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Correlation of penetrant transport with polymer free volume: additional evidence from block copolymers

Mary E. Rezac[a,*] and Tilo John[†b]
[a]*Georgia Institute of Technology, School of Chemical Engineering, Atlanta, GA 30332-0100, USA*
[b]*Institute für Thermische Verfahrenstechnik, Universität Karlsruhe, Karlsruhe, Germany*
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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 vapours. 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 is discussed. © 1997 Elsevier Science Ltd.

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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 and coworkers[1–4] and Koros, Paul and others[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 can be found by

$$V_F = V - V_0 \qquad (2)$$

Where V is the experimentally observed specific volume and V_0 is an estimate of the specific volume occupied by the polymer at zero Kelvin. The specific volume is taken as the inverse of the polymer bulk density. A group contribution approach was used in the calculation of V_0. The van der Waals specific volume, V_W, of the polymer was calculated by group contribution and equated to the occupied volume

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[*] To whom correspondence should be addressed
[†] Present address: BASF, Mannheim, Germany

by

$$V_0 = 1.3 V_W \tag{3}$$

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 a 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 negligible downstream pressure, the permeability coefficient can be written as the product of a diffusion coefficient and a sorption coefficient:

$$P = DS \tag{5}$$

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 straightforward[15]. Therefore, the literature frequently reports permeability coefficients exclusively. As a result, several authors have attempted to apply Cohen and Turnbull's theory to correlate permeability coefficients with the free volume[16–22]. While such an extension has little theoretical basis, the correlations are often quite good. Successful correlations 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 Vrentas, Duda and coworkers[23–25]. These authors 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 Vrentas and Duda 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 Vrentas and Duda model requires information relating to variations in polymer viscosity above and below T_g, thermal expansion coefficients of the glassy and rubbery state, molar volume of solvent, rheological 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 behaviour 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):

$$\ln P = x_1 \ln P_1 + x_2 \ln P_2 \tag{6}$$

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 behaviour 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 the penetrant. The weight change was determined with an electromicrobalance incorporated in a vacuum system that allowed the exposure of the candidate material to a vapour of the solvent of interest. The system has been previously described in detail[27].

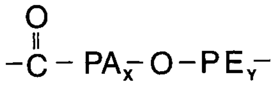
Materials

Polymers. A series of PEBAX® block copolymer samples in the form of pellets was kindly supplied by Elf Atochem (Philadelphia, PA). 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 polytetramethylene 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, CO). 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 those reported by Faruque and Lacabanne for this PEBAX® polymer[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^{-1}. 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 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



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

Figure 1 General monomeric repeat structure of PEBAX®

Table 1 Physical properties of the PEBAX® samples

	PEBAX®				Nylon 12
	2533	3533	5533	6333	
'x'	2.68	3.42	14.85	19.30	–
'y'	27.80	26.00	24.70	16.60	–
Weight percentage of PA	21.6	27.1	62.2	75.8	100
FFV	0.172	0.168	0.141	0.131	0.120[a]
$T_{g\ \mathrm{PTMO}}$ (°C)	−76	−72	−65	−60	–
$T_{m\ \mathrm{Crystalline\ PTMO}}$ (°C)	12	7	None detected	None detected	–
T_g Nylon (°C)	70	68	66	72	–
$T_{m\ \mathrm{Crystalline\ PA}}$ (°C)	137	142	160	170	178[a]

[a]Reference [33]

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 cm.

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 aluminium 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 vapour pressures were in good agreement with those reported by Reid *et al.*[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. The constant 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^{-1}) 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,

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

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[15] showed that for cases of non-constant 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 deviations from the exact solution of Fick's second law. This 'short-time method' was used in this study to analyse 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 coefficients reported in this paper are the average of the results of the short- and 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

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 [cm^3 (STP) cm^{-3} polymer cmHg^{-1}]	$D_{AVG} \times 10^8$ (cm^2 s^{-1})	$P \times 10^{10}$ [cm^3 (STP) cm cm^{-2} cmHg^{-1} s^{-1}]
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^{-1}]	$D_{AVG} \times 10^8$ (cm^2 s^{-1})	$P \times 10^{10}$ [cm^3 (STP) cm cm^{-2} cmHg^{-1} s^{-1}]
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

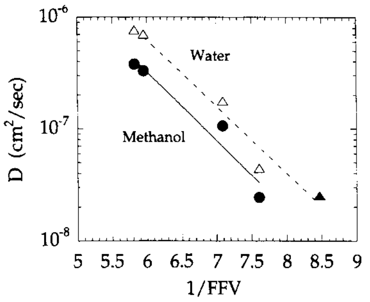


Figure 2 Correlation between inverse fractional free volume of PEBAX® polymers and the measured diffusion coefficients for methanol and water at 30°C. Correlation coefficients for water and methanol are 0.996 and 0.993, respectively. Water data denoted with solid triangle (at $1/FFV = 8.5$) is for the transport of water through pure Nylon 12[33]

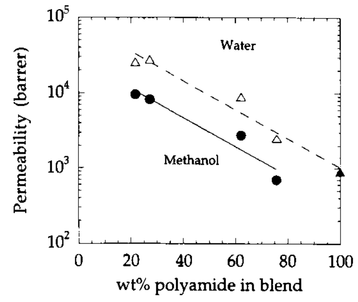


Figure 3 Influence of PEBAX® blend composition on the permeability of water and methanol at 30°C. Correlation coefficients for water and methanol are 0.966 and 0.990, respectively. Water data denoted with solid triangle (at polyamide content = 100%) is for the transport of water through pure Nylon 12[33]

entirely to changes in the measured diffusion coefficient. This supports the use 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. Furthermore, 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. Thus, any phase separation present 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 vapour 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 analysed 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. The successful 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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