<table>
<thead>
<tr>
<th>1. REPORT DATE (DD-MM-YYYY)</th>
<th>2. REPORT TYPE</th>
<th>3. DATES COVERED (From - To)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>4. TITLE AND SUBTITLE</th>
<th>5a. CONTRACT NUMBER</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>6. AUTHOR(S)</th>
<th>5b. GRANT NUMBER</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</th>
<th>8. PERFORMING ORGANIZATION REPORT</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</th>
<th>10. SPONSOR/MONITOR'S ACRONYM(S)</th>
</tr>
</thead>
</table>

Air Force Research Laboratory (AFMC)  
AFRL/PRS  
5 Pollux Drive  
Edwards AFB CA 93524-7048

<table>
<thead>
<tr>
<th>11. SPONSOR/MONITOR'S NUMBER(S)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>12. DISTRIBUTION / AVAILABILITY STATEMENT</th>
</tr>
</thead>
</table>

Approved for public release; distribution unlimited.

<table>
<thead>
<tr>
<th>13. SUPPLEMENTARY NOTES</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>14. ABSTRACT</th>
</tr>
</thead>
</table>

20030127 205

<table>
<thead>
<tr>
<th>15. SUBJECT TERMS</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>16. SECURITY CLASSIFICATION OF:</th>
<th>17. LIMITATION OF ABSTRACT</th>
<th>18. NUMBER OF PAGES</th>
<th>19a. NAME OF RESPONSIBLE PERSON</th>
<th>19b. TELEPHONE NUMBER (include area code)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. REPORT</td>
<td>b. ABSTRACT</td>
<td>c. THIS PAGE</td>
<td>A</td>
<td>(661) 275-5015</td>
</tr>
<tr>
<td>Unclassified</td>
<td>Unclassified</td>
<td>Unclassified</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Unclassified

19a. NAME OF RESPONSIBLE PERSON: Leilani Richardson
19b. TELEPHONE NUMBER: (661) 275-5015
MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO) 31 Oct 2001

Brent D. Viers, et al., "Basic and Applied Research on Hybrid Organic/Inorganic Materials for Propulsion and Space"

PDMS Langmuir Blodgett Analysis

- Inherent dimensionality effects

![Graph showing various curves]

PDMS terminated with ▲ di COOH;
X mono COOH; ● di Si(CH$_3$)$_3$; — di OH

- Highly sensitive to functionality


Results – P-A Isotherms of POSS Samples

POSS Samples ($T = 22.5^\circ C$)
- Isobutyltrisilanol
- Cyclopentyltrisilanol
- Cyclohexyltrisilanol
- Octaisobutyl

Weak Interactions

Stronger Interactions

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited
Results – BAM of Isobutyltrisilanol-POSS

- Non-equilibrium phase transition induced by pressure
- Supersaturation results in non-equilibrium 2-D dendritic growth of the more condensed phase
- Pressure relaxation drives the system to the equilibrium state characterized by round domains
- Observed in a few other surfactant systems*

*Iimora, K.-I.; et al. Langmuir 2001, 17, 4602

POSS-PDMS Blends

\[ \Delta G^{\sigma} = \int_{\Pi} (A_{12} - x_1 A_1 - x_2 A_2) d\Pi \]

A

B

$<A>/\AA^2\text{monomer}^{-1}$

$\Pi / nM/m^2$
Basic and Applied Research on Hybrid Organic/Inorganic Materials for Propulsion and Space

POSS is NOT just the smallest silica

**Dr. Brent D. Viers**
Propulsion Sciences Division
Edwards Air Force Research Lab

---

**POSS = Polyhedral Oligomeric Silsesquioxane**

- Traditional silsesquioxane chemistry focused on "T-Resins"
- The maximization of property enhancements in polymers results from interaction at the molecular level (Edwards AFRL/PRSM → POSS monomers)
Motivation – Filled Nanofluids

Blends Confined at the Air/Water Interface

Small Sample Requirements

1-2 nm “2-D” Polymer, Interphase, & Inorganic Core

Subphase Affinity is an Important Variable
• A/W poor solvent for PDMS & PtBA → solvent exclusion
• A/W good solvent for PVAc → chain swelling
  (must consider water’s contribution)
Experimental – Π-A Isotherm Studies

How the balance measures surface pressure:

\[
\Pi = \gamma_0 - \gamma = \frac{F_0 - F_{\text{obs}}}{2(L + t) \cos \theta}
\]

Molecular Phases in an Isotherm

- Liquid Phase
  - Suitable for LB-Transfer

- Gaseous Phase

L1-G and I = (L1-L2) Coexistent Phases
Brewster’s Law

Incident Beam

\[ \theta_b \]

Air

Reflected Beam

Reflected Beam

For a clean interface, the image should be uniformly dark as no light is reflected.

30mW@688nm (100:1 p+s light)

Monitor

p-Polarizer

Black Plate

Surface heterogeneity (>20μm) is observable by this technique.

30mW@688nm (100:1 p+s light)

**Polymers** — Structural Models for Adhesive Polymers

POSS Derivatives
- Octaisobutyl-POSS
- Isobutyltrisilanol-POSS
- Cyclopentyltrisilanol-POSS
- Cyclohexyltrisilanol-POSS

PTBA: \( M_n = 25k \)

PVA: \( M_n \approx 1280k \)

PTACT: \( M_n \approx 2k \)
PDMS Langmuir Blodgett Analysis

- Inherent dimensionality effects

- Highly sensitive to functionality


- "al." should not be capitalized
- Please add a comma after "al." to separate the journal name

Results - P-A Isotherms of POSS Samples (T= 22.5°C)

- Isobutyltrisilanol
- Cyclopentyltrisilanol
- Cyclohexyltrisilanol
- Octaisobutyl

POSS Samples (T= 22.5°C)

Weak Interactions

Stronger Interactions
Results – BAM of Octaisobutyl-POSS

Octaisobutyl-POSS
10.5 Å²・molecule⁻¹
T = 22.5°C

Results – BAM of Isobutyltrisilanol-POSS

Isobutyltrisilanol-POSS
7.5 Å²・molecule⁻¹
T = 22.5°C

Scales correspond to 500 μm.
Results – BAM of Isobutyltrisilanol-POSS

- Non-equilibrium phase transition induced by pressure
- Supersaturation results in non-equilibrium 2-D dendritic growth of the more condensed phase
- Pressure relaxation drives the system to the equilibrium state characterized by round domains
- Observed in a few other surfactant systems

*Imura, K.-I.; et al. Langmuir 2001, 17, 4602

I suggest adding a comma here to separate the authors from the journal name.

\[ \Delta G^* = \int_{A_2}^{A_1} (A_2 - x_1 A_1 - x_2 A_2) d\Pi \]
Results – 80 wt% iBu7T7/PtBA Blend

- Ideal uniform blends (0-100 wt% POSS, 1-3), LB<50 wt% POSS
- Dendritic domains form at 4 (50-100 wt%) POSS, size ↑ as POSS ↑, round domains (POSS < 50 wt%)
- Banded structure ⇒ PtBA collapse
- 6* = 60 wt% iBu7T7/PtBA blend

Results – 35 wt% Octaisobutyl-POSS/PDMS

Scales correspond to 500 μm.
Results – 35wt% Octaisobutyl-POSS/PVAc

- PVAc/iBu₈T₈: Non-ideal mixing like PDMS/iBu₈T₈
- Unlike PDMS system, POSS is almost completely excluded from the interface!!

Scales correspond to 500 μm.

Results – 50wt% Isobutyltrisilanol-POSS/PDMS

Scales correspond to 500 μm.
Summary: POSS Blends

- POSS derivatives exhibit surfactant properties that vary with structure.
- Homogeneous films with near ideal mixing for iBu\textsubscript{7}T\textsubscript{7}+PDMS, PVAc or PtBA (P < 18 mN\textcdot m\textsuperscript{-1}), but BAM shows samples are dispersions.
- For P > 18 mN\textcdot m\textsuperscript{-1}, non-equilibrium dendritic domains form for pure iBu\textsubscript{7}T\textsubscript{7} & iBu\textsubscript{7}T\textsubscript{7}+PtBA (>50wt% POSS), round domains as POSS
- iBu\textsubscript{7}T\textsubscript{7}+PDMS uniform dispersions (>mm), iBu\textsubscript{7}T\textsubscript{7}+PVAc immiscible (>mm)
Model POSS Polymers- POSS Norbornene

Both block and random copolymers were synthesized.

The amount of POSS was varied from 0 to 50 wt. % POSS.

POSS-block-norbornene

Only a single Tg is observed from the norbornene block.

The POSS-norbornene block does not give rise to any transition up to 350°C.

While polymers of POSS-styryl and acrylates show the same behavior.
Morphology of POSS/PN Diblock Copolymers (TEM)

10wt% of CyPOSS
- CyPOSS is more soluble in the polymer matrix than CpPOSS
- Also seen for random polymers, resulting in a greater $\Delta T_c$ for CyPOSS

Morphology of POSS/PN Diblock Copolymers (TEM)

30wt% of CyPOSS
30wt% of CpPOSS
Morphology of POSS/PN Diblock Copolymers (TEM)

30wt % of CyPOSS

Morphology of POSS/PN Diblock Copolymers (TEM)

30wt % of CpPOSS
Morphology of POSS/PN Diblock Copolymers (TEM)

60 wt% of CyPOSS

60 wt% of CpPOSS

DSC Data for Random Copolymers

- Random copolymerization: Material with a single Tg is obtained that increases with increasing POSS content.
- Effect stronger than that observed for POSS-styryl, but not as large as for POSS-acrylics.
Tensile Storage Modulus Variation with POSS Content at Three Temperatures

Up to 50 weight % of POSS-nobornene was incorporated into the nobornene copolymer without adversely affecting the room temperature modulus, and increasing the use temperature of these materials over 50 °C.

TEM of 50CpPOSS/PN & 50CyPOSS/PN

"Coarse" Cylinder Nanostructure (Diameter ~ 12nm)  "Fine" Cylinder Nanocstructure (Diameter ~ 6nm)

CyPOSS-rich domains may entrain more unoriented PN chains than CpPOSS-rich domains, which could reduce the recoverable strain.
TEM of 4X drawn 50CpPOSS/PN & 50CyPOSS/PN

Reanalysis of the Random 50 CyPOSS/PN System

- Strong anisotropy and correlations noted—hints at assembled structure
Summary: POSS copolymers

- A variety of POSS "monomers" can be copolymerized into common systems (styrenic, acrylics, polyimides, etc.)
- The polymerization parameters don't appear to be greatly affected, and the POSS is compatible with the matrix (optically transparent)
- The model POSS-norbornene copolymers show distinct differences in mechanical behavior and morphology for differences in POSS corona chemistry (cyclopentyl vs. cyclohexyl)
- Evidence of larger scale structures.

Variations on the theme-POSS corona chemistry

Different POSS corona polymers being synthesized

\[ R = \text{cyclohexyl, isobutyl, cyclopentyl, phenyl} \]
Polymeric Materials for Aerospace

- Offer many advantages
  - Lightweight
  - Easy to process
  - Versatility
  - Optically transparent or opaque
  - Rubbery or stiff
  - Conductive or insulating
- However, their use is limited due to severe degradation in operation (Low Earth Orbit, high speed, high flux)

POSS Reinforcement-Pi-K motor

CHAR-063 ABLATION RATE
EPDM-Kevlar STANDARD (S10) / EPDM-V, T, (T10)

![Graph showing ablation rate comparison](image)
POSS Reinforcement-CSD tests

- 40-lb ITM Motor
- A series of POSS/EPDMs were tested
- Most promising was VI8T8

Goal: Develop Multi-Functional, Space-Resistant Materials

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation Energy (eV)</th>
<th>λ (nm)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-H, C=N</td>
<td>3.9</td>
<td>320</td>
<td>Kaption®</td>
</tr>
<tr>
<td>C=N</td>
<td>3.2</td>
<td>390</td>
<td>Kaption®</td>
</tr>
<tr>
<td>CF₂-CF₂</td>
<td>4.3</td>
<td>290</td>
<td>FEP Teflon®</td>
</tr>
<tr>
<td>CF₃-F</td>
<td>5.5</td>
<td>230</td>
<td>FEP Teflon®</td>
</tr>
<tr>
<td>Si-O</td>
<td>6.3</td>
<td>150</td>
<td>Nanocomposite</td>
</tr>
<tr>
<td>Zr-O</td>
<td>8.1</td>
<td>150</td>
<td>Nanocomposite</td>
</tr>
<tr>
<td>Al-O</td>
<td>5.3</td>
<td>230</td>
<td>Nanocomposite</td>
</tr>
</tbody>
</table>

Objectives
- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials
- Self-Passivating/Self-Rigidizing/Self-Healing based on organic/inorganic nanocomposite incorporation
Atomic Oxygen Resistance of POSS Siloxane

XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

<table>
<thead>
<tr>
<th>Sample Treatment</th>
<th>O  (at%)</th>
<th>C  (at%)</th>
<th>Si  (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received</td>
<td>18.5</td>
<td>65.0</td>
<td>16.6</td>
</tr>
<tr>
<td>2.0 hr</td>
<td>33.8</td>
<td>48.4</td>
<td>17.8</td>
</tr>
<tr>
<td>24.6 hr</td>
<td>49.1</td>
<td>22.1</td>
<td>28.8</td>
</tr>
<tr>
<td>63.0 hr</td>
<td>55.7</td>
<td>16.3</td>
<td>28.0</td>
</tr>
<tr>
<td>4.75 hr air</td>
<td>52.6</td>
<td>19.5</td>
<td>27.7</td>
</tr>
</tbody>
</table>

High Resolution C 1s and O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.
High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b) after a 2-hr exposure to the hyperthermal AO flux, and (c) 4.75-hr air exposure following the 63-hr AO exposure.

Summary: Aerospace Polymers

- POSS can be compatibilized into traditional systems in high loadings (>50 wt%), allowing great opportunity for ceramic formation
- The reactive POSS corona, or the incompletely oxidized silsesquioxane core might favor the formation of the protective ceramic coating