for more than 24 h. The solvent resistance of the membranes was due to the chemical reaction with DAMP, which converted the imide bonds of the P84 in amide bonds linking the polymer chains, as confirmed by FTIR analyses (Figure 2). The reaction was carried out in ethanol solution because of the high affinity between the

polymer and this solvent, which can swell the membranes and render more accessible the reaction sites on the polymer chains. The comparison of the FTIR spectra of the membranes before and after the reaction with DAMP confirmed the complete cross-linking [Figure 2(A,B)]. The typical imide bands were identified in the spectra of the membranes uncrosslinked at 1780 cm^{-1} (asymmetric stretch of C=O imide group), 1719 cm^{-1} (symmetric stretch of C=O imide group), and 1362 cm^{-1} (C–N stretch). These bands disappeared completely in the spectra of the crosslinked membrane, instead characterized by the typical signals of the amide at 1640 cm^{-1} (C=O stretching) and 1535 cm^{-1} (C–N stretch).

The membranes prepared from the dope solution-containing water or ethanol were characterized by a lower permeance in comparison with the membrane prepared from the NMP solution (P84-0; Table I). These results were due to the less porous structure obtained in the presence of these nonsolvent, in agreement with the previous SEM observation. However, the permeance of all the support membranes is relatively high if compared with a NF membrane. Considering the water permeance, the typical range of NF membranes is $1.4\text{--}12\text{ L h}^{-1}\text{ m}^{-2}\text{ bar}^{-1}$; the permeance of the membranes reported in Table I fall in the range of the ultrafiltration-microfiltration (respectively, $10\text{--}50$ and $>50\text{ L h}^{-1}\text{ m}^{-2}\text{ bar}^{-1}$);⁶ as a consequence, all of them can be potentially used as support for a composite NF membrane, because they offer a negligible mass transfer resistance than a NF membrane.

The solvent fluxes depended linearly from the TMP in the range between 0.5 and 2 bar.

The permeance of the membranes, calculated from the slope of the flux versus TMP curve, resulted to be strongly influenced by the viscosity (Figure 3) and molar volume of the solvents, as well as, from the affinity between the solvent and the polymer (Table II).

In all cases, the higher permeance was obtained with the CH_3CN characterized by a lower viscosity. On the contrary,

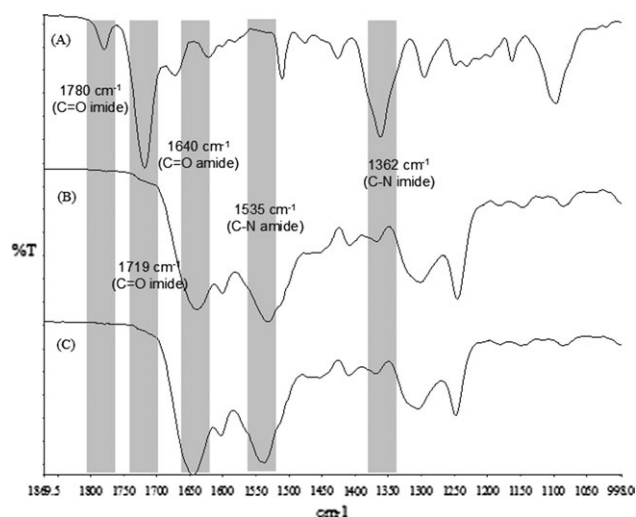


Figure 2. ATR-FTIR spectra of the P84-W4 membrane before (A) and after the cross-linking with DAMP (B), and the spectra of the crosslinked composite PHC-5 membrane (C).

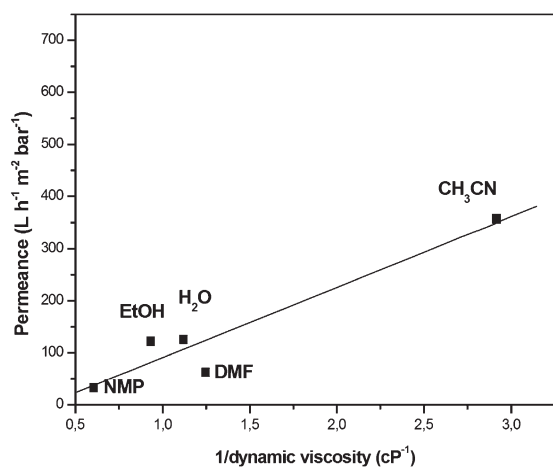


Figure 3. Permeance of of the P84-W4 membrane versus the reciprocal of the solvent dynamic viscosity.

NMP permeance was the lowest, because the higher viscosity. A lower difference in permeance was observed between EtOH and H₂O having intermediate viscosity between the solvent used. However, the membrane permeance was also influenced by the mutual affinity between the solvent and the polymeric matrix. Despite the lower viscosity of the DMF respect to the previous two solvents, its permeance through the P84-based membranes resulted lower, because DMF is a good solvent for the uncrosslinked membrane and, despite the crosslinked membranes were stable in this solvent, it can swell the membrane reducing the effective pore size. Moreover, DMF has a higher molar volume than water and ethanol. The membrane selected as support for the PHC was the P84-W4, because it conjugated an appropriate structure (sponge-like, no macrovoids) with high permeance (Figure 1 and Table I). A PHC membrane was prepared by coating and controlled solvent evaporation of a P84 co-PI solution (5 wt % in a mixture 50 : 50 wt % NMP : THF) on the crosslinked P84 co-PI support. Finally, in order to have a composite membrane completely stable in organic solvents, also, the selective layer was crosslinked by reaction with DAMP (membrane code PHC-5). The FTIR spectra of the PHC-5 membrane confirmed the conversion of the imide bonds in amide bonds also for the coating layer [Figure 2(C)]. Before the coating, the support membrane was immersed in glycerol in order to fill the pores with this nonvolatile substance. The impregnation step is fundamental, because it avoids the intrusion of the coating solution inside the pores of the support, with consequent excessive increase of the mass transport resistance. The use of glycerol also avoids the partial pore collapse of the support due to the large capillary forces during the drying of water-filled membranes.¹² Moreover, the P84 membranes, if directly dried from water, were subject to strong asymmetric tension caused by the water evaporation from the pores, and, as a consequence, they tend to curl, resulting rigid and fragile. On the contrary, the membranes dried after the impregnation step, were flexible, easy to be handled, and to be fixed on a glass plate obtaining a flat surface for the application of the coating layer. Not only at macroscopic scale, but also on a microscopic scale, the impregnation procedure rendered the support more

suitable for the coating procedure, because it offered a more smooth surface. The AFM analysis of the support clearly indicated that the impregnation with glycerol reduced the surface roughness. The R_w , R_q , and R_{max} values of the support dried from water resulted to be 13.6, 18.4, and 184 nm, respectively; the same parameters for the support impregnated with glycerol before drying, were 3.32, 4.18, and 33.5 nm. The SEM analyses of the PHC-5 membrane revealed that the coated layer was composed of a denser structure on the up side and a nodular porous sub-structure with not interconnected pores [Figure 4(A)].

The solvent evaporation from the surface of cast liquid film increased the polymer concentration in the top layer and therefore resulted in the vitrification of the polymer matrix, which forms a nodular structure. The formation of the voids in the substructure can be due to different factors: residual traces of the less volatile solvent (NMP) remained entrapped after the polymer solidification and removed only rinsing the membrane was rinsed in water; the diffusion of glycerol from the support layer to the upper layer because of its high affinity for the NMP; the diffusion of water vapor from the atmosphere into the polymer film.

The PHC-5 membrane was characterized in pure solvent permeation test and retention experiments using a neutral molecule as solute model (Solvent Blue 35). The composite membrane resulted completely stable in DMF and NMP, and no delamination phenomena were also observed after 96 h of immersion in NMP and permeation and rejection test at 30 bar [Figure 4(B)]. The comparison of the permeance and rejection of the support (P84-W4) with the composite membrane (PHC-5) revealed that the upper layer was the mass transport limiting and selective layer (lower permeance and higher rejection of the composite membrane; Figure 5). As expected, for all the membranes, the permeance of the pure solvent was higher than the permeance of the solution with Solvent Blue 35.

The type of solvents, in which the molecule to be retained was dissolved, affected the rejection. The Solvent Blue 35 rejection in DMF for the PHC-5 membrane was 46%, and the rejection in NMP was 62%. This difference can be explained considering not only the higher DMF solution permeance respect to the more viscous NMP solution permeance (Figure 5), and the consequence higher solvent dragging effect, but also the higher affinity of the solute for the DMF than for NMP. The solubility parameter (δ) of the Solvent Blue 35 was calculated using the Fedors' group contribution method¹⁸ and resulted to be $25.7 \text{ J}^{1/2} \text{ cm}^{-3/2}$. This value is more close to the δ value of the

Table II. Dynamic Viscosity (η), Molar Volume (V), and Solubility Parameter (δ) of the Solvents Used¹⁸

	η (cP @25°C)	V (cm ³ mol ⁻¹)	δ (J ^{1/2} cm ^{-3/2})
CH ₃ CN	0.343	85.10	19.50
DMF	0.802	77	24.9
H ₂ O	0.894	18.00	48.00
EtOH	1.074	58.40	26.25
NMP	1.65	96.4	22.9

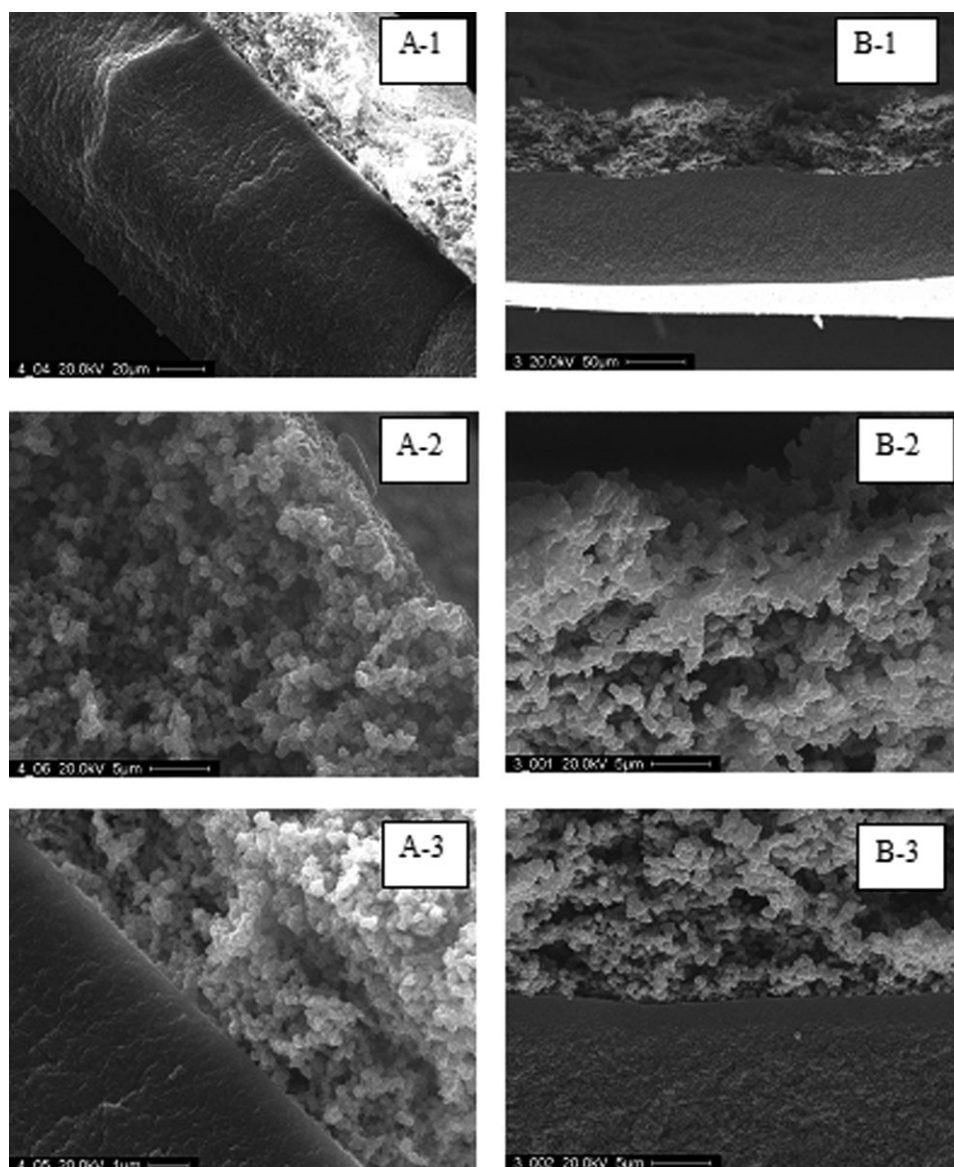


Figure 4. SEM images of the cross section of the PHC-5 membranes as prepared (A) and after immersion in NMP for 4 days and successive permeation and rejection test in NMP at 30 bar (B). (1) Whole cross section; (2) particular of the up side; (3) particular of the interface between the two layers.

DMF than to the δ value of the NMP (Table II). To test the long-term stability of the composite membrane in polar aprotic solvent, the PHC-5 membrane was immersed in NMP for 96 h (aging test). The high compatibility between the two layers of the composite membranes was able to avoid any delamination of the “aged” membrane [Figure 4(B)].

Moreover, the membrane “aged” in NMP had higher permeance, then the sample conditioned in NMP for only 24 h, but similar rejection [Figure 5(B)].

These differences in permeance were probably due to residual traces of glycerol in the composite membrane, which are completely removed after immersion for long time in NMP, which is a good solvent for the glycerol.

Although the optimization of the PHC membranes is still in progress, the preliminary results clearly demonstrated the high

potentiality of this new type of membranes for separations in organic solvents.

CONCLUSIONS

In this work, the proof of the concept of PHC membranes, in which the selective layer is made of the same material of the support, was demonstrated. The use of the same material for the preparation of both, the selective and the support layer, has the advantage of a better affinity and adhesion between the two systems and can allow an increase of the long-term stability of the composite membranes, reducing the possibility of delamination phenomena.

Porous co-PI (P84) membranes were prepared by NIPS method. Macrovoids with finger-like structure were present in the membrane cast from a P84 (21 wt %) solution in NMP (79 wt %). However, these macrovoids totally disappeared adding a small

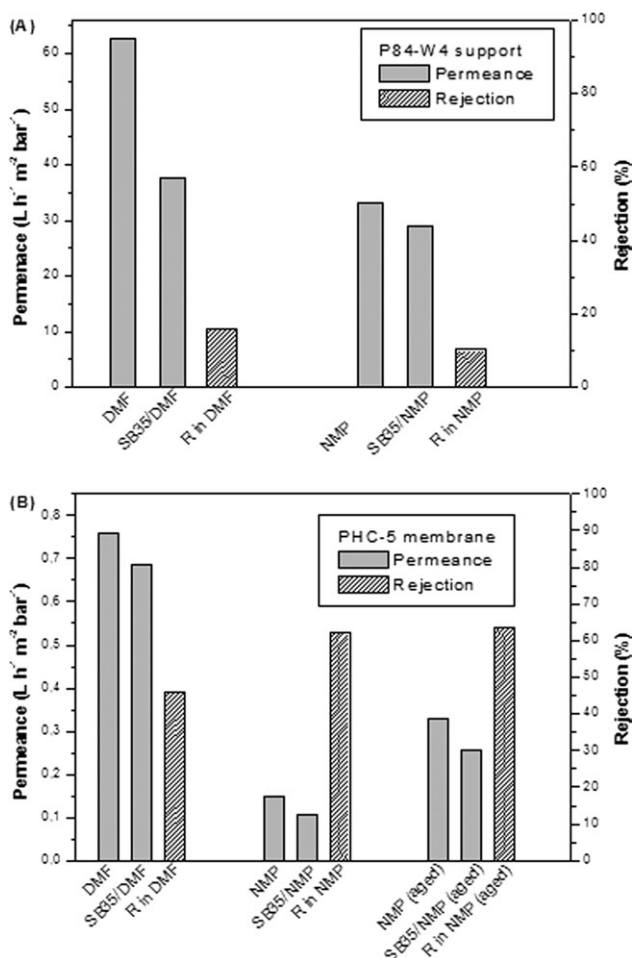


Figure 5. Permeance of pure solvent (DMF or NMP), and rejection and permeance of Solvent Blue 35 solution (SB35 in DMF or SB35 in NMP) of the membrane support (P84-W4; A) and the composite membrane (PHC-5; B). All the membrane were conditioned in the target solvent for 24 h before the permeation test except in the case of the results marked as “aged” in which the PHC-5 membrane was soaked in NMP for 96 h. The experiments were carried out at 2 bar for P84-W4 and 30 bar for PHC-5 at 25°C ± 3°C.

quantity of water (4 wt %) in the dope solution obtaining a porous membrane with sponge-like structure (P84-W4). The suppression of the finger-like macrovoids was explained by the change of the kinetics of the liquid-liquid demixing from instantaneous to delayed because of the increase of the solution viscosity. The optimized support ensured high-compression resistance and high permeance. Moreover, after crosslinking with a diamine (DAMP), it was completely stable in polar aprotic solvent like NMP and DMF in which the original copolymer was soluble. The selected P84-W4 membrane was used as support for the coating of a P84 solution, which after controlled solvent evaporation and crosslinking with DAMP, formed the selective layer of the PHC membrane for OSN applications. This composite membrane resulted to be completely stable in NMP also over long times (96 h). No delamination problems were observed, and the rejection of Solvent Blue 35 of the membrane was maintained (63.5%). The results obtained are promis-

ing and potentially can be extended to other polymers, which, like PI, can be rendered insoluble in the original solvents by an appropriate crosslinking. However, it is fundamental to further improve the membrane transport properties obtaining a more tight and less thick selective layer in order to improve both permeance and selectivity.

ACKNOWLEDGMENTS

Ms Eun Woo Lee is gratefully acknowledged for her collaboration in the preparation of some of the supports. This work was carried out in the framework of the FP7 project NEMOPUR (New Molecular Purification Technology for Pharmaceutical Production, grant agreement n 214226).

REFERENCES

- Vandezande, P.; Gevers, L. E. M.; Vankelecom, I. F. *J. Chem. Soc. Rev.* **2008**, *37*, 365.
- Peeva, L.G.; Malladi, S.; Livingston, A. In *Comprehensive Membrane Science and Engineering*, Vol. 2; Drioli, E., Giorno, L., Eds.; Elsevier: Oxford, **2010**; p 91–111.
- Vanherck, K.; Cano-Odena, A.; Koeckelberghs, G.; Dedroog, T.; Vankelecom, I. F. *J. Membr. Sci.* **2010**, *353*, 135.
- Soroko, I.; Lopes, M. P.; Livingston, A. *J. Membr. Sci.* **2011**, *381*, 152.
- Aberg, C. M.; Ozcam, A. E.; Majikes, J. M.; Seyam, M. A.; Spontak, R. *J. Macromol. Rapid Commun.* **2008**, *29*, 1461.
- Mulder, M. *Basic Principles of Membrane Technology*; Kluwer: Dordrecht, **1991**.
- Strathmann, H.; Kimmerle, K. *Desalination* **1990**, *79*, 283.
- Soroko, I.; Makowski, M.; Spill, F.; Livingston, A. *J. Membr. Sci.* **2011**, *381*, 163.
- Cadotte, J. E.; Petersen, R. I. In: *Synthetic Membranes*, ACS Symposium Series 153, A.F. Turbak, Ed., Vol. 1: *Desalination*; American Chemical Society: Washington D.C., **1981**, p 305–325.
- Kools, W. U.S. Pat. 020,948,5A1 (**2003**).
- Livingston. In *Organic Solvent Nanofiltration: An Emerging Molecular Separation Technology*, Proceeding of the ICOM 2011 Conference, Amsterdam, The Netherlands, July 24–29, **2011**; ICOM1828.
- Gevers, L. E. M.; Aldea, S.; Vankelecom, I. F. J.; Jacobs, P. A. *J. Membr. Sci.* **2006**, *281*, 741.
- <http://www.p84.com> (accessed June 1).
- Han, J.Y.; Oh, H.-H.; Choi, K.J.; Min, B.R. *J. Appl. Polym. Sci.* **2011**, *122*, 2653.
- Fontananova, E.; Jansen, J. C.; Cristiano, A.; Curcio, E.; Drioli, E. *Desalination* **2006**, *192*, 190.
- Soroko, I.; Livingston, A. *J. Membr. Sci.* **2009**, *343*, 189.
- Ren, J.; Li, Z. *Desalination* **2012**, *285*, 336.
- Van Krevelen, D. W. In *Properties of Polymers, Their Correlation with Chemical Structure, Their Numerical Estimation and Prediction from Additive Group Contributions*; Elsevier: Amsterdam, **1990**.