SUPEROLEOPHOBIC SURFACE FORMATION ON FLUOROPOLYMER / NANOCOMPOSITE SURFACES

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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

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Baseline fluoropolymer Nanocomposite

• Hi-Sil233 (PPG Industries):
  - precipitated amorphous silica
  - Surface area, BET: 135 m²/g
  - Silanol group density: 5-12 nm⁻²
  - Average particle size: 22 nm

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

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Diameter (nm)</td>
<td>22</td>
</tr>
<tr>
<td>BET Surface Area (m²/g)</td>
<td>92</td>
</tr>
<tr>
<td>BET C Constant</td>
<td>21</td>
</tr>
<tr>
<td>Water Vapor Uptake (wt%)</td>
<td>2.8</td>
</tr>
<tr>
<td>Wt % Fluorine</td>
<td>9.9</td>
</tr>
<tr>
<td>Grafting Density (chains nm⁻²)</td>
<td>1.6</td>
</tr>
<tr>
<td>Graft Layer Molar Volume (cc)</td>
<td>311</td>
</tr>
<tr>
<td>Average Thickness of Graft (nm)</td>
<td>0.8</td>
</tr>
</tbody>
</table>

5 mg/mL fluoropolymer in AK225G Viton® Extreme ETP-600S: DuPont terpolymer consisting of ethylene, tetrafluoroethylene, perfluoro(methylvinyl) ether, and bromotetrafluorobutene


Spray Coating Process

• Silica Types
  • FF-Modified Hi-Sil233
  • Unmodified Hi-Sil233
  • FF-Modified 7 nm fumed silica, 390 m²/g, Aldrich)

• fluoropolymer Types
  • Viton Extreme ETP-600S (described previously)
  • Technoflon BR 9151: Solvay Solexis pentapolymer consisting of Vinlylidene (VF₂), HFP (hexafluoropropylene), TFE (tetrafluoroethylene), PMVE (perfluoromethylvinylether CF₂=CF-OCF₃) 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/cm².
Coating Morphology

Top-down (upper panels) and cross-sectional (lower panels) views of FF-Hi-Sil233 / Viton coatings with silica to fluoropolymer 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

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

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
Elemental Composition of FF-Hi-Sil233 /Viton Surfaces

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

Pink = F; Green = Si

20 wt% FF-Hi-Sil233

80 wt% FF-Hi-Sil233
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.
Similar water repellence for FF-Hi-Sil233 for different fluoropolymer types. Somewhat lower receding angles for Technoflon® at low loading.
Effect of Silica Type on Silica Particle Morphology

Hi-Sil233 Precipitated

Aldrich Fumed 7 nm

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

400x  4000x  50000x

400x  12000x  24000x
Morphology of FF-Fumed Silica / Viton Nanocomposites

80 wt% FF-Fumed Silica in Viton®

Smotherer surface should limit fine sale roughness
With fumed silica, the transition to superhydrophobic behavior requires a higher silica loading, likely due to the smoother nature of the silica aggregates.
Hexadecane Contact Angles for FF-Silica Nanocomposites

Despite similar contact angles at low loadings, systems incorporating Viton® achieve superoleophobic behavior, while those based on Technoflon® do not.
Morphology of Untreated Hi-Sil233 / Viton Nanocomposites

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

Smother surface, leads to higher weight fractions needed for liquid repellence
Fluorine tends to be evenly distributed among interstices of aggregate, may be slightly enriched near bottom, but does not pool on the surface.

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