Application of Surface Modifying Macromolecules in Polyethersulfone Membranes: Influence on PES Surface Chemistry and Physical Properties

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ABSTRACT: Novel surface modifying macromolecules (SMMs) were developed for incorporation into polyethersulfone (PES) membranes, intended for pervaporation applications. These materials were synthesized with a diisocyanate, polypropylene oxide (PPO), and a fluoro-alcohol, and characterized for elemental analysis, molecular weight, and glass transition temperatures. PES/SMM blends with eight types of SMMs were characterized for surface and physical properties and compared with PES. Water droplet contact angle measurements and X-ray photoelectron spectroscopy data showed that the SMMs migrated to the surface and rendered the PES material more hydrophobic. While advancing contact angle data were equivalent to those of pure Teflon™, the highest average values of receding angles of these systems were less than those of commercial Teflon™. The opaqueness of PES/SMMs films and data from differential scanning calorimetry experiments showed that the SMMs were either immiscible or only partially miscible with PES. It was also observed, for a fixed PES concentration of 25 wt %, that increases in the molecular weight of the SMMs and the weight fraction of PPO in the SMMs led to phase separation in the ternary PES/SMMs/dimethylacetamide (i.e., membrane casting solution) system. On the other hand, in the binary PES/SMMs system (i.e., cast membrane film), an increasing weight fraction of fluorine in the SMMs contributed to an increase in the phase separation. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1363–1378, 1999

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INTRODUCTION

With an increasing interest for the use of pervaporation membrane technology in the food, bio-

technology, pharmaceutical, and other industries[1], a polyethersulfone (PES) pervaporation membrane with improved selectivity towards organic compounds would have the possibility of overcoming some practical problems with the currently available membranes. These include high manufacturing costs[2] and poor membrane stability.[3] However, there are few reports in the literature on the use of PES in pervaporation pro-

cesses, particularly for the concentration of organic compounds from dilute aqueous solution. PES is an attractive material for pervaporation membranes because it is mechanically stable and commercially available at a relatively low cost.

It is well documented that surface chemistry and morphology play an important role in the transport of a penetrant in a membrane.[4,5] It is also known that a hydrophobic membrane surface tends to favor organic selectivity in the separation of aqueous solutions.[6–8] Therefore, it could be hypothesized that the performance of a PES membrane as an organic selective membrane could be improved by enhancing its surface hydrophobicity. Surface modification can be carried out using a number of methods such as coating, grafting, surface treatment, and so on.[9–12] Another attractive method involves the addition or blending of surface active components into the polymer casting solution.[13,14] If successful, this method could render the surface of a membrane hydrophobic while maintaining the membrane's original bulk properties. Furthermore, it would permit the production of the desired asymmetric membrane in a single casting step rather than the two required by the alternative techniques mentioned earlier.

In previous work, novel surface modifying macromolecules (SMMs) were synthesized using copolymeric block structures and were introduced into polyurethanes.[15] These SMMs had an amphipathic structure consisting of a main polyurethane chain terminated with two low polarity polymer chains (i.e., fluorine segments). In this latter work, it was demonstrated that the SMMs dramatically altered the surface chemistry of the polymers to render them hydrophobic, but introduced minimal changes in the bulk nature of the materials. It was therefore hypothesized that SMMs could also be incorporated into PES materials and would migrate to the surface in order to alter the latter's properties, thus making the PES membrane surface hydrophobic and hence potentially improving its pervaporation performance.

The mobilization of the SMMs to the PES surface would occur as a result of a driving force for spontaneous surface migration in order to minimize the interfacial energy.[16] In a polymer blend, thermodynamic incompatibility between polymers usually causes the separation of polymers to occur. If the polymer system is equilibrated in air, the polymer with the lowest surface energy will concentrate at the air interface and reduce the

system's interfacial tension as a consequence. Since the surface characteristics of the SMM modified PES materials are anticipated to be largely determined by the SMMs's low polarity components, monomers making up the SMMs can be chosen to give a specific property.[13,14,17] It is preferable to use a fluorine-based component due to additional features such as surface lubrication, reduced fouling and increased chemical resistivity associated with the carbon–fluorine (C–F) bond.[18–20]

The objectives of this study were (1) to assess if SMMs could be blended with PES, to what extent they could be blended, and which step(s) of the SMMs synthesis could be a parameter(s) for manipulating them in order to improve compatibility with PES, and (2) to show that SMMs do migrate to the PES surface and, in doing so, create a hydrophobic surface.

EXPERIMENTAL

SMM Synthesis

Methylene bis-phenyl diisocyanate (MDI, Eastman Kodak, Rochester, NY) was distilled at 0.025 mmHg before use. Polypropylene diol (PPO) of average molecular weight 425 (Aldrich, St. Louis, MO) was degassed at 0.5 mmHg for 24 h before use to remove residual water. The fluoro-alcohol intermediate (Zonyl BA-L, Van Waters and Rogers, Montreal, PQ, Canada) had a variable number (m) of (CF_2) repeating units where m ranged from 4 to 12 (see Figure 1). Zonyl BA-L was distilled at 0.025 mm Hg to yield three major fractions. The description and physical state of each fraction are listed in Table I. Fractions Low and High were used in this work. The chemical structure of the synthesis reagents are given in Figure 1. N,N-dimethylacetamide (DMAC, Aldrich, St. Louis, MO) was used as the reaction solvent and was distilled at 0.5 mmHg within 24 h before use. 1,1,2-trichloro-trifluoroethane (HPLC grade) was supplied by BDH (Toronto, ON, Canada) and was used "as is."

SMMs were synthesized using a two-step solution polymerization under a nitrogen atmosphere. First, a prepolymer was made by reacting MDI with PPO; then the fluoro-alcohol was reacted with the prepolymer to yield the SMMs. A typical batch of SMMs were synthesized according to the following procedure. MDI and PPO were dissolved separately in 50 mL of DMAC. The PPO–

Figure 1 Chemical structures of SMMs synthesis reagents.

DMAC solution then was stirred and preheated to about 40°C in a glass reactor. The MDI–DMAC solution then was added in one step to the reactor. This reaction mixture was stirred for three h at 40–50°C. At the end of this period the fluoro-alcohol intermediate was dissolved in 50 mL of DMAC and was added to the prepolymer solution. This last step of the reaction was carried out for 15 h at room temperature. Upon completion, the reaction mixture was slowly added into distilled water while stirring, in order to precipitate the SMMs. The precipitate was further washed three times (for periods of 24 h) with distilled water to leach out trace solvent and water-soluble unreacted components. The SMMs then were dried in an air-circulating oven at 50°C for two days. Once dry, the material was ground into fine particles to increase surface area and then was washed three times with 1,1,2-trichloro-trifluoroethane to remove traces of unreacted fluoro-alcohol. The final SMM material was dried in an air-circulating oven at 50°C for two days. This was followed by drying at 0.5 mmHg at the same temperature for one additional day in order to remove trace amounts of washing solvent.

A nomenclature was adopted with the general form MPBijkXY(n), where M, P, and B represent MDI, PPO, and BA-L respectively; i, j, and k represent the stoichiometry used for the three reactants, respectively; X is the type of BA-L fraction used where H is the high boiling fraction of BA-L and L is the low boiling fraction (Table I); and Y is the prepolymer reactant concentration that varied between a reduced value of 75% (R) and 100% (N) of a set concentration value for a particular reaction stoichiometry (ijk). The number n in parenthesis represents the batch number for the synthesis. Therefore, an SMM with the code MPB322HN(1) represents the polymer made from reacting MDI, PPO, and BA-L, using a 3:2:2 mole ratio, with the High fraction of BA-L at a normal (N) reactant concentration of 0.3 mmol/mL MDI and 0.2 mmol/mL PPO; the batch number is (1). Without the synthesis batch number (e.g., MPB322HN), the notation signifies a general class of SMMs sharing the same synthesis formula and reaction method. The reactant mole ratio (RMR), the prepolymer reactant concentration (RC), and the fraction of BA-L (FB) are experimental variables defined for the synthesis of the SMMs. The latter three variables were assessed for their effect on SMM character using a two-level (+ and −), three-variable factorial study (2^3) defined below. The statistical analysis was carried out using STAT-Graphics [Statistical Graphics Corporation (©1985–91 Ver.5.0.)].

Table I   Physical Data of Zony BA-L

BA-L Fraction	m[a]	Vapor Temperature Range at 0.025 mmHg (°C)	Average Molecular Weight	Physical Appearance
Low	4–8	50–55	440	colorless liquid
Medium	8–10	60–65	490	soft, white solid
High	>10	70–90	590	white solid

[a] m is related to the number of repeated (CF_2) groups in the molecule.

1. For reactant stoichiometry, a + represents 3 : 2 : 2 diisocyanate : polyol : fluoro-alcohol mole ratio, whereas a − represents a 2 : 1 : 2 ratio of the respective reagents.

2. For the chemical nature of the fluoro-alcohol, a + represents the High fraction from the BA-L distillation, whereas a − represents the Low fraction.

3. For the reactant concentration in the prepolymer stage, a + represents 0.3 mmol/mL of diisocyanate and 0.2 mmol/mL of polypropylene diol for the 3 : 2 : 2 formula ratio, while for the 2 : 1 : 2 formula, a + represents 0.2 mmol/mL of diisocyanate and 0.1 mmol/mL of polypropylene diol. The − indicates reactant concentrations equal to 75% of those for the + case.

Membrane Base Material

The PES used for the preparation of membrane samples was Victrex 4800P supplied by ICI Advanced Materials, Cleveland, England. Prior to use PES was dried in an air-circulating oven for 4 h at 150°C to remove absorbed moisture. DMAC was used as solvent and was distilled at 0.5 mmHg within 24 h before use.

Elemental Analysis

Bulk elemental composition (carbon, nitrogen, and fluorine) for each SMM was determined by Guelph Chemical Laboratory (GCL), Guelph, ON, Canada. These values are reported in units of weight percent. Nitrogen is specifically associated with the urethane bond in the main chain of the SMM and is related to the MDI component, while fluorine is only associated with the fluoro-alcohol. The method used to determine the monomer content from the weight percent of a characteristic element in the material has been described elsewhere.[21] In this report, f_z is the weight percent of a given fluoro-alcohol, while f_m and f_p are weight fraction values of MDI and PPO in a given SMM, respectively. It must be noted that there is a distinction between the amount of fluorine associated with the weight fraction of the fluoro-alcohol molecule (f_z) of a particular BA-L fraction (i.e., BA-L High or BA-L Low) in the SMMs. Hence, for the same value of f_z, SMMs synthesized with BA-L High and Low will have different molecular distributions of fluoro-alcohol since BA-L High has a longer polyfluoro-chain than BA-L Low.

Gel Permeation Chromatography (GPC)

Average molecular weights (relative to polystyrene standards) for a batch of SMMs were determined by GPC. The average molecular weights and the polydispersity are reported as relative values with respect to polystyrene standards. These values were used for a comparative basis between SMMs synthesis batches and have no meaning in absolute terms. Three Waters Ultrastyragel columns (10^3, 10^4, and 10^5 Å pore sizes, Mississauga, ON, Canada) and a differential refractive index detector (Waters 410, detector, Mississauga ON, Canada) were used. The solvent phase was HPLC-grade dimethylformamide (supplied by BDH, Toronto, ON, Canada) containing 0.05 M LiBr. The flow rate was 1 mL/min, and the column temperature was kept at 80°C.

Differential Scanning Calorimetry (DSC)

The glass transition temperatures (T_g) of SMMs, PES, and PES/SMM mixtures were determined by DSC. A DuPont DSC 910 system (Mississauga ON, Canada) equipped with a low temperature cell was used. Sample weights consisted of 5–10 mg of powder (synthesized SMMs) or films (membranes). PES and PES/SMM films were prepared from casting solutions consisting of 25 wt % PES with 0, 0.5, 1.0, or 2.0 wt % SMM in distilled DMAC solvent. The filtered solution was cast onto a clean glass slide to form a thin film. The slide was then placed into an air-circulating oven at 110°C for 10 min, followed by drying at room temperature for 24 h in a dry air-circulating oven and an additional 24 h of drying under vacuum (room temperature, ~ 1 mmHg). The films were then dried by a solvent exchange procedure involving four consecutive overnight immersions in aqueous solutions of increasing ethanol concentrations (25, 50, 75, and 100 vol % ethanol). After the last immersion, the films were dried under vacuum for 24 h at room temperature. DSC experiments were performed under 50 mL/min of nitrogen purge over a temperature range of −125–260°C with a heating rate of 20°C/min. The sample was first heated to 260°C followed by a 10-min isothermal period to remove any trace of solvent. Next, the sample was cooled to −125°C at 40°C/min with liquid nitrogen and then heated for a second time to 260°C at 20°C/min. Thermograms were analyzed using DuPont's General V.4.0D software (Mississauga ON, Canada). Two characteristic values for the T_g are (1) the T_g width defined by the range of the transition tem-

perature and (2) the midpoint T_g, given as the temperature at which half of the total change in specific heat capacity has occurred. Another value, the change in specific heat capacity for the range of the transition (ΔCp, J/g $\cdot$ °C), was also reported. The convention for reporting the midpoint T_g has been used by several authors[22–26], and in this study they are reported as the midpoint of the inflection curve from the second heating.

X-ray Photoelectron Spectroscopy (XPS)

The surfaces of the PES/SMM films were characterized by XPS at the Centre for Biomaterials, University of Toronto, Toronto, ON, Canada. Film casting was identical to the protocol described in the previous section, and solutions were prepared as described in the section on contact angles. After casting, films were separated from glass slides by immersion in distilled water and were marked for the side exposed to air. They were then washed with HPLC-grade 1,1,2-trichloro-trifluoroethane (TCTFE, supplied by BDH, Toronto, ON, Canada) (2 × 1 minute rinses) to remove traces of silicone contamination.[27] Each sample then was rinsed with distilled water and put in an aluminum dish, covered with a non-lint tissue, and dried under vacuum at room temperature for 24 h to remove all traces of solvent. The samples then were placed inside a sterile plastic pouch and sent for analysis.

The XPS information for samples consisted of two parts: low- and high-resolution spectra. At low resolution, information regarding elemental composition in terms of relative atomic percent was obtained. At high resolution, chemical bond types were detected by measuring the relative binding energy shift for carbon 1s electrons (C1s). For the low-resolution data, the relative intensities were normalized with respect to the intensity of the elemental carbon content, whereas the high-resolution data were normalized with respect to the C–C shift signal. This format has been previously adopted by other groups.[28]

The XPS spectra were obtained on a Leybold MAX 200 XPS system (Leybold, Cologne, Germany). Unfiltered Mg K$_\alpha$ X-ray radiation was used as the excitation source. The source was run at 12 kV and 25 mA. Atomic percentages of the elements present were derived from spectra run in a low-resolution mode (pass energy = 192 eV), which then were normalized to the unit transmission of the electron spectrometer. The spectral

regions of interest also were run in a high-resolution mode (pass energy = 48 eV). Binding energy and peak areas were obtained by use of the numerical routines provided with the spectrometer. The energy scale of the spectrometer was calibrated to Ag3d$_{5/2}$ and Cu2p$_{3/2}$ peaks at 368.3 eV and 932.7 eV, respectively. The binding energy scale then was shifted to place the C1s feature present at 285.0 eV. Large-area analysis was performed (2 × 4 mm or 4 × 7 mm) so that exposure of the samples to the X-rays would be minimized while sufficient signal-to-noise ratios could be obtained for the spectral features. Low and high-resolution data were collected at two take-off angles (θ'') 15° and 90° (angle θ'' is measured relative to the horizontal plane of the sample surface). The layer characterized at the 90° take-off angle was representative of the top 10 nm of the surface, while that characterized at the 15° take-off angle was representative of the top 2 nm of the surface.

Contact Angle Measurements

The relative hydrophobicity of a surface can be qualitatively determined by measuring the contact angle of a water drop deposited onto the surface. Contact angle values depend on the surface chemistry, its roughness, and its heterogeneity.[29] While the Gibbs analysis predicted that there would only be one contact angle,[30] this situation only arises for an idealized smooth, homogeneous, and nondeformable surface. Real systems are rarely in thermodynamic equilibrium, and this is particularly relevant in the case of polymer surfaces.[31] A fundamental characteristic of wetting is the ability of a liquid drop to adopt several different but stable angles on a solid surface. Two relatively reproducible angles are the largest and the smallest, which are called the advancing angle θ_{adv} and the receding angle θ_{rec}, respectively. In this study, both of these angles will be measured. Their difference, $\theta_{adv} - \theta_{rec}$, also referred to as the hysteresis, will be reported on as well.

Films for contact angle measurements were prepared on glass slides. The slides were soaked in chromic acid solution for 24 h and rinsed with distilled water, followed by drying in a 100°C oven prior to use. Casting solutions (see the Differential Scanning Calorimetry section) were allowed to stand at room temperature for 48 h in order to detect the occurrence of any phase separation within the solution phase. Solutions that maintained a single phase were filtered through a

Table II   SMM Characteristics (Reported as the Mean of Three Polymer Batches and % Standard Error [s.e.])

SMM Formulation	M_w (s.e.) (10^4)	M_n (s.e.) (10^4)	f_z (s.e.)	f_m (s.e.)	f_p (s.e.)	T_g Width (s.e.), (°C)	T_g Midpoint (s.e.), (°C)
MPB322HN	2.7 (10%)	1.6 (6%)	0.20 (6%)	0.36 (10%)	0.43 (6%)	16 (5%)	29 (8%)
MPB322HR	2.2 (7%)	1.4 (4%)	0.17 (39%)	0.42 (4%)	0.41 (12%)	13 (5%)	20 (13%)
MPB212HN	1.6 (11%)	1.1 (6%)	0.30 (16%)	0.37 (5%)	0.33 (9%)	13 (21%)	34 (5%)
MPB212HR	1.8 (9%)	1.1 (6%)	0.18 (12%)	0.43 (10%)	0.39 (6%)	13 (13%)	29 (5%)
MPB322LN	2.5 (15%)	1.5 (11%)	0.11 (35%)	0.51 (18%)	0.39 (16%)	14 (0%)	19 (20%)
MPB322LR	1.9 (5%)	1.3 (3%)	0.14 (10%)	0.41 (6%)	0.45 (4%)	15 (2%)	24 (5%)
MPB212LN	1.3 (9%)	0.9 (5%)	0.31 (3%)	0.39 (2%)	0.30 (5%)	14 (2%)	28 (5%)
MPB212LR	1.5 (13%)	1.0 (2%)	0.21 (12%)	0.49 (2%)	0.30 (5%)	14 (4%)	27 (7%)

M_w and M_n are the polystyrene equivalent weight average molecular weight and number average molecular weight, respectively; f_z is the weight fraction of fluoro-alcohol in the material; f_p is the weight fraction of PPO; and f_m is the weight fraction of MDI.

0.5 μm pore–size Teflon™ membrane filter prior to film casting. The films then were cast and processed in a similar manner to that described in the Differential Scanning Calorimetry section. Contact angles for each surface were measured immediately following the drying procedure.

Water θ_{adv} and θ_{rec} values of PES and PES/ SMM films were measured using a Ramé-Hart, Model A-100 goniometer (Mountain Lakes, NJ). Distilled water was purified using a Barnstead NANOpure II unit, and the initial water drop (2.0 $\times 10^{-4}$ mL) was deposited onto the film surface with a Ramé-Hart, Model 100-10 microlitre gas tight syringe (Mountain Lakes, NJ). The volume of the drop was slowly increased and then decreased by adding water to and withdrawing water from it using the microsyringe. The procedure was repeated three times prior to the contact angle measurements. On the third water addition, a contact angle reading, just prior to the sudden movement of the three-phase interface, was recorded as the θ_{adv} value. Water was then withdrawn until the onset of another sudden movement of the three-phase interface to give the θ_{rec} reading. A total of two slides were prepared for the PES solution and for each of the PES/SMM solutions. Ten readings were performed at random locations on the surface of each slide. After these sets of readings were taken, the films were then used for XPS measurements.

RESULTS AND DISCUSSION

SMM Characterization

The average material characteristics, along with their respective percent standard errors relative to the averages for each type of SMMs synthesized, are presented in Table II. The experimental error associated with the GPC method itself was only 2–3%; therefore, any standard error for molecular weight numbers greater than the latter value originates from the synthesis of the SMMs. In general, the standard errors for weight average molecular weights were all on the order of 10%. Based on the data in Table II, the standard errors did not appear to be strictly correlated to any of the three experimental variables, although a reduction in the concentration of prepolymer reactants seemed to decrease the error associated with M_w and M_n. The results of the factorial analysis showed that an increase in RMR or the combined effect of RMR/RC increased the molecular weight of the SMM ($p < 0.05$). This is not a surprise, since Peebles[32] indicated that the length of the isocyanate terminated chain, which is synthesized in the prepolymer reaction, is more difficult to control when the diisocyanate concentration is high and the diisocyanate/diol ratio is low.

Table II also contains the weight fraction of each component for the different SMMs. For the purpose of comparison, the theoretical weight fractions of the components were calculated, assuming a 100% conversion of the three monomers (see Table III). The actual f_z values reported in Table II are significantly lower than the theoretical values in Table III. Another immediate observation from the data in Table II is that the standard errors associated with f_z were high for MPB322HR and MPB322LN. Based on the information available at this time, it is not possible to associate stoichiometry, reaction concentration, or BA-L type with the elevated standard errors observed for these two materials. However, it

Table III   Theoretical Weight Fractions of MDI (f_m) : PPO (f_p) : BA-L (f_z) in SMMs, Assuming 100% Conversion

Reactant Mole Ratio, BA-L Fraction	f_z	f_m	f_p	$f_m + f_p$
3 : 2 : 2, High	0.42	0.27	0.31	0.58
3 : 2 : 2, Low	0.36	0.30	0.34	0.64
2 : 1 : 2, High	0.56	0.24	0.20	0.44
2 : 1 : 2, Low	0.49	0.28	0.23	0.51

should also be considered that other variables that were not systematically varied may be in part responsible for the high standard errors associated with f_z. For instance, these may be related to reaction kinetics and/or the reactivity of the hydroxyl group on the fluoro-alcohol relative to the hydroxyl group on PPO molecule. With the exception of MPB322LN, the percent standard error for f_m and f_p values were maintained to less than 12%. This would indicate that, in general, the reproducibility of the prepolymer synthesis step was better than that of the end-capping step.

The factorial study showed that only the RMR had a significant effect on the weight fraction of PPO in the SMM (f_p). The effect of all other variables on f_p was insignificant (based on $p < 0.05$). The change in f_p produced by changing the RMR was 0.083. The theoretical change (average of the changes within the high and low BA-L fractions, Table III) in f_p with a change in RMR was calculated as being 0.11 when all other variables were constant. Hence, the experimental value approaches that of the theoretical one. RMR and FB were the only variables that had significant effects on f_z ($p < 0.05$). The effect of the RMR on f_z was expected since an increase in RMR (change from 2 : 1 : 2 to 3 : 2 : 2) would increase the prepolymer molecular weight and therefore decrease f_z. The increased fluorine chain length of the high fraction of BA-L contributes to the observed increase for an increase in the FB variable. The average T_g width and midpoint T_g for the SMMs are also reported in Table II. In this work, the SMMs were heated at a constant rate (20°C/min) to a temperature higher than their T_g (i.e., 260°C). This procedure allows the polymers to be as close as possible to a state of free arrangement and hence independent of the history of sample processing. In general, there were no crystallization endotherms detected for any of the SMMs from −50°C up to 260°C, which indicates that the

polymers were amorphous within this temperature range. The nonsymmetrical chain structure inherent in the PPO segments will minimize the formation of semicrystalline structures.[33] RMR, FB, and FB + RC had a significant effect on the midpoint T_g, but no effect was observed on the T_g width. It is to be noted that BA-L Low is a liquid while BA-L High is a solid (Table I), and hence it may be expected to see an increase in midpoint T_g for SMMs synthesized with the respective fluoro-alcohols. The effect of RMR on the midpoint T_g values was also expected since an increase in RMR increased both the molecular weight of the SMM and f_p, the weight fraction of the PPO component, which acts as an internal plasticizer to reduce T_g values.[33]

PES/SMM Solution Behavior

The complete miscibility of one polymer into another has been shown to be rare.[28,34,35] Even when a common solvent is added (one that is infinitely soluble with each of the polymeric constituents alone), two polymers usually cannot coexist in a homogenous solution beyond a concentration of a few percent.[36] Hence, prior to assessing the SMMs's ability to alter the performance of PES membranes in pervaporation processes, its behavior with respect to membrane manufacturing methods must be studied. Specifically, in the case of pervaporation membrane formation, a homogenous phase in solution is considered important since various membrane fabrication techniques require this criterion in the casting of thin films.[4]

It was beyond the scope of this work to generate complete phase diagrams for PES and all of the SMMs. Instead, a fixed concentration of PES at 25 wt % was used to study solution effects. This concentration was selected since this was a working concentration used in studies previously reported by Matsuura and colleagues.[5] The solvent used for preparing the solutions was DMAC, and two distinct batches of SMMs for each formulation were used in order to comment on the reproducibility of observations with a specific formulation. The selected batches represent SMMs with the highest and lowest measured molecular weights for a particular formulation and were such that the molecular weights did not vary by more than 10% within a pair of SMMs batches with the same formulation.

The casting solution appearance for various PES/SMMs/DMAC mixtures (see Table IV) was

Table IV   Solution Appearance of PES/SMM Blends at Various Concentrations of SMMs in Solution. The Wt % of PES was Kept at 25 Wt %, and the Solvent was DMAC

SMM Formulation	PES/SMM with 0.5 Wt % SMM	PES/SMM with 1.0 Wt % SMM	PES/SMM with 2.0 Wt % SMM
MPB322HN(1)	0	1	1
MPB322HN(3)	1	1	2
MPB322HR(2)	0	0	0
MPB322HR(3)	0	0	0
MPB212HN(2)	0	0	1
MPB212HN(3)	0	0	1
MPB212HR(1)	0	0	0
MPB212HR(2)	0	0	0
MPB322LN(2)	0	1	2
MPB322LN(3)	0	1	1
MPB322LR(1)	0	0	0
MPB322LR(2)	0	0	1
MPB212LN(2)	0	0	0
MPB212LN(3)	0	0	0
MPB212LR(2)	0	0	0
MPB212LR(3)	0	0	0

0 = clear solution; 1 = cloudy, one phase; 2 = two phases.

recorded after the mixtures were allowed to stand for two days at room temperature (25°C). There were three observable states: clear, cloudy but only one phase, and two phases. Phase separation was identified as either cloudy or observed two phases. On average, the order of phase behavior from poor to good for the range of concentrations studied was MPB322HN = MPB322LN < MPB212HN < MPB322LR < MPB322HR = MPB212HR = MPB212LN = MPB212LR. This trend was consistent for both batches of the eight formulations. All mixtures showed a decrease in miscibility as the concentration of SMMs increased. In general, the SMMs synthesized with the RMR of 2 : 1 : 2 seemed to show consistently better phase behavior than those synthesized with the 3 : 2 : 2 ratio. It can be concluded then that the RMR had some effect on the phase behavior of SMMs. However, a more rigid experimental analysis over a range of PES concentrations will be needed to confirm this at a statistical level.

As discussed in the previous section, the RMR significantly affected the average molecular weight, the weight fraction of PPO (f_p) and the weight fraction of BA-L (f_z) in the SMMs. All of these properties could influence solution behavior. However, it is seen from Table IV that the type of BA-L did not have any clear effect on the phase behavior within this SMM concentration

range. Also, since the weight fraction of MDI in SMM (f_m) was not significantly affected by the RMR, it could be concluded that the effect of the RMR on phase behavior was due mainly to the weight fraction of PPO in the SMM. Since molecular weight and (f_p) were shown to increase with increasing RMR (i.e., going from 212 to 322), it is interesting to note that the two materials with the best miscibility (i.e., MPB212LN and MPB212LR) also have the lowest PPO content and the lowest molecular weight (see Table II). Conversely, the two materials with the highest molecular weight (i.e., MPB322HN and MPB322LN) are the least miscible in the ternary system.

The Miscibility of PES/SMM Film Components

For solutions that did not separate into two distinct phases, films were prepared according to methods described for DSC studies. The films obtained were qualified according to optical characteristics (opaque or transparent), surface patterns, and differences in morphology (see Table V). The classification for nontransparent films were (1) "uniform" if the surface was smooth and had no distinguishable feature, (2) "somewhat uniform" if it was smooth but had some kind of pattern, and (3) "phase separated" if distinct phases were visually observed.

Table V   Film Appearance of PES/SMM Blends at Various Concentration of SMMs in Casting Solution. The Concentration of PES in Solution was Fixed at 25 Wt %, and the Solvent was DMAC

SMM Formulation	PES/SMM with 0.5 Wt % SMM	PES/SMM with 1.0 Wt % SMM	PES/SMM with 2.0 Wt % SMM
MPB322HN(1)	0	1	2
MPB322HN(3)	1	1	N/A
MPB322HR(2)	0	0	0
MPB322HR(3)	0	0	0
MPB212HN(2)	1	1	2
MPB212HN(3)	1	1	2
MPB212HR(1)	0	0	0
MPB212HR(2)	0	1	1
MPB322LN(2)	0	0	N/A
MPB322LN(3)	0	0	0
MPB322LR(1)	0	0	2
MPB322LR(2)	0	0	0
MPB212LN(2)	0	1	1
MPB212LN(3)	0	1	1
MPB212LR(2)	0	0	0
MPB212LR(3)	0	0	0

00 = transparent; 0 = opaque and uniform; 1 = opaque and somewhat uniform; 2 = phase separated; N/A = not applicable due to phase separation of solution.

The results in Table V show that all PES/SMM mixtures were immiscible, at least by visual observation. Similarly to the situation with the ternary solution, the ability of a given SMM to yield a single macroscopic phase across the concentration range was of interest since films with distinct morphological regions are not usually practical for pervaporation membrane applications. Therefore, a good SMM would only yield small morphological changes, if any, with increasing concentration when mixed with PES. Based on this criterion, the order of the degree of phase separation of SMMs was classified from poor to good as MPB322HN < MPB212HN < MPB212LN < MPB322LN < MPB322LR < MPB212HR < MPB322HR = MPB212LR. A similar behavior between the two batches for a given SMM formulation was again observed. However, it must be emphasized that these results are based only on qualitative visual inspection, and further work should include a more quantitative measure of phase separation in order to provide definite conclusions.

While in general, increasing the amount of SMMs decreased the miscibility, it was not readily clear from the data as to which experimental variable and its associated characteristics (see Table II) determined the degree of phase separation in the binary polymers. There was a

trend associated with the RC. SMMs synthesized with a reduced RC (i.e., polymer with an R in the nomenclature) had a reduced incidence of distinct phase separation. The discussion on the SMM characterization data reported that RC by itself had an effect only on the weight fraction of the prepolymer. When the RC was lowered (i.e., "R"), the weight fraction of the prepolymer showed a significant increase. It was further indicated that RC alone did not exert any effect on the content of the individual components making up the prepolymer (i.e., PPO and MDI); hence, the relationship was specific to the combination of the two, which is equal to $1 - f_z$. Therefore the only clear parameter that is influenced by RC is f_z. Hence, it can be concluded that the miscibility of the SMMs in the cast film is highly dependent on the f_z content. Interestingly enough the three SMMs with the lowest miscibility in the cast films (i.e., MPB322HN, MPB212HN, and MPB212LN) are three of the materials with the highest f_z values (see Table II). However, the fact that the MPB212LR has an f_z value similar to that of MPB322HN but yet has one of the best miscibilities in the PES cast film indicates that other parameters are involved.

In conclusion, while the data for the ternary system suggested that the PPO content was an important factor in determining the miscibility of

Figure 2 Average midpoint T_g of PES and PES/SMM blends (with standard error) for SMMs synthesized with (a) BA-L High and (b) BA-L Low.

the SMMs in the PES solution, this parameter does not appear to be a key factor in assessing this set of SMMs's miscibility in the cast film. It should be noted that Krause[35] and Paul[37] have indicated that the transition of apparently miscible polymer–polymer mixtures from a ternary state with a solvent to a binary one with only polymers can be unpredictable. Specifically, the solvent type can mislead the results since binary polymer mixtures can be immiscible, although their ternary compositions showed otherwise.[35]

Thermal Properties of Cast PES/SMM Films

Miscible polymer pairs are usually optically transparent and show only one intermediate T_g for all compositions.[35] Hence, the miscibility of polymer systems can be detected by measuring its T_g values.[35] To study the miscibility of SMMs in PES, the thermal analysis of random samples cut from uniform and somewhat uniform films were performed (see Table V for films with these criteria). The midpoint T_g (see Figure 2), the T_g width (see Fig. 3), and change in specific heat capacity at the T_g (ΔCp) (see Fig. 4) of the blends were recorded. Since the observations made from the data in Table V indicated that none of the films were transparent, it was expected to find two T_g

values for these materials; however, only one T_g was observed. It is possible that the transitions for the SMMs were not readily detected due to the limited sensitivity of the instrument. This difficulty in measuring the secondary transition at low concentrations was also reported by Burns and Kim.[26] The recorded midpoint T_g values for the blends were those of a PES–rich phase, but they were slightly lower than that of the pure PES, which was recorded at 220°C and also has been reported by others.[38] There were no statistical differences for the behavior of PES/SMM blends for the three concentrations of SMM, indicating the midpoint T_g's lack of sensitivity to the quantity and the distribution of SMM in the polymer.

The width of the T_g transition region for polymers has previously been associated with their microheterogeneity.[39,40] The reported T_g widths in Figure 3 indicate that the PES/SMMs blends have higher heterogeneity than the pure PES material, as the T_g widths are almost double. This was expected due to the effect of SMMs on phase separation, previously noted (see Table V). There were no distinguishable trends among the blends. This is rather surprising since it would have been expected from the data in Table V that an increase in SMM concentration would increase the degree of heterogeneity.

Figure 3 Average T_g width of PES and PES/ SMM blends (with standard error) for SMMs synthesized with (a) BA-L High and (b) BA-L Low.

Figure 4 Change in specific heat capacity (ΔCp) at the T_g of PES and PES/SMM blends (with standard error) for SMMs synthesized with (a) BA-L High and (b) BA-L Low.

Burns and Kim had suggested after a series of studies[26] that a decrease in the change of specific heat capacity at the T_g of the rich-phase polymer component with an increase in the concentration of the poorer phase component was an indication of partial miscibility. As illustrated in Figure 4, only PES/MPB212HR and PES/MPB322LR exhibited degrees of partial miscibility with some confidence (with the given standard errors), whereas a clear immiscibility was observed with the rest of the blends. How this apparent partial miscibility influences solution behavior and solid phase behavior cannot be determined at this time due to the lack of complete phase diagrams.

PES/SMM Surface Characterization by XPS

As discussed previously, it was anticipated that the incorporation of the surface active additive would result in the surface migration and concentration of SMMs to the topmost layer of the membrane surface. XPS is an ideal tool for the study of elemental and chemical group composition within the top 10 nm of the surface. In this work, the film surfaces prepared from PES and MPB322HN, MPB322LN, MPB212HN, and MPB212LN were studied using samples cast from solutions of 0.5,

1.0, and 2.0 wt % SMM. In the case of MPB322HN and MPB212HN, the films at 2.0 wt % SMM were phase-separated samples. The purpose of using the latter samples was to determine if there would be a difference in surface composition when the phase separation phenomenon occurred. The spatial resolution of XPS is limited to 200 μm,[34] which means that there can be large uncertainties associated with extending the results obtained for a particular "spot" studied by XPS to another area. In the case of homogeneous polymers or high molecular weight copolymers, a certain macroscopic homogeneity can be assumed to be valid.[31] However, in this work this is no longer the case because of the heterogeneous nature of the system. Therefore, for each experimental group a certain confidence level was assured by using two separately cast films for the same batch of SMMs and analyzing both in order to generate averages. In addition, two analysis sites on each film were studied. Hence, averages for each element or chemical group were generated with a total of four measurements, and these averages were reported for each SMM/PES combination.

The fluorine content is associated only with the SMMs, and the F/C ratio (see Figure 5) is indicative of the SMM's polyfluoro segment. The high-resolution data from XPS provided information on the PES/SMM composition through two ratios: —CF$_2$—/C—C (Figure 6) and —CF$_3$—/—CF$_2$ (Figure 7), where chemical groups were assigned according to binding energy shifts.[40] Based on the chemical structure of the fluoro-alcohol (Figure 1), the latter of these two ratios represents the degree of end-on orientation of the polyfluoro-segment since the CF$_3$ group is only located at the tail of this segment. Data showing the —CF$_3$—/—CF$_2$ ratio in Figure 7 indicate a trend in which the orientation of the SMMs's polyfluoro ends is predominantly towards the surface. This is supported by the observation showing a consistent increase of the —CF$_3$—/—CF$_2$ ratio from 90° (top 10 nm) to 15° take-off angle (top 2 nm).

Results in Figures 5–7 clearly show the presence of fluorine at the surface of the materials. While it appears that fluorine content at the surface is increasing with increased SMM loading, the intensity ratio is undergoing high fluctuations, thus making it impossible to quantify these changes. Similarly, it was difficult to quantify differences for the fluorine and fluorine group content between the upper surface (15° take-off angle) and lower surface (90° take-off angle) of the materials since the variability from site to site

Figure 5 XPS analysis at different take-off angles, for atomic fluorine with respect to atomic carbon: (a) 0.5, (b) 1.0, and (c) 2.0 wt % of SMM in the PES casting solution.

was so high. It is suspected that the heterogeneous nature of the materials (as suggested by the miscibility studies, Table V) contributed to the amount of variability seen in the XPS data.

The fact that there were no significant differences in fluorine and fluorine group content among the four different SMMs and the layers studied is not particularly surprising. Ward and colleagues[13] had previously indicated that it would take little surface active material to saturate a surface. This was shown experimentally in work by Kasemura and colleagues for modified epoxy resins.[14] Therefore, it would appear that at concentrations of 0.5 wt % SMMs or greater there is a significant amount of SMMs present in order to saturate the surface regions of PES.

Based on the elemental analysis data the average F/C ratio of the bulk SMMs materials themselves (i.e., MPB322HN, MPB212HN, MPB322LN, and MPB212LN) were calculated to be 0.24, 0.38, 0.10, and 0.3, respectively. Figure 5 shows that the average F/C values obtained by XPS for the PES/SMM mixtures are comparable and higher, suggesting that the surface is composed of almost 100% SMMs and in some cases consist primarily of the fluorine tails themselves.

Figure 6 XPS analysis at different take-off angles, for —CF_2— groups with respect to C—C: (a) 0.5, (b) 1.0 and (c) 2.0 wt % of SMM in the PES casting solution.

Figure 7 XPS analysis at different take-off angles, for —CF_3 group with respect to —CF_2—: (a) 0.5, (b) 1.0, and (c) 2.0 wt % of SMM in the PES casting solution.

It was interesting to note that the PES/MPB322HN and PES/MPB322LN surfaces that had exhibited phase separation (Tables IV and V) were not differentiable from the other materials using the XPS technique. It therefore can be hypothesized that migration of SMMs to the surface occurs before the phase-separation phenomenon.

Surface Energetics of PES/SMM Materials

The concentration of the SMMs at the polymer–air interface was indicated by XPS results; however, XPS has limited lateral resolution (~ 200 μm).[34] The use of contact angle measurements is a practical means of obtaining surface information over a larger area of the surface. In this work, water was used as the test liquid to provide a direct measure of surface hydrophobicity in air. The average advancing contact angle (θ_{adv}) for the PES/SMMs surfaces with the eight types of SMMs are shown in Figure 8, whereas their average receding angle (θ_{rec}) are plotted in Figure 9. All surfaces containing SMMs are more hydrophobic than the pure PES surface and, in general, the contact angles increase with increasing concentration of SMMs. The exception was PES/MPB322HN, where (θ_{adv}) and (θ_{rec}) indicate that saturation was reached at 0.5 wt % SMMs. The surface of the PES membrane containing SMMs synthesized with BA-L High generally had higher contact angles (θ_{adv} and θ_{rec} values) than those containing SMM synthesized with BA-L Low. PES/SMMs mixtures related to the former groups

achieved θ_{adv} values close to that of Teflon™ (i.e., 116°[22]). However, the highest average values of receding angles of these same systems (Figure 9) was not as close to the value of pure Teflon™, which is 92°.[22] There was no trend correlating θ_{adv} values with either RMR or RC. On the other hand, the θ_{rec} value was consistently higher for SMMs synthesized with an RMR of 212 versus 322 (see Figure 9). Hence, unlike the XPS results, the contact angle data show that the surface characteristics of PES/SMM blends were dependent on the specific SMM formulation and the concentration of SMM.

Model of SMM/PES System

By combining the information from the T_g data, XPS analysis, and contact angle measurements, it is possible to propose a model for the structure of the SMM/PES membrane. A schematic of the conceptual state for this system is illustrated in Figure 10. The DSC thermal analysis data indicated that there would be phases of SMM dispersed in PES. The size of these dispersed phases in some cases must be less than 100 μm (limit of visual detection). The shape of these phases would likely be spherical in order to minimize interfacial tensions,[30,31] since the general morphology of immiscible and partially miscible systems has been noted as being spherical domains of one material within the rich phase of the other material.[41] The XPS results showed that for at least the top 10-nm surface layer there were elevated levels of

pure SMMs. Future work will attempt to validate this proposed model using various microscopy techniques, such as atomic force microscopy, polarized light microscopy, and confocal microscopy.

CONCLUSIONS

The following conclusions were drawn from the above experimental results:

1. The increasing weight fraction of PPO in the SMMs and increasing SMMs molecular weight contributed to an increased phase separation in the ternary PES/SMM/DMAC system, where the composition of PES was fixed at 25 wt %. However, increasing the weight fraction of the prepolymer in the SMM and hence decreasing the fluorine content contributed to a decreased phase separation in the binary PES/SMM system (i.e., cast solid phase).
2. XPS and contact angle studies showed that

Figure 8 Advancing contact angle (δ_{adv}) for surfaces of PES/SMM blends containing SMMs synthesized with (a) BA-L High and (b) BA-L Low. Note: Data for 2.0 wt % of MPB322HN and MPB212HN were not obtained because the surface roughness that resulted from phase separation made it impossible to obtain reliable data.

Figure 9 Receding contact angle (δ_{rec}) for surfaces of PES/SMM blends containing SMMs synthesized with (a) BA-L High and (b) BA-L Low. Note: Data for 2.0 wt % of MPB322HN and MPB212HN were not obtained because the surface roughness that resulted from phase separation made it impossible to obtain reliable data.

SMMs have successfully migrated to the surface of PES.
3. XPS studies indicated a similar surface chemistry for all materials containing MPB322HN, MPB322LN, MPB212HN, and MPB212LN, within the 2- to 10-nm surface range.
4. Contrary to the XPS data, the contact angle data do indicate that these material differ in their chemical modification effect at the surface. All SMMs influenced the surface energetics of PES. The polymer systems PES/MPB322HN, PES/MPB212HN, PES/MPB212HR, and PES/MPB212LN achieved θ_{adv} values close to that of Teflon™. However, the highest average values of receding angles of these systems were lower than that for Teflon™.

Figure 10 Conceptual model of a typical cast PES/SMM surface produced in this work. Note: the expanded and top views are not to scale with the side view.

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