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Project Title: Emulsion-Templated Organo-Gel Constructs for Oil-Water Separation

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Executive Summary: This research project focuses on water separation from emulsions in hydrocarbon oils using hierarchical, porous polymer constructs that include macrovoids of a few tens of micrometer in diameter created by emulsion-templating of a set of polymer organogels. The polymer organogels contain solid polymer strands organized in 3D meso-(typical pore 30 nm) and macroporous (typical pore 100 nm) networks from thermo-reversible gelation or nucleation and growth mechanisms. The central idea of this project are porous materials development and evaluation of expedited demulsification of water-in-oil emulsions as an energy-efficient alternative to traditional demulsification technologies based on chemical agents and heating. The meso- and macropores and macrovoids of polymer gels offer large specific surface area for interactions with the surfactants. The macrovoids and large pore volume (>90%) allow high liquid throughput. In year 1 of the project, two emulsion-templated polymer gel systems were studied -syndiotactic polystyrene (sPS) and polyurea. Specifically, the coalescing filtration efficiency of emulsified water droplets in model hydrocarbon oil was evaluated by continuously pumping emulsions through a layer of sPS gels. Emulsion-templated sPS gels were developed using prior knowledge existing in PI's group. Concurrently, emulsion-templated polyurea gel system was developed. Polyurea and sPS gel systems cover a broad range of surface energies for interactions and adsorption of surfactants of different HLB values. The rapid spreading and preferential adsorption of the surfactants on polymer strands are key to release of water droplets and rapid emulsion breakup. The results from year 1 reveal that emulsion-templated sPS gels exhibit greater than 97% single-pass efficiency for removal of emulsified water droplets in n-heptane. The results also show that oil-in-oil emulsion-templating is a viable method for inclusion substantial macrovoids in polyurea gels.

Oil-water Separation Using Emulsion-templated sPS Gel

Emulsion-templated syndiotactic polystyrene gels were prepared following a method reported earlier¹. Briefly, sPS pellets of molecular weight 300,000 g/mol were dissolved in toluene at 100 °C at a concentration of 0.06 g/mL.

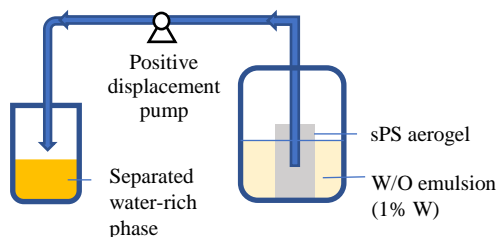


Figure 1. Filtration setup used for separation of oil-water emulsions.

Deionized water and sorbitan monooleate (SPAN®80) surfactant were added to sPS solution to obtain an emulsion. The volume fraction of water was varied in the range 20-50% by volume and SPAN80 concentration was maintained at 1.5 wt% of the total emulsion. The emulsion was poured into glass molds and subsequent quenching led to the formation of a three-dimensional polymeric gel with water droplets locked inside. The gels were aged in the molds for over 12 hours after which they were solvent exchanged with ethanol and finally with liquid carbon dioxide at supercritical conditions to form the sPS aerogel foam with >90 % porosity consisting of macrovoids of typical diameter 30 μm and macropores of typical diameter 100

nm. These materials were used in separation of water droplets with most probable diameter 40 nm from an emulsion in n-heptane.

The wetting characteristic of sPS aerogel foams was inferred from contact angle values of water and heptane on compressed, solid sPS aerogel disc. The sPS aerogel surface is superhydrophobic. Therefore, this separation media is expected to reject water and allow the oil-phase (n-heptane) to pass through.

The filtration setup used to perform the experiments is shown in **Figure 1**. The aerogel foam was created with a hollow channel spanning half the depth of the aerogel monolith. A delivery tube was inserted in the hollow channel and the W/O emulsion prepared by mixing 1 wt% deionized water in n-heptane in the presence of SPAN®80 surfactant was allowed to flow through the immersed aerogel cylinder under vacuum created by a positive displacement pump. The water-rich phase was collected in a beaker and analyzed using a particle sizing system. The level of emulsion in the beaker was maintained to ensure constant liquid flux. The droplet size distribution of water in the emulsions before and after filtration was determined using Accusizer 780, PALS – Particle Sizing Systems (FL).

The internal structures of sPS aerogel foams produced with 20% volume of water are presented in **Figure 2**, showing co-existence of interconnected networks of macrovoids and macropores. The contact angle of n-heptane and deionized water on compressed sPS aerogel surface was determined using a Rame Hart goniometer to be respectively 24° and 124°. The low contact angle of n-heptane and high contact angle of water on sPS surface endorse respectively wetting of sPS aerogel foams by n-heptane and rejection of water droplets. The droplet size distribution for the emulsions before and after filtration was characterized using the Accusizer 780. The water droplet size distribution curves in original emulsion (labeled Before Filtration) and water-rich emulsions (labeled Run 1 and Run 2) are presented in **Figure 3**. It is inferred that most probable size of water droplets changed from ~ 40 μm in original emulsion to ~10 μm in water-rich emulsion phase, indicating substantial expedited coalescence of larger water droplets in single passage through the aerogel foam materials. Filtration efficiency was computed from the volume of water in original emulsion and the water-rich emulsion. The data included in **Figure 3** revealed filtration efficiency values of 98.3% in Run 1 and 97.5% in Run 2. We attribute such performance to adsorption of surfactant molecules onto sPS polymer strands as shown in Figure 2(b), thus destabilizing emulsified water droplets. We are currently evaluating the fractions of surfactant adsorbed on sPS layer. Future work is planned to assess the effects of greater fraction of macrovoids on n-heptane flux through the media and the separation efficiency.

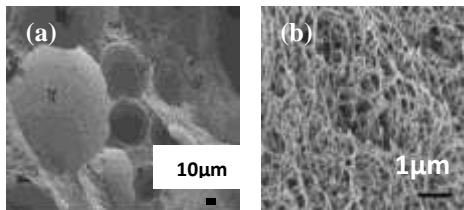


Figure 2. Scanning electron microscope images of sPS aerogel foams showing (a) macrovoids and (b) macropores.

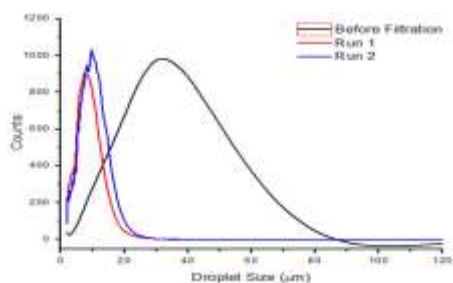


Figure 3. Droplet size distributions.

Design of Emulsion-Templated Mesoporous-Macroporous Polyurea Gels And Aerogels

A sol-gel process was used to obtain porous polyurea gels with three-dimensional, chemically crosslinked solid networks with meso- and macropores filled with a liquid achieved via an oil-in-oil (O/O) emulsion². The polyurea gels offer co-existing, interconnected networks of substantial mesopores in conjunction with macropores and emulsion-templated macrovoids. In addition, polyurea offers different surface energy compared to sPS to be effective in selectively adsorbing surfactants of a different set of HLB values. Polyurea gel was synthesized in dimethyl formamide from aromatic isocyanate and water mixtures with inherently produced mesopores and macropores. In conjunction, a set of pores of diameter a few tens of micrometer (macrovoids) were introduced via O/O emulsion-templating using n-heptane. The stability of O/O emulsion was an issue in view of a relatively long gel time of 23-75 min of polyurea. This was mitigated by using high concentration of surfactants. The results showed that polyethylene-polypropylene block copolymer surfactant exerted significant influence on the gel time, polymer strand size in the gel network, stability of the emulsion, and the specific surface area of the solids network. An increase of n-heptane volume fraction led to an increase

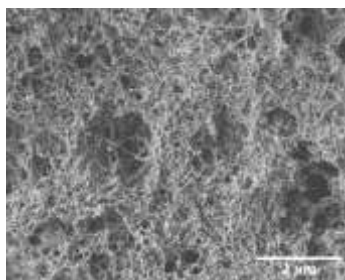


Figure 4. SEM image of polyurea aerogel with 30% n-heptane dispersed phase, 30 wt% surfactant.

of porosity aided by an increase of macrovoid fraction. The scanning electron microscope images revealed open porous interconnects among macrovoids and denser polymer strands at the surfaces of n-heptane droplets, as shown in **Figure 4**.

References:

1. Teo, N.; Jana, S. C. Open Cell Aerogel Foams via Emulsion Templating. *Langmuir* **2017**, *33* (44), 12729–12738. <https://doi.org/10.1021/acs.langmuir.7b03139>.
2. Mawhinney, K., Jana, S.C. Design of Emulsion-Templated Mesoporous-Macroporous Polyurea Gels And Aerogels. *ACS Applied Polymer Materials*, minor revision.