Effect of Particle Size on Gas Permeability of Filled Superglassy Polymers

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Introduction

Filled polymeric systems are widely used in a number of industries, including membrane and barrier applications. Generally, incorporating inert, nonporous fillers into a polymer membrane results in a decrease in its gas permeability. This permeability reduction results because filler particles typically lower both gas solubility and gas diffusivity within the polymer. In the simplest case, gas solubility in a polymer/filler composite, S_f, is the solubility in the volume fraction of polymer present; that is, $S_f = S(1 - \varphi)$, where φ is the filler volume fraction and S is gas solubility in the polymer. Filler particles also increase the average path length experienced by gas molecules traversing the membrane. Consequently, the gas diffusion coefficient in the composite, D_f, is the diffusion coefficient in the unfilled polymer, D, reduced by a tortuosity factor τ, defined to be the ratio of the average diffusion path length in the filled polymer to that in the unfilled polymer; that is, $D_f = D/\tau$. Therefore, as gas permeability in the composite polymer, P_f, is the product of gas solubility and gas diffusivity (i.e., $P_f = S_f D_f$), P_f usually decreases relative to P_o, the unfilled polymer permeability, with increasing volume fraction of filler.[1]

A simple relationship between filler volume fraction in a polymer composite and the associated relative permeability, P_f/P_o, has been derived by Nielson[2] and others[1,3] by analogy from an electric conductivity expression first proposed by Maxwell[4] for heterogeneous media. As might be expected, P_f/P_o decreases monotonically with increasing filler content, and this relationship has been demonstrated to hold, at least qualitatively, for several filled polymer systems.[1,3] Other alternate relationships[5−7] have also been proposed to describe permeability in polymer composites. Each of these expressions accounts for the impact of filler volume fraction on relative permeability, and some also describe the effect of filler particle aspect ratio. However, all of these theoretical models predict P_f/P_o to be independent of the average size of spherical filler particles.

High-free-volume (i.e., superglassy) polymers such as poly(1-trimethylsilyl-1-propyne) [PTMSP] and poly(4-methyl-2-pentyne) [PMP] display unique and unexpected gas permeability behavior because of their unusual microstructure.[8] Gas permeabilities in these amorphous, glassy materials are higher than those in any other known polymer, including silicone rubber.[9−11] The anomalous gas transport properties of superglassy polymers have been explained in terms of poor packing of the polymer chains due to their backbone stiffness (a consequence of the high degree of unsaturation) and bulky pendant groups.[8] This very poor chain packing is postulated to lead to a particularly nanoporous morphology consisting of large, interconnected free volume elements in these polymers.[12,13] Such interconnected pathways, though not large enough to support Knudsen flow, are adequate to confer very high gas permeability to superglassy materials, as compared to the much lower permeability of common polymers, which lack these rapid diffusion channels.

Recently, the addition of fumed silica nanoparticles to PTMSP and PMP was found to increase permeability with increasing filler content up to a level as high as 30 vol %.[14−16] This behavior is completely contrary to that in traditional filled polymer systems where, as mentioned, permeability typically decreases with increasing filler loading. The unusual transport behavior in filled superglassy polymers has been ascribed to the ability of the tiny fumed silica particles to disrupt chain packing in these rigid polymers, leading to an increase in system free volume. This enhanced free volume in filled superglassy polymers has been confirmed by both positron annihilation lifetime spectroscopy[14−16] and ^{129}Xe NMR.[17] It has also been noted that, in addition to filler concentration, filler particle size appears to affect permeability in filled superglassy systems as well. In a previous study,[14] five fillers with different particle diameters (7−500 nm) and different surface chemistries (precipitated silica, hydrophilic and hydrophobic fumed silicas, carbon black, and α-alumina powder) were added to PMP. At a fixed filler volume fraction, different PMP/filler nanocomposites showed significant differences in gas permeability. In general, it appeared that smaller filler particles produce larger increases in permeability at a constant filler volume fraction.[14] However, the widely different surface chemistries of the fillers used made it difficult to unambiguously interpret the effect of particle size on permeability.

Here we seek to clarify the issue of particle size by reporting for the first time data showing clearly that, at constant filler volume fraction, gas permeability in PTMSP/fumed silica nanocomposites increases with decreasing filler size. These results are compared with those previously obtained for PMP, and a rationale for the effect of filler particle size on gas permeability in filled superglassy polymers is discussed.

Experimental Section

The PTMSP was kindly synthesized by Permea, Inc. (St. Louis, MO) using $TaCl_5$ catalyst. Fumed silicas having different primary particle sizes, ranging from 7 to 40 nm, were supplied by Cabot Corp. (Cab-O-Sil TS-530; Tuscola, IL) and Degussa Corp. (Aerosil R 812, R 972, and RX 50; Piscataway, NJ). Because these fumed silicas have been hydrophobized with trimethylsilyl groups (TS-530, R 812, and RX 50) or dimethylsilyl groups (R 972) via surface treatment with hexamethyldisilazane or dimethyldichlorosilane, respectively, their surface chemistries can be considered essentially equivalent for the purpose of our study. The PTMSP/fumed silica nanocomposite films were prepared by solution-casting physically blended mixtures of PTMSP and silica filler in toluene according to a procedure described elsewhere.[16,17] Resultant

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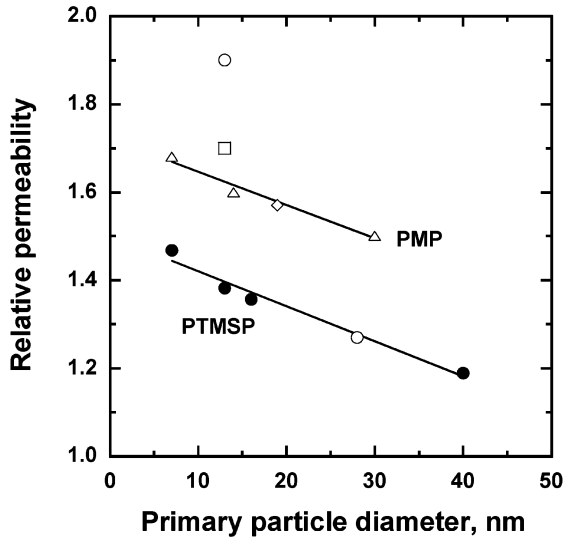

Figure 1. Effect of filler primary particle size on relative gas permeability (P_f/P_o) in filled PTMSP at constant filler volume fraction of ~0.13. Data for PTMSP loaded with fumed silicas (Cab-O-Sil TS-530; Aerosil R 812, R 972, and RX 50) having essentially equivalent hydrophobic surface chemistries were obtained with pure nitrogen at 21 °C and are shown as filled circles (●). Uncertainty in relative permeability data for PTMSP is roughly ±10% from a propagation-of-error analysis. For comparison, previously reported 25 °C methane permeation data[14] for PMP containing various fillers at the same volume fraction of 0.13 are shown as open symbols [○, hydrophobic Cab-O-Sil fumed silicas TS-530 and TS-720; △, hydrophilic Cab-O-Sil fumed silicas EH-5, M-5, and L-90; ◇, precipitated silica Hi-Sil 233; □, carbon black Monarch 1300]. For PMP, the line drawn here passes through the data points for hydrophilic fumed silicas.

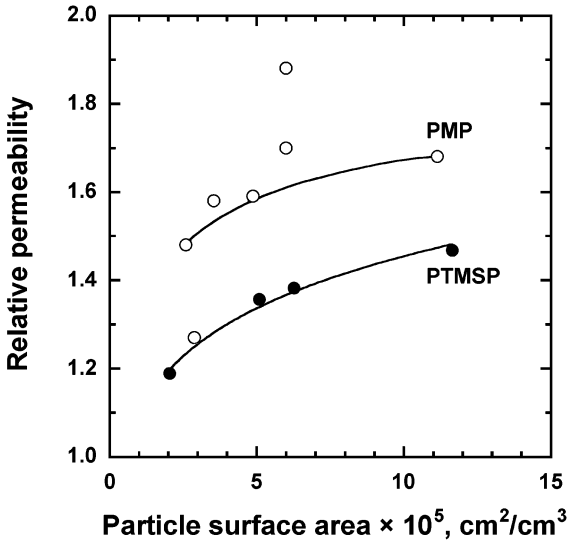

Figure 2. Effect of total filler particle surface area on relative gas permeability (filled/unfilled) in filled PTMSP and PMP at constant filler volume fraction of ~0.13. Filled PTMSP data (●) were obtained in this study with pure nitrogen at 21 °C. Filled PMP data (○) from ref 14 were determined with pure methane at 25 °C and are replotted here with respect to particle surface area for comparison. Fillers used are those identified in Figure 1.

dried films measured 80−95 μm thick and contained ~13 vol % (30 wt %) fumed silica. Pure nitrogen permeability of the filled PTMSP films was determined with an uncertainty of ±7% at 21 °C with a constant-pressure/variable-pressure apparatus.[18] The feed pressure used in the experiments was 50 psig; the permeate pressure was maintained at 0 psig (atmospheric).

Results and Discussion

Figure 1 presents the relative permeability of PTMSP nanocomposite films containing 13 vol % fumed silica as a function of primary particle diameter of the filler. Consistent with earlier results,[16,17] the permeability of superglassy PTMSP is increased by the addition of nanoparticles. This departure from traditional filled polymer behavior has been attributed to the rigid nature of superglassy polymers, which limits their ability to accommodate nanoparticles without significant chain packing disruption and a resultant increase in system free volume.[16] In addition to enhanced permeability, the effect of filler particle size on permeability in filled PTMSP is also evident in Figure 1. Relative permeability in the PTMSP/silica nanocomposites decreases linearly (correlation coefficient $R^2 = 0.97$) as the silica primary particle size increases from 7 to 40 nm. This result, while not predicted by conventional filled polymer theory, is qualitatively consistent with previously reported data for several different filler types in PMP, which are also plotted in Figure 1 for comparison.[14] Relative to the data for filled PMP, the filled PTMSP data exhibit much less scatter presumably because filler particle surface chemistry is not a variable in the PTMSP system.

The strong correlation between relative permeability and primary particle diameter of filler is unexpected, not only because of theoretical considerations pointing to filler volume fraction as the only important parameter but also because fumed silica is unlikely to exist as discrete, individual particles in a polymer matrix. Most commercial applications of fumed silica rely on its well-known ability to form aggregate structures when dispersed in various media. Microscopic studies of PMP/fumed silica nanocomposites show the presence of silica aggregates in the 100 nm size range.[14,15] Because PTMSP/fumed silica films were prepared by a similar physical-dispersion/solution-casting method used to make PMP/silica composites, it is likely that fumed silica clustering also occurs in the PTMSP system. Whether the size of the silica aggregates scales with primary particle diameter, though, is unknown.

Regardless of the extent of filler clustering, the number of filler particles inserted into a polymer matrix at fixed volume fraction increases as particle size decreases. In our filled PTMSP/fumed silica system, the number of filler particles per cubic centimeter of composite increases by approximately 2 orders of magnitude when particle size decreases from 40 to 7 nm. Correspondingly, the particle surface area also increases substantially, so that there is much more potential polymer−filler interfacial area in PTMSP containing 7 nm particles than in PTMSP containing the same volume fraction of 40 nm particles. (Of course, because of particle−particle contact, the polymer−filler interfacial area is not necessarily equal to the particle surface area; nevertheless, it is likely that these two parameters correlate.) As illustrated in Figure 2, relative permeability in the nanocomposites increases with increasing filler particle surface area. This result suggests that the locus of rapid mass transport in these filled superglassy polymers is at the polymer−filler interface. Presumably, rigid PMP or PTMSP chains are unable to pack efficiently around the periphery of silica filler particles, resulting in a low-density polymer−filler interfacial

region. The relatively high free volume in this area would allow gas molecules to diffuse more rapidly compared to their movement in the bulk polymer. Consequently, as interfacial area is increased by reducing filler particle size, gas permeability increases.

To our knowledge, except for studies on high-aspect-ratio particles used to enhance membrane barrier properties, the only other investigation of the effect of filler particle size on membrane transport properties is recent work by Tantekin-Ersolmaz et al.[19] These authors report that, at fixed concentration of zeolite filler, the permeability of silicone rubber membranes decreases with decreasing zeolite particle size. This result was attributed to increased mass transfer resistance at polymer−filler interfaces, which are present in greater number for smaller particles.[19] This finding is very different from the permeation behavior observed in the filled superglassy polymer systems where permeability *increases* with decreasing particle size. Nevertheless, in both silicone rubber and superglassy systems, the apparent effect of filler particle size on permeability appears to be related to the amount of polymer−filler interfacial area and the relative ease of molecular diffusion in this interfacial region. For a flexible elastomer (silicone rubber) filled with micron-scale zeolites, the polymer−filler interface represents an area of increased resistance to mass transport. In contrast, for superglassy polymers (PTMSP and PMP), the inability of rigid polymer chains to wrap around nanoscale silica particles results in a relatively high-free-volume interface where rapid gas diffusion is permitted.

Conclusion

At a constant volume fraction of nonporous fumed silica nanoparticles with essentially equivalent surface chemistries, gas permeability of PTMSP/silica nanocomposites increases linearly with decreasing primary particle size. This dependence is in contrast to simple theoretical treatments predicting that permeability in filled polymers varies solely with filler volume fraction. It appears that the unusual behavior in this and other filled polymer systems recently examined is related to the overriding influence of the polymer−filler interfacial layer on molecular transport.

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