# Silicon-Containing Polymers and Composites

**Authors:** Joseph M. Mabry

**Performing Organization:**
Air Force Research Laboratory (AFMC)
AFRL/RZSM
9 Antares Road
Edwards AFB CA 93524-7401

**Funding Agency:**
Air Force Research Laboratory (AFMC)
AFRL/RZ
5 Pollux Drive
Edwards AFB CA 93524-7048

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**Abstract:**
Many hydrophobic surfaces exist in nature, but there is no naturally occurring oleophobic surface. There is plenty of academic and commercial interest in the development of oleophobic surfaces. The focus is on commercially available textiles. This presentation shows that fluoroPOSS are superhydrophobic. FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic. Superhydrophilic and superoleophobic surfaces have been developed. Such surfaces are ideal for the separation of both free-oil and oil-water emulsions. These membranes, for the first time, allow continuous-flow oil-water emulsion separation. Functionality will allow the covalent attachment of these low energy materials to substrates of choice.

**Security Classification:**
- **a. Report:** Unclassified
- **b. Abstract:** Unclassified
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Silicon-Containing Polymers and Composites

Silicones and Silicone-Modified Materials
ACS National Meeting
28 March 2012

Joseph M. Mabry
Air Force Research Laboratory
Propulsion Materials & Applications
joseph.mabry@edwards.af.mil
(661) 275-5857

Distribution Statement A: Approved for public release; distribution unlimited.
Motivation

• Many hydrophobic surfaces exist in nature but there is no naturally occurring oleophobic surface

• Plenty of academic and commercial interest in the development of oleophobic surfaces

• Focus on commercially available textiles
Non-wetting surfaces

Contact angles with water:

- Superhydrophilic: \( \theta \sim 0^\circ \)
- Hydrophilic: \( 0^\circ < \theta < 90^\circ \)
- Hydrophobic: \( \theta > 90^\circ \)
- Superhydrophobic: \( \theta^* > 150^\circ \)

Similarly, superoleophobic surfaces display contact angle \( \theta^* > 150^\circ \) with oils or alkanes.
Nanocomposite Materials

Silicon-containing compounds

- POSS
- Nanosilicas
- Layered silicates
- Linear silicates
Fluorinated POSS Synthesis

\[ R_f\text{SiX}_3 \xrightarrow{\text{OH}^-/\text{H}_2\text{O}} \text{solvent} \]

\[ R_f = -\text{CH}_2\text{CH}_2(\text{CF}_2)_n\text{CF}_3 \]

\[ n = 0, 3, 5, 7 \]

Angew Chem (2008)

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Hydrophobic Materials

- Spin-cast surface of Fluorodecyl POSS
- ~4 μm rms roughness by AFM
- 154° Water contact angle

Angew Chem (2008)
Low Surface Energy Materials

\[ \gamma_c = 5.5 \text{ mN/m} \text{ by Zisman analysis} \]

\[ R = -\text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3 \]

Similarly, GG analysis results in surface energy calculation of: \( \gamma_c = 8 \text{ mN/m} \)

Contacting liquids:
- hexadecane (\( \gamma_N = 27.5 \text{ mN/m} \)), dodecane (25.3), decane (23.8), octane (21.6), heptane (20.1), and pentane (15.5)

ACS AMI (2010)

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Water/Oil Repellant Nanocomposites

88° 128°

40° increase in water contact angle!

10% POSS

Polychlorotrifluoroethylene (PCTFE)

PCTFE with 10% Fluorodecyl₁₈T₈

Increase in hexadecane contact angle less than desired
Water, $\gamma_{LV} = 72.1$ mN/m

Hexadecane, $\gamma_{LV} = 27.5$ mN/m

On most surfaces, $\theta_{oil} < \theta_{water}$. This is because the surface tension ($\gamma_{lv}$) of water is significantly higher than that for oils.
Electrospun Surfaces

- ‘Beads on a string’ morphology, with high roughness and porosity
- A single step process - surface turns superhydrophobic for all POSS concentrations > 10 wt%

*Science* (2007)

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Effect of Surface Texture

Each surface is composed of PMMA+POSS – 44 wt% blend; contact angle for hexadecane on corresponding spincoated surfaces = $q_{\text{adv}} = q_{\text{rec}} = 79^\circ$.

Beads

Beads + Strings

Strings

Superoleophobic!

Hexadecane

$\*_{\text{adv}} = 156^\circ$

$\*_{\text{rec}} = 150^\circ$

Water contact angles

$\*_{\text{adv}} = \*_{\text{rec}} = 165^\circ$

Hexadecane

$\*_{\text{adv}} = 153^\circ$

$\*_{\text{rec}} = 141^\circ$

Hexadecane

$\*_{\text{adv}} = 147^\circ$

$\*_{\text{rec}} = 120^\circ$

$\*_{\text{adv}} = \*_{\text{rec}} = 163^\circ$

$\*_{\text{adv}} = \*_{\text{rec}} = 162^\circ$

Comparison with Lotus Leaf

Coat with electrospun fibers

44 wt% POSS

Water

Hexadecane


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Critical role of re-entrant texture ($\psi < 90^\circ$)

$\theta < 90^\circ$ ; $\psi < 90^\circ$

It is possible to support a composite interface even if $\theta < 90^\circ$

Re-entrant curvature : $180^\circ > \theta > 0^\circ$

Lotus Leaf

Cylinders / Fibers

Designing Omniphobic Surfaces

• Constructing super-repellent surfaces
  – Three key ingredients

  - Surface Chemistry ($\theta_e$)
  - Roughness ($r$)
  - Surface Geometry ($\psi$)

PMMA + 44 wt% POSS electrospun coating (beads on a string) morphology

Science (2007)

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The Dip-Coating Process

Hexadecane ($\gamma_v = 27.5 \text{ mN/m}$) on an as-received commercial polyester fabric

Hold for 1-5 min

Solution of fluorodecyl POSS in Asahiklin (30 mg/ml)

Dip

Dry (heat in oven at 60°C for 20 minutes)

Before

After dip-coating with a solution of fluorodecyl POSS

Adv Mater (2008)

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Dip-Coated Polyester Fabric

Before coating

After coating with fluorodecyl POSS in Asahiklin (30 mg/ml)

γₐ = 22.7 mN/m  γₐ = 27.5 mN/m  γₐ = 50.8 mN/m  γₐ = 72 mN/m

Methanol  Hexadecane  Methylene Iodide  Water

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Dip-coating process for conformal coating of textured surfaces

Before Dip-coating

Anticon 100 polyester fabric

Hexadecane

50:50 mixture, total solids = 10 mg/ml

Dip in Asahiklin solution for 5 minutes

Air dry to remove solvent

Heat treat at 60 °C for 30 minutes

R_f = -CH_2-CH_2-(CF_2)_7-CF_3
Fluorodecyl POSS
γ_{sv} ≈ 8 mN/m

Tecnoflon® (BR9151)
Fluoro-elastomer from Solvay-Solexis
γ_{sv} ≈ 18 mN/m

EDAXS spectrum for fluorine
At low POSS concentrations many surfaces are both superhydrophobic and superoleophilic ($\theta_{alkane} \approx 0^\circ$). Thus, these porous surfaces form ideal membranes for separating mixtures / dispersions of alkanes (oils) and water.

But...water is more dense than hydrocarbons!

*Science* (2007)

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Hydrophilic Membranes

A and B. Neat x-PEGDA dip-coated stainless steel mesh 100 and polyester fabric C. An apparatus with a mesh 100 coated with neat x-PEGDA Both water and rapeseed oil permeate through.

Manuscript in preparation

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**PEGDA + Fluorodecyl POSS**

- Can hydrogen bond with water
- Photo-crosslinkable
- AFM Phase images of spin-coated PEGDA + POSS films
- Fluorodecyl POSS molecules preferentially segregate to the air interface and crystallize.

Fluorodecyl POSS

\[ R_f = -\text{CH}_2\text{-CH}_2\text{-}(\text{CF}_2)_7\text{-CF}_3 \]

**Pure PEGDA**

**10% POSS**

**20% POSS Under water**

**20% POSS**

\[ \gamma_{sv} \approx 8 \text{ mN/m} \]

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Surfaces with inherent re-entrant curvature dip-coated with PEGDA + POSS blends

PEGDA surface reconfiguration leads to superhydrophilic behavior.

Manuscript in preparation
Free Oil – Water separation

Stainless steel mesh coated with PEGDA + 20 wt% fluorodecyl POSS.

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A simple, scalable, gravity-based system for the separation of both oil-in-water and water-in-oil emulsions. This is one of the first gravity-based systems to achieve such high emulsion separation efficiencies.

Manuscript in preparation

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Oil-Water Emulsion Separation

Our system: PEGDA + 20% FPOSS

Flux (L/hr·m²)

Cycles

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Separation Efficiency

- 99% Oil
- 78% Oil
- 0.1% Oil

- Feed
- Permeate
- Retentate

Manuscript in preparation

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Incompletely condensed silsesquioxane synthesis yields a disilanol capable of functionalization with dichlorosilanes.*
X-Ray Crystal Structure of Disilanol

- Crystal structure is dimeric via intra- and intermolecular hydrogen bonding between silanols.
- $M_r$, monoclinic, space group $P2(1)/c$, $a=11.84(10)$ Å, $b=57.11(6)$ Å, $c=19.06(2)$ Å, $\alpha = 90.00^\circ$, $\beta = 92.21(10)$ $^\circ$, $\gamma = 90.00^\circ$, $V = 12878(2)$ Å$^3$


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Edge Capping Reactions

\[ R = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3 \]
\[ R_1 = \text{CH}_3 \]
\[ R_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)CHCH}_2 \]

- Edge capping reactions typically have 40-70% yield
- Main side product is starting material (recycled)
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes

Macromer/RBM = 4178 g/mol

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Edge Capping Reactions

\[ \text{R} = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3 \]
\[ \text{R}_1 = \text{CH}_3 \]
\[ \text{R}_2 = \text{CH}_2\text{CH}_2\text{CH}_2\text{OC(O)CHCH}_2 \]

- Typically 40-70% yield
- Main side product is starting material (recycled), formed during base addition
- Disilanol can revert back to closed cage during reaction
- Reactions take 5-10 minutes
- Si ratio (1:2:2:4)
- **New Si peak!**
1H NMR Characterization of Compounds

$^{19}$F NMR taken in diethyl ether. $^1$H NMR taken in C$_6$F$_6$/CDCl$_3$ mixture.

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F-POSS Structures Synthesized

\[ R = \text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3 \]

-29.5 ppm

-17.8 ppm

-32.1 ppm

-17.8 ppm

-45.5 ppm

-17.1 ppm

-17.9 ppm

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## Initial Copolymerizations

\[
\text{MMA} \quad \text{(MW = 100 g/mol)}
\]

\[
\text{MMA-F-POSS} \quad \text{(MW = 4179 g/mol)}
\]

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<tr>
<th>Sample #</th>
<th>Weight (g)</th>
<th>Weight (MMA)</th>
<th>Weight (MMA-F-POSS)</th>
<th>Monomer (mmol)</th>
<th>Mol Ratio (MMA:MMA-F-POSS)</th>
<th>Initiator (mol %)</th>
<th>Conversion (%)</th>
<th>Weight (%) FPOSS*</th>
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<td>1</td>
<td>0.085</td>
<td>1.31</td>
<td>6.3</td>
<td>MMA (mmol)</td>
<td>MMA-F-POSS (mmol)</td>
<td>0.5</td>
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<td>2</td>
<td>0.362</td>
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<td>21.6</td>
<td>MMA (mmol)</td>
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*Weight (%) of F-POSS was calculated from elemental analysis of Fluorine content in the final polymer.

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Summary

- FluoroPOSS are superhydrophobic
- FluoroPOSS polymer composite surfaces can be superhydrophobic and superoleophobic
- Superhydrophilic and superoleophobic surfaces have been developed
- Such surfaces are ideal for the separation of both free-oil and oil-water emulsions
- These membranes, for the first time, allow continuous-flow oil-water emulsion separation
- Functionality will allow the covalent attachment of these low energy materials to substrates of choice
Acknowledgements

Profs. Gareth McKinley & Bob Cohen
Superoleophobic Surfaces

Professor Anish Tuteja
Oil/Water Separation Membranes

Polymer Working Group
Fluorinated POSS

Financial Support

Air Force Office of Scientific Research

Air Force Research Laboratory, Propulsion Directorate

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Polymer Working Group

The Polymer Working Group at Edwards Air Force Base:

Ms. Dana Pinson
Dr. Sean Ramirez
Mr. Pat Ruth
Dr. Tim Haddad
Ms. Vandana Vij
Dr. Greg Yandek

Dr. Andy Guenthner
Mr. Brian Moore
Dr. Joe Mabry
Mr. Kevin Lamison
Dr. Josiah Reams

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Air Force Research Laboratory, Propulsion Directorate

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<td>Silicon Cyanate Esters</td>
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<td>Sean Ramirez</td>
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QUESTIONS?

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