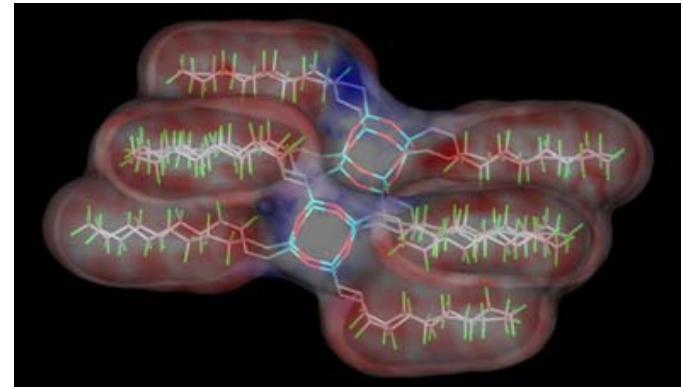
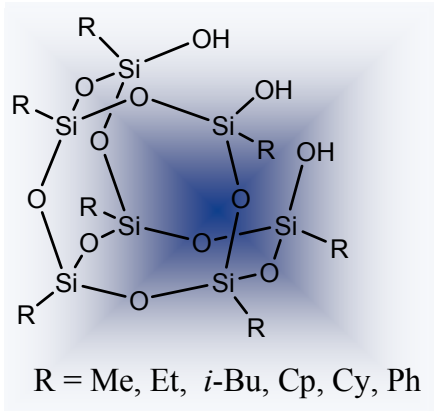


From Nanoscience to Nanotechnology: The Development and Application of Polyhedral Oligomeric Silsesquioxanes (POSS) as Versatile, Engineering Nanomaterials.

21 September 04



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Applications Branch

AFRL/PRSM

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Report Documentation Page

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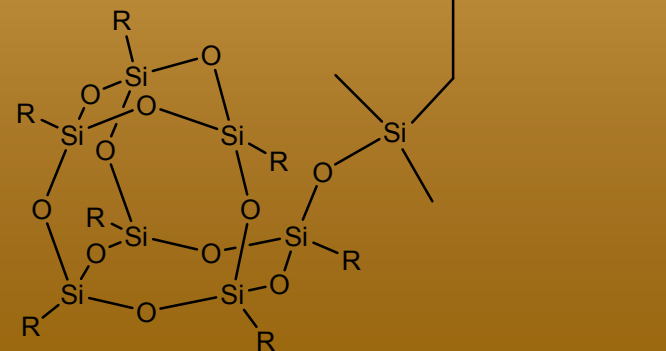
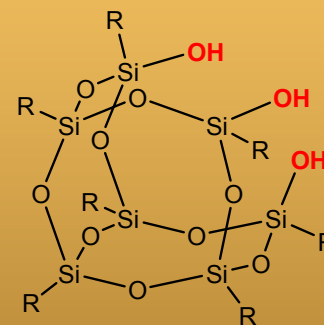
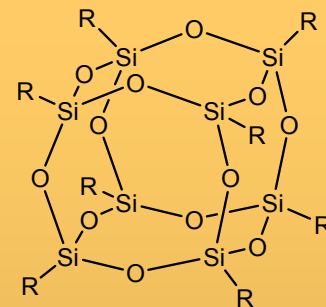
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|---|------------------------------------|--|----------------------------|----------------------------------|---------------------------------|
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| | | 5b. GRANT NUMBER | | | |
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| a. REPORT unclassified | b. ABSTRACT unclassified | c. THIS PAGE unclassified | | | |



POSS: Where We Were (1996)



- **Cost: \$5,000-\$10,000/lb**
- **Volume: ~20 lbs/yr**
- **Production time: min 11 days,
max 6 months**
- **Versatility: ~6 POSS feedstocks
~30 POSS macromers**
- **No successful POSS blends**
- **Made only by U.S. Government**





What Property Enhancements Can You Get From Using POSS?



increased T_g

increased T_{dec}

enhanced blend miscibility

reduced flammability

extended temperature range

oxidation resistance

reduced heat evolution

increased oxygen permeability

altered mechanicals

lower density

lower thermal conductivity

reduced viscosity

disposal as silica

thermoplastic or curable

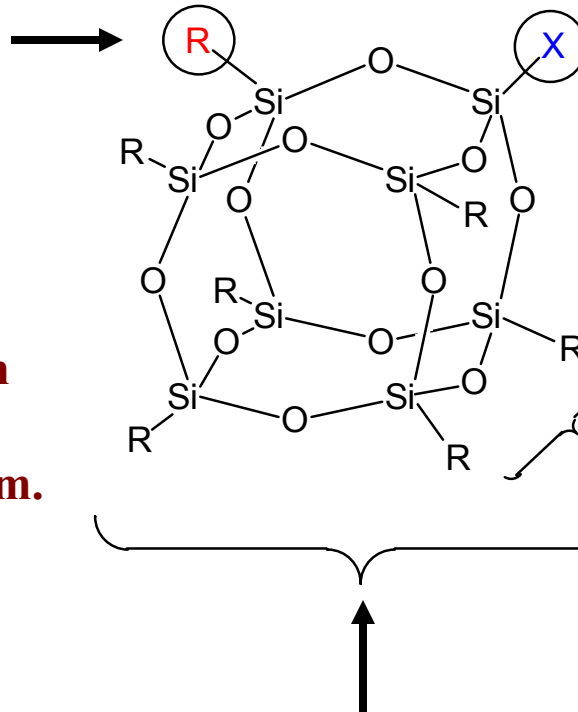
Beat competitors' patents!



Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS[®]) Molecule



Nonreactive organic (R) groups for solubilization and compatibilization.



May possess one or more functional groups suitable for polymerization or grafting.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

• Think of it as functionalized sand, or smallest particle of sand possible

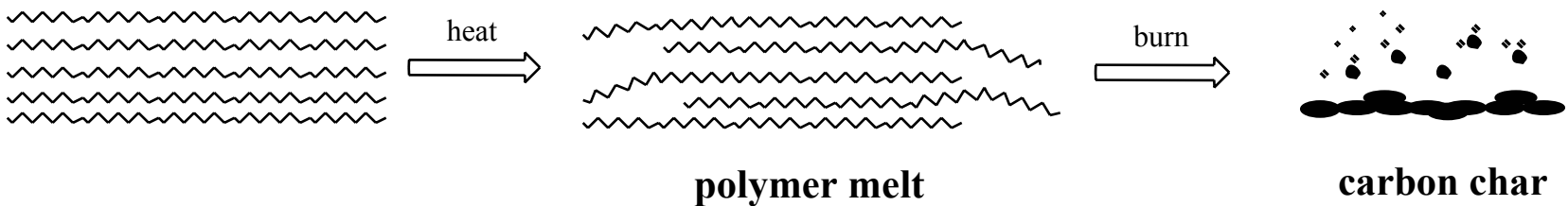


Oxidation Resistance/Reduced Flammability, Smoke & Heat Evolution

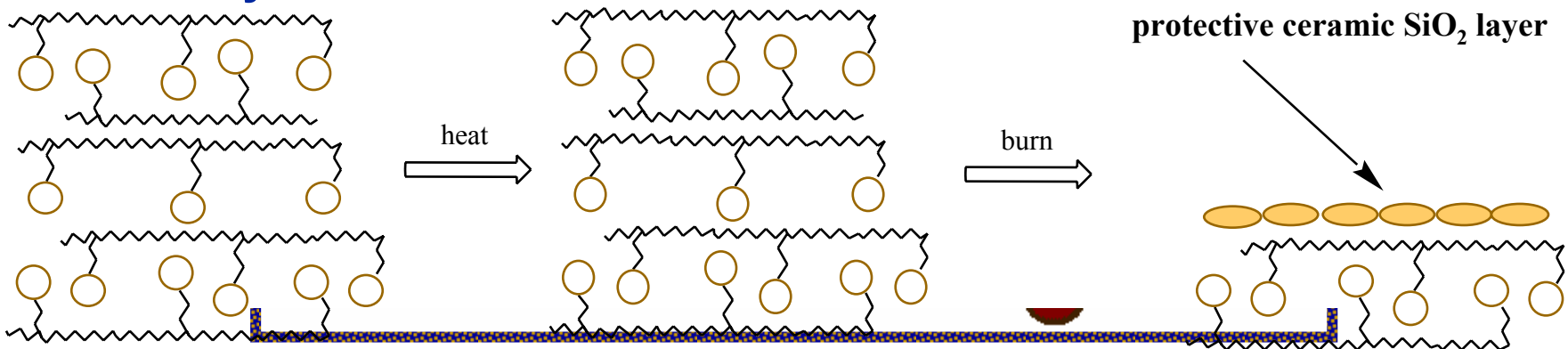


- Only organic groups on POSS cage can burn
- Silicon groups on POSS are only partially oxidized and form a ceramic silicon dioxide (SiO_2) layer in-situ
- POSS can form a char layer that stops the burning process

Polymer



POSS Polymer

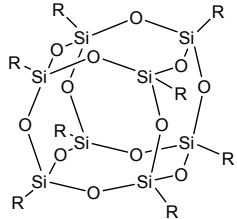




How to use POSS (Blends or Drop-In Nanofillers)

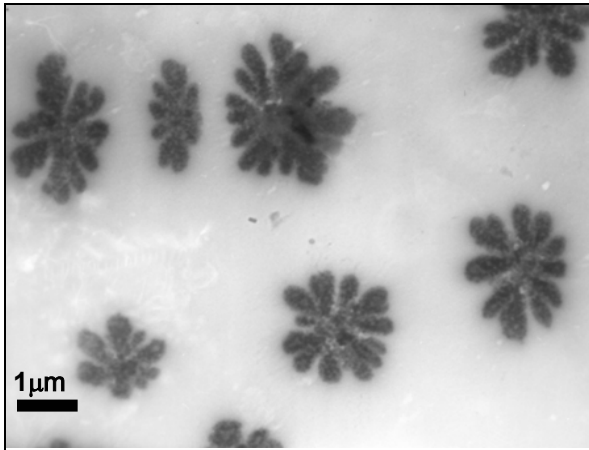


50 Wt % POSS Blends in 2 Million MW PS

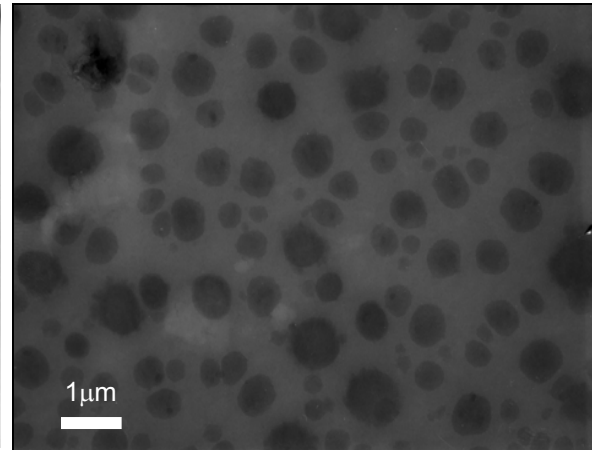


R = cyclopentyl

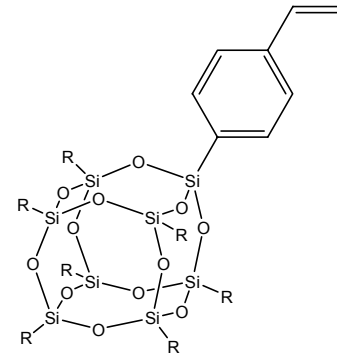
Cp₈T₈



Domain Formation

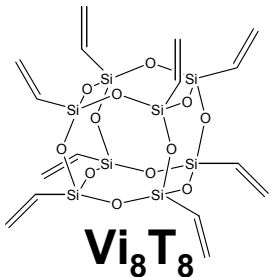


Partial Compatibility

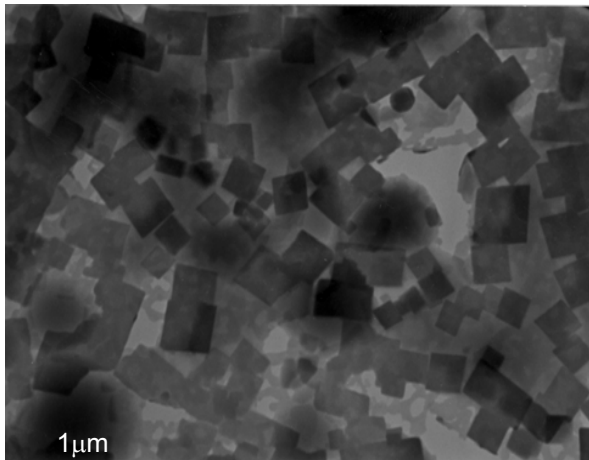


R = cyclopentyl

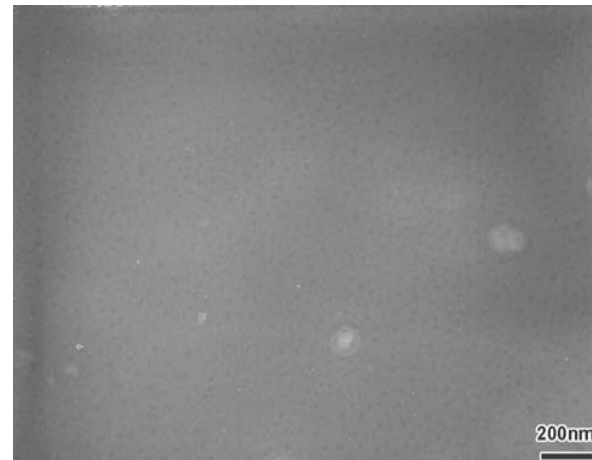
Cp₇T₈Styryl



Vi₈T₈



Immiscible POSS Crystallites



**Complete Compatibility-
POSS Nanodispersion/Transparent**



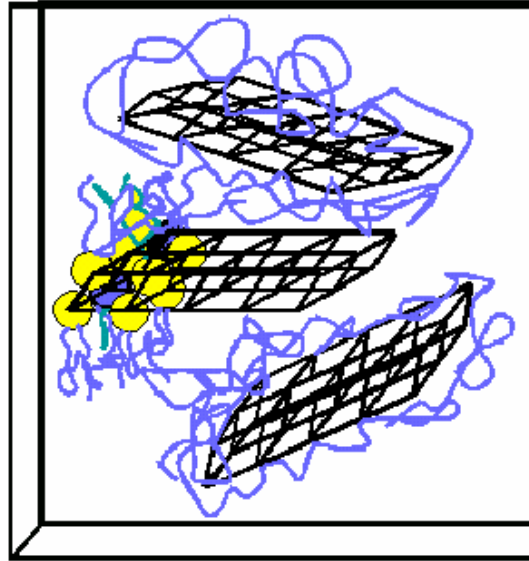
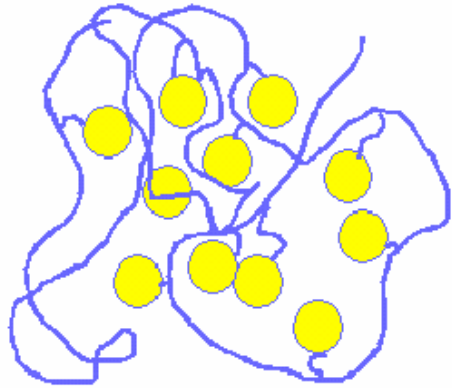
Phenethyl₈T₈



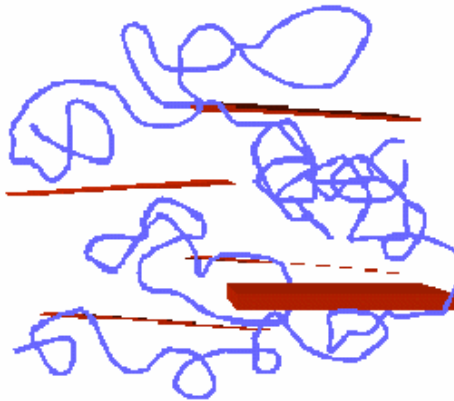
Coughlin Building Block Model (POSS Blends & Copolymers)



Bottom-up Approach (Self-Assembly)



Top-down Approach

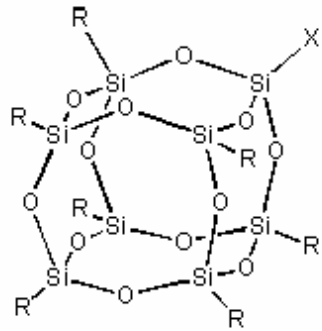


Bryan Coughlin-UMass

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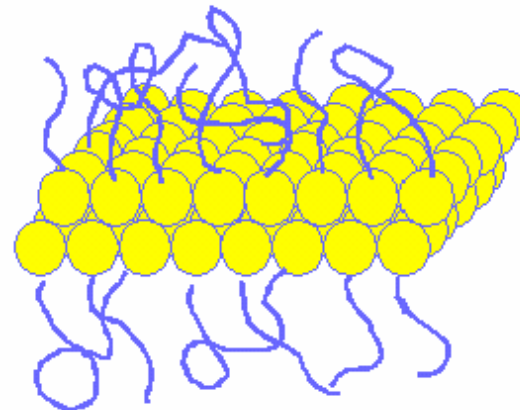
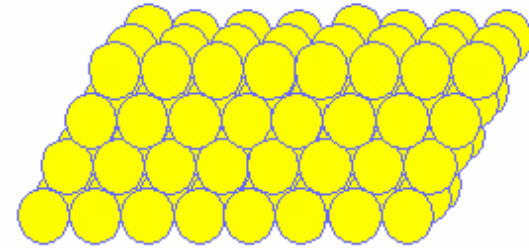
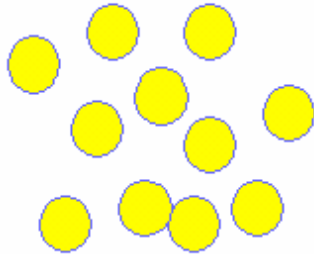
Coughlin Model Continued (building from the ground up)



≡

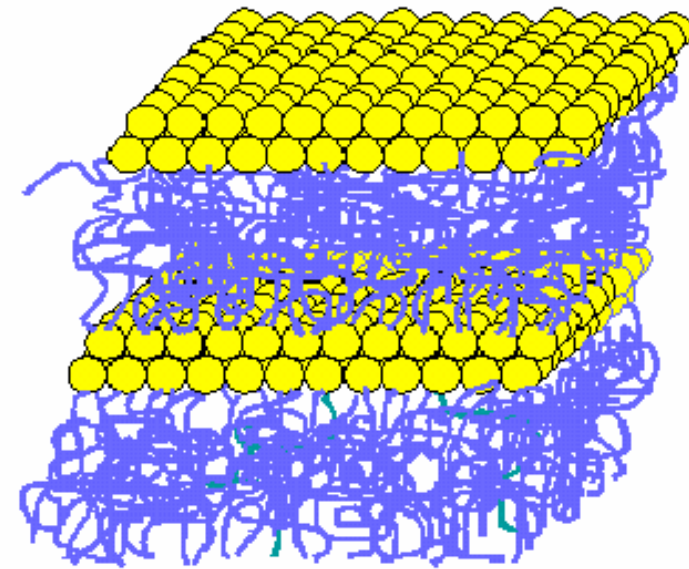
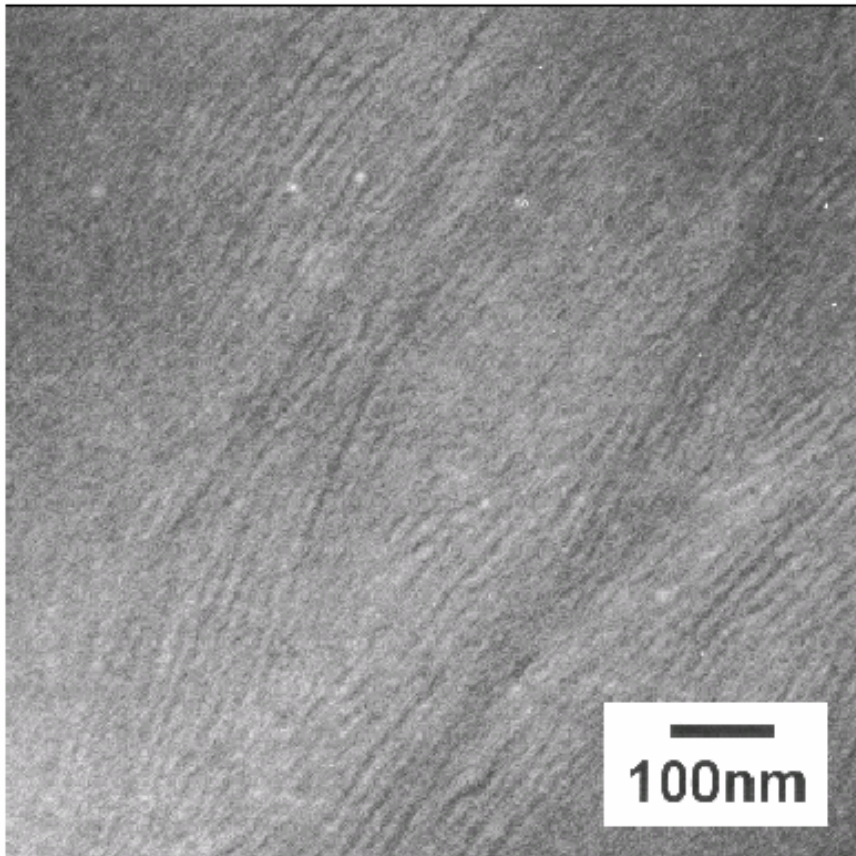


1. As a solid, POSS crystallizes





Nanoengineering with POSS



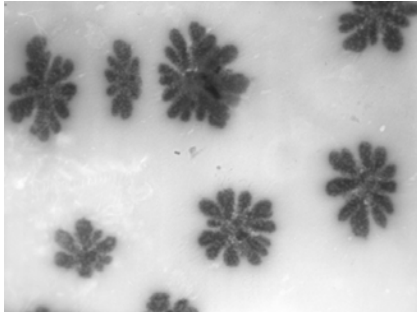
Bryan Coughlin-UMass

PBD-POSS4 (43wt%POSS)

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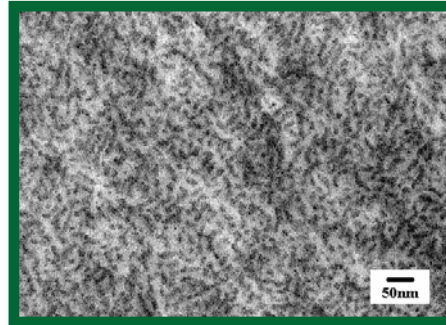


Dimensionality Control (Crystallite/Aggregate Size)

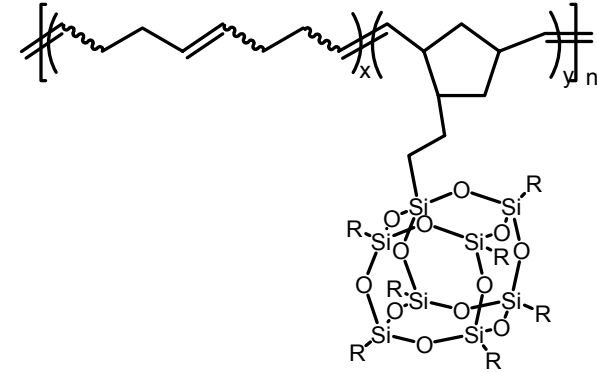


Domain Formation

50% CyPOSS/PN

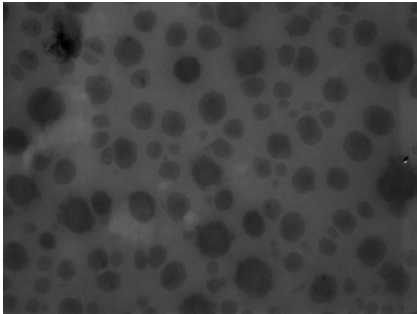


12 nm coarse cylinders (2x ↑T_g over CpPOSS)



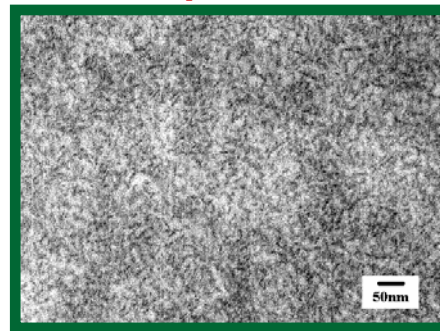
PBD-POSS (43wt%POSS)

2000 SAB



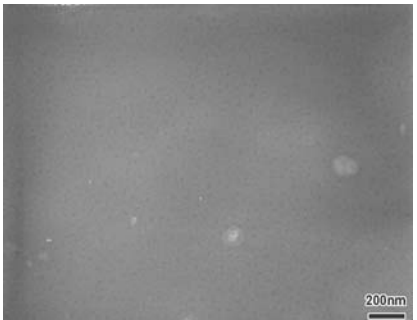
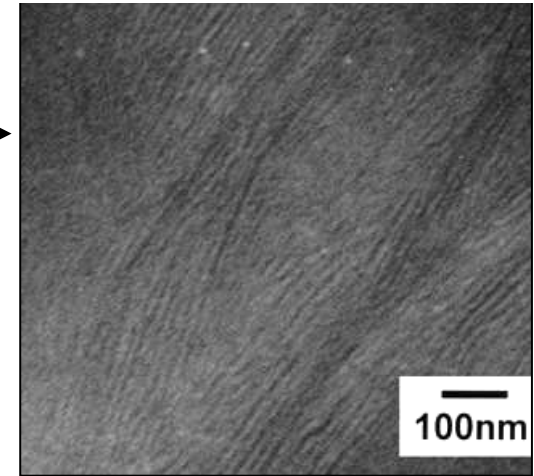
Partial Compatibility

2002 SAB

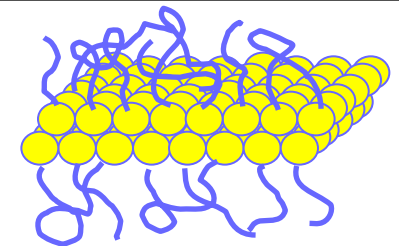


6 nm fine cylinders

2004 SAB



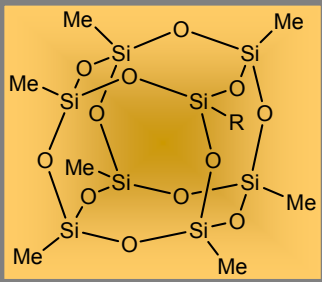
Complete Nanodispersion





Prof. Andre Lee i-PP/POSS Blends



|  | Dow data | Neat <i>i</i> -PP (processed) | <i>i</i> -PP blended 2 wt% Methyl ₈ T ₈ | <i>i</i> -PP blended 5 wt% Methyl ₈ T ₈ | <i>i</i> -PP blended 10 wt% Methyl ₈ T ₈ |
|--|------------------------------------|------------------------------------|--|--|--|
| Tensile Strength @ Yield; ASTM D638 | 5000 psi (34.5 MPa) | 4800 psi (33.0 MPa) | 5000 psi (34.5 MPa) | 5100 psi (35.1 MPa) | 5200 psi (35.8 MPa) |
| Flexural Modulus (0.05 in/min); ASTM D790A | 240,000 psi (1.655 GPa) | 235,000 psi (1.620 GPa) | 251,000 psi (1.730 GPa) | 255,000 psi (1.757 GPa) | 262,000 psi (1.80 GPa) |
| HDT @ 66 psi, as injected; ASTM D648 | 210 °F (99 °C) | 210 °F (99 °C) | 221 °F (105 °C) | 239 °F (115 °C) | 255 °F (124 °C) |
| Impact Izod @25C ASTM D256A | 0.5 ft-lb/in | 0.55 ft-lb/in | 0.55 ft-lb/in | 0.62 ft-lb/in | 0.75 ft-lb/in |

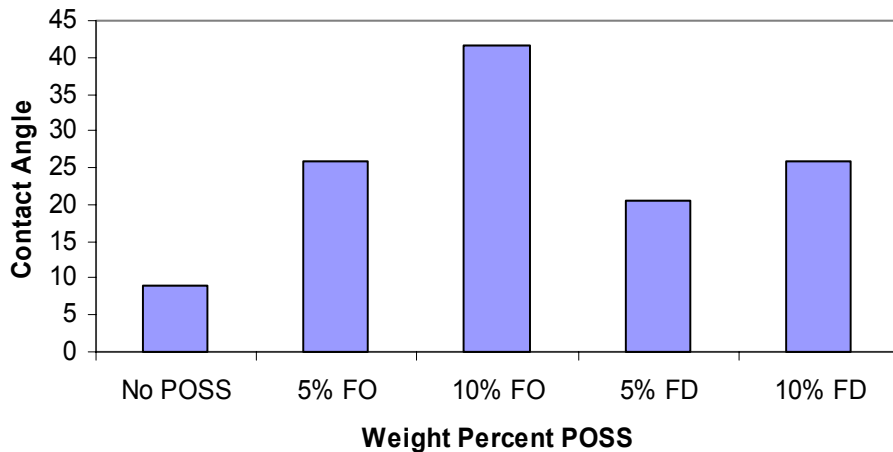
- The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.**



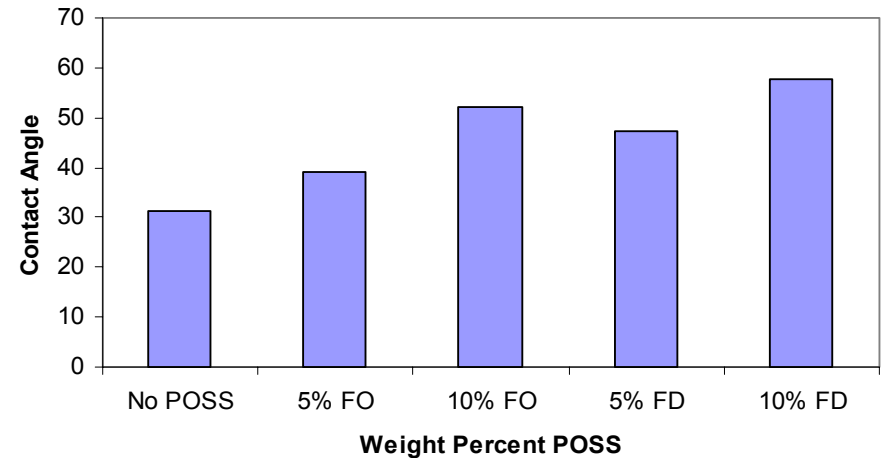
Oleophobicity Improvement

Kel-F (PCTFE) & POSS Blends

Decane (Fuel) Contact Angles



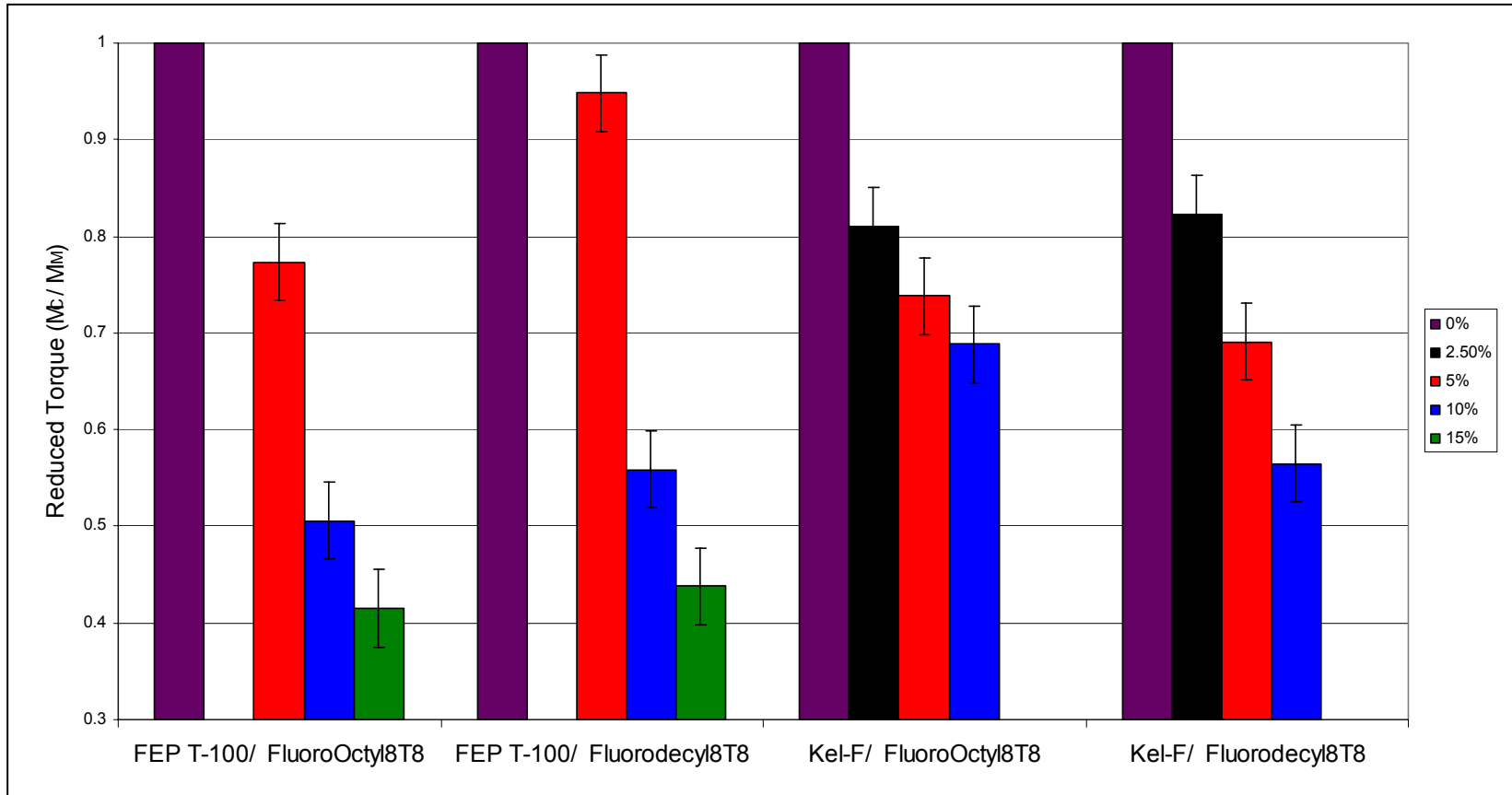
Hexadecane (Fuel) Contact Angles



- 10 wt% FluoroPOSS in Kel-F increases the contact angle (decane: $9^\circ \rightarrow 42^\circ$, hexadecane: $31^\circ \rightarrow 58^\circ$).



Fluoropolymer Processing Aid

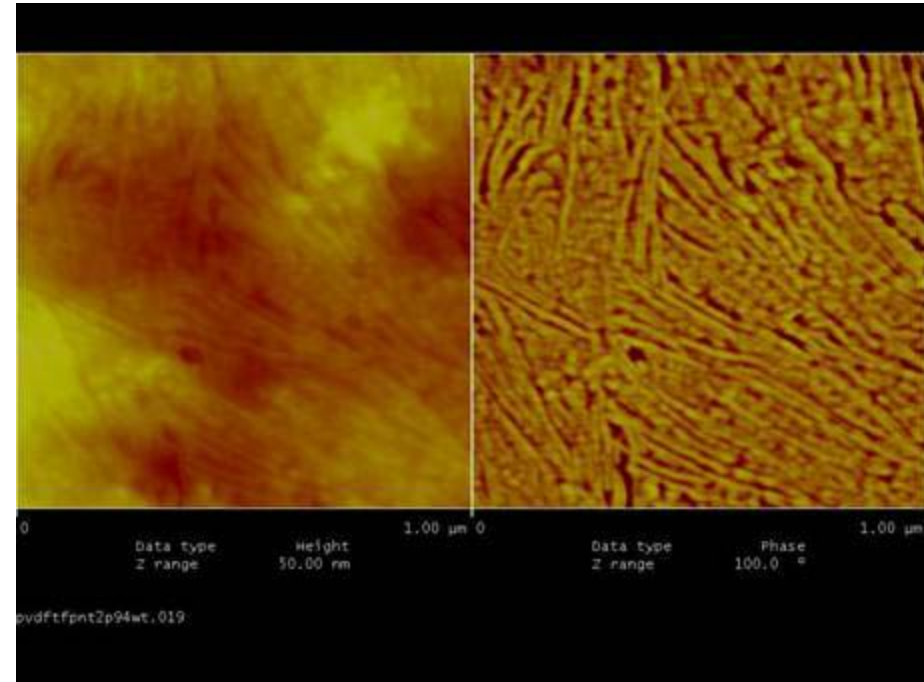
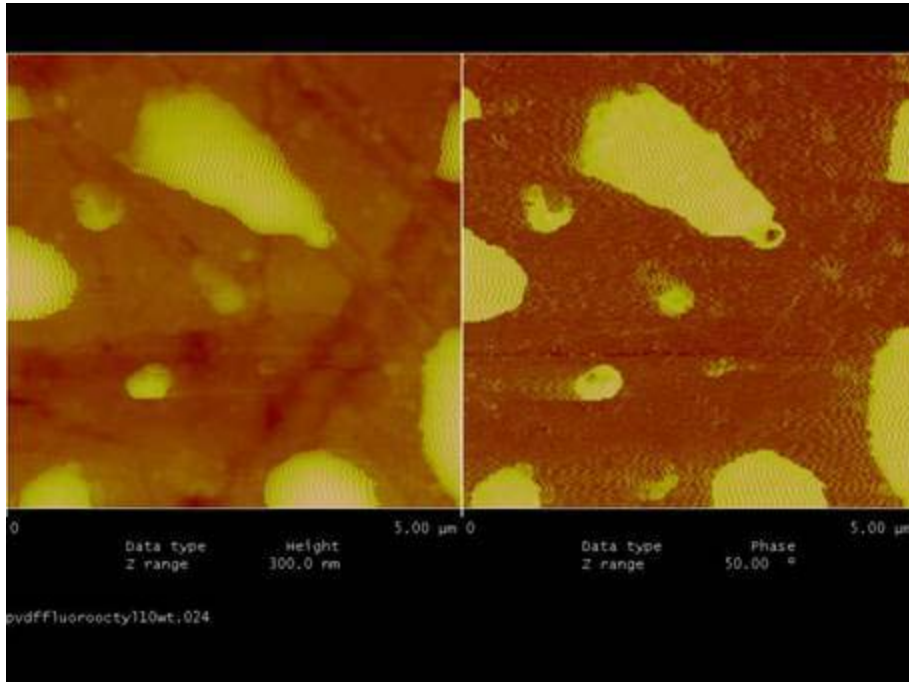


- FluoroPOSS acts as a processing aid during the blending into both FEP and Kel-F without affecting the mechanical properties.

DISTRIBUTION A. Approved for public release; distribution unlimited.



PVdF/FluoroPOSS AFMs



- **Fluorooctyl POSS is largely incompatible with PVdF, probably due to its large fluorine content.**
- **Fluoropropyl POSS, on the other hand, is highly compatible with PVdF. Fluoropropyl POSS has a similar F/H ratio to PVdF.**

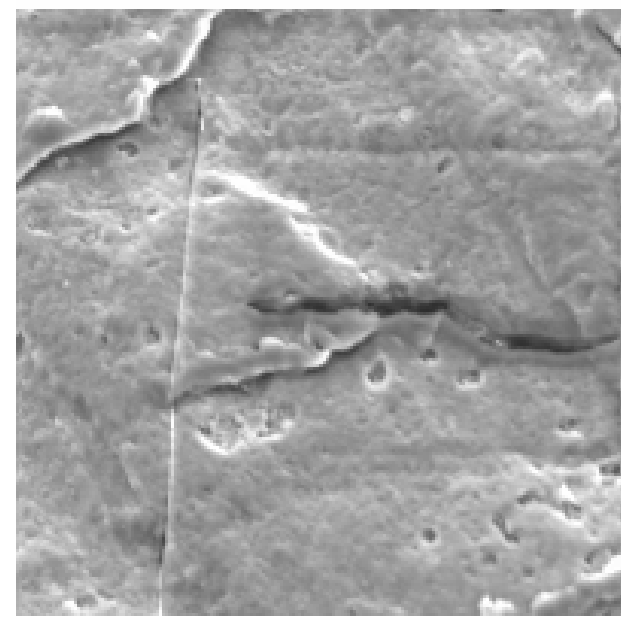
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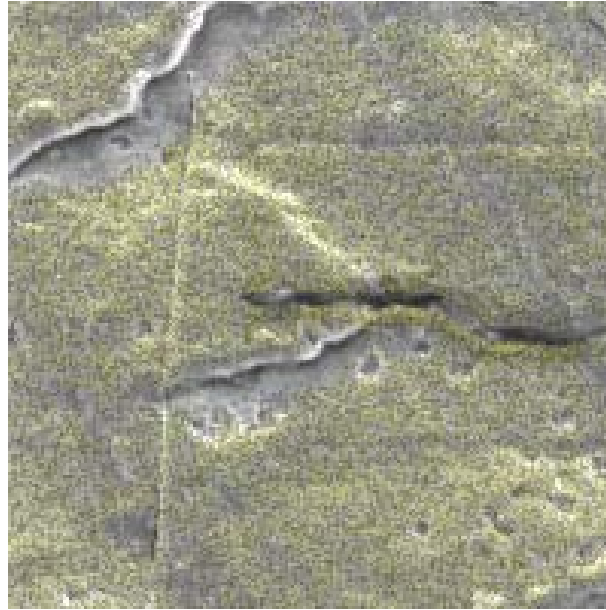
PVdF/FluoropropylInTn SEMs



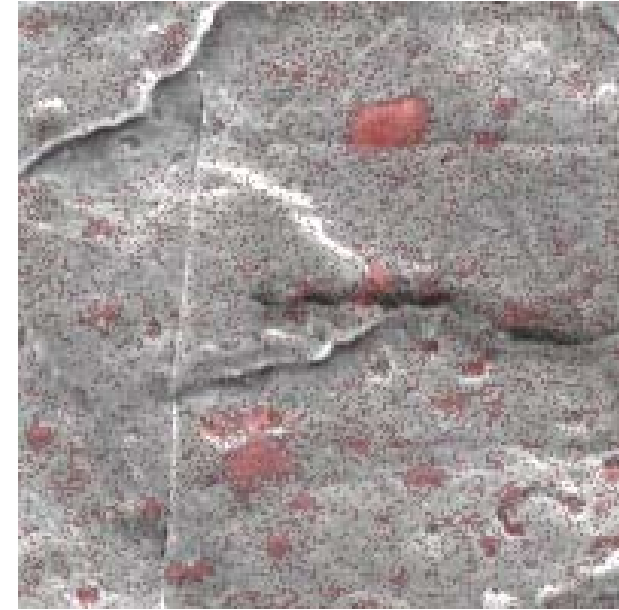
SEM



SEM Image



Carbon Map



Silicon Map

- **SEM Image taken on cross-section of 1/4 inch thick sample bar.**
- **Good dispersion is observed in silicon map.**

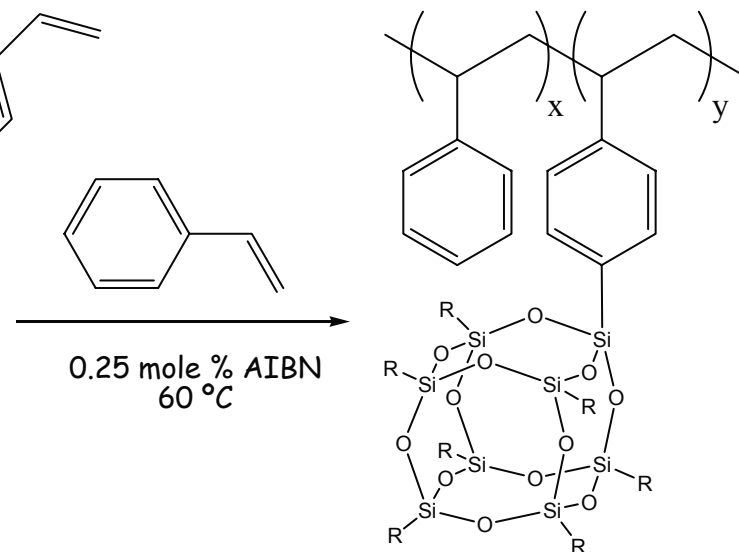
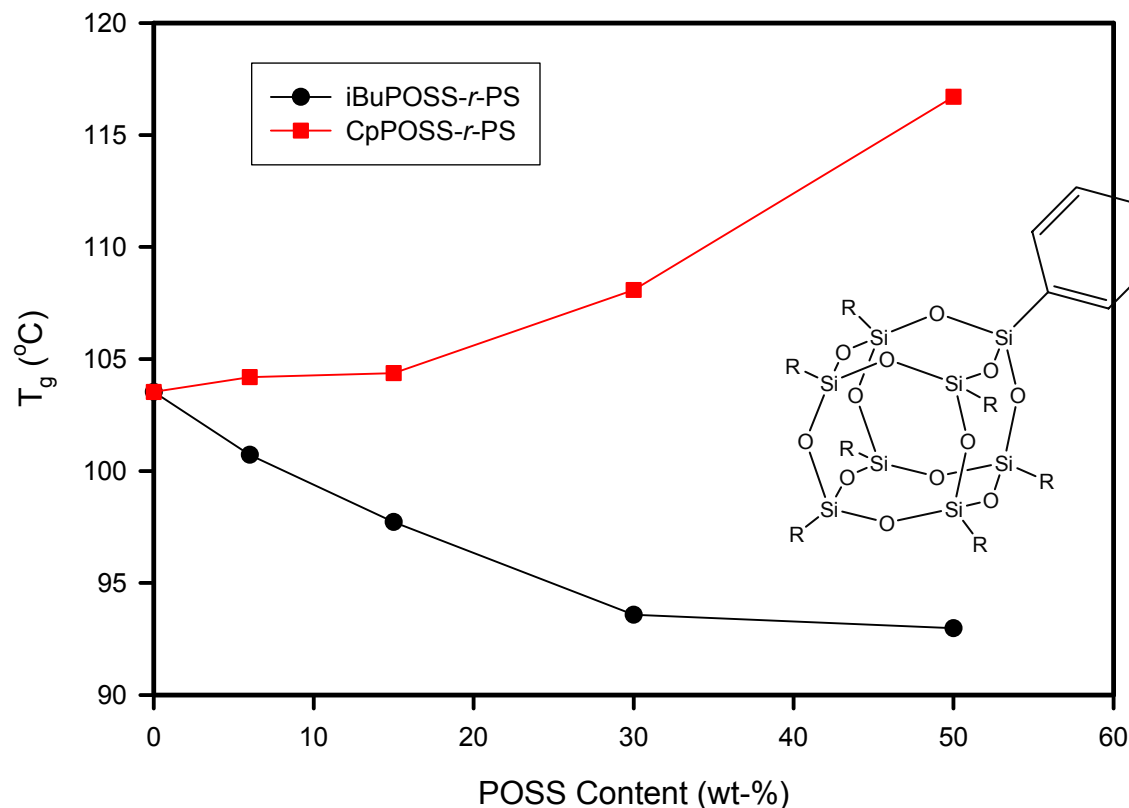


Glassy Polymer POSS-Polystyrene



DISTRIBUTION A. Approved for public release; distribution unlimited.

- In 2Q03 developed high molecular weight POSS-Polystyrene (R=Cy, Cp, i-Bu) resulted in:
 - Chain entanglement criteria, Good mechanical properties, Processability



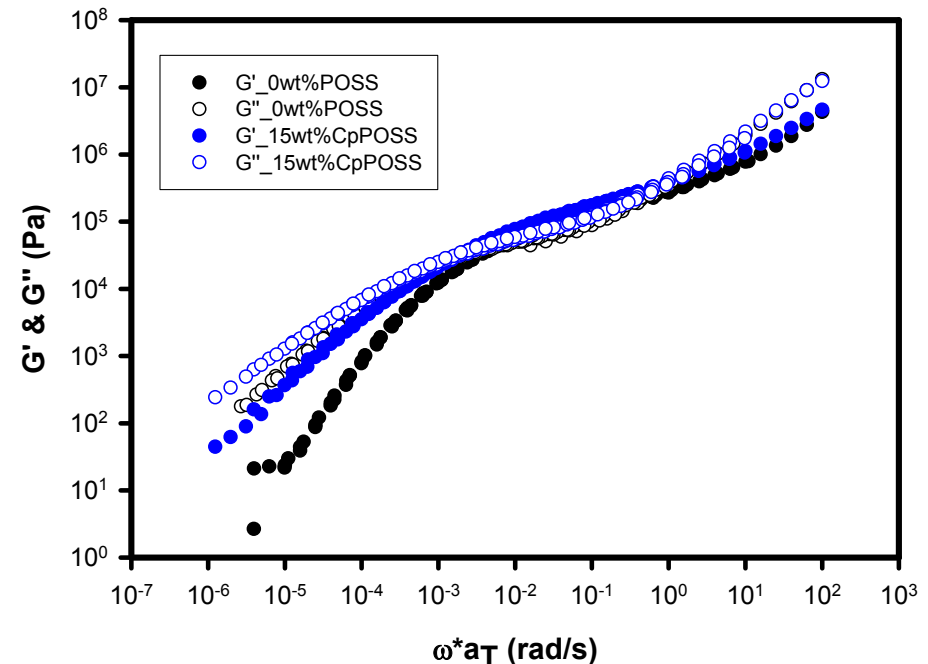
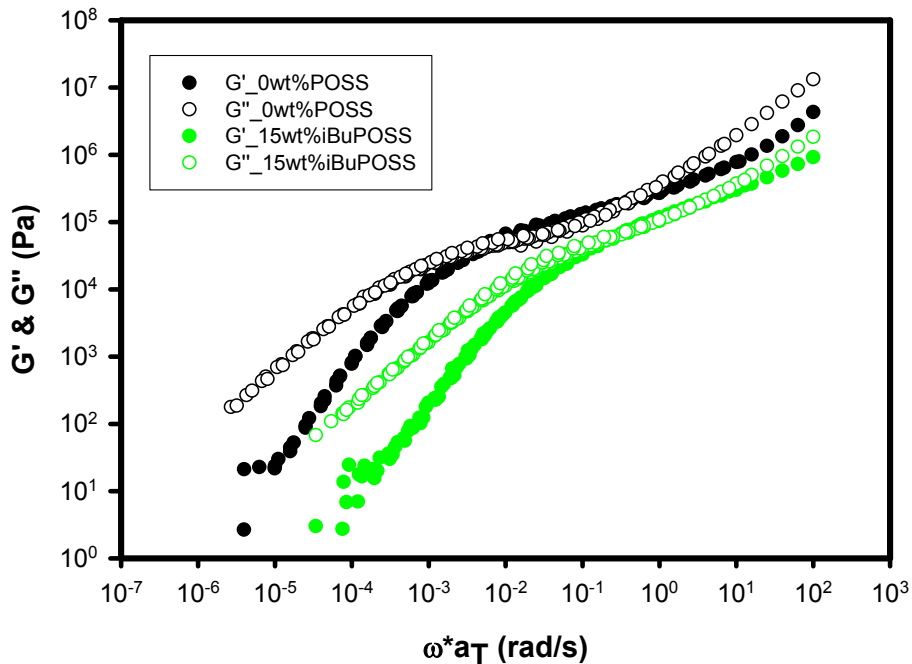


Glassy Polymer POSS-Polystyrene



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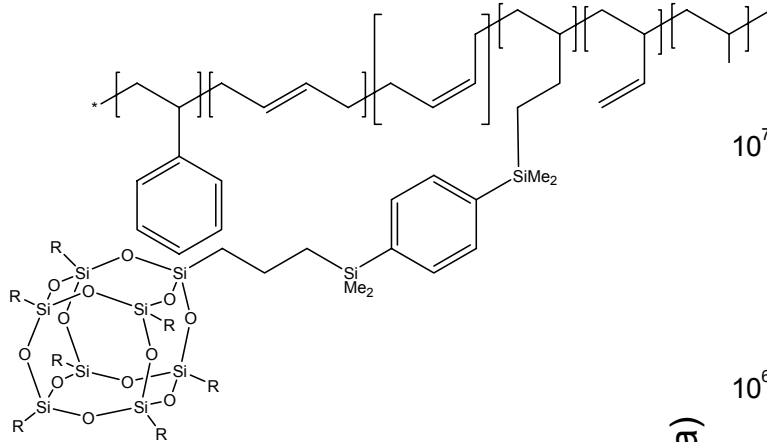
Reference Temperature = 120°C, 15% POSS



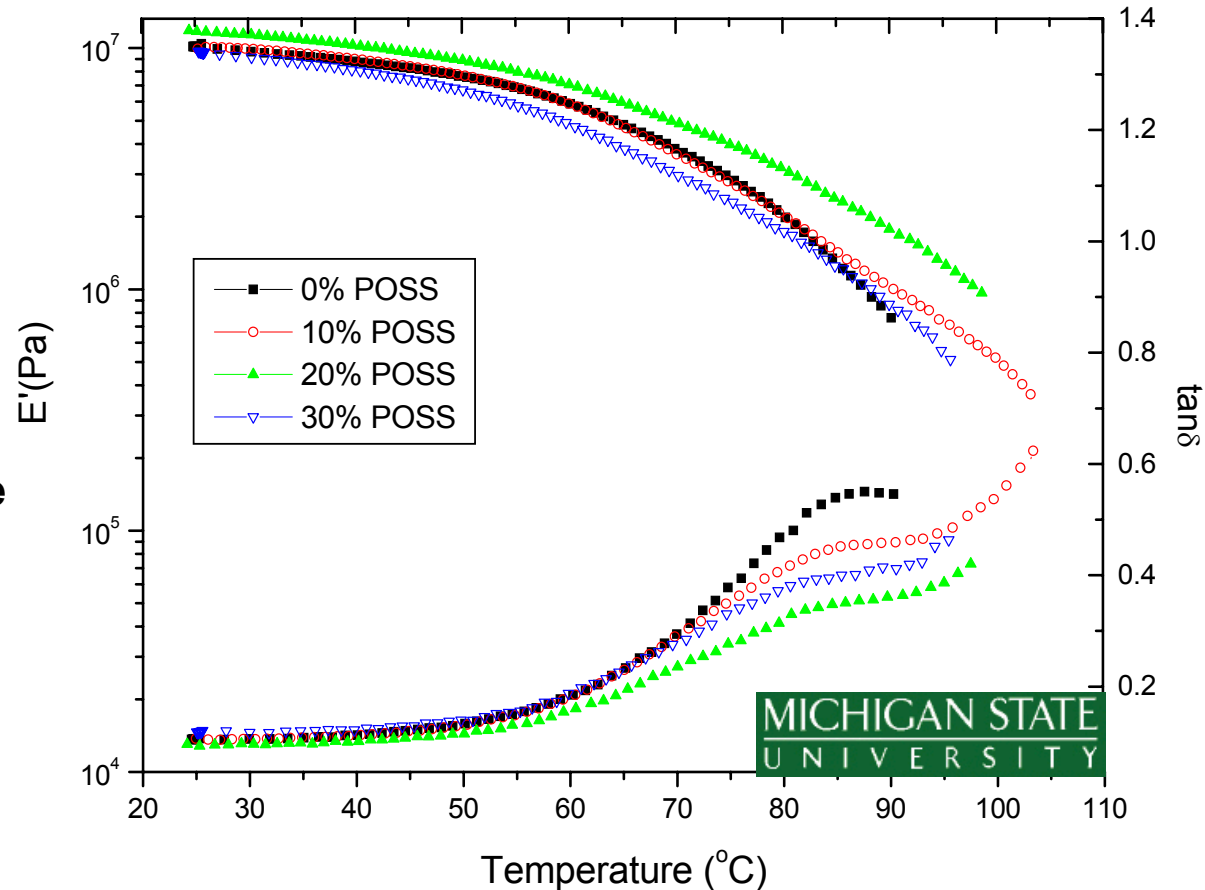


POSS-Kraton Copolymer

POSS styrene-butadiene-styrene (SBS) copolymer



- 20 wt% POSS sample had the best retaining modulus.
- POSS reinforces both styrene & butadiene segments.



- **POSS-SBS copolymers have much better high temperature performance.**



Nanostructured™ POSS Chemicals Physical Form of Products



**Hybrid
Plastics™**



Crystalline Solids

Wide melting range 24°C to 400°C+

Waxes

Liquids & Oils

Wide viscosity range 40cSt. to 400cSt

>120 POSS Monomers, Polymers and Feedstocks Available

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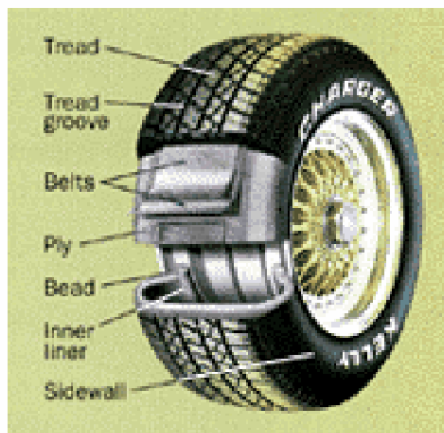
Dave Scheraldi: POSS PET



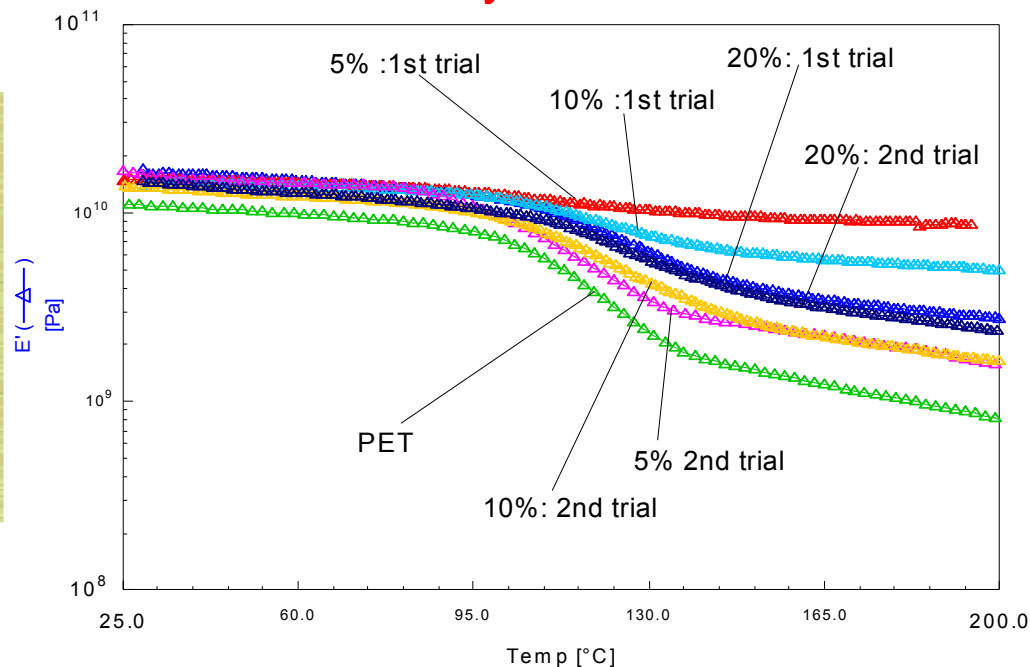
Tires are typically
Reinforced with PET
Fabrics

PET Tg
polymer 78° C
HMLS yarn ~ 110° C

Internal Tire Temperature
~ 120° C



TrisilanolisooctylPOSS PET Blend



Scheraldi (Case Western) and KOSA investigating processing parameters for POSS blended with PET tire cord

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POSS Conference 2002



Masanori Ikeda: Flame resistant POSS PPE



Asahi-KASEI Corporation: Hybrid Plastics Asian Distributor

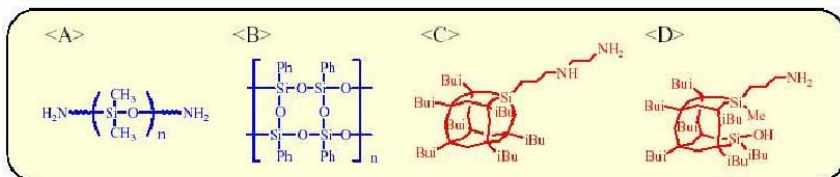
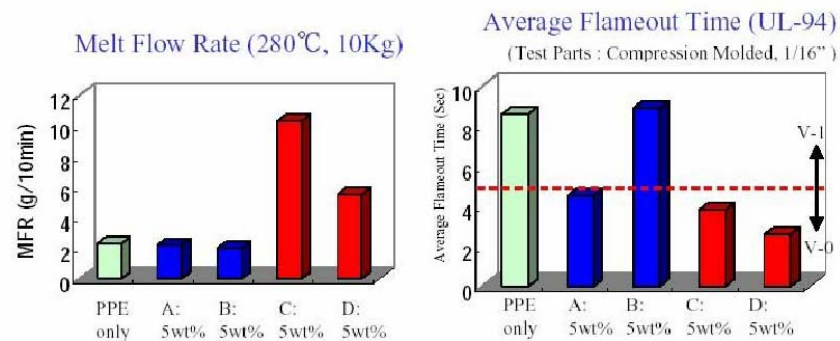


Figure 8. Effects of Additives on MFR and Anti-Flammability

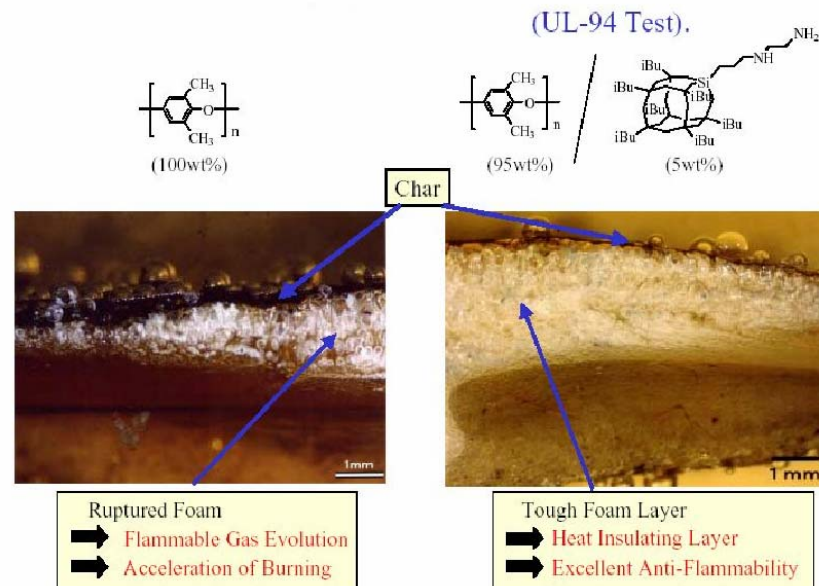


Figure 10. Cross Section Photograph of Burned Test Piece

Isobutyl POSS cage in PPE gives:

- superior flame retardance
- imparts superb processability
- excellent HDT is maintained

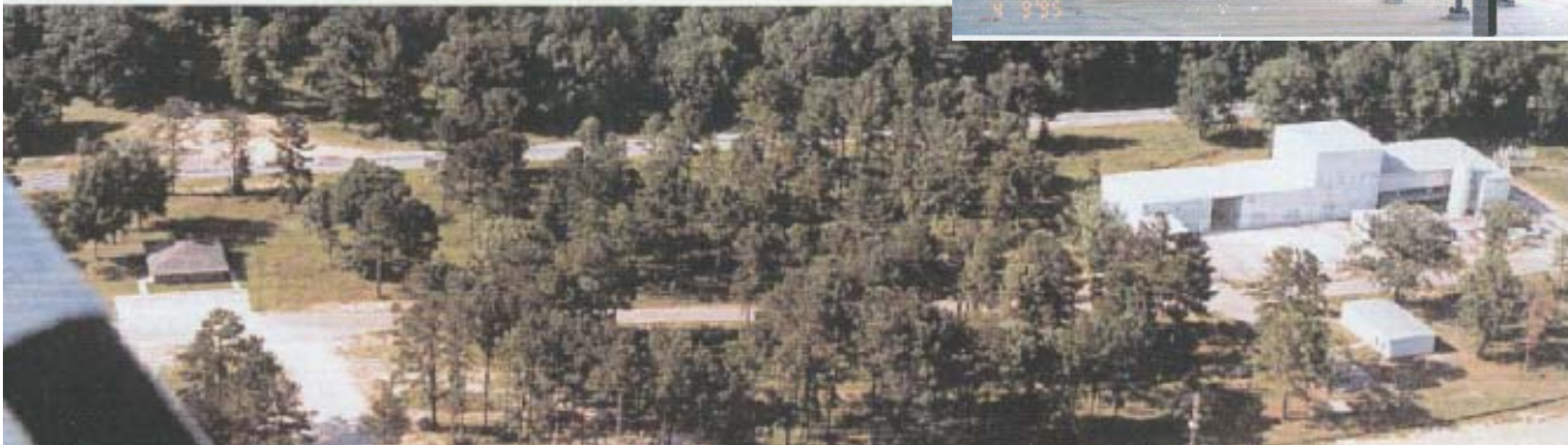
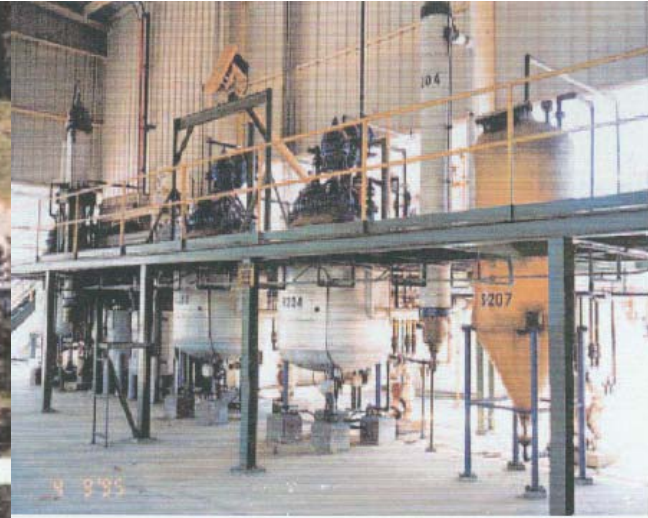
DISTRIBUTION A. Approved for public release; distribution unlimited.

POSS Conference 2002



Hybrid Plastics

Tech Transfer Partner (The Nanotech Part)



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Southern Mississippi – Corporate Headquarters and Production
Southern California – Laboratory and Chemistry Research
USM “Southern Miss” Lab – Technical Support & Polymer Formulation



Hybrid Plastics: 4'x8' Panel



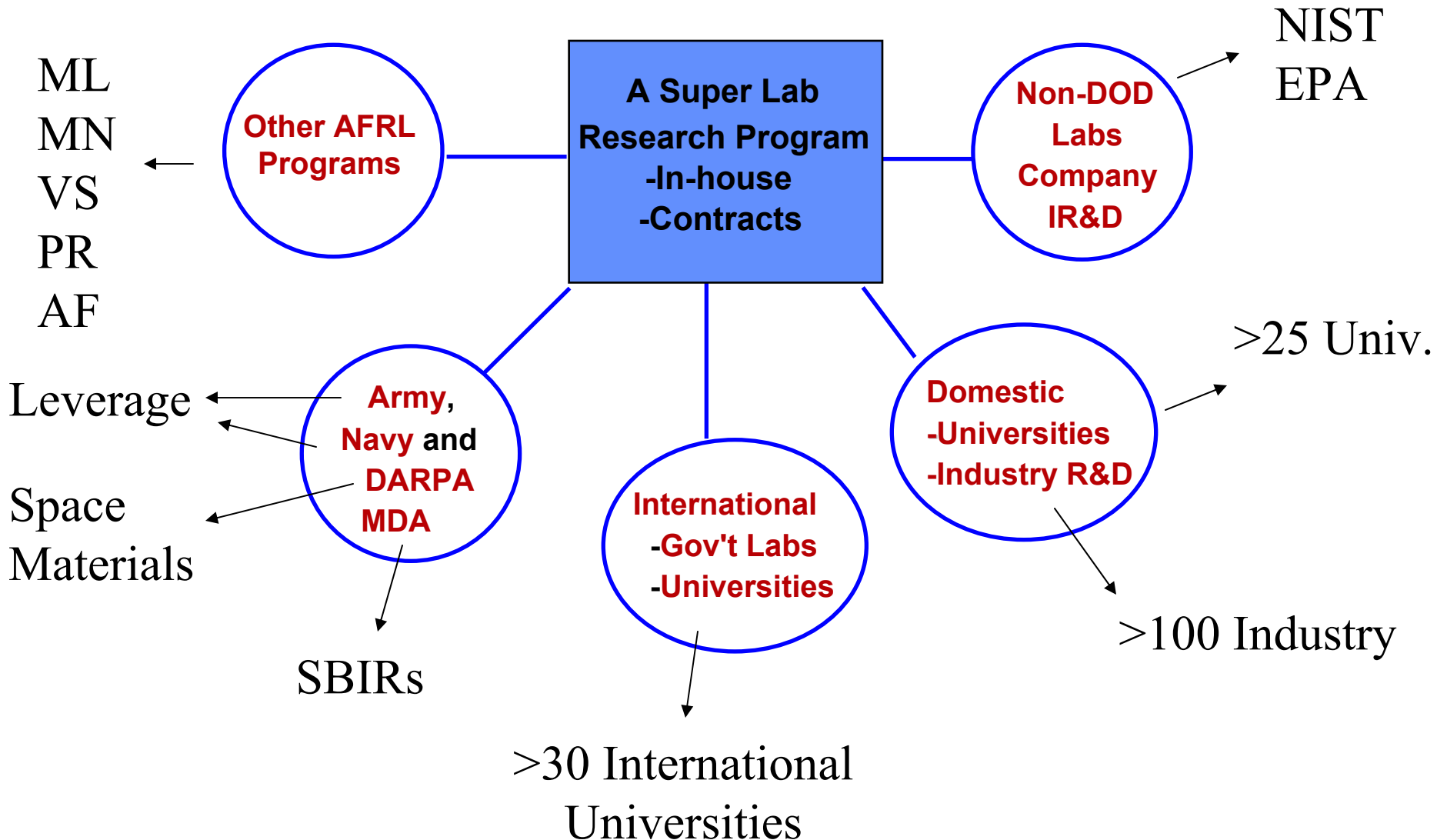
VARTM of 4'x8' panel



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A Super Lab Created from the Ground Up (AFRL Edwards)



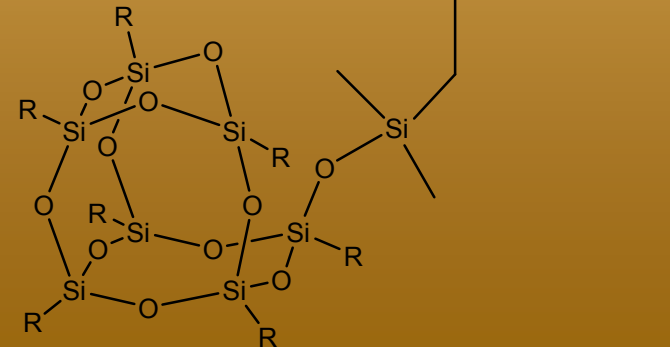
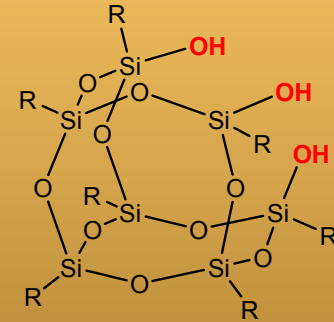
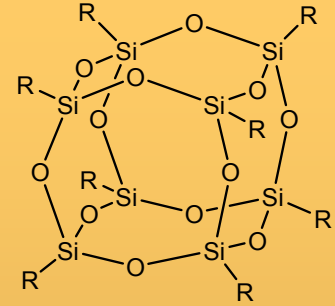


POSS: Where Are We Now (2004)

1996 data in red



- **Cost:** \$20-\$5000/lb (**\$5000-\$10,000/lb**)
- **Volume:** Multi-ton (**~20lb/yr**)
- **Production time:** min 1 hour (**11 days**),
max 14 days (**6 months**)
- **Versatility:** >120 POSS (**36 POSS**)
monomers, feedstocks, polymers
- **Many successful POSS blends**
- **Commercialized by Hybrid Plastics**
www.hybridplastics.com





Why Use POSS?

- **Multifunctionality – including no negative effects on processing (or can even get improvements)**
- **Properties previously not attainable (extended temp range, flame retardancy)**
- **Turnkey Utility**
- **The ultimate control of molecular architect**