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Water Vapor Sorption and Diffusion in Glassy Polymers

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SUMMARY: By establishing relationships between polymer structure and gas permeation behavior, significant advances have been made in designing materials for membrane separation of gas mixtures. However, the situation is not so well understood when water vapor is one of the components since water molecules may interact with the polymer (plasticization) or each other (clustering) in ways that complicate the structure-property relationships. In addition, accurate measurement of water sorption, diffusion, and permeation is more complicated than for gases because of the unique hydrogen bonding capability of water, e.g., its tendency to strongly adsorb on high-energy surfaces and high heat of vaporization. A progress report on a broad program to understand water sorption and diffusion in glassy polymers that may be of interest for membrane applications is outlined; specific strategies include studies of structurally related polymers and miscible blends of hydrophobic/hydrophilic polymer pairs.

Introduction

Separation of gases using polymeric membranes has become a well-developed technology over the past two decades [1]. Glassy polymers have emerged as the materials of choice for such applications because they offer the best combination of selectivity versus productivity; they generally possess adequate mechanical properties and many can be formed into composite or asymmetric structures needed for high flux. High permeability glassy polymers can be achieved by appropriate design of the repeat unit structure that leads to a high free volume or low chain packing efficiency. High selectivity is achieved by limiting the mobility of the polymer chains by making rotational motions about the chain axis difficult. For gases like H_2, O_2, N_2, CH_4 and even CO_2, interactions between the gas molecules and the polymer segments represent, at most, second order considerations in the selection or design of the polymeric membrane material[1].

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However, the situation is not so simple when one of the components is water vapor since it can interact with polymer segments and itself much more strongly than most gases; thus, these interactions become an important consideration in the design of membrane materials for separation of water from gas streams[2, 3].

Gas Permeability Behavior

Extensive investigations have been reported on the optimization of the repeat unit structure of glassy polymers in search of materials that simultaneously maximize permeability (productivity) and selectivity since this is the key to successful gas separation membrane systems. The results of these studies have been reduced to group contribution methods that permit prediction of permeation properties in terms of repeat unit molecular structure[4,5]. More empirical correlations of selectivity-permeability data appear to identify upper-bound relationships[6] for each gas pair beyond which better combinations of permeability and selectivity have not yet been found and may not be possible. This level of predictability, or at least regularity, of permeation behavior in terms of polymer structure no doubt stems from some simplifications that apply for simple gas molecules. The permeability coefficient, P, can be factored into diffusion, D, and solubility, S, coefficients as follows

$$P = DS$$

For gases in glassy polymers, these coefficients depend somewhat on the gas pressure in ways that are well described using the so-called "dual sorption" theory applicable for glassy polymers[1]; however, such effects are relatively unimportant in the boarder picture to be considered here.

For simple gases, the solubility coefficient varies in a quite predictable way from one gas to another (based on the condensability of the gas) but relatively less from one polymer to another[7]. The diffusion coefficient varies according to the molecular size of the gas molecule and the fractional free volume, FFV, of the polymer. As a result of this consideration, the permeability coefficient of a given gas can be rather successfully correlated with the fractional free volume of the polymer[1]. These simplifications stem from the relatively weak interactions of the gas molecules with the polymer segments and with themselves.

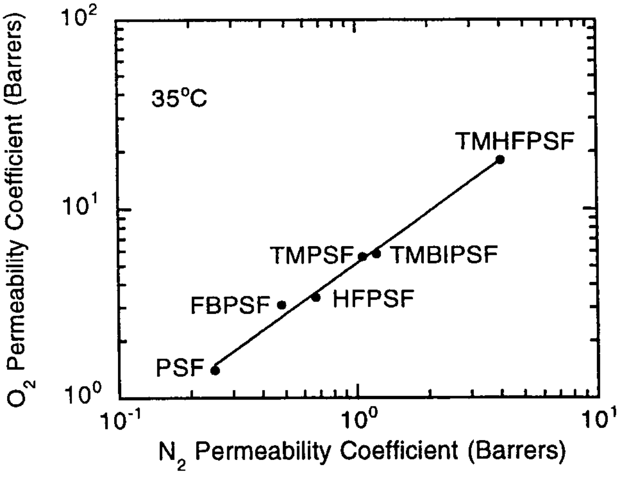

Figure 1 Illustration of a high degree of correlation between the permeability of a series polysulfone polymers to O_2 and N_2

A consequence of these issues is that, for the most part, the structural factors of a polymer that influence the permeability of one gas similarly affects the permeability of another gas.

This fact is conveniently illustrated for the gas pair O_2 and N_2 in a series of polysulfones where various substitutions on the aromatic rings (TM = tetramethyl) or the connector group (HF = hexafluoro ispropylidene, FB = fluorene bisphenol, BI = biphenol, etc.) of the bisphenol-A based polysulfone, PSF, have been made2).

The result is a near perfect correlation between the permeability coefficients for O_2 versus that for N_2 as seen in Figure 1.

Water Vapor Permeation Behavior

For a penetrant like water that can strongly interact with the polymer or with itself, the types of simplifications mentioned above for gases may not apply. First, the solubility of water in a polymer depends strongly on the interaction of the water molecules with the polymer repeat unit and does not fall within any predictable progression of behavior for other gas molecules. In other words, the solubility coefficient for water may vary enormously from one polymer to another based on the water-polymer interaction. In addition, the solubility coefficient may depend strongly on the water vapor activity.

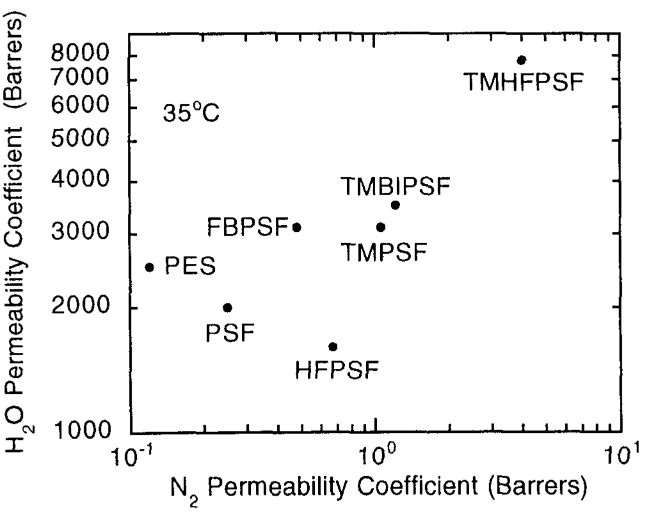

Figure 2 Illustration of the lack of correlation between the permeability of water vapor and N_2 gas for a series of polysulfones

The diffusion coefficient for water in glassy polymers does, as in the case of gases, depend on the polymer fractional free volume[2, 3]. However, this relationship is complicated by two factors: (1) plasticization of the polymer as a result of high levels of water sorption that changes the mobility of the polymer segments, usually the glass transition temperature is lowered as a result, and (2) clustering of water molecules with one another which causes the size of the diffusing unit to be larger than individual molecules. The first causes the diffusion coefficient to be higher than expected while the latter causes it to be lower[2], when both factors are eliminated or held constant, the diffusion coefficient of water varies in a predictable way with polymer fractional free volume.

The consequence of the above considerations is that water vapor permeability is not influenced by polymer structure in the same predictable fashion observed for simple gas molecules. This is illustrated in Figure 2 where the water vapor permeability is plotted versus the N_2 permeability for the same series of polysulfones considered in Figure 1. Clearly, there is not a simple correlation between permeability coefficients in Figure 2 as was found in Figure 1.

There is a need for membrane systems that efficiently remove water vapor from gas streams with little loss of gas through the membrane, e.g., dehydration of natural gas. The optimization of polymer structure for such applications involves additional factors than for simple gas pairs like O_2/N_2 and is the subject of recent investigations.

Water Vapor Sorption and Diffusion in Miscible Polymer Blends

A potentially useful way to modify the permeation behavior of penetrants in a systematic and continuous way is via miscible polymer blends. For water, this could be a powerful approach when one polymer is hydrophilic and the other is hydrophobic. Given the fact that polymer blend pairs are thermodynamically not likely to be miscible8), it would seem unlikely that many miscible hydrophilic/hydrophobic pairs would exist. However, Table 1 identifies a number of such systems.

Table 1 Miscible Blends Of Hydrophilic/Hydrophobic Polymer Pairs

Water Soluble Polymer	Hydrophobic Polymer	Reference
Polyethyloxazoline	Styrene/acrylonitrile copolymers	9
Polyethyloxazoline	Phenoxy	9
Polyethyloxazoline	Polyethersulfone	3
Poly(N-vinyl-2-pyrrolidone)	Phenoxy	10, 11
Poly(N-vinyl-2-pyrrolidone)	Macrocyclic polyether-polyamide	12
Poly(vinyl methyl ether)	Polystyrene	13-16
Poly(vinyl methyl ether)	Phenoxy	17
Poly(ethylene oxide)	Phenoxy	17
Poly(ethylene oxide)	Polyethersulfone	18
Poly(ethylene oxide)	Poly(epichlorohydrin)	19
Poly(ethylene oxide)	Poly(methyl methacrylate)	19

Water sorption and diffusion has been reported for several of the systems described in Table 1.3, 20-23) It has been shown that the extent of water sorption can be increased quite substantially by adding a hydrophilic, or even water-soluble polymer, to the hydrophobic polymer. However, in many cases, the diffusion coefficient is discussed as the hydrophilic

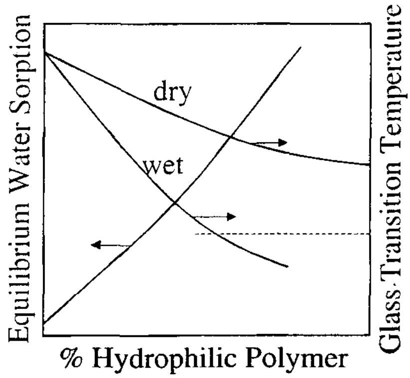

Figure 3 Water sorption and glass transition temperature behavior of miscible blends of a hydrophobic polymer with a hydrophilic polymer

component is added since these are generally polar materials that have strong self-associations which lead to low fractional free volume.3) Thus, water vapor permeability may not increase as a result of blending the hydrophilic polymer with the hydrophobic material.3)

Miscible blends of hydrophilic polymers with hydrophobic base polymers are an attractive approach for continuously varying the interaction with water without synthesis of new polymers as mentioned above. However, there are some natural stability limits that must be considered. As more and more water is sorbed into such a mixture, the relative environment for the two types of polymers is altered dramatically. The hydrophilic component is thermodynamically compatible with the water environment whereas the hydrophobic component is not. If the mobility of the mixture permits, the two polymers, while miscible with each other, will escape to separate phases in the presence of water; one rich in the hydrophobic component where little water is sorbed and the other rich in the hydrophilic component where the water content is high. Figure 3 illustrates the criteria for such phase segregation. As the fraction of hydrophilic polymer in the blend increases, the equilibrium uptake of liquid water increases. The glass transition temperature of the blend in the absence of water (dry) is a unique function of blend composition; in most of the cases in Table 1, the Tg of the hydrophilic polymer is lower than that of the hydrophobic polymer. In the presence of water, the Tg of the blend (line labeled wet) is decreased by plasticization from the sorbed water. The extent of plasticization becomes larger as the content of the hydrophilic polymer increases. At some point, the Tg of the water saturated blend (wet) is reduced below ambient temperature (dotted line) and enough mobility exists for phase separation of blends having a higher content of hydrophilic polymer than that defined by this condition.3, 20)

It is interesting to note that such blends can be extremely resistant to extraction of the water-soluble polymer or to disintegration. Below the critical content of hydrophilic polymer, the Tg of the blend in the wet state is above ambient and there is insufficient chain mobility for extraction in liquid water. Even beyond the point of phase separation, a surprising level of integrity of the highly swollen structure and resistance to extraction has been observed in some instances. This has been attributed to the formation of two-phase morphologies like that illustrated in Figure 4. Segments of the hydrophilic polymer are trapped in the hydrophobic domains, and these domains are tied to one another as suggested to form a highly swollen but kinetically stable structure.[20)]

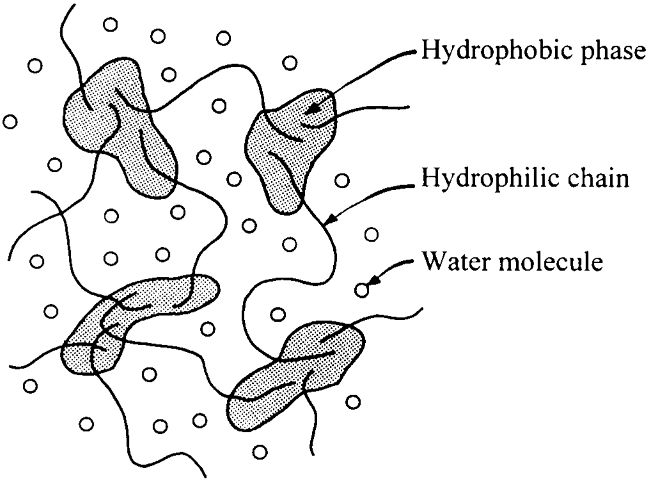

Figure 4 Schematic of the phase morphology of a miscible blend of hydrophobic/hydrophilic polymers that has phase separated due to water sorption

Summary

There are some important applications of polymeric membranes for separations involving water as one of the components. The optimization of polymer structure for these cases involves additional considerations than the well-studied case of separations involving only simple gases. A few strategies for designing polymers for such applications and understanding the transport-structure relationships have been reviewed here..

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