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MEMORANDUM FOR PRS (In-House Publication)

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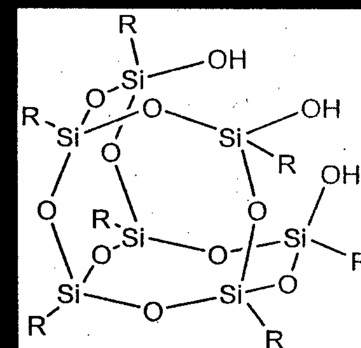
SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-136**
Phillips, Shawn; Haddad, T.S., Blanski, R.L., "Molecularly Reinforced Polymers" (VuGraphs)

2001 International Symposium on Nanocomposites **(Statement A)**
(Chicago, IL 25-27 June 2001)(Deadline: 24 June 2001)

POSS Nanostructured Chemicals: Past & Present

Dr. Shawn H. Phillips
Polymer Working Group
Air Force Research Lab, Edwards



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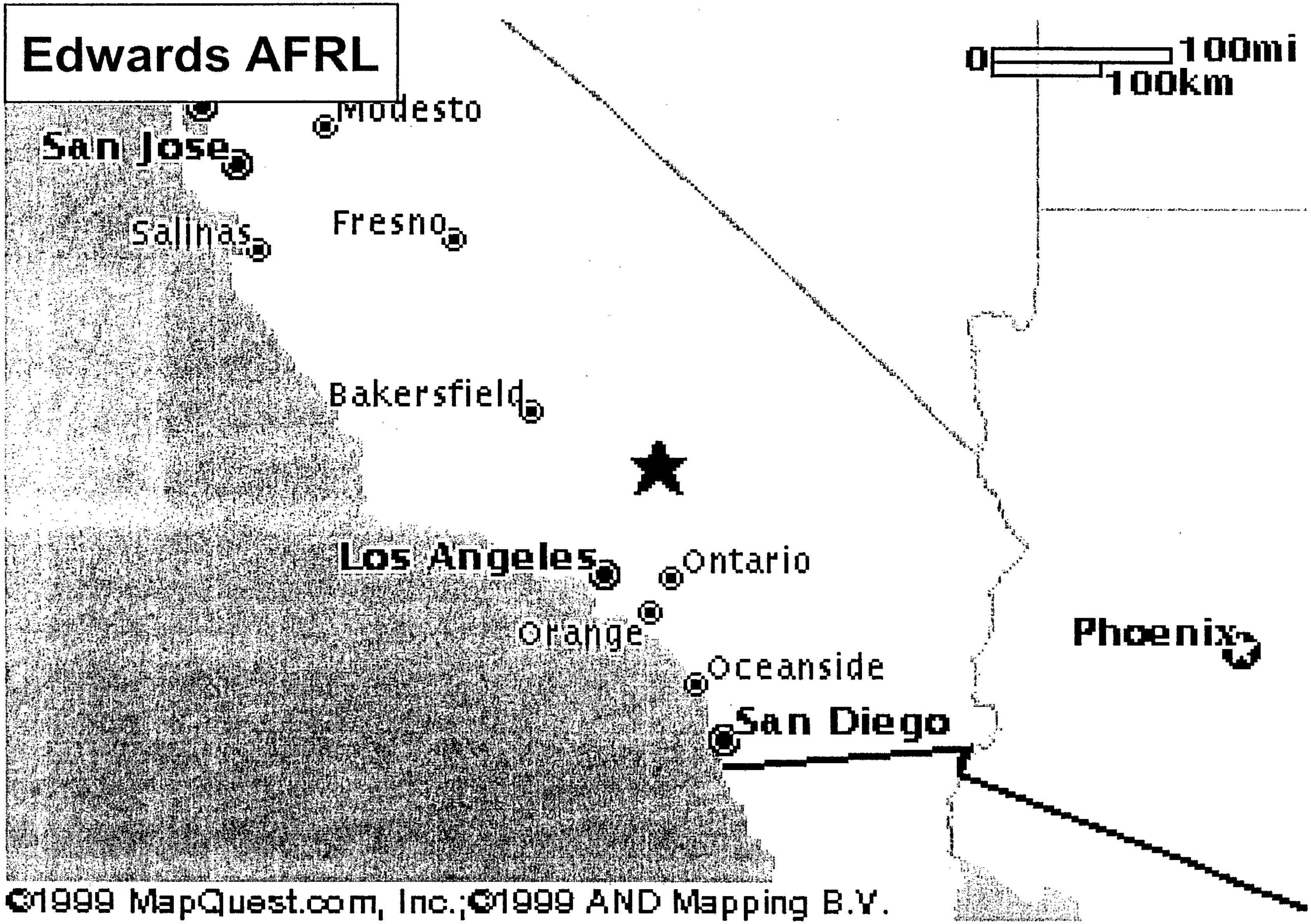
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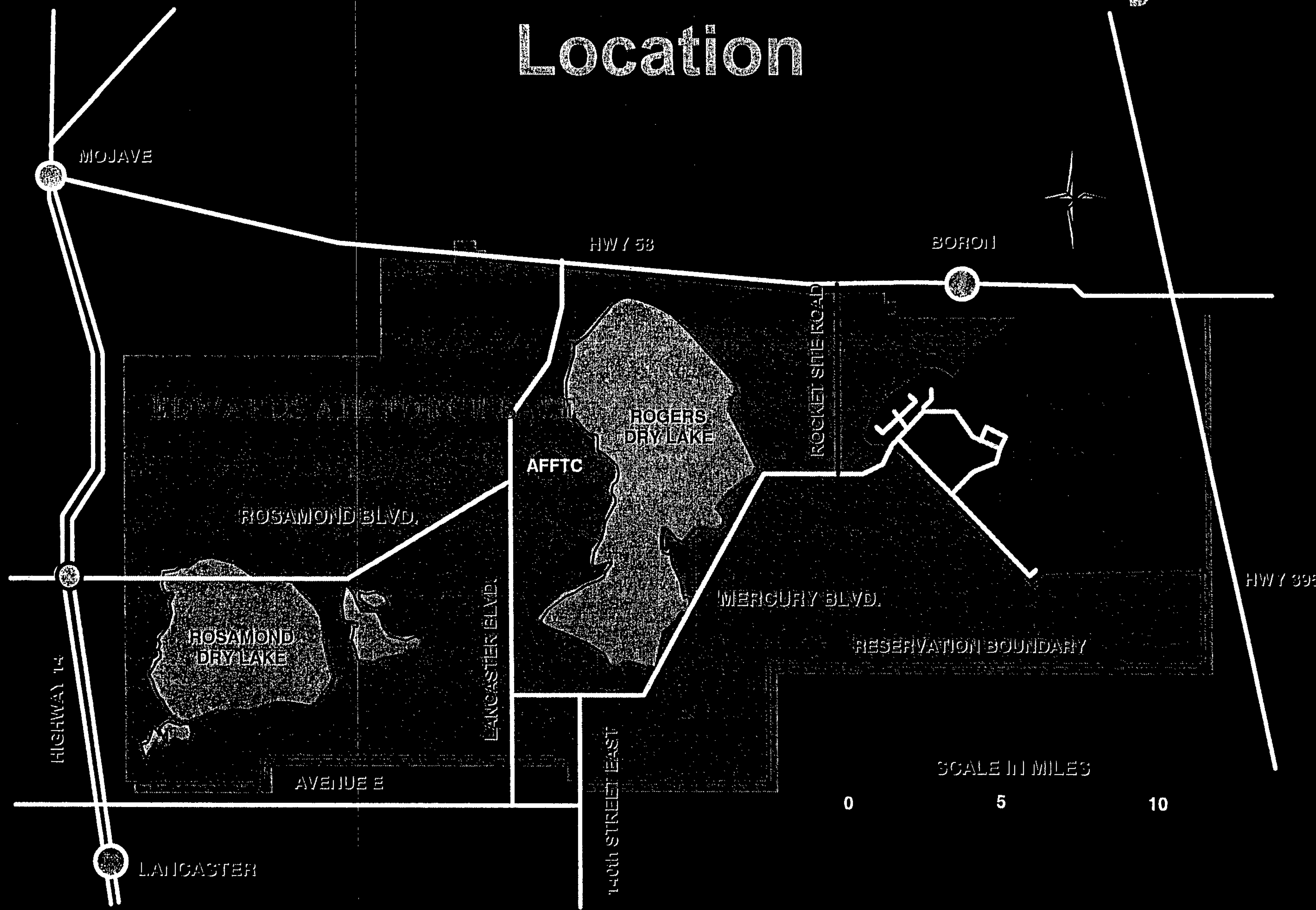
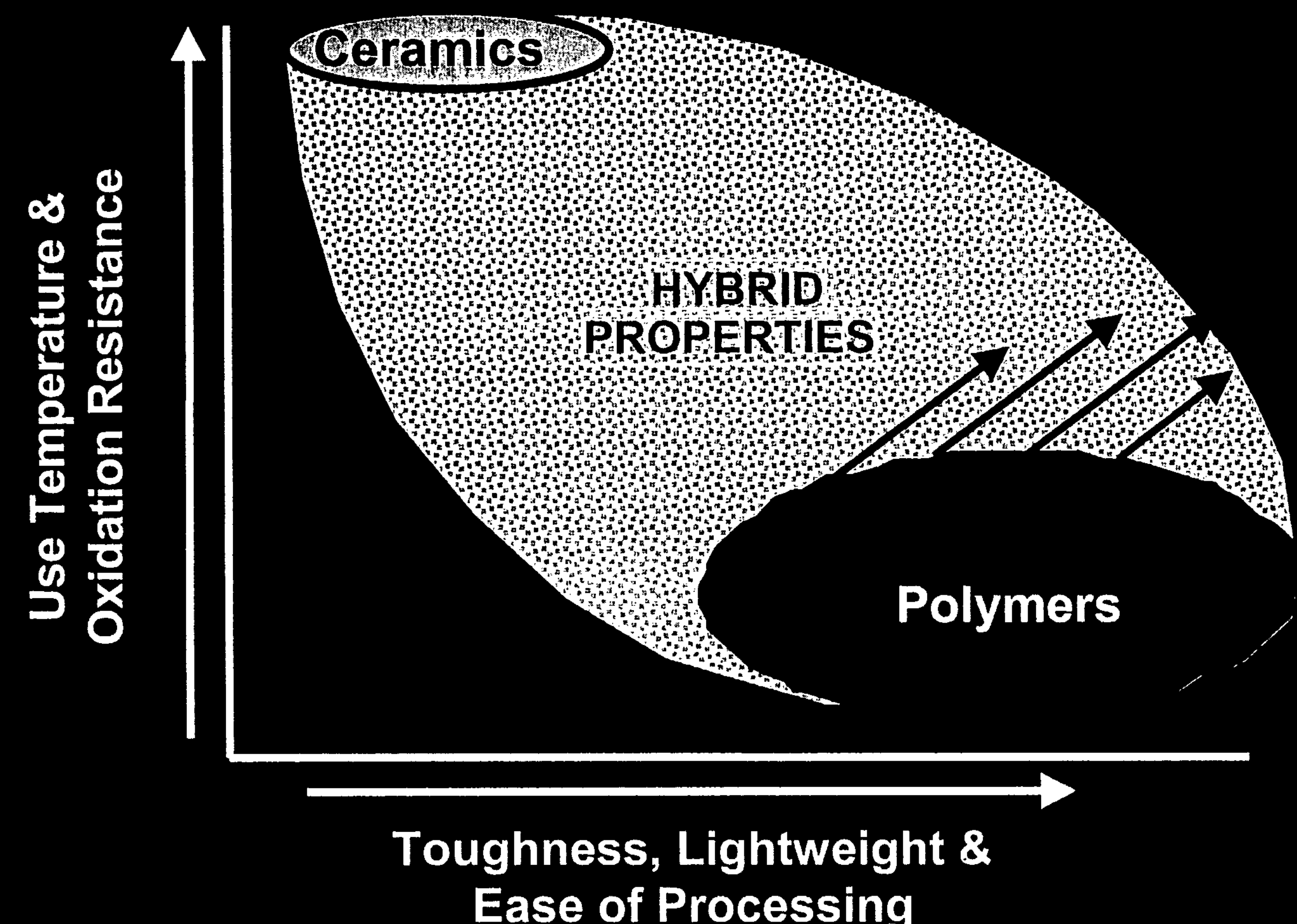
Air Force Research Laboratory Location



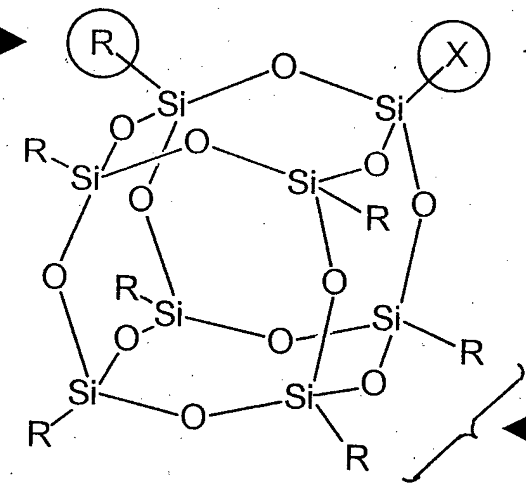
Multiple Applications/Multi-Function



- Improve High Performance Polymers/ Transform Commodity Polymers into High performance Polymers
- Develop Multi-Functional Materials/ Replace Metal Parts with Polymers

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.

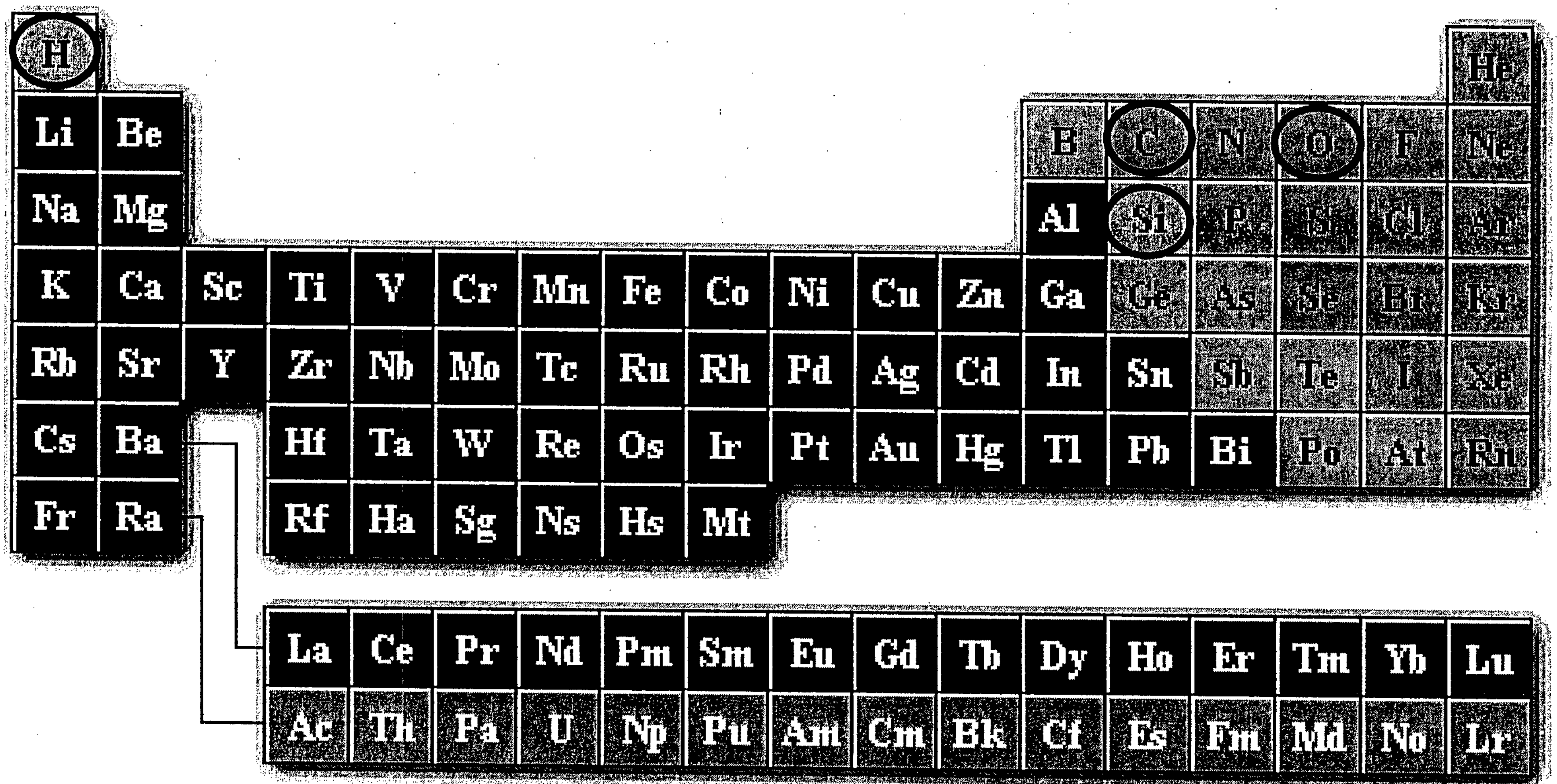
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

The maximization of property enhancements in polymers results from interaction at the nano-level (Edwards AFRL/PRSM ---> POSS monomers)

Physical Aspects

Particle Type	Particle Diameter
polymer segments	5 - 50 Å
C60 "buckeyball"	7 Å
Cy_8T_8 POSS	15 Å
silicate layer	10-100 Å
random polym. coils	50 - 100 Å
colloidal silica	90 - 800 Å
max. extended lengths	80 - 90,000 Å
crystalline lamallae	10 - 90,000 Å
fillers / atmospheric dust	20 - 1,000,000 Å

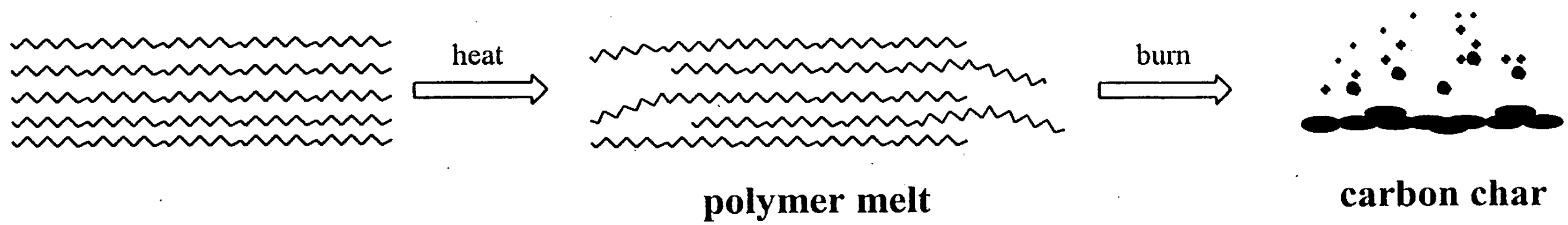
Why does POSS incorporation result in dramatic property enhancements?



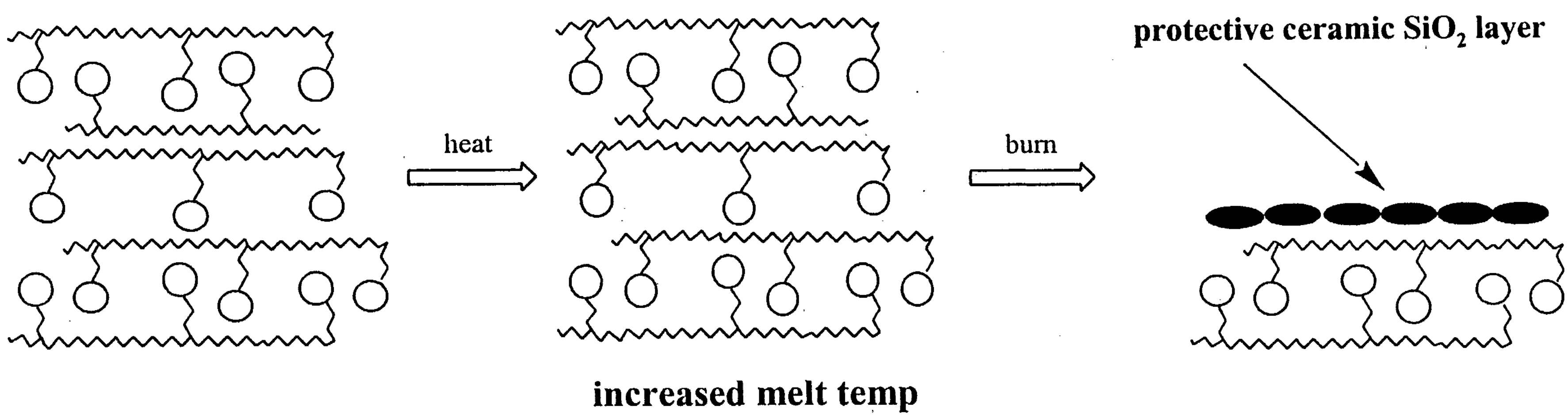
Chemical Composition

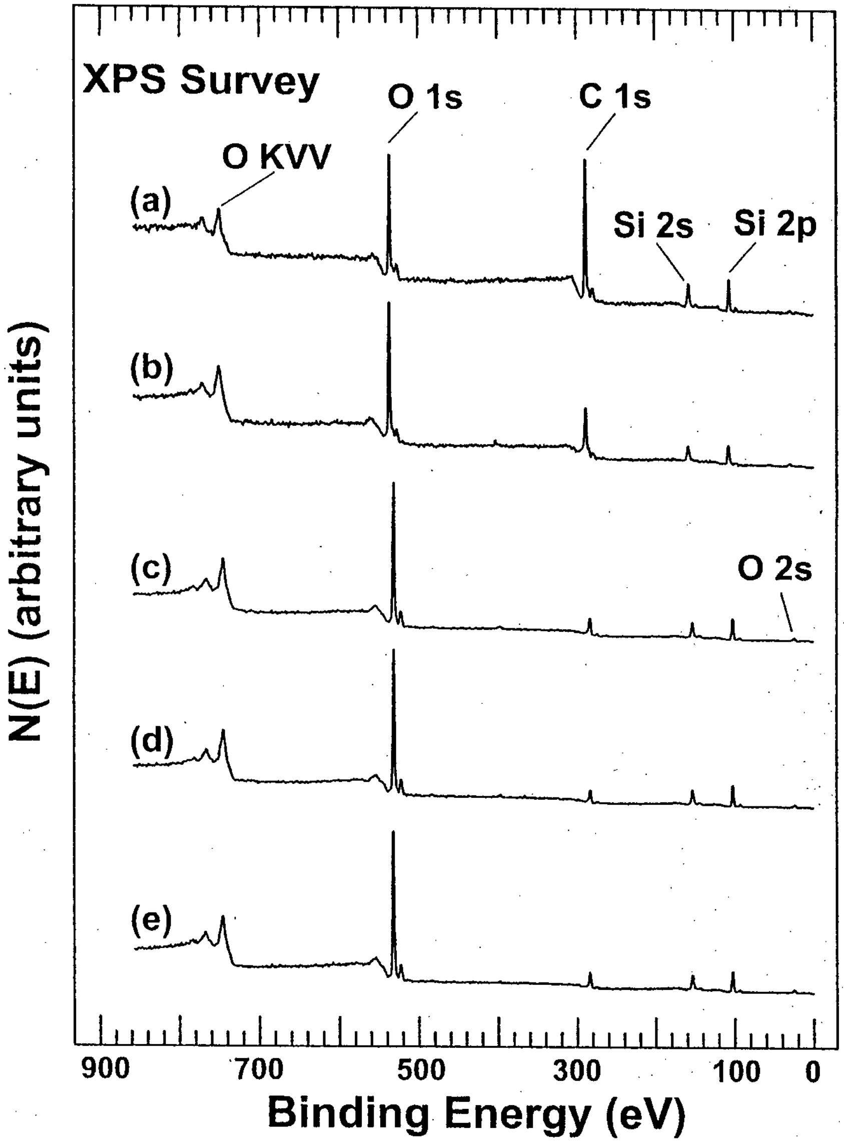
POSS for Flame Retardant Materials

Traditional Polymer

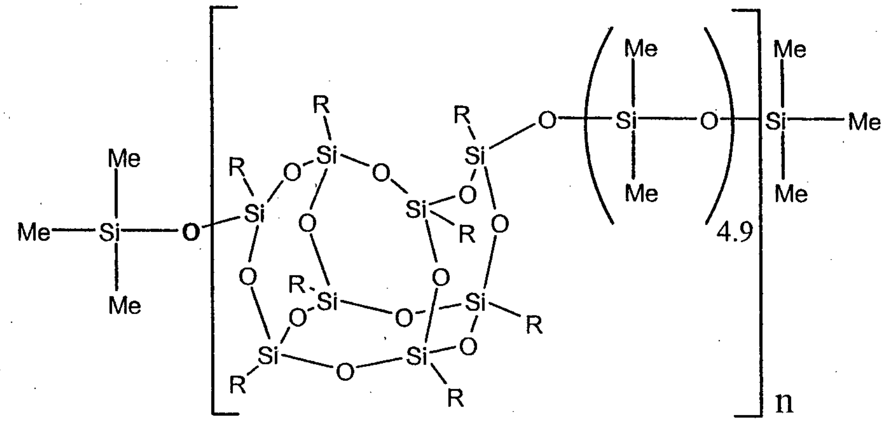


POSS Polymer



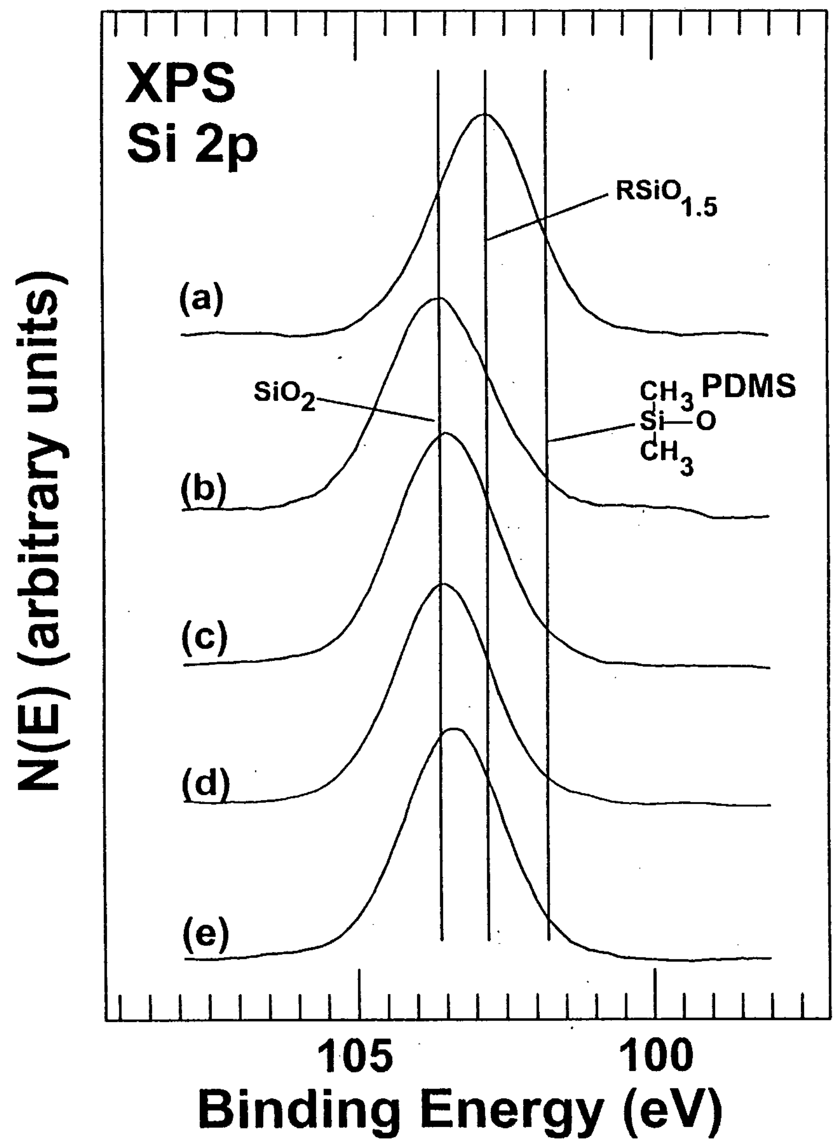


POSS Siloxane



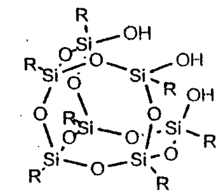
Sample Treatment	O	C	Si
As entered	18.5	65.0	16.6
2.0 hr	33.8	48.4	17.8
24.6 hr	49.1	22.1	28.8
63.0 hr	55.7	16.3	28.0
4.8 hr air	52.8	19.5	27.7

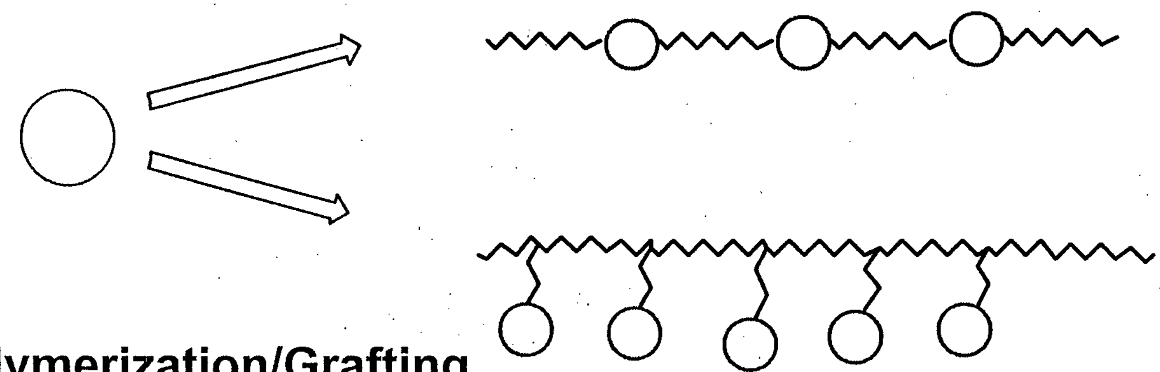
XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.



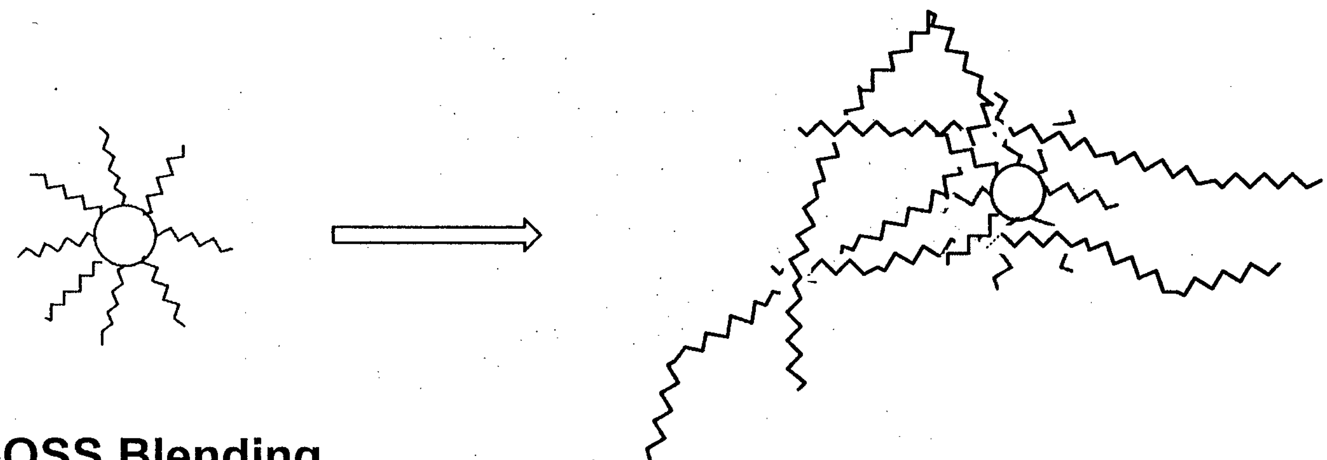
High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.

POSS Polymer Incorporation





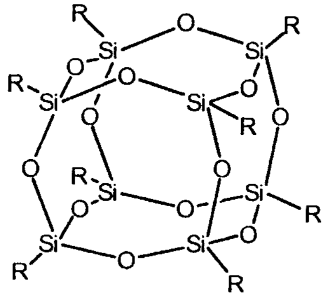
POSS Copolymerization/Grafting



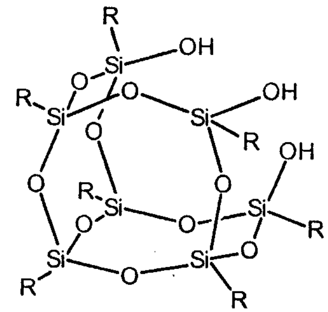
POSS Blending

Size & Shape

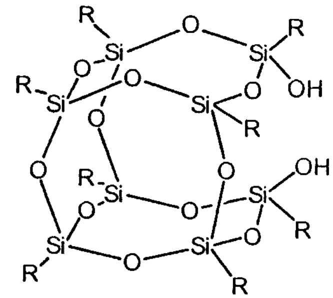
POSS Diversity



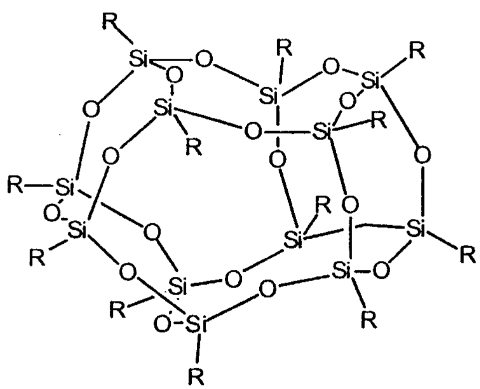
R = Methyl, Isobutyl, Cyclopentyl, Cyclohexyl, Isooctyl, Phenyl, Phenethyl, Octadecene



R = Isobutyl, Cyclopentyl, Cyclohexyl, Isooctyl, Ethyl



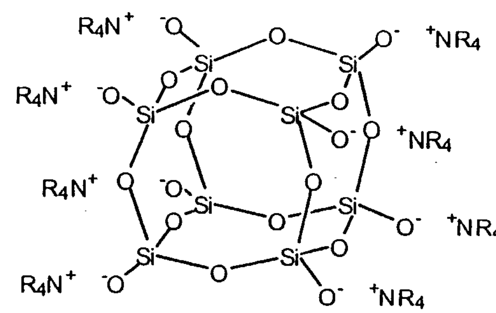
R = Isobutyl, Cyclopentyl, Cyclohexyl, Isooctyl



R = Phenyl, Trifluoromethylpropyl

Polydisperse Cages
(T_8, T_{10}, T_{12})

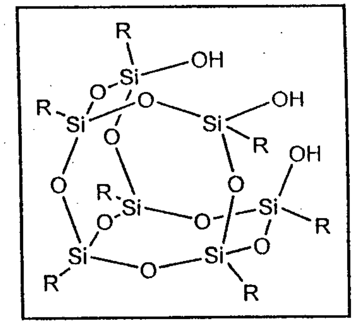
R = Vinyl, Phenethyl

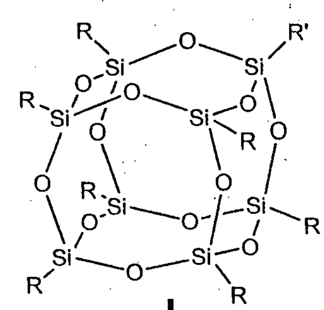


R = Methyl

Hybrid Plastics

POSS Monomer/Polymer Trees





halides
alcohols
esters
acids
bisphenols
acid chlorides
aryldiacids

nitriles
amines
isocyanates
arylbisamines
arydiisocyanates

silanes
silanols
siloxanes

olefins
styryls
acrylics

norbornyls
cyclopropyls
epoxies

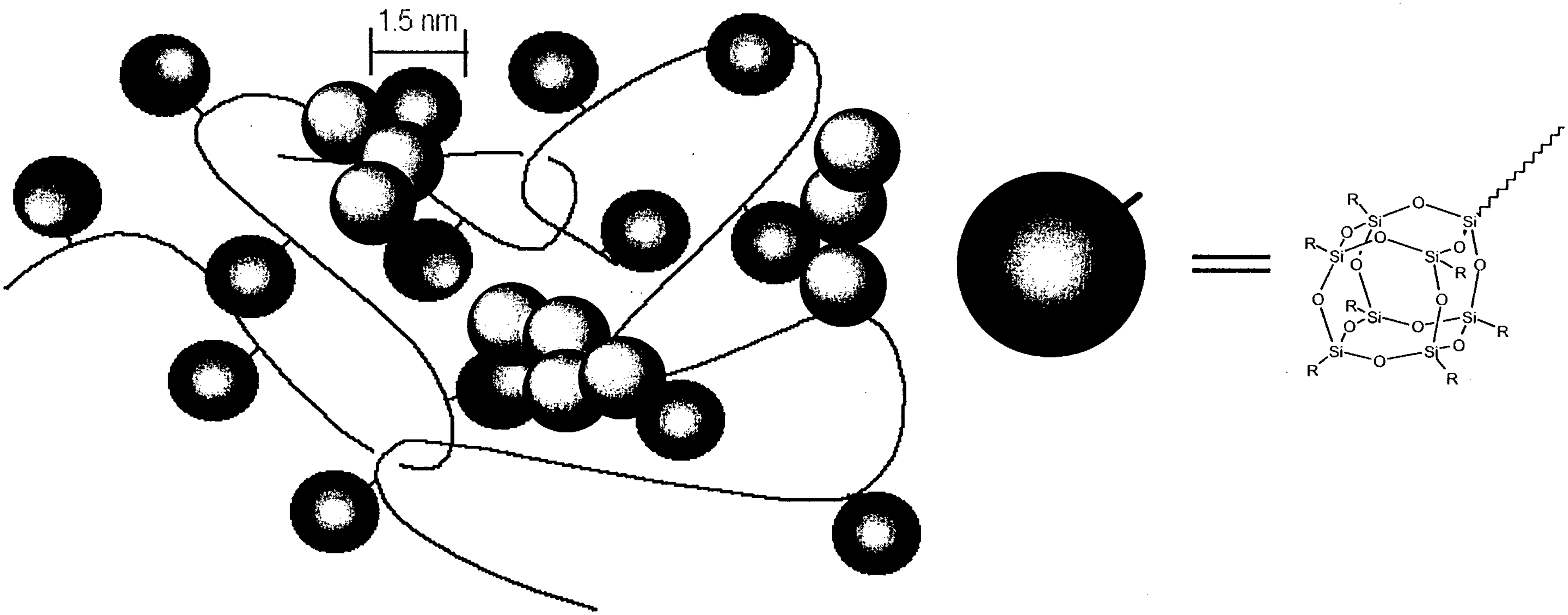
"POSS-technology is sustainable via dual-use markets"

<u>>100 polymer systems</u>

- POSS-rubber*
- POSS-urethane*
- POSS-epoxy*
- POSS-phenolic*
- POSS-imide*
- POSS-teflon

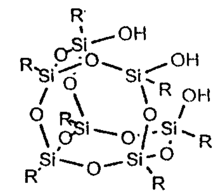
monomers and polymers.

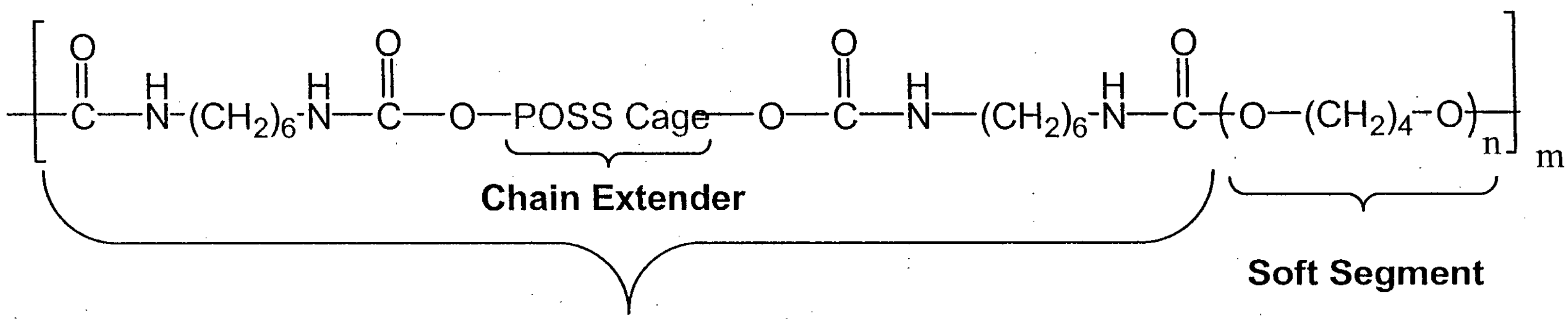
Conceptual Model for POSS Polymers



POSS-POSS interactions?
Entanglement?
Aggregation?

POSS-polyurethane Properties





POSS-polymer improvements

Up to 300 °C increase in the melt transition temperature (rheology studies show the transition from an oil to a true thermoplastic elastomer)

Up to a 100 °C increase in T_{dec} (29 wt% POSS, still TPE)

Up to 10X increase in moduli (>400% elongation with no destruction of hard segments))

17% POSS incorporation ----> 3X increase in Hardness (Shore A)

Prof. Andre Lee - Michigan State University

	Dow data	Neat *i*-PP (processed)	*i*-PP blended 2 wt% $Methyl_8T_8$	*i*-PP blended 5 wt% $Methyl_8T_8$	*i*-PP blended 10 wt% $Methyl_8T_8$
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, 1% secant); 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.**

Key Roadblocks for POSS Materials, Sept. 1998

- **Time for Production of POSS feedstocks**
- **Cost of POSS feedstocks/monomers/polymers**
- **Volume of POSS feedstocks/monomers**
- **Structure/Property Relationships**
- **Blends & Processing**

POSS™ Commercialization and Cost Reduction Campaigns

In October 1998 Hybrid Plastics and the Air Force Research Laboratory entered into a Cooperative Research and Development Agreement (CRADA) for the commercialization of POSS™ Nanotechnology.

Technical Objective:

- Commercialization of POSS™ Technology.

Also in October 1998 Hybrid Plastics was awarded a 3-year, \$2 million grant by NIST's Advanced Technology Program (ATP) to reduce the cost of POSS Nanostructured™ Chemical Technology by a factor of 100.

Technical Objective:

- Reduce costs of POSS™ Technology from \$1000-\$5000/lb to \$10-50/lb.

Hybrid Plastics

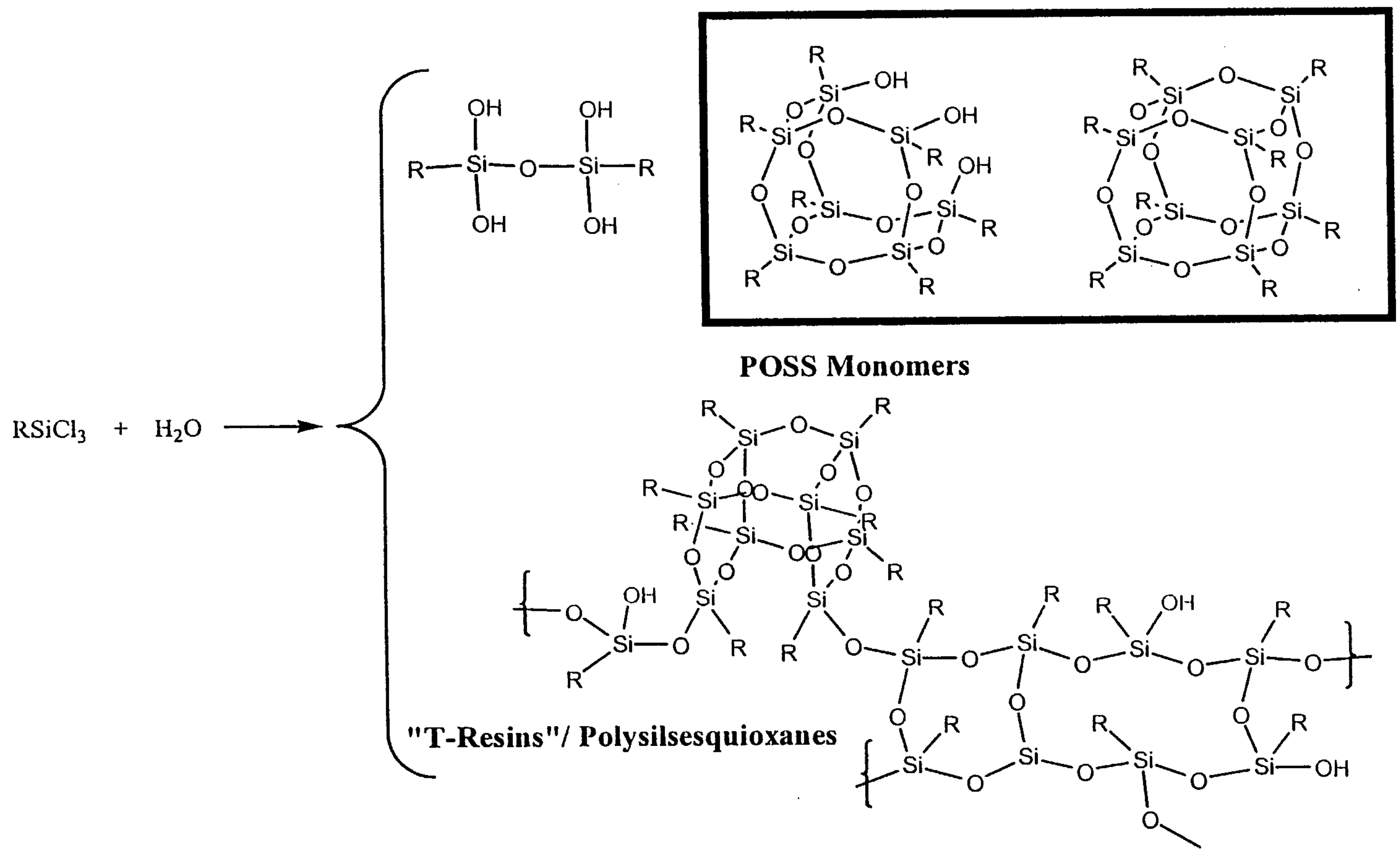
POSS™ Commercialization and Cost Reduction Campaign

Technical Challenges:

- Develop processes for the synthesis of nanostructures from low cost feedstocks.
- Increase efficiency of processes:
  - ➢Increase concentration at least 5 fold.
  - ➢Increase yield to >95%.
  - ➢Increase selectivity for desired products.
- Decrease reaction times from days to hours.
- Develop processes suitable for large scale (kilo-ton) production.
- Develop technology portfolio which will allow:
  - ➢Selective manipulation SiO framework.
  - ➢Control of stereochemistry.
  - ➢Control of functionality.
  - ➢Type of reactive functionality.
  - ➢Degree of reactive functionality

Hybrid Plastics

Volume Increase, Price Reduction

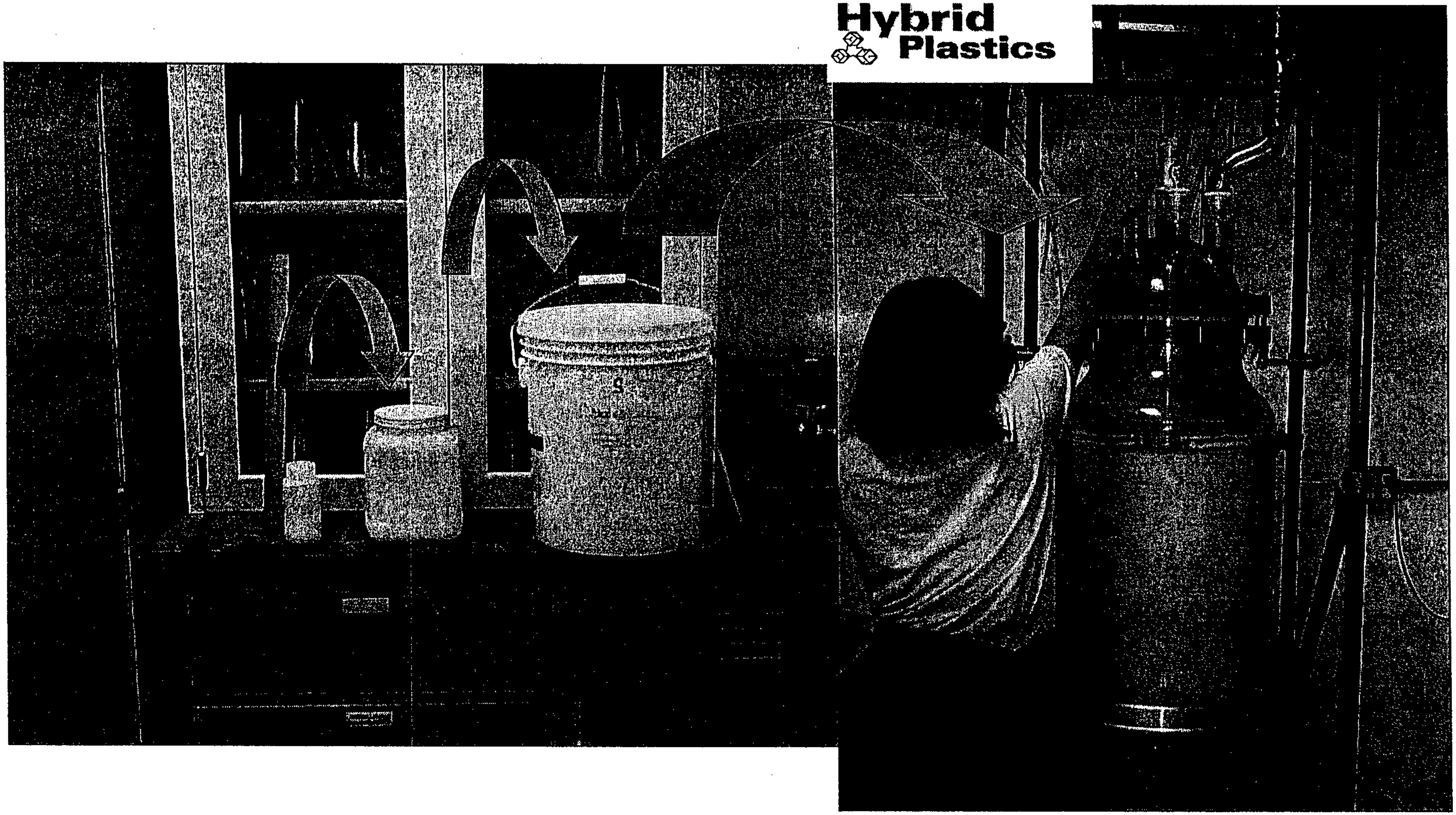


- Traditional silsesquioxane chemistry focused on "T-Resins"
- Hybrid Plastic's new proprietary routes have resulted in high yields, selectivity, increased []s, and lower cost starting materials

↑ ?

Technology Transfer = Scalability = Price Reduction, Sustainability

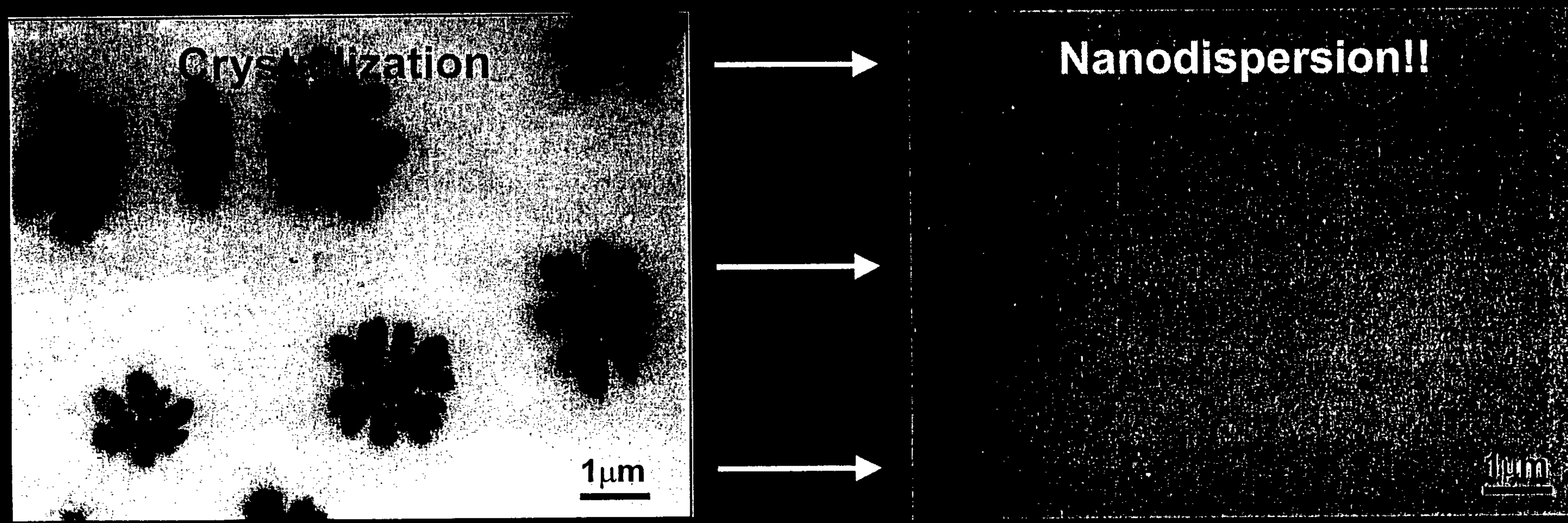
Hybrid Plastics



Time	1991	1994	1998	2000
Quantity	< 50g	2-5 lb	20-40 lb	> 400 lb
Price	???	$1000-5000/lb	$1000-5000/lb	$20-250/lb

Plant

6.1 NWV: Processing/Blending

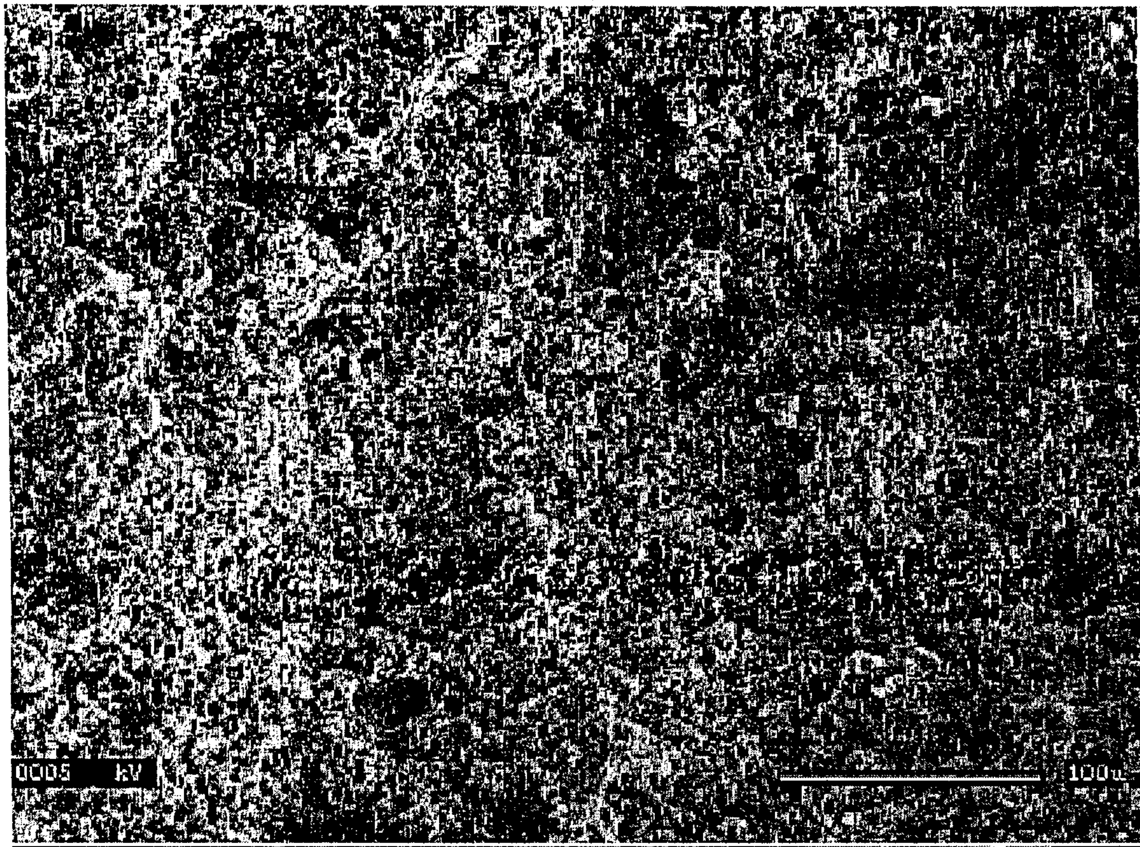


Tech Challenge: Insolubility of POSS monomers in polymer matrices

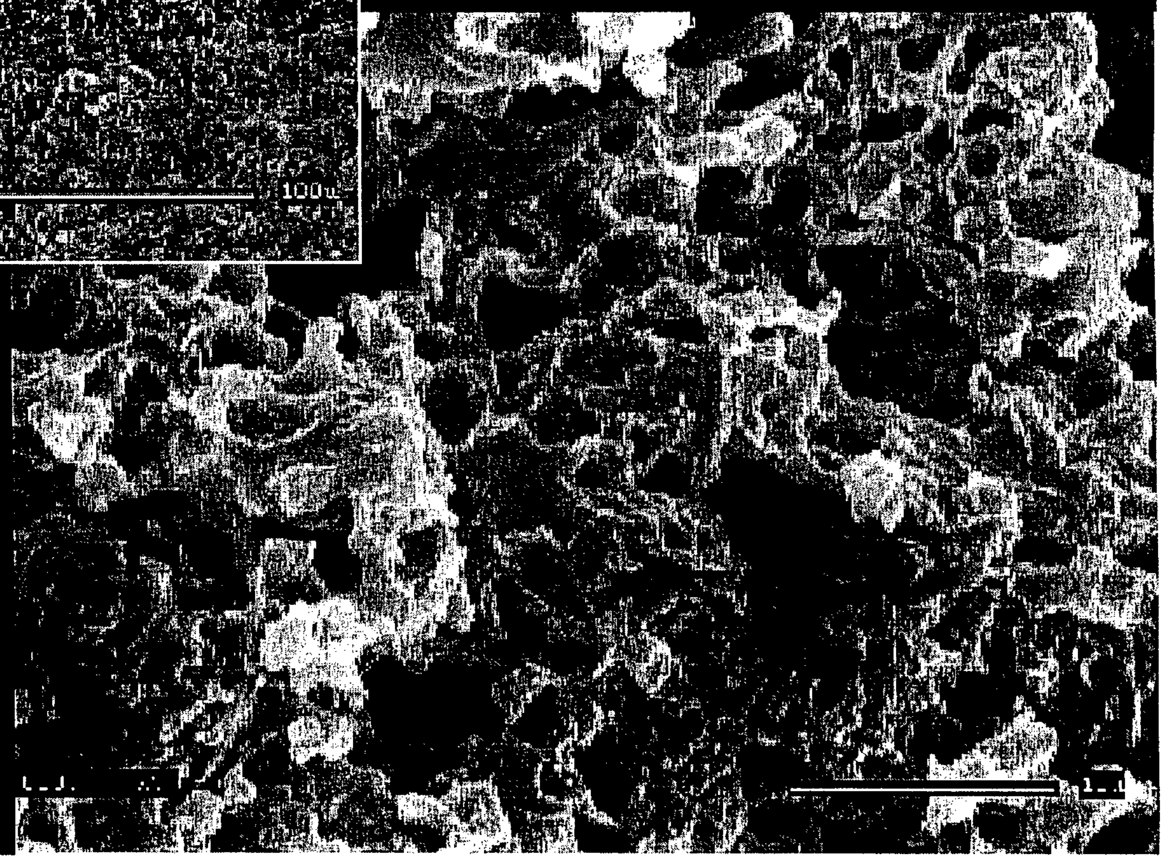
Success + synthesis of a nanodispersed POSS-Polypropylene (demos)

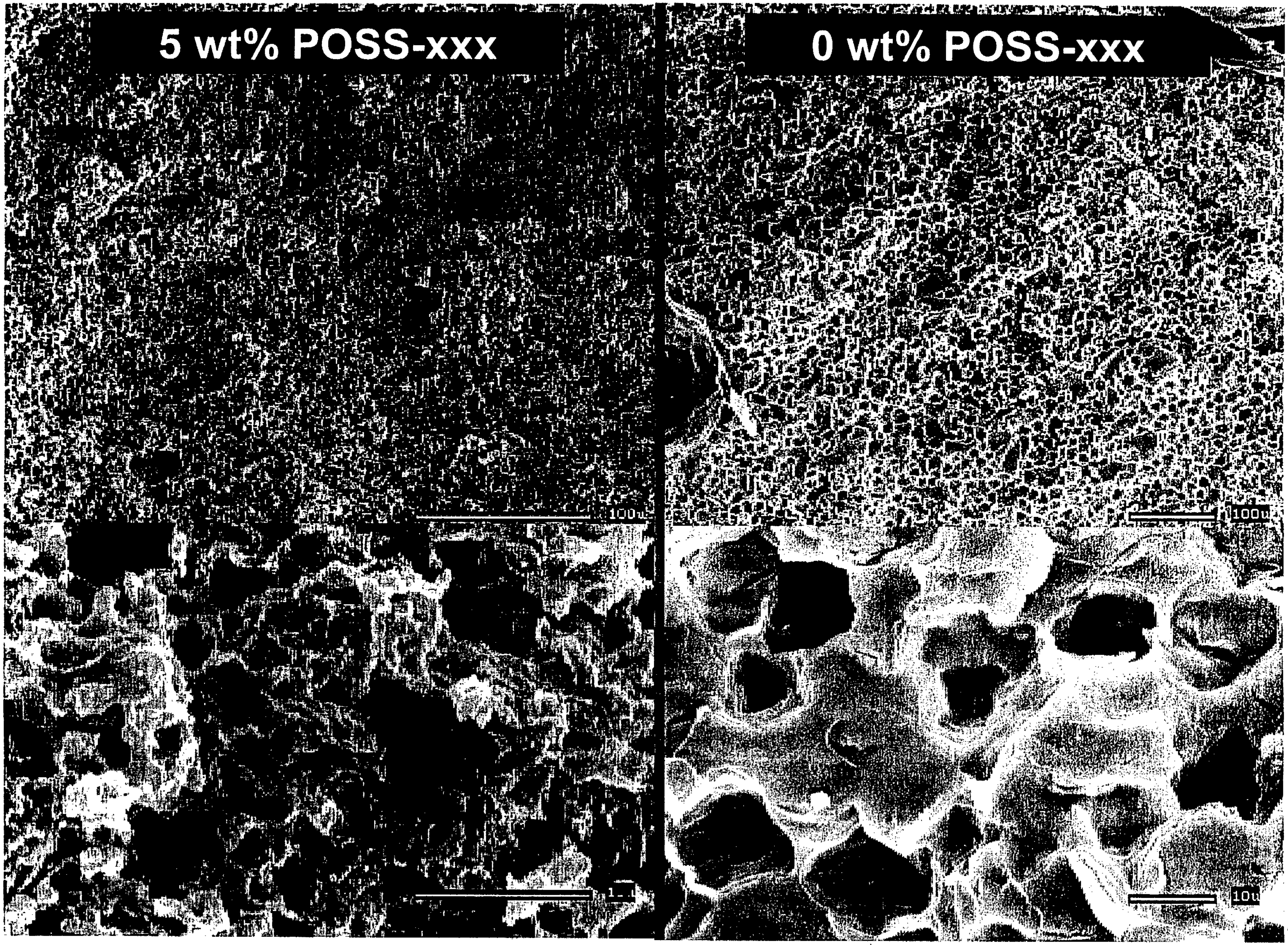
Result: R&D100 Award in 2000

5 wt% POSS-xxx Microfoamed by WMR (DUS&T)

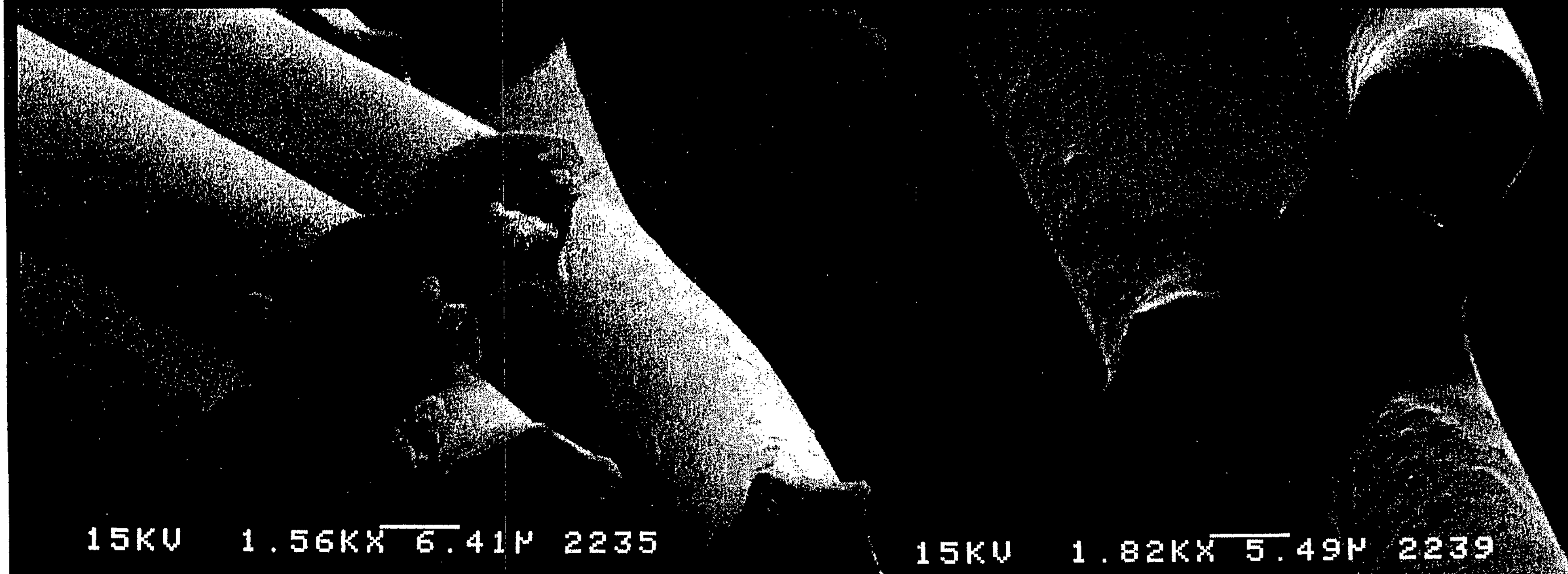


- Fairly uniform foaming
- >25% weight reduction*
- 33% increase in compression strength & fracture toughness




5 wt% POSS-xxx
0 wt% POSS-xxx
100u
100u
1.u
10u

POSS for fiber coatings

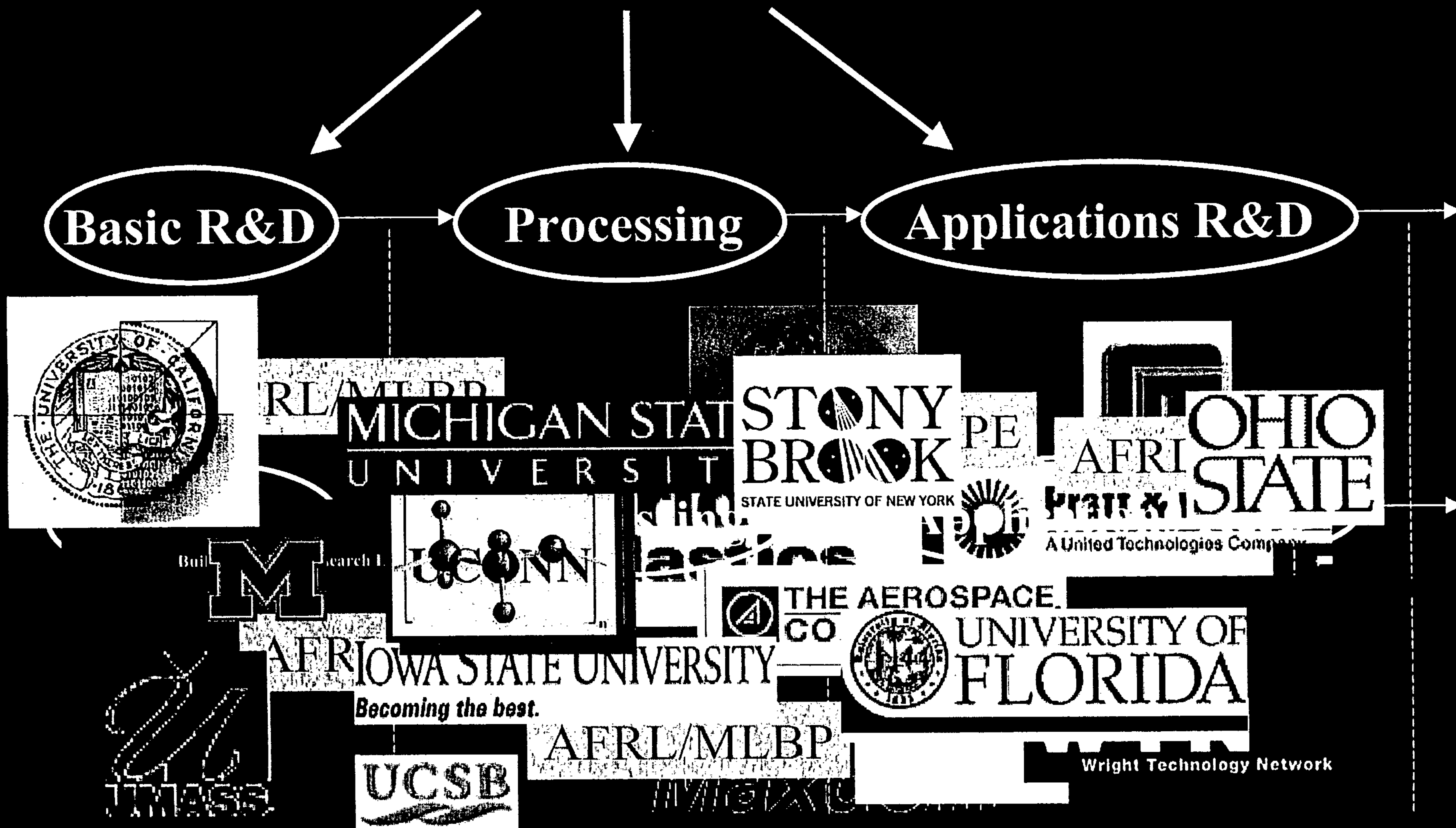


Uncoated and coated riton fibers

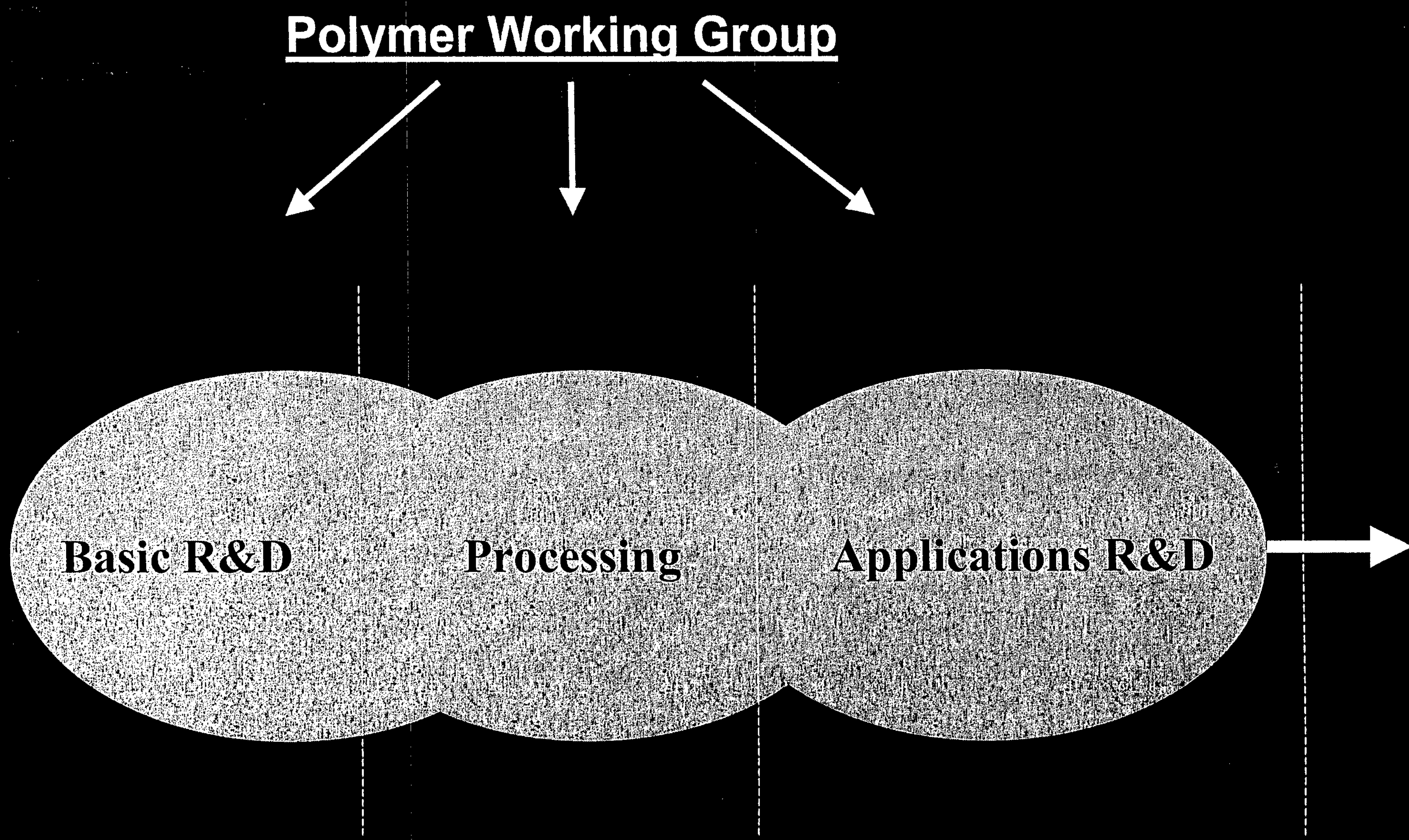
Successfully developed low-cost, efficient coating process

Programmatics: Dual Use & Leveraging

Polymer Working Group



Programmatics: Dual Use & Leveraging



CONCLUSIONS

Academic/Government Lab Collaborations are essential

Polymer Working Group

Basic R&D goal for controlling/understanding POSS affects on polymer properties is already ahead of schedule (including processing).

Cost, Volume and Production time goals have all been met thanks to Hybrid Plastics & Prof. Frank Feher.

Understanding processing is a key area that is being heavily worked.

POSS applications within government are on critical paths, while industrial interest has increased exponentially with technology transfer in 1998.