

## ACS PRF Doctorate New Investigator Award Progress Report 2018-2019

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| PRF#                    | 57353-DNI5  |
| Project Title           | Colloidal Interaction between Oil Droplets and Oleophobic Surfaces and its Implications |
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### Brief Description of Task and Primary Objective

This past year we have continued to investigate the oil-surface interaction with force spectroscopy as outlined in our proposal. In our previous report we used AFM force spectroscopy to measure the interactions between model foulants, oil and organics, and surfaces with different roughness and wetting properties. We found that the strongest and longest-range interactions for both oil and organics exist with rough hydrophobic surfaces. To further elucidate the effect of surface wetting properties on the oil-surface interaction in this past year we probed the interaction between oil droplets and surfaces with different wetting properties underwater. Specifically, we used a force tensiometer where milliliter sized oil droplets were directly placed on the probe and used to measure underwater oil-surface interactions. We compared force curves between crude oil droplets and a commercial hydrophobic membrane and three composite hydrophilic membranes with varied amounts of low-surface-energy functional groups. The primary objective of the studies in this past year were to elucidate the effect of low-surface-energy groups on oil-fouling resistance in model membrane applications, such as membrane distillation.

### Brief Description of Methods

We used a commercial PVDF membrane for the in-air hydrophobic (in-air and underwater oleophilic) surface (PVDF, Fig. 1). We casted a chitosan-silica nanoparticle solution onto the commercial PVDF membrane to produce an in-air hydrophilic and underwater oleophobic surface with little low-surface-energy functional groups (CTS-PVDF, Fig. 1). We spray coated a mixture of the CTS containing perfluorooctanoate (PFO) onto the commercial PVDF membrane to produce an in-air hydrophilic and underwater oleophobic surface with low-surface-energy perfluoroalkyl functional groups (CTS/PFO-PVDF, Fig. 1). Finally, we created an in-air hydrophilic and underwater oleophobic membrane surface with even more low-surface-energy perfluoroalkyl functional groups by spray coating an anionic fluorosurfactant (FS) onto the CTS/PFO-PVDF membrane surface (FS/CTS/PFO-PVDF, Fig. 1).

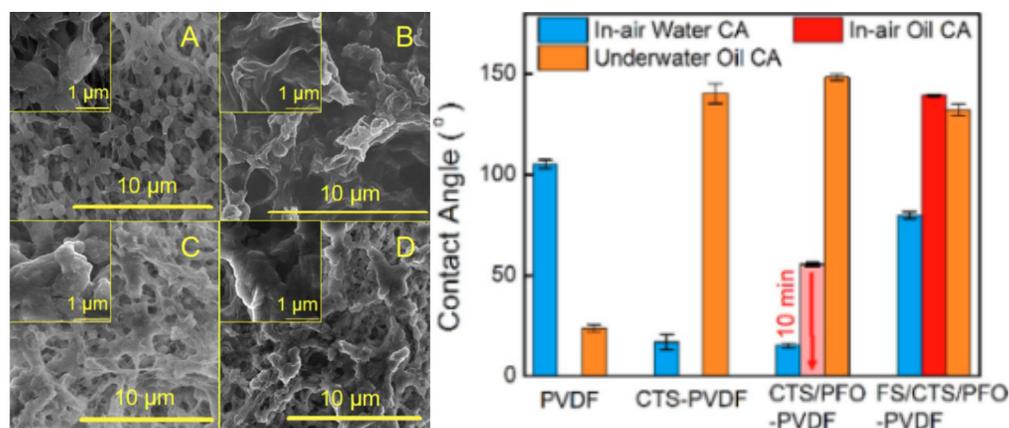


Figure 1. SEM images of (A) pristine commercial PVDF membrane, (B) CTS-PVDF composite membrane, (C) CTS/PFO-PVDF composite membrane, and (D) FS/CTS/PFO-PVDF composite membrane. (Right) Contact angles (CA) of water and mineral oil in-air and oil underwater on the four membrane surfaces. For the CTS/PFO-PVDF membrane, the in-air oil CA was initially 55° but after 10 min went to 0°.

We performed tensiometer force spectroscopy by attaching membrane coupons to the bottom of a transparent test cell and filling it with water. A small droplet (~6  $\mu$ L) of crude oil was carefully hung onto the submerged ring-shaped force probe using a syringe. The force probe with attached oil droplet approached the surface at 0.3 mm/min until contact then immediately retracted at the same speed. An explanation of this tensiometer based force spectroscopy and data analysis was included in our proposal (Figure 6 in ACS PRF Proposal).

### Summary of Results

We performed force spectroscopy experiments on the four submerged membrane surfaces described in Fig. 1 with an oil droplet on the force probe. The force curves are presented in Fig. 2A. The probe was initially zeroed in water and placed near the surface. The advancing stage yields flat, 0  $\mu$ N, force curve from displacement of 0 to 1 mm as the

probe approaches the submerged surface at constant speed. After contact, the force probe retracted at the same constant speed, stretching the oil droplet until it split, depicted as a sharp decline in adhesion force during the receding stage.

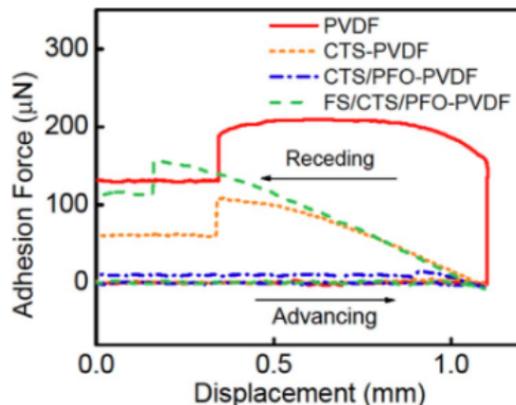


Figure 2. Force curves for the interactions of a crude oil droplet with the four membranes from Fig. 1 underwater. The initial position of the droplet was set as zero. The oil droplet containing probe advanced at constant speed until contacting the membrane, where it immediately retracted to its original location at that same constant speed.

Upon contacting, the strong hydrophobic interaction between PVDF membrane and oil droplet resulted in sharp adhesion force increase whereas a small but discernible repulsive force was measured upon contact for the composite membranes. However, some long-range attraction was observed for the composite CTS-PVDF and FS/CTS/PFO-PVDF membranes indicated by longer oil-droplet rupture distances on these membranes, comparable even to the PVDF membrane. For the CTS/PFO-PVDF membrane the oil droplet readily detached from the surface during the receding stage and furthermore negligible adhesion force was measured relative to the other membrane surfaces throughout the experiment.

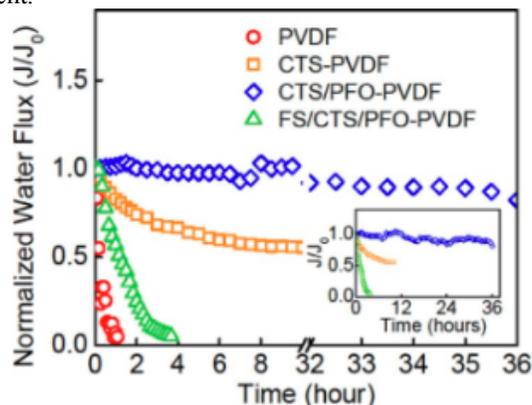


Figure 3. Normalized water flux for the four membranes from Fig.1 over time. The feed was 1000 ppm (by weight) crude oil-in-water emulsion. The feed inlet temperature was maintained at 60°C and the permeate inlet temperature was maintained at 20°C. The cross-flow velocities were held constant in all experiments.

We performed direct contact membrane distillation experiments with the four membranes to evaluate their oil fouling resistance (Fig. 3). The feed solution was 1000 ppm (by weight) crude oil-in-water emulsion and each membrane flux was normalized by the initial (unfouled) flux. As the normalized water flux drops below 1.0, the membrane surface is being blocked due to oil fouling. As we expected based on the force spectroscopy in Fig. 2, the CTS/PFO-PVDF membrane exhibited robust oil fouling resistance for 36 hours. A manuscript has been published based on this work.

### Career and Educational Impact

This project has significant impact on my career because it allows me explore a new direction that differs from the research performed for doctoral dissertation and as a postdoctoral associate. The funding also supported a PhD student who graduated last winter and is now doing a postdoc at Yale University because of his excellent academic achievement.