334d Permeability Enhancement in Nanoparticle Filled Polymeric Membranes

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Traditionally, the addition of impermeable particles to rubbery polymeric membranes reduces light gas and vapor permeability as particle loading increases. This phenomenon is well known for barrier materials, and there are numerous models, such as one derived by Maxwell, that accurately predict permeability decrease in membranes filled with impermeable particles.[1]

Recently, nanoparticle filled polymers have been prepared that have over an order of magnitude higher light gas (i.e., CO2, N2, O2, H2) permeability with little or no change in selectivity relative to that of the unfilled polymer, which runs counter to traditional filled polymers. This phenomena has been observed in a broad range of polymeric materials, from high free volume stiff-chain polyacetylenes and crosslinked poly(ethylene oxide) to commodity materials such as 1,2-polybutadiene and poly(ethylene-co-1-octene). The degree of permeability enhancement is polymer and particle loading dependent, and our studies include a wide range of polymer and particle chemistries, including situations where the polymer and particle can react. Moreover, nanocomposite light gas permeability and selectivity are highly dependent on nanoparticle surface chemistry. The nanoparticles are nonporous and are primarily from the metal oxide family (MgO, SiO2, TiO2, etc.). Some of the particles are available as small as 2.5 nm primary particle diameter. These nanocomposites have been characterized using light gas sorption and permeation to monitor gas transport properties as well as SEM and TEM to characterize particle distribution within the polymer matrix.

Using appropriate nanoparticle and polymer combinations permits preparation of nanocomposite membranes that are over 90 weight percent nanoparticles. In such instances, it has been necessary to investigate fractional free volume and membrane void space behavior to characterize the structure of materials with such extremely high nanoparticle loadings.

[1] R. M. Barrer, J. A. Barrie and M. G. Rogers, Heterogenous Membranes: Diffusion in Filled Rubber, Journal of Polymer Science, Part A: Polymer Chemistry, 1 (1963) 2565-2586.