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

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MEMORANDUM FOR PRS (In-House Contractor Publication)

FROM: PROI (STINFO) 08 May 2002

Tim Haddad (ERC) and Brent Viers (PRSM), “Organic Polymers Modified with Inorganic Polyhedra”

Canadian Society for Chemistry
(2-5 June 2002, Vancouver, Canada) (Deadline: 31 May 2002)
ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA.

Timothy S. Haddad and Brent D. Viers
ERC Inc., Air Force Research Lab,
10 E Saturn Boulevard
Edwards Air Force Base, CA 93524

Nanostructured composites of thermoplastics and inorganic clusters have been developed by incorporating polyhedral oligomeric silsesquioxane (POSS) macromers into organic polymers. These hybrid inorganic/organic thermoplastics based on styrenes, acrylates, imides, norbornenes or siloxanes, are reinforced by covalently linking monodisperse inorganic POSS clusters to the polymer backbone. A typical POSS-macromer, $R_3P(SiO_{1.5})$, is a well-defined octomeric polyhedron containing a single "P" functionality for polymerization and seven "R" groups to solubilize and compatibilize the inorganic filler with the organic matrix. A nanoreinforcement effect from the POSS groups is strongly influenced by the seven "R" groups (cyclopentyl, cyclohexyl, isobutyl or phenyl). Covalently attached POSS groups result in significant change to the observed characteristic relaxation time of the polymer; rheological measurements on molten polymer indicate that interactions between the POSS groups generate a reversible network material with rubbery properties. TEM images show that the inorganic POSS moieties associate to form a nanoscale network within the polymer matrix.

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ORGANIC POLYMERS MODIFIED WITH INORGANIC POLYHEDRA

Tim Haddad and Brent Viers
ERC Inc., Air Force Research Lab
Hybrid plastics can bridge the differences between ceramics and polymers.
Anatomy of a POSS Macromer

Nonreactive organic (R) groups for solubilization and compatibilization.

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

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

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

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

R-Groups
- cyclohexyl
- phenyl
- cyclopentyl
- isobutyl
POSS Silanol Synthesis

\[
\text{SiCl}_3 + \text{H}_2\text{O} / \text{Acetone} \rightarrow \text{R} = \text{Cyclohexyl}
\]

\[
\text{SiCl}_3 + \text{H}_2\text{O} / \text{Acetone} \rightarrow \text{R} = \text{Cyclohexyl, Cyclopentyl, Cycloheptyl}
\]

Feher et al: JACS, 1989, p 1741;
Organometallics, 1991, p 2526
POSS Macromers For Nanocomposites

**R-Groups**
- cyclohexyl
- phenyl
- cyclopentyl
- isobutyl

Halides          Nitriles          Silanes          Styryls
Alcohols         Amines           Silanols         α-olefins
Esters           Isocyanates      Silylchlorides   Acrylics
Bisphenols       Epoxides         Norbornenyls   

POSS-based macromers are now available through either Geleste or Aldrich
POSS technology is commercialized by Hybrid Plastics in Fountain Valley CA
# Why POSS and Why Nano?

<table>
<thead>
<tr>
<th>Field</th>
<th>Property</th>
<th>Critical Length</th>
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<tbody>
<tr>
<td>Electronics</td>
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<tr>
<td>Optical</td>
<td>Quantum Well</td>
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<td>Wave Decay</td>
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<td></td>
<td>Secondary Structure</td>
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<td>Mechanics</td>
<td>Dislocation Interaction</td>
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<td>Entanglement Rad.</td>
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<td>Therm-Mech.</td>
<td>Chain Motion</td>
<td>0.5-50 nm</td>
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<tr>
<td>Nucleation</td>
<td>Defect</td>
<td>0.1-10 nm</td>
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<tr>
<td></td>
<td>Critical Nucleus Size</td>
<td>1-10 nm</td>
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<tr>
<td></td>
<td>Surface Corrugation</td>
<td>1-10 nm</td>
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<tr>
<td>Catalysis</td>
<td>Surface Topology</td>
<td>1-10 nm</td>
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<tr>
<td>Biology</td>
<td>Cell Walls</td>
<td>1-100 nm</td>
</tr>
<tr>
<td>Membranes</td>
<td>Porosity Control</td>
<td>0.1-5 nm</td>
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</tbody>
</table>

- 1 mm: Sewing Needle, Razor Blade Thickness
- 100 µm: Human Hair, Most Cells & Fibers
- 10 µm: Bacteria, Fillers & Polymer Morphology
- 1 µm: Viruses & Nanofillers, POSS® Building Blocks, Macromolecules
- 1.0 nm: Atoms / Small Molecules
- 0.1 nm: Atoms / Small Molecules
- Maximizing property enhancements through changes at the nano level
- Polymer miscibility vs. POSS/POSS interactions
POSS Polymer Incorporation

POSS Bead

POSS Pendent

POSS Crosslinking

POSS Blending

Size & Shape
50 Wt % POSS Blends in 2 Million MW Polystyrene

$\text{Vi}_8\text{T}_8$

$\text{Phenethyl}_8\text{T}_8$

Nanodispersion!!
DMA of 10 Wt % POSS in isotactic Polypropylene
The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.
TMA of Pendent POSS-Siloxanes

![Graph showing dimension change vs. temperature for different values of Z and Y.]

- Z = 2.0
- Z = 1.5
- Z = 1.0
- Z = 0, Y = 9.3
- Z = 0, Y = 0

![Chemical structure of POSS-Siloxanes with labels for Z and Y.]
Hydrosilation to High MW PDMS

Used 5 weight % POSS

There are about 7 POSS-macromers per PDMS chain
Comparison of Three T8-POSS Macromers

PDMS + 5 wt % POSS
Blue = cyclopentyl
Red = cyclohexyl
Purple = isobutyl

Loss Modulus $G''$ (Pa)

Temperature °C

$\tan(\delta)$

Chemical structures:
- Blue: Cyclopentyl
- Red: Cyclohexyl
- Purple: Isobutyl
Comparison of Two POSS Polyhedra

PDMS + 5 wt %
CyclohexylPOSS
Red = T8-POSS
Blue = T7-POSS

Loss Modulus $G''$ (Pa)

Temperature °C
DMA of 30 wt % POSS Polystyrenes

- Comparison of isobutyl, cyclopentyl & cyclohexyl
- Bulk polymerized samples
TMA Plot Comparison For POSS-Styryl and POSS-EthylStyryl Polymers
(R = Cyclohexyl and Cyclopentyl)
Both block and random copolymers were synthesized. The wt. % POSS was varied from 0 to 50 wt. % POSS. An ideal polymerization would yield polymers with 500 monomer units.

0 wt % POSS, 0 mole % POSS: $x = 500$, $y = 0$
10 wt % POSS, 1 mole % POSS: $x = 495$, $y = 5$
50 wt % POSS, 8 mole % POSS: $x = 460$, $y = 40$
Storage Modulus and Loss Tangent

Cyclohexyl Relaxation: 14.7 kcal/mol

Various Wt.% Cyclohexyl POSS/Polynorbornene Random Copolymers
TEM of Random POSS Norbornenes

50CyPOSS/PN

"Coarse" Cylinder Nanostructure (Diameter ~ 12nm)

50CpPOSS/PN

"Fine" Cylinder Nanodstructure (Diameter ~ 6nm)

CyclohexylPOSS-rich domains may entrain more unoriented polynorbornene chains than CyclopentylPOSS-rich domains.
O-Atom Etching Experiment

8.47 x 10^{20} \text{ atoms cm}^{-2}

Kapton 10 wt\% POSS
Average etch depth: 2.2 \mu m

Kapton H Standard
Average etch depth: 25.4 \mu m
Summary

- The successful incorporation of nano-sized inorganic clusters (POSS) into a wide variety of polymers has been demonstrated.

- These POSS clusters have a remarkable effect on the thermal transitions and mechanical properties of the polymers they are copolymerized into.

- The POSS effect on the properties of analogous polymers shows a dependency on the type of alkyl group on the POSS cluster.

- TEM images of randomly copolymerized polymers illustrate this dependency, as the size of the POSS domains are alkyl-group dependent.

- Rheology of high molecular weight PDMS grafted with small amounts of POSS illustrates a dependence on both the POSS-alkyl-group and POSS shape.
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