Surface Modification of Polyvinylidene Fluoride Pervaporation Membranes

Mohamed Khayet
Dept. of Applied Physics I, Faculty of Physics, University Complutense of Madrid, 28040 Madrid, Spain

Geeta Chowdhury and Takeshi Matsuura
Industrial Membrane Research Institute, Dept. of Chemical Engineering, University of Ottawa,
Ottawa, Ont., K1N 6N5, Canada

Polyvinylidene fluoride (PVDF) membranes were surface-modified using fluorinated surface-modifying macromolecules (SMMs) additives. The membranes were prepared using the phase-inversion method. Two novel SMM formulations were used. The effect of some relevant parameters, such as the solvent evaporation time, evaporation temperature, and concentration of SMM in the PVDF casting solution, was considered. The prepared membranes were characterized in terms of the contact angle analysis, the liquid entry pressure of water measurements, and the scanning electron microscopy. Pervaporation experiments were conducted for dilute chloroform/water binary mixtures. Based on the contact angle analysis, the incorporation of SMM into the PVDF casting solution produced membranes with higher surface hydrophobicity. The pervaporative performance of the prepared membranes was investigated, and the relationship between the surface characteristics of the modified PVDF membranes and the chloroform separation discussed.

Introduction

It is well documented that surface chemistry and morphology of the membranes play an important role in the transmembrane transport of penetrants (Matsuura, 1993). Generally, hydrophobic membrane surfaces tend to favor organic selectivity in the separation of aqueous solutions by pervaporation (PV) (Huang, 1991). Therefore, it can be hypothesized that if the hydrophobicity of the membrane is enhanced, the organic selectivity of this membrane can be improved. In the membrane literature, various techniques were carried out for surface modification of polymer membranes. Those are physical (e.g., coating, UV treatment, plasma treatment), chemical (e.g., wet treatment, grafting), or bulk modification (e.g., polymer blends) (Ganbassi et al., 1996). The simple and attractive method, frequently used, is the addition or blending of surface-active components into the casting polymer solution. Generally, the resulting polymer surface properties are quite different from those of the bulk polymer, because of the surface localization of the additives (Pinnau and Freeman, 2000). The driving force for the surface migration and the orientation of the additive's chemical groups at the membrane surface is the tendency to minimize the interfacial energy. Based on this procedure, in our previous studies (Matsuura et al., 1999; Pham et al., 1999; Hamza et al., 1997; Ho et al., 2000), surface-modifying macromolecules (SMMs) with a hydrocarbon tail containing fluorine were blended into polyethersulfone (PES) polymer solutions. The type of surface-modifying macromolecules employed has a copolymeric nature. It has an amphipathic structure, theoretically consisting of a main polyurethane chain terminated with two low-polarity polymer chains (that is, fluorine segments). It was observed that during the solvent evaporation from the SMM/PES casting film, SMM migrated to the film surface, rendering the surface of the obtained membrane more hydrophobic than the bulk-membrane phase. Because only a small concentration of SMM was added to the dope solution, usually less than 5 wt. %, the bulk properties of the base polymer remained relatively unchanged. The measured water contact angle over the membrane surface increased from 76°

Correspondence concerning this article should be addressed to M. Khayet.

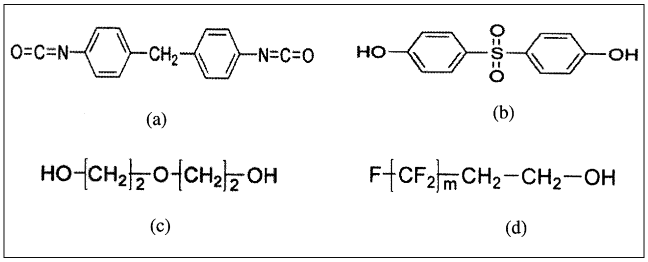


Figure 1. Chemical structures of SMM reagents.

(a) Methylene bis-*p*-phenyl di-isocyanate (MDI); (b) dihydroxy diphenyl sulfone (DPS); (c) diethylene glycol (DEG); (d) fluoroalcohol Zonyl (BA-L).

for the PES membrane to 116° for the SMM-modified PES membrane, which was close to the contact angle of the commercial polytetrafluoroethylene (PTFE) membrane. The localization of SMM in the membrane surface was also confirmed by X-ray photoelectron spectroscopy (XPS) analysis, scanning electron microscopy (SEM), and atomic force microscopy (AFM) (Pham et al., 1999; Hamza et al., 1997; Ho et al., 2000).

Several formulations of SMMs were synthesized with different combinations and stoichiometrics of the reagents: di-isocyanates [such as methylene bis-*p*-phenyl di-isocyanate (MDI), 1,6-hexane di-isocyanate (HDI)], polyols [such as polypropylene dioxide (PPO), polycaprolactone diol (PCL), polytetramethylene oxide (PTMO)], and different fractions of a monofunctional fluorinated alcohol (BA-L) (Ho et al., 2000; Tang et al., 1996, 1997a,b). Attempts were made to find the effects of various types of SMMs and different membrane casting conditions to SMM migration. It was found that the solubility in the base polymer depends on the additive's molecular weight, its molecular structure, and its low polar component, which can be controlled by various factors, such as the main chain length, the number of C-F bond, and the type of chemicals used to synthesize the main chain (Matsuura et al., 1999; Pham et al., 1999; Hamza et al., 1997; Ho et al., 2000; Tang et al., 1996, 1997a,b). PES membranes modified by SMM exhibited low surface energies, high chemical resistance, and good mechanical strength. Those membranes were tested for use in ultrafiltration and pervaporation applications. In comparison to the unmodified PES membranes, SMM surface-modified membranes were susceptible to less fouling in the treatment of cutting machine oil/water emulsion by ultrafiltration (Hamza et al., 1997), and could be used to remove chloroform from water by pervaporation (Fang et al., 1994; Mahmud et al., 1996, 2001).

As a continuation of the membrane-surface modification research program, two novel types of SMMs were used for incorporation into polyvinylidene fluoride (PVDF) material to develop pervaporation membranes for possible separation of volatile organic compounds (VOCs) from water. It is known that PVDF is a chemically inert fluoropolymer, can tolerate high-temperature feed solutions, and is "hydrophobic" material. It is more hydrophobic than PES; however, it is less hydrophobic than polypropylene (PP) and polytetrafluoroethylene (PTFE). The reported values of the contact angle of PVDF are lower than 90°. Owens and Wendent (1969) presented a value of 82°, Huang et al. (2000) obtained a value of 75°, Nunes and Peinemann (1992) gave a value of 80°. In this work, the measured values of the advancing and the receding contact angles of the prepared PVDF membranes are 82.3° ± 2.1° and 75.2° ± 2.0°, respectively.

Attempts are made in this work to prepare pervaporative flat-sheet SMM modified and unmodified PVDF membranes using the phase-inversion method and employing two types of SMMs to increase the hydrophobicity of the PVDF membranes. The influence of different solvent evaporation periods, evaporation temperatures, and SMM concentrations in the PVDF casting solution was studied. The membranes were characterized by the contact-angle measurements and SEM. PV experiments were carried out for chloroform/water binary mixtures. The relationship between the membrane surface characteristics and the PV permeation properties of aqueous chloroform solutions is discussed.

Experimental Studies

Materials

Materials Used for SMM Synthesis. The SMMs were kindly supplied by the Department of Biomaterials, Faculty of Dentistry, University of Toronto. They were synthesized using

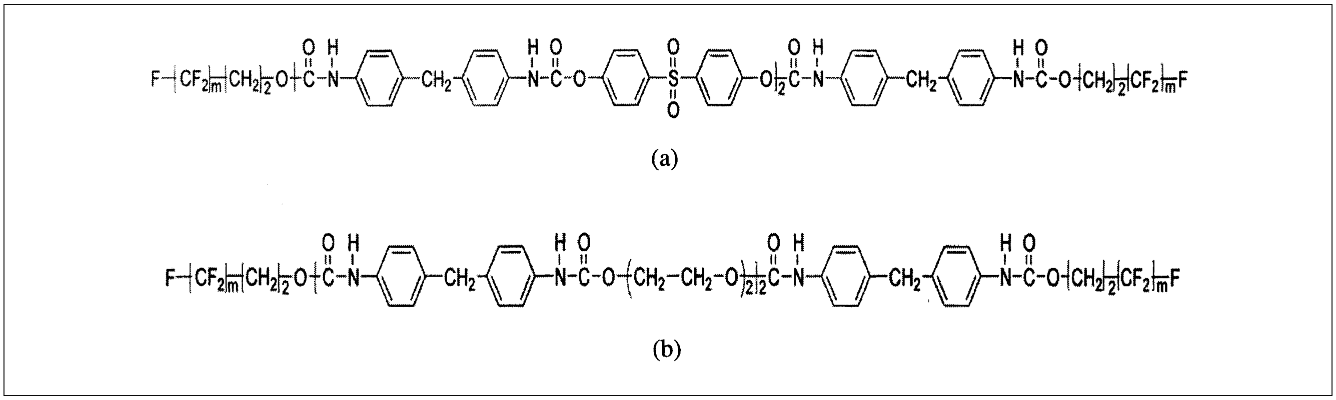


Figure 2. Chemical structures of SMMs.

(a) MDI:DPS:BA-L (SMM1); (b) MDI:DEG:BA-L (SMM2).

methylene bis-*p*-phenyl di-isocyanate (MDI, Eastman Kodak), two polyols: dihydroxy diphenyl sulfone (DPS), and di-ethylene glycol (DEG) from Aldrich Chemical Company, and a monofunctional fluorinated alcohol (Zonyl BA-L, DuPont Chemical from Waters & Rogers, Montreal), which is a fluorotelomer intermediate with a variable number of (CF_2) repeat units in the molecule in the range of 4 to 12. This fluoroalcohol was distilled under vacuum (3.33 Pa) at a temperature between 50 and 55°C to yield a low fraction, with a repeat unit number from 4 to 8, an average molecular weight of about 443, and a fluorine content of 49.6 wt. % (Pham et al., 1999). More details of the conditions and method for separating fractions of the fluoroalcohols are given elsewhere (Pham et al., 1999; Tang et al., 1996; Ho, 1997). *N,N*-Dimethylacetamide (DMAC, Aldrich Chemical Company) was used as a solvent for the reaction of the di-isocyanate with the polyol. Prior to their use, all reagents and solvents were distilled to remove trace impurities and degassed to remove moisture using material preparation procedures described extensively by Ho (1997). The chemical structures of the SMM reagents (MDI, DPS, DEG, and BA-L) are presented in Figure 1.

Materials Used for Preparation of the Membranes. The base polymer used in this work is polyvinylidene fluoride (PVDF), Kynar grade 740 (Elf Autochem, Philadelphia). DMAC was employed as a solvent to prepare the polymer casting solution. Surface modifying macromolecules [MDI:DPS:BA-L (SMM1) and MDI:DEG:BA-L (SMM2)] were used (see Figure 2). Ethanol (GR grade, Merck, 99%) was used for the solvent exchange method. Distilled water and formamide (BDH chemicals, 99%) were used for the contact angle measurement.

Synthesis and characterization of surface-modifying macromolecules

Two SMM formulations were synthesized for this study using a two-step solution polymerization method under a controlled nitrogen atmosphere inside a glove box. In the first step, a prepolymer was prepared by reacting the di-isocyanate (MDI) with either DEG or DPS in a common solvent of DMAC. This mixture formed a urethane prepolymer solution. In the second step, the oligomeric fluoroalcohol BA-L (low fraction) was added to the prepolymer to cap the molecules, resulting in a solution of SMMs. The reaction molar ratio of MDI:polyol:BA-L was 3:2:2. Details of the synthesis conditions were outlined in earlier publications (Ho et al., 2000; Tang et al., 1996, 1997a,b). The chemical structure of the two prepared SMMs is given in Figure 2.

Fluorine elemental analysis was made and the polystyrene equivalent molecular weights of the prepared SMM polymers were determined. The analytical procedure used was detailed by Ho (1997).

Membrane preparation

Pervaporative flat-sheet membranes were prepared by the phase-inversion method. First, 20 wt. % of PVDF was dissolved in DMAC and stirred at approximately 328 K for about 12 h to ensure the complete dissolution of the polymer. The polymer dope prepared was transparent and homogenous at room temperature. This polymer solution was used to prepare the unmodified PVDF membranes. For the preparation of SMM-modified PVDF membranes, different concentrations of SMM (≤ 4 wt. %) were dissolved into the prepared PVDF casting solutions and the solutions were allowed to stir in an orbital shaker at room temperature for at least 8 h. The resulting solutions were filtered through a 0.5-μm Teflon filter, under a pressure of 2.41×10^5 Pa, to remove nonsoluble contaminants. The mixture was then degassed over night at room temperature. The PVDF polymer solutions with and without SMM were poured onto glass plates for casting at room temperature using a casting bar. The cast films together with the glass plates were immersed immediately in distilled water at 294.2 K for at least 1 h or introduced in an oven with forced air circulation for solvent (DMAC) evaporation under a controlled temperature for a predetermined period of time. The evaporation temperature was varied from 293 K to 373.2 K. The films were further immersed in distilled water at approximately 294 K for at least 1 h. During gelation, the membrane spontaneously peeled off the glass plate. Those membranes were subjected to solvent exchange after gelation. First the membranes were immersed for approximately 4 h in an aqueous ethanol solution (50 wt. %) and then in pure ethanol for 24 h. Furthermore, the membranes were dried at room temperature for about 6 h, and then dried under vacuum for 24 h.

Membrane characterization

Contact-Angle Studies. Contact angle measurements provide information over a large area of the membrane surface, while other techniques, used for the characterization of the membrane surface, such as X-ray photoelectron spectroscopy (XPS), have limited lateral resolution. In this work, contact angles of liquid on the air surface of all the prepared SMM-modified and -unmodified membranes were measured at room temperature by using a contact-angle-meter 14-in. Horizontal Beam Comparator (SCHERR ST TUMICO, Model 22-2000 Series). Initial drops of 3 μL were deposited on the membrane surface, employing a tight syringe that was adjusted to 5×10^{-4} m above the membrane surface. Direct measurements of the advancing contact angle, which is a measure of the hydrophobic character of the surface, and the receding contact angle, which is a measure of the relative hydrophilic character of the surface, were carried out at 10 different spots on each membrane sample.

Liquid Entry Pressure of Water Measurements. Membrane liquid entry pressure of water (LEPw) is the pressure that must be applied to pure water before it penetrates into dried membrane pores. This pressure depends on the pore size and on the hydrophobicity of the membrane. It decreases as the pore size increases and/or the contact angle decreases. The apparatus used is shown in Figure 3. The method used for this measurement was described earlier by Smolders and Franken (1989). The membrane was placed in the static stainless cell between the feed side (the upper chamber) and the permeate side (the lower chamber) connected to a digital capillary flowmeter (Varian Optiflow 420). First, a slight pressure ($\approx 0.3 \times 10^5$ Pa, gauge) was applied to the system for at least 600 s, then the pressure was increased stepwise, with an increment of 0.68×10^3 Pa. The pressure at which a

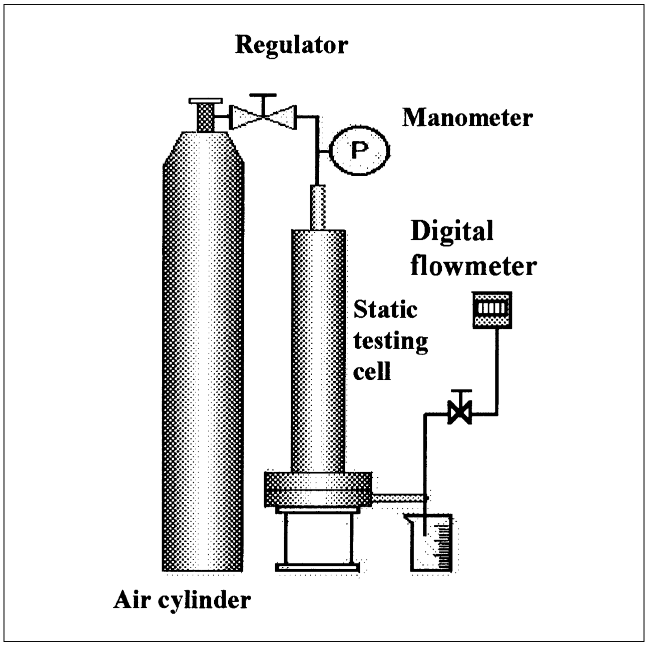


Figure 3. Experimental system used for the membrane liquid entry pressure of water (LEPw) measurement.

continuous flow is observed in the permeate side is the membrane LEPw.

Scanning Electron Microscopy. The SMM modified and unmodified PVDF membranes prepared with the methods mentioned earlier were examined by a scanning electron microscopy (SEM, JEOL Model JSM-6400). The samples were positioned on a metal support and coated by 60% gold and 40% palladium under vacuum in a sputtering system HUMMER VII that provides a 2×10^{-9} into 3×10^{-9} m conductive coating on the samples. The SEM pictures of both surface and cross section of the membranes were taken at various magnifications.

Pervaporation Experiments. Pervaporation experiments were carried out using the apparatus described in Figure 4. It is constituted by a static stainless cell connected to a heating system through its jacket to control the temperature of the liquid feed. The membrane was placed between the upper chamber (feed side) and the lower chamber (permeate side), having an effective area of about 9.84×10^{-4} m^2. The total volume of the upper chamber is 381.7×10^{-6} m^3. The temperature was measured, after steady state was reached, inside the cell by a sensor connected to a digital meter with an accuracy of ±0.1 K. The liquid feed was allowed to stir inside the cell by using a graduated magnetic stirrer. A vacuum pump (Welch DuoSeal 1400), which was associated to a vacuum pressure controller (MKS Type 651), was connected to the permeate side of the cell to remove the vapor. The downstream pressure was measured by a digital pressure transducer with an accuracy of about $\pm2\%$. Two glass cold traps filled automatically with liquid nitrogen were installed to recover the permeate. In every case, the flux of the membrane was determined from the weight of the condensate collected in each trap for a predetermined period of time. The compositions of the feed and permeate were determined using a gas chromatograph, Varian 3300, equipped with Alltech Chemipack C18, 80/100 Column. Practically, all pervaporation experiments were repeated at least two times to ensure reproducibility of the measurements, and the separation factor was calculated using the following expression

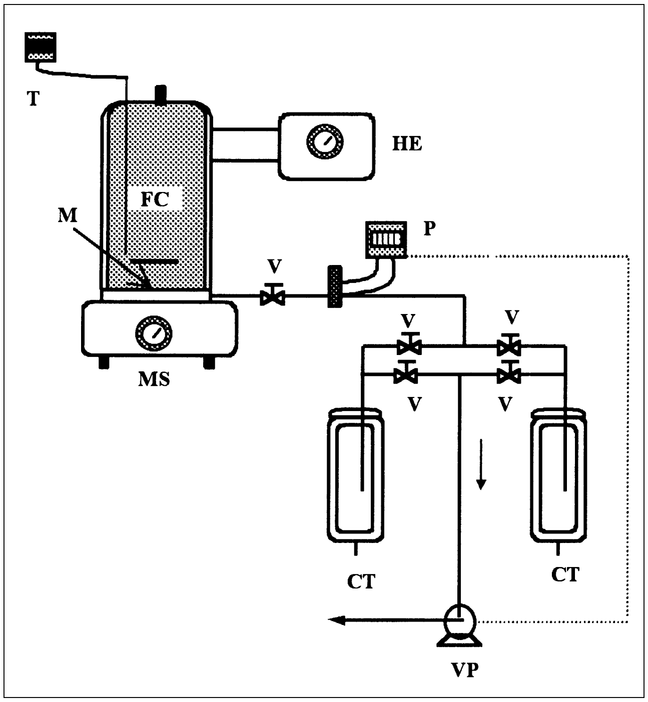


Figure 4. Experimental setup used for the pervaporation experiments.

(M) Membrane; (FC) feed container; (HE) heat exchanger; (T) temperature sensor; (MS) magnetic stirrer; (V) valve; (P) vacuum pressure controller; (CT) cold trap; and (VP) vacuum pump.

$$\alpha = \frac{[C_{ch}/C_w]^{\text{permeate}}}{[C_{ch}/C_w]^{\text{feed}}}, \tag{1}$$

where C_{ch} and C_w are the concentrations of chloroform and water, respectively.

Theory

The contact angle, θ, was determined from the following equation (Pinnau and Freeman, 2000)

$$\theta = \cos^{-1}\left(\frac{\cos\theta_a + \cos\theta_r}{2}\right), \tag{2}$$

where θ_a and θ_r are the advancing contact angle and the receding contact angle, respectively.

The surface energy of the membranes was estimated from the contact-angle measurements to water and formamide on the SMM surface-modified and -unmodified PVDF membranes. The following equations, taken from Owens and

Wendent (1969), were employed:

$$(1+\cos\theta)\gamma_l = 2\left[\left(\gamma_s^d\gamma_l^d\right)^{1/2}+\left(\gamma_s^p\gamma_l^p\right)^{1/2}\right] \tag{3}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p, \tag{4}$$

where θ is the contact angle, γ_s and γ_l are the surface free energies of the solid and liquid, respectively. The superscripts d and p refer to the dispersion and polar-force components, respectively.

The solubility parameter of the membranes, δ, is an indicator for the hydrophobicity of a polymer surface. This was calculated from Eq. 5

$$\delta = (e_{\mathrm{coh}})^{1/2} \tag{5}$$

where e_{coh} is the cohesive energy density of the membrane surface, which can be determined from the surface free energy by using the following equation

$$\gamma_s = 0.75(e_{\mathrm{coh}})^{2/3}, \tag{6}$$

where γ_s is the surface free energy, which can be calculated from the contact-angle measurement and using Eqs. 3 and 4. The adopted values of γ_l, γ_l^d and γ_l^p for water were 72.8 mJ/m^2, 21.8 mJ/m^2, and 51.0 mJ/m^2, respectively, while for formamide those values were 58.2 mJ/m^2, 39.5 mJ/m^2, and 19.0 mJ/m^2, respectively (Van Krevelen, 1990). By measuring the contact angle, θ, of water and formamide on the membrane surface, simultaneous equations are obtained from Eq. 3, which can be solved for γ_s^d and γ_s^p. In Eq. 6, to obtain a value of e_{coh} in 10^6 J/m^3, the value of γ_s must be in mJ/m^2. The solubility parameter, δ (in 10^3 J$^{1/2}$/m$^{3/2}$), could then be determined from Eq. 5 using the obtained value of e_{coh}.

Results and Discussion

SMM properties

Molecular properties of SMM1 and SMM2 are given in Table 1 (Mandeep, personal communication, 2000; Ho, 1997; Ho et al., 2000). The fluorine content of the two SMMs is almost similar and the polystyrene equivalent weight average molecular weights (MW) is more than two times higher for the SMM2.

Different SMMs were synthesized with the polyols: polypropylene dioxide (PPO) and polycaprolactone diol (PCL) (Ho et al., 2000). It was observed that SMM synthesized with PCL had a higher molecular-weight value and lower fluorine content relative to the SMM synthesized with PPO segments. It must be pointed out that the SMMs used in this work with DPS and DEG had higher fluorine content than the SMMs prepared with PPO and PCL even though the same type of fluoroalcohol (BA-L low fraction) was used.

Table 1. Properties of SMMs

SMM	Fluorine Content (wt. %)	Molec. Wt.* (MW)/10^4	Polydispersity
SMM1 (MDI:DPS:BA-L)	20.00	0.6±0.1	1.2±0.1
SMM2 (MDI:DEG:BA-L)	19.79	1.6±0.1	1.4±0.1

*Molecular-weight values are reported as polystyrene equivalent weight-average molecular weights.

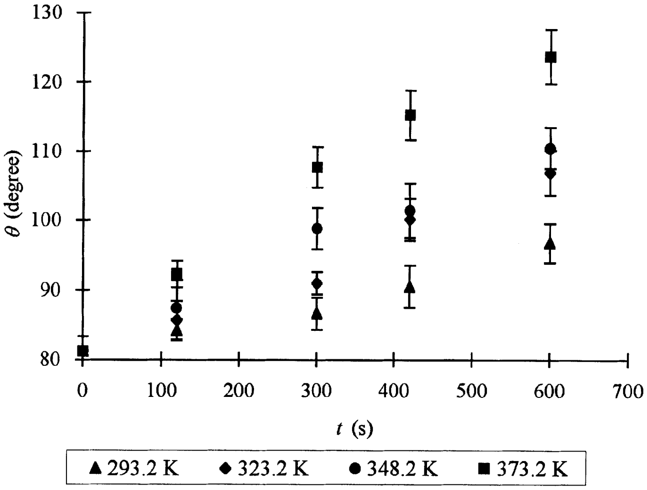


Figure 5. Contact angle vs. solvent evaporation time for the modified membranes with SMM1 (MDI:DPS:BA-L).

SMM concentration in the casting solution, 2 wt. %; solvent evaporation temperatures: 293.2 K, 323.2 K, 348.2 K and 373.2 K.

As mentioned in the experimental part, flat-sheet PVDF membranes were prepared without and with different SMM contents in the casting solution. The membrane preparation steps involved a solvent evaporation in a preheated oven for various time intervals under different temperatures. Contact angle analysis was performed to assess the relative wettability of those membranes. The influence of different experimental conditions is discussed below.

Effect of solvent evaporation period

Figure 5 shows the experimental values of the contact angle θ as a function of the solvent evaporation time, t, at four different solvent evaporation temperatures: 293.2 K, 323.2 K, 348.2 K, and 373.2 K, for the modified PVDF membranes with a concentration of 2% of SMM1 (MDI:DPS:BA-L) in the PVDF casting solution.

Using SMM1 as a polymer additive in the PVDF casting solution, the contact angle of water on the surface of the modified PVDF membrane increased with an increase in the solvent evaporation time and with the solvent evaporation temperature. In contrast, it was found that the contact angle of the unmodified PVDF membranes did not change significantly, remaining around a value of 78.8°±2.1° (θ_a = 82.3°± 2.1°, θ_r = 75.2°±2.0°). The increase in the contact angle suggests that the surface of the modified PVDF membrane became more hydrophobic. This result indicates that during solvent evaporation, the SMM molecules migrate to the membrane surface in order to minimize the surface free energy of the SMM/PVDF system. A similar effect of blending SMMs was observed for polyethersulfone (Hamza et al., 1997; Ho et al., 2000) and polyurethanes (Tang et al., 1996, 1997a,b).

It is worth noting that the measured LEPw of the membranes prepared with evaporation time up to 420 s is higher than the LEPw of the unmodified PVDF membrane, 29.7×10^5 Pa. However, for the membranes prepared with an evaporation time of 600 s, the LEPw is very low ($<7\times10^4$ Pa) in spite of their very hydrophobic surface. This fact was observed for both the SMM-modified and -unmodified membranes. This can be explained by the morphological changes of those membranes. SEM pictures of unmodified (Figure 6a) and modified PVDF membranes (Figures 6b and 6c) are presented. Unmodified membranes were prepared with an evaporation temperature of 373.2 K and an evaporation time of 420 s. Both modified PVDF membranes were prepared with 2 wt. % of SMM1 and an evaporation temperature of 373.2 K. The evaporation time was 420 and 600 s for the modified membranes presented in Figures 6b and 6c, respectively. The apparition of pores is observed when the membranes were exposed to 600 s of solvent evaporation time. The morphology change occurring at more than 600-s evaporation period did not depend on the presence or the absence of SMM in the casting solution or the type of SMM. It must be mentioned that the observed pores on the membrane surfaces may affect the contact angle measurements (Ganbassi et al., 1996).

Similar tests were carried out with the modified membranes prepared with the SMM2 (MDI:DEG:BA-L). Figure 7 shows the obtained values of the contact angle vs. evaporation time for the modified PVDF membranes with both SMMs prepared at two different evaporation temperatures: 293.2 K and 373.2 K. The concentration of SMM in the PVDF casting solution was 2 wt. % for both SMM1 and SMM2.

As can be seen in Figure 7, the same behavior between the contact angle and evaporation time is observed for both SMMs. The contact angle increased with an increase in the solvent evaporation time and the evaporation temperature. A visual inspection of the data permits the statement that, without solvent evaporation (at $t=0$), the contact angle of the modified membranes using both SMMs are higher than the contact angle of the unmodified PVDF membrane, and the contact angle is higher for SMM2 than for SMM1. The obtained values are $87.2°\pm3.1°$ ($\theta_a=89.5°\pm2.3°$, $\theta_r=84.8°\pm3.9°$) for SMM2 and $81.2°\pm2.2°$ ($\theta_a=88.9°\pm1.4°$, $\theta_r=73.4°\pm2.9°$) for SMM1.

Moreover, at a solvent evaporation temperature of 293.2 K, there is no significant difference between the contact angles for SMM1 and SMM2, except for the data at $t=0$. Probably, an evaporation period longer than 600 s is required to observe the difference between these two SMMs. On the other hand, the contact angle of SMM1 is significantly larger than SMM2 at 373.2 K. This means that the SMM1 migrates more easily to the PVDF surface than the SMM2, and the migration is faster at a high temperature. This may be due to the fact that the molecular weight of SMM1 is less than that of SMM2, whereas the fluorine contents of both SMMs are almost the same, as shown earlier in Table 1.

It should be noted that the LEPw of the SMM-modified membranes prepared with SMM2 decreased from 31.7×10^5 Pa to 4.1×10^4 Pa when the solvent evaporation time was increased from 420 to 600 s. This is related to the pore formation in the membrane with 600 s of evaporation as stated before (see Figure 6). It should also be noted that a decrease in the thickness of the membranes from 72.0 μm to 50.1 μm was observed when the evaporation time was increased from zero to 420 s, even if the same casting blade was used for the preparation of the films.

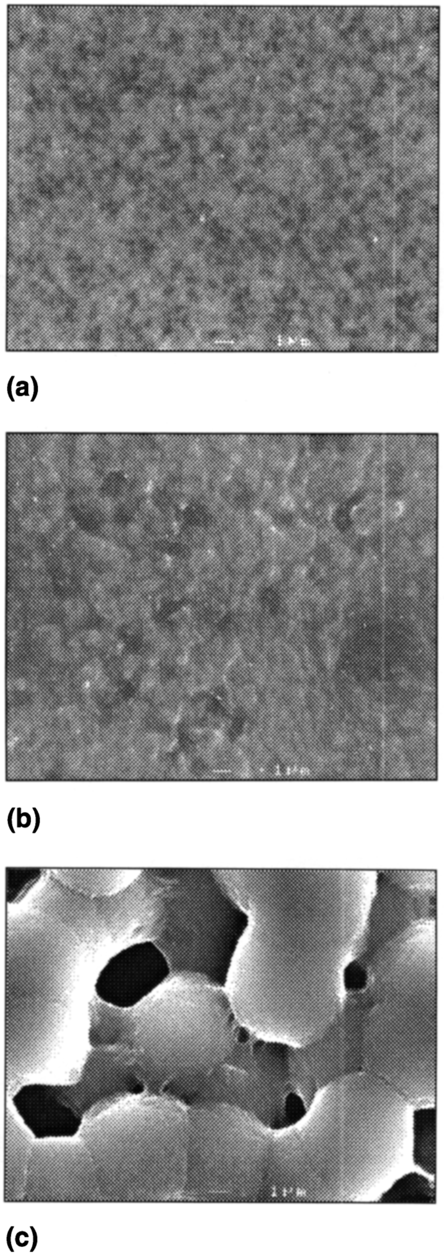


Figure 6. SEM pictures of unmodified (a) and modified PVDF membranes with SMM1, SMM concentration in the casting solutions, 2 wt. %; solvent evaporation temperature, 373.2 K; evaporation time, 420 s (b) and 600 s (c).

Under optimum conditions, that is, 420 s of solvent evaporation time and 373.2 K of evaporation temperature, the obtained contact angles for the modified PVDF membrane with

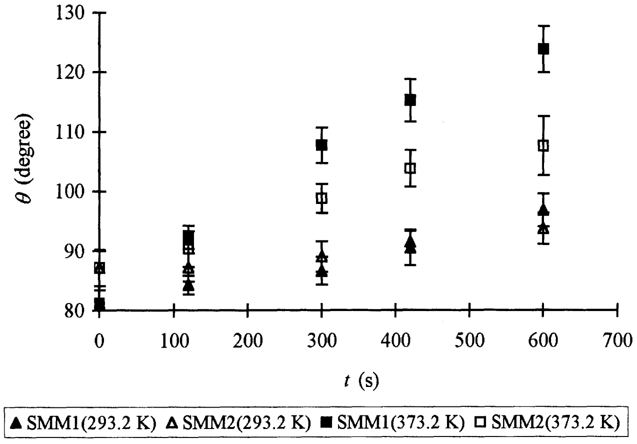


Figure 7. Contact angle vs. solvent evaporation time for the modified membranes with both SMM1 (MDI:DPS:BA-L) and SMM2 (MDI:DEG:BA-L).

SMM concentration in the casting solutions, 2 wt. %; solvent evaporation temperatures: 293.2 K and 373.2 K.

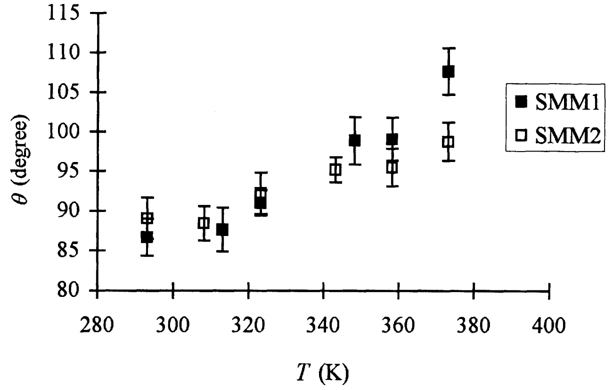


Figure 8. Contact angle vs. solvent evaporation temperature for the modified PVDF membranes with both SMM1 and SMM2.

SMM concentration in the casting solutions, 2 wt. %; solvent evaporation time, 300 s.

SMM1 ($\theta = 115.2° \pm 3.6°$, $\theta_a = 120.5° \pm 3.1°$, $\theta_r = 110.2° \pm 4.06°$) were equivalent to those of polytetrafluoroethylene [Teflon; $\theta_a = 116°$, $\theta_r = 92°$ (Hamza et al., 1997)]. However, the contact-angle values measured for the modified PVDF membrane under the same conditions, but with SMM2, were lower ($\theta = 103.8° \pm 3.0°$, $\theta_a = 110.7° \pm 3.1°$, $\theta_r = 97.1° \pm 2.9°$). Generally, the hysteresis, which is the difference between the advancing and the receding contact angles, was higher for membranes modified with SMM2 than with SMM1, but it was always lower than the hysteresis of the polytetrafluoroethylene material. This indicates that the stability of the hydrophobic character of the surface is higher for modified PVDF membranes.

Effect of evaporation temperature

The effect of the evaporation temperature on the contact angle is shown in Figure 8 for both SMM1 and SMM2. The concentration of SMM in the PVDF casting solution and the evaporation period were maintained at 2 wt. % and 300 s, respectively.

It should be noted that the LEPw and the thickness of the membranes were maintained around 31×10^5 Pa and 57 μm, respectively.

Figure 8 indicates that for both types of SMM-modified PVDF membranes, the contact angle increased with an increase in evaporation temperature. This may be related to the increase in the solvent evaporation with temperature.

Effect of SMM concentration

To study the effect of the SMM content in the PVDF casting solution, modified PVDF membranes were prepared with SMM concentrations from zero to 4 wt. %. The solvent evaporation temperature and evaporation time were kept constant at 373.2 K and 300 s, respectively. The two formulations of SMMs were used. In Figure 9, the contact angle of water on the surface of the prepared membranes was plotted vs. the SMM concentration in the PVDF casting solution. As can be seen in this figure, the surface of the PVDF membrane containing SMM1 generally had contact angles (θ_a and θ_r values) higher than the membranes containing SMM2. For both SMMs, the contact angle of water on the modified PVDF membranes increased with an increase in the SMM content in the casting solution and seems to level off at higher SMM concentrations.

Based on X-ray photoelectron spectroscopy (XPS), Pham et al. (1996) stated that it would take only a little surface-active material ($\approx$ 0.5 wt. %) to saturate the surface of PES films. The F/C ratios at the surface of the PES/SMM film were comparable to or higher than the F/C ratio of SMM itself, when the SMM concentration was 0.5 wt. % or above in the casting solution. This suggests that the surface was composed of almost 100% SMM, and in some cases consisted primarily of the fluorine tails themselves. In this study, from

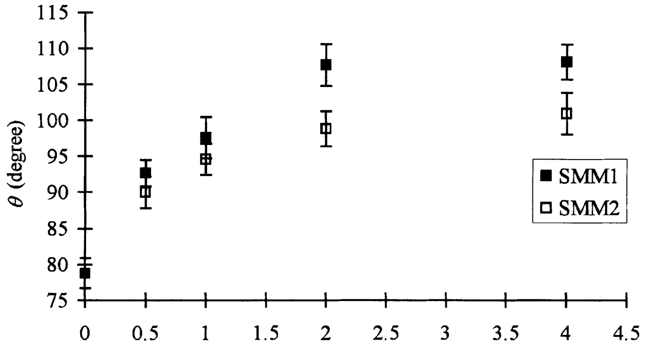


Figure 9. Contact angle vs. SMM concentration in the PVDF casting solution for both SMM1 and SMM2.

Solvent evaporation temperature, 373.2 K; solvent evaporation time, 300 s.

Figure 9, it can be anticipated that saturation of the PVDF membrane surface can be reached at about 2 wt. % of the SMM in the PVDF casting solution.

It should be pointed out that the LEPw for these modified SMM membranes was almost the same (≈ 31.7×10^5 Pa) and the thickness was about 60 μm.

The contact-angle analysis therefore demonstrates that the surface characteristics of PVDF/SMM blend membranes are dependent on the specific SMM formulation, solvent evaporation time, evaporation temperature, and the concentration of SMM.

Furthermore, the solubility parameter and the surface free energy of the membranes prepared with different concentrations of SMMs, from zero to 4 wt. %, were estimated by the contact angles for water and formamide on the surface of the membranes and by using Eqs. 3–6. Table 2 shows the experimental results. It can be observed that the contact angle of the membranes with SMM1 is higher in the entire SMM concentration range and that the corresponding solubility parameter is lower. For both PVDF/SMM blends, the solubility parameter decreases as the concentration of SMM is increased. For the modified PVDF membranes with SMM1, the solubility parameter decreased by 27.3% when the concentration of SMM was increased from zero to 4 wt %. In the case of SMM2, it decreased by 24.8%.

The estimated value of the solubility parameter of PVDF material from the group contribution using the method of Hoftyzer and Van Krevelen is about 15.7×10^3 $J^{1/2}/m^{3/2}$ (Van Krevelen, 1990). This value is very close to the reported value, 16.1×10^3 $J^{1/2}/m^{3/2}$, obtained in this work for the unmodified PVDF membranes. In contrast, Bottino et al. assumed for PVDF a solubility parameter of 23.2×10^3 $J^{1/2}/m^{3/2}$. This value was obtained from the highest limiting viscosity number that corresponds to hexamethylphosphoramide (Bottino et al., 1988). On the basis of the contact-angle observations, Hansen found a solubility parameter of 19.2×10^3 $J^{1/2}/m^{3/2}$ (Bottino et al., 1988). These values are higher than the values obtained in this work. The discrepancy may be due to the fact that both the advancing and the receding contact angles were taken into consideration in this work.

Pervaporation experiments

Pervaporation experiments were made for the unmodified PVDF membranes and for the modified membranes with the two formulations of SMMs. The membranes used in these experiments were prepared with different concentrations of SMMs, from zero to 4 wt. %, maintaining solvent evaporation time and evaporation temperature at 300 s and 373.2 K, respectively.

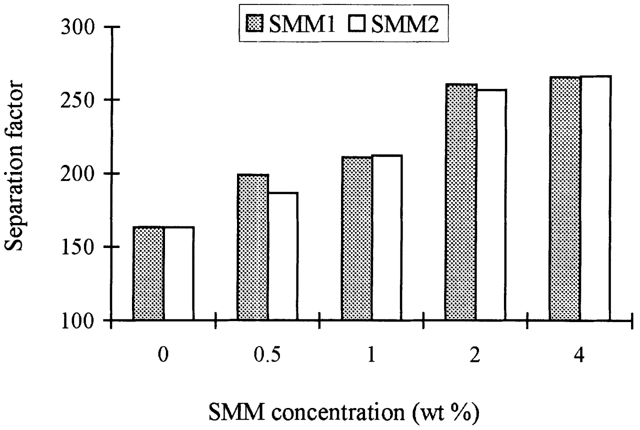


Figure 10. Chloroform separation factor as function of the SMM concentration in the PVDF casting solution for both SMM1 and SMM2.

Modified membranes: solvent evaporation temperature, 373.2 K; solvent evaporation time, 300 s. Pervaporation experiments: feed temperature, 298.2 K; permeate pressure, 1,666.5 Pa; stirring rate, 53.3 rps (maximum stirring); initial chloroform concentration, ≈ 1 kg/m^3.

In pervaporation experiments, the temperature was maintained at 298.2 K, the downstream pressure at 1666.5 Pa, the stirring rate of the magnetic stirrer was 53.3 rps (maximum stirring), and the initial chloroform concentration in the feed side was about 1 kg/m^3. The experimental results, including separation factor, total permeate flux, chloroform, and water permeation fluxes, are presented as a function of the concentration of SMM in Figures 10, 11, 12a, and 12b, respectively.

It is interesting to note that the separation factor of the PVDF membranes can be enhanced by the addition of the SMM to the PVDF casting solution (see Figure 10). Under the same experimental conditions, the separation factor increased by 62.8% by adding 4 wt. % of SMM1 to the PVDF casting solution and by 63.3% when 4 wt. % of SMM2 was added to the casting solution, in comparison with the unmodified PVDF membrane. This means that the chloroform enrichment in the permeate side could be increased with an increase in the amount of SMM. It must be mentioned that

Table 2. Surface Properties of SMM Modified and Unmodified PVDF Membranes

SMM	SMM Content (wt. %)	Contact Angle (°) Water	Contact Angle (°) Formamide	γ_s (mJ/m^2)	e_{coh} (10^6 J/m^3)	δ (10^3 $J^{1/2}/m^{3/2}$)
SMM1 (MDI:DPS:BA-L)	0	78.8±2.1	63.2±1.6	30.49	259.25	16.10
	0.5	92.7±1.8	73.1±2.2	25.77	201.43	14.19
	1	97.6±2.9	77.9±1.9	23.39	174.14	13.20
	2	107.7±2.9	86.8±2.0	20.09	138.64	11.77
	4	108.2±2.4	87.3±2.2	19.95	137.16	11.71
SMM2 (MDI:DEG:BA-L)	0	78.8±2.1	63.2±1.6	30.49	259.25	16.10
	0.5	90.0±2.2	71.3±2.2	26.33	208.01	14.42
	1	94.6±2.2	75.3±1.9	24.48	186.49	13.66
	2	98.8±2.4	80.6±2.0	21.25	150.87	12.28
	4	100.9±2.9	82.2±2.2	20.82	146.27	12.09

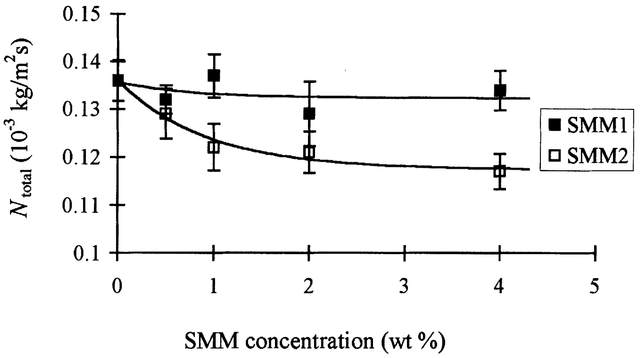


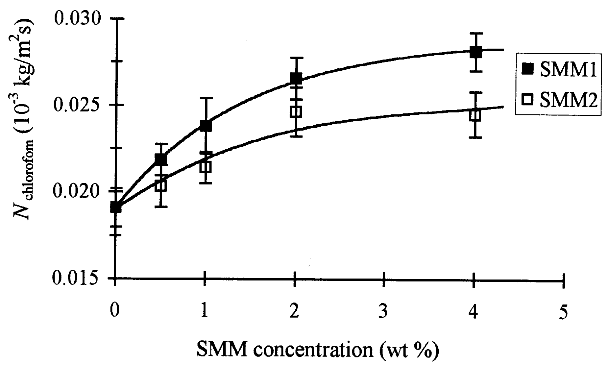
Figure 11. Total permeate flux vs. SMM concentration in the PVDF casting solution for both SMM1 and SMM2; same membranes and pervaporation conditions as in Figure 10.

the solubility parameter of water is 47.9×10^3 J$^{1/2}$/m$^{3/2}$. Then the difference in solubility parameters between water and the prepared membranes increases with an increase in the SMM content in the PVDF casting solution. The higher the solubility parameter difference, the lower the water/polymer affinity. In the pervaporation system discussed in this work, chloroform is the minor component and water is the major component that is more preferentially repelled by the membranes as the hydrophobicity is increased. Accordingly, the addition of fluorinated SMM in the PVDF casting solution enhances the enrichment of chloroform in the permeate, with a corresponding decrease of the permeate water flux.

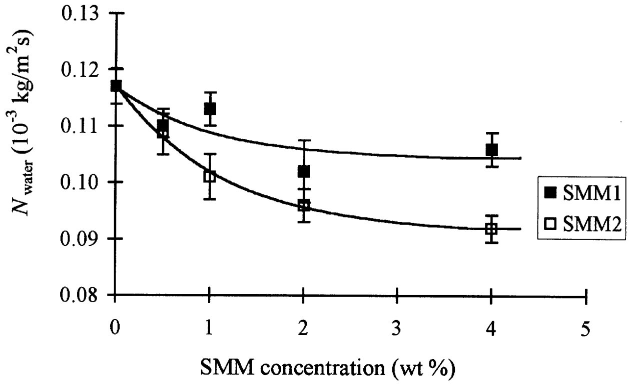
Figure 10 shows that a further increase in the SMM concentration from 2 wt. % does not necessarily enhance the separation factor. This behavior is linked to the contact-angle measurement presented in Figure 9.

Figure 11 shows that the total pervaporative flux tends to decrease with an increase in SMM concentration. When using the SMM2, the permeate flux decreased by about 14%, while for SMM1 the decrease was only about 5.2%. A similar result was also obtained with PES/SMM blend (Fang et al., 1994).

Figure 10 shows that the chloroform/water selectivity was almost the same for both SMMs. Nevertheless, as can be observed in Figure 12a, the flux of chloroform through the modified PVDF membranes with SMM1 was clearly higher than that which corresponds to membranes modified with SMM2. From Figure 12b, the permeate water flux is higher for the surface-modified PVDF membranes with SMM1. The permeate water flux decreased by 21.4% when 4 wt. % of SMM2 was added to the PVDF casting solution, while for SMM1 the decrease was only about 9.4%. This result is contrary to the contact-angle measurements presented previously in Figure 9, since a lower water flux is expected for a membrane of higher contact angle. This fact suggests that the selectivity of the surface-modified PVDF membranes is associated not only to the surface characteristics but also to the membrane bulk structure. Figure 13 shows cross-sectional pictures of unmodified (Figure 13a) and modified PVDF membranes with SMM1 (Figure 13b) and SMM2 (Figure 13c). These membranes were prepared with an evaporation temperature of 373.2 K and evaporation time of 300 s. The modified membranes were prepared with 2 wt. % of SMM concentration in the casting solution. A fingerlike structure is observed for the membranes prepared from solutions containing SMM1. This can affect the diffusion process through the membranes. The formation of the fingerlike structure may be explained by means of the solubility parameter. The solubility parameters of the two formulations of SMM were estimated by applying the additivity rule to each group contribution using the method of Hoftyzer and Van Krevelen (Van Krevelen, 1990). The solubility parameter differences between SMM and the solvent DMAC (22.5×10^3 J$^{1/2}$/m$^{3/2}$) and between SMM and the polymer PVDF (15.7×10^3 J$^{1/2}$/m$^{3/2}$) were both smaller in the case of the SMM2. It can be hypothesized that the compatibility is better between the SMM2 and the PVDF/DMAC system. Consequently, it takes longer to remove the solvent from the PVDF/SMM2 structure and the polymer precipitation rate is slower, resulting in a sponge-type structure. Hence, the difference in the membrane structure suggests that the chloroform selectivity of the modified PVDF membranes must be associated not only to the surface characteristics but also to the diffusion through the membrane.



(a)



(b)

Figure 12. Partial permeate flux vs. SMM concentration in the PVDF casting solution for both SMM1 and SMM2.

(a) Permeate chloroform flux; (b) permeate water flux. Same membranes and pervaporation conditions as in Figure 10.

Conclusions

Polyvinylidene fluoride (PVDF) flat-sheet membranes were modified by surface-modifying macromolecules (SMMs) in

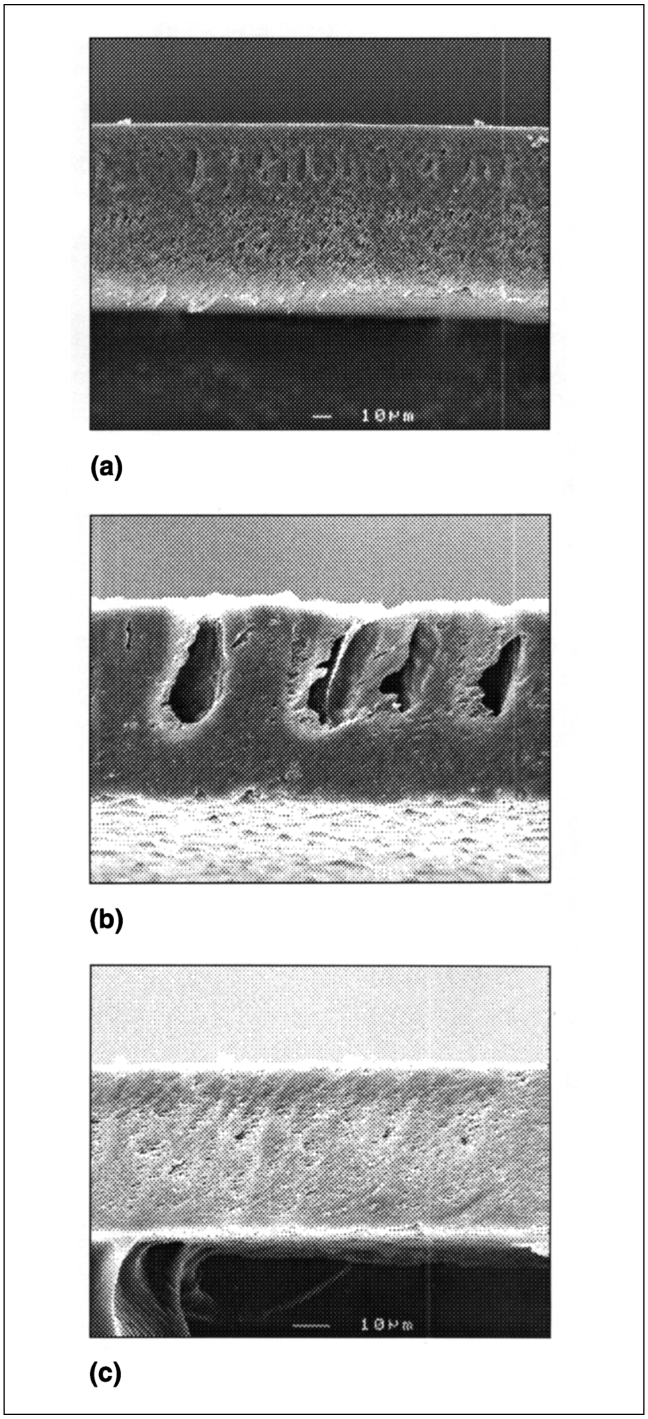


Figure 13. SEM cross-sectional pictures of the (a) unmodified and (b) modified PVDF membranes with SMM1 and (c) SMM2. Concentration in the casting solutions, 2 wt. %; solvent evaporation temperature, 373.2 K; evaporation time, 300 s.

order to improve their pervaporative performance. Two types of SMMs were used. It was observed that:

1. The contact angle of the PVDF membranes increased remarkably with the addition of the SMMs. This demonstrates that the SMM was localized on the PVDF membrane surface, rendering it more hydrophobic.

2. The increase in the contact angle of the PVDF-modified membranes depends on the solvent evaporation time, evaporation temperature, SMM concentration in the PVDF casting solution, and the SMM formulations.

3. From the LEPw measurement and the SEM analysis, it was observed that pores are formed at 600 s of solvent evaporation time, both for the modified and the unmodified PVDF membranes.

4. The chloroform separation factor increases with an increase in the concentration of SMM in the PVDF casting solution.

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Notation

c = SMM concentration in the PVDF casting solution, wt. %
C = chloroform concentration, kg/m^3
e_{coh} = cohesive energy density, J/m^3
LEPw = liquid entry pressure of water, Pa
MW = polystyrene equivalent molecular weight
N = permeate flux, kg/m$^2\cdot$s
R = gas constant, J/mol$\cdot$K
t = time, s
T = temperature, K

Greek letters

α = separation factor
δ = solubility parameter, J$^{1/2}$/m$^{3/2}$
γ = surface free energy, mJ/m^2
θ = contact angle, °

Subscripts and superscripts

a = advancing contact angle
ch = chloroform
l = liquid
r = receding contact angle
s = solid
$total$ = total flux
w = water
d = dispersion-force component
p = polar-force component

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