

ACS PRF Doctorate New Investigator Award Progress Report 2017-2018

PRF#	57353-DNI5
Project Title	Colloidal Interaction between Oil Droplets and Oleophobic Surfaces and its Implications
P.I. Name (Affiliation)	Shihong Lin (Vanderbilt University)

Brief Description of Task and Primary Objective

In the past year we have pursued the tasks described in our proposal to elucidate the colloidal interaction between oil droplets and oleophobic surfaces using force spectroscopy with atomic force microscope (AFM). Specifically, we employed AFM force spectroscopy to compare the interaction between a colloidal probe and a model substrate surface with different properties. The two colloidal probes we used include a polyethylene (PE) particle ($\sim 5 \mu\text{m}$) and a carboxylated polystyrene (C-PS) particle ($\sim 4.5 \mu\text{m}$), both attached onto the tip of an AFM cantilever. The soft (deformable) and hydrophobic PE colloidal probe represents an oil droplet, whereas CP colloidal probe are often used to investigate surface fouling by organics because the carboxylic groups are abundant in many of the natural organic foulants. We also prepared four types of model substrate surfaces, including smooth surfaces that are hydrophilic (underwater oleophobic) and hydrophobic (underwater oleophilic), and rough surfaces, that are hydrophilic (underwater oleophobic) and hydrophobic (underwater oleophilic). The primary objective of the study in the past year was to investigate the impact of surface roughness and wetting properties on the interaction between surface and the two representative foulants.

Brief Description of Methods

We used quartz microscope slides as the model flat smooth surface. Both the scanning electron microscope (SEM) image (Fig. 1A) and the AFM surface topography analysis (Fig. 1C) suggest that the quartz microscope slides are very smooth with very small local roughness. We modified such slides by depositing silica nanoparticles (SiNPs) with an average diameter of $\sim 200 \mu\text{m}$. These SiNPs were fabricated using the standard Stober method. The SiNPs deposit was sintered at 600°C for one hour, which resulted in a surface morphology that is similar to a microfiltration membrane. Both the SEM image (Fig. 1B) and the AFM surface topography analysis (Fig. 1D) suggest that the SiNPs coated quartz microscope slides are very rough with significant local roughness. Specifically, the local roughness for the SiNPs coated surface is nearly two orders of magnitudes higher than that of the smooth, unmodified surface.

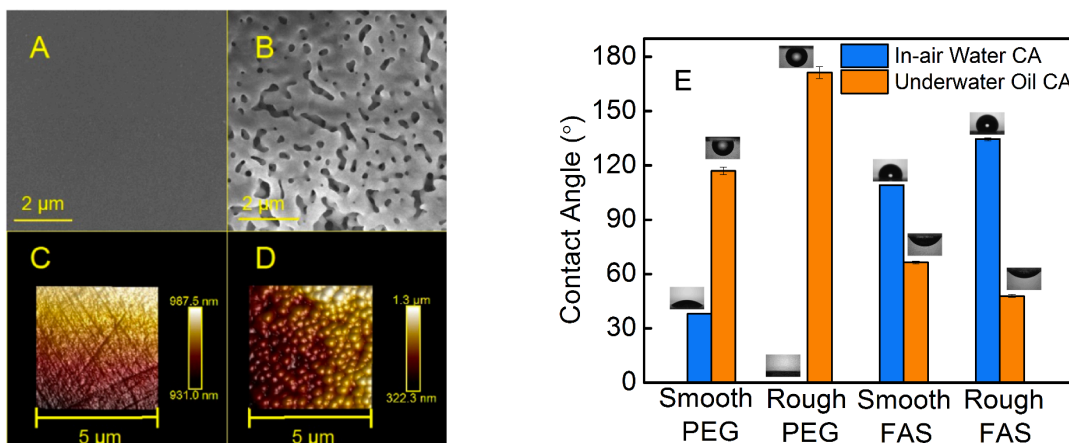


Figure 1. SEM images of (A) a smooth, unmodified quartz surface, and (B) a rough surface prepared by sintering SiNPs. AFM images of (C) a smooth, unmodified quartz surface, and (D) a rough surface prepared by sintering SiNPs. (E) in-air water CA (blue) and underwater oil CA (orange) of the four surfaces with different wettability and surface texture.

To modify the wetting property of the smooth and rough substrate surfaces, we used saline chemistry to coat the surfaces by grafting polyethylene glycol (PEG) to make the surfaces in-air hydrophilic, and by fluorinated alkyl saline (FAS) to make the surfaces in-air hydrophobic. The wetting properties of the fabricated surfaces were characterized using contact angle (CA) measurements. Both in-air CA and underwater oil (mineral oil) CA were measured using an optical goniometer. The CA of the different surfaces are summarized in Fig. 2. Specifically, the smooth surface coated with PEG (smooth PEG) was in-air hydrophilic and underwater slightly oleophobic; the SiNPs-coated rough surface coated with PEG (rough PEG) was in-air superhydrophilic (with no measurable water CA) and underwater superoleophobic; the smooth surface coated with FAS (smooth FAS) was in-air slightly hydrophobic and underwater slightly oleophobic; and the rough surface coated with FAS (rough FAS) was in-air very hydrophobic (but not superhydrophobic) and underwater oleophobic.

We performed colloidal probe force spectroscopy in 10 mM aqueous solution of NaCl. We controlled the trigger force, ramp size, and ramp rates. For each sample, force spectroscopy was conducted at 300 different positions of the surface to obtain interaction force curves which were analyzed using the built-in software with the AFM.

Summary of Results

We performed a large number of force spectroscopy experiments using the two colloidal probes (PE and C-PS) and the four model surfaces (smooth/hydrophilic, rough/hydrophilic, smooth/hydrophobic, rough/hydrophobic). The data is summarized in

Fig.2. Specifically, Fig. 2A to 2H are representative approach (or extension) curves (red) and retraction curves (blue), whereas Fig. 2I to 2P are the statistics of adhesion force and rupture distance, the eight different interactions. The following primary conclusions can be drawn from the data. A manuscript is in preparation based on the data collected in this work.

Probe	Surface Wettability	Roughness	Major observation			
			Extension	Retraction	Adhesion force	Rupture distance
C-PS	Hydrophilic	Smooth	Negligible	Small attraction	4.1 ± 0.4 nN	43.3 ± 4.2 nm
C-PS	Hydrophilic	Rough	Negligible	Negligible attraction	0.7 ± 0.4 nN	26.2 ± 11.0 nm
C-PS	Hydrophobic	Smooth	Small attraction	Significant attraction	92.8 ± 45.2 nN	163.3 ± 38.2 nm
C-PS	Hydrophobic	Rough	Significant attraction	Very strong and long-ranged attraction	241.3 ± 29.7 nN	1373.7 ± 142.2 nm
PE	Hydrophilic	Smooth	Negligible	Moderate attraction	17.8 ± 4.2 nN	282.6 ± 56.0 nm
PE	Hydrophilic	Rough	Negligible	Small attraction	3.5 ± 2.3 nN	75.3 ± 40.9 nm
PE	Hydrophobic	Smooth	Small attraction	Strong, long-ranged attraction	346.1 ± 35.5 nN	1156.6 ± 160.0 nm
PE	Hydrophobic	Rough	Significant attraction	Strong, very long-ranged attraction	439.9 ± 31.0 nN	2036.0 ± 198.4 nm

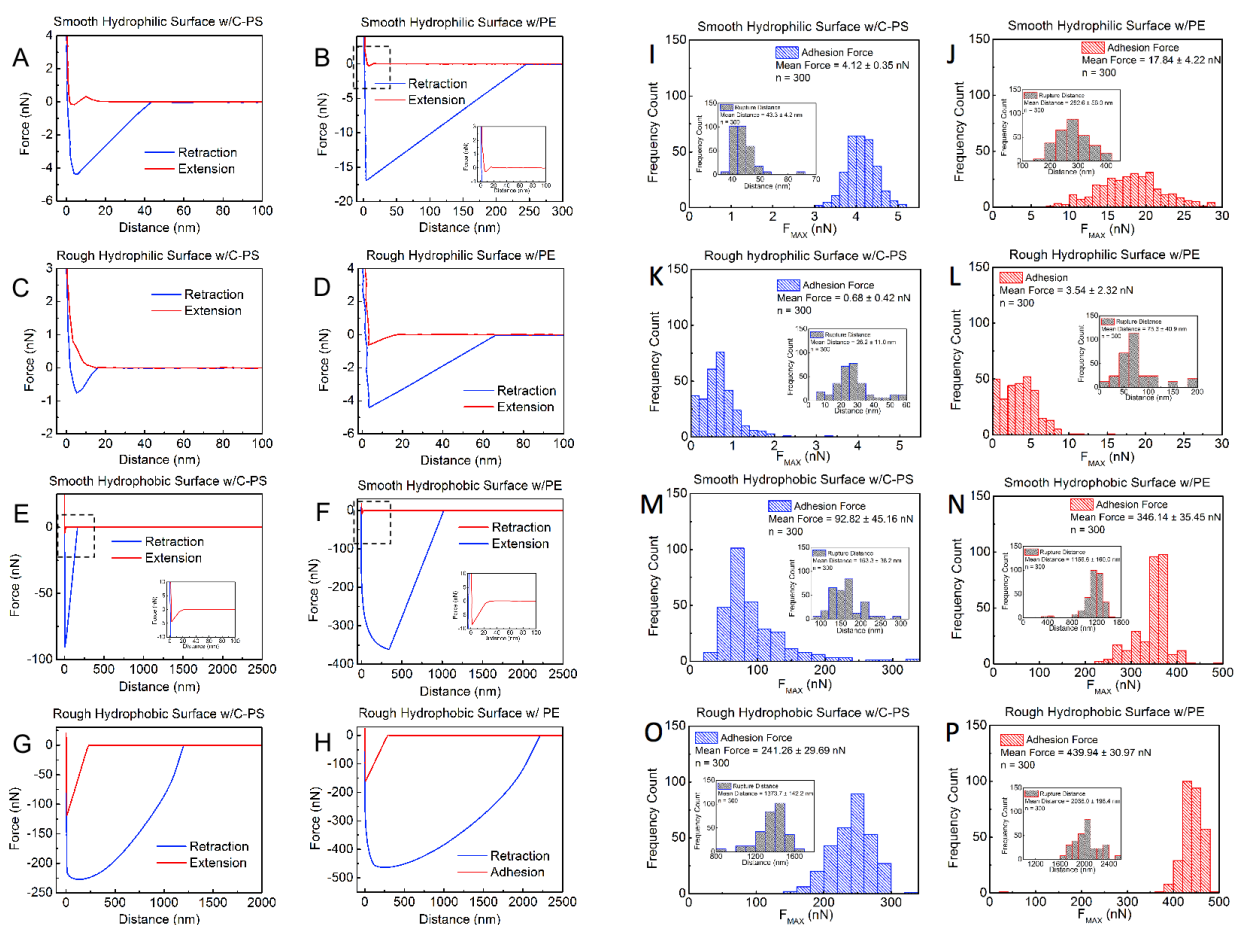


Figure 2. (A) to (H) approach (blue) and retraction (red) force curves (A to H); (I) to (P) maximum adhesion force and rupture distance statistics. The type of colloidal probe and substrate surface is given on the title of each panel.

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 supports a PhD student who just graduated this month and now goes onto doing a postdoc at Yale University because of his excellent academic achievement.