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Final Report

Membrane Technology for Recovery of Organic Vapors in the Paper Industry

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The Georgia Consortium for Technological Competitiveness in Pulp and Paper

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Executive Summary

Motivation

Hazardous Air Pollutants (HAP's), including methanol, have become a focus for reduction of gas/vapor emissions from pulp and paper mills. Methanol is used in this work as the representative volatile organic carbon, since it constitutes the majority compound, and is the focus of regulatory activity. This research program examined the ability to use an emerging technology (membrane vapor separation) for the selective separation of methanol from gas/vapor streams to minimize emissions from significant point sources. The recovery of methanol using membrane permeation would provide a simple and rugged process (no moving parts, recovery of methanol as a byproduct) and compliance with current and future emissions regulations.

Summary of Work

This project includes an evaluation of possible changes in pulp storage tank operation (a major point of methanol emissions), search for an optimized membrane polymer, membrane formation, and a preliminary system design.

Recirculation of the gas/vapor mixture through the open volume at the top of a high density pulp storage tank would be an advantageous process to extract methanol. This requires changes from the current free convection stacks often used on storage tanks. A blower would be used to feed a vapor/air mixture from the storage tank to the membrane vapor separation unit. The membrane unit would separate the majority of the methanol from the stream, and the methanol depleted stream is returned to the tank to extract more methanol.

Several polymers were tested for their selectivity for water, methanol, and air. Selectivities for methanol over air are very high, exceeding a factor of 1000 (see Appendix A). However, water was also found to be very selectively transported through the membrane, leading to unwanted dehydration of the feed stream, and excessive membrane area requirements. This problem is currently being addressed in work sponsored by the U.S. DOE (steam purge on the membrane permeate side).

Formation of high performance composite membranes from candidate polymers was shown in the laboratory. This confirms that membranes can be produced for this process by commercial suppliers.

Using the permeability data obtained in this work, and under the assumption that water is not permeating significantly (steam purge, see below), the needed membrane area to treat the methanol from a high density pulp storage tank (about 14 m^2) would be easily incorporated in three commercial-size spiral wound membrane modules. The practical feasibility of the steam purge is currently being investigated in a project sponsored by the U.S. Department of Energy.

Background

Table 1 shows a comparison of different organic vapor control technologies. The advantages of membrane separations are significant.

	Methanol recovered	*Regenerate /dispose of adsorbent*	*Sludge generated*	*Startup/shutdown procedure*	*Tolerates feed changes*
Membrane Separation	**yes**	**no**	**no**	**simple**	**yes**
Adsorption	possible	yes	no	yes	limited
Bio Reactor	no	no	yes	complex	no

Table 1: Comparison of alternative control methods for methanol emissions.

Membrane vapor separation is being evaluated here as a potential technology for the recovery of methanol [Peinemann, et al., 1986]. 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 solvent recycling.

The vapor separation device itself contains no moving parts. Modularity of the system allows expansions and adaptation to the volume to be treated. The targeted result of the membrane separation process is recovery of nearly all organics as liquids for easy re-use, transport or disposal. Through internal recycling schemes, the process can be adapted to feeds with low or high concentrations.

Technical Approach

Methanol was chosen as the model organic, since it is the majority component, when compared with other materials emitted in gas and vapor form.

There are numerous point sources of methanol emissions in a mill. Individual treatment of each of these points is not practical. Rather, we have chosen a significant source in the early stages of the process (pulp storage) where we hope to recover a large fraction of the methanol from the system and thereby minimize all downstream emissions. Once the methanol is transported downstream with the pulp to the paper machine, it will be virtually impossible to capture it without incurring prohibitive costs. Therefore, removal as early as possible is our approach.

A membrane material capable of recovering methanol while allowing the majority of the water and air to pass through the unit would be ideally suited for this application. The basic principle is shown in Figure 1. 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 the interaction of polymers with methanol is available, experimental evaluation of candidate polymers was made. This evaluation entails determination of basic material properties (sorption, diffusion) of candidate polymers when contacted with methanol, water, and air.

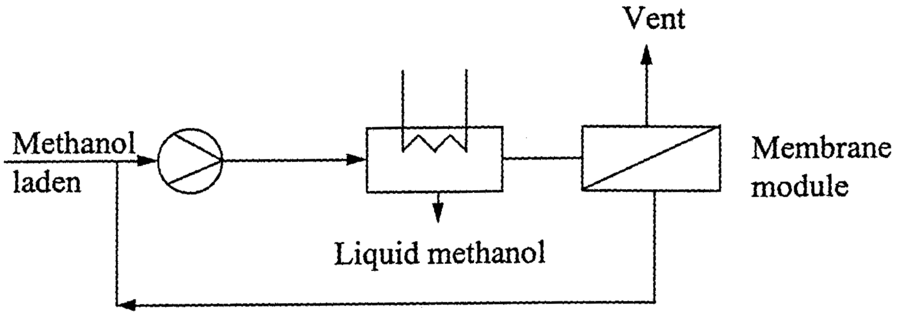

Figure 1: Selective removal of methanol from vapor-laden air streams (Process by MTR, Inc.).

Deliverables and Progress Made

Work on this project was completed in fiscal year 1997. Two presentations relating to this work were made at international meetings. Further, two publications in refereed journals are in preparation. References for these publications are as follows:

Rezac, M. E., John, T., and Pfromm, P. H., "Effect of Copolymer Composition on the Solubility and Transport of Water and Methanol in a Series of Polyether Amides", accepted, J. Appl. Pol. Sci., 1997. (See Appendix A)

Rezac, M. E. and John, T., "Correlation of Penetrant Transport with Polymer Free Volume: Additional Evidence from Block Copolymers", accepted Polymer, 1997. (See Appendix B)

Rezac, M. E., John, T., and Pfromm, P., "Methanol Recovery in the Pulp and Paper Industry by Membrane Vapor Separation," Fifth World Congress on Chemical Engineering, San Diego, CA, paper 54d, July 15, 1996.

Pfromm, P. H., John, T., and Rezac, M. E., "Membrane Vapor Separations for Methanol Recovery", AIChE National Meeting, Chicago, IL, paper 135b, November, 1996

Progress made to date follows each item.

1. *Develop modified operation of pulp storage tank for maximum HAP recovery.*

A literature search was completed to assess high density pulp storage tank operation and methanol emissions. The current practice of venting through an open stack could be replaced by recirculation of the vent gases through the membrane separation unit (Figure 2).

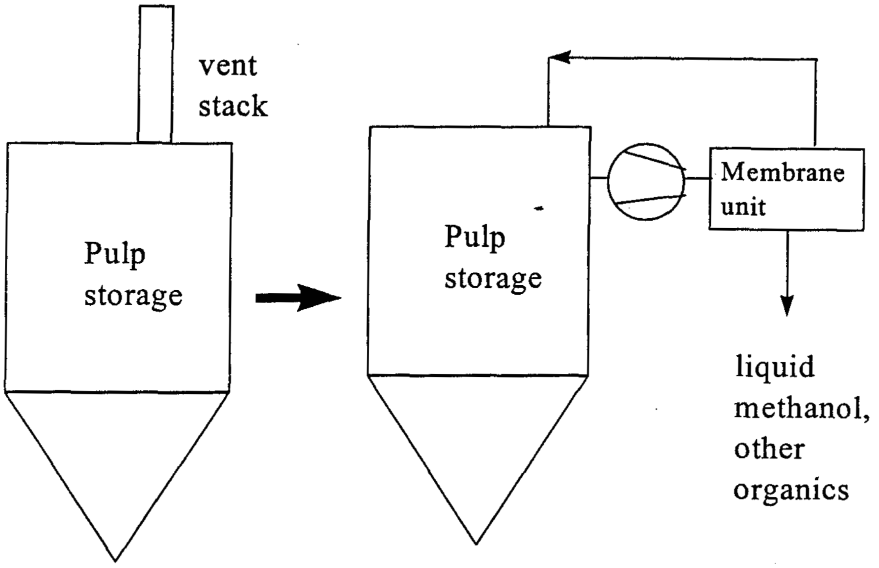

Figure 2: Modified high density pulp storage tank operation with recovery of volatile organics.

This would maximize and facilitate methanol and HAP removal from the tank, since the concentrations would be increased. Also, methanol would not be transferred downstream, but would be captured early on.

Recirculation would increase the concentration of methanol in the gas/vapor mixture fed to the membrane unit. Internal changes to the tank towards a maximized exposure of pulp entering the tank to the methanol extracting gas/vapor stream would also be beneficial. Ideas can be drawn, for example, from technology used in bleaching of pulp with gaseous ozone. Here, a similar gas/pulp contact is desired as in the extraction of methanol from the pulp.

2. *Optimized Membrane Polymer for HAP recovery*

During the first year of this project (July, 1995 - June, 1996) we evaluated the ability of polyetheramide copolymers to recover methanol from air streams. We discovered that these polymers were very effective at recovering methanol.

Unfortunately, they were not capable of selectively removing methanol from a stream containing both methanol and water vapor. Rather, to achieve effective recovery of the organic component, essentially all of the water had to be permeated as well. While this is not a serious technical problem, it greatly increases the membrane equipment size required and thus the capital costs. Therefore, during this portion of the research, we have evaluated membranes which may provide improved separation of methanol from water.

Initially, we had evaluated rubbery polymers because they are known to have a high affinity for organics over air. Unfortunately, they have very poor separation capacity for methanol over water. Recently, Schult and Paul [1996] reported on the ability of a series of polysulfones to transport water. While they did not consider the transport of methanol (or other lower alcohols) through these polymers, the work provided guidance in the selection of a second series of polymers. We have evaluated a series of rigid substituted polynorbornenes for this application. The general structure of the polymer is shown in Figure 3. We looked at a series of polymers where R was a linear methyl, butyl, hexyl, or decyl chain.

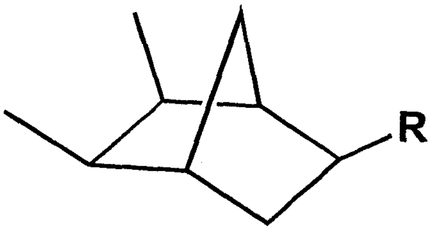

Figure 3: Repeat structure of the polynorbornenes evaluated.

To expedite the measurements, we screened these materials by measuring their capacity to transport permanent gases. Evaluation of the ability of the polymer to separate oxygen from nitrogen will provide an indication of the ability to separate methanol from water, based on our experience from the previous work. High separation for methanol from water would be expected from materials which selectively separate oxygen from nitrogen. The complete results of this evaluation have been accepted for publication [Dorkenoo, et al., 1997].

The material with the highest separation selectivity for oxygen from nitrogen, the methyl-polynorbornene, was evaluated for its ability to transport both water and methanol. The transport rates through this polymer were an order of magnitude slower than through the previously evaluated polyetheramides, and the ability to separate methanol from water was only marginally improved. Based on these initial results, it appears that it will not be easily possible to locate a commercial polymer which has both high transport rates for methanol, *and* high methanol/water selectivities.

3. *Laboratory-scale membranes for HAP recovery.*

Research has been conducted to evaluate the ability to form either integrally-skinned asymmetric membranes or multi-layer composite membranes. Initial studies focused on the use of model polymers in this evaluation. We have demonstrated the ability to efficiently form both types of membranes [Dudley, 1997; Rezac et al., 1997 A}. Continued evaluation of these membranes is anticipated in the on-going DOE project (see below).

4. *System Design*

Assumptions are made to estimate a full scale system (see NCASI, Technical Bulletin No. 677, 1994):

- production of 1372 oven dried tons of pulp per day (softwood)
- emission from high density pulp storage vent is 5.0 pounds of methanol per hour

Using a methanol permeability as determined in the laboratory (see Appendix A, 8,090 * 10^{-10} cm^3(STP) cm/cm^2 cmHg s) the membrane area can be estimated. Assumptions are:

- zero stagecut
- a permeate steam purge to avoid permeation of water is used
- a membrane thickness of 20,000 Angstrom
- a methanol feed partial pressure of 0.76 cmHg is present (1vol% methanol in the gas stream)

The needed area can be estimated according to

$$A = \frac{V * l}{P * \Delta p} \qquad (1)$$

where A is the area in cm2, V is the volumetric flux of methanol vapor, l is the effective membrane thickness, P is the permeability in cm^3(STP) cm/cm^2 cmHg s, and Δp is the partial pressure driving force in cmHg.

The resulting estimated membrane area to remove the methanol from this specific high density storage tank is 14 m^2, which can be accommodated in three commercial spiral wound membrane modules.

The steam purge option allows this minimized membrane area. If water were allowed to permeate, the needed membrane area would be a multiple of the area estimated above, since membranes are about as permeable for water as for methanol, but water is present in much higher concentration in the feed.

Future Directions

In an attempt to overcome the limitation of imperfect methanol/water selectivities in the polymers available, we are evaluating a major engineering modification to the system shown in Figure 1. In this modification, a steam sweep gas will be employed on the permeate side of the membrane. In so doing, the vacuum pump will be eliminated from the system, and the driving force for water permeation through the system will be minimized. Thus, the membrane area can be greatly reduced. Research on this technique is being conducted under a grant from the Department of Energy.

References

Dorkenoo, K. D., Pfromm, P. H., and Rezac, M. E., "Gas Transport Properties of a Series of High TG Polynorbornenes with Aliphatic Pendant Groups," J. Poly. Sci., Poly. Phys. Ed., accepted for publication, 1997. (See Appendix A)

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Rezac, M. E., John, T., and Pfromm, P. H., "Effect of Copolymer Composition on the Solubility and Transport of Water and Methanol in a Series of Polyether Amides", J. Appl. Pol. Sci., **65** (1997) 1983 (See Appendix A). B

Rezac, M. E. and John, T., "Correlation of Penetrant Transport with Polymer Free Volume: Additional Evidence from Block Copolymers", accepted for publication, Polymer, 1997 (See Appendix B). C

Schult, K. A., and D. R. Paul, J. Appl. Poly. Sci., 61 (1996) 1865.

Appendix A

Paper: Rezac, M. E., John, T., and Pfromm, P. H., "Effect of Copolymer Composition on the Solubility and Transport of Water and Methanol in a Series of Polyether Amides"

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

Key words: PEBAX™; methanol and water sorption and diffusion; membrane vapor separation; pulp and paper industry

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.

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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-

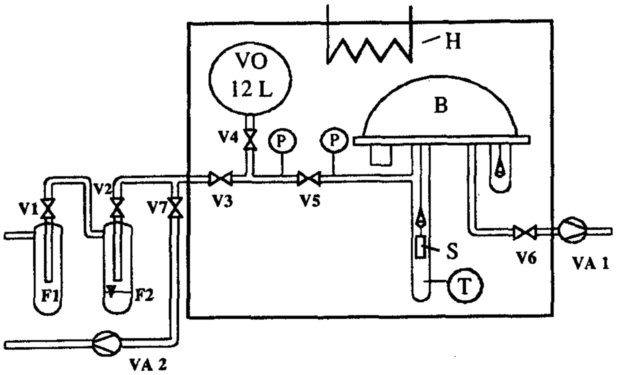


Figure 1 Schematic of apparatus for dynamic sorption–desorption measurements. (B) Cahn microbalance, (H) heater, (V) valve, (VO) ballast volume, (F) flask, (VA) vacuum pump, (S) sample, (T) temperature indicator, (P) pressure gauge.

view lists experimental data for water uptake in Nylon 12 of 12.6 to 13.8 cc(STP)/cc Polymer at 25 ± 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} cm^2/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

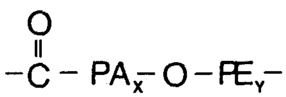
The absorption–desorption kinetics and the solubility of methanol vapor, water vapor, and dry air in a series of PEBAX™ polymers and PDMS were studied by a gravimetric method. This method consists of measuring the rate of weight gain or loss of a sample due to sorption or desorption. The weight change 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, hangdown 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 ± 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.



$$-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{PA}_X-\mathrm{O}-\mathrm{PE}_Y-$$

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

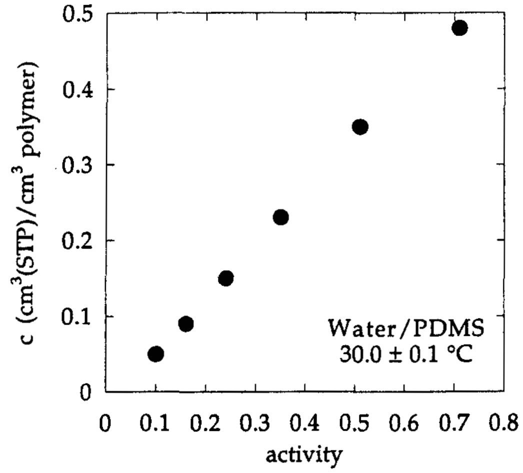


Figure 3 Solubility of water in PDMS as a function of activity at 30°C.

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/cm^3.[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

$$c = \frac{22414 |M_f - M_i|}{MW \cdot V_p} \tag{1}$$

where c is the equilibrium concentration of the penetrant [cm^3(STP)/cm^3 polymer]; 22414 is the volume (cm^3) 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 (cm^3). Standard conditions were taken as 0°C and 1 atm.

The solubility coefficient, S, is defined as:

$$S = c/p \tag{2}$$

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:

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

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-

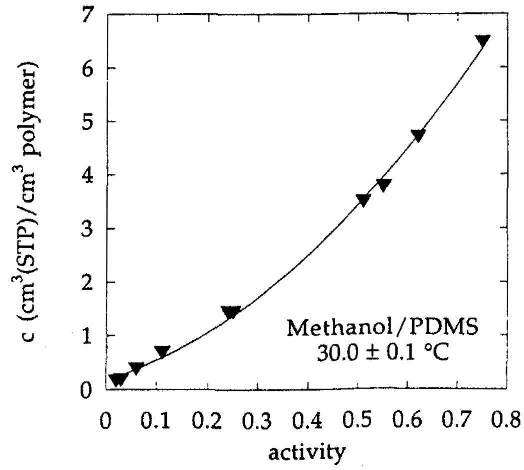


Figure 4 Solubility of methanol in PDMS as a function of penetrant activity. The dark line represents the data published by Favre.[5]

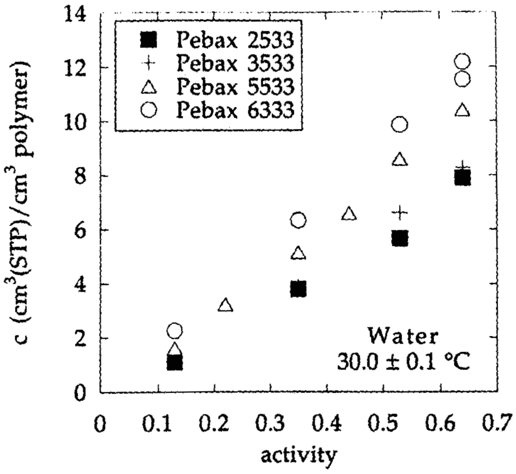


Figure 5 Solubility of water in a series of PEBAX® polymers as a function of activity.

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 ± 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 ± 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 ± 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 ± 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 linear 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.

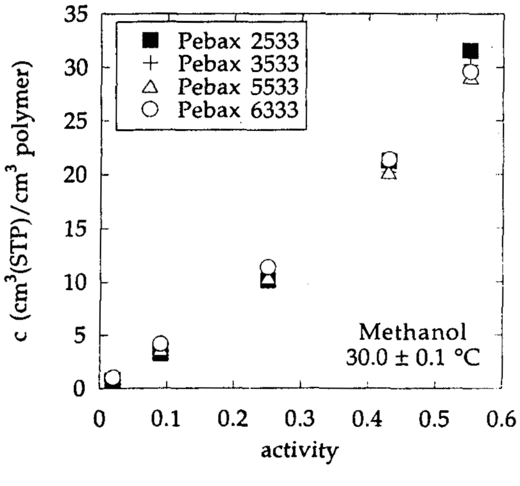


Figure 6 Solubility of methanol in a series of PEBAX™ polymers as a function of activity at 30°C.

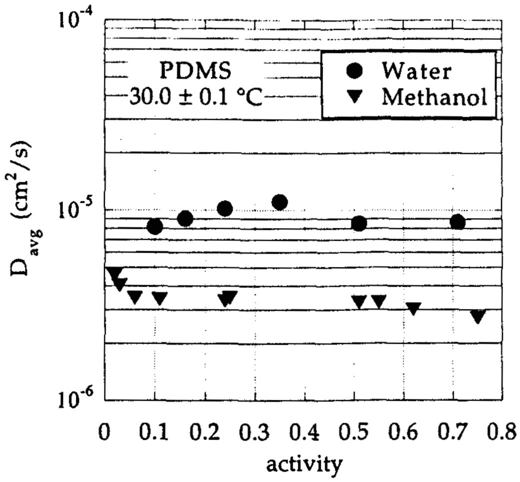


Figure 7 Average diffusion coefficient for water and methanol in PDMS as a function of penetrant activity.

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

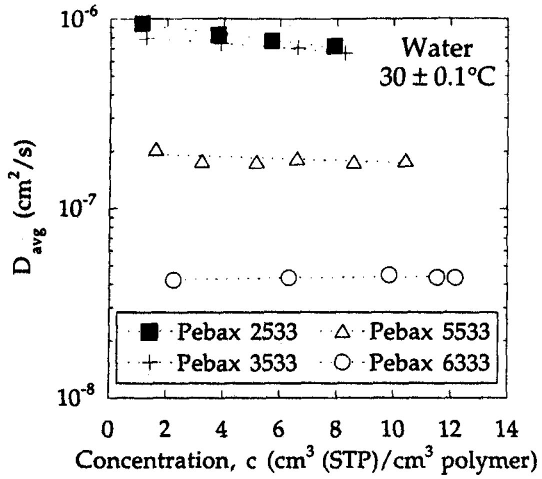


Figure 8 Average diffusion coefficient for water in a series of PEBAX™ polymers as a function of penetrant concentration. Lines drawn as visual aid.

measured here range from 0.8 to 1.1 × 10^{-5} cm^2/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} cm^2/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 plasticization 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} cm^2/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-

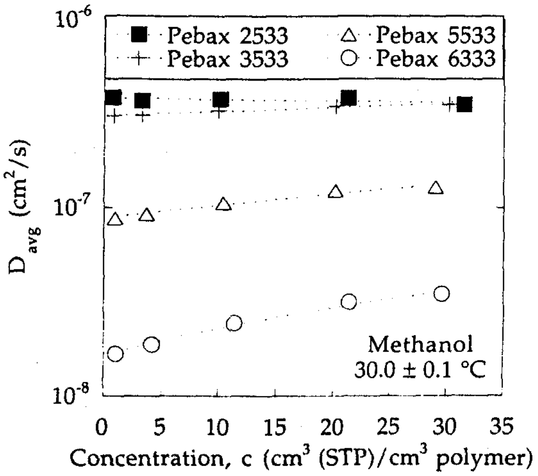


Figure 9 Average diffusion coefficient for methanol in a series of PEBAX™ polymers as a function of penetrant concentration. Lines drawn as visual aid.

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

	Permeability (Barrer)			Ideal Selectivity	
PEBAX™ Grade	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 behavior 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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Appendix B

Paper: Rezac, M. E. and John, T., "Correlation of Penetrant Transport with Polymer Free Volume: Additional Evidence from Block Copolymers"

Correlation of Penetrant Transport with Polymer Free Volume: Additional Evidence from Block Copolymers

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ABSTRACT

The transport rates of methanol and water through a series of PEBAX® block copolymers were measured and correlated with the fractional free volume. Excellent agreement between the logarithm of the diffusion coefficient and the inverse of the fractional free volume of the polymer was observed. This provides new evidence of the utility of the free volume theory to describe the transport of highly condensable vapors. Correlation was also quite good when the logarithmic additivity relationship was employed. This relationship has been previously shown to correlate the properties of homogenous blends with copolymer composition. The successful use of this theory for a series of blends that exhibit two glass transition temperatures will be discussed.

Keywords: diffusion in polymers, free volume theory, copolymers, polyetheramide, methanol, water

Running title: Free volume correlations for copolymer transport

Polymer, 1997, in press.

INTRODUCTION

The rate of gas transport across a solid polymeric film is determined by the process conditions (feed composition, temperature, and partial pressure) as well as by the chemical structure of the polymer. Many studies have attempted to quantify and generalize the relationship between chemical structure and gas transport. Notable are those of Stern[1-4] and Koros and Paul.[5-8] These studies have focused on the use of permanent gases as test penetrants and on systematic variation of the polymeric backbone or side groups. Our analysis of a series of block copolymers minimizes ambiguities in the interpretation of the results due to variations in the chemical makeup of the polymer backbone or pendant groups. The research reported here examines the gas transport of highly condensable penetrants in a series of block copolymers. Block copolymers are rarely examined. Yet, they offer the unique opportunity to systematically examine gas transport without the influence of side group interactions. The physical properties of these materials vary as the copolymer content changes, however, the chemical constituents of the polymer remain constant.

Through a detailed analysis of the transport of condensable penetrants in a series of block copolymers, we have provided further information in the continuing attempt to correlate the polymer structure with transport properties.

BACKGROUND

Cohen and Turnbull have suggested that diffusion in a rubbery polymer is the result of redistribution of free volumes within a matrix and migration of the penetrant among these free volumes.[9] Diffusion can therefore occur if a hole exists that is large enough for a molecule to enter this newly formed hole. From the evaluation of transport in liquids, Cohen and Turnbull found that the probability that a volume large enough exists for such a jump could be described by the following equation.

$$P\,(v^*) = \exp\,(-\gamma v^*/v_F) \qquad (1)$$

Where P is the probability for a hole of sufficient size, v^*; γ is a constant; and v_F is the average free volume in the material. Barrer and Fergusson[10] found linear relations between the probability of the existence of a hole and the diffusivity. Therefore, the free volume model suggests a linear relationship if the logarithm of the diffusion coefficient is plotted versus the polymer's free volume. Lee has shown that such a correlation can be applied both above and below the polymer's glass transition temperature.[11]

A major limitation of the quantitative use of this theory is the lack of a clear working definition of "free volume".[12-14] Specific free volume and fractional free volume have been suggested. Each method has proven useful. The following simple definitions for specific and fractional free volume have been proposed and employed. Specific free volume:

$$V_F = V - V_o \qquad (2)$$

Where V is the experimentally observed specific volume and Vo is an estimate of the specific volume at zero degree Kelven. A group contribution approach was used in the calculation of the latter. The van der Waals specific volume, Vw, of the polymer was calculated by group contribution and equated to the occupied volume by:

$$V_o = 1.3\,V_W \qquad (3)$$

as suggested by Bondi.[12]

The fraction free volume has been defined as the ratio of the specific free volume, to the observed specific volume:

$$FFV = \frac{V_F}{V} \tag{4}$$

Cohen and Turnbull's theory has been used to correlate the rate of penetrant diffusion in a polymer with its "free volume". Examination of penetrant transport in polymers is often concerned with the rate of penetrant migration across the film, or the permeation rate. This rate can be used in the design of polymeric membranes for separation or barrier packaging. For the case of negligable downstream pressure, the permeability coefficient can be written as the product of a diffusion coefficient and a sorption coefficient:

$$P = D\,S \tag{5}$$

In principle, each of these coefficients can be measured independently. However, for low sorbing penetrants such as oxygen, nitrogen, and helium accurate measurement of the sorption and diffusion coefficients is difficult. Yet, direct measurement of the permeability coefficient of such gases is straight forward.[15] Therefore, the literature frequently reports permeability coefficients exclusively. As a result, several authors have attempted to apply Cohen and Turnbull's theory to the correlate permeability coefficients with free volume.[16-22] While such an extension has little theoretical basis, the correlations are often quite good. This supports the proposition by these authors that the expected level of sorption is nearly constant for a given penetrant over a wide range of free volumes if the chemical nature of the polymer is varied only minimally. For systems in which D and S were independently measured, this proposition is generally confirmed.[21]

Several modern theories of gas transport in polymers have been developed based on work of Cohen and Turnbull. Notable among these are those of Duda and Vrentas and coworkers.[23-25] Duda and Vrentas have attempted to develop a predictive theory and to account for differences in the chemical nature of the polymer and the penetrant. However, the complexity of the Duda and Vrentas model has limited its use.

While the Cohen and Turnbull model can accurately correlate transport rates to a single parameter, the polymer free volume, the Duda and Vrentas model requires information relating to variations in polymer viscosity above and below Tg, thermal expansion coefficients of the glassy and rubbery state, molar volume of solvent, reological data, and diffusivity data for the solvent in the glassy polymer as a function of temperature. The correlative power of the model appears to be quite high, better than that of Cohen and Turnbull in certain circumstances. However, the use of the model has been limited by the amount of experimental data required.

Weinkauf and Paul used free volume theory to describe the behavior of a series of copolymers.[26] The copolymers exhibited only a single melting exotherm and a single glass transition temperature. The theory showed a good correlation with the experimental data.

Weinkauf and Paul also demonstrated that the copolymer permeability could be correlated using logarithmic additivity as shown in equation 6.

$$\ln P = x_1 \ln P_1 + x_2 \ln P_2 \qquad (6)$$

where x_i is the volume fraction of component i, and P_i is the permeability of the homopolymer. Equation 6 provides a simple model by which to predict the behavior of miscible mixtures or copolymers prior to actual synthesis and evaluation.

EXPERIMENTAL

The absorption-desorption kinetics and the solubility of methanol and water in a series of polyamide-polyether block copolymers were studied by a gravimetric method. This method consists of measuring the rate of weight gain or loss of a sample material due to absorption or desorption, respectively, of penetrant. The weight change was determined with an electromicrobalance incorporated in a vacuum system that allowed the exposure of the candidate material to a vapor of the solvent of interest. The system has been previously described in detail.[27]

Materials

Polymers

A series of PEBAX® block copolymer samples in the form of pellets was kindly supplied by Elf Atochem (Philadelphia, Pennsylvania). PEBAX® grades 2533, 3533, 5533, and 6333 were evaluated. The general chemical formula for PEBAX® is given in Figure 1.

PA represents polyamide and PE is a polyether segment. In the PEBAX® series studied here, Nylon 12 and polytetrametylene oxide (PTMO) were used in varying ratios. An elemental analysis for carbon, hydrogen, nitrogen and oxygen (C, H, N, and O) was performed by Huffman Laboratories (Golden, Colorado). The number of repeat units of polyamide and polyether in each monomer segment (subscripts "x" and "y" in Figure 1) was calculated. In this calculation, initial guesses for "x" and "y" were based on Faruque and Lacabanne.[28] Using these values 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 1. The fractional free volume for each material is also reported. Fractional free volumes were calculated using the method of Bondi[12] with values for the structural groups from van Krevelen.[29]

The glass transition temperatures of the various polymers 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 1. Thermal analysis of these materials indicated two distinct glass transition temperatures as well as crystalline melting peaks near 10 °C 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°C 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 were between 0.0125 and 0.0470 centimeter.

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 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/cm^3.[30]

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.[31]

TREATMENT OF EXPERIMENTAL DATA

Sorption

The equilibrium sorption for each penetrant was calculated using:

$$c = \frac{22414|M_f - M_i|}{MW \cdot V_p} \tag{7}$$

where c is the equilibrium concentration of the penetrate absorbed in $cm^3(STP)/cm^3$ polymer, at a pressure, p, and at the given temperature. 22414 represents the volume, in cm^3, of one mole of penetrant at STP (°0 C and 1 atm); M_f is the mass shown by the balance at equilibrium (final) and M_i is the mass shown at the beginning of an experiment (initial), both in grams. MW is the molecular weight of the penetrant, in g/mol; and V_p is the polymer volume, in cm^3.

Diffusion coefficients

Diffusion coefficients were evaluated using the non-steady state of the sorption and desorption curve according to Crank.[32] At short times:

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{\delta^2}\right)^{1/2} \tag{8}$$

This "short-time method" was used in this study to analyze the data.

Crank and Park[15] also introduced the long-time method to calculate the diffusion coefficient from experimental data. The long-time method proposes a linear relationship in a plot of $\ln(1- M_t/M_\infty)$ versus time, t:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \left(\frac{\pi^2 D}{\delta^2}\right)t \tag{9}$$

Agreement between the values of the diffusion coefficient calculated using those two methods was very good supporting the accuracy of the calculated values.

The diffusion coefficient reported in this paper are the average of the results of the short-time and the long-time values. Furthermore, the average of the results of the sorption and the desorption runs is used.

Permeation Coefficients

The permeation coefficients reported were calculated using equation (5), where S is the sorption coefficient and is defined as $S = C/p$. Here, the average slope of a plot of equilibrium sorption versus pressure up to the activity reported is used as S.

RESULTS

Sorption isotherms for both methanol and water in each of the PEBAX® polymers were measured over the activity range of 0 to approximately 0.75 at 30 °C. Complete analysis of the influence of activity on molecular transport is provided in a separate publication.[27] Here, we have chosen to evaluate only a single intermediate activity for each penetrant. Up to the activities discussed, the sorption isotherms were linear with respect to penetrant activity. Therefore, one may conclude that no significant swelling of the polymer matrix has occurred.

Measured solubility coefficients, diffusion coefficients, and calculated permeability coefficients for each of the polymers are reported in Table 2 for methanol and in Table 3 for water. Each of the values reported is the average of the measured values obtained from a paired absorption-desorption run.

For the polymers and penetrants examined, the solubility is essentially constant. Therefore, variations observed in the permeability coefficient can be attributed almost entirely to changes in the measured diffusion coefficient. This supports the extension of the free volume theory for correlations of the permeability coefficient with minimal inaccuracy.

DISCUSSION OF RESULTS

A plot of the diffusion coefficients of both water and methanol in the PEBAX® series as a function of inverse fractional free volume is presented in Figure 2. An excellent correlation between the fractional free volume of the copolymer and the diffusion coefficient of either water or methanol is demonstrated. Further, data from the literature is included for water transport through pure Nylon 12. This data fits well with the experimentally measured trend. No data for the transport of methanol through the homopolymers was found in the literature.

Several, potentially significant, variations exist between the results reported here and those reported in the literature for the correlation of transport properties with a polymer's free volume. The polymers studied here exhibit two glass transition temperatures indicative of phase separation. Yet, the materials are optically clear and the molecular weight of each segment in the repeat unit is relatively short indicating that if phase separation is present, it is on a local molecular scale. Nevertheless, the free volume theory provides very good correlation for the transport properties of these materials.

The highly condensable components water and methanol were used as test penetrants. While the free volume theory is hypothetically applicable to any penetrant in any pseudo-liquid system, essentially all of the published correlations are for test penetrants that are much less condensable than water and methanol, typically carbon dioxide, nitrogen, or methane. We must note, however, that the analysis presented here is at relative vapor activities under which no swelling of the polymer matrix was observed. Under bulk swelling conditions, this correlation may not provide sufficient detail to fully describe the diffusion process.

The extension of the free volume theory of Cohen and Turnbull to highly condensable components in block copolymers provides unique evidence for the usefulness of the theory to correlate transport properties and the fractional free volume of a polymer.

The permeability data for these polymers has been analyzed using the logarithmic additivity model described in equation (6). While the permeability values for the homopolymers are not known, it appears that the block copolymers follow this simple relation (as can be seen in Figure 3). Our data confirms that equation (6) provides a simple method for the prediction of the properties of block copolymers. The excellent fit of equation (6) provides further support that the transport properties of the polymers examined here behave in a manner consistent with homogenous polymer blends.[26]

CONCLUSIONS

Correlations between polymer free volume and penetrant diffusion coefficients, first proposed by Cohen and Turnbull have been successfully applied to a series of block copolymers with methanol and water as the test penetrants. The excellent agreement between the overall polymer free volume and the diffusion coefficients provides an opportunity to tune the copolymer content to achieve a wide range of desired transport properties. Extension of the free volume theory to a series of block copolymers and highly condensable penetrants provides further evidence of its general utility.

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Table 1: Physical properties of the PEBAX® samples.

	PEBAX®				
	2533	3533	5533	6333	Nylon 12
"x"	2.68	3.42	14.85	19.30	-
"y"	27.80	26.00	24.70	16.60	-
weight % PA	21.6	27.1	62.2	75.8	100
FFV	0.172	0.168	0.141	0.131	0.120[a]
T_g PTMO (°C)	-76	-72	-65	-60	-
T_m Crystalline PTMO (°C)	12	7	None Detected	None Detected	-
T_g Nylon (°C)	70	68	66	72	
T_m Crystalline PA (°C)	137	142	160	170	178[a]

a: Reference 33

Table 2: Solubility, Diffusion, and Permeability Coefficients for Methanol in a Series of PEBAX® Polymers at 30 °C and Methanol Partial Pressure of 40 cmHg (methanol activity = 0.25).

Polymer	S (cm³ (STP) /cm³ polymer • cmHg)	$D_{AVG} \times 10^8$ (cm²/s)	P X 10¹⁰ (cm³ (STP) cm /cm²•cmHg•s)
Pebax 2533	2.53	38.0	9600
Pebax 3533	2.48	33.0	8200
Pebax 5533	2.58	10.6	2740
Pebax 6333	2.86	2.45	700

Table 3: Solubility, Diffusion, and Permeability Coefficients for Water in a Series of PEBAX® Polymers at 30 °C and Water Partial Pressure of 20 cmHg (water activity = 0.64).

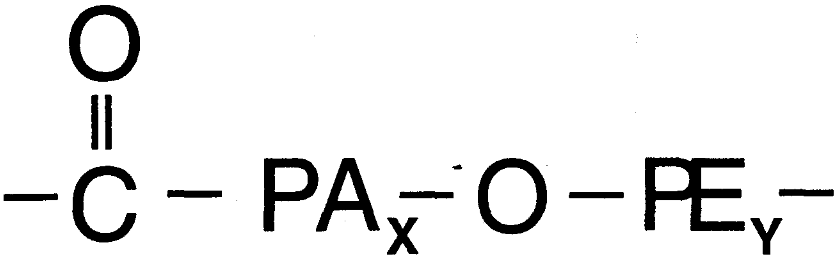
Polymer	S (cm^3 (STP) /cm^3 polymer • cmHg)	D_{AVG} X 10^8 (cm^2/s)	P X 10^{10} (cm^3 (STP) cm /cm^2•cmHg•s)
Pebax 2533	4.37	73.0	31870
Pebax 3533	4.06	66.4	26930
Pebax 5533	5.11	17.9	9150
Pebax 6333	5.70	4.35	2480

Legand for Figures:

Figure 1: General monomeric repeat structure of PEBAX®

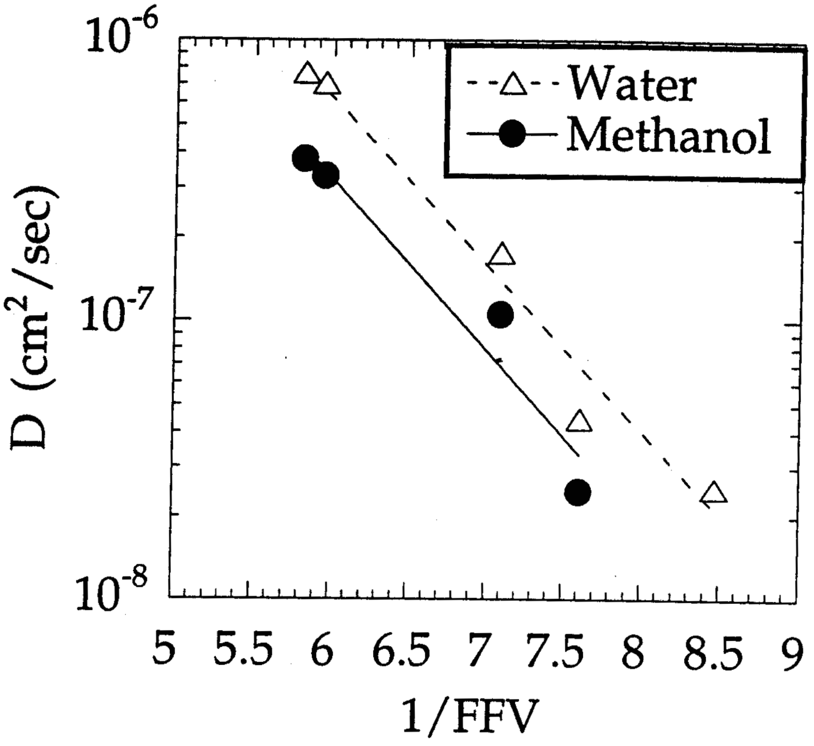
Figure 2: Correlation between inverse fractional free volume of PEBAX® polymers and the measured diffusion coefficients for methanol and water at 30 °C. Correlation coefficients for water and methanol are 0.996 and 0.993, respectively.

Figure 3: Influence of PEBAX® blend composition on the permeability of water and methanol at 30°C. Correlation coefficients for water and methanol are 0.966 and 0.990, respectively.

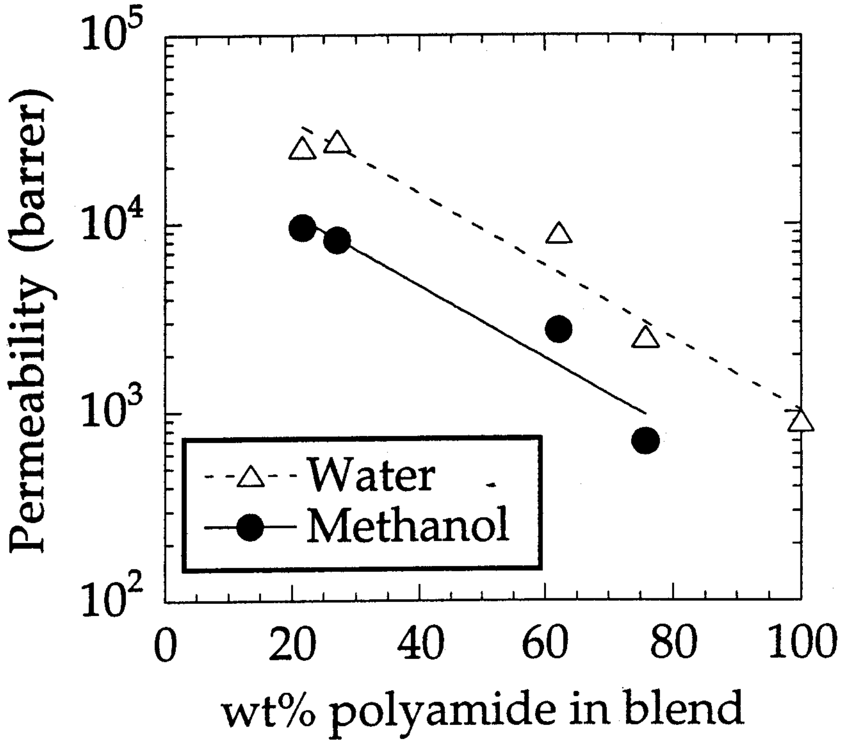


$$-\overset{\overset{\displaystyle O}{\|}}{C}-PA_X-O-PE_Y-$$

Polymer, Rezac & John, Figure 1



Polymer, Rezac & John, Figure 2



Polymer, Rezac & John, Figure 3