Hybrid Membrane Materials Comprising Organic Polymers with Rigid Dispersed Phases

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Dispersing highly selective rigid "inserts" such as zeolites and carbons into polymers can produce novel membrane materials with improved gas mixture permselectivity. Rigid inserts frequently cause the permeability in an "interphase" surrounding individual inserts to differ markedly from the intrinsic permeability of the matrix polymer. While existing theoretical models describe permselectivity reasonably well, they fail to predict the absolute permeabilities for individual components in such hybrid media. In fact, the degree of deviation from the simple model predictions provides insight into the detailed properties of the interphase, which has been neglected in previous analyses of these hybrid materials. Extension of an existing model provides a framework to analyze gas permeation properties of model systems with rigid molecular sieve inserts in glassy matrices. Inhibited segmental motion due to surface attachment and matrix contraction at the interface during preparation of these materials is hypothesized as the key cause of the observed behavior. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 311–321, 2004

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Introduction

Membranes have rapidly emerged as a fourth major paradigm for doing bulk separations of gases and now challenge distillation, absorption, and adsorption processes in key areas such as hydrogen purification, nitrogen recovery from air, and natural gas purification. Improvement in the separation performance of membranes without a significant increase in cost per square foot would promote replacement of the more traditional gas separation technologies with membranes.

So-called "mixed matrix" materials are heterogeneous structures comprised of permeable "inserts" embedded in a polymer matrix. The mixed matrix membrane concept combines the advantages of each phase: high selectivity of the inserts and

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Table 1. Potential Applications of Molecular Sieving (MS) and Selective Surface Flow (SSF) Mixed Matrix Membranes Application List Adapted from Lee and Koros (2002) (HC = Hydrocarbon)

Category	Gas Components	Application	Mixed Matrix Insert Phase
Hydrogen	H_2/N_2	Ammonia purge gas	MS
	H_2/CH_4	Refinery hydrogen recovery	MS
	H_2/CO	Synthesis gas ratio adjustment	SSF
	H_2/O_2	Fuel cells	MS
Air	O_2/N_2	N_2-enriched air for inerting	MS
		O_2-enriched air for combustion	MS
		O_2 for respiration therapy	MS
Acid gases	CO_2/CH_4	Enhanced oil recovery; recover CO_2 for reinjection	MS
		Natural gas and landfill gas sweetening	MS
	H_2S/CH_4	Sour gas sweetening	SSF
	CO_2/N_2	Digester gas treatment	SSF
Drying	H_2O/HC	Hydrocarbon drying	MS/SSF*
	H_2O/Air	Air drying	MS/SSF*
Hydrocarbons	HC/Air or HC/N_2	Pollution control; stack gas or solvent recovery	SSF
	HC/N_2	Upgrading low-BTU gas	SSF
	HC/HC	Dew pointing of natural gas	MS/SSF†
Helium	He/HC	Helium recovery from gas wells	MS
	He/N_2	Helium recovery from diving air mixtures	MS

* An insert could potentially show both molecular sieving and selective surface flow for water, because it is both small and condensable.
† If there is insufficient size difference between the penetrants, they could likely be separated using selective surface flow inserts.

desirable mechanical properties and economical processability of polymers. Recent studies have demonstrated the remarkable separation properties of these mixed matrix materials, exhibiting performance well beyond the intrinsic properties of the polymer matrix. These studies have considered different *molecular sieving* inserts, including zeolites (Duval et al., 1993; Jia et al., 1991; Kulprathipanja et al., 1988; Mahajan and Koros, 2000, 2002a,b) and carbon molecular sieves (Duval et al., 1993; Vu et al., 2003a,b) with several polymer matrices. In principle, the concept can also be extended to include microporous media that operate by a so-called "*selective surface flow*" mechanism (Anand et al., 1997; Nicholson, 1997; Sircar et al., 1999). In this latter case, larger-pored rigid solids enable the selective adsorption and surface diffusion of the more condensable component in a mixture, while excluding the less condensable component. The less condensable component is often the smaller of the two penetrants; thus, selective surface flow offers a novel way to selectively enhance the permeation of an otherwise slower diffusing large penetrant. The mixed matrix paradigm, therefore, is extremely broad, potentially opening avenues to economical high performance materials with applications across a wide spectrum of important applications. The possible "matches" of the technology to applications are noted in Table 1.

In this article, experimental results are compared with theoretical models that have been employed by previous researchers to predict permeation behavior of heterogeneous membranes. The permeability and selectivity are the most important factors that determine a material's utility as a gas separation membrane. The permeability, which is a thickness and driving force normalized flux, of penetrant "A" can be represented as the product of the average diffusion and sorption coefficients in the membrane (Koros and Fleming, 1993)

$$P_A = D_A \times S_A \tag{1}$$

Permeabilities are customarily given in Barrers where 1 Barrer $= 1 \times 10^{-10}(\mathrm{cc_{STP}} \cdot \mathrm{cm} \cdot \mathrm{cm}^{-2} \cdot \mathrm{s}^{-1} \cdot \mathrm{cmHg}^{-1}) = 3.35 \times 10^{-16}(\mathrm{mol} \cdot \mathrm{m} \cdot \mathrm{m}^{-2} \cdot \mathrm{s}^{-1} \cdot \mathrm{Pa}^{-1})$. A second important parameter, the ideal selectivity, or permselectivity, equals the permeability of penetrant A divided by the permeability of a second, "rejected" penetrant, "B", when the pressure on the permeate side of the membrane is zero

$$\alpha_{AB} = \frac{P_A}{P_B} \tag{2}$$

Since the permeability of the slower gas is used as the denominator, the selectivity is greater than one. This provides a basis to compare different materials since the permeabilities of a given penetrant, and, hence, the ideal selectivities, are intrinsic properties of homogeneous materials. The ideal selectivity is convenient to use since new materials, including those in this work, are typically first tested with equipment that operates essentially at vacuum on the permeate side.

In general, both the permeability and selectivity of a material depend on the compositions of the feed and permeate and the history of the sample. Nevertheless, history dependence is not marked in dense films, such as those tested here, nor were they tested under conditions where composition dependence would be expected to be important, so these two effects can be neglected to focus on key primary effects.

A detailed discussion of the transport mechanism of each of the material classes considered here is beyond the scope of this work. Nevertheless, an overview understanding of each of the mechanisms by which transport occurs in each material will be helpful. Penetrants first sorb into and then diffuse through polymers. This occurs when a large enough transient gap is formed in the polymer next to the penetrant due to thermally induced motions of the polymer chain segments, enabling sub-nanometer random "jumps" (Koros and Fleming, 1993). The selectivity of two gases in a polymer depends on their relative condensabilities and the properties of the polymer that affect the rate at which thermally induced gaps are formed (Freeman, 1999). In molecular sieves with pores of approxi-

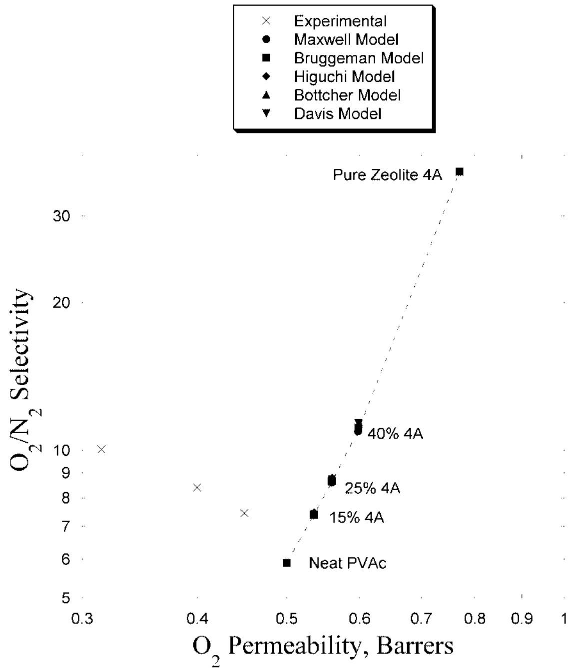

Figure 1. Comparison of model predictions with experimental data for zeolite 4A filled PVAc at 35°C.

1 Barrer = 3.35×10^{-16} (mol · m · m^{-2} · s^{-1} · Pa^{-1}).

mately the same size as the penetrants, diffusion proceeds through a transition state by overcoming repulsions from atoms comprising the transport-regulating pores (Singh and Koros, 1996). Diffusion selectivity in these materials can be quite high, depending on the size and shape differences between penetrants. For materials with pore dimensions much larger than the penetrants, surfaced selective flow becomes more important (Sircar et al., 1999). In this case, more condensable penetrants are favored over less condensable penetrants, and the selectivity can be quite high. The rate of improvement in the gas separation capabilities of neat polymers has slowed, so adding these more selective zeolites and carbons as inserts into the polymers offer an opportunity to realize a more dramatic improvement in the gas separation capabilities of membranes.

To illustrate the types of effects of interest, consider Figure 1 for 5 μm type 4A zeolites dispersed in PVAc. In such a case with good matrix-sieve compatibility, the *selectivity* is adequately described by the ratio of permeabilities of O_2 and N_2 estimated from existing models. On the other hand, the absolute *permeability* of each component is increasingly poorly described as sieve loading increases. This work demonstrates that simple modifications to existing models can account for an "interphase" extending from the sieve surface into the polymer matrix. Such an interphase is believed to arise from a region of altered polymer chain mobility near the sieve surface and is consistent with earlier related observations. Reduced segmental mobility has been postulated as the cause of lower-than-predicted sorption in filled polymer systems (Manson and Chiu, 1973). Reduced mobility near a filler leads to nonadditive mechanical property effects on the modulus of filled polymer systems. For instance, Galperin and Kwei and Kwei and Kumins postulate such modulus-enhancing effects in TiO_2-filled poly(vinyl acetate) systems (Galperin and Kwei, 1966; Kwei and Kumins, 1964). This increase in modulus is frequently accompanied by an increase in the T_g of the polymer matrix (Lewis and Nielsen, 1970; Theocaris and Spathis, 1982). Similar regions of reduced polymer mobility have also been postulated to decrease the permeability of semicrystalline polymers (Michaels and Parker, 1959; Michaels et al., 1963) and to increase the rigidity and glass transition temperature of random ionomers (Eisenberg et al., 1990). However, in these two cases, the dispersed phase is on such a fine scale that the entire matrix can be affected.

Mixed matrix membrane performance can be predicted using various theoretical expressions, including models by Maxwell (1873), Bruggemann (1935), Higuchi and Higuchi (1960), Bottcher, (1945), and Davis (1977). Several studies have compared predictions of analogous two phase polymer systems with these various models (Bouma et al., 1997; Petropoulos, 1985), demonstrating that the models produce similar predictions for the low volume fraction materials considered here. This fact is supported by the comparison of predictions from several models presented in Figure 1 for the PVAc-zeolite 4A system. Clearly, none of these existing models reproduce the trend observed in the data. In all of the recent work summarized in this article, the aspect ratio of the disperse phase was close to unity. For more complex, nonunity aspect ratio flakes, the work of Cussler would need to be considered (Cussler, 1990; Cussler et al., 1988). This complicates the analysis still further, so only the simpler unity aspect ratio case is considered here.

The effective steady-state permeability of a composite material can be given by the following expression (Bouma et al., 1997; Petropoulos, 1985)

$$\boldsymbol{P}_{mm} = \boldsymbol{P}_c\left[\frac{n \cdot \boldsymbol{P}_d + (1-n)\boldsymbol{P}_c + (1-n)\phi_d\,(\boldsymbol{P}_d - \boldsymbol{P}_c)}{n \cdot \boldsymbol{P}_d + (1-n)\boldsymbol{P}_c - n\phi_d\,(\boldsymbol{P}_d - \boldsymbol{P}_c)}\right] \quad (3)$$

where $\boldsymbol{P}_{mm}$ is the effective permeability of a penetrant in the composite material with a volume fraction (ϕ_d) of dispersed phase (d) in a continuous matrix phase (c); $\boldsymbol{P}_c$ and $\boldsymbol{P}_d$ are the penetrant permeabilities in the continuous and dispersed phases, respectively; and n is a shape factor for the dispersed phase. The limit of $n = 0$ corresponds to parallel transport through a laminate and can be expressed as an arithmetic mean of the dispersed and continuous phase permeabilities

$$\boldsymbol{P}_{mm} = \boldsymbol{P}_c(1-\phi_d) + \phi_d\boldsymbol{P}_d \quad (4)$$

The limit of $n = 1$ corresponds to transport through a laminate in series

$$\boldsymbol{P}_{mm} = \frac{\boldsymbol{P}_c\boldsymbol{P}_d}{\boldsymbol{P}_d(1-\phi_d) + \phi_d\boldsymbol{P}_c} \quad (5)$$

The predictions of the parallel and series models bound the expected behavior of mixed matrix materials. The result for a dilute suspension of spherical particles ($n = 1/3$) is known as the Maxwell equation

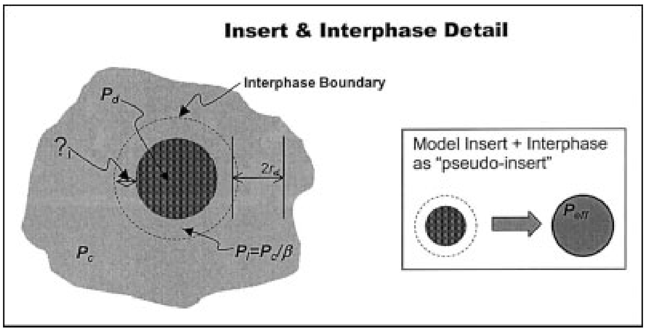

Figure 2. Parameters for the modified Maxwell model.

$$P_{mm} = P_c\left[\frac{P_d + 2P_c - 2\phi_d(P_c - P_d)}{P_d + 2P_c + \phi_d(P_c - P_d)}\right] \tag{6}$$

This model was originally developed (Maxwell, 1873) to describe the permittivity of a dielectric. The constitutive equation governing electrical potential and the flux through membranes are analogues, permitting the application of Maxwell's equation to transport in mixed matrix membranes. This model provides a simple, quantitative framework to predict the transport properties of mixed matrix materials when the transport properties of the constituent phases are known, especially at relatively low dispersed phase volume fractions. Since other models usually give similar predictions without providing a simple, intuitive physical framework of the transport process, the Maxwell model was used in this work as the basis for a more complex model incorporating *interphase effects.*

Modified Maxwell Model

The three-phase polymer, insert, and interphase can be described as an idealized two-phase system with the matrix polymer being one phase and the combined insert and interphase constituting the other, as shown in Figure 2. It is possible to model these materials as an idealized two-phase system, because the insert must be encapsulated by the interphase for practical applications. The combined insert and interphase can be envisioned as a "pseudo-insert" phase. These concepts were first proposed by Mahajan (2000). Erdem-Senatalar et al. report a limiting case using the effective medium theory (the model of Davis (1977)) to calculate the overall permeability of the membrane based on these concepts where the interphase is assumed to be in series with the dispersed insert (Erdem-Senatalar et al., 2001). However, as mentioned above, the series model predicts only one of the bounds of the expected behavior, and the Maxwell model gives a more realistic representation of the transport process.

A similar three-phase model can be applied to describe mixed matrix membranes with poor polymer-insert contact (Mahajan and Koros, 2002a). Poor bonding (such as interfacial voids or more subtle poor packing) results in "sieve-in-a-cage" morphology and may cause a "leaky interface." A mechanism is proposed as the cause of this morphology in Moore et al. (2003). Modeling the permeation behavior in this case is discussed extensively by Mahajan and Koros (2002a), so it is not duplicated here. In this extreme case, the interphase is comprised of the void between the polymer and insert. If the thickness of the void surrounding the inserts could be controlled, it could be a design variable to effectively create new materials with higher free volume and thus more facile transport pathways. Nanoscopic inserts have been used to achieve this purpose (He et al., 2002; Merkel et al., 2002). On the other hand, long-term stability of these materials may be limited, so that achieving a well bonded interface with the internal pores properly selected may be preferred. In the results section, due to the lack of data for large pored inserts (operating under a surface selective flow mechanism), attention will be focused on the types of smaller-pored inserts relying on molecular sieving for separation.

It is not surprising that the interphase in well-bonded cases can possess properties different from both bulk phases. In this work, the interphase is comprised of the region of rigidified polymer within the zone of influence of the insert, wherein the polymer properties are affected by the insert. The Maxwell model can be used to calculate the permeability of the "pseudo-insert" phase with the insert dispersed in the continuous interphase. Thus, applying Maxwell's equation, one can obtain the effective permeability of the "pseudo-insert" phase

$$P_{\text{eff}} = P_I\left[\frac{P_d + 2P_I - 2\phi_s(P_I - P_d)}{P_d + 2P_I + \phi_s(P_I - P_d)}\right] \tag{8}$$

where P_{eff} is the effective permeability of the "pseudo-insert" phase, P_d is the permeability of the insert, P_I is the permeability of the interphase, and ϕ_s is the volume fraction of the insert phase within the "pseudo-insert" phase. The volume fraction ϕ_s is given by the following expression

$$\phi_s = \frac{\phi_d}{\phi_d + \phi_I} = \frac{r_d^3}{(r_d + \ell_I)^3} \tag{9}$$

Here, ϕ_d and ϕ_I are the overall volume fractions in the membrane of the insert and the interphase, respectively; r_d is the insert radius; and the interphase thickness is denoted ℓ_I, as shown in Figure 2. Because of the nature of the interphase, ϕ_s can be greater than the "dilute" volume fractions at which the Maxwell model is typically applied. Justification for the use of Maxwell's model for the pseudo-insert phase is given below. The value of the dispersed "pseudo-insert" permeability P_{eff} can be used in a nested application of Maxwell's model, along with the continuous polymer phase permeability P_c, to obtain a predicted permeability P_{3MM} for three-phase mixed matrix materials

$$P_{3MM} = P_M\left[\frac{P_{\text{eff}} + 2P_c - 2(\phi_d + \phi_I)(P_c - P_{\text{eff}})}{P_{\text{eff}} + 2P_c + (\phi_d + \phi_I)(P_c - P_{\text{eff}})}\right] \tag{10}$$

As $\phi_d + \phi_I$ increases toward one, the interphases of neighboring insert particles overlap so that the whole matrix is rigidified. In this case, the matrix will, in fact, have effective properties different from the neat polymer. This can be envisioned to occur near the close pack density, which is ~74% for monodisperse spheres. This volume fraction ($\phi_d + \phi_I$) roughly corresponds to the case for our 35–40% (ϕ_d) 4A filled films, although the 4A particles are cubical and not monodisperse, so they pack better. Overlapping will be more likely as the insert loading is increased, or as the interphase thickness is increased.

Thus, if one can estimate the interphase volume fraction, or equivalently, the thickness, and the interphase permeability, the Maxwell model can easily be extended to these more complicated systems. The permeability of the polymer in the interphase $\mathbf{P}_I$ is assumed to be decreased by a chain immobilization factor β. Permeability in the amorphous regions of semicrystalline polymers is treated in a similar manner (Michaels and Parker, 1959; Michaels et al., 1963). The parameter β is found to be a weak function of penetrant size in the semicrystalline materials. In our work, β is assumed to have a fixed value for all penetrants, since the size of the penetrants studied here are reasonably similar. The other parameter in the model ℓ_I is the interphase thickness, that is, the distance from the insert in which the polymer chains have reduced mobility. This model provides a useful way to estimate an effective thickness of the interphase, which is very difficult to probe using other methods. For example, rigidification near glass fibers has been measured using an atomic force microscope (Hodzic et al., 2000; VanLandingham et al., 1998), but the thickness was difficult to accurately quantify and this technique will be difficult to implement with particulate filled composites.

Use of the Maxwell model for concentrated suspensions (>20%) is usually not recommended. This could occur either in the calculation of the "pseudo-insert" phase permeability P_{eff} or the overall permeability of the mixed matrix membrane, P_{3mm}. However, Petropoulos found little deviation for $P_d/P_c \sim 10$ (P_d/P_I in the calculation of P_{eff}) between the Maxwell model and more rigorous models for fcc and bcc lattices of spheres until the interparticle gaps became quite narrow (Petropoulos, 1985). For an fcc lattice of spheres, this occurs as ϕ_d (ϕ_s in the calculation of P_{eff}) approaches 74%. For the systems considered here ($\phi_d < 40\%$), ϕ_s was found to be ~50% for the zeolites, and ~68% for the CMS particles. The corresponding P_d/P_I values for our insert with surrounding rigidified interphase are 4.6 for O_2 and 0.75 for N_2. These are even closer to 1 than the P_d/P_c of 10 used by Petropoulos, so even smaller deviations would be expected. As a further check, we used the parallel and series models in place of the Maxwell model for the pseudo-insert phase for the PVAc-zeolite 4A system. Since these models serve as upper and lower bounds for two-phase structures, this allows a measure of the maximum error attributable to choosing a particular model, such as the Maxwell model. At the intermediate loading (25%) for the PVAc-zeolite 4A system, this results in a model permeability uncertainty of ~0.8 Barrers and a model selectivity uncertainty of ~1.5. This uncertainty does not extend to include the calculations corresponding to a single application of the Maxwell model to this system, indicating that there must be an interphase effect, which can only be modeled by accounting for an interphase. Another assumption that requires some justification is the assumption that the particle shape (such as spheres vs. cubes) is unimportant so long as the aspect ratio is approximately unity. Again, we rely on the work of Petropoulos, who showed similar predictions for models using spherical and cubical dispersed phases (Petropoulos, 1985). Thus, the model proposed here is valid to at least a first-order approximation of the physical reality. There are undoubtedly some second-order effects, such as the particle shape and size distributions, that have been neglected in this analysis, but modeling these effects will likely require detailed computer simulations, and is beyond the scope of this work and unnecessary to demonstrate the importance of the interphase.

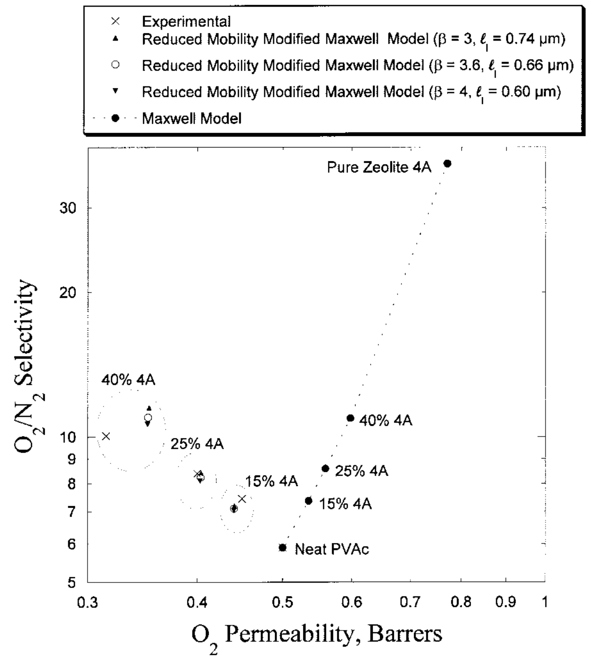

Figure 3. Comparison of experimental data with predictions from the Maxwell model and the reduced mobility modified Maxwell model for zeolite 4A filled PVAc at 35°C.

1 Barrer = 3.35×10^{-16}(mol · m · m^{-2} · s^{-1} · Pa^{-1}).

Results and Discussion

As mentioned above, the results section focuses on interphase effects in mixed matrix membranes prepared with molecular sieving inserts since they have been studied most extensively. Figure 3 presents the observed data and modified Maxwell model predictions for the zeolite 4A-poly(vinyl acetate) (PVAc) system (Mahajan and Koros, 2000). Figure 4 provides similar data for the zeolite 4A-BAPB-BPADA and the zeolite 4A-Ultem® (GE Plastics, Pittsfield, MA) systems (Mahajan and Koros, 2002b). BAPB-BPADA is based on the monomers 2,2′-bis(4-aminophenoxy)biphenyl and bisphenol A tetracarboxylic dianhydride, as shown in the reference. Carbon molecular sieve materials are also viable molecular sieving inserts, as shown in Figure 5 for carbon molecular sieves (CMS) dispersed in Matrimid® (Ciba-Geigy, Ardsley, NY) (Vu et al., 2003a,b). The detailed preparation methods for each membrane are described in the references cited; however, it is important to note that all of these membranes were found to have well-adhered polymer-sieve interfaces. Poorly adhered polymer-sieve interfaces frequently lead to artificially high permeabilities with no change or a slight decrease in permselectivity (Mahajan and Koros, 2002a; Zimmerman et al., 1997). Moreover, these membranes were all cast from solvents too large to enter the sieve pores and dried sufficiently to remove the solvent from the matrix phase prior to testing. Both zeolite 4A and the CMS used in this study have pore sizes and structures (3-D) ideally suited to the separation of oxygen and nitrogen or carbon dioxide and methane. Finally, the zeolites were activated at 250°C under vacuum to remove any sorbed components (that is, water). Mixed matrix membranes were put into permeation cells immediately after drying to minimize the potential for adsorption of water from the atmosphere. The zeolite 4A used in this work has a cubic morphology, with a sidelength of ~5 μm, while the approximately spherical CMS particles had a smaller size, closer to 1 μm.

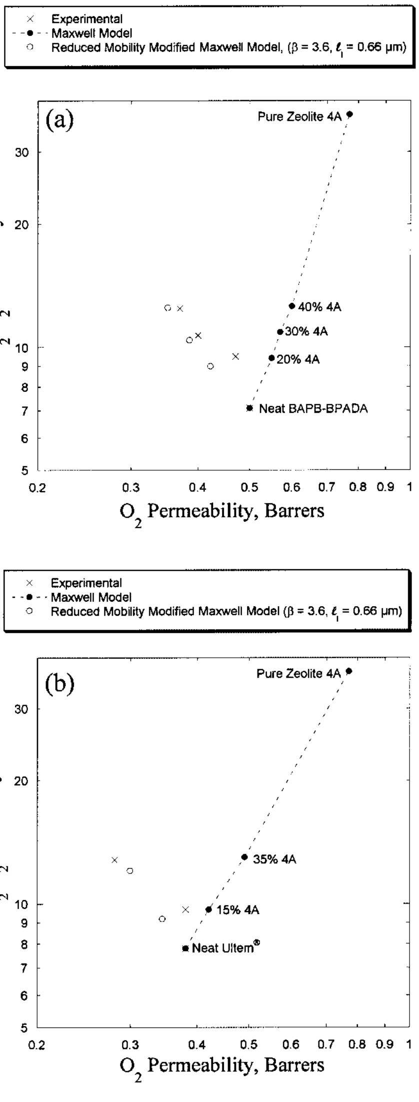

Figure 4. Comparison of experimental data with predictions from the Maxwell model and the reduced mobility modified Maxwell model at 35°C.

(a) Zeolite 4A in BAPB-BPADA; (b) zeolite 4A in Ultem. 1 Barrer = 3.35 × 10^{-16}(mol · m/m^2 · s · Pa).

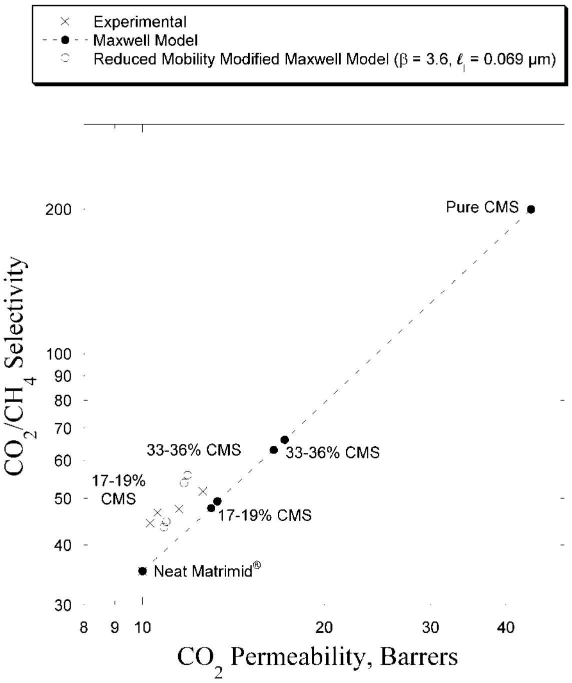

Figure 5. Comparison of experimental data with predictions from the Maxwell model and the reduced mobility modified Maxwell model for CMS filled Matrimid at 35°C.

1 Barrer = 3.35 × 10^{-16}(mol · m · m^{-2} · s^{-1} · Pa^{-1}).

All of the above cases show significant improvement in *permselectivity* beyond the matrix polymer with increasing fraction of the sieve phase in these membranes. However, increasing deviation from the simple Maxwell model predicted *permeability* is observed. The permselectivity was usually within experimental error of the Maxwell model prediction. At the outset, several possible hypotheses were considered to explain this lower-than-predicted permeability, including: poor choice of model, incorrect neat polymer or pure sieve data, blockage of the sieve pores by residual solvent or adsorbed polymer, and reduced mobility of the polymer chains near the sieve surface. Based on the results presented in the following discussion, reduced polymer mobility in an interphase at the insert surface appears to offer the most plausible explanation for transport properties observed in these mixed matrix membranes. The existing models gave similar results (see Figure 1), and so it was clear that they were inadequate to describe the phenomenon observed here. The reasons for ruling out the other potential causes: (i) incorrect neat polymer or pure sieve data and (ii) blockage of the sieve pores by residual solvent or adsorbed polymer are discussed in the appendices.

The observed deviations between predicted and observed permeabilities, which are attributed to inhibition of polymer chain mobility near the polymer-sieve interface, are also consistent with observations of decreased chain mobility reported by researchers working on related problems (Galperin and Kwei, 1966; Manson and Chiu, 1973; Michaels and Parker, 1959; Michaels et al., 1963). An increasing deviation from the simple Maxwell model due to a zone of reduced permeability near the sieve is expected to become more pronounced as the sieve loading increases, since a greater fraction of the polymer matrix would be affected. This trend is clearly apparent in all of the experimental data for these systems. The basic Maxwell model assumes uniform polymer permeability throughout the matrix and, thus, cannot account for these effects, but the modified Maxwell model detailed earlier can be used to examine such effects.

The predictions obtained using this "reduced mobility modified Maxwell model" are also given in Figures 3 and 4 for the zeolite 4A filled membranes. Only the modified Maxwell model displays the proper trend of decreasing permeability with increasing sieve fraction, clearly fitting the experimental data better than any of the existing models. The parameters β and ℓ_I were fit to the data by minimizing the sum of the errors in the oxygen and nitrogen permeabilities for all the zeolite 4A filled membranes. The error was calculated as the difference between the predicted and experimental permeabilities, normalized by the experimental permeabilities so that more permeable membranes did not have undue influence on the fit. The chain immobilization factor β calculated in this manner is 3.6, which is similar to chain immobilization factors in related studies involving semi-crystalline polymers mentioned earlier (Michaels and Parker, 1959; Michaels et al., 1963). This method of global error minimization requires that all the membranes filled with zeolite 4A have the same region of influence, ℓ_I of 0.66 μm. Calculations for different values of β (3 and 4) for the PVAc-zeolite 4A case in Figure 3 show that the predictions are not very sensitive to the values used for β and also that the region of influence is relatively insensitive to the value used for β. The Matrimid-CMS data (Figure 5) was fit by assuming β was the same as for the zeolite filled materials. However, because the CMS are much smaller than zeolite 4A, a smaller radius of influence of 0.069 μm was required to fit the Matrimid-CMS data. This system is also better modeled with the reduced mobility modified Maxwell model.

A better fit of the data can be obtained by optimizing each polymer-sieve system with separate values of the parameters β and ℓ_I (see Appendix C). However, the trends are more important than the actual fit and the model appears to provide a useful framework to capture the trends. The modified Maxwell model assumes a simple expression with a step change in polymer permeability in the interphase, followed by bulk matrix permeability outside the zone of influence. In reality, the permeability presumably changes continuously from a low value close to the sieve to bulk matrix permeability far from the surface. Another complication is that the zeolite 4A sieves are actually cubic; however, assuming they are spherical makes little difference since the aspect ratio is still near unity. More complicated functions relaxing some of these assumptions can ultimately be incorporated into the framework of the modified Maxwell model to provide a more accurate description of these systems. Currently, however, there is insufficient experimental data to justify additional complications and this simple framework appears quite useful.

Recent molecular dynamic simulations of mixed matrix materials have also shown decreased polymer chain mobility and permeability near an interface (Bohning et al., 1999) further supporting the analysis above. The simulation studies looked at a fully siliceous zeolite (ZK4) and poly(dimethylsiloxane) (PDMS), an amorphously-packed rubbery polymer. While the results of that investigation did show reduced chain mobility and consequently decreased movement of individual penetrant molecules, the results did not provide a quantitative number for the decline in permeability. Further work in the area, however, could be used to guide better modeling of these complex transport phenomena, especially if quantitative trends could be identified.

If the matrix surrounding the sieve has reduced mobility, the T_g should increase. This T_g-elevation phenomenon is also postulated to occur, in the absence of other effects, in semi-crystalline polymers with proportionate increases in crystallinity (Andrews and Grulke, 1999). The results suggest that the presence of an insert can affect the fundamental properties (such as T_g) of the polymer matrix when good segmental-level attachment exists between these two phases. Increases in T_g have also been observed with organic-inorganic hybrid materials employing *in situ* growth of dispersed nano silica in silicone rubber and in polyetherimide (that is, Ultem) matrices (Nunes et al., 1999). A correlation of polymer chain mobility or stiffness with T_g increases has been noted for random ionomers (Eisenberg et al., 1990). To explain this phenomenon, Eisenberg et al. have proposed a model that suggests that the mobility of a polymer chain in the "immediate vicinity" of these "multiplet-clusters," or ionic aggregates, can become restricted relative to the chains in the bulk polymer (Eisenberg et al., 1990). They propose that the multiplet-clusters with anchored polymer chains act as effective crosslinks in the bulk polymer to increase the T_g of the material. The glass transition temperatures of CMS filled Matrimid mixed matrix films were determined by differential scanning calorimetry (DSC) (Perkin-Elmer DSC 7 connected to Thermal Analysis Controller (TAC) 7/DX, Norwalk, CT). The T_g for each film was determined from the heat flow vs. temperature curve obtained from the second heating cycle using the onset method. All of the Matrimid films showed increases in T_g of about 15°C, regardless of loading. This may indicate that the interphases overlap to such a degree that the entire matrix has reduced chain mobility. Given an interphase thickness of 0.069 μm (see Figure 5), the affected fractions of the matrix are $\sim$10 and 25% at $\sim$17 and 34% sieve loading, respectively. This is at odds with the DSC data, although Theocaris reports that different methods frequently give different estimates of the influence of an insert (Theocaris and Spathis, 1982). The independent observation of increased T_g in the presence of inserts and suppressed permeabilities certainly provides evidence for reduced chain mobility in an interphase.

Mechanism

Effects on segmental mobility due to surface attachment may not have a long range of influence, but additional, longer range effects can be envisioned. For instance, reduced chain mobility surrounding the dispersed phase may also be due to inhibited isotropic contraction of the polymer at the polymer-insert interface. This effect, illustrated in Figure 6, results from contraction as the casting solvent evaporates. Once the matrix phase of the nascent film becomes vitrified, the polymer chains are effectively frozen in position relative to one another. In a pure polymer film, the entire polymer matrix contracts isotropically as the solvent evaporates beyond the vitrification point. However, in a mixed matrix film, the polymer in contact with the rigid insert is unable to contract. As the rest of the polymer matrix contracts, a stress forms in the layer of polymer surrounding the insert. It is likely that the polymer within this region will have different properties than the bulk polymer, thereby forming the interphase. This hypothesis is analogous to an explanation for the rigidification in filled epoxy composites (Manson and Chiu, 1973). However, in the case of the filled epoxy composites, mismatched thermal contraction, rather than solvent evaporation causes the contraction of the matrix phase and resulting rigidification at the interphase. Both solvent evaporation and cooling result in a decrease in the volume occupied by the polymer matrix, so similar effects should be observed in both cases. Thus, while heating above the T_g should relieve solvent evaporation induced stresses, cooling below the T_g will

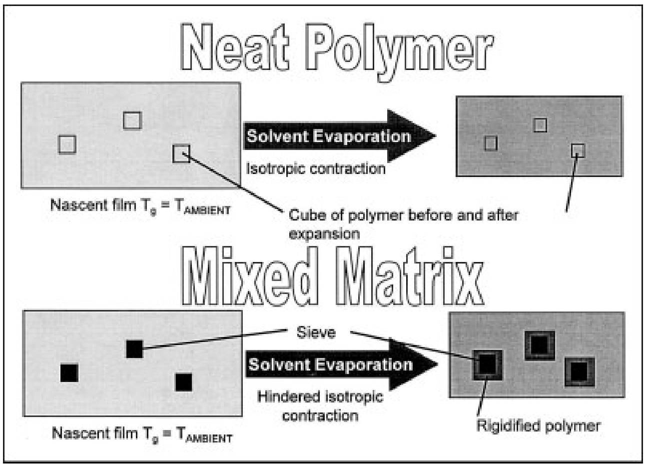

Figure 6. Detail of formation of the rigidified interphase via inhibited isotropic contraction.

reintroduce similar, smaller compressive stresses. Others have also postulated reduced chain mobility at an interface when the contraction is due to cooling below the T_g of the polymer (Kraus and Gruver, 1970; Nielsen and Lewis, 1969) or curing of the polymer matrix (Theocaris and Spathis, 1982). Such effects would undoubtedly impact many aspects of heterogeneous systems, including the transport properties.

If inhibited isotropic contraction is the cause of the rigidified polymer near the sieve surface, the interphase thickness should be a function of the size of the dispersed domain, with smaller sieves having smaller interphases, because they inhibit contraction less. Indeed, the observed zone of influence for 1 μm CMS particles was an order of magnitude smaller than for 5 μm zeolite particles. However, this is circumstantial evidence at best for the "inhibited contraction" hypothesis since the polymers are likely to interact differently with the two inserts. However, inhibited contraction should affect only the thickness of the interphase. If the interphase is thought of as a polymer-sieve surface area multiplied by the interphase thickness, changing the particle size at constant sieve volume fraction has two effects. Decreasing the particle size dramatically increases the polymer-sieve interaction area, and this may dwarf the hypothesized decrease in the interphase thickness. Thus, even if the interphase thickness is reduced for smaller particles, there may be a greater overall decrease in chain mobility compared to larger particles at constrant volume fraction. Clearly, additional study is required to investigate the hypothesis of "inhibited contraction."

Conclusions

This work introduces a potential new kind of mixed matrix material that can be used to separate more condensable, typically larger, components from a mixture. Such a material would incorporate selective surface flow inserts into appropriate polymer matrices to achieve high selectivities. Together with molecular sieving mixed matrix materials, these membranes represent a new paradigm in gas separation technology. When fully developed, it should make membranes more competitive with the three conventional gas separation technologies.

A modified model was presented to predict the performance of mixed matrix membranes. While simplistic in nature, this model is the only one that can properly account for the observed permeabilities of mixed matrix materials. This model assumes that the insert has an associated "interphase" a finite distance from the sieve surface into the polymer matrix. Within this interphase, the mobility of the polymer chains is reduced, leading to reduced permeability. This phenomenon can have a large effect on the overall permeability of mixed matrix membranes; however, the effect on permselectivity remains small since similar sized penetrants undergo similar permeability drops in the rigidified region. Other potential explanations for the lower-than-predicted permeabilities do not match the observed trends and appear less plausible. The presence of a rigidified interphase is further supported by increases in the T_g of polymer-CMS films. These effects may be caused by inhibited contraction at the polymer-insert interface during the formation of these materials, which would result in compressive stresses in the polymer near the particle.

Decreased chain mobility should affect not only the transport properties, but also the mechanical properties. So, it may be interesting to examine the effect of inserts on the mechanical properties of membranes. Some potential applications require high-pressure feeds, so changes in mechanical properties may be important. From a more fundamental standpoint, it is desirable to know how the decreased chain mobility affects both penetrant diffusion and sorption in the interphase. Reduced chain mobility would presumably affect the diffusion coefficient, but if there are any packing effects, the sorption coefficient may also be affected.

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Appendix A: Effects of Transport Property Uncertainty

As noted in the discussion, it is unlikely that the deviation between predicted and experimental permeabilities can be attributed to inaccurate values of the permeabilities of the polymer matrix or the molecular sieve. Aside from BAPB-BPADA, the polymers in this work are well-studied, and the neat polymer properties agree well with the literature. Neat polymer transport properties are relatively simple to measure; so, there is no reason to doubt the properties reported here for neat BAPB-BPADA. The transport properties of the CMS materials were directly characterized by preparing pure, dense, flat-sheet CMS membranes (Steel, 2000) so their properties are also accurately known. Zeolite permeabilities cannot be measured directly because defect-free zeolite membranes cannot be prepared (Caro et al., 2000). Therefore, zeolite permeability was estimated with Eq. 1 as the product of the diffusion and sorption coefficients determined by gravimetric sorption measurements, as described by Zimmerman (1997).

Although care was taken to select reasonable diffusion and sorption coefficients for zeolite 4A, there may be a difference between the actual and estimated permeability of the zeolite 4A. While the estimates of the transport properties of zeolite 4A may not be as accurate as the transport properties measured via gas permeation, this alone cannot account for the observed deviations in experimental and predicted permeabilities. Assuming that the estimated permeability and selectivity of zeolite 4A are incorrect, the Maxwell model can be used to calculate the zeolite permeabilities based on the experimental permeabilities for the mixed matrix membranes and known neat polymer permeabilities. This exercise results in a variation in the calculated sieve properties at each sieve loading, with negative slow gas sieve permeabilities necessary at some loadings to account for the data. Clearly, negative permeabilities are physically unrealistic, indicating that there is a new phenomenon here causing deviation from the Maxwell model, and not a major discrepancy between the actual and estimated properties of zeolite 4A.

Appendix B: Effects of Pore Blockage

Another possibility investigated was potential blockage of the sieve pores by the solvent used to prepare the films. Molecular models of zeolite 4A and the solvents used to prepare the zeolite based membranes were made with Harvard Apparatus (Holliston, MA) CPK space-filling molecular models. These molecular models indicated that it was unlikely that the solvents used for the zeolite based membranes in Figures 3 and 4 could enter the zeolite pores. Because the pore size of the CMS used here is similar to that of zeolite 4A, it is also unlikely that they are blocked by the presence of residual solvent. Work with a material similar to PVAc demonstrated the effect of zeolite pore blocking by a solvent known to fit into the pores of zeolite 4A (Qin, 1999). The results of this investigation are reported in Table B1. Mixed matrix materials were prepared using zeolite 4A and hydrolyzed poly(vinyl acetate) (40% hydrolyzed) (Polysciences, Warrington, PA), cast from methanol. Methanol *is* small enough to enter the pores of zeolite 4A and would also be expected to interact favorably with these hydrophilic sieves, making it difficult to remove if present (Becila et al., 1980). This would lead to blocked pores, essentially making the zeolite impermeable. The observed performance of the mixed matrix membrane prepared from methanol was far below the Maxwell model prediction for open pores, but well matched by a Maxwell prediction assuming *closed pores* (Table B1, Row 3). The selectivity was the same as that of the polymer and the permeability was significantly lower than expected for open pores, indicating that the zeolite pores were indeed filled with methanol. Similar membranes were then prepared with dichloromethane, which is too large to enter the pores, and successful (unblocked) mixed matrix membranes resulted. The performance was close to that predicted for open pores (Table B1, Row 4). The preceding discussion rules out solvent pore blocking as the cause of the difference in observed and predicted permeabilities.

The discussion above does not preclude partial blockage by strongly adsorbed polymer. Even though the polymer chains are extremely unlikely to enter these small pore sieves, they could still block some of the pores by covering them. Despite their flexibility, polymer chains could possibly impede the flow of gas into the sieve pores. These effects could add resistance to gas flow, leading to reduced permeabilities depending on sieve loading. This scenario was examined further by modeling and testing an appropriate surrogate system.

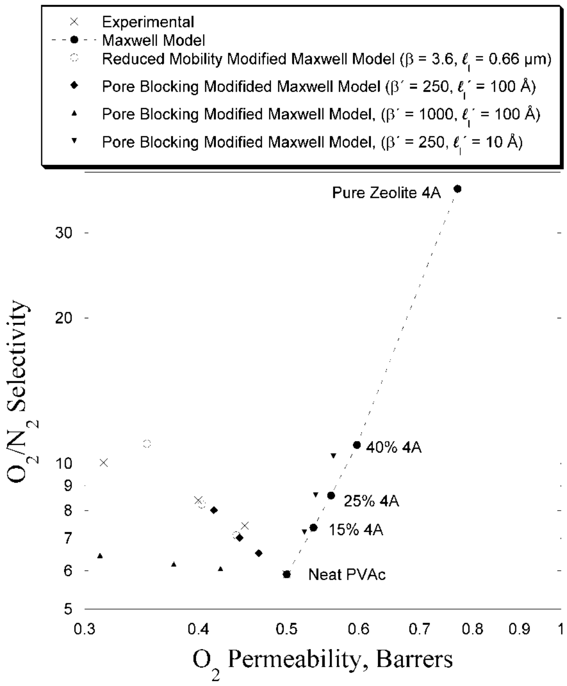

Figure B1. Comparison of experimental data with selected model predictions for PVAc-zeolite 4A mixed matrix membranes at 35°C.

1 Barrer = 3.35 × 10^{-16} (mol · m · m^{-2} · s^{-1} · Pa^{-1}).

Sieve pore blocking can also be explored using the modified Maxwell model. For this case, one can assume a decline in permeability in a small layer *inside* the sieve instead of outside in the polymer. The parameters used for this model are similar to those for reduced chain mobility, but are referred to as β; the decline in permeability of the outer layer of the sieve relative to the bulk sieve, and ℓ'_I, the thickness of this region. Note that in this case ℓ'_I extends a short distance into the sieve. One can assume the decline in permeabilities to be much greater than the reduced chain mobility case, since a fraction of the pores near the surface can actually be blocked. Some of the parameters used and the resulting predictions are shown in Figure B1, along with the Maxwell model and reduced mobility model predictions. The best match is obtained with the reduced mobility modified Maxwell model. It may seem that a suitable choice of parameters could give a good fit even for the pore blocking mechanism, but the sieve volume fraction for the

Table B1. Summary of Experimental Data and Model Predictions for 40% *Hydrolyzed* PVAc-Zeolite 4A Mixed Matrix Membranes at 35°C (All Data Taken from Qin (1999))

	O_2 Permeability (Barrer)		O_2/N_2 Permselectivity	
Mixed Matrix Films	Experimental	Maxwell Model Predictions	Experimental	Maxwell Model Predictions
Neat 40% hydrolyzed PVAc (0 vol % 4A)	0.28	0.28	6.7	6.7
Pure zeolite 4A	0.77	0.77	37	37
15 vol. % 4A in PVAC cast from methanol	0.22	0.23 Assumes closed 4A	6.7	6.7 Assumes closed 4A
15 vol. % 4A in PVAC cast from dichloromethane	0.29	0.33 Assumes open 4A	8.0	8.6 Assumes open 4A

1 Barrer = 1 × 10^{-10} (mol · m · m^{-2} · s^{-1} · Pa^{-1}) = 3.35 × 10^{-16} (mol · m · m^{-2} · s^{-1} · Pa^{-1}).

Table B2. Comparison of Observed Data for a PVAc-Zeolite 3A Mixed Matrix Membrane with Predicted Performance at 35°C (Note that the Parameters for the Modified Maxwell Model Are the Same as for Those Used for the PVAc-Zeolite 4A Membrane in Figure 3)

	O_2 Permeability (Barrer)			O_2/N_2 Permselectivity		
Mixed Matrix Films	Experimental	Maxwell Model Predictions	Modified Maxwell Model Predictions*	Experimental	Maxwell Model Predictions	Modified Maxwell Model Predictions*
Neat PVAc (0 vol. % 3A)	0.50	0.50	0.50	5.9	5.9	5.9
Pure zeolite 3A	0	0	0	N/A	N/A	N/A
15 vol. % 3A	0.32	0.40	0.33	6.2	5.9	5.9

* 4A particles are assumed to be 5 μm in size (that is, diameter). The chain immobilization factor β was 3.6, and the thickness of the region of influence ℓ_I was 0.66 μm.
1 Barrer = 1×10^{-10} (mol · m · m^{-2} · s^{-1} · Pa^{-1}) = 3.35×10^{-16}(mol · m · m^{-2} · s^{-1} · Pa^{-1}).

predictions must correspond to the sieve volume fractions of the experimental data. One can obtain a line that fits the *trajectory* of the experimental data, but the predictions at the actual sieve loadings do not correspond to experimental observations for the same sieve loadings. On the other hand, the modified Maxwell model predictions for reduced polymer mobility calculated at various loadings (shown in Figure B1) correspond to the experimental loadings.

The results presented in Figure B1 suggest that pore blocking by adsorbed polymer alone cannot account for the deviations, but it could still be operating in combination with reduced chain mobility. To further understand the mechanism and to confirm which of the two phenomena was dominant, experiments were performed with zeolite 3A filled poly(vinyl acetate). The cation in zeolite 3A is potassium instead of sodium, as in zeolite 4A. Since the potassium cation is larger than the sodium cation, the pore size in zeolite 3A is 3.0 Å, instead of 3.8 Å in zeolite 4A (Breck, 1974). Although the cation within the pore structure is different for these two zeolites, their surfaces are very similar, so interaction of PVAc with the surfaces of these two zeolites should be comparable. The smaller pore size of zeolite 3A makes it impermeable to both oxygen and nitrogen. Thus, mixed matrix membranes prepared with zeolite 3A in PVAc provide a surrogate system to study potential reduced chain mobility effects without the possibility for pore blockage by the polymer, since zeolite 3A is already impermeable. Therefore, any experimental permeability lower than the Maxwell model prediction (with $\boldsymbol{P}_d = 0$) for this system *must be* attributed to reduced chain mobility and reduced polymer permeability in the interphase. Furthermore, if reduced chain mobility is the only effect occurring, the adjustable parameters in the modified Maxwell model β and ℓ_I for the PVAc-zeolite 3A system should be similar to those for the PVAc-zeolite 4A system. If both reduced chain mobility and pore blockage were operating in the PVAc-zeolite 4A system, one would expect only reduced chain mobility in PVAc-zeolite 3A system. In this case, the result should be a smaller deviation from the Maxwell model in the PVAc-zeolite 3A system than the PVAc-zeolite 4A system.

Mixed matrix materials were prepared at 15% loading with zeolite 3A and PVAc using the same solvent and procedure used to prepare the PVAc-zeolite 4A membranes. The results of the experiment are summarized in Table B2 along with predictions using the Maxwell model and the modified Maxwell model for reduced chain mobility. The parameters used for the reduced chain mobility modified Maxwell model are the ones that gave a reasonable fit with the PVAc-zeolite 4A system (Figure 3). The estimates from the reduced chain mobility modified Maxwell model *are much closer to the observed values* than the simple Maxwell model predictions, strongly suggesting that reduced chain mobility is indeed the cause of the observed deviations.

Appendix C: Individual Fitting Parameters for the Reduced Mobility Modified Maxwell Model

The parameters (ℓ_I and β) for individual systems obtained by a least-squares fit of the reduced mobility modified Maxwell model normalized by the experimental permeability are listed below in Table C1. While there is clearly some variability between the chain immobilization factors for the three polymers used with zeolite 4A, the interphase thicknesses are reasonably close given the approximate nature of the modeling. Without further study, it is not possible to say whether the differences in the chain immobilization factors for the three materials used with zeolite 4A (and similarly for the three different classes of polymers they represent) are significant.

Table C1. Best Fits (ℓ_I and β) of the Parameters in the Reduced Mobility Modified Maxwell Model for the Systems Studied in this Work

	Zeolite 4A Dispersed In:			CMS Dispersed In:
Mixed Matrix Films	PVAc	BAPB-BPADA	Ultem	Matrimid
ℓ_I; interphase thickness, μm	0.64	0.66	0.88	0.046
β; chain immobilization factor	4.2	3.0	2.6	4.9

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