Effect of Copolymer Composition on the Solubility and Diffusivity of Water and Methanol in a Series of Polyether Amides

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ABSTRACT: Sorption and diffusion of water and methanol in polydimethylsiloxane and a series of PEBAX™ copolymers (polyether block amide copolymers) were measured over a wide range of activities near room temperature. The goal was to identify a membrane material for separation of the hazardous air pollutant methanol from wet air streams in the pulp and paper industry. The PEBAX™ copolymer series used here allows a unique insight into transport of small molecules, because solubilities are virtually constant, while diffusion coefficients vary. This is due to the similar chemical structure, but different chain mobility of the homopolymers. The grade PEBAX™ 2533 is most promising for the separation process due to high solubility and diffusivity. The unwanted simultaneous highly selective separation of methanol and water from the targeted air/vapor streams will be addressed in future work. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1983–1993, 1997

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INTRODUCTION

Methanol vapor present in water wet air streams has clearly been identified as one of the major hazardous air pollutants emitted from pulping and papermaking operations.[1] In a typical pulp and paper mill using the Kraft process,[2] methanol is emitted at many points in the process. As wood is chemically treated to liberate individual cellulose fibers that will be made into paper, the lignin, an organic network polymer present in the wood, is decomposed into lower molecular weight organic compounds. These processes are carried out in an aqueous phase medium at high pH. Very large amounts of water are employed. Conventional equipment (washers, holding tanks) is not pressure tight, and operates above ambient temperature. Many of the separation stages operate in "open" systems where loss of some of the aqueous phase in the form of vapors occurs. The dissolved organics present as byproducts from chemical pulping may have a much higher vapor pressure than water, and therefore, partition preferentially into the vapor phase. Methanol is the most significant example.

Major equipment and processing changes would be required to eliminate all air–liquid contacts currently present in pulp and paper mills.

Failing this, the partial migration of organics from the liquid to the air phase will continue. It is unrealistic to expect that complete renovation of a majority of mills will occur, due to the prohibitive investment costs that are involved. Entirely novel methanol control technologies are not currently realistic. However, methanol must be captured, because it will have to be removed from the process in a controlled fashion. Therefore, we have chosen to focus our efforts on the recovery of organics from mixtures with air, with methanol as the representative example.

The ultimate goal of our work is a technology that can be used as a retrofit to existing mills to control hazardous air pollutant emissions. Methanol is the most prominent contributor to these emissions and will serve as our model compound.[1] We chose to investigate membrane vapor separation for this purpose.

Polymeric membranes have inherently high selectivities for organics over air. Membrane vapor separation units are rugged and can be built to treat point sources.[3] The organics are recovered as liquids without cumbersome regeneration or disposal problems that occur with adsorption or bioremediation.

Membrane vapor separation is being evaluated here as a potential technology for the recovery of methanol. In this process, organic vapors are separated from the feed stream by permeation through an ultrathin polymeric membrane with outstanding affinity for the organic component. Current industrial-scale applications of this process include recovery of fuel vapors from tank farms and recycling of solvents and chemicals.[4]

The vapor separation membrane module itself contains no moving parts. Modularity of the system allows expansions and adaptation to the volume to be treated. Ideally, the result of the membrane separation process is recovery of nearly all organics in liquid form for easy reuse, transport, or disposal. Through internal recycling schemes, the process can be adapted to feeds with low or high concentrations.

TECHNICAL APPROACH

A membrane material capable of recovering methanol while allowing the majority of the water and air to pass through the unit is required for this application. The affinity of the membrane material for a minor component of the feed stream (methanol) allows removal of a highly concentrated solvent vapor by permeation through the membrane.

As only limited data regarding diffusivity of water and methanol from the vapor phase through polymers is available, experimental evaluation of candidate polymers was made. This entails determination of basic transport properties (sorption, diffusion) of candidate polymers when contacted with methanol, water, and air. The initial material evaluation is reported here.
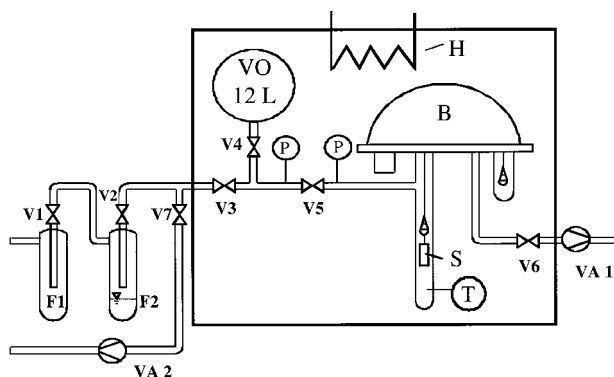
PREVIOUS STUDIES

The system polydimethylsiloxane (PDMS)/water was included in the work presented here to validate the experimental technique by comparison with existing data (see discussion). After many years of experimental work (e.g., refs. 5–7), the diffusivity of water in PDMS remains under discussion. A review and additional data has recently been published.[8] Watson and Baron challenge the view that clustering of water molecules decreases the diffusion coefficient with increasing water sorption. Our data appears to support this view.

The literature yielded no comparable results for the diffusivity of methanol in PDMS beyond Favre et al.[5]

The transport properties of polyether block amides (PEBAX™), especially for water and methanol, have rarely been reported in the literature. Some PEBAX™ grades show a very high affinity for water. Therefore, this polymer was chosen to investigate the separation of methanol from air streams. The availability of a wide range of copolymers allows unique insights in structure/ property relationships. Optimization of the polymer for the separation process may then be possible. Depending on chemical composition, PEBAX™ grades can exhibit two glass transition temperatures far below and above room temperature. PEBAX™ has been evaluated for the separation of liquid acetone/water mixtures by pervaporation.[9] Although the grade of PEBAX™ was not given, the low acetone selectivity may indicate a grade with low polyamide content. Permeability coefficients cannot be derived, because the effective membrane thickness was not given.

It is of some interest to investigate the literature for the transport properties of homopolymers made from the monomer units of PEBAX™. Copolymer properties could then potentially be predicted.[10] The transport properties of the system polyamide/water have been reviewed.[11] This re-

Figure 1 Schematic of apparatus for dynamic sorption–desorption measurements. (B) Cahn microbalance, (H) heater, (V) valve, (VO) ballast volume, (F) flask, (VA) vacuum pump, (S) sample, (T) temperature indicator, (P) pressure gauge.

view lists experimental data for water uptake in Nylon 12 of 12.6 to 13.8 cc(STP)/cc Polymer at $25 \pm 5°C$ and an activity of 0.6. This data clearly confirms the magnitude and trend of water sorption in PEBAX™ grades with increasing polyamide content (Fig. 5). Using a model,[11] a diffusion coefficient of 5.4×10^{-9} cm²/s of water in Nylon 12 at unit activity and 30°C can be predicted. Considering the many assumptions for the model, this value corresponds reasonably well with another source.[12] The decrease in the diffusion coefficient of water with increasing polyamide content of PEBAX™ grades as found in this work is generally confirmed.

Unfortunately, no studies of the diffusivity of water or methanol in polytetramethylene oxide (PTMO) were found in the literature. Therefore, no attempt could be made at predicting copolymer properties from the homopolymers.

EXPERIMENTAL

The absorption–desorption kinetics and the solubility of methanol vapor, water vapor, and dry air in a series of PEBAX™ polymers and PDMS were studied by a gravimetric method. This method consists of measuring the rate of weight gain or loss of a sample due to sorption or desorption. The weight change is determined with an automatic electromicrobalance incorporated in a vacuum system as shown in Figure 1.
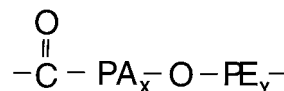
An electronically controlled beam balance was used (Cahn Instruments, Inc.; Cerritos, CA; Model D-200). On both sides of the beam, hang-

down wires with sample baskets were suspended in glass tubes. One basket holds sheets of the sample material; the other holds tare weights. For the configuration employed, the balance had a maximum load-carrying capacity of 3.5 g and was capable of registering weight changes of up to 750 mg with a sensitivity of 1 mg.

The vacuum system consisted of two flasks, F1 and F2, to generate the solvent vapor, a ballast volume (approximately 12 L) to reduce pressure fluctuations during the runs due to absorption, and two vacuum pumps with cold traps (VA1: Precision Scientific, Model D25. VA2: Edwards, Model E2M2). Pump VA1 was used to evacuate the system up to valve V5 during the desorption runs, and pump VA2 was used to evacuate the remainder of the system and to adjust the vapor pressure prior to sorption experiments. The pressure was measured with two absolute pressure transducers (MKS, range 0–1000 cmHg and 0–100 cmHg). The temperature inside the isolated chamber (black box in Fig. 1) was held at $30 \pm 0.1°C$.

For gas absorption, a sample of known thickness is placed on the hangdown wire. Valve V5 is closed and the system evacuated with pump VA1. In this stage, any remaining penetrants are removed. Solvent is filled in Flask F2 at room temperature. Valve V1 was closed and the left part of the system was evacuated with pump VA2 to remove any air. To start the run, valve V6 is closed and data recorded every 5 s. After 60 s valve V5 is carefully opened and the sample exposed to the solvent vapor. Typically, about 30 s is required for the pressure in the balance system to reach steady state. No data for this initial transient pressure period was used in the analysis. Sorption was allowed to continue for a period of at least 20 times the half-time (time for 50% final penetrant uptake).

Desorption measurements followed each absorption measurement. Valve V5 was closed and the data recording started. After 60 s, valve V6 was opened to evacuate the system. This pump was capable of evacuating the system within several seconds. The run was terminated after the same time had elapsed as during absorption.

Figure 2 Chemical structure of PEBAX™.

Table I   Physical Properties of the Different PEBAX™ Grades

	PEBAX™			
	2533	3533	5533	6333
"x" (number of PTMO groups per repeat unit)	2.68	3.42	14.85	19.30
"y" (number of PA groups per repeat unit)	27.80	26.00	24.70	16.60
Weight percent PA	21.6	27.1	62.2	75.8
T_g PTMO (°C)	−76	−72	−65	−60
T_m crystalline PTMO (°C)	12	7	None detected	None detected
T_g PA (°C)	All between 65 and 75			
T_m crystalline PA (°C)	137	142	160	170

MATERIALS

Polymers

The polymers used in this study were Polydimethylsiloxane (PDMS) and polyether block amide (PEBAX™).

The PDMS films were cast from commercially available components (General Electric) with no fillers or additives. As solvent, toluene was used. The sample was dried at room temperature for 2 weeks and at 100°C for 48 h under vacuum (vacuum pump equipped with an aluminum oxide backdiffusion trap). The density of PDMS is reported to be 1.02 g/cm^3.[13] The thickness, δ, was evaluated with a thickness gauge at 21 positions on the sample. The arithmetic average was 0.502 ± 0.074 mm. The glass transition temperature, T_g, was measured using differential mechanical thermal analysis to be −123°C. This is in good agreement with the published value.[13]

A series of PEBAX™ samples in the form of pellets was generously supplied by Elf Atochem (Philadelphia, PA). PEBAX™ 2533, 3533, 5533, and 6333 were evaluated. The general chemical structure of PEBAX™ is given in Figure 2.

PA represents polyamide, and PE is a polyether segment. In the PEBAX™ series studied here, Nylon 12 and polytetramethylene oxide (PTMO) were present in varying ratios. An elemental analysis for carbon, hydrogen, nitrogen, and oxygen was performed by Huffman Laboratories (Golden, CO). The number of repeat units of polyamide

and polyether in each monomer segment (subscripts "x" and "y" in Fig. 2) were calculated. Initial guesses for "x" and "y" were based on the literature.[14,15] Using these guesses and the known structure of Nylon 12 and PTMO, the resultant mass fraction of each element was calculated. These calculated values were compared to the experimentally measured mass fractions and an overall error (defined as the sum of the error for each element) was minimized via iteration. The results are reported in Table I.
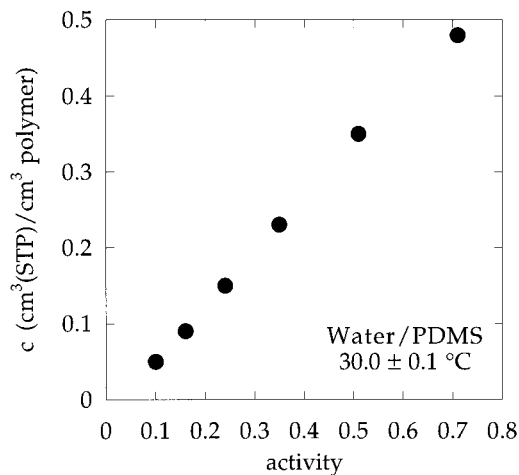
The T_gs were measured using differential scanning calorimetry (DSC) under nitrogen. Scans were run from −100 to 200°C at a heating rate of 10°C/min. The measured values are reported in Table I. Thermal analysis of the PEBAX™ grades indicated two distinct glass transition temperatures as well as crystalline melting peaks near 10 and 140°C.

PEBAX™ films were melt extruded using a Haake Buckler extruder fitted with a flat film die. The extrusion temperature ranged from 140 to 180°C, depending on the material. The motor speed was varied between 5 and 30 rpm. Sample thickness was controlled by the motor speed and the speed of the take up roller. Sample thicknesses are reported in Table II.

All films were optically clear and remained so throughout the preparation and testing process. Samples were dried under vacuum for 14 days at 40°C. The vacuum pump was equipped with an aluminum oxide backdiffusion trap. Following

Table II   Thickness and Standard Deviation for PEBAX™ Samples

	PEBAX™ 2533	PEBAX™ 3533	PEBAX™ 5533	PEBAX™ 6333
Thickness, δ (mm)	0.470 ± 0.011	0.470 ± 0.023	0.432 ± 0.023	0.125 ± 0.005

Figure 3 Solubility of water in PDMS as a function of activity at 30°C.

drying, all samples were stored in a desiccator until further use. The density of the PEBAX™ grades tested was reported to be 1.01 g/cm³.[16]

Solvents

Methanol (Fisher Chemical, technical grade, 99.9% purity) and water were used. Both penetrants were subjected to a series of freeze–thaw cycles before use. The measured vapor pressures were in good agreement with those reported by Reid, Prausnitz, and Poling.[17]

TREATMENT OF EXPERIMENTAL DATA

Solubility

The equilibrium sorption for each penetrant was calculated using

$$c = \frac{22414 \, | M_f - M_i |}{MW \cdot V_p} \qquad (1)$$

where c is the equilibrium concentration of the penetrant [cm³(STP)/cm³ polymer]; 22414 is the volume (cm³) of 1 mol of penetrant at standard temperature and pressure; M_i and M_f are the initial and final masses (g), respectively; MW is the molecular weight of the penetrant (g/mol); and V_p is the polymer volume (cm³). Standard conditions were taken as 0°C and 1 atm.

The solubility coefficient, S, is defined as:
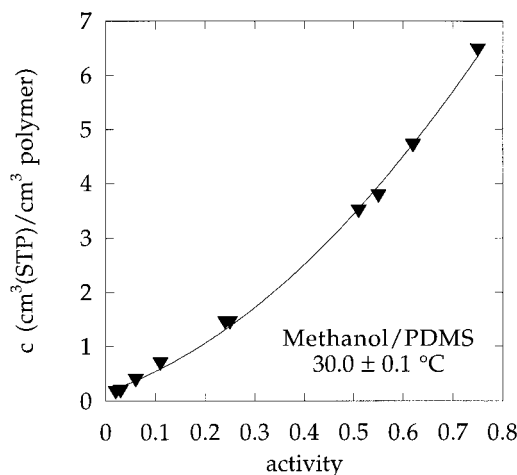
$$S = c/p \qquad (2)$$

where p is the vapor pressure. Solubility coefficients were needed to calculate permeability coefficients. The permeability coefficients at low activities were of interest for the methanol separation process. Therefore, eq. (2) could be used directly, because the concentration c is linearly related to the vapor pressure in this range.
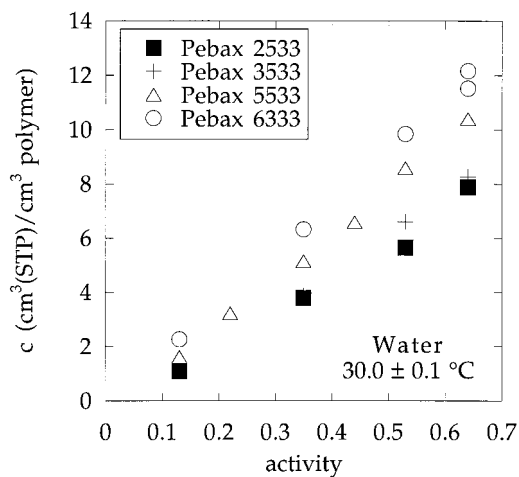
Diffusion Coefficients

The diffusion coefficient can be determined from the transient portion of the sorption process. The necessary relationships were obtained from the solution of Fick's second law by Crank[18] obeying boundary conditions equivalent to the ones in this study. At short times, the diffusion coefficient can be estimated from a plot of M_t/M_∞ versus the square root of time:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{\delta^2} \right)^{1/2} \qquad (3)$$

where M_t and M_∞ are the weight gain by the sample at time t and at equilibrium, respectively, δ is the thickness of the sample, and D is the mutual diffusion coefficient. This equation is only valid for applications with a constant diffusion coefficient. However, Crank and Park[19] showed that for cases of nonconstant D, the average diffusion coefficient over the entire experimental range is calculated. This method can be applied up to a normalized mass uptake M_t/M_∞ of 0.6 with negligible devia-

Figure 4 Solubility of methanol in PDMS as a function of penetrant activity. The dark line represents the data published by Favre.[5]

Figure 5 Solubility of water in a series of PEBAX™ polymers as a function of activity.

tions from the exact solution of Fick's second law. The short-term method was used in this study to analyze the data. The time required to bring the sample environment from vacuum to the vapor pressure of the run is small compared to the experimental timescale, but not zero. The raw experimental data (weight vs. time) was therefore shifted so that a zero time/zero uptake intercept of the linear regression (up to $M_t/M_\infty = 0.6$) was obtained.

Crank and Park[19] also introduced the long-term method to calculate the diffusion coefficient from experimental data. The long-term method proposes a linear relationship in a plot of $\ln(1 - M_t/M_\infty)$ versus time t:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D}{\delta^2}\right)t \qquad (4)$$

This method was used for a normalized mass uptake between 0.5 and 0.85. The uncertainty of the starting time has negligible influence on the results of the long-term method. The starting time determined through the shift of the raw experimental data to satisfy the zero time/zero uptake intercept was used (see above). Agreement between the diffusion coefficients from the short- and long-term methods was very good. This shows the high reliability of the results obtained here.

The reported diffusion coefficients were calculated by first averaging the results of the short-term and the long-term method for each sorption and desorption experiment. Then, the final value

is obtained by averaging the results of the corresponding sorption–desorption runs.

Permeation Coefficients

The permeation coefficient of each penetrant has been calculated as the product of the diffusion and sorption coefficients according to

$$P = DS \qquad (5)$$

RESULTS

Solubility Measurements

To ensure that the data obtained were accurate, the sorption of water and methanol in PDMS was measured and compared to values reported in the literature.

PDMS/Water

The solubility of water in PDMS was determined at $30.0 \pm 0.1°C$ over the pressure range of 4 to 21 cmHg, or an activity range of 0.13 to 0.64. Experimental results are presented in Figure 3 in the form of a solubility isotherm. The isotherm is linear, indicating that the sorption can be described by Henry's law for this activity range. The solubility of water in PDMS is quite low (<0.5 $cm^3(STP)/cm^3$ polymer at an activity of 0.7).

The behavior of water in PDMS has been the subject of recent analysis by a number of researchers. Unfortunately, there is some discrepancy as to the exact numerical results. The compliance with Henry's law over this activity range, and the order of magnitude of the sorption found in our work are consistent with the published data.[5]

PDMS/Methanol

The solubility of methanol in PDMS was measured at $30.0 \pm 0.1°C$ over the pressure range 4 to 122 cmHg, or an activity range from 0 to 0.75. Experimental results are presented in Figure 4. As with the sorption of water, the sorption of methanol is linearly related to the applied penetrant pressure at low penetrant activities. However, at activities above about 0.3, there is clear curvature in the sorption isotherm, indicating that Henry's law no longer applies. Furthermore, the absolute value of sorption of methanol is an

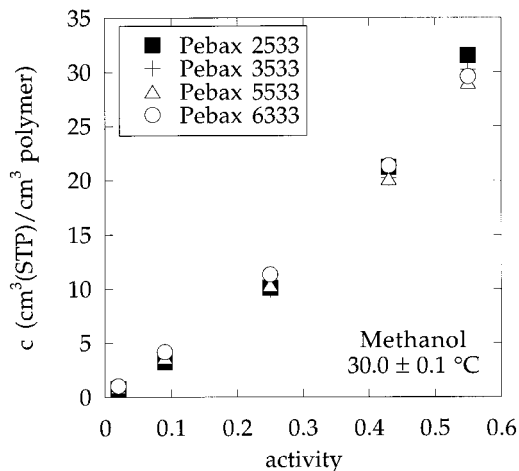order of magnitude greater than the sorption of water.

The results for the measurements with PDMS were compared to those reported by Favre[5] after correcting for temperature (solid line in Fig. 4). Temperature correction was performed using the interaction parameter calculated with the equations from Koningsveld and Kleinjtens.[20] The Favre data was obtained with a vapor permeation module. The agreement between our data and that of Favre is quite good. This is a very good validation of our experimental method.
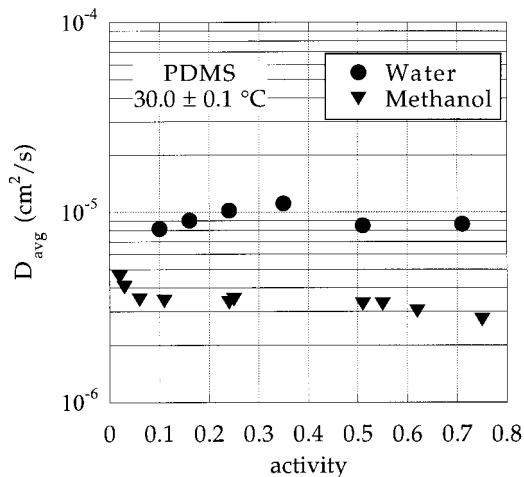
PEBAX™/Water

The solubility of water in a series of PEBAX™ polymers was determined at $30.0 \pm 0.1°C$ over the pressure range of 4 to 21 cmHg, or an activity range of 0.13 to 0.64. Experimental results are presented in Figure 5. Each of the isotherms is essentially linear with activity and shows no pronounced swelling or plasticization behavior. Interestingly, the total sorption, at a given activity, is not markedly affected by the polymer composition. Slight increases in the sorption of water are observed in the order of increasing PA content of PEBAX™ 2533 < 3533 < 5533 < 6333.

PEBAX™/Methanol

The solubility of methanol in the PEBAX™ series was determined at $30.0 \pm 0.1°C$ over the pressure range of 4 to 90 cmHg, or an activity range of 0.02 to 0.55. Experimental results are presented in Figure 6. Each of the isotherms is essentially lin-

Figure 7 Average diffusion coefficient for water and methanol in PDMS as a function of penetrant activity.

ear and shows no pronounced swelling or plasticization behavior. The total sorption, at a given penetrant activity, is essentially unaffected by the polymer composition. Within experimental error, all four polymers exhibit the same total sorption.
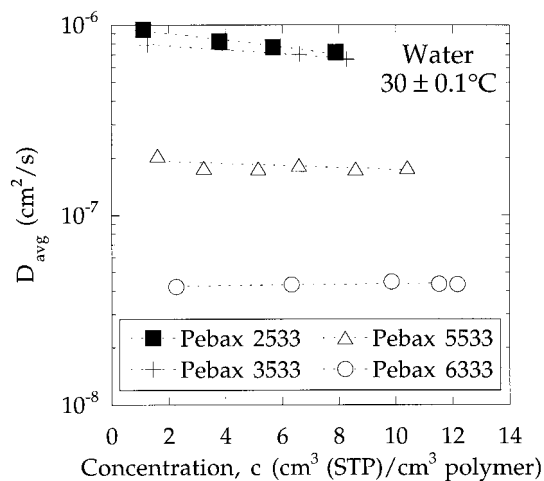
DIFFUSION COEFFICIENTS

PDMS/Water/Methanol

The mutual diffusion coefficients, D, for water and methanol in PDMS were determined from the absorption and desorption rates using both the short-time and long-time methods as discussed above. The results are presented in Figure 7. The diffusion coefficients for both water and methanol are nearly independent of activity over the conditions investigated.

A recent publication by Watson and Baron reviews published diffusion coefficients for water in PDMS.[8] In contrast to previously published data,[5,6] which demonstrate decreases in the diffusion coefficient with increasing penetrant concentration, Watson and Baron report an essentially constant diffusion coefficient over a wide concentration range. The published values of diffusion coefficients as summarized by Watson and Baron vary by nearly an order of magnitude.

The data reported here is in acceptable agreement with that of Watson and Baron. In both data sets, the diffusion coefficient is observed to be independent of penetrant concentration. The average diffusion coefficient measured by Watson and Baron was 1.2 to 1.9×10^{-5} cm^2/s.[8] The values

Figure 6 Solubility of methanol in a series of PEBAX™ polymers as a function of activity at 30°C.

Figure 8 Average diffusion coefficient for water in a series of PEBAX™ polymers as a function of penetrant concentration. Lines drawn as visual aid.

measured here range from 0.8 to 1.1×10^{-5} cm²/s. Considering the variability in the previously reported data, this agreement was deemed acceptable.

PEBAX™/Water

The diffusion coefficient of water in the PEBAX™ series was measured under the same conditions as the sorption isotherms. The results are presented in Figure 8, which shows that the diffusion coefficients are essentially independent of concentration over the interval investigated. However, there are marked differences in the diffusion coefficient of water in each of the four PEBAX™ grades. The trend is (increasing diffusion coefficient with decreasing polyamide content): 2533 ≈ 3533 > 5533 > 6333.

The absolute value of the diffusion coefficients ranges from approximately 3×10^{-8} to 1×10^{-6} cm²/s.

PEBAX™/Methanol

The mutual diffusion coefficient of methanol in the PEBAX™ series was measured under the same conditions as the sorption isotherms. The results are presented in Figure 9, which shows that for grades 2533 and 3533, the diffusion coefficients are essentially independent of concentration over the interval investigated. Concentration dependence, which was not apparent in Figure 6, is clearly apparent here for PEBAX™ grades 5533 and 6333. This is most likely due to the plasticiza-

tion of PEBAX™ grades 5533 and 6333 by methanol.

There are marked differences in the diffusion coefficient of methanol in each of the four polymers investigated. The trend in diffusion coefficients is the same as for water (increasing diffusion coefficient with decreasing polyamide content). The absolute values of the diffusion coefficients range from approximately 1.5×10^{-8} to 4×10^{-7} cm²/s.
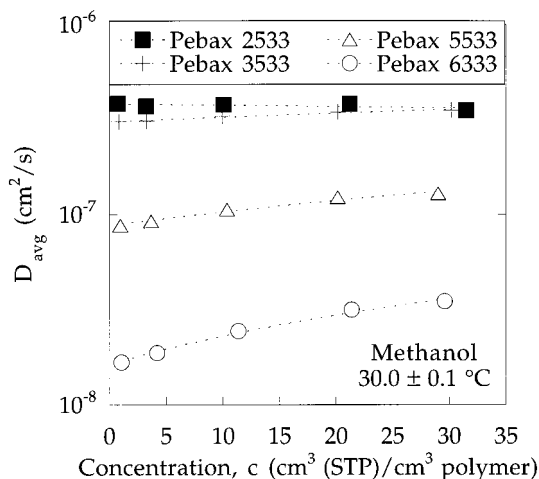
Permeation Coefficients

In the analysis of the membrane separation process, the relative rates of permeation through the polymer matrix is the key material property. Therefore, for each of the penetrants, the permeability has been calculated from eq. (5). In Table III, the calculated permeability for each material is reported at an activity similar to the level that would be encountered in the methanol recovery application of interest.

Due to the very low sorption of air in the polymer samples, the inaccuracy of the reported permeabilities for this penetrant is relatively high, estimated as ±50%. The relative inaccuracies are only approximately ±2% for the reported permeability coefficients of methanol and water.

DISCUSSION OF RESULTS

Membrane Separation Process

Ideally, if a membrane process were to be employed in recovery of vaporous methanol from hu-

Figure 9 Average diffusion coefficient for methanol in a series of PEBAX™ polymers as a function of penetrant concentration. Lines drawn as visual aid.

Table III   Calculated Permeability Coefficients and Selectivities for Methanol, Water, and Air Transport through PEBAX™ Polymers

PEBAX™ Grade	Permeability (Barrer)			Ideal Selectivity	
	Methanol[a]	Water[b]	Air[c]	Methanol/Air	Methanol/Water
2533	8090	25600	4.4	1840	0.32
3533	6840	27450	5.1	1340	0.25
5533	2250	8910	2.1	1070	0.25
6333	520	2590	0.3	1730	0.20

1 barrer $= 10^{-10}$ cm^3 (stp) cm/cm^2 s cmHg.
[a] Methanol activity, 0.09.
[b] Water activity, 0.53.
[c] Air pressure, 73 cmHg.

mid air streams, it would preferentially permeate the methanol while excluding nearly all water and air from the permeate. Further, the rate of methanol transport should be as fast as possible, thereby minimizing the size of the membrane unit required. An appreciation for the ability of a particular material to complete this separation can be gained by evaluation of the ideal separation factors in Table III.

The ideal separation factor, defined as the ratio of the independently measured single-component permeation coefficients, provides a useful measure of the actual separation for polymers that exhibit Henry's law type sorption if there is no strong interaction of the various penetrants, and if the polymer does not undergo plasticization or swelling.[21] For the activity ranges of interest, swelling was not evident from the sorption measurements.

Each of the polymers in the PEBAX™ series evaluated here exhibits an outstanding ability to separate methanol from air, with selectivities of greater than 1000. PEBAX™ grade 2533 would appear to be the most attractive for this separation based on its high methanol permeability.

However, none of these polymers demonstrates the ability to selectively remove methanol from a water-wet air stream. Because these materials actually transport water faster than methanol, the permeate would consist of a methanol/water mixture, and the retentate would be a well-dried air stream. Thus, the goal of methanol recovery could be realized, but only at the added expense of a very large membrane area, which would be required to transport both the minor constituent (methanol) and the contaminant water.

Efforts are underway to overcome these limitations. We will report in the future on modifications

of the mode of operation that will make full use of the high methanol selectivities, while avoiding problems with water permeation.

Transport Properties of Copolymers

The series of PEBAX™ polymers investigated is interesting in that although the films evaluated are optically clear, thermal analysis clearly demonstrates two distinct T_gs. Evaluation of Table I indicates that the thermal properties of the polymer are not influenced by the relative composition of polyether and polyamide segments. This is indicative of a microphase separated polymer.[22,23] The possible presence of two distinct phases in the polymers evaluated introduces some complications in the analysis.

The polyether phase has a T_g well below room temperature. Therefore, sorption into this phase would be expected to obey Henry's law with linear sorption isotherms up to the activity at which swelling becomes apparent. However, the polyamide segment has a T_g of approximately 40°C above the measurement temperature. Therefore, dual-mode type sorption isotherms, as are typical of glassy materials, may be expected from this fraction of the polymer.

Evaluation of the sorption isotherms for water and methanol in PEBAX™ (Figs. 5 and 6) indicates that, within the experimental error, all isotherms are linear with penetrant activity. Even for grade 6333, which is approximately 75 wt % glassy polyamide, no dual-mode behavior is observed.

A number of factors may be contributing to this behavior. First, the overall sorption measured is the sum of sorption into the rubbery PTMO phase and into the glassy PA phase. Any dual-mode be-

havior that may be present in the PA phase could be masked when superimposed on that of the PTMO phase.

It is further possible that the PA phase itself exhibits little or no dual mode sorption behavior. Stern has reported on the sorption of ethane and butane into polybutylmethacrylate over a range of temperatures traversing the T_g.[24] Even at temperatures 30°C above T_g, the sorption isotherm exhibited no dual-mode behavior. Rather, for the entire temperature range that was covered, the sorption isotherms were well described by Henry's law. Stern attributed this to the fact that the T_g is a temperature range, rather than a singular temperature.

Influence of Polymer Structure on Transport Properties

The copolymers evaluated here provide a unique look at a series of materials with essentially constant solubility, but varying diffusion coefficients.

Equilibrium sorption is determined by thermodynamic interactions between the polymer and the penetrant.[25] Thus, changes in the chemical nature of the polymer (such as changes in polarity) may manifest themselves as changes in the level of equilibrium sorption. In the series of polymers evaluated here, the relative content of polyether and polyamide groups is varied. The two constituents, PTMO and PA, have the chemical structures of $-(CH_2)_4-O-$, and $-NH-(CH_2)_{11}-CO-$, respectively. Because both materials have rather long aliphatic components, the chemical affinity of each for water and methanol is expected to be similar. This is consistent with the virtually constant equilibrium sorption for each of the block copolymers.

While the chemical nature of each of the blocks of the copolymer are nearly equivalent, their thermal behavior is not. At the evaluation temperature, the PTMO is in the rubbery range, and the PA has glassy characteristics. Thus, the kinetic behavior (chain mobility) of the two, which controls the rate of diffusion, is markedly different. These differences manifest themselves as differences in the diffusion coefficients. As the content of PA in the copolymer increases, the measured, average diffusion coefficient decreases. The diffusion coefficient in these materials is well correlated with the weight fraction of PA in the copolymer.

CONCLUSIONS

The PEBAX™ materials evaluated here can be used to selectively separate methanol from air, but not methanol from water. The 2533 grade appears to be the most promising based on its high permeation rates. If one of these materials were to be used in a membrane system for the recovery of methanol from water-wet air streams, the permeate product would be a mixture of methanol and water. Research is under way that will address this limitation, while simultaneously making full use of the very high methanol/air selectivities.

The PEBAX™ materials are unique in several respects. Because of the similar chemical nature of the two components of the copolymer, the equilibrium sorption of water and methanol in each of the polymers is essentially equivalent. However, the diffusion coefficient decreases markedly as the glassy polyamide content is increased.

Although the PEBAX™ polymers exhibit two T_gs, they are optically clear. Therefore, microphase separation is probable, but, if present, it must be present on a local scale only. The sorption isotherms of these materials (even those with up to 75 wt % glassy polyamide) obey Henry's law and show no evidence of dual-mode behavior. This may be attributable to masking of the sorption in the glassy phase by sorption into the rubbery phase. In addition, the presence of only minimal dual-mode behavior in the glassy phase could be explained by the close proximity of the measurement temperature to T_g.

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