

Study on Surface Modification by Surface-Modifying Macromolecules and Its Applications in Membrane-Separation Processes

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ABSTRACT: Surface-modifying macromolecules (SMMs) are oligomeric fluoropolymers synthesized by polyurethane chemistry and tailored with fluorinated end groups. In the literature, several formulations of SMMs have been developed and blended with base polymers of polyurethanes and polyethersulfone for surface modification. It has been shown that SMMs migrate to the surface and the fluorine end groups orient themselves toward the air-polymer interface, reducing the surface energy of the hydrophilic base polymer to values close to that of polytetrafluoroethylene (Teflon). Because only a small amount of SMMs was needed, the bulk properties of the base polymer remained relatively unchanged. The properties of the SMM polymers were characterized, including molecular weights, elemental analysis,

and thermal transitions. The morphology and surface properties of the SMM-modified and unmodified membranes were assessed. The use of SMMs has been tested for use in ultrafiltration, pervaporation, and biomedical applications. SMM-modified membranes offer advantages over unmodified membranes and the use of SMMs will continue to be the focus of future studies. This study reviews the recent development of surface-modifying macromolecules (SMMs) and SMM-blended membranes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2902–2916, 2003

Key words: surface-modifying macromolecules; polyethersulfone; polyurethanes; surface properties; fluoropolymers

INTRODUCTION

It is well documented that the surface chemistry and morphology of membranes play an important role in the transmembrane transport of penetrants.¹ To enhance the overall performance of a membrane, it is often necessary to modify the membrane material or its structure. Generally, the objective for modification is not only to increase the flux and/or selectivity but also to improve the chemical resistance (i.e., solvent resistance, swelling, or fouling resistance), control of pore size, and elimination of defects.

The first reported membrane-modification method involved annealing of porous membranes by heat treatment.² In the membrane literature, various techniques were carried out for surface modification of polymer membranes: physical, chemical, or bulk mod-

ification (i.e., polymer blends).³ Recently, Pinnau and Freeman² gave a summary of some of the most commonly practiced membrane-modification methods such as surface coating, chemical treatment (fluorination, crosslinking, pyrolysis), annealing with heat treatment, and solvent treatment. A less common approach to modifying the properties of a polymer is to introduce additives that can migrate to the film surface and alter the surface chemistry while leaving the bulk properties intact.⁴ Ward et al.⁴ were apparently the first to synthesize a polyurethane block copolymer, to be used as a surface modifying additive for the development of a new biomedical polyurethaneurea. They showed that this method is efficient because only a small weight percentage of additive was required to modify the surface properties while maintaining the bulk properties unaltered.

There are obvious advantages in the use of surface fluorination,⁵ although most commercial fluoropolymers are difficult to process. In copolymers, fluorinated segments are usually enriched at the surface. This fact was the basis for the development of surface-modifying macromolecules (SMMs), which are oligomeric fluoropolymers synthesized by polyurethane

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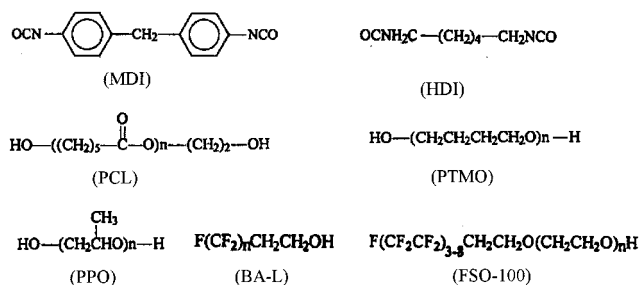


Figure 1 Chemical structures of reagents used for the synthesis of surface-modifying macromolecules (SMMs): methylene bis(*p*-phenyldiisocyanate) (MDI), hexamethylene diisocyanate (HDI), polycaprolactone diol (PCL), polytetramethylene oxide (PTMO), polypropylene diol (PPO), and the fluoroalcohols BA-L and FSO-100.

chemistry and tailored with fluorinate end groups. It has an amphiphatic structure consisting theoretically of a main polyurethane chain terminated with two low polarity polymer chains (i.e., fluorine segments).

Tang et al.⁶⁻⁹ designed a series of SMMs to obtain an effective surface modification of polyester-urea-urethane with improved additive stability. Matsuura et al.¹⁰ proposed a membrane surface modification by blending polymer active additives (SMMs) into the polyethersulfone base material. The goal was to prepare, in a single casting step, membranes with high hydrophobicity and chemical resistivity at a low cost, to be competitive with other hydrophobic membranes such as polydimethylsiloxane (PDMS) or polytetrafluoroethylene (PTFE). Since then, other series of SMM formulations were synthesized with different combinations and stoichiometries of different reagents, and blended with polyethersulfone. Attempts were made to determine the effects of various types of SMMs and different membrane-casting conditions on SMM migration to the top membrane surface. The performance of the SMM-modified membranes was tested for use in ultrafiltration, pervaporation, and in biomedical applications. Therefore, the purpose of this study was to give an overview of the development of SMMs and SMM-modified membranes with a view toward the future direction of SMM applications.

SYNTHESIS OF SURFACE-MODIFYING MACROMOLECULES

Materials used for SMM synthesis

The materials commonly used for SMM synthesis are a diisocyanate, a polyol, a fluoroalcohol, and a solvent. Until now, the principal diisocyanates used for SMM preparation have been methylene bis-*p*-phenyl diisocyanate (MDI) and hexamethylene diisocyanate (HDI). The chemical structures of these diisocyanates are illustrated in Figure 1. The polyols employed were

polypropylene diol (PPO), polycaprolactone diol (PCL), and polytetramethylene diol (PTMO). The most commonly used solvent is *N,N*-dimethylacetamide and the oligomeric fluoroalcohols used are commercial products of Zonyl (BA-L) (MW 443 g/mol) and Zonyl (FSO-100) (MW 730 g/mol) obtained from DuPont Chemical (Rockville, MD) and designated in this study as B and F, respectively. The molecular weight distribution of the latter compounds may vary, giving a range in fluorine content. The fluoroalcohols were distilled into three molecular weight fractions, low (L), intermediate (I), and high (H), by varying the distillation conditions. The first fraction, distilled at 102°C and atmospheric pressure, was a clear liquid; the second fraction was a white semisolid material distilled between 70 and 80°C under vacuum (i.e., 0.01 mmHg); and the last fraction, distilled between 80 and 100°C under a vacuum of 0.01 mmHg, was a very pale yellow solid. Additional details of the conditions and methods of fractionating the fluoroalcohols were given by Pham,¹¹ Pham et al.,¹² and Ho.¹³ Because the diisocyanates readily react with water to form diamines, before 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.¹³ The chemical structures of the SMM reagents are presented in Figure 1.

SMM synthesis

The SMMs were synthesized by a two-step solution polymerization method. The initial step involved the reaction of a diisocyanate with a polyol in a common solvent, dimethylacetamide (DMAC). This mixture formed a urethane prepolymer solution. The reaction was then terminated by the addition of an oligomeric fluoroalcohol. The resulting polymer was then precipitated with distilled water, washed in 30 vol/vol % acetone/water mixture to leach out unreacted monomer, and finally dried in an oven at 50°C. The latter step was repeated three times. The two polymerization steps were performed in a controlled atmosphere of a prepurified nitrogen inside a glove box. Temperature, solvent volume, reactant mole ratio, reactant concentration, and stir rate were important parameters in determining the size distribution of the SMMs. Various SMM formulations were synthesized with different combinations and stoichiometries of the above-cited reagents. Details of the synthesis conditions were outlined in earlier publications.^{6-9,11,13,14} In Table I, a list of the SMMs together with the reactants used and the reaction molar ratio of the diisocyanate : polyol : fluoroalcohol (distilled fraction of the fluoroalcohol) are summarized. As an example, the reactions of the

TABLE I
Bulk Properties of Different Formulations of Surface-Modifying Macromolecules (SMMs)

SMM polymer	SMM formulation and reaction stoichiometry ^a	M_{zo} (10 ⁴) ^b	M_n (10 ⁴) ^b	Polydispersity (M_w/M_n) ^b	Fluorine content ^c	Reference(s)
SMM1	MDI : PPO(425) : B(H) 3 : 2 : 2	2.67	1.62	1.65	13.57	[11,12,17,26]
SMM2	MDI : PPO(425) : B(H) 3 : 2 : 2 (R)	2.23	1.42	1.57	11.37	[11–13,17,18,24,28]
SMM3	MDI : PPO(425) : B(H) 2 : 1 : 2	1.63	1.06	1.54	19.77	[11,12,17]
SMM4	MDI : PPO(425) : B(H) 2 : 1 : 2 (R)	1.80	1.14	1.58	12.13	[11,12,17]
SMM5	MDI : PPO(425) : B(L) 3 : 2 : 2	2.53 2.52	1.53 1.97	1.65 1.28	5.77 11.36	[11,12] [13,14]
SMM6	MDI : PPO(425) : B(L) 3 : 2 : 2(R)	1.93	1.32	1.46	7.93	[11,12]
SMM7	MDI : PPO(425) : B(L) 2 : 1 : 2(R)	1.27	0.92	1.38	17.13	[11,12]
SMM8	MDI : PPO(425) : B(L) 2 : 1 : 2(R)	1.53	1.02	1.50	11.57	[11,12]
SMM9	MDI : PPO(425) : F(L) 3 : 2 : 2	1.81	1.31	1.38	21.01	[13,14,24]
SMM10	MDI : PPO(425) : F(I) 3 : 2 : 2	1.81	1.35	1.34	16.30	[13,14]
SMM11	MDI : PPO(425) : F(H) 3 : 2 : 2	1.93	1.53	1.27	14.20	[13,14]
SMM12	MDI : PCL(530) : B(L) 3 : 2 : 2	2.89	2.26	1.28	8.58	[13,14,24]
SMM13	MDI : PCL(530) : F(L) 3 : 2 : 2	2.05	1.59	1.29	17.15	[13,14]
SMM14	MDI : PCL(530) : F(I) 3 : 2 : 2	2.07	1.63	1.27	16.70	[13,14]
SMM15	MDI : PCL(530) : F(H) 3 : 2 : 2	3.09	2.49	1.26	10.81	[13,14]
SMM16	HDI : PTMO(1000) : B(I) 4 : 3 : 2	11	5.50	2.0	NF	[6,7]
SMM17	HDI : PTMO(1000) : B(L) 2 : 1 : 2	3.0	2.0	1.5	7.98	[6]
SMM18	HDI : PTMO(1000) : B(L) 3 : 2 : 2	24	13.3	1.8	NF	[6]
SMM19	HDI : PTMO(1000) : B(H) 2 : 1 : 2	9.7	4.62	2.1	0.72	[6]
SMM20	HDI : PTMO(1000) : B(I) 2 : 1 : 2	14	4.5	3.1	0.10	[6]
SMM21	HDI : PPO(1000) : B(L) 2 : 1 : 2	2.2 1.6	1.69	1.3	12.44 18.87	[6,7]
SMM22	HDI : PPO(1000) : B(I) 3 : 2 : 2	4.8 3.3	3.00	1.6	3.95 9.37	[6–8]
SMM23	HDI : PTMO(1000) : B(H) 3 : 2 : 2	6.1 5.5	3.05	2.0	0.71 3.83	[6,7]
SMM24	HDI : PPO(1000) : B(H) 3 : 2 : 2	2.6 4.63	1.63	1.6	5.11 4.63	[6,7]
SMM25	HDI : PTMO(1000) : B(I) 3 : 2 : 2	5.0 4.6	2.94	1.7	4.97 5.50	[6–8]
SMM26	HDI : PTMO(1000) : B(L) 4 : 3 : 2	18	9	2.0	NF	[6,7]
SMM27	HDI : PTMO(1000) : B(H) 4 : 3 : 2	7.1	4.18	1.7	3.28	[6,7]

^a (L), (I), and (H) refer to the low, intermediate, and high fractions of the fluoroalcohols (BA-L designated by B and FSO-100 designated by F). R refers to the reduced prepolymer reactant concentration to 75%.

^b M_{zo} is the polystyrene equivalent weight-average molecular weight and M_n is the number-average molecular weight.

^c NF, not found.

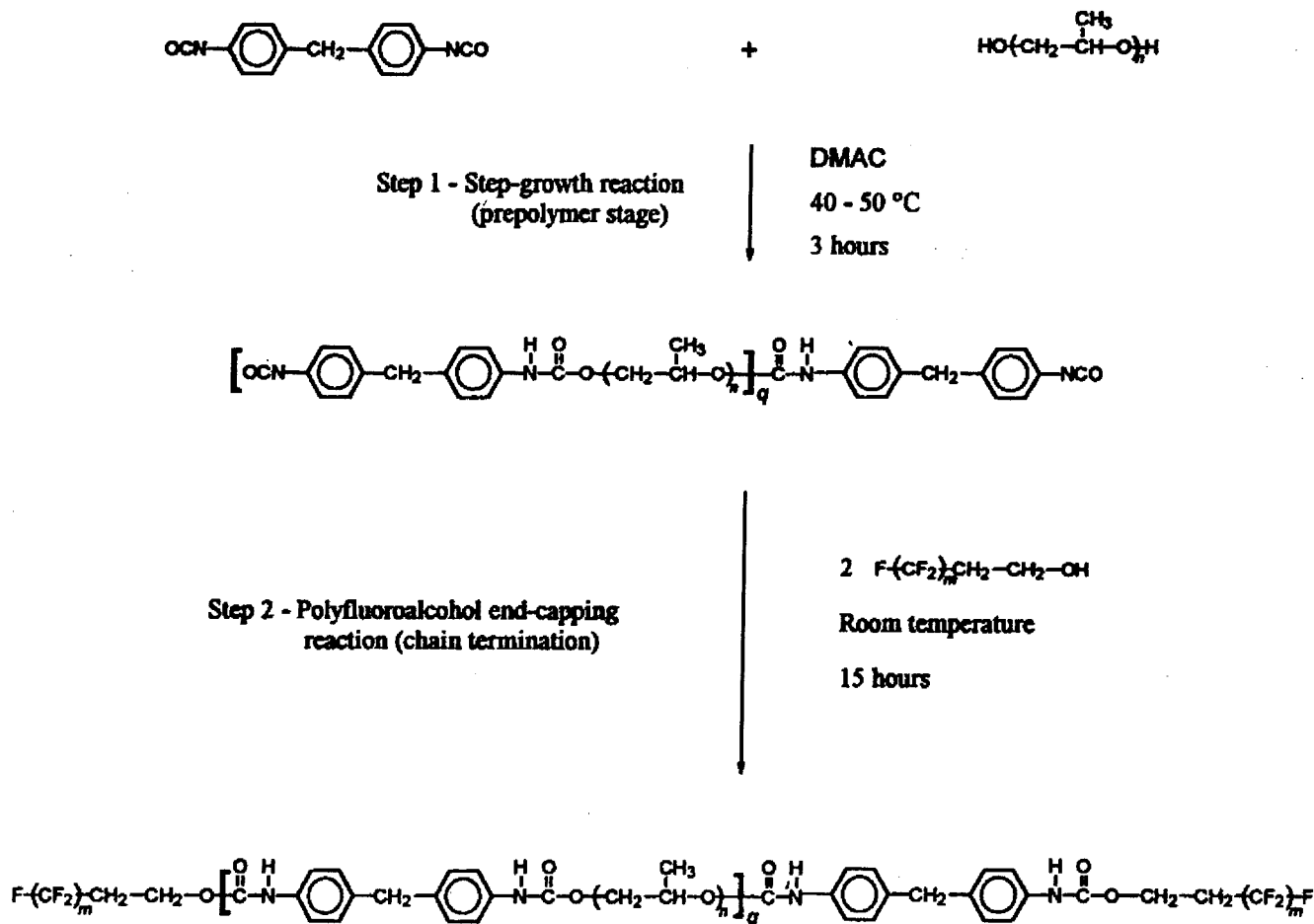


Figure 2 Reaction scheme for synthesis of surface-modifying macromolecules (SMMs).

synthesis of the SMM (MDI : PPO : B) is detailed in Figure 2 for a 3 : 2 : 2 stoichiometric ratio.

SMM CHARACTERIZATION

Molecular weight analysis of SMMs

The most common method of determining polymer molecular weight is size exclusion chromatography (SEC), also known more descriptively as gel permeation chromatography (GPC). This methodology was described previously in Tang et al.⁶⁻⁸ and Pham et al.,¹² and the instrumentation details may be found in Ho.¹³ First, a direct standard calibration curve was generated by use of polystyrene polymer standards with known molecular weights. Subsequently, the molecular weight values of the SMMs [i.e., the weight-average molecular weight (M_w) and the number-average molecular weight (M_n)] were reported as polystyrene equivalent molecular weights (see Table I).

The reported values of the SMM average molecular weight (M_w) ranged between 1.2×10^4 and 2.4×10^5 and in all cases the measured molecular weight was

greater than the value predicted by the reaction stoichiometry. In fact, the molecular weight value of the SMM is primarily determined by the size of the prepolymer generated in the first step of the reaction; this is because the fluorine-containing reactant is monofunctional and theoretically cannot allow for further increases in the molecular weight.

Ho et al.¹⁴ observed that the SMMs containing PCL as the soft segment had higher molecular weight values and generally had lower fluorine content than those with PPO segments. Tang et al.⁶ noted that the SMMs synthesized with PPO generally had lower molecular weight values than those containing PTMO. As can be observed in Table I, the molecular weight of the SMMs synthesized with the fluoroalcohol B(L) (i.e., SMM5, SMM12) was higher than the corresponding SMMs prepared with F(L) (i.e., SMM9, SMM13), despite the fact that both types of fluoroalcohols have relatively low molecular weights. These differences may be attributed to a preferential reaction of the isocyanate groups with the hydroxyl groups that are not directly pendant to the fluoro segment. It is hy-

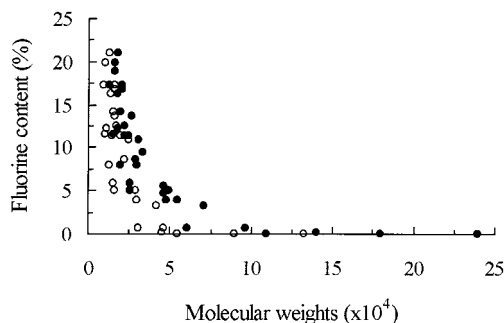


Figure 3 Plot of fluorine content versus molecular weights of SMMs. (●) Weight-average molecular weight (M_w), (○) number-average molecular weight (M_n).

pothesized that SMMs containing a high distillation fraction of fluoroalcohol should have high molecular weight. The work of Ho et al.¹⁴ confirmed this hypothesis for SMMs containing PCL and PPO soft segments. Pham et al.¹² studied the effect of the reactant mole ratio (RMR), the prepolymer reactant concentration (RC), and the type of polyfluoroalcohol on the SMM average molecular weights. It was found that an increase in RMR (change from 2 : 1 : 2 to 3 : 2 : 2) or the combined effect of RMR and RC increased the molecular weight of the SMM. In addition, Pham¹¹ and Pham et al.¹² reported that the ratio of M_w/M_n (i.e., polydispersity) was not affected significantly by any of these experimental variables.

Elemental fluorine analysis

The method used to determine the fluorine content in SMM was reported previously in Tang et al.,⁶ Pham,¹¹ and Ho et al.¹⁴ The fluorine content of the different SMMs is also given in Table I.

The highest fluorine content of the SMMs was 21% for SMM9. It can be hypothesized that SMMs containing a high fraction of fluoroalcohol should have higher fluorine content than SMMs synthesized with intermediate or low fractions when the prepolymer chains were equivalent. However, the experimental results showed no clear trend in this regard. This contradiction may be explained by some of the unanticipated differences in the reaction kinetics of the various agents used. Ho¹³ and Ho et al.¹⁴ observed a decrease in fluorine content of SMMs synthesized with F(L) to F(H) (i.e., SMM9, SMM10, SMM11 and SMM13, SMM14, SMM15) and associated this result to the corresponding increase in polyethylene oxide (PEO) chain lengths. Tang et al.⁶ observed that the fluorine contents for various SMMs were significantly lower than anticipated values based on reactant stoichiometries.

Figure 3 shows the relation between the fluorine content and the molecular weight for different SMMs.

The data show a general trend in which the fluorine content decreased with an increase in the SMM molecular weight. No specific trend was found between the distilled fluoroalcohol fraction and SMM fluorine content. This further indicates that the most significant contribution to the molecular weight of SMMs was the size of the prepolymer chain and not the size of the fluorine tail, given that the addition of the fluoroalcohol was a chain-terminating step. The above trend (i.e., lower fluorine content corresponding to higher molecular weight) can be explained in several ways. One possibility is that, during the fluoroalcohol capping procedure, unreacted hydroxyl groups from the polyol reacted with the diisocyanate end-capped prepolymer.

Thermal transition analysis

The thermal properties of polymers and polymer blends are important considerations for industrial applications. One important property is the glass-transition temperature (T_g), which is the temperature, or range of temperatures, below which the polymer is in a glassy state and above which it is rubbery. A conventional method of thermal characterization is differential scanning calorimetry (DSC), in which the thermal property monitored is the change in enthalpy. The DSC samples consisted of 5–10 mg of synthesized SMM or they were prepared by casting SMM solutions (i.e., 10 wt % in DMAC) into films, followed by complete evaporation of solvent. Before DSC scanning, the SMM samples were equilibrated at a low temperature using liquid nitrogen and then heated at a predetermined rate to a high temperature. Two values characterize the T_g measurements: (1) the T_g width, defined by the range of the transition temperature; and (2) the midpoint T_g , given as the temperature at which half of the total change in specific heat capacity has occurred. Table II summarizes the thermal properties of different types of SMMs.

Tang et al.⁶ reported that the T_g of the SMMs was highly dependent on the polyol used and the SMMs containing a PPO soft segment showed higher T_g values than those containing PTMO. This result is related to the T_g value of pure PPO (-70°C), which is higher than the T_g of pure PTMO (-79.8°C).¹⁵ Ho et al.¹⁴ found that the T_g values for SMMs containing PCL soft segments were generally lower than those for SMMs containing PPO segments. In fact, the SMMs synthesized with PCL have slightly higher molecular weight values compared to those prepared with PPO segments. Pham¹¹ reported that the reactant mole ratio, the reactant concentration, and the type of fluoroalcohol did not show any correlation with the variation in glass-transition temperature. The relationship between the SMM midpoint T_g values and their relative

TABLE II
Glass-Transition Temperatures of SMMs

SMM polymer	Onset T_g (°C) ^a	Final T_g (°C) ^b	T_g width (°C)	Midpoint T_g (°C)	References
SMM1	19	36	16	29	[11,12,17,26]
SMM2	14	27	13	20	[11-13,17,18,24,28]
SMM3	27	41	13	34	[11,12,17]
SMM4	21	34	13	29	[11,12,17]
	12	26	14	19	[11,12]
SMM5	-7.7	3.9	11.6	-1.2	[13,14]
SMM6	16	31	15	24	[11,12]
SMM7	21	34	14	28	[11,12]
SMM8	19	33	14	27	[11,12]
SMM9	-14.5	-1.5	13.1	-6.4	[13,14,24]
SMM10	-10.8	4.1	14.9	-0.9	[13,14]
SMM11	-20.4	-7.2	13.2	-13.0	[13,14]
SMM12	-23.4	-13.5	9.9	-18.1	[13,14,24]
SMM13	-20.1	-9.1	11.0	-12.5	[13,14]
SMM14	-24.1	-11.9	12.2	-15.7	[13,14]
SMM15	-25.5	-16.8	8.6	-20.6	[13,14]
SMM21	-53.2	-47.1	6.1		[6,7]
SMM22	-53.6	-47.5	6.1	-50	[6-8]
SMM23	-72.3	-61.2	11.1		[6,7]
SMM24	-53.0	-47.6	5.4		[6,7]
SMM25	-73.7	-63.3	10.4	-65	[6-8]

^a Temperature at which the transition started.

^b Temperature at which the transition ended.

molecular weights showed that T_g decreased with increasing molecular weight and has a closer linear relationship with M_n than with M_w (see Fig. 4). This type of relation was documented earlier by Turi.¹⁶ In fact, the heterogeneous nature of the components contributes to the decrease in T_g with increasing molecular weights. It must be noted that the SMMs synthesized with different fractions of fluoroalcohol had similar T_g midpoints and, despite the difference in the T_g midpoints, there was little difference in the SMM T_g widths. The T_g widths of the SMMs ranged between 5 and 16°C (see Table II). This parameter is a measure of the heterogeneity within the glassy phase of the SMMs, which may be attributable either to the distribution of polymer chain lengths or to their copolymeric composition.

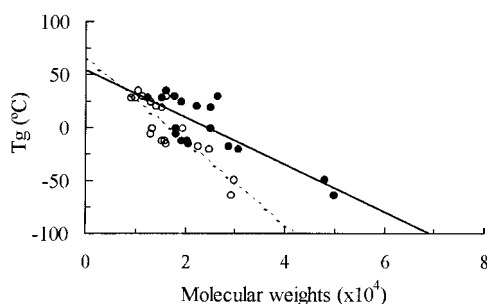


Figure 4 Plot of glass-transition temperature (T_g) versus molecular weights of SMMs. (●) Weight-average molecular weight (M_w), (○) number-average molecular weight (M_n).

PREPARATION OF MEMBRANES

SMMs have previously been blended with base polymers of polyurethanes (PU)⁶⁻⁸ and polyethersulfone (PES).¹⁰

For the preparation of the SMM-modified and unmodified polyurethane membranes, polyester-urea-urethane, referred to as TDI : PCL : ED, was the base polymer to which the SMM was added.⁶⁻⁸ The base polymer was synthesized by a conventional two-step polymerization procedure under nitrogen atmosphere. The first step involved the reaction of 2,4-toluene diisocyanate (TDI) with polycaprolactone diol 1250 (PCL) in dimethyl sulfoxide (DMSO) for 2 h over the temperature range of 60–70°C. The second step was carried out at room temperature with ethylene diamine (ED). The reaction stoichiometry of TDI : PCL : ED was 2.2 : 1 : 1.2. The product was precipitated with distilled water and dried in a 50°C oven for 48 h. For further purification, the polymer was dissolved again in DMSO and precipitated again in distilled water. After the polymer was washed with distilled water, it was dried in a 50°C oven for 48 h, and then dried under vacuum for 24 h. Polyurethane surfaces were then prepared by a dip-coating technique. Before being coated, glass slides were cleaned with chromic acid and subsequently coated with a polymer solution and dried in an oven at 50°C for 12 h. Four coatings were needed to generate an optically smooth surface. The coating solutions consisted of 10 wt % of

TDI : PCL : ED in DMAC to prepare the unmodified PU membranes or mixtures of SMM with TDI : PCL : ED in DMAC for preparation of SMM-modified PU membranes.

The phase-inversion method was used to cast the SMM-modified and unmodified PES membranes. The base polymer used was polyethersulfone (PES, Victrex 4100P). Before use, PES was dried in an air-circulating oven at about 150°C for about 4 h to remove absorbed moisture. The polymer solutions were prepared by dissolving predetermined amounts of PES and polyvinylpyrrolidone (PVP) of molecular weight 1×10^4 or 4×10^4 (from Sigma Chemical, St. Louis, MO) in *N,N*-dimethylacetamide or *N*-methylpyrrolidone (NMP) as solvent. For the preparation of the SMM-modified PES membranes, different amounts of SMMs, all less than 5 wt % of the solutions, were added to the casting solutions. After complete dissolution of the polymers, the solutions were filtered and subsequently thin films were prepared by casting the polymer solutions onto smooth glass plates to a predetermined thickness. The cast films together with the glass plates were immersed directly into ice-cold water or placed in an oven with forced air circulation for a predetermined period (from 0 to 16 min) at a temperature of 95°C, for solvent evaporation, followed by immersion into an ice-cold water bath. During gelation, the membrane spontaneously peeled off from the glass plate. The membranes were then dried by a solvent-exchange method using ethyl alcohol/water solutions of different concentrations (25, 50, 75 and 100 vol/vol %). The duration of each immersion was 24 h. In this technique, water in the membranes is replaced with ethyl alcohol, which is subsequently air-evaporated at room temperature to yield the final dry membranes.

SMM-MODIFIED AND UNMODIFIED MEMBRANE CHARACTERIZATION

Contact angle studies

The relative hydrophobicity of a membrane surface can be qualitatively determined by measuring the contact angle of a water drop deposited onto the membrane surface. The apparatus used for air contact angle studies is commonly known as a goniometer (Ramé-Hart, Mountain Lakes, NJ) in which ultrapure water, 5 to 10 μL , is pumped from a microsyringe onto the surface of the film. Both the advancing and the receding contact angles can be measured by increasing or decreasing the volume until the three-phase boundary moves over the surface. The advancing contact angle measurements reflect the hydrophobic character of the material, whereas the receding contact angle is considered to represent the high energy surface compo-

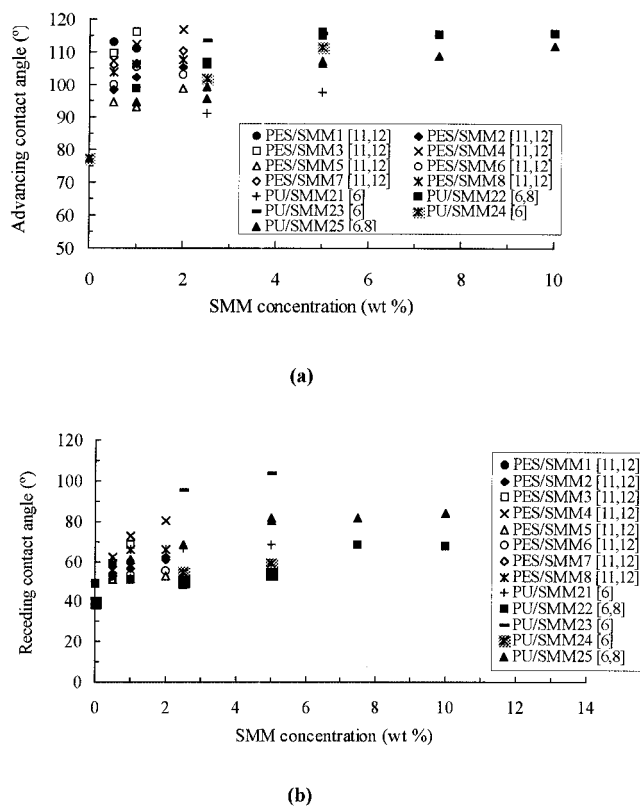


Figure 5 Plots of contact angles versus SMM concentration for the SMM-modified and unmodified PU and PES membranes without PVP: (a) advancing contact angle; (b) receding contact angle.

nent that is a measure of the relative hydrophilic character of the surface. The difference between the advancing and receding contact angles is the contact angle hysteresis, which gives an indication of the heterogeneity of the surface.

Flat-sheet SMM-modified and unmodified PES membranes with and without PVP as well as the SMM-modified and unmodified PU membranes were subjected to contact angle studies to assess the relative wettability of those membranes.

Hamza et al.¹⁷ and Pham et al.¹² reported values of the advancing and receding contact angles of unmodified PES membranes about 76.9° and 49.3°, respectively, whereas Tang et al.^{6,8} obtained 77.3° for the advancing contact angle and 39.6° for the receding contact angle of unmodified PU membrane. It was found that the incorporation of SMM in the PES and PU solutions produced more hydrophobic film surfaces, which was reflected in the increased contact angle values. In general, the contact angles increased with increasing the concentration of SMMs until a plateau value was reached, as can be observed in Figure 5. This was attributed to the presence of SMMs at the surface of the membranes and more directly to the hydrophobic nature of the SMM fluorine tails. In

other words, the SMMs migrated to the surface of the polymer mixture, yielding a new hydrophobic surface. Fang¹⁸ estimated that a very small amount, not more than a few wt % of SMM, is required to cover the membrane surface completely. Factors such as the SMM formulation, its concentration, the base polymer, the membrane thickness, solvent evaporation temperature and time, type of polyfluoroalcohol, and reactant mole ratio of SMM synthesis may affect the migration of SMM to the surface.

Tang et al.⁸ observed that the PU membranes modified with SMMs containing PPO (such as SMM22) showed higher advancing contact angle values than those of the PU membranes modified with SMMs containing PTMO (such as SMM25), suggesting a different arrangement of SMM within the surface. They also reported that the contact angle hysteresis of the surfaces modified by the SMMs containing PTMO was lower than that of the surfaces modified with the SMMs containing PPO. This result was attributed to the enhanced ability of PTMO segments to crystallize and to the fact that the SMMs synthesized with PTMO had higher molecular weights and longer chains than the SMMs having PPO segments.

Hamza et al.¹⁷ and Pham et al.¹² studied the effect of SMMs on PES membranes prepared by casting solutions containing 25 wt % PES in DMAC and different concentrations of SMMs (i.e., 0, 0.5, 1, and 2 wt %). With the addition of SMM in the casting solution, there was an increase in the hydrophobicity and the surface of the modified PES membranes with SMMs containing high fractions of the fluoroalcohol [B(H)] generally had higher contact angles. Of particular note is the fact that there was a significant increase in the contact angles even at low concentrations of the SMM additive in the PES solutions (i.e., ≤ 2 wt %). Pham et al.¹² could not correlate the contact angle data alone with the reactant mole ratio and the prepolymer reactant concentration, although the study did recommend the combination of a high fraction of the fluoroalcohol Zonyl (BA-L) and 2:1:2 chemistry to achieve elevated contact angle values for the SMM/PES blend.

Pham et al.,¹¹ Fang,¹⁸ and Ho et al.¹⁴ measured the contact angles of the SMM-modified and unmodified PES membranes prepared using PVP. Ho et al.¹⁴ reported values of the advancing and receding contact angles for the unmodified PES/PVP membranes of 67.2 and 26.0°, respectively, Pham et al.¹¹ obtained very similar values (i.e., 65.9 and 23.0°) by using double the amount of PVP in the PES casting solution (i.e., 6 wt %), and Fang¹⁸ obtained 68 and 21° with 6 wt % PVP. These values are lower than those reported by Hamza et al.¹⁷ and Pham et al.¹² for "pure" PES membranes. This indicates the presence of PVP in the membrane surface because it is hydrophilic.¹⁹ PVP acted

also as a compatibilizer, allowing for preparation of casting solutions with greater SMM contents. In fact, it was observed that the addition of SMMs increased the contact angles even though the membranes were prepared from solution with PVP.^{11,13,14}

Ho et al.¹⁴ studied the influence of the soft-segment type in the SMM formulation as well as the type of the fluoroalcohol. It was found that the SMMs containing PCL segments showed higher advancing contact angles than those with PPO segments, a result attributed to the lower molecular weights of the SMMs synthesized with PCL, which facilitated their migration to the surface, and to the relatively higher fluorine contents, which increased the surface content of the hydrophobic component. They also found that SMMs containing B(L) produced membranes with higher advancing contact angles than those with F(L) and attributed this effect to the absence of the hydrophilic PEO segments within the fluoroalcohol B(L).

X-ray photoelectron spectroscopy (XPS) analysis

On the basis of the contact angle results discussed previously, it was anticipated that the incorporation of the SMMs would result in the surface migration and concentration of SMMs. Tang et al.,^{7,8} Pham et al.,¹² Fang,¹⁸ and Ho et al.¹⁴ confirmed this result by studying both the chemical and the elemental group compositions at the surfaces using XPS. This method is widely used to provide quantitative and qualitative chemical information of the top 1–20 nm of a surface.²⁰ Generally, the samples are analyzed at a series of takeoff angles (measured from the surface sample to the X-ray lens) to determine whether a compositional gradient exists near the surface. The background and theory relevant to this complementary analytical method were discussed elsewhere.²¹

From the SMM chemical structure (see Fig. 2) it can be noted that fluorine content is associated only with SMMs. Figure 6 presents the fluorine content in the membrane measured at the takeoff angle of 15° versus the fluorine content in SMM itself. For the same concentration of fluorine in SMM, the modified PU membranes with SMM reported by Tang et al.^{7,8} exhibited higher fluorine content than the modified PES membranes with SMM prepared by Pham et al.¹² and Ho et al.¹⁴

Tang et al.^{7,8} not only observed a significant increase in fluorine content for all SMM-modified PU surfaces, compared to the base polymer (unmodified PU membranes), but also a fluorine enrichment toward the outermost surface. Similar observations were made by Pham et al.¹² and Ho et al.¹⁴ for the SMM-modified PES membranes. It was also noted that on the SMM-modified surfaces, there was a decrease in carbon content associated with an increase in SMM concen-

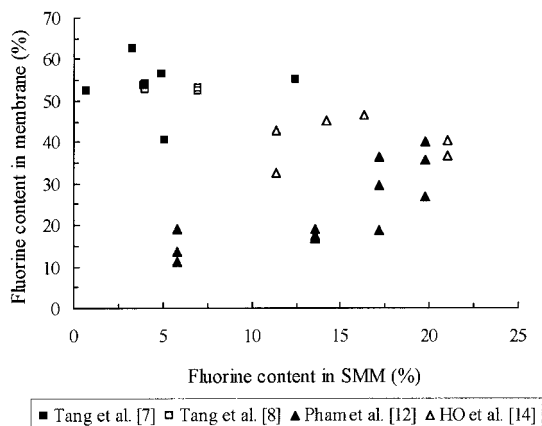


Figure 6 Plot of fluorine content in SMM-modified membranes as a function of fluorine content in SMM obtained at takeoff angle 15°.

tration, and this was accompanied by an increase in nitrogen content, which is believed to be associated with the diisocyanate group within the SMM chain.^{13,14}

Tang et al.⁸ found that an increase in the SMM concentration did not significantly change the fluorine content within the top surface of the PU membranes. In contrast, as discussed previously, the contact angles were more sensitive to the SMM concentration. Based on the elemental analysis data, Pham et al.¹² reported that little surface active additive was necessary to saturate the surface. Tang et al.⁸ observed that the elemental composition was almost identical for both PU membrane surfaces modified with the SMMs containing PPO and PTMO (i.e., SMM22 and SMM25). Pham et al.¹² and Ho et al.¹⁴ reported the same result for the PES membranes modified with SMMs containing PPO and PCL soft segments. Again, this result is significantly different from the trends observed in the contact angle data. The most obvious reason for this difference is that contact angle depends on many factors other than the fluorine content.

Suk²² studied the effect of membrane thickness and evaporation period on SMM migration to the top surface of PES membranes analyzed by XPS. It was reported that more surface migration of SMMs was detected for a thinner membrane, the surface migration of SMM increased with an increase in evaporation period, and no surface migration of SMM was detected when membranes were prepared with a zero evaporation period.

Based on the chemical structure of the fluoroalcohol (see Fig. 1), the ratio CF_3/CF_2 represents the degree of orientation of the polyfluoro segment, given that the CF_3 group is located only at the tail of this segment. It was found that the CF_2 and CF_3 contents decreased as the takeoff angle increased and the ratio of CF_3/CF_2

was high at the top layer, indicating that the CF_3 end of the fluorine tail is preferentially oriented outward from the surface.^{11,12} Furthermore, the materials that contain a high concentration of fluorine atoms (CF_2 and CF_3) at the surface show a significant depletion of C—C groups. This again suggests that the XPS-detectable layer is dominated by the SMM fluorine tails.

Thermal properties

Differential scanning calorimetry (DSC) was also used to characterize the thermal transition of SMM-modified and unmodified membranes. Figure 7 shows the T_g and the T_g width values as a function of the SMM concentration in the PES and in the PES/PVP blends. In studies led by Pham and Ho,^{11–14} it was found that the midpoint T_g values of the SMM-modified PES membranes were those of the PES-rich phase. They were slightly lower than that of the pure PES, which was recorded at 220°C. Tang et al.⁶ observed that the thermograms for the SMM-modified PU membranes were identical to that of the pure base material. In addition, no difference in the behavior of the SMM-modified membranes was found for different concentrations of SMMs. These results suggest that the mac-

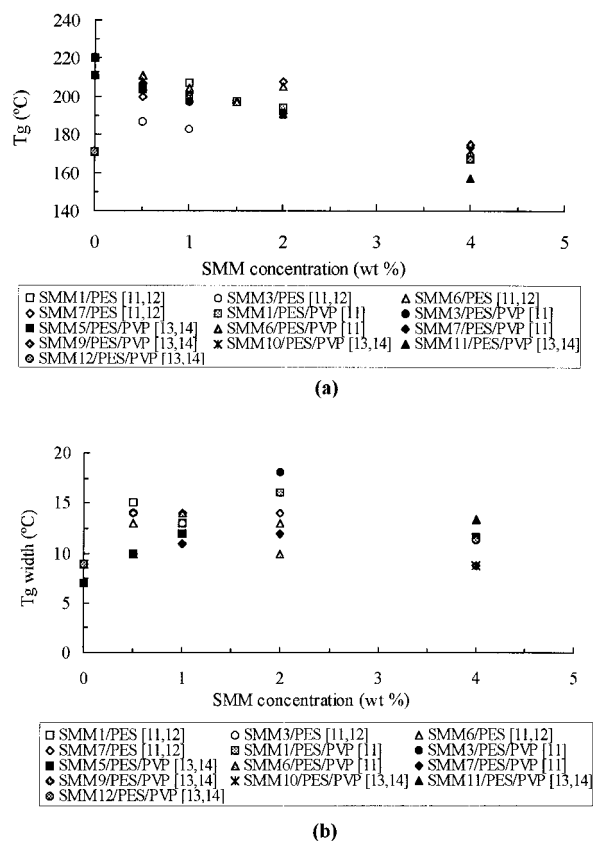


Figure 7 Plots of glass-transition temperature (a) and T_g width (b) of the membranes versus SMM concentration.

romolecules were not evenly distributed throughout the bulk material, but rather had migrated to the surface of the polymer and had little impact on the bulk phase microstructure.

The T_g value of the PES/PVP membrane (172°C was reported by Ho et al.¹⁴ and 211°C was reported by Pham¹¹) was lower than that of the pure PES membrane (220°C), indicating a plasticizing effect that was related to the presence of PVP in the membrane after the preparation procedure. It is also interesting to note that the T_g width of PES/PVP membranes was the same as that of pure PES (7°C). This was expected because PES and PVP are miscible in all proportions, as stated by Lafrenière et al. (see Miyano et al.¹⁹). Ho et al.¹⁴ observed that the addition of 4 wt % SMMs to PES films cast from solutions containing PVP (3 wt %) did not change the midpoint T_g (Fig. 7). On the contrary, Pham¹¹ found that the PES/SMM membranes had significantly lower T_g values than those of the PES membrane when using 6 wt % PVP. It is worth mentioning that the width of the transition region was previously associated with microheterogeneity of the material, as stated by Cortázar et al.²³ Pham¹¹ and Pham et al.¹² observed that the SMM-modified PES membranes had higher heterogeneity than the pure PES material, given that the T_g widths were almost double. Pham¹¹ reported that the microheterogeneity of the materials containing low SMM concentration was seen to be reduced by the presence of PVP in casting solutions, although the effect of PVP on T_g width was lost at SMM concentrations greater than 2 wt %.

Because only one T_g was observed for the SMM-modified membranes, one might conclude that the SMMs were relatively miscible in the PES material. However, as will be shown later, polarized microscopy analysis of SMM/PES membranes revealed the presence of phase-separated structures in the form of spherical microdomains. In fact, the single observable T_g may have resulted from the low concentration of SMMs (≤ 5 wt %) in the bulk material and therefore a T_g for the SMM phase was not detected.

Tensile strength and elongation tests

The effect of SMMs on the mechanical properties of PES membranes was performed by measuring the maximum tensile strength and percentage elongation of the SMM-modified and unmodified PES membranes. Suk²² conducted those experiments using membranes prepared in the same way as described above (Preparation of Membranes) from a casting solution with a composition of 10 wt % PES and 10 wt % PVP ($M_w = 10^4$) in the solvent NMP. The concentrations of SMM6 were 0 and 1.5 wt %. It was found that the tensile strength and percentage elongation of the

SMM-modified PES membranes were higher than those of the unmodified PES membranes. The tensile strength increased about 17.8 and 6.7% for the PES membranes containing SMM6 at a moving head speed of 2 and 5 mm/min, respectively; and the percentage elongation increased about 71% at a moving head speed of 2 mm/min and about 132.6% at a moving head speed of 5 mm/min for the SMM-modified PES membrane. This result may be attributed to the fact that SMM was synthesized on the basis of polyurethane chemistry, given that the chemical structure of polyurethanes yielded elastomers with high tensile strength.

Microscopy observations

Various microscopy techniques such as polarized microscopy (PM), confocal microscopy (CM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to examine the morphology and the structural characteristics of the SMM-modified and unmodified membranes.

Ho et al.¹⁴ stated that polarized microscopy technique provided the clearest evidence of the heterogeneous nature resulting from SMM addition to PES. The PM pictures of the unmodified PES membranes were clear and transparent, and no microstructures could be observed. However, microdomains appeared within the SMM-modified PES membranes and their size depended on the type of SMM used and on their chemical compositions.

Confocal microscopy was used by Ho,¹³ in reflectance mode, to study the internal morphology of SMM-modified PES membranes. A gradual depletion of the number of the microdomain structures throughout the bulk of the membrane material from the top membrane surface down to a depth of 6 μm was observed. This observation supports the XPS data, which suggested a selective migration of SMMs to the air-surface interface.

Based on the AFM images, the SMM-modified PES membranes were found to be rougher than the unmodified PES membrane and the obtained size of the microdomains was similar to that measured by confocal microscopy.¹⁴ Morphological analysis was also performed by use of SEM. Minnery²⁴ observed that the SMM-modified PES membranes underwent phase dispersion, and the size and number of the dispersed-phase elements increased as the solvent evaporation time increased. Minnery²⁴ also reported that the SEM does not provide any information about the composition of the top surface, which was shown by Ho et al.¹⁴ using confocal spectroscopy to be populated by circular (or spherical) SMM-rich domains embedded in a matrix of PES.

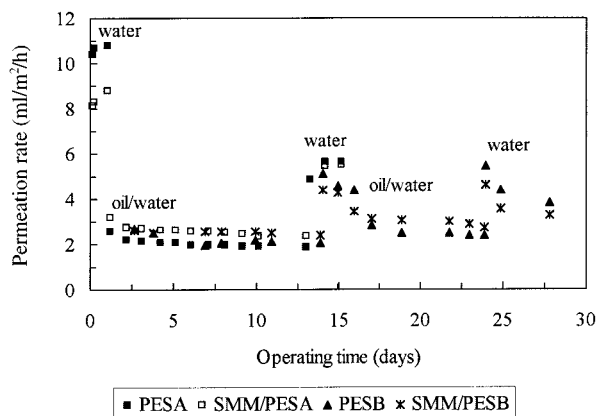


Figure 8 Plot of permeation rate of water and 10 vol/vol % cutting oil/water mixture through SMM-modified and unmodified PES membranes.

Finally, through these microscopy studies, it was confirmed that surface modification was achieved by the migration of SMM-concentrated microdomains to the air-membrane interface and the diameter of the dispersed phase observed by Ho¹⁴ ranged from 0.1 to 3 μm .

SMM-MODIFIED MEMBRANE APPLICATIONS

Ultrafiltration application

SMM-modified and unmodified membranes were tested to study the effect of SMM on permeation rate, separation factor, and fouling during ultrafiltration. Hamza et al.¹⁷ tested the performance of the PES membranes prepared from two concentrations of the PES (22 and 17 wt %), PVP of molecular weight 10^4 (7 wt %), and different concentrations of SMM7, from 0 to 1.35 wt %, in a common solvent of DMAC. Cutting oil (Texaco Soluble Oil), which readily produces emulsions, was used to prepare the aqueous feed solution of 10% by volume.

Figure 8 shows the performance, for both water and cutting oil/water as feeds, of the membranes PESA (PES 22%, PVP 7%, SMM 0%, DMAC 71%), PESB (PES 17%, PVP 7%, SMM 0%, DMAC 76%), SMM/PESA (PES 22%, PVP 7%, SMM 1%, DMAC 70%), and SMM/PESB (PES 17%, PVP 7%, SMM 1%, DMAC 75%). The oil separation factor of those membranes was more than 90% and, as can be observed in Figure 8, the enhanced fouling effect was very clear for all membranes, resulting in a significant decrease of the permeation rate of oil/water mixture compared to that of pure water. It was observed that the SMM-modified PES membranes have a superior performance, reflected in their higher flux when treating oil/water emulsions, than the unmodified membranes. On the contrary, when the feed is pure water

the membranes containing SMM exhibited lower permeation flux. In fact, as stated previously, the incorporation of SMM increased the hydrophobicity of the PES membranes. Tang et al.,⁶⁻⁸ Pham et al.,¹² Ho et al.,¹⁴ and Hamza et al.¹⁷ confirmed that the receding contact angle measurements suggested that the hydrophobic character was still maintained after exposing the films to water. This tends to decrease pure water permeation rates. On the other hand, the addition of SMM reduced the gel formation when the feed was changed to oil/water emulsion, resulting in higher flux of the SMM-modified PES membranes as compared to that of the unmodified membranes. Correspondingly, the oil gel layer resistance of the SMM-modified PES membranes generally decreased with an increase of the SMM content in the casting solutions. These results indicate that PES-modified membranes by SMM were less susceptible to fouling by oil/water emulsions, as reflected in their consistent ability in having higher product rates than those of unmodified membranes.

This result is the most controversial issue because it is generally believed that hydrophilic membranes are less fouled than hydrophobic ones. Cornelissen et al.²⁵ stated in a general overview in membrane technology that membranes prepared from hydrophilic materials are better than hydrophobic materials with respect to adsorptive fouling. Hydrophilicity and hydrophobicity are not the only criteria to govern fouling. Membrane polymer/solute interaction must also be taken into consideration.

Pervaporation applications

The pervaporation performance of PES membranes prepared by incorporating SMMs and unmodified PES membranes was evaluated by experiments with chloroform/water mixtures^{11,18,26-28} and alcohol/water mixtures (i.e., ethanol and methanol).²⁴ The pervaporative performance of the SMM-modified and unmodified PES membranes was studied by examining the effect of solvent evaporation time, SMM and PVP content in the casting solution, feed concentration, feed temperature, and permeate pressure.

Fang et al.²⁶ studied the effect of solvent evaporation period (i.e., from 2 to 16 min) on the pervaporative performance of the unmodified PES and SMM-5 modified PES membranes prepared from casting solutions containing 25 wt % PES and 6 wt % PVP ($M_w = 4 \times 10^4$) in the solvent DMAC. It was found that PES membranes prepared with an evaporation time less than 7 min were water selective compared with those having longer evaporation time that were chloroform selective, and the total permeation rate decreased with evaporation time.

For an evaporation time of 7 min SMM5-modified PES membranes (with 0 to 3.5% SMM5) were also chloroform selective. Similar SMM-modified membranes (1.5% SMM6) were evaluated by Mahmud et al.²⁷ with the same apparatus and procedures, and 11 ppm chloroform aqueous solutions. They also found high total carbon concentrations in the permeate, as expected based on the work of Fang et al.²⁶ But upon further investigation using more detailed chromatographic separation of the permeate and a run with a distilled water feed, they were able to establish that the main organic compound in the permeate was ethanol and not chloroform. The ethanol, retained from the ethanol-water exchange (drying) process, was being leached from the membrane. When the ethanol leaching was eliminated (by eliminating the ethanol drying process) the membranes were highly water selective. Thus, based on their analytical technique used, Fang et al.²⁶ claims of chloroform enrichment are suspect. Minnery²⁸ and Fang¹⁸ examined the effect of solvent evaporation period (i.e., 1, 3, and 5 min) on both the SMM-modified and unmodified membranes prepared using the polymer solution containing 25 wt % PES and 6 wt % PVP ($M_w = 4 \times 10^4$) in DMAC with the addition of 0.5 wt % of SMM6. They observed a reduction of the permeated flux of both the SMM-modified and unmodified PES membranes with increasing evaporation time, and all the membranes were water selective.

Minnery²⁸ investigated the effect of PVP on the pervaporative performance of the SMM-modified and unmodified PES membranes. Different concentrations of PVP were used (i.e., from 0 to 8 wt %). The membranes were prepared using 0 and 0.5 wt % SMM6 and 25 wt % PES in the solvent DMAC. The solvent evaporation time was 7 min and the feed mixture was 1000 ppm chloroform. He observed that below 2 wt % PVP, the SMM-modified membranes preferentially permeated water and for some measurements, no chloroform was detected in the permeate. Above this point, the modified membranes increasingly concentrated chloroform in the permeate, up to a factor of fourfold greater than that in the feed. In contrast, the unmodified PES membranes rejected chloroform over the entire range of PVP concentrations and the chloroform rejection tended to decrease as the amount of PVP increased. The permeated flux was lower for the unmodified membranes than it was for the SMM-modified membranes and tended to increase as the concentration of PVP increased. This is to be somewhat expected, given the role of PVP as a pore former. Hence, the greater the percentage of PVP in the casting solution, the greater the pore sizes. Perhaps, increasing the amount of PVP allows for the migration of enough SMM to the surface, and thermodynamically reverses the selectivity. In fact, increasing the percentage of

PVP in the casting solution allows more SMM to be present at the surface, producing an organophilic surface, thus increasing the concentration of organics at the membrane/feed liquid interface, which would increase the flux.

Minnery²⁸ also conducted pervaporation tests with SMM7-modified and unmodified PES membranes to study the impact of SMM concentration and feed concentration for an alternative SMM. The feed concentration impact tests (6% PVP, 7 min evaporation time and 0 or 0.5% SMM-7) showed that these membranes were water selective for feed concentration ranging from 100 to 1000 ppm. The tests for membranes with SMM7 concentrations ranging from 0 to 3.5% (6% PVP, 7 min evaporation time, chloroform feed = 1000 ppm) also showed that these membranes were water selective. It is interesting to note that for SMM modified membranes prepared with 6% PVP, 3% SMM, 7 min evaporation time, chloroform feed = 1000 ppm, those using SMM6 were chloroform selective while those using SMM7 were water selective. Thus, for certain conditions the SMM type will have a significant impact on the membrane performance.

Minnery²⁴ studied the effect of SMM on the pervaporative performance of PES membranes using three feed mixtures, ethanol, distilled water, and a ternary mixture of 65 wt % water, 30 wt % ethanol, and 5 wt % methanol. The membranes were prepared with a 7-min solvent evaporation time from casting solution containing 25 wt % PES, 6 wt % PVP ($M_w = 10^4$), and SMM6 in DMAC. The concentration of SMM was either 0 or 1 wt %. For both the SMM-modified and unmodified PES membranes, it was found that the flux was a function of temperature, following an Arrhenius-type dependency. Those experiments were conducted between 25 and 70°C. There was no significant difference between the activation energies of the SMM-modified and unmodified PES membranes, and the obtained activation energies were 7 kcal/mol for water and 11.6 kcal/mol for ethanol.

In his study, Minnery²⁴ measured the pervaporation flux in modified and unmodified membranes as a function of the downstream pressure using two types of feed, water and ethanol. Both membranes exhibited a similar trend (Fig. 9). The permeated flux decreased, gradually approaching a minimum plateau as the downstream pressure increased, and a minimum was attained when the downstream pressure was equal to, or greater than, the vapor pressure of the liquid feed (2.6 kPa at 22°C for water and 6.6 kPa at 22°C for ethanol). The pore flow model provided a good fit for permeation of water and ethanol as a function of pressure.^{29,30}

The effect of the feed concentration on the performance of the membranes synthesized with and without SMM modification was also investigated by Min-

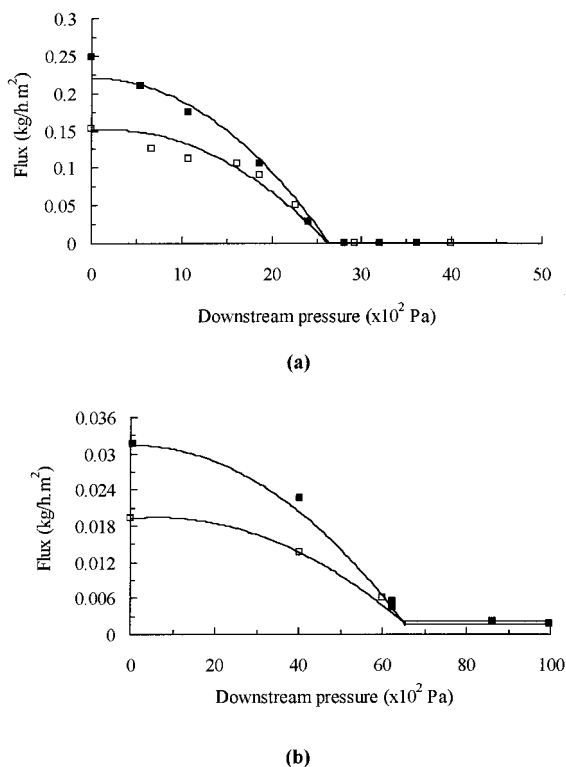


Figure 9 Plot of pervaporation performance for chloroform/water mixtures of SMM-modified and unmodified PES membranes.

ner²⁴ by use of aqueous ethanol solutions (from 0 to 100% ethanol). It was observed that both membranes showed fairly similar performances. The modified membrane exhibited a slightly higher mean permeated flux than the unmodified membrane and the mean water selectivity of the unmodified membrane was slightly greater than that of the modified membrane. As stated earlier, PVP is a hydrophilic pore former.¹⁹ The presence of some residual PVP in the final membrane matrix may act to increase the hydrophilicity, resulting in an increase in flux and water selectivity. Another possibility is that the addition of SMM could provide a hydrophobic/hydrophilic balance that would improve the separation of ethanol from water. As a matter of comparison, these membranes do not exhibit a separation factor high enough to be considered competitive in the dehydration of ethanol.³¹ The experimental result exhibited a sufficiently high flow rate but the separation factor was approximately two orders of magnitude too low to be competitive.

Biomedical applications

SMM-modified membranes were tested for blood compatibility with respect to fibrinogen adsorption

and biodegradation mediated by lysosomal enzymes released from inflammatory cells.^{7,8,13}

Polyurethane is one of the most important classes of thermoplastic elastomers, widely used in many biomedical applications because of its excellent physical properties.³² However, there is a controversy regarding the biostability of this material.³³ Tang et al.^{7,8} used SMM additives to reduce the hydrolytic degradation of polyurethanes by lysosomal enzymes. Samples were prepared by coating on small hollow glass tubes polymer solutions made from 10 wt % of radiolabeled base polyester-urea-urethane (¹⁴C-TDI/PCL/ED) and SMM in DMAC. The radiolabeled ¹⁴C-TDI/PCL/ED was prepared using the same polymerization steps indicated above (Preparation of Membranes) for the preparation of TDI/PCL/ED, but using radiolabeled 2,4-toluene diisocyanate (¹⁴C-TDI). The enzyme selected for the biodegradation tests was cholesterol esterase (CE). The radiolabeled products provided a measure of polymer degradation by the enzymes. Tang et al.² mixed nine different types of SMMs with ¹⁴C-TDI/PCL/ED at different SMM concentrations (i.e., 1, 2.5, and 5 wt %). They found that five of the SMMs (i.e., SMM21, SMM22, SMM23, SMM24, and SMM25) enhanced the hydrolytic stability of the polyester-urea-urethane against degradation by cholesterol esterase, whereas the other four SMMs (i.e., SMM17, SMM19, SMM20, and SMM27) enhanced degradation of the base polymer. They observed that there was no inhibition of biodegradation when the fluorine content in the SMM was extremely low or nondetectable by bulk analytical methods and when the SMM molecular weight was very high (such as SMM16, SMM18, SMM26). No relationship was found between biodegradation results and the molecular weight or fluorine content of the SMMs that showed inhibition of degradation.⁷

Tang et al.⁸ carried out long-term biodegradation experiments, which lasted for 34 weeks, using different concentrations of SMM22 and SMM25. They found that the inhibition effect increased by increasing the SMM concentration in the mixture and the long-term biodegradation results of the two SMMs showed almost the same inhibition of degradation, even though their molecular weights and fluorine content differed. Tang et al.⁷ reported that a SMM concentration of 1 wt % was sufficient to allow for a significant protection of the hydrolyzable bonds from degradation and suggested that some SMM molecules were more stable at the surface than others. Therefore, Tang et al.⁸ tested the biostability of the SMM materials themselves to hydrolytic degradation by cholesterol esterase. Radiolabeled SMMs (¹⁴C-SMM22 and ¹⁴C-SMM25) were synthesized as described above using radiolabeled hexamethylene diisocyanate (¹⁴C-HDI) and then mixed with nonradiolabeled polyester-urea-urethane

(TDI/PCL/ED). Tang et al.⁸ found that the SMM was significantly more stable than the base polymer itself and SMM22 appeared to stabilize more than SMM25.

Protein adsorption studies were carried out to assess the interaction of the modified polymer with blood components as a measure of potential procoagulation activity. Tang et al.⁸ evaluated the SMM-modified and unmodified (TDI/PCL/ED) membranes using SMM22. The concentration of the fibrinogen solutions ranged from 0 to 1 g/L. Reduction of almost 50% in fibrinogen adsorption was observed for diluted fibrinogen solutions, and at higher fibrinogen concentrations (0.5 g/L) a difference of only 20% was reached. This implies that the SMM-modified membranes have relatively lower affinity to retain fibrinogen. Ho¹³ conducted the same experiments using SMM-modified and unmodified PES hollow fibers prepared from polymer solution containing 30 wt % PES, 1.5 wt % PVP, and 0 or 4 wt % SMM. Eight different types of SMMs were used (SMM5, SMM9–SMM15). Once again, it was found that surface modification with SMMs reduced the amount of protein adsorbed compared to unmodified PES fibers. The addition of 4 wt % SMM to PES hollow-fiber membranes reduced the adsorption of fibrinogen by as much as 36% compared to “pure” PES, and generally SMMs containing PPO soft segments were more effective than SMMs containing PCL soft segments in reducing fibrinogen adsorption.

Because fibrinogen has been directly linked to platelet activities, activation of the intrinsic coagulation pathway, and interactions with leukocytes,³⁴ it was anticipated that the chemistry of the SMMs might differentiate the potential activation of blood components on the modified membranes. However, from preliminary results of the *in vitro* whole blood studies carried out by Ho,¹³ it was not possible to draw conclusions on the relative activation of platelets and leukocytes by PES hollow-fiber membranes. Ho attributed this fact to donor variability, unreliable sources of antibody, irregular roughness features, and the presence of surface contaminants on the membranes. More recent studies by Jahangir et al.³⁵ demonstrate that the SMM-containing surfaces show a substantial reduction in platelet activation and adhesion.

Finally, it may be concluded that the SMM additive played two simultaneous roles, the anticoagulant role of protein at the surface and enhancement of the biostability of polyurethane. More research must be done in this area.

A FINAL NOTE AND FUTURE DIRECTIONS

The surface energy of the SMM-blended membranes is close to that of the commercial polytetrafluoroethylene (PTFE) membrane. It is clear that the addition of

SMMs will lower the surface tension of the base material, producing relatively more hydrophobic surfaces through the migration and concentration of SMMs at the surface, without dramatically changing the membrane bulk properties. The SMM-modified membranes exhibited low surface energies, high chemical resistance, and good mechanical strength. Compared to the unmodified membranes, SMM surface-modified membranes were susceptible to less fouling during ultrafiltration (i.e., higher fouling resistance) and could thus be used for separation of volatile organic compounds from aqueous solutions by pervaporation and for biomedical applications to reduce the material's susceptibility to hydrolysis degradation and protein adsorption. However, SMMs are not universal and do require a preliminary assessment of substrate compatibility. Much research and development effort are required to ascertain the effect of SMMs on the morphology and performance of SMM-blended membranes. Further investigations to elucidate the factors that influence the kinetics of the migration of SMM to the membrane surface (i.e., evaporation time, membrane thickness, evaporation temperature) will be an important goal in future work. Designing novel types of SMMs, blending the SMMs in other hydrophilic base polymers such as polyetherimide (PEI), use of other membrane configurations (i.e., capillary and hollow fibers), and application of SMM-modified membranes in other processes such as membrane distillation or gas separation would be considered new and important contributions to membrane science and technology.

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