

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE Technical Paper	3. DATES COVERED (From - To)
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4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER 2303
	5e. TASK NUMBER M1A3
	5f. WORK UNIT NUMBER 346127
	8. PERFORMING ORGANIZATION REPORT

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/PRS 5 Pollux Drive Edwards AFB CA 93524-7048	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

20030127 205

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT A	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Leilani Richardson
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) (661) 275-5015

18. ~~Illegible text~~

2303M1 / 3

MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

31 Oct 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2001-218**
Brent D. Viers, et al., "Basic and Applied Research on Hybrid Organic/Inorganic Materials for
Propulsion and Space"

American Chem Soc Wkshp: Org/Inorg Hybrids
(Napa, CA, 17-20 November 2001) (DEADLINE: 16 Nov 01)

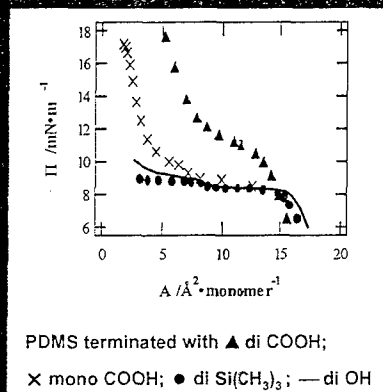
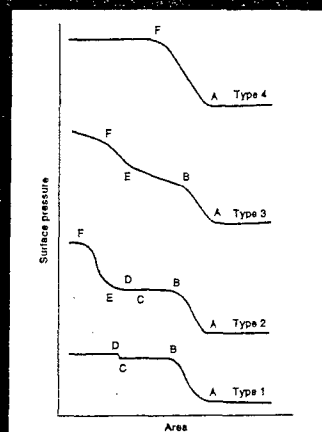
(Statement A)



PDMS Langmuir Blodgett Analysis



- Inherent dimensionality effects



PDMS terminated with ▲ di COOH;
× mono COOH; ● di Si(CH₃)₃; — di OH

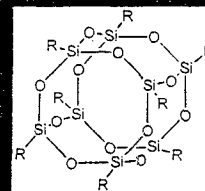
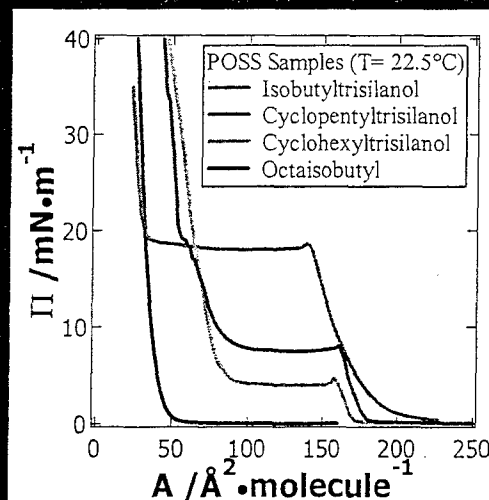
- Highly sensitive to functionality

Lenk, Koberstein, et. Al. *Langmuir*, **10**, 1857, (1994)

13

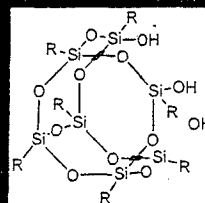


Results – P-A Isotherms of POSS Samples



R₈T₈

Weak Interactions



R₇T₇

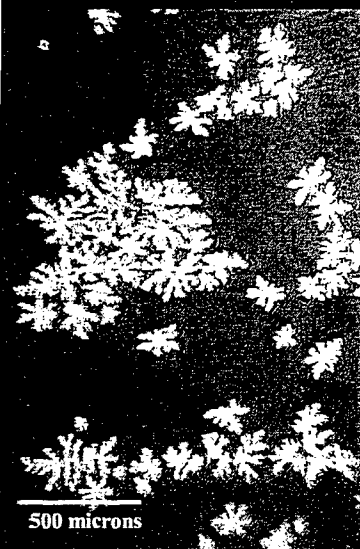
Stronger Interactions



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

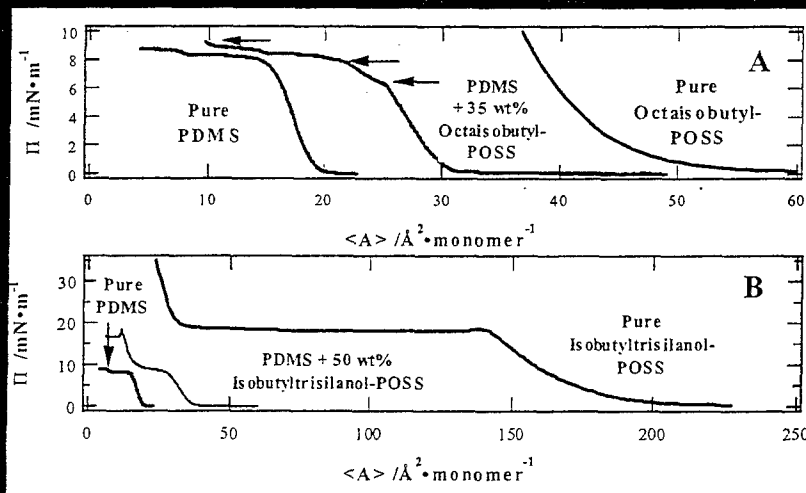
17



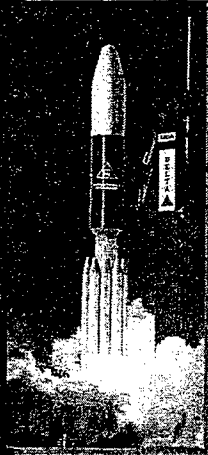
POSS-PDMS Blends



$$\Delta G^{\sigma} = \int_{\Pi}^{\Pi^*} (A_2 - x_1 A_1 - x_2 A_2) d\Pi$$



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Basic and Applied Research on Hybrid Organic/Inorganic Materials for Propulsion and Space

POSS is NOT just the smallest silica

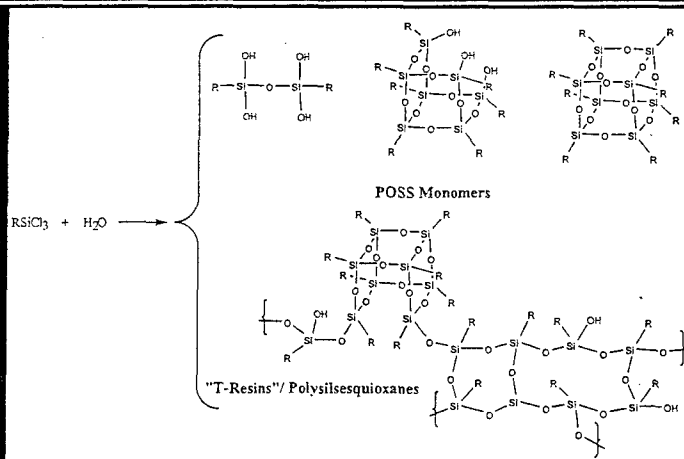
Dr. Brent D. Viers
Propulsion Sciences Division
Edwards Air Force Research Lab

Dr. Shawn H. Phillips, Dr. Timothy S. Haddad, Dr. Rusty Blanski, Maj. Steve Svejda Ph.D.,
Prof. Andre Y. Lee, Justin Leland, Pat Ruth, Brian Moore,
Capt. Rene Gonzalez, Prof. Patrick T. Mather, Prof. Frank Fehrer, Prof. Benjamin S. Hsiao,
Professor Alan Esker, Katie Farmer, Joe Polidan

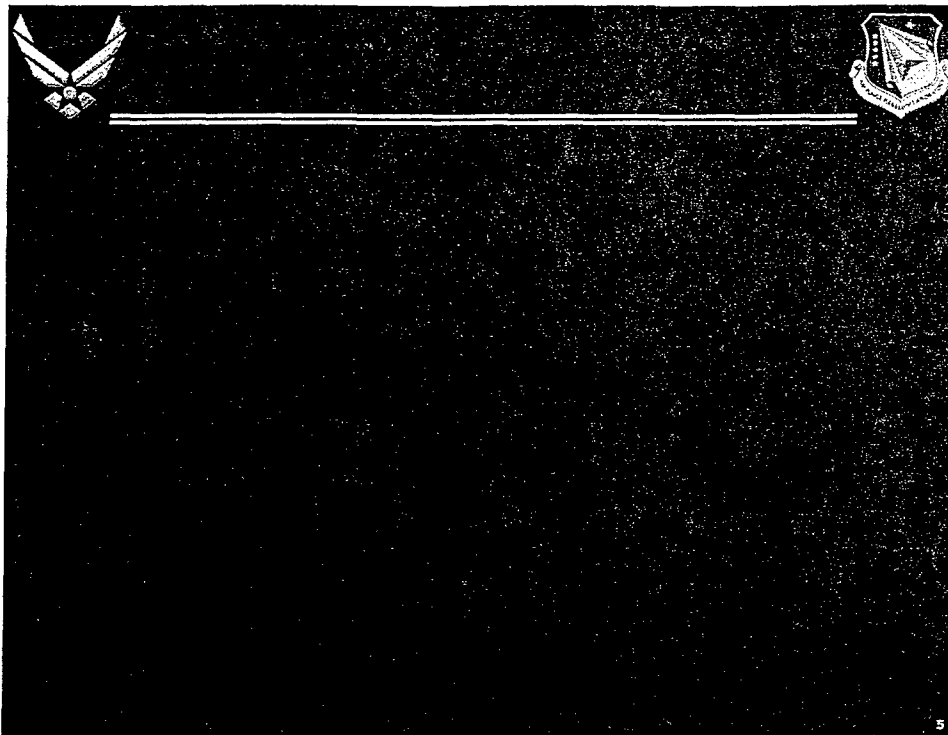
Dr. Joseph D. Lichtenhan, Dr. Joseph A. Schwan



POSS = Polyhedral Oligomeric Silsesquioxane



- Traditional silsesquioxane chemistry focused on "T-Resins"
- The maximization of property enhancements in polymers results from interaction at the μ -level (Edwards AFRL/PRSM $\rightarrow$ POSS monomers)



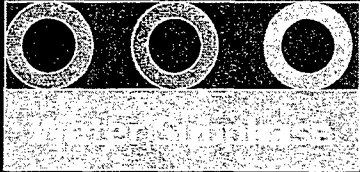
What is
suppose
← to be on
this slide?



Motivation – Filled Nanofluids



Blends Confined at the Air/Water Interface



Small
Sample
Requirements

}

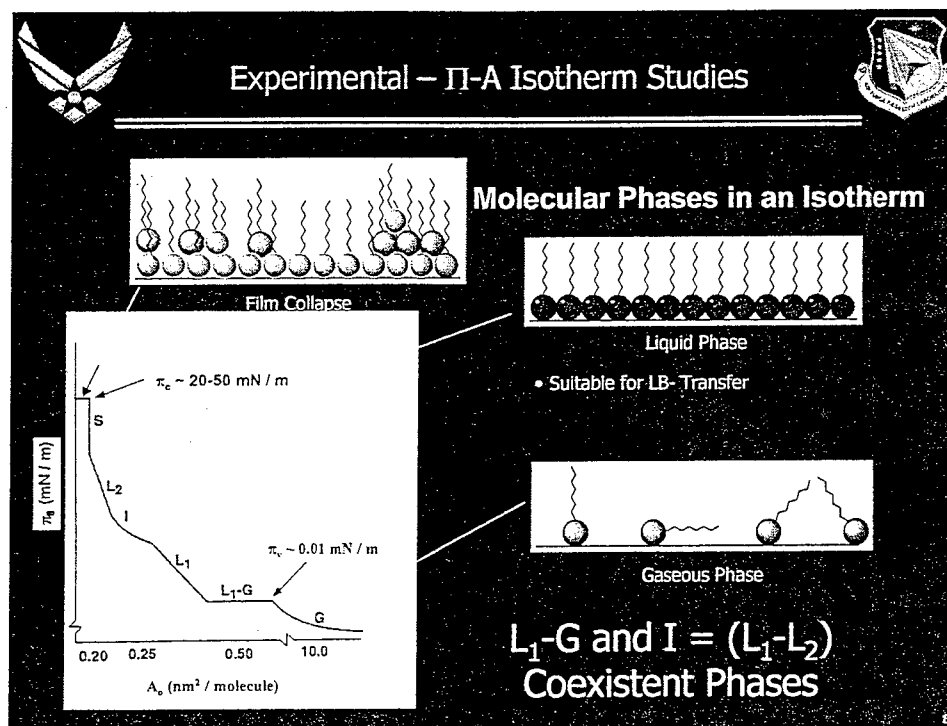
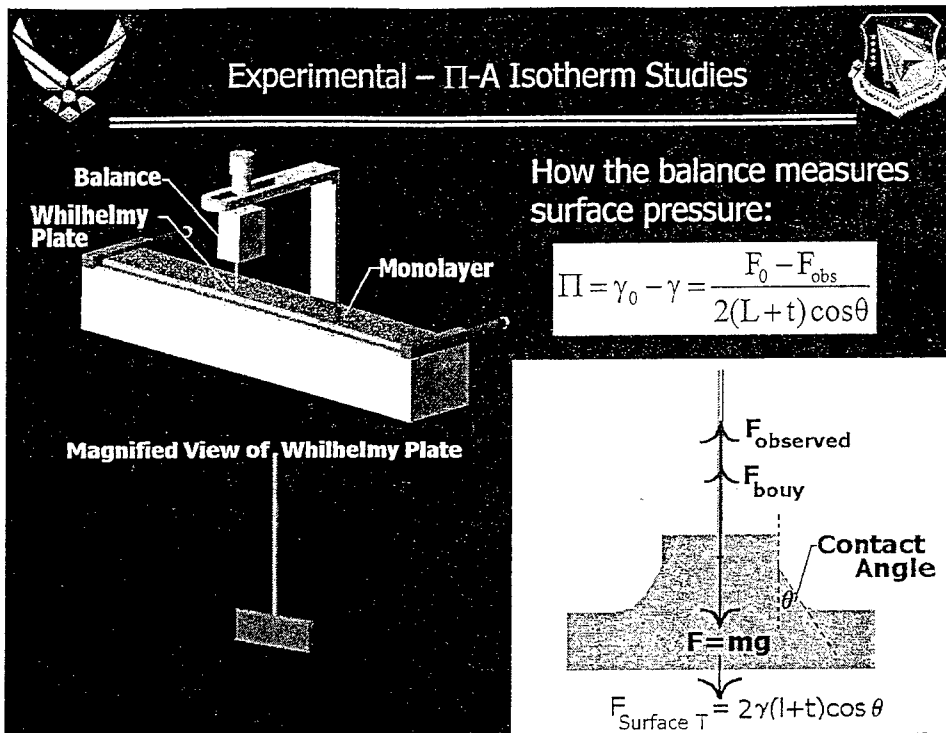
1-2 nm
"2-D"

Polymer,
Interphase,
& Inorganic
Core

Subphase Affinity is an Important Variable

- A/W poor solvent for PDMS & PtBA $\Rightarrow$ solvent exclusion
- A/W good solvent for PVAc $\Rightarrow$ chain swelling
(must consider water's contribution)

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Experimental – Brewster Angle Microscopy



Brewster's Law →

Incident Beam

Reflected Beam

Air

θ_b



Refracted Beam

Halliday, D., Resnick, R., Fundamentals of Physics, p.870 (1988)

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Experimental – Brewster Angle Microscopy



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

Monitor

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



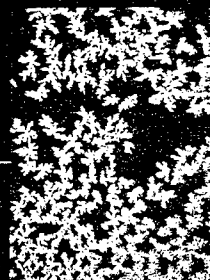
p-Polarizer

Black Plate

10



Monitor



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

p-Polarizer

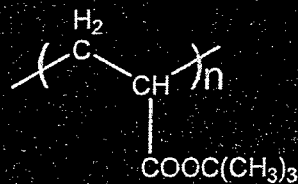
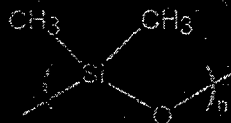
Black Plate

Film

1



Polymers – Structural Models for Adhesive Polymers



PEO3: $M_n \approx 2k$ PVAc: $M_n \approx 1280k$ PtBA: $M_n \approx 25k$

POSS Derivatives

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

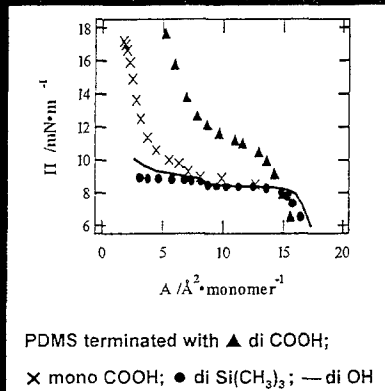
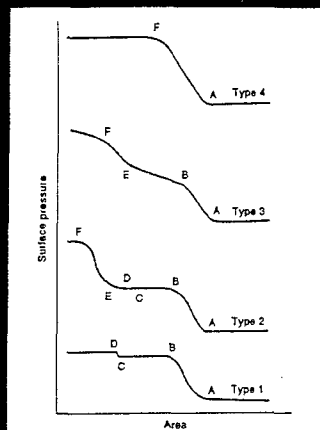
1



PDMS Langmuir Blodgett Analysis



- Inherent dimensionality effects



PDMS terminated with ▲ di COOH;

× mono COOH; ● di Si(CH₃)₃; — di OH

- Highly sensitive to functionality

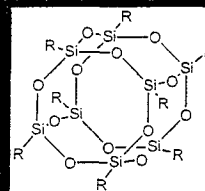
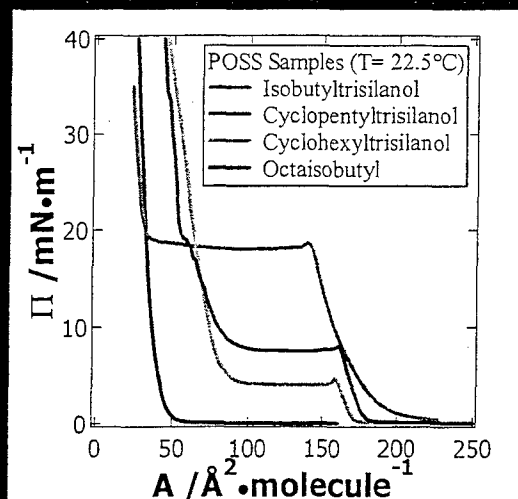
Lenk, Koberstein, et. Al. *Langmuir* 10, 1857

- “al.” should not be capitalized

- Please add a comma after “al.” to separate the journal name

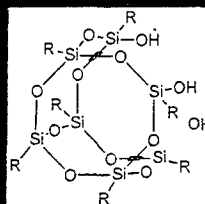


Results – P-A Isotherms of POSS



R₈T₈

Weak Interactions



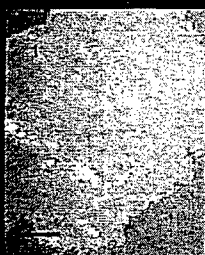
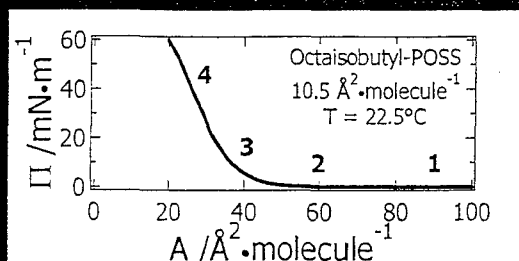
R₇T₇

Stronger Interactions





Results – BAM of Octaisobutyl-POSS

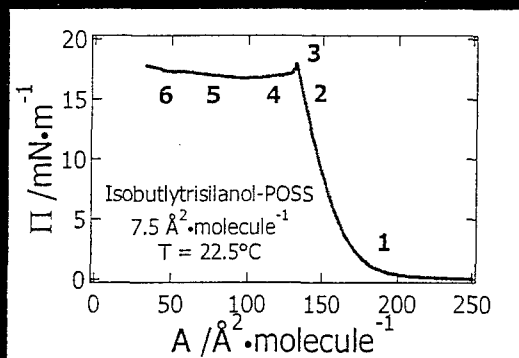


Scales correspond to 500 μm .

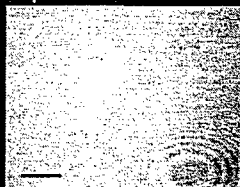
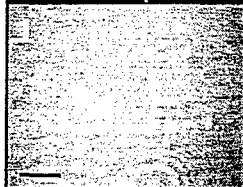
15



Results – BAM of Isobutyltrisilanol-POSS

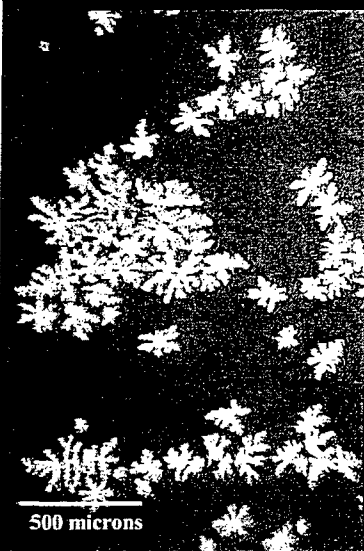


Scales correspond to 500 μm .





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- Non-equilibrium phase transition induced by pressure
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*Timora, K.-I.; et al. *Langmuir* 2001, 17, 4602

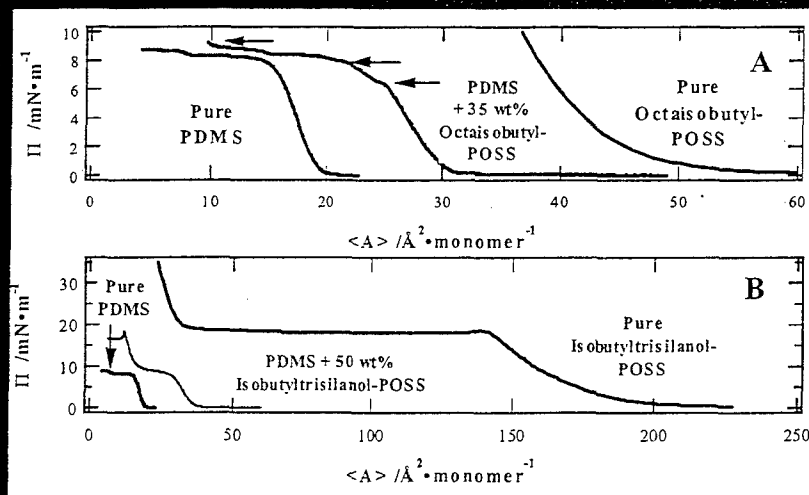
I suggest adding a comma here to separate the authors from the journal name



POSS-

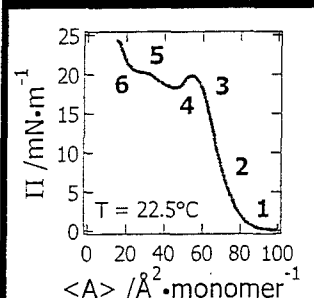


$$\Delta G^{*,\sigma} = \int_{\Pi}^{\Pi'} (A_{12} - x_1 A_1 - x_2 A_2) d\Pi$$





Results – 80 wt% iBu₇T₇/PtBA Blend

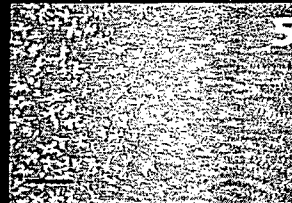
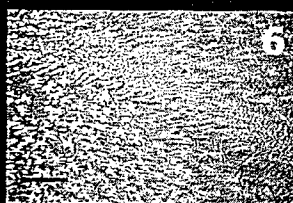
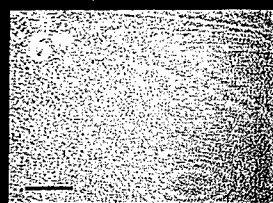


- Ideal uniform blends (0-100 wt% POSS, 1-3), LB < 50 wt% POSS

- Dendritic domains form at 4 (50-100 wt%) POSS, size ↑ as POSS ↑, round domains (POSS < 50 wt%)

- Banded structure $\Rightarrow$ PtBA collapse

- 6* = 60 wt% iBu₇T₇/PtBA blend

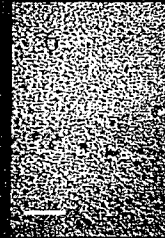
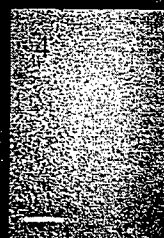
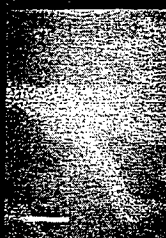
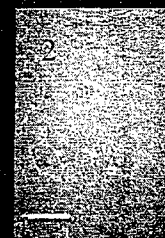
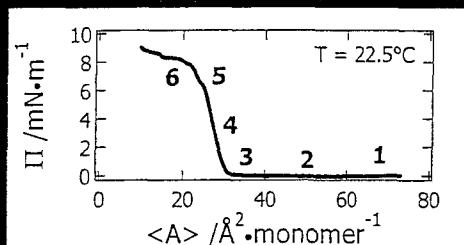


Scales correspond to 500 μm.

19



Results – 35wt% Octaisobutyl-POSS/PDMS

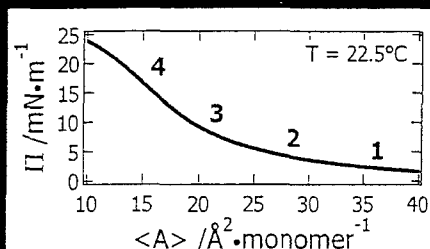


Scales correspond to 500 μm.

20

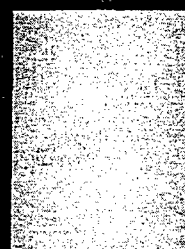
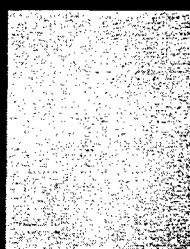
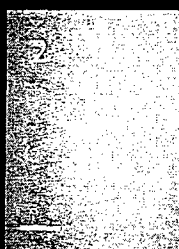
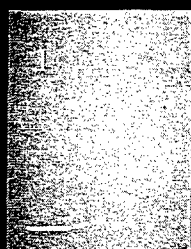


Results – 35wt% Octaisobutyl-POSS/PVAc



•PVAc/ iBu_8T_8 : Non-ideal mixing like PDMS/ iBu_8T_8

•Unlike PDMS system, POSS is almost completely excluded from the interface!!!

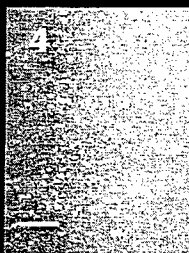
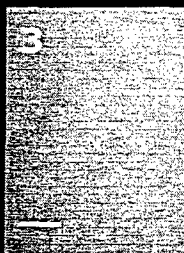
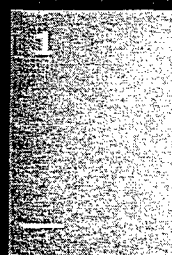
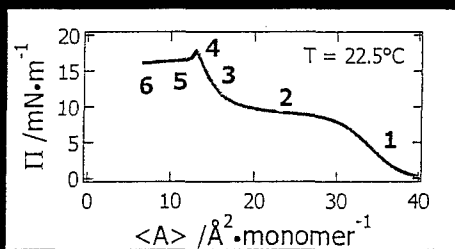


Scales correspond to 500 μm .

21



Results – 50wt% Isobutyltrisilanol-POSS/PDMS

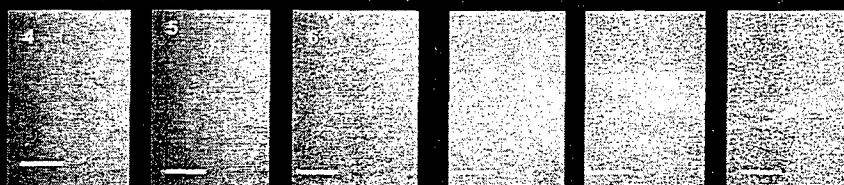
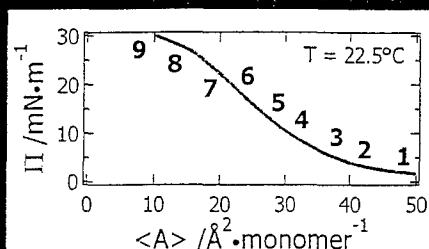


Scales correspond to 500 μm .

22



Results – 50wt% Isobutyltrisilanol-POSS/PVAc



Scales correspond to 500 μm .

23



Summary: POSS Blends



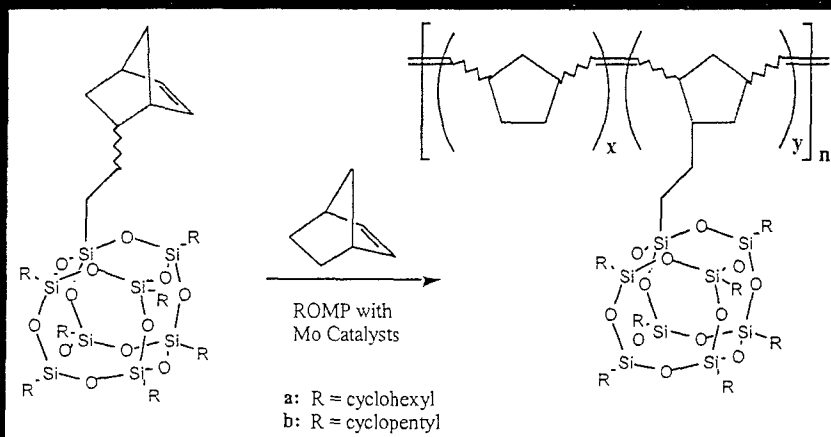
- POSS derivatives exhibit surfactant properties that vary with structure
- Homogeneous films with near ideal mixing for $i\text{Bu}_7\text{T}_7$ +PDMS, PVAc or PtBA ($P < 18 \text{ mN}\cdot\text{m}^{-1}$), but BAM shows samples are dispersions
- For $P > 18 \text{ mN}\cdot\text{m}^{-1}$, non-equilibrium dendritic domains form for pure $i\text{Bu}_7\text{T}_7$ & $i\text{Bu}_7\text{T}_7$ +PtBA (>50wt% POSS), round domains as POSS⁻
- $i\text{Bu}_7\text{T}_7$ +PDMS uniform dispersions (>mm), $i\text{Bu}_7\text{T}_7$ +PVAc immiscible (>mm)



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Model POSS Polymers- POSS Norbornene



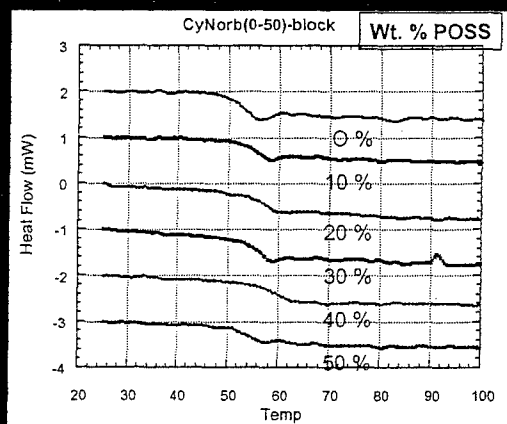
• Both block and random copolymers were synthesized.

• The amount of POSS was varied from 0 to 60 wt. % POSS.

25



POSS-block-norbornene



• Only a single Tg is observed from the norbornene block.

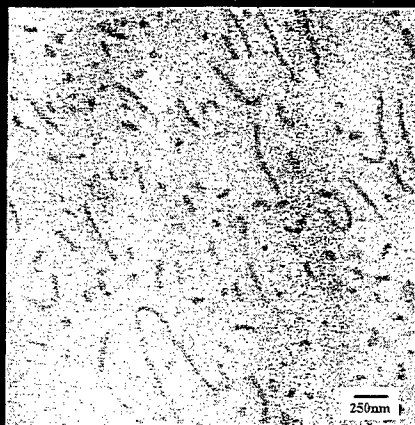
• The POSS norbornene block does not give rise to any transition up to 300 °C

• Some polymers of POSS-styrene and acrylate show the same behavior.

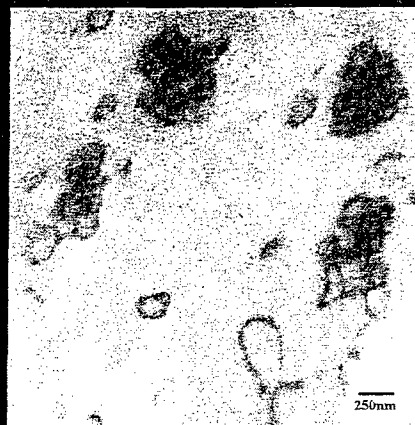
26



Morphology of POSS/PN Diblock Copolymers (TEM)



10wt% of CyPOSS



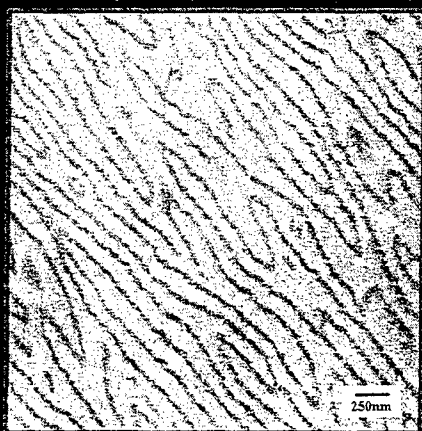
10wt % of CpPOSS

- CyPOSS is more soluble in the polymer matrix than CpPOSS
- Also seen for random polymers, resulting in a greater ΔT_g for CyPOSS

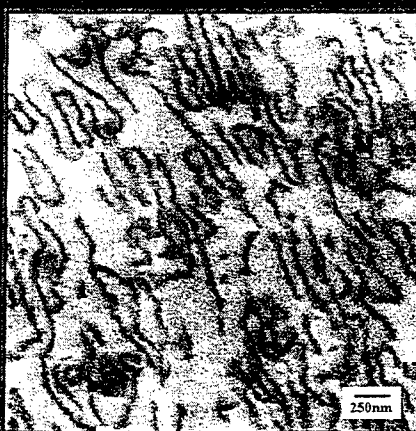
27



Morphology of POSS/PN Diblock Copolymers (TEM)



30wt % of CyPOSS



30wt% of CpPOSS

28



Morphology of POSS/PN Diblock Copolymers (TEM)



30wt % of CyPOSS

29



Morphology of POSS/PN Diblock Copolymers (TEM)

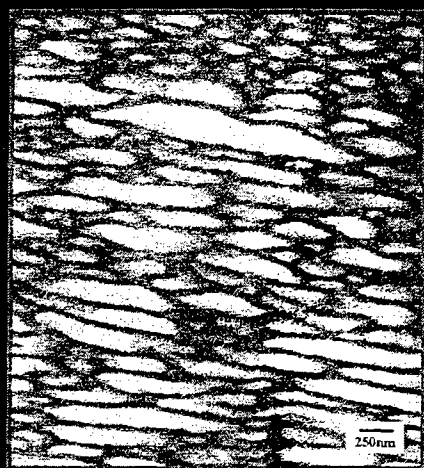


30wt % of CpPOSS

30



Morphology of POSS/PN Diblock Copolymers (TEM)



60wt% of CyPOSS

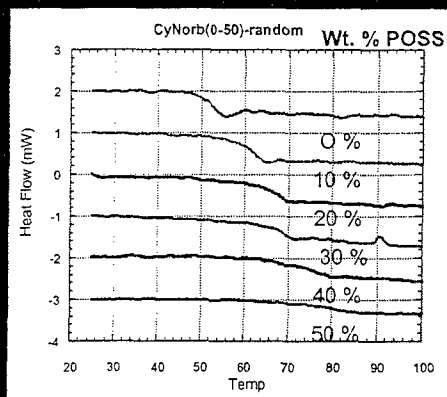


60wt% of CpPOSS

31



DSC Data for Random Copolymers

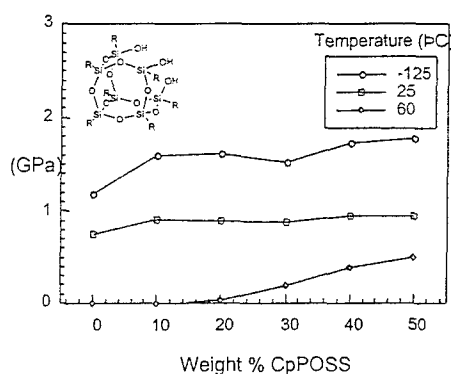
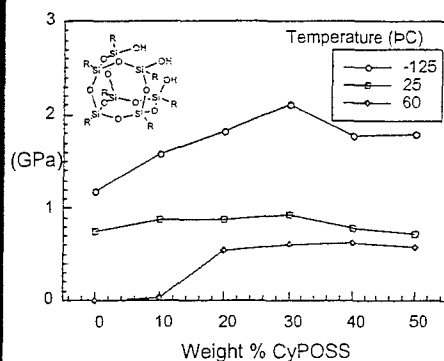


- Random copolymerization: Material with a single Tg is obtained that increases with increasing POSS content
- Effect stronger than that observed for POSS-styryl, but not as large as for POSS-acrylics.

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Tensile Storage Modulus Variation with POSS Content at Three Temperatures



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

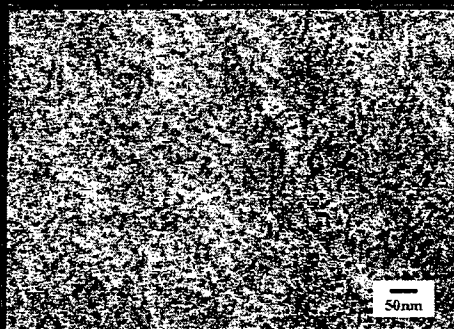
33



TEM of 50CpPOSS/PN & 50CyPOSS/PN

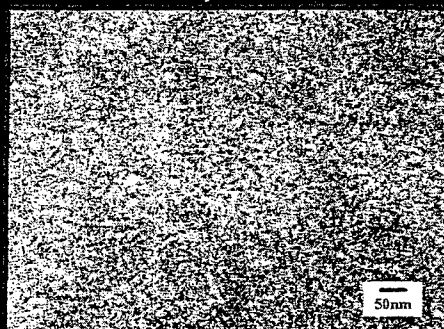


50CyPOSS/PN



"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

50CpPOSS/PN



"Fine" Cylinder Nanodstructure
(Diameter ~ 6nm)

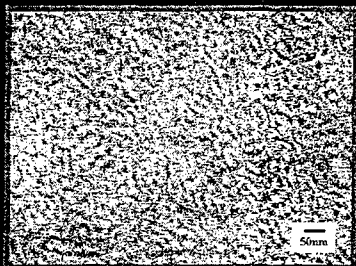
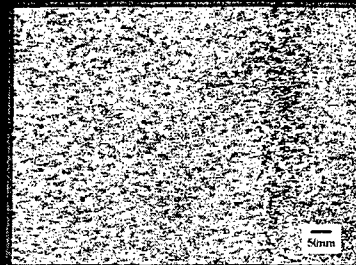
CyPOSS-rich domains may entrain more unoriented PN chains than CpPOSS-rich domains, which could reduce the recoverable strain.

← Nanostructure?

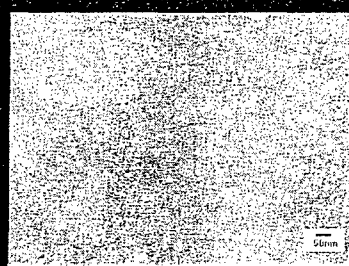
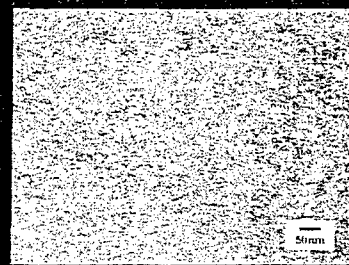
34



TEM of 4X drawn 50CpPOSS/PN & 50CyPOSS/PN



50CyPN



50CpPN

Draw Direction
⊙

Draw Direction
↑

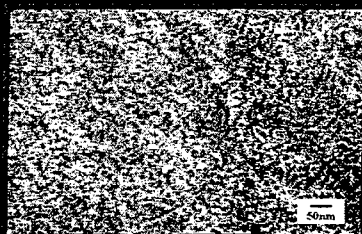
35



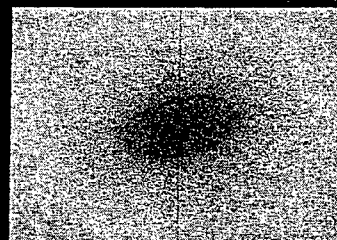
Reanalysis of the *Random* 50 CyPOSS/PN System



50% CyPN



FT reconstruction



- Strong anisotropy and correlations noted-hints at assembled structure

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Summary: POSS copolymers

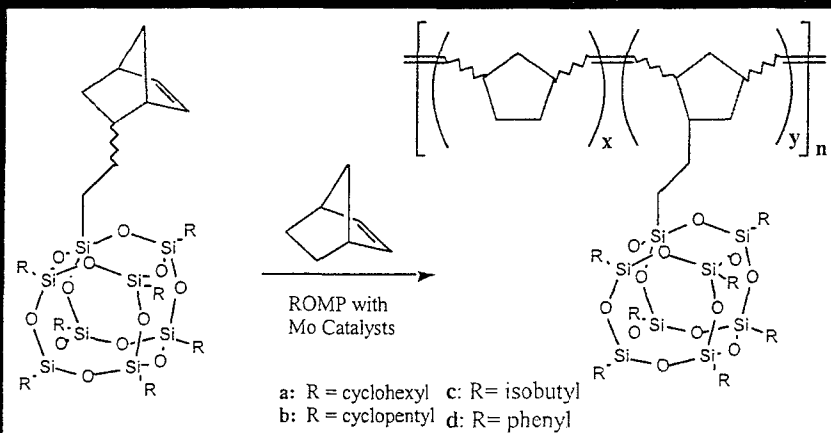


- A variety of POSS "monomers" can be copolymerized into common systems (styrenic, acrylics, polyimides, etc.)
- The polymerization parameters don't appear to be greatly affected, and the POSS is compatible with the matrix (optically transparent)
- The model POSS-norbornene copolymers show distinct differences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

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Variations on the theme-POSS corona chemistry



• Differing POSS corona polynorbornenes being synthesized

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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)

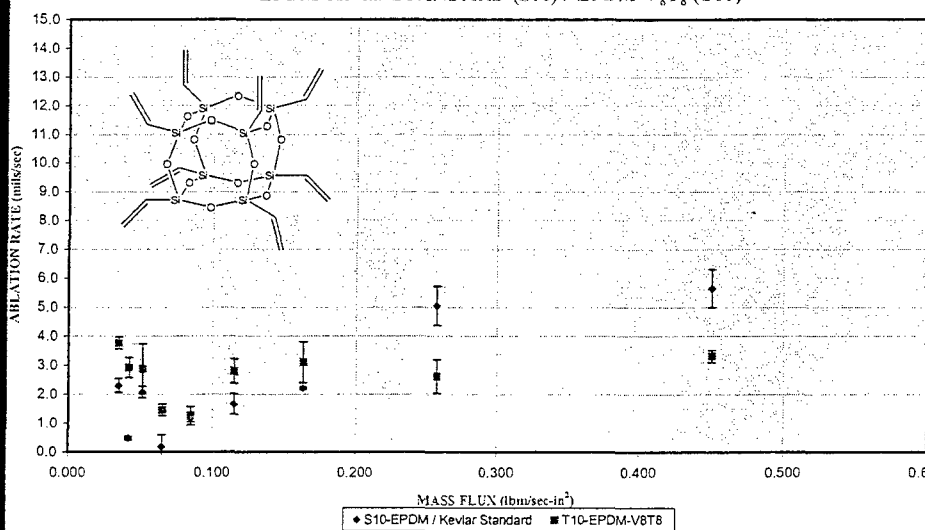
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POSS Reinforcement-Pi-K motor

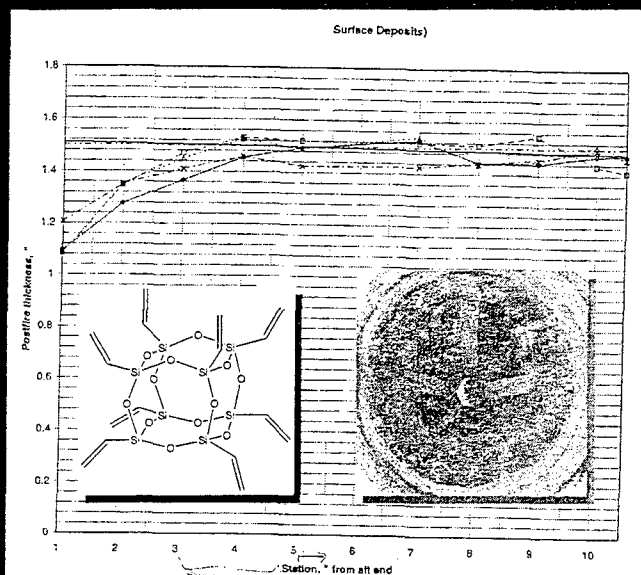


CHAR-063 ABLATION RATE
EPDM-Kevlar STANDARD (S10) / EPDM-V₈T₈ (T10)





POSS Reinforcement-CSD tests



•40-lb ITM Motor

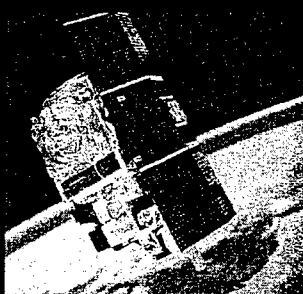
•A series of POSS/EPDMs were tested

•Most promising was Vi8T8

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Goal: Develop Multi-Functional, Space-Resistant Materials



Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

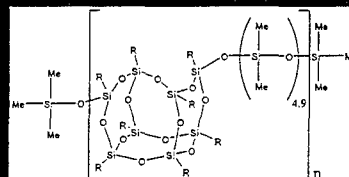
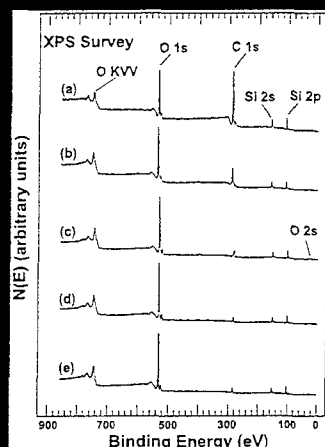
Objectives

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

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Atomic Oxygen Resistance of POSS Siloxane



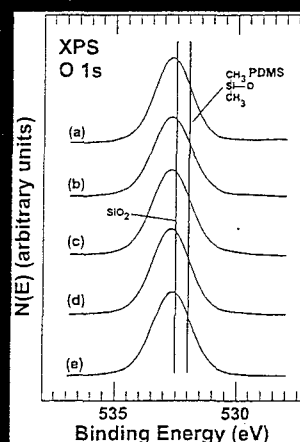
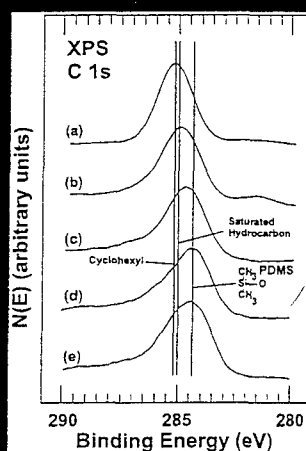
Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

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.

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Atomic Oxygen Resistance of POSS Siloxane

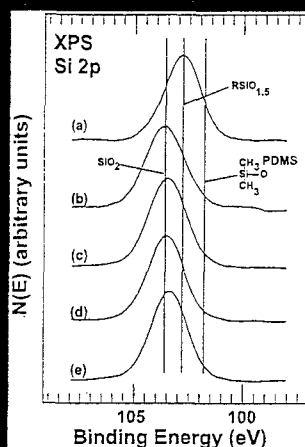


High Resolution C 1s and O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

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Atomic Oxygen Resistance of POSS Siloxane



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 (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.

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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

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