“Hybrid POSS-Polymer Technology for Rocket & Space Applications”

Nanostructured™ Chemicals Workshop
September 7th, 1999

Dr. Shawn H. Phillips
AFRL/PRSM - Polymer Working Group
Propulsion Sciences Division
Edwards Air Force Research Lab
MISSION STATEMENT

Create and Transition Propulsion and Power Technology for Military Dominance of Air and Space

Air Force Research Laboratory
Edwards AFB / Propulsion Directorate

OTV
IPD
CARBON / CARBON
HEDM
ESEX
OTV
ESEX
HEDM
Dr. Tim Haddad & Brian Moore: Basic Research - POSS size and R group effects
Applications - Jet Canopies, Insulation, Space

Dr. Rusty Blanski & Justin Leland: Basic Research - POSS blends and additives
Propulsion Applications - Lubes, Capacitors

Dr. Shawn Phillips & Rebecca Marshman: Basic Research - High temp. polymers, resin coatings
Applications - LRE ducting tubing/Insulation

Capt Steve Svejda, Ph.D.: Basic Research - High temp. polymers
Applications - Case & Motor Insulation

Pat Ruth: Basic Research - NWV polymer processing, blending
Applications - Capacitors, Insulation

Dr. Brent Viers: Basic Research - Surface Science & Mechanical Properties
Applications - Coatings

Lt. Rene Gonzalez: Basic Research - AO resistance, surface degradation

Capabilities: Monomer/Polymer Synthesis, Polymer Characterization/Processing,
Applications R&D, Full-Analytical Facilities
POSS = Polyhedral Oligomeric Silsesquioxane

Traditional silsesquioxane chemistry focused on “T-Resins”

The maximization of property enhancements in polymers results from interaction at the nano-level (increased surface area)
Management Philosophy

Polymer Working Group

AFRL/MLBP

Industry

JPL/NASA

Industry

Academic

AFRL/MLBP

Industry

NIST

Aerospace

Hybrid Plastics Technology Transfer

Basic
Management Philosophy

Polymer Working Group

Basic R&D  Processing  Applications R&D
In-House R&D

Polymer Working Group

Basic R&D → Processing → Applications R&D

POSS-Monomers
Existing POSS-Polymers
New POSS-Polymers
POSS-Polymers for Space
Surface Science
Property Enhancements via POSS

Observed in POSS-Copolymers and Blends

- increased $T_g$
- increased $T_{dec}$
- enhanced blend miscibility
- reduced heat evolution
- extended temperature range
- oxidation resistance
- reduced flammability
- increased oxygen permeability
- altered mechanicals
- lower density
- lower thermal conductivity
- reduced viscosity
- disposal as silica
- thermoplastic or curable
- Beat Competitors’ Patents!
New POSS Monomers

Goal 1: Develop lower-cost, more-soluble POSS Monomers

Goal 2: Target 2-3 new monomers for specific polymer systems

Goal 3: Size/Shape/Geometries for structure/property studies

Modeling POSS Formation - Prof. Mark Gordon
Existing POSS-Polymers

POSS-Norbornyls: Increased Tg by 25 C, Decreased heat evolution by 23%, low and high temperature increased tensile storage moduli

POSS-PDMS: Increase Tg over 150 C, oxidation and VUV resistance

POSS-Polyurethanes: 10x increase in modulus, 3x increase in Shore A hardness, 100 C increase in decomposition temperature

Can anyone fully characterize every possible POSS-polymer?

Goal: Be able to predict/control the physical and mechanical Property enhancements from POSS incorporation.

Technical Issues:
- Are there enough varieties of monomers available for such a study?
- Can Modeling/simulation aide in this effort?
- Is there enough financial resources for such an effort?
New POSS-Polymers

Goal: Determine if POSS incorporation into high-performance Polymers will improve SOTA systems.

Have Targeted Four Polymer Systems:
POSS-Polyimides
POSS-Epoxies
POSS-Polyphenylenes
(POSS-Polycarbonates)

R = Styrenyl
Objectives

• Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x

• Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

Goal: Develop Multi-Functional, Space-Survivable Materials

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation Energy (eV)</th>
<th>λ (nm)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C₆H₄-C(=O)-</td>
<td>3.9</td>
<td>320</td>
<td>Kapton®</td>
</tr>
<tr>
<td>C-N</td>
<td>3.2</td>
<td>390</td>
<td>Kapton®</td>
</tr>
<tr>
<td>CF₃-CF₃</td>
<td>4.3</td>
<td>290</td>
<td>FEP Teflon®</td>
</tr>
<tr>
<td>CF₂-F</td>
<td>5.5</td>
<td>230</td>
<td>FEP Teflon®</td>
</tr>
<tr>
<td>Si-O</td>
<td>8.3</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>
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</tbody>
</table>
In-House R&D

Polymer Working Group

Basic R&D → Processing → Applications R&D

POSS-Monomers
Existing POSS-Polymers
New POSS-Polymers
POSS-Polymers for Space
Surface Science

POSS-Copolymers/Grafts
POSS-Blends
Processing Understanding/Optimization
In-House Facilities/Equipment

Twin screw micro-compounder of 5g capacity

Small scale micro-injection molding machine for <4g of polymer
In-House Facilities/Equipment

50cc High-Temperature Brabender
1 ton pneumatic press
24 ton hydraulic press
Single-screw extruder
Pelletizer
Programmable Vacuum Oven
Tensile testers (plastics to metals)
Film extruder/rollers
DMTA, Rheometer (both < 1 yr. old), modulated-DSC, TGA-FTIR,
300 & 400 MHz NMR, HPLC’s, GPC, GC’s, GC-MS
Scratch Tester, Abrasion Tester, Durometer
Spin Coater
POSS-Copolymers/Grafts

Goal: Demonstrate the ease of processing of POSS-polymers
And determine how processing affects polymer properties.

Technical Issues:
• Can traditional processing equipment be utilized for such polymers?

• Agglomeration/aggregation of POSS units over time

• Decomposition of polymer due to heightened processing temperatures
POSS Blends

Goal: Develop POSS monomers that are nanodispersed throughout the polymer matrix.

Twin Screw Extruder mixing of PP and Me₈T₈

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Load (N)</th>
<th>Torque (N·M)</th>
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</thead>
<tbody>
<tr>
<td>PP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>3600</td>
<td>4.65</td>
</tr>
<tr>
<td>1</td>
<td>3150</td>
<td>4.35</td>
</tr>
<tr>
<td>2</td>
<td>2950</td>
<td>4.10</td>
</tr>
<tr>
<td>3</td>
<td>2800</td>
<td>3.95</td>
</tr>
<tr>
<td>PP/Me₈T₈</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0 (10 wt. %)</td>
<td>3300</td>
<td>4.35</td>
</tr>
<tr>
<td>1</td>
<td>2950</td>
<td>4.05</td>
</tr>
<tr>
<td>2</td>
<td>2800</td>
<td>3.95</td>
</tr>
<tr>
<td>3</td>
<td>2800</td>
<td>3.90</td>
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</table>
In-House R&D

Polymer Working Group

Basic R&D → Processing → Applications R&D

- POSS-Monomers
- Existing POSS-Polymers
- New POSS-Polymers
- POSS-Polymers for Space Surface Science

- POSS-Copolymers/Grafts
- POSS-Blends
- Processing Understanding/Optimization

- SRM Insulation
- LRE Ducting
- LRE Casing
- High Temperature Lubricants
- Jet Canopies
- Space-Survivable Polymers
- Radomes/Capacitors
- Creep-Resistant Seals
IHPRPT
SOLID ROCKET MOTOR
BOOST/ORBIT TRANSFER & TACTICAL MATERIALS - Edwards AFRL/PRSM

July 2000

- Integrated High-Payoff Rocket Propulsion Technology
- IHRPRPT Material Working Group
- Solid Rocket Motors
  Dr. Shawn Phillips
  Edwards AFRL/PRSM
# IHPRPT Goals (SRM B&OT)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Cost</th>
<th>ISP (SEC)</th>
<th>Mass Fraction</th>
</tr>
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<tbody>
<tr>
<td>Baseline</td>
<td>$5M</td>
<td>248.3</td>
<td>0.927 (Wp=107,754) (Wt=116,240)</td>
</tr>
<tr>
<td>Phase I</td>
<td>15%</td>
<td>$750K</td>
<td>0.938</td>
</tr>
<tr>
<td>Phase II</td>
<td>25%</td>
<td>$1,250K</td>
<td>0.945</td>
</tr>
<tr>
<td>Phase III</td>
<td>35%</td>
<td>$1,750K</td>
<td>0.953</td>
</tr>
</tbody>
</table>

**Payoffs (Athena II) Phase III 2010**
- Weight Reduction: 35%
- Payload Increase: 93%
- Cost Reduction: $2,047/lb (was $5,000/lb)
CASTOR 120® COST

- MOTOR - $5 million (FY94 dollars)
- INSULATED CASE - » 27%
- NOZZLE - » 20%
- THRUST VECTOR SYSTEM - » 9%
- PROPELLANT - » 31%
- MISCELLANEOUS - » 13%
CASTOR 120® MASS PROPERTIES (lbs)

- MOTOR - 116,240
- INSULATED CASE - 4,858
- NOZZLE - 1,985
- THRUST VECTOR SYSTEM - 600
- PROPELLANT - 107,754
- MISC. - 1,043
• CASTOR 120® MOTOR
  8 GRAPHITE EPOXY CASE (ERL 1908 RESIN/T1000 FIBER)
  8 FILLED NBR/EPDM INTERNAL INSULATION
  8 HTPB PROPELLANT WITH RADIAL SLOT GRAIN DESIGN
  8 COLD GAS BLOWDOWN, HYDRAULIC, TVC
  8 SUBMERGED NOZZLE
<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>MATERIAL/PROCESS CANDIDATES</th>
</tr>
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<tbody>
<tr>
<td>NOZZLE</td>
<td></td>
</tr>
<tr>
<td>- Low-Eroding Throats</td>
<td>(A) Free-standing Refractory Liner*</td>
</tr>
<tr>
<td></td>
<td>- Tungsten</td>
</tr>
<tr>
<td></td>
<td>- HfC, HfN</td>
</tr>
<tr>
<td></td>
<td>- Tungsten/Rhenium</td>
</tr>
<tr>
<td></td>
<td>(B) Low Cost Rapid Densification of Carbon-Carbon*</td>
</tr>
<tr>
<td>INSULATION</td>
<td></td>
</tr>
<tr>
<td>- Sprayable Technologies</td>
<td>(A) Sprayable Insulation*</td>
</tr>
<tr>
<td></td>
<td>(B) Ceramic-Forming Polymer Precursor*</td>
</tr>
<tr>
<td></td>
<td>(C) Low Density Ablation Resistant Polymers*</td>
</tr>
<tr>
<td>CASE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(A) Low Cost Mandrels</td>
</tr>
<tr>
<td></td>
<td>(B) Composite Integrity Program*</td>
</tr>
<tr>
<td>NOZZLE</td>
<td></td>
</tr>
<tr>
<td>- Low Cost Components</td>
<td>(A) Net Molded Structural Components</td>
</tr>
<tr>
<td></td>
<td>- MXC-150</td>
</tr>
<tr>
<td></td>
<td>- Lytex Compounds</td>
</tr>
<tr>
<td></td>
<td>(B) Commercial Ablative Materials*</td>
</tr>
<tr>
<td>CASE</td>
<td>(A) Enhanced High Temperature Resins*</td>
</tr>
<tr>
<td></td>
<td>(B) Integrated Case/Insulation*</td>
</tr>
<tr>
<td>NOZZLE</td>
<td>(A) Tape Wrap Process for Low Density Exit Cone Liner</td>
</tr>
<tr>
<td>- Exit Cone Ablative</td>
<td>(B) Molded Exit Cone Liner</td>
</tr>
<tr>
<td></td>
<td>(C) NARC Rayon Based Carbon Cloth Phenolic Replacement Material</td>
</tr>
</tbody>
</table>

*Programs that will apply to Tactical, in addition to B/OT*
Goal: 50% Lower Erosion of Insulation (44% weight reduction, 7.4% booster payload increase) – Phase III IHPRP

Objective: Development of Ceramic Forming Polymer

Technical Issues:
• Development/modification of insulation chemistry to incorporate pre-ceramic polymers

• Char formation/erosion under different operational conditions/prediction capabilities

• Achieving good adhesion and physical properties at the insulation/case interface
POSS for Flame Retardant Materials

**Traditional Polymer**

Heat \(\rightarrow\) polymer melt \(\rightarrow\) burn \(\rightarrow\) carbon char

**POSS Polymer**

Heat \(\rightarrow\) increased melt temp \(\rightarrow\) protective ceramic SiO\(_2\) layer
Solid Rocket Motors Insulation

A) Insulation containing POSS monomers
B) Convergent Cone
C) Convergent Cone + Insulation
Convergent Cone SRM Insulation Tests

<table>
<thead>
<tr>
<th>Propellant</th>
<th>XXXX</th>
<th>XXXXX</th>
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<tbody>
<tr>
<td>Ave Pressure</td>
<td>1340 psi</td>
<td>1310 psi</td>
</tr>
<tr>
<td>Duration</td>
<td>6.5 sec</td>
<td>6.3 sec</td>
</tr>
<tr>
<td>Insulation /Filler</td>
<td>POSS-Allyl (25%)</td>
<td>POSS-Octavinyl (25%)</td>
</tr>
<tr>
<td>Stn No.</td>
<td>e</td>
<td>Ma No.</td>
</tr>
<tr>
<td>0</td>
<td>3.5</td>
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<td>4.0</td>
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<td>9.8</td>
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<td>6</td>
<td>33</td>
<td>.02</td>
</tr>
<tr>
<td>7</td>
<td>47</td>
<td>.01</td>
</tr>
</tbody>
</table>

Negative numbers represent the formation of a structural char
In-House SRM Insulation Testing

Objective: Low Cost/Low Volume Screening of New Materials for Rocket Motor Insulation

Capabilities:
• Test facilities developed at Edwards AFRL (2 ¾” Pi-K Motor)

• Volume of material reduced from 5 Kg to 75 g

• Cost (synthesis, part fabrication, ablation test, analysis) reduced to 1K!!

• Rapid testing of 5-6 samples per day.
Goal: Replace low-pressure metal ducting with plastics (80% duct weight decrease, 15% upper stage thrust-to-weight increase)

Can plastics replace metal/aluminum parts of LRE’s?

- every 10 lbs. of metal replaced would result in a $40,000-$80,000 weight savings
- significant cost/time savings due to processing
- 2-4x increase in strength and stiffness over other advanced thermoplastics (PC, PPS, TPI, PEEK, PEI).

- Better reported hoop strength and **predicted** burst pressures than any other molded structure.

- One of the first rigid-rod polymers that isn’t intractable or insoluble.

- Demonstrated cryo and permeability resistant properties.

- POSS incorporation improves use temperature
Nanomaterials for Case Insulation

Goal: Replace expensive, heavy fibers in composites with cheap, light natural fibers

Accomplishments:

• Synthetic and curing methodology for reproducible POSS resin to be used as coating
• Developed patented breakthrough process for thin-film coatings of natural fibers
• Initial crude flammability tests showing significant flame retardancy and ability to self-extinguish
Nanomaterials for Case Insulation

Uncoated and coated riton fibers

FY01 Goals:

- Scale-up of POSS resin and patented coating process
  - >100 g fiber at a time, then 500 g at a time
- Incorporate (modified) coated fibers into epoxy resin
- Determine physical and mechanical properties of fibers and composite material
High Temp Lubricants

Goal: Replace ester-based lubricant with modified POSS lubricant.

Objectives:
- Fluid with working temperature range of -40° to 600° F (IHPTET)
- Ester lubricants limited to 400 °F: POSS monomer $T_{\text{dec}} = 590$ °F
- 600 °F lube = 1.5-1.6x T/W improvement
POSS Materials for Aerospace
High Temperature & Lightweight

Jet Canopies

POSS-based Transparent Materials

• Mach 2.x speeds limited by plastic canopy (need increased HDT)

• Target Engagement Times can be reduced by increasing flight speed

POSS-MMA increases use temp. by 150 °C
POSS-polycarbonate currently being prepared
Combining with nanocellular foam process

WMR’s Current High Performance Foam

Cell Sizes can be Tailored From Nano To Several mm
Monomers & Polymers Research

- Fundamental studies ---> polymer property understanding (POSS structure, POSS miscibility, polymer type).
- Polymer Processing ---> reactive processing, polymer blends, composites
- AFOSR/Star Team, R&D 100 Award, FLC Technology Transfer Award

Applications Research

- Lightweight, low-cost, high-temperature, high-strength
- Utilize economical small-scale SRM insulation screening for large scale testing
- Dual-Use = Sustainability