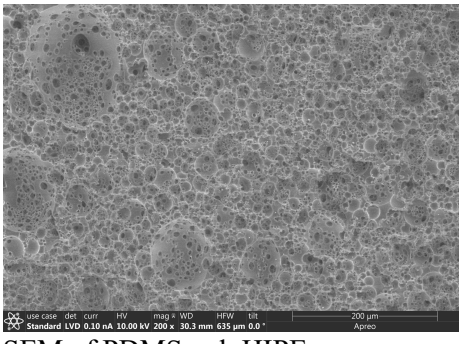
Title: Polydimethylsiloxane porous polymers for the synthesis of new materials.
PI: Ayres
Potential Co-I: Beaucage
Number of Graduate Students/Post Docs: 1 PD + 1 GS
Timespan: Two years
Budget: $300 000

Porous elastomeric polymers are used in a wide range of possible applications including biomaterials and catalysis due to their elastomeric behavior, biocompatibility, gas permeability, thermal stability, and specific hydrophobic and dielectric properties. More recently, they were also shown to exhibit specific acoustic properties, including low sound velocities through the materials (from 40-120 m/s). These soft acoustic metamaterials have been prepared from commercially available reagents such as poly(dimethyl siloxane) (PDMS) and lead to materials with negative acoustic indices when dispersed as small porous beads in a continuous matrix.

One method to prepare highly porous materials is using emulsion templating with polymerized high internal phase emulsions (polyHIPEs). This has been used to prepare porous PDMS materials. The term *high* is defined as when the volume fraction of the dispersed phase of the emulsion exceeds 74% of the global volume. An emulsion with 24-74% dispersed phase by volume is called a *medium* internal phase emulsion (MIPE), and *low* internal phase emulsions (LIPEs) contain less than 24% of dispersed phase by volume. Polymerized emulsions are formed after polymerization of a monomer in the continuous phase, and a porous network is obtained after removal of the dispersed phase. This method is compatible with both hydrophilic and hydrophobic monomers depending if a water-in-oil (w/o) or oil-in-water (o/w) emulsion is used. For example, free radical polymerization of styrene and a divinylbenzene cross-linker is often used in synthesis of hydrophobic polyHIPE materials and hydrophilic monoliths have been prepared using acrylamide and *N*,*N*′-methylenebisacrylamide. It has been suggested that a constraint with using free radical polymerization techniques is a lack of network homogeneity, leading to unpredictable materials properties including irreproducible Young's modulus. A way to circumvent this constraint may be to use macromolecular orthogonal coupling reactions (or "click chemistry"), such as thiol-ene reactions. This reaction can occur between functionalized polymers or small molecules, and macromolecular thiol-ene reactions have been reported using cross-linked silicones. These reactions enable the properties of the final polyHIPE to be tuned based on stoichiometric ratios of the reactants and permit post-polymerization functionalization or secondary click-reactions.


SEM of PDMS polyHIPE

Our recent work demonstrated the synthesis of soft polyMIPEs using a macromolecular thiol-ene reaction to prepare porous networks. The ratio of

the thiolated-PDMS to the vinyl-terminated PDMS does not affect the properties of the initial emulsion, or porosity of the resulting polyMIPE, but the stoichiometric ratio of the PDMS reagents does control the storage moduli of the materials. The materials properties of the polyMIPEs could also be directly controlled by the amount of surfactant used to stabilize the emulsion and the volume of dispersed phase. Significantly, acoustic measurements show that the materials exhibit very low values of the sound velocity (~40 m/s), a value rarely attained in any solid materials.

We propose to extend this work by synthesizing new elastomeric polyHIPEs and polyMIPEs with active functional groups decorating the surface of the materials. These functional groups can be used for complexing, for example, nanoparticles for catalytic applications or hydrogels for fluid uptake and filtration applications. The materials will be characterized using mechanical analysis, electron microscopy, and scattering techniques as we described in our previous work. These materials will be hierarchical in nature, as the polyHIPE materials will be prepared based on combinations of polymer chemistry assembled into emulsion formulations and then the polyHIPEs will be subsequently modified with value added soft or hard materials.