

## 72f Designing Nanoporous Polymers Using Sol-Gel Techniques for Permeation Membrane and Thermal Insulation Applications

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The objective of this talk is to discuss the methods of designing nanoporous polymeric materials based on sol-gel techniques for permeation membrane and thermal insulation applications. First the design of nanoporous polymer membranes based on an epoxy-amine sol-gel technique and the subsequent characterization of transport properties will be discussed. Transport properties of a porous membrane depend upon its ability to facilitate molecular motions which could be random or directed by specific interaction effects. The random molecular motion or diffusion takes place through the pore or free volume in the membrane and the directional transport mechanisms are facilitated by the interactions between the permeant and the functional groups on the pore interface. Thus designing nanoporous polymer networks for these applications involves controlling the network and pore structures and the resulting transport properties by tailoring the pore size, structure and pore interface activity/functionality. A novel method of designing membranes with controlled nanoporous structures was developed based on reactive encapsulation of a solvent (RES) using step-growth polymerization without micro/macroscale phase separation. The step-growth system of epoxy-amine (diglycidyl ether of bisphenol A - EPON 828 and 4,4'-methylenebis(cyclohexylamine)) in the presence of tetrahydrofuran (THF) as a chemically inert solvent gave the miscibility characteristics required for the reactive encapsulation to occur. This system unlike the conventional systems based on micro/macroscale phase separation resulted in homogenous nanoporous structures and their porosity and pore size could be directly influenced by changing the solvent content. Fundamental transport properties such as permeability (P), diffusivity (D) and partition coefficient (K) of the membrane were determined using permeation and equilibrium sorption studies. Permeation experiments showed that the permeability of the permeant (phenyl glycidyl ether – PGE) through the membrane increased with the solvent content. These experiments were analyzed using a pseudosteady state assumption. It was found that both diffusion and solubility characteristics of the membranes were influenced by the solvent content. Increasing the solvent content improved the diffusion characteristics significantly in comparison to the solubility effects. This effect could be potentially used in designing separation membranes as the diffusion limitations of the membranes could be effectively improved by increasing the solvent content while significantly maintaining the permeation behavior due to the interaction or solubility effects.

Nanoporous polymers could be potentially used as materials for thermal insulation. Currently polymeric foams with pores in the micron length scale are used as insulation materials which can almost match the thermal conductivity of air ( $\sim 24 \text{ mW/m}\cdot\text{K}$  at  $25^\circ\text{C}$ ), but going below this requires a new generation of highly nanoporous materials that take advantage of the Knudsen effect. The thermal conductivity of insulation materials is due to conductive heat transfer through the solids, through gas molecules that occupy the pores and due to radiative transport. In the conventional polymer foams the major contribution to the thermal conductivity is due to intermolecular collisions between gas molecules within the pores. Reducing the pore sizes to nanoscopic level would increase the collisions between the gas molecules and the pore walls i.e. Knudsen effect, such an effect could be potentially used to reduce the thermal conductivity. In addition, porosity in these materials should be as high as possible in order to reduce the contribution due to heat conduction through the solids. Thus for effective thermal insulation, materials with high porosity ( $\geq 90\%$ ) and nanoscopic ( $\sim 100 \text{ nm}$ ) pores are required. In order to design such materials, solvogels were synthesized based on widely used polyurethane chemistry and subsequently dried under ambient conditions. The objective here was to control the reaction, solvation and phase separation characteristics of the system to design materials with optimal nanoporous structure for thermal insulation applications. The nanoporous structures obtained using this method were characterized using SEM, nitrogen adsorption and mercury intrusion techniques. These analyses showed that the polyurethane based sol-gel technique can be used to design materials with the desired pore size

and porosity. Future work would involve measuring the thermal conductivities and analyzing these materials for the presence of Knudsen effects. Evidence of such effects could be potentially used to design advanced nanostructured materials that could be used as effective thermal insulators.