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# SUPEROLEOPHOBIC SURFACE FORMATION ON FLUOROPOLYMER / NANOCOMPOSITE SURFACES

15 October 2014


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# Outline

- Fluoropolymer / Fluorinated Silica Nanocomposites
  - Less Binder -> More Roughness -> Superoleophobicity
- Effect of Fluoropolymer Type
- Effect of Silica Particle Type
  - Fumed vs. Precipitated
  - Fluorinated vs. Non-fluorinated

Acknowledgements: Air Force Research Laboratory, Air Force Office of Scientific Research (AFOSR) – program support; PWG Team Members!

# Baseline fluoropolymer Nanocomposite

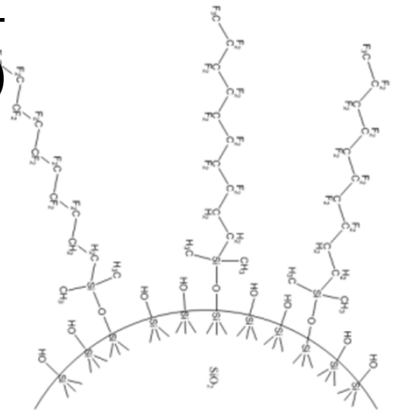
- Hi-Sil233 (PPG Industries):
  - -precipitated amorphous silica
  - -Surface area, BET: 135 $m^2/g$
  - -Silanol group density: 5-12 $nm^{-2}$
  - -Average particle size: 22 nm

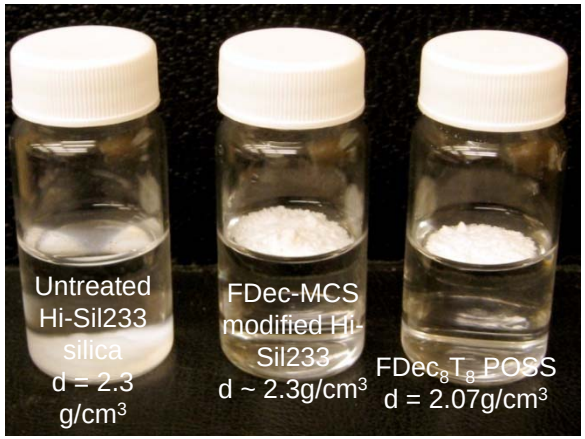
5 mg/mL fluoropolymer in AK225G

Viton® Extreme ETP-600S: DuPont terpolymer consisting of ethylene, tetrafluoroethylene, perfluoro(methylvinyl) ether, and bromotetrafluorobutene

Properties of 1H,1H,2H,2H-heptadecafluorodecyl(dimethyl)chloro-silane-treated Hi-Sil233 (FF-Hi-Sil233)

| | |
|---|---|
| Average Diameter (nm) | 22 |
| BET Surface Area ($m^2/g$) | 92 |
| BET C Constant | 21 |
| Water Vapor Uptake (wt%) | 2.8 |
| Wt % Fluorine | 9.9 |
| Grafting Density (chains $nm^{-2}$) | 1.6 |
| Graft Layer Molar Volume (cc) | 311 |
| Average Thickness of Graft (nm) | 0.8 |






Campos, R.; Guenthner, A. J.; Haddad, T. S.; Mabry, J. M. "Fluoroalkyl-functionalized Silica Particles: Synthesis, Characterization, and Wetting Characteristics", *Langmuir*, 27,10206-10215 (2011).

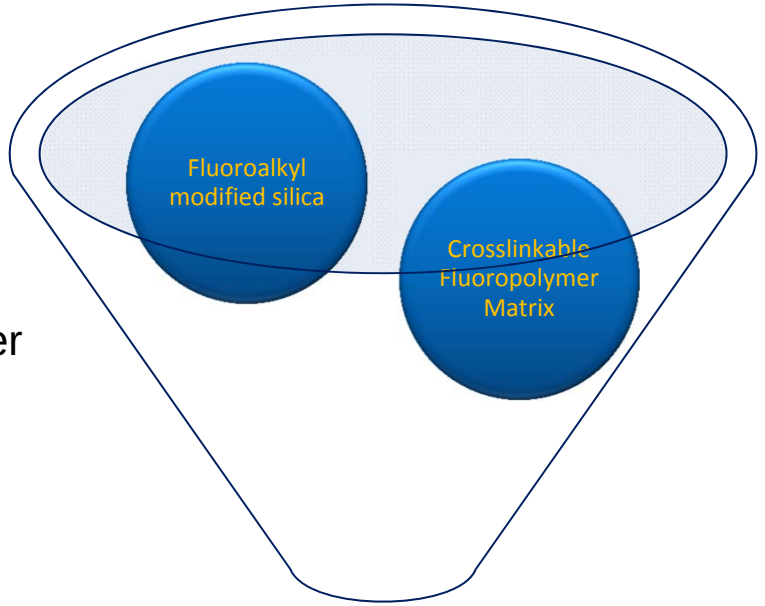
Campos, R.; Guenthner, A. J.; Meuler, A. J.; Tuteja, A.; Cohen, R. E.; McKinley, G. H.; Haddad, T. S.; Mabry J. M. "Superoleophobic surfaces through control of stochastic sprayed-on topography", *Langmuir*, 28, 9834-9841 (2012).

# Spray Coating Process

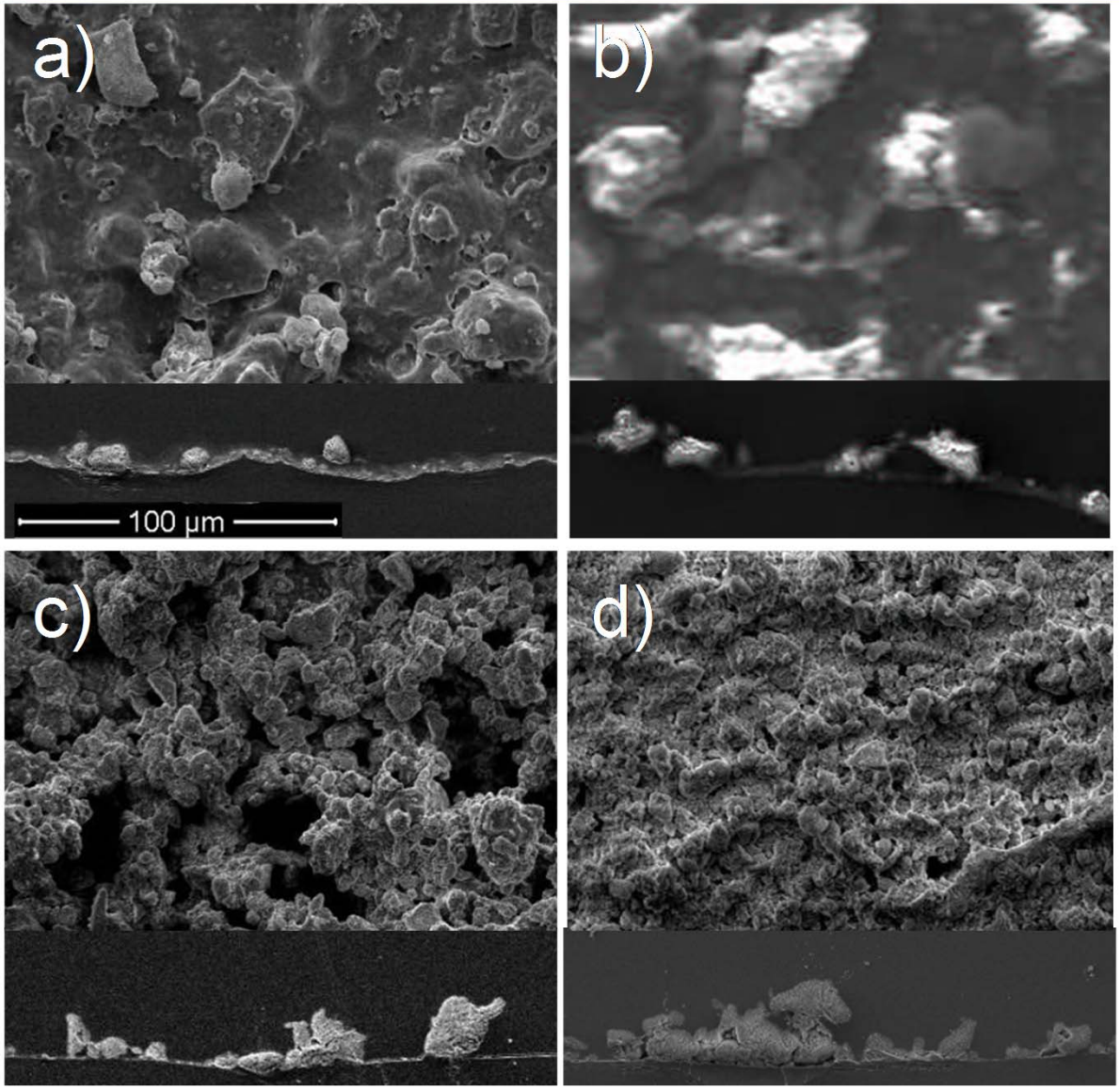
- Silica Types
  - FF-Modified Hi-Sil233
  - Unmodified Hi-Sil233
  - FF-Modified 7 nm fumed silica, 390 $m^2/g$, Aldrich)

- fluoropolymer Types
  - Viton Extreme ETP-600S (described previously)
  - Technoflon BR 9151: Solvay Solexis pentapolymer consisting of Vinylidene ($VF_2$), HFP (hexafluoropropylene), TFE (tetrafluoroethylene), PMVE (perfluoromethylvinylether $CF_2$=CF-$OCF_3$) and ethylene

- Spray coating done via airbrush (Paasche, VLSTPRO) with a 1.06 mm diameter tip using compressed air (25 psi). The airbrush was repeatedly passed over the substrate laterally at an approximate distance of 15-20 cm from the substrate until 20 mL of the coating mixture had been deposited. The resultant deposition level is around is 20 $mg/cm^2$.



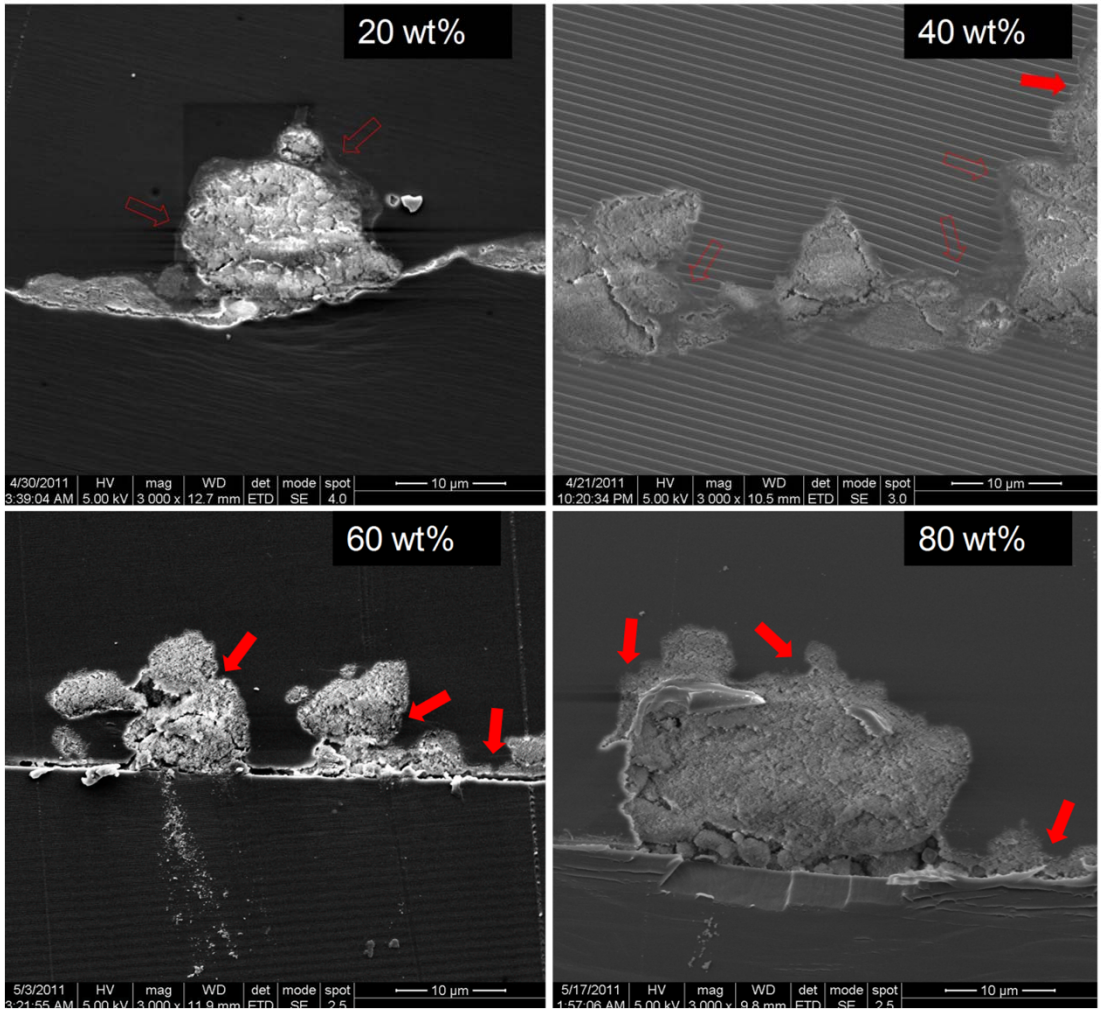

# Coating Morphology




Top-down (upper panels) and cross-sectional (lower panels) views of FF-Hi-Sil233 / Viton coatings with silica to fluoro-polymer ratios of:
a) 20:80 (wt) b) 40:60 (wt)
c) 60:40 (wt) d) 80:20 (wt)

At low loadings, “islands” of FF-silica float in a “sea” of fluoropolymer. At higher loadings, the FF-silica forms larger and larger aggregates, with little or no fluoropolymer between aggregates

# Effect of Binder on Sub-Micron Roughness

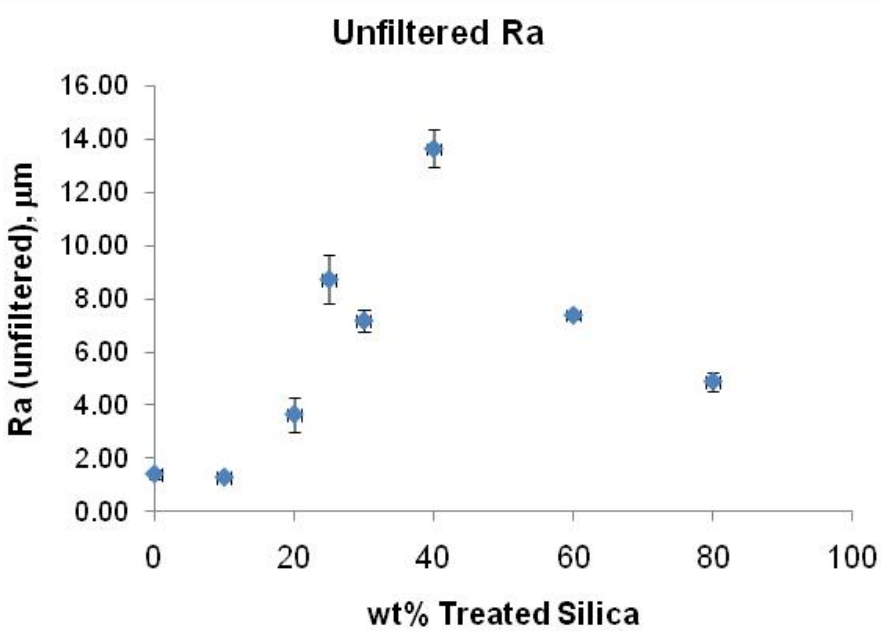


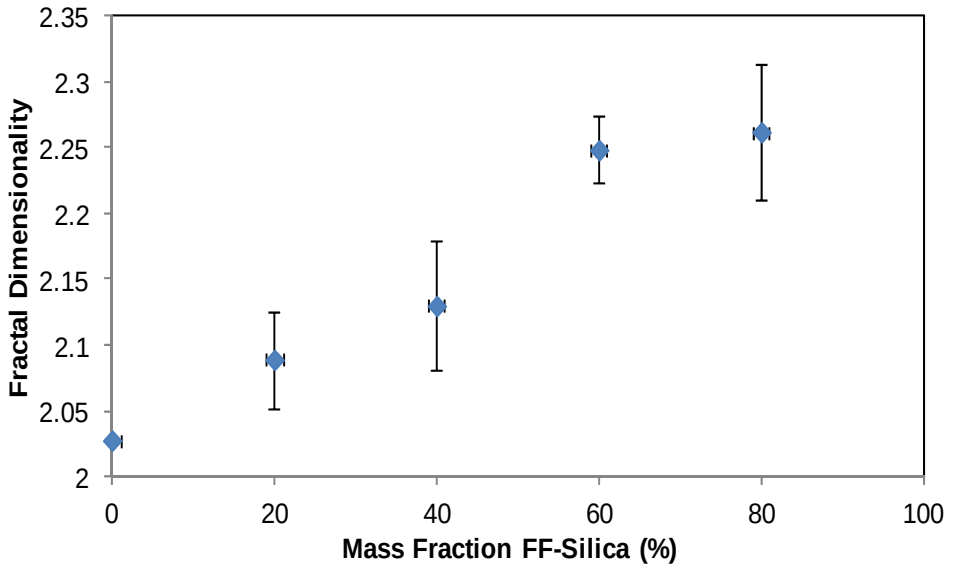

Cross-sectional morphology of FF-Hi-Sil233 / Viton coatings at the FF-silica loading levels indicated. Unfilled arrows indicate fine features in the silica particle that are filled in by binder; filled arrows indicate where such features are conformal to the surface.

The fluoropolymer binder "fills in" fine features in the coating surface that would otherwise be present

# Quantification of Nanocomposite Roughness Characteristics

FF-Hi-Sil233 / Viton®



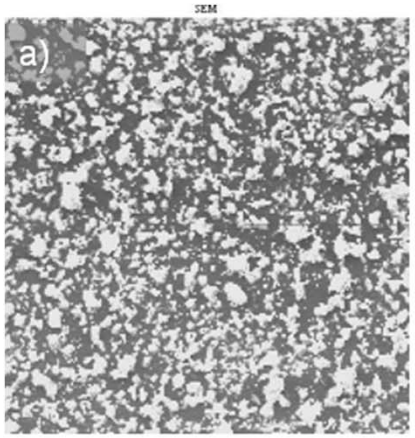



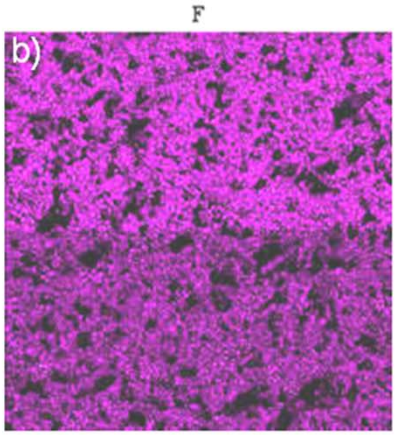

Average roughness as measured by interferometry, sensitive to features larger than about 1 µm

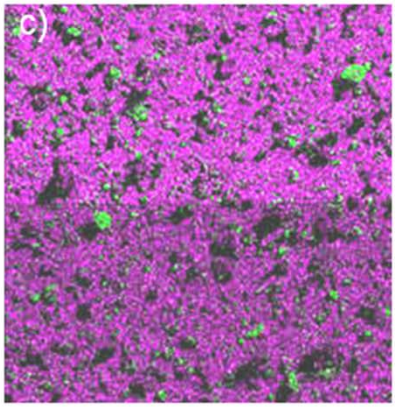
Fractal dimensionality as measured by cross-sectional SEM; sensitive to features from 0.1 - 10µm

At higher silica loading levels, the roughness exists principally at sub-micron length scales

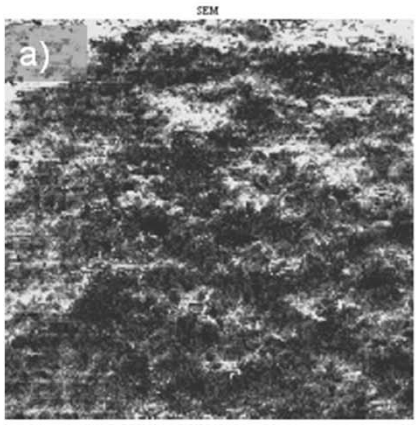
# Elemental Composition of FF-Hi-Sil233 /Viton Surfaces

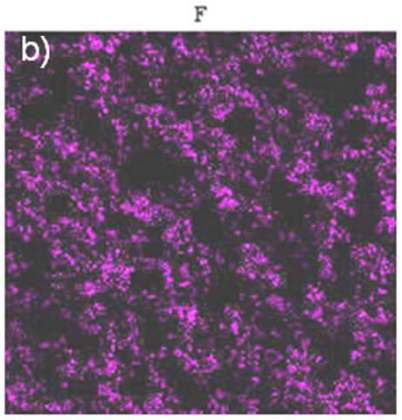


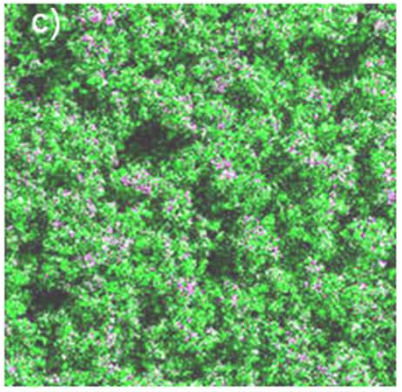




20 wt% FF-Hi-Sil233



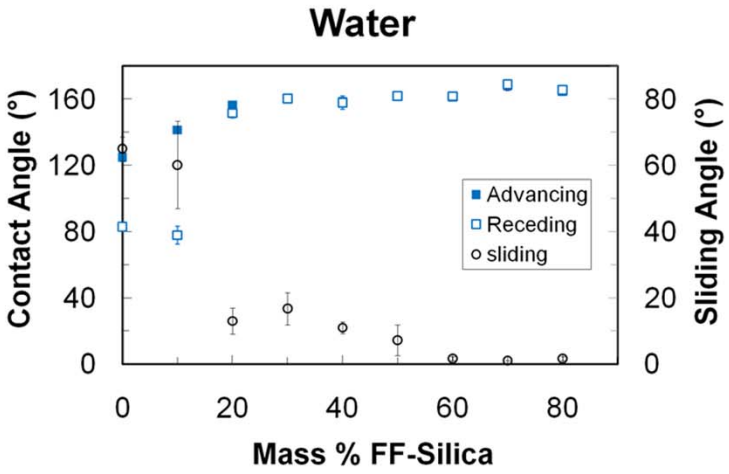



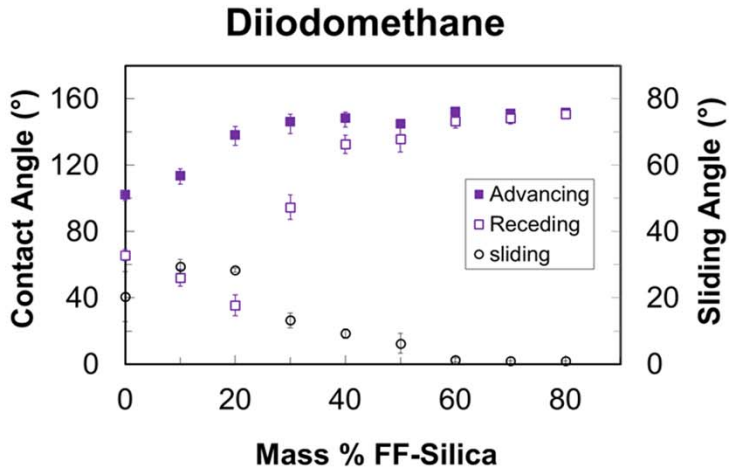

80 wt% FF-Hi-Sil233

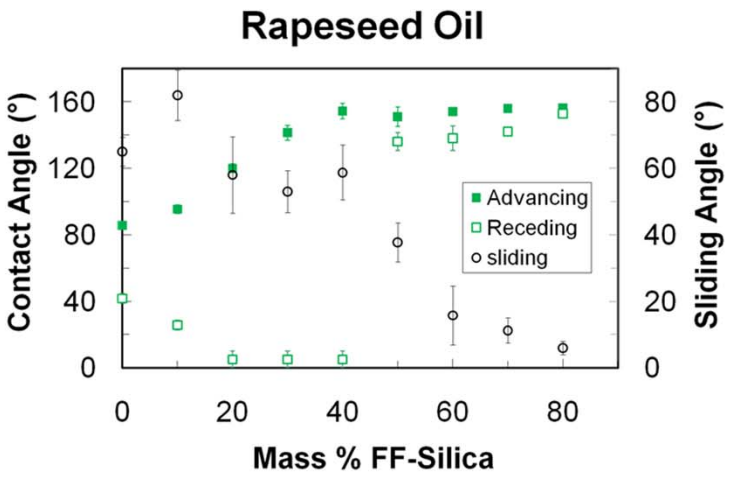
Pink = F; Green = Si

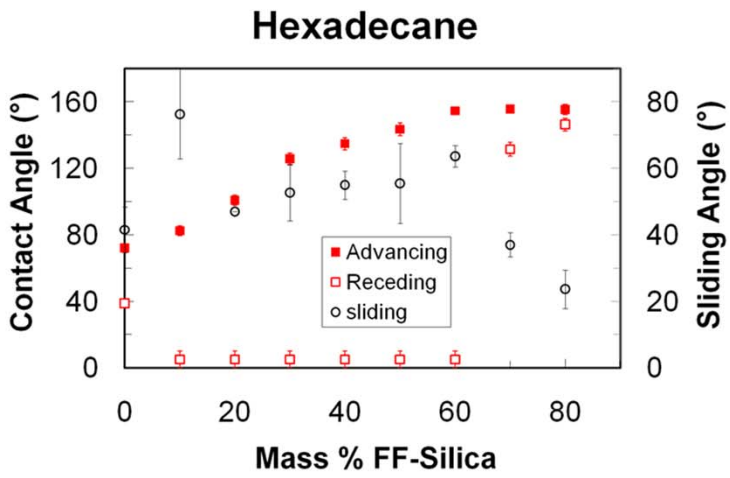
At 80 wt% loading, any binder pools on the surface are few and isolated

# Superamphiphobicity of FF-Silica / Viton Surfaces



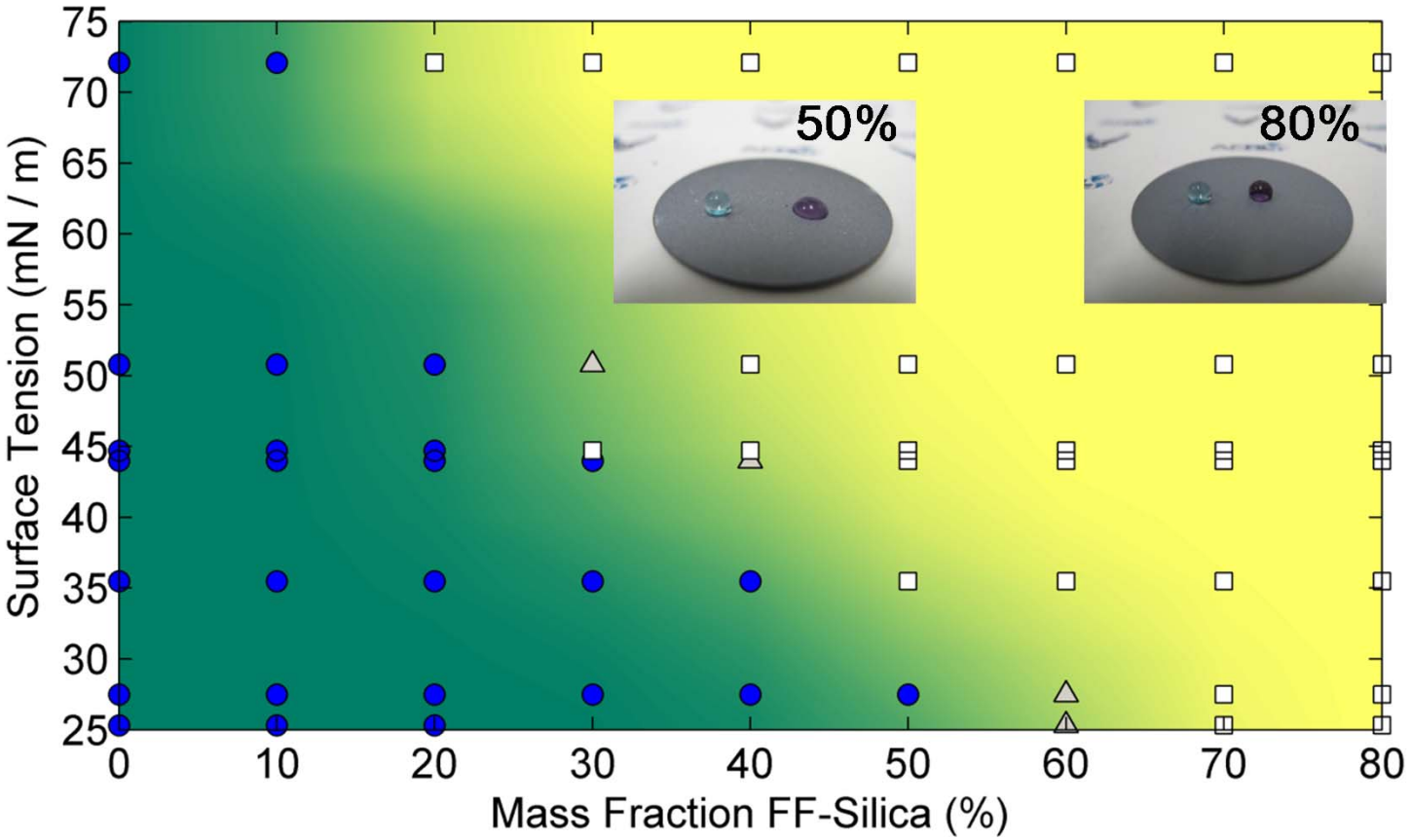



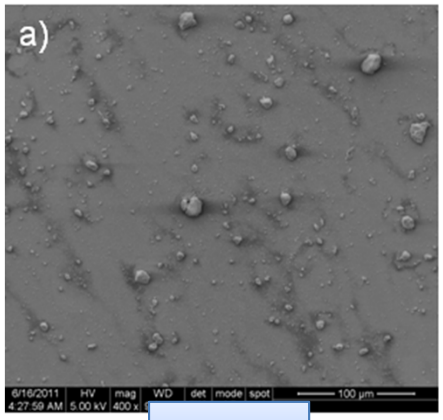

Liquid repulsion characteristics can be tuned by adjusting the level of FF-silica

# Superamphiphobicity of FF-Silica / Viton Surfaces

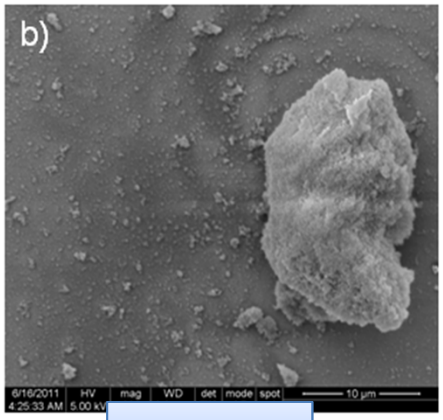



Parameter map showing liquid repulsion characteristics; filled symbols = fully wetted state; open symbols = Cassie-Baxter state; triangles = mixed behavior

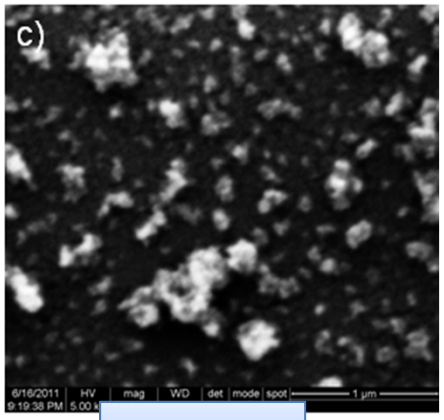
# Effect of Silica Type on Silica Particle Morphology




400x

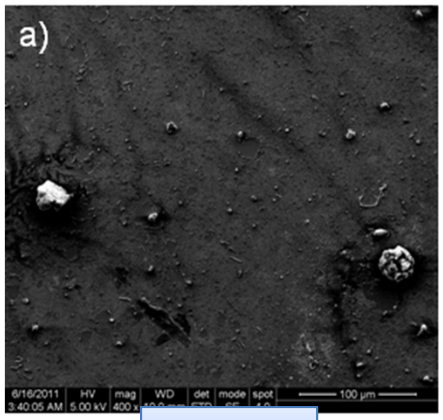



4000x




50000x

Hi-Sil233 Precipitated

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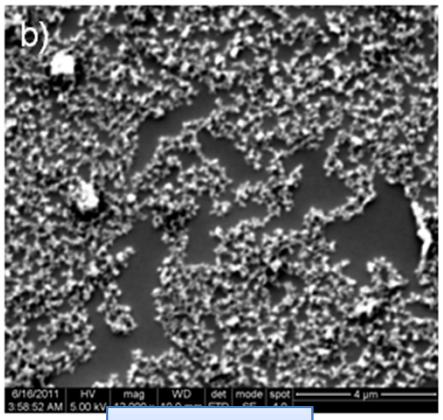
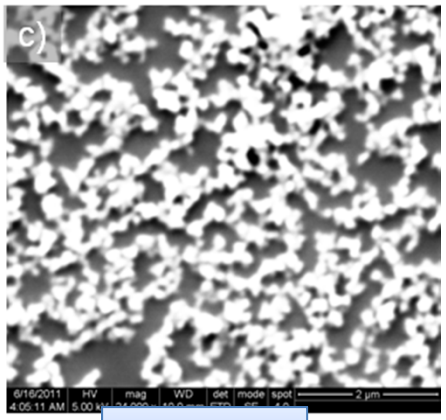



12000x

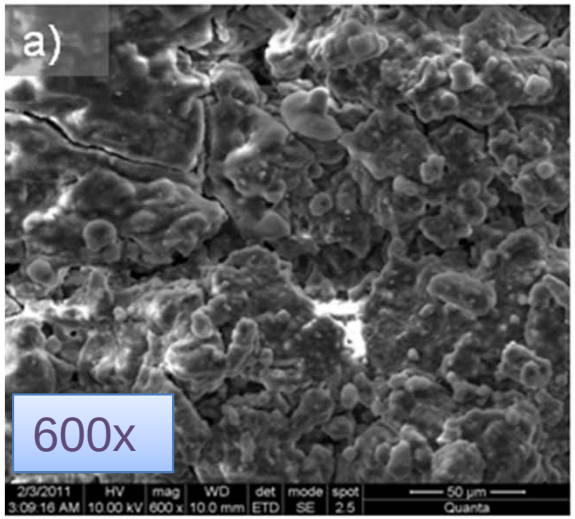


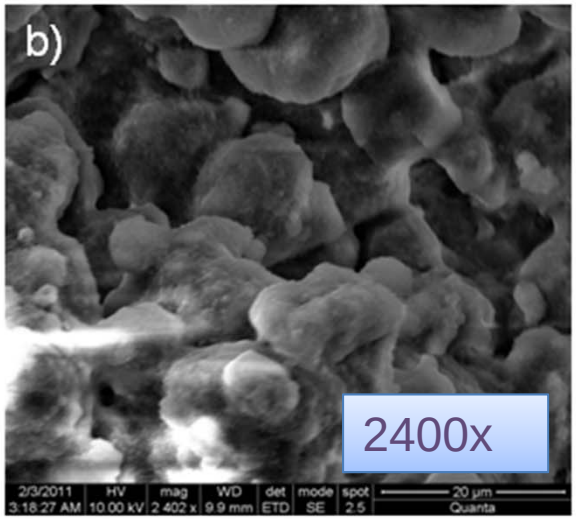

24000x

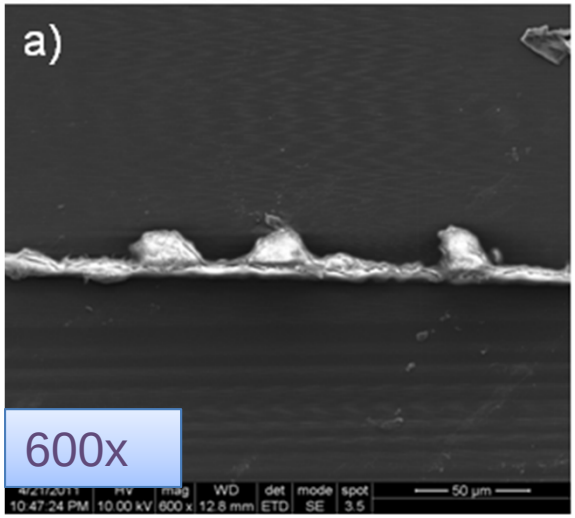
Aldrich Fumed 7 nm

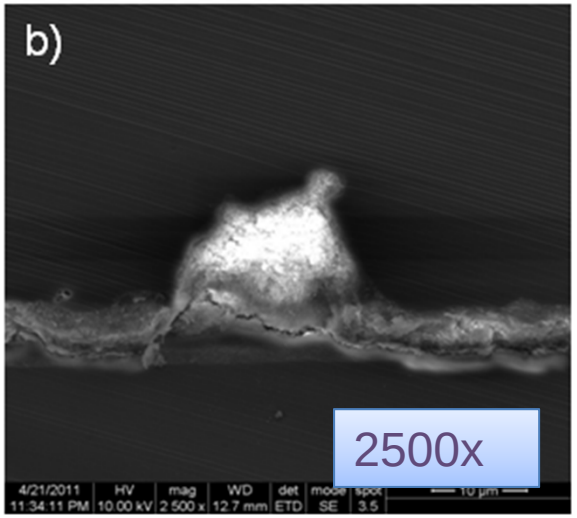
Hi-Sil morphology is more variable, with more large aggregates

# Morphology of FF-Fumed Silica / Viton Nanocomposites



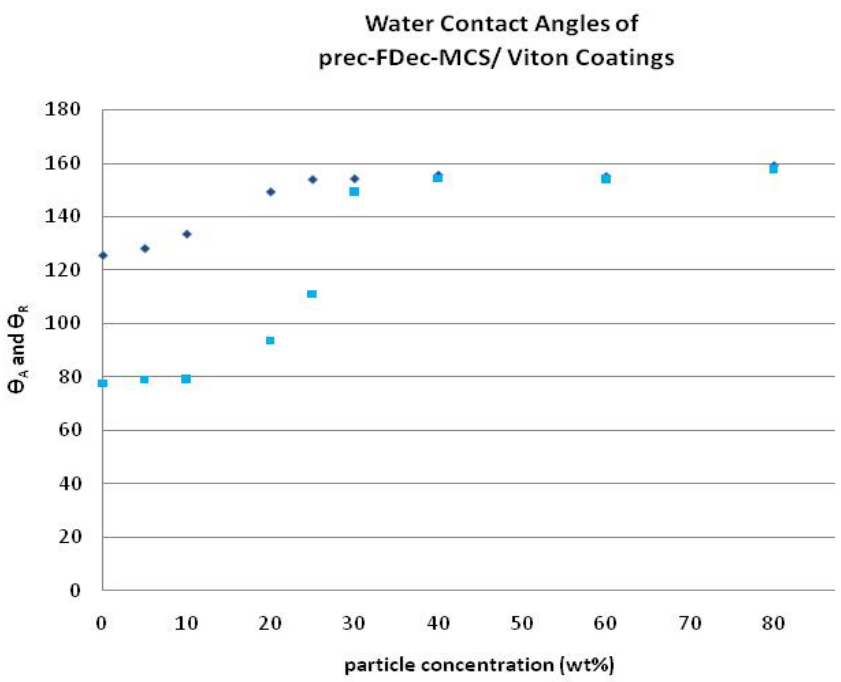




80 wt% FF-Fumed Silica in Viton®

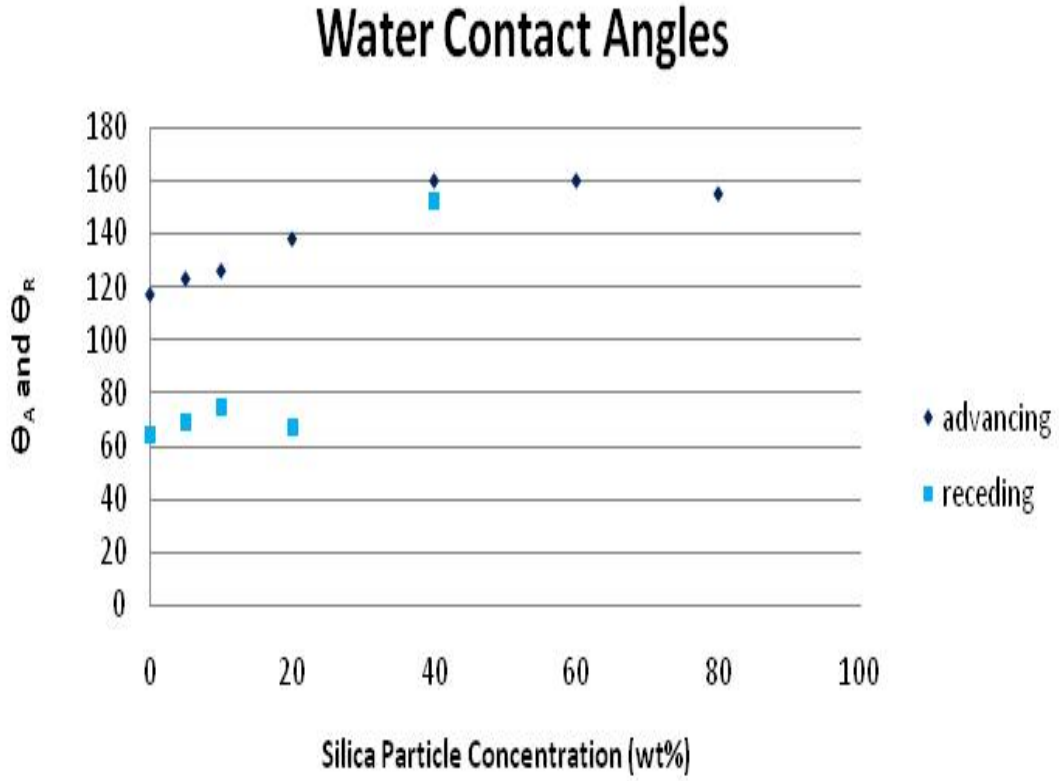
Smoother surface should limit fine sale roughness

# Water Contact Angles for FF-Silica Nanocomposites

FF-HiSil233 in Viton®



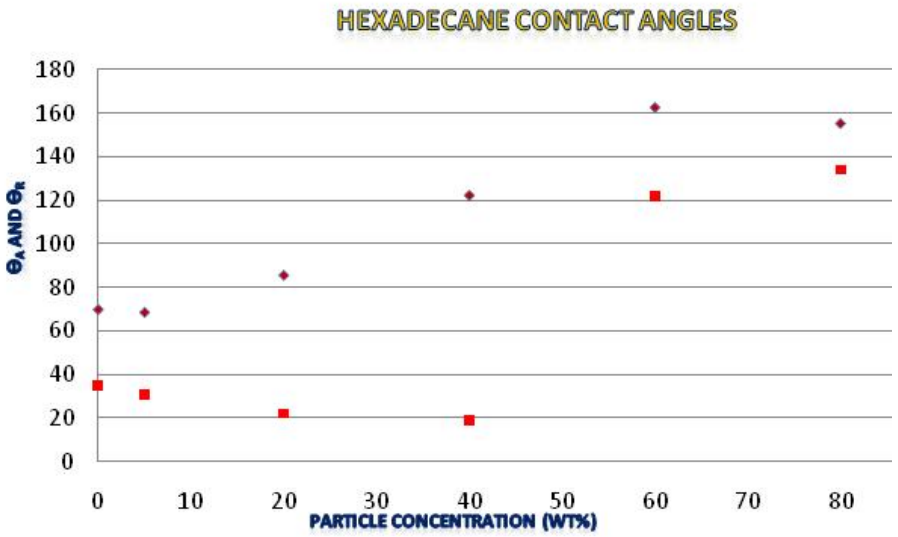

FF-HiSil233 in Technoflon®



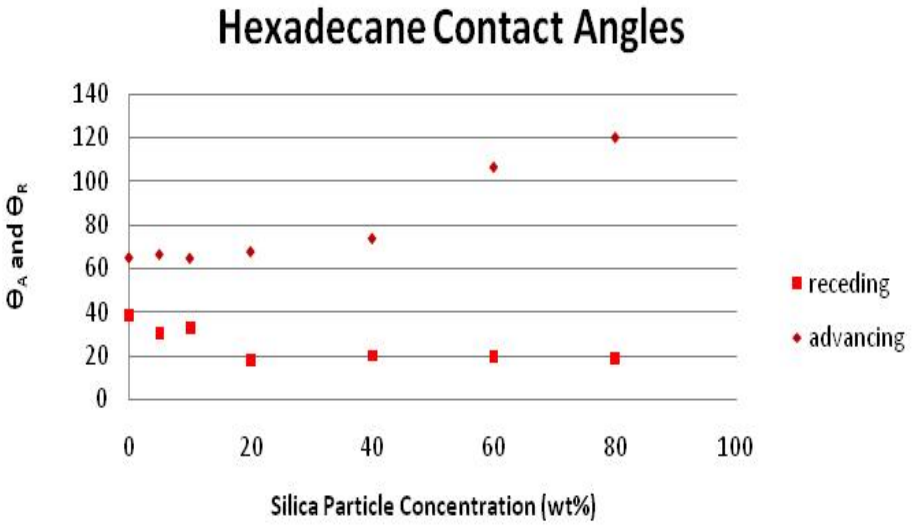

Similar water repellence for FF-Hi-Sil233 for different fluoropolymer types.
Somewhat lower receding angles for Technoflon® at low loading

# Hexadecane Contact Angles for FF-Silica Nanocomposites

FF-HiSil233 in Viton®



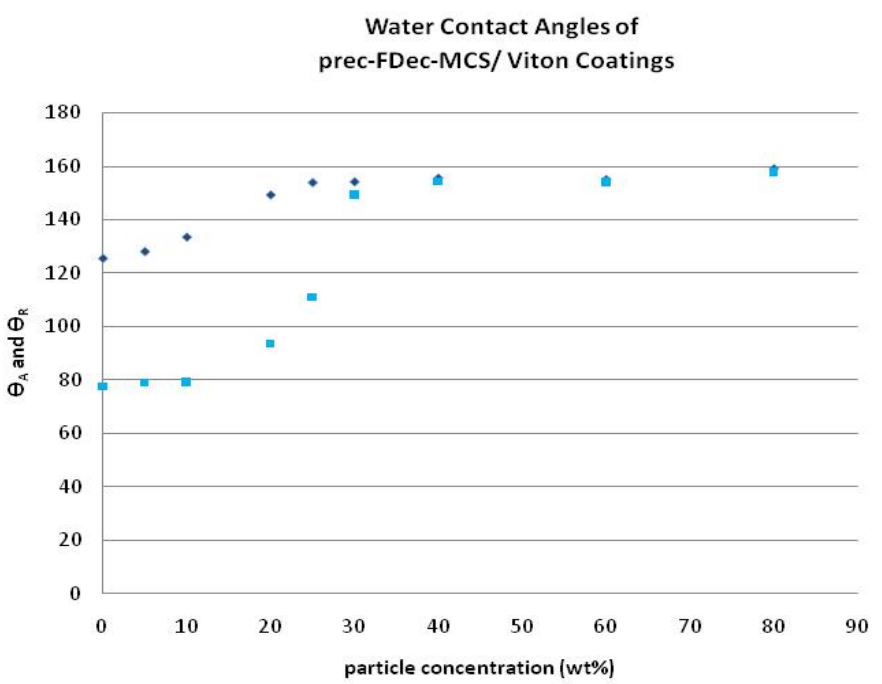

FF-HiSil233 in Technoflon®



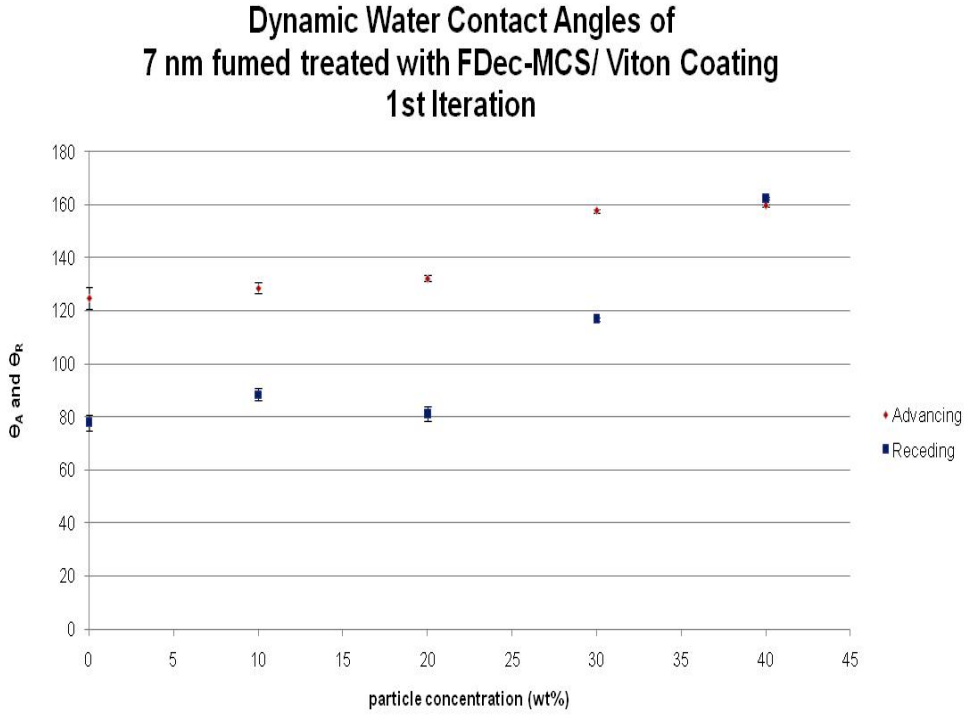

Despite similar contact angles at low loadings, systems incorporating Viton® achieve superoleophobic behavior, while those based on Technoflon® do not

# Water Contact Angles for FF-Silica Nanocomposites

## FF-HiSil233 in Viton®

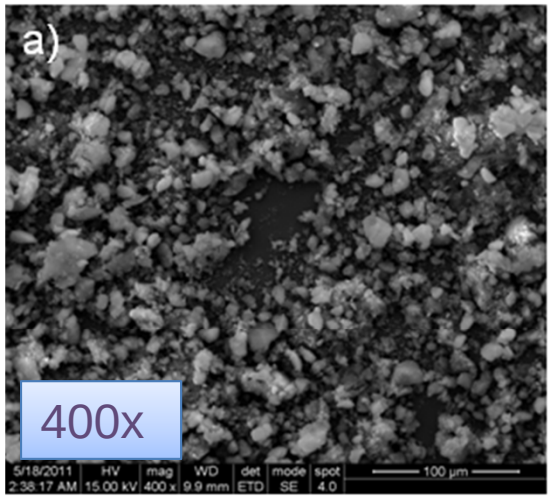


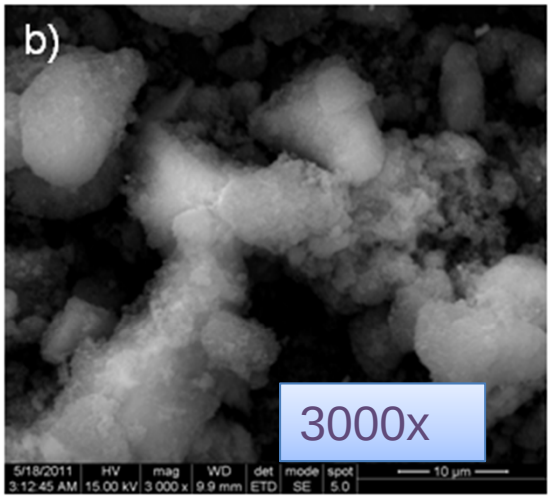

## FF-Fumed Silica in Viton®



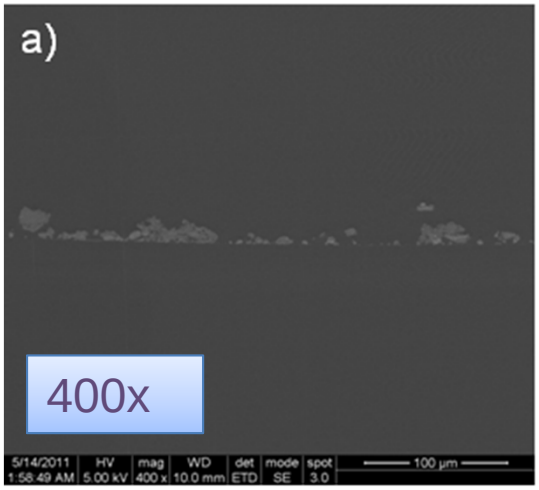

With fumed silica, the transition to superhydrophobic behavior requires a higher silica loading, likely due to the smoother nature of the silica aggregates

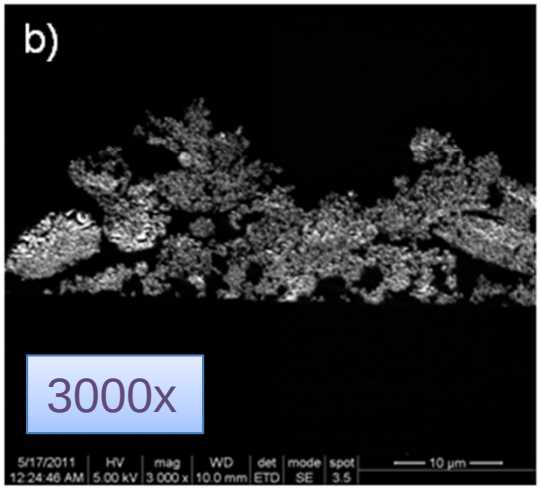
# Morphology of Untreated Hi-Sil233 / Viton Nanocomposites

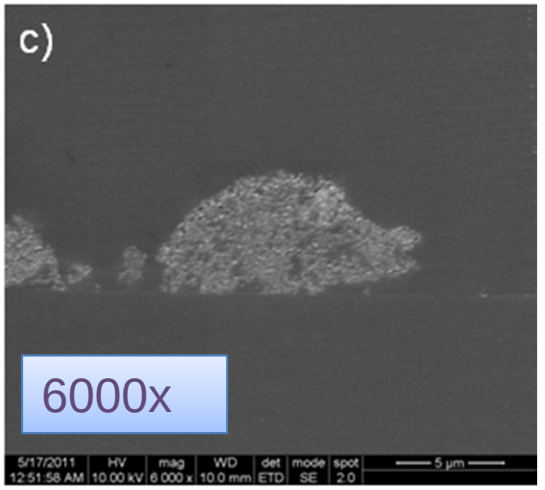



Hi-Sil233 Precipitated Silica, 80 wt% in Viton®, no treatment

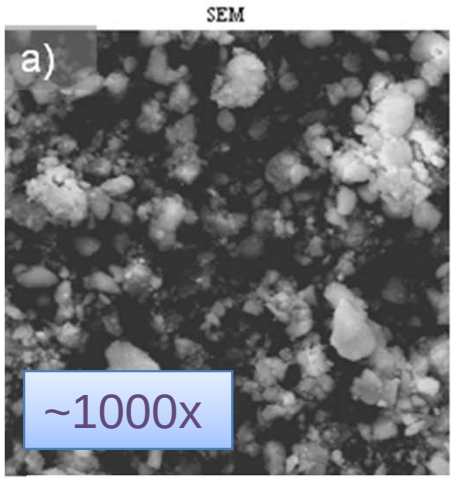


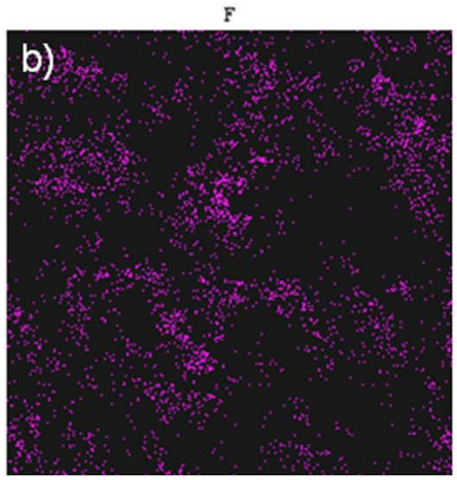



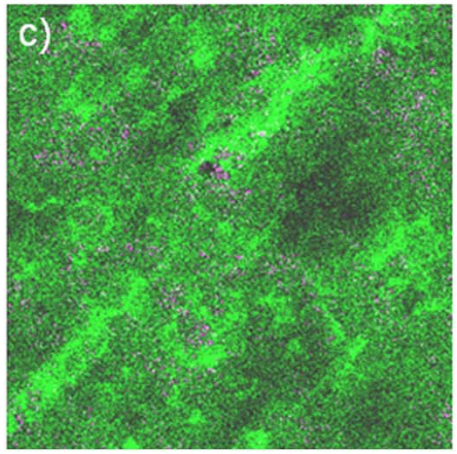




Smoother surface, leads to higher weight fractions needed for liquid repellence

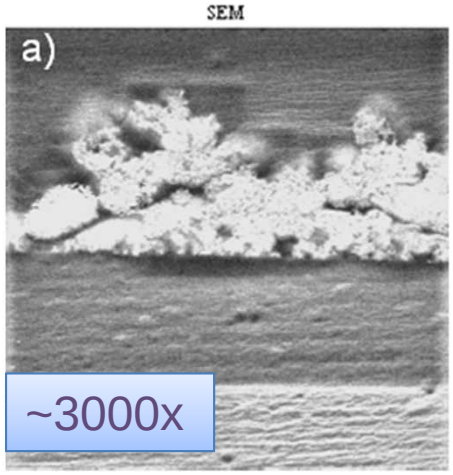
# Morphology of Untreated Hi-Sil233 / Viton Nanocomposites

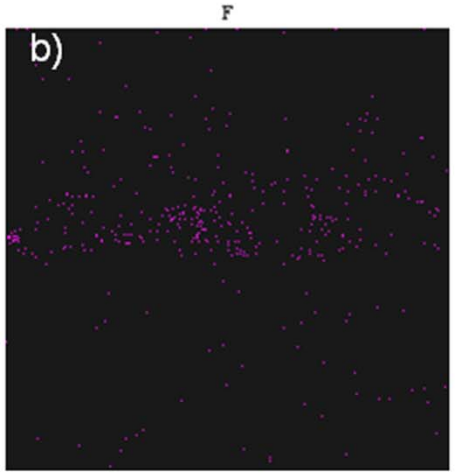


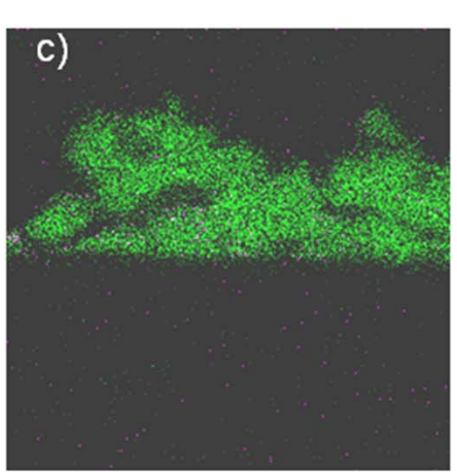




Hi-Sil233 Precipitated Silica, 80 wt% in Viton®, no treatment

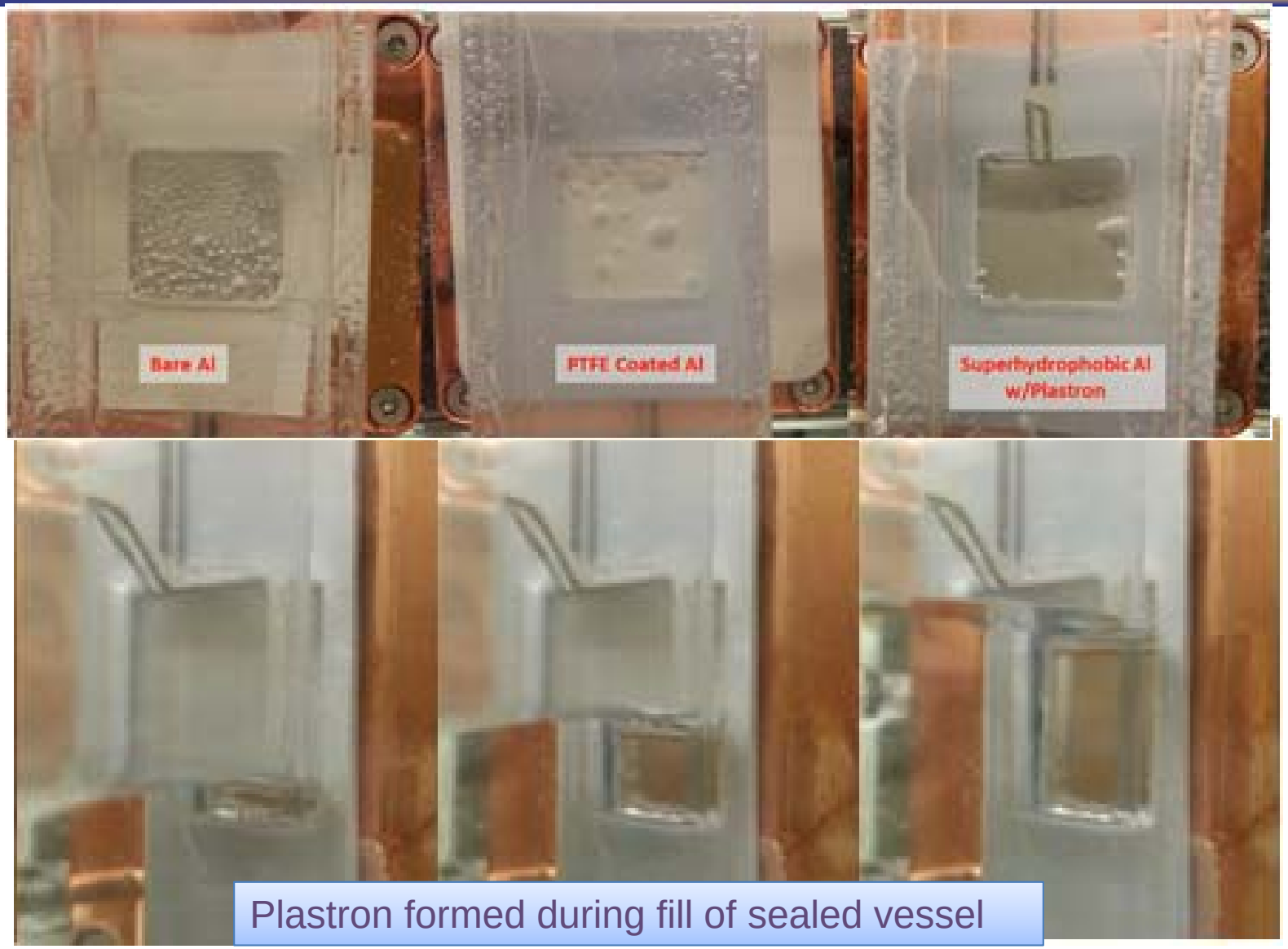



Fluorine tends to be evenly distributed among interstices of aggregate, enriched near bottom, but does not pool on the surface

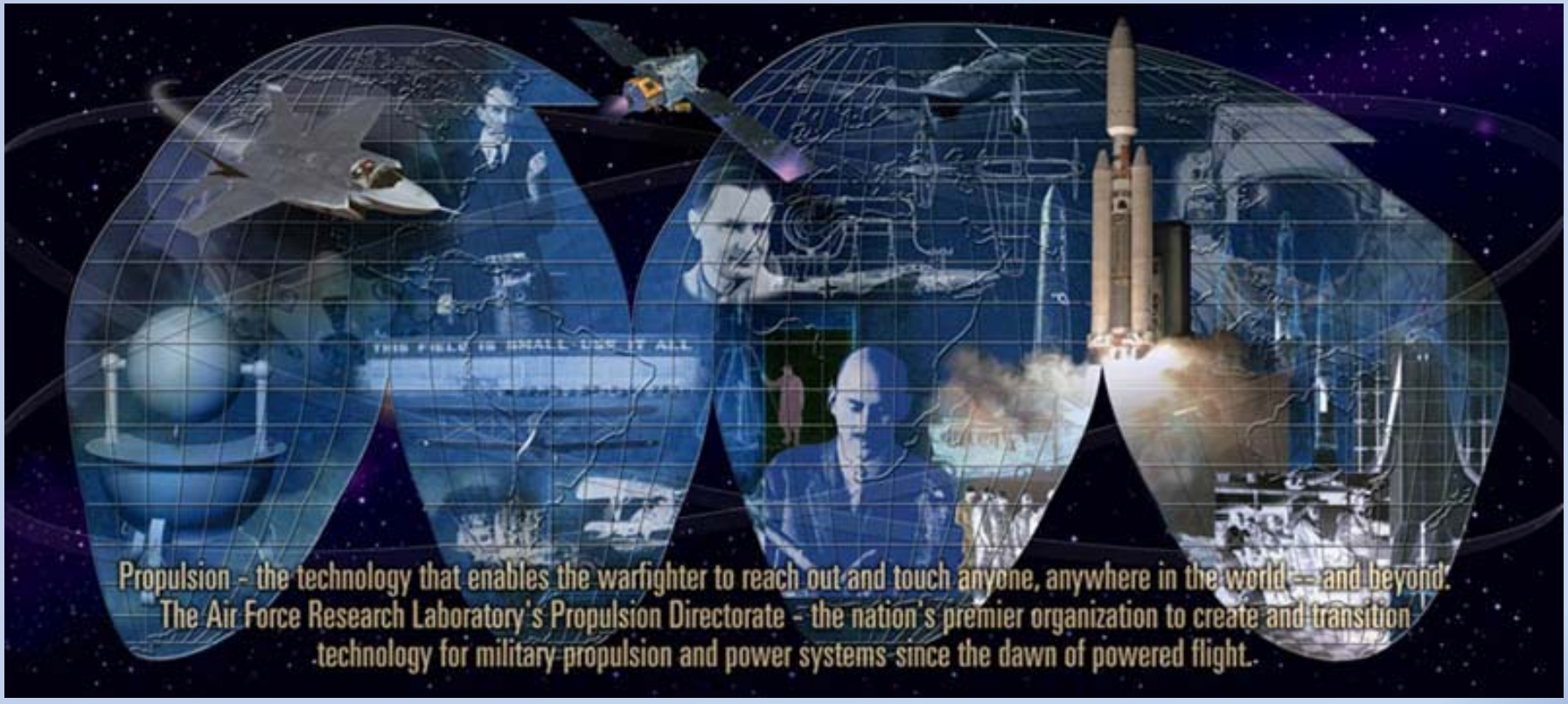
# FF-Silica Nanocomposites Support Plastron Formation




Plastron formed during fill of sealed vessel

# Summary

- Fluoroalkyl-functionalized silica particles and fluoropolymers can be spray coated on to a variety of substrates to form superamphiphobic surfaces
- The morphology of these silica / fluoropolymer sprayed surfaces is dominated by the roughness characteristics of the silica aggregates, and the degree to which the fluoropolymer creates a smoother surface topography
- In general, at low silica loadings, excess fluoropolymer eliminates roughness at the smallest length scales, decreasing the liquid repellence of the surface
- In experiments to date, precipitated silica, which tends to form aggregates with roughness across a wider range of length scales, has produced greater liquid repellence than fumed silica
- In untreated silica at the highest loadings, fluoropolymer does not appear to cover the surface evenly enough to produce a high level of liquid repellence

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