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MEMORANDUM FOR PRS (In-House Publication)

FROM: PROI (STINFO)

01 May 2003

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2003-114**
6270 Shawn Phillips (AFRL/PRSM), "T^2 Success within the Material Applications Branch of AFRL's Propulsion Directorate"

National Symposium Federal Lab Consortium
(Phoenix, AZ, no date provided) (Deadline: 06 May 2003 – RUSH per Dr. Corley) (Statement A)

T^2 Success within the Material Applications Branch of AFRL's Propulsion Directorate

- *Nanostructured™ Chemical Technology Based on POSS*
- *Rapid Processing for the Densification of Carbon-Carbon*

Dr. Shawn Phillips
Chief, AFRL/PRSM
Propulsion Directorate
Air Force Research Laboratory
Shawn.phillips@edwards.af.mil

SMJ CARBON

Hybrid Plastics™

- Quick Note on Technology Transition

- Technology Transfer Success Stories w/in AFRL/PRSM
  - The Stories on:
    - a new chemical feedstock with no current market (yes with some science)
    - a new processing technology that already has an existing market.
  - That was then and this is now

- What will be contained in the Success Stories
  - Setting up collaborations
    - Spin-off companies (CRADAs)
    - Industrial Interest (NDAs, STTRs, SBIRs)
    - Industrial Funding (CRADAs)
  - Leveraging of resources (TIAs, CRADAs, NDAs, STTRs, SBIRs, PRDAs, DARPA, AFOSR, Academic Collaboration/Consultants)

The Council for Chemical Research Collaboration Success Award for 2001/2

POSS

2000 FLC Technology Transfer Award

Hybrid Plastics™

Commercialization and Solution Development

UCI University of California, Irvine

Discovery Research

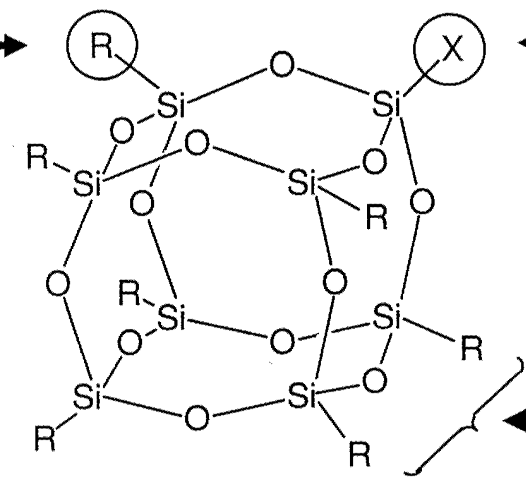
AIR FORCE RESEARCH LABORATORY

Basic and Applied Research

Anatomy of a Polyhedral Oligomeric Silsesquioxane (POSS™) Molecule

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.



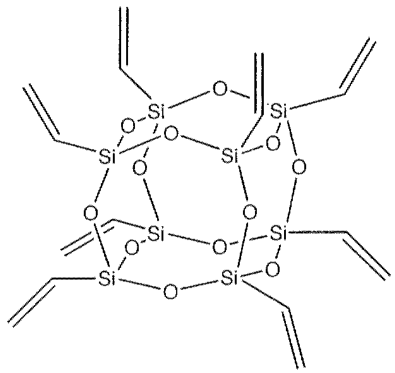
May possess one or more functional groups suitable for polymerization or grafting.

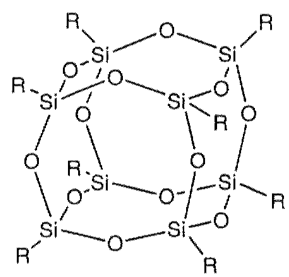
Thermally and chemically robust hybrid (organic-inorganic) framework.

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

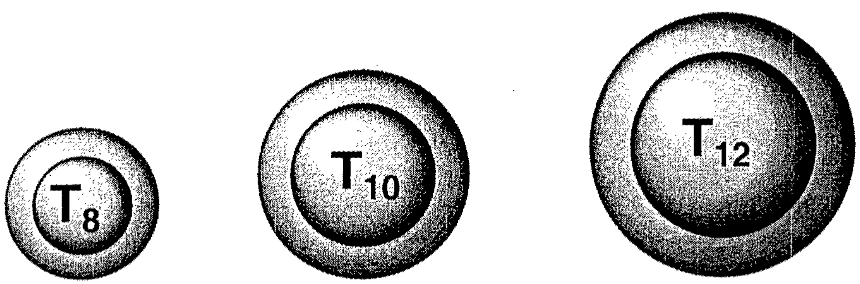
POSS®: Versatile Feedstock Development

Completely Condensed

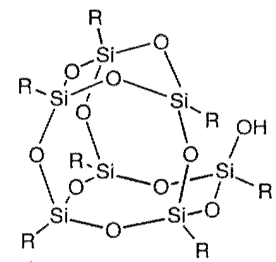




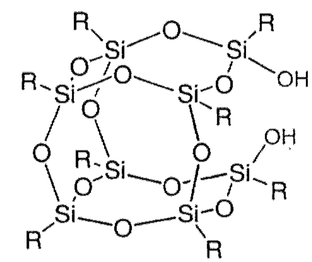
R = Me, Et, *i*-Bu, Cp, Cy, i-Octyl, Ph



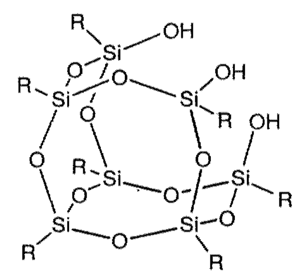
Incompletely Condensed



R = Cp, Cy, *i*-Bu

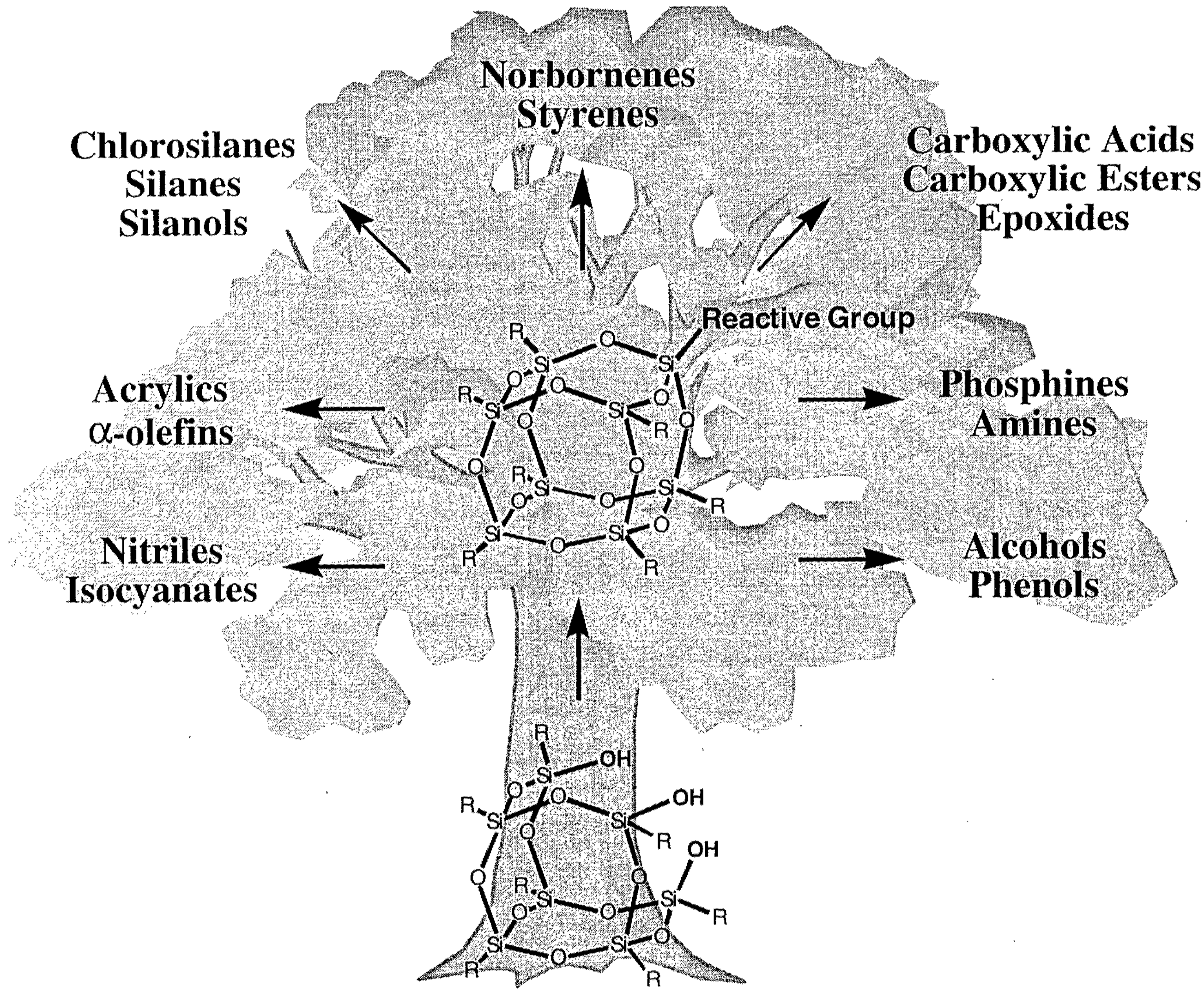


R = Cy, Cp, i-Bu, Et



R = *i*-Butyl, Et

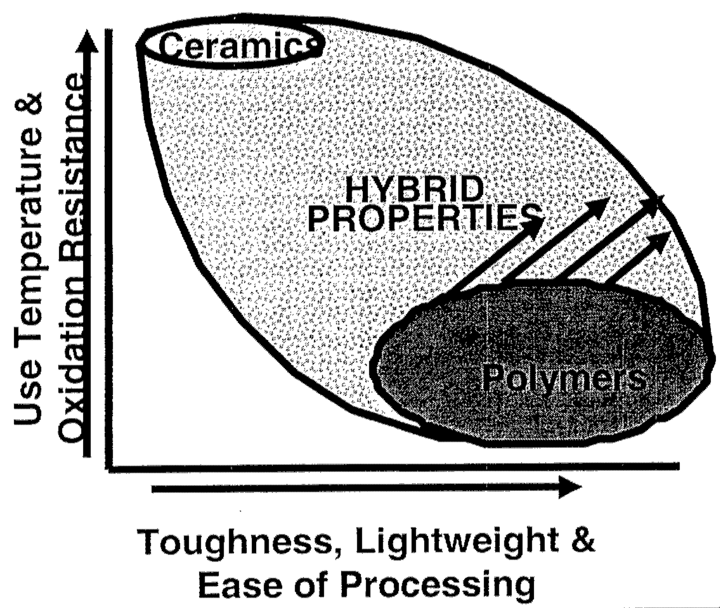
Functionalized POSS™-Monomers



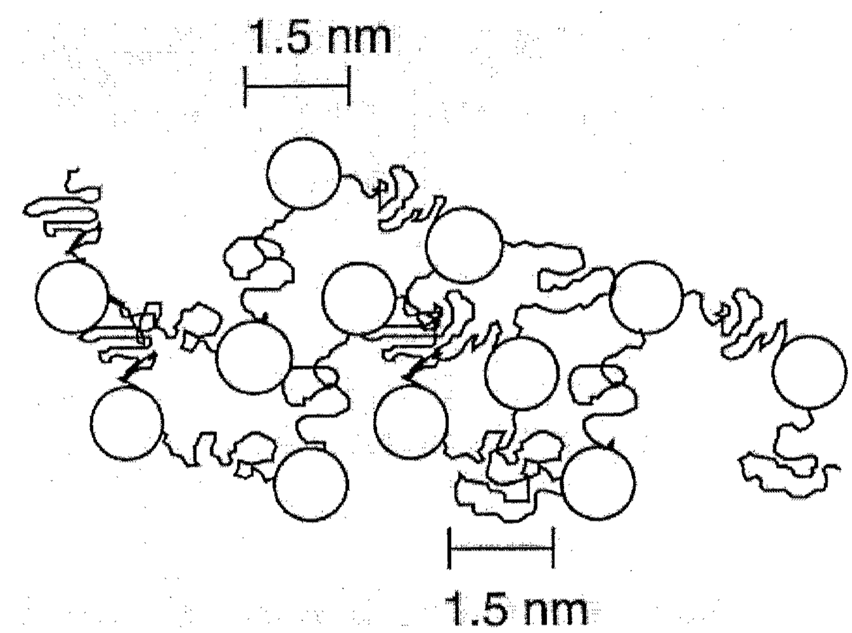
Hybrid Plastics currently offers over 180 Nanostructured™ Chemicals

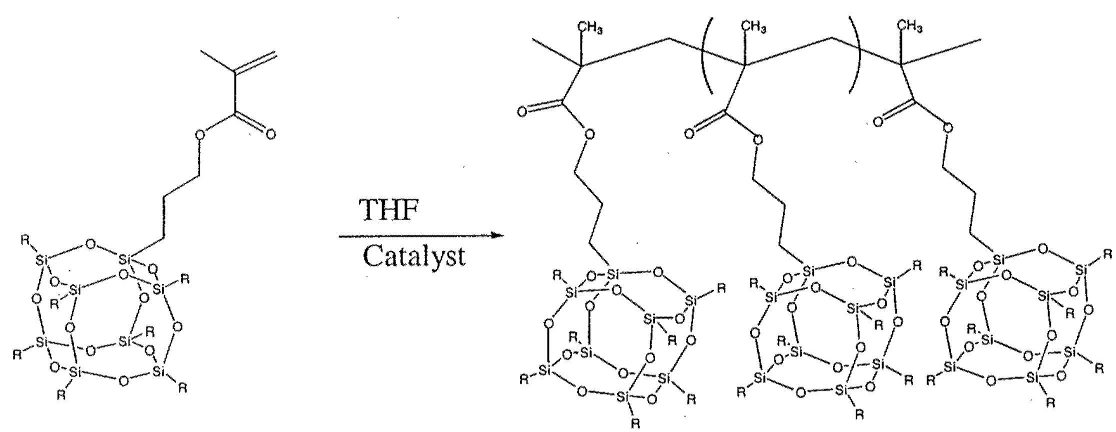
Key Aspects of POSS™ Technology

Hybrid (inorganic/organic) Composition



Nanostructured™ Chemical Reinforcement

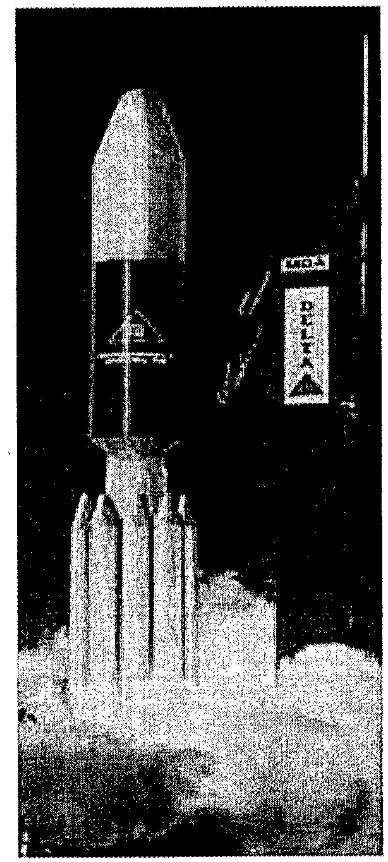




POSS™ technology does not require manufacturers to retool or alter existing processes.

Lichtenhan et. al. *Macromolecules* **1993**, *26*, 2141.
Lichtenhan, *Polym. Mater. Encyclopedia* **1996**, *10*, 7768.

Where Are We Now?



2nd CRADA:

Focused on POSS Polymer Synthesis & Scale-up
(1st CRADA for new feedstocks/monomers)

Research:

New Monomers & Feedstocks (>180) - simplicity
Control & Prediction of Property Enhancements

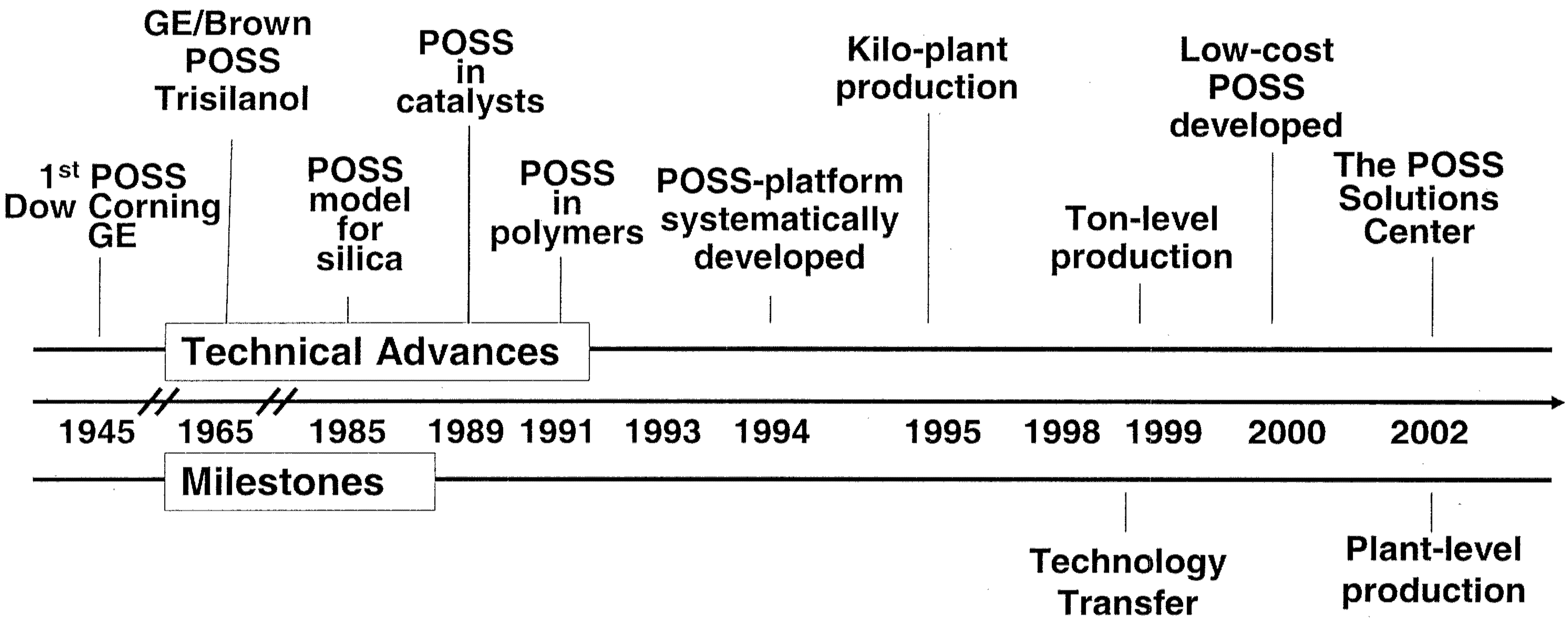
Production:

Multi-Ton Production Capability!!!
10-100x Reduction in Cost (monomer dependent)!!!

Application:

Critical & High-Risk Paths for Air Force Applications
Incorporation and R&D Testing by Numerous Companies

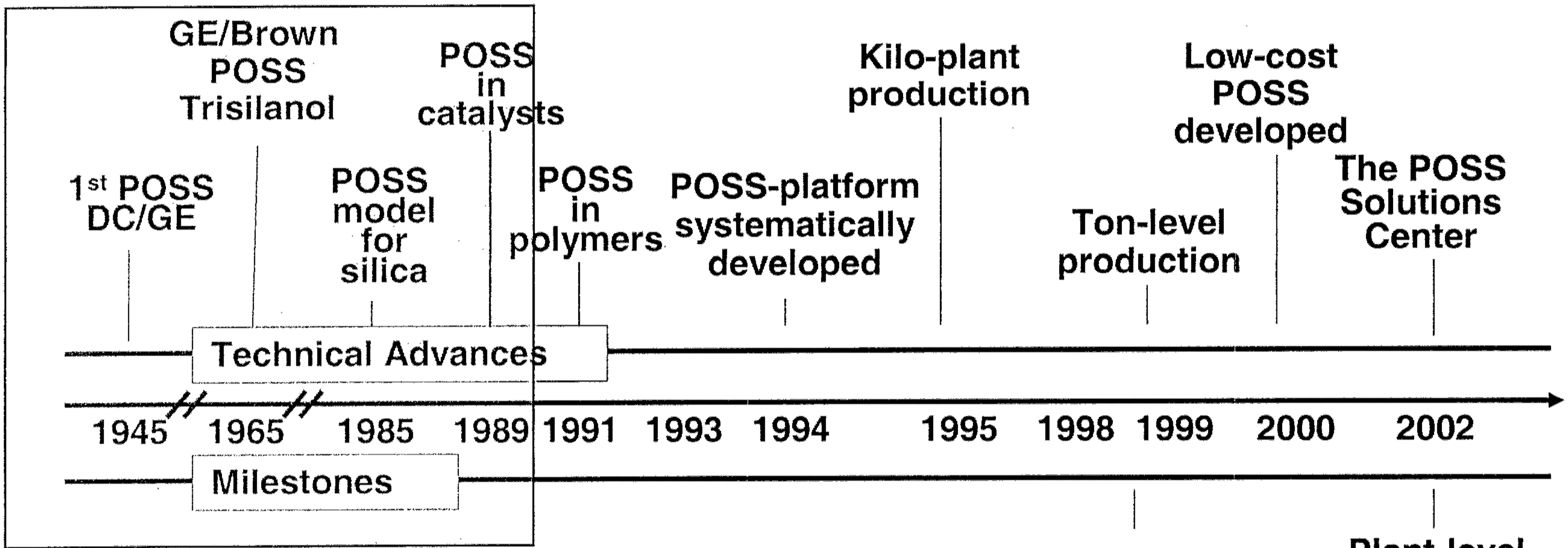
POSS™-Technology Timeline



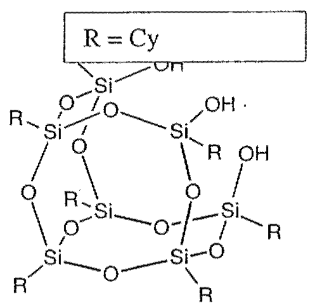
UCI — Chemistry

Air Force — Chemistry & Polymers

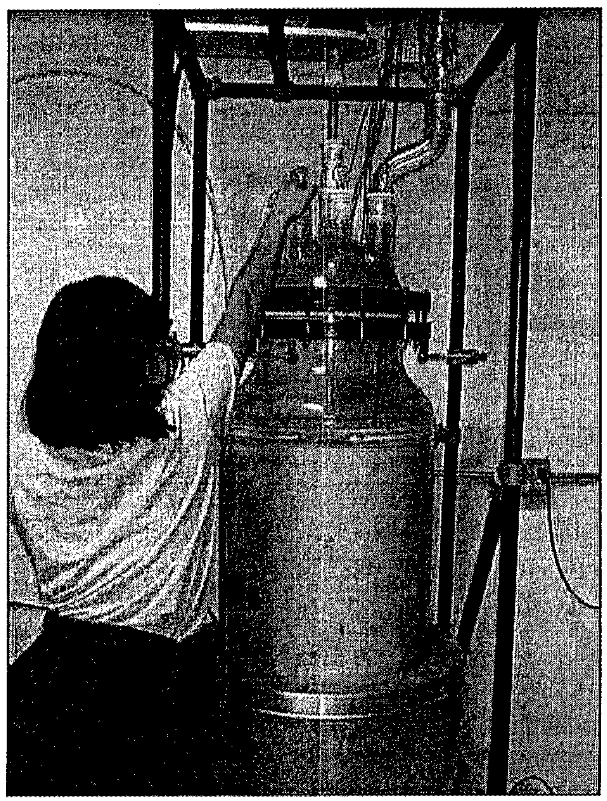
Hybrid Plastics — Commercial Solutions



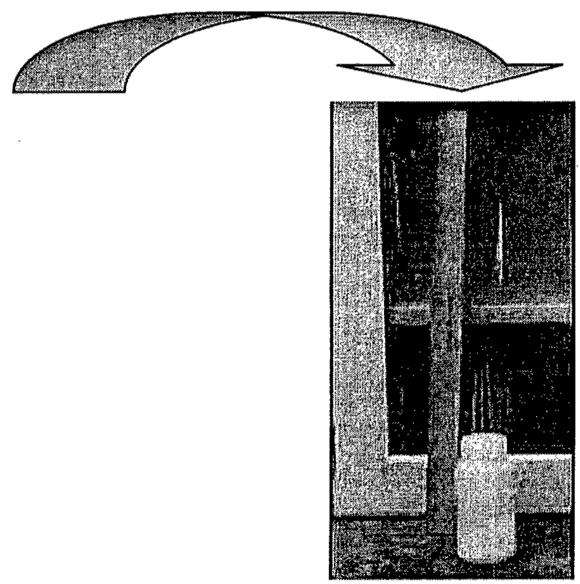
- NSF Funding
- 3 Academic Groups

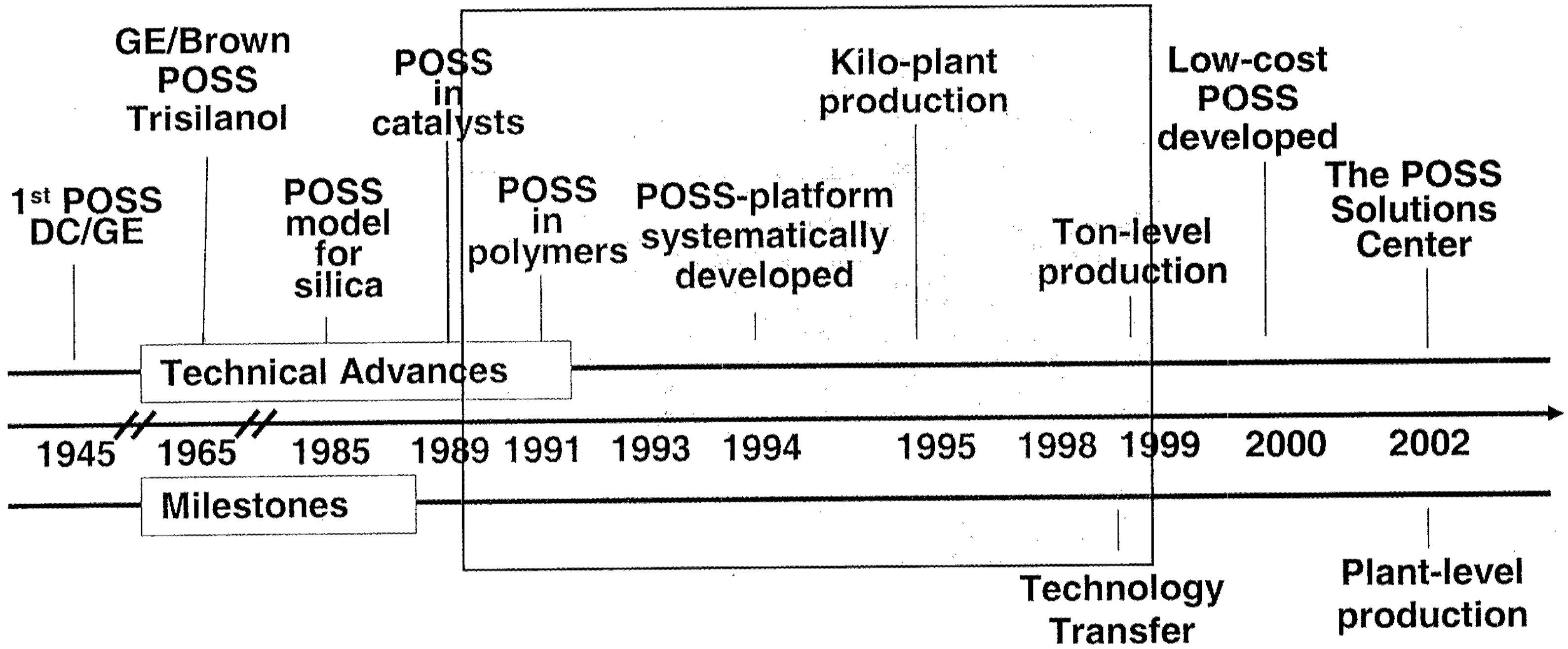


R = *i*-Butyl, Et



Reverse Scale-up?

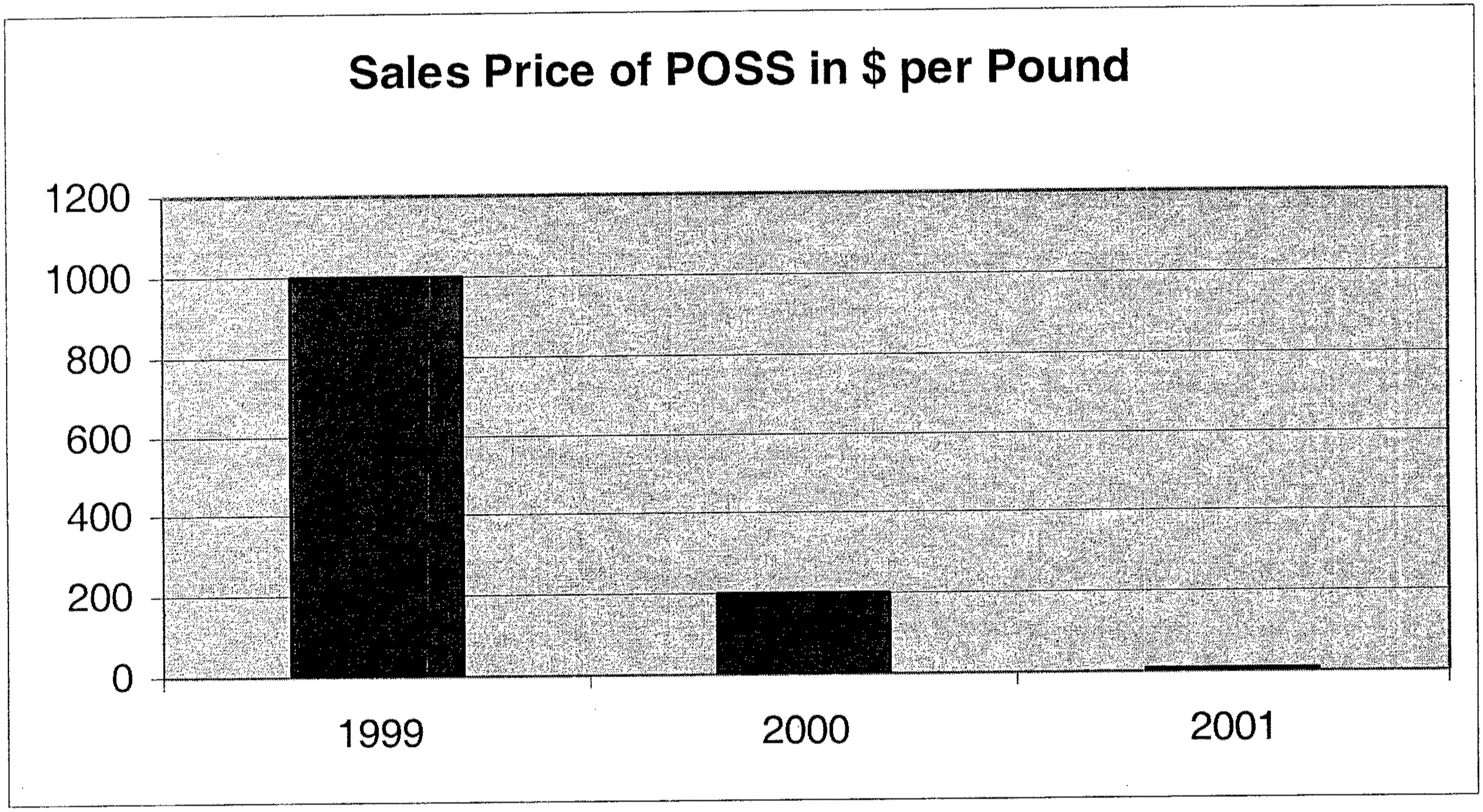




- 1992 AFOSR Funding of AFRL/PRSM
- 1992 AFRL Funding of AFRL/PRSM
- 1994-1998 Numerous NDAs, small funding to Universities
- 1994-??? Over 8 SBIRs focused on POSS Applications
- 1997 AFOSR funds academics for POSS research
- 1998 CRADA
- 1998 Multi-Million dollar ATP Grant for price reduction

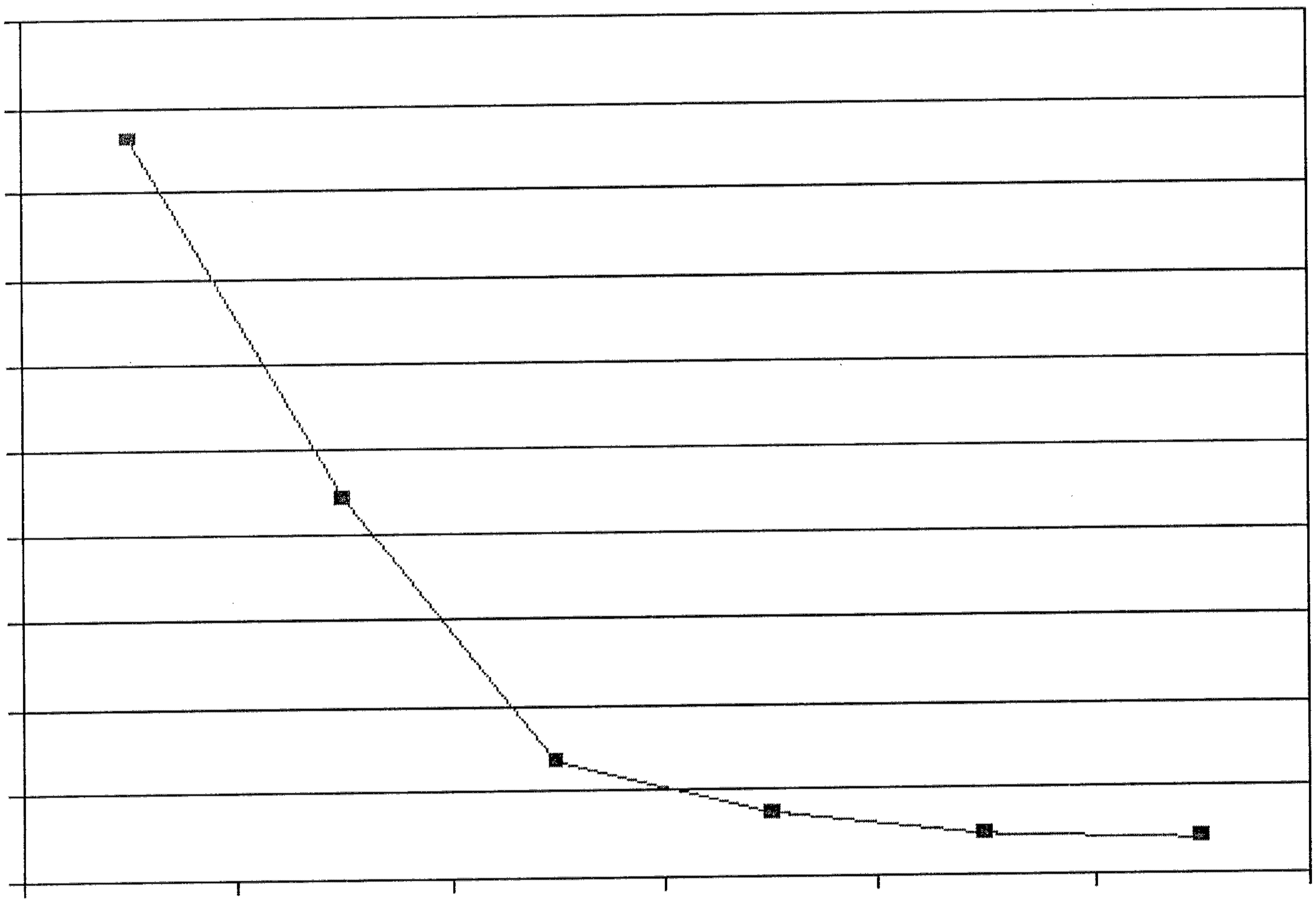
Leveraging DOC program

NIST ATP Funded Cost Reduction

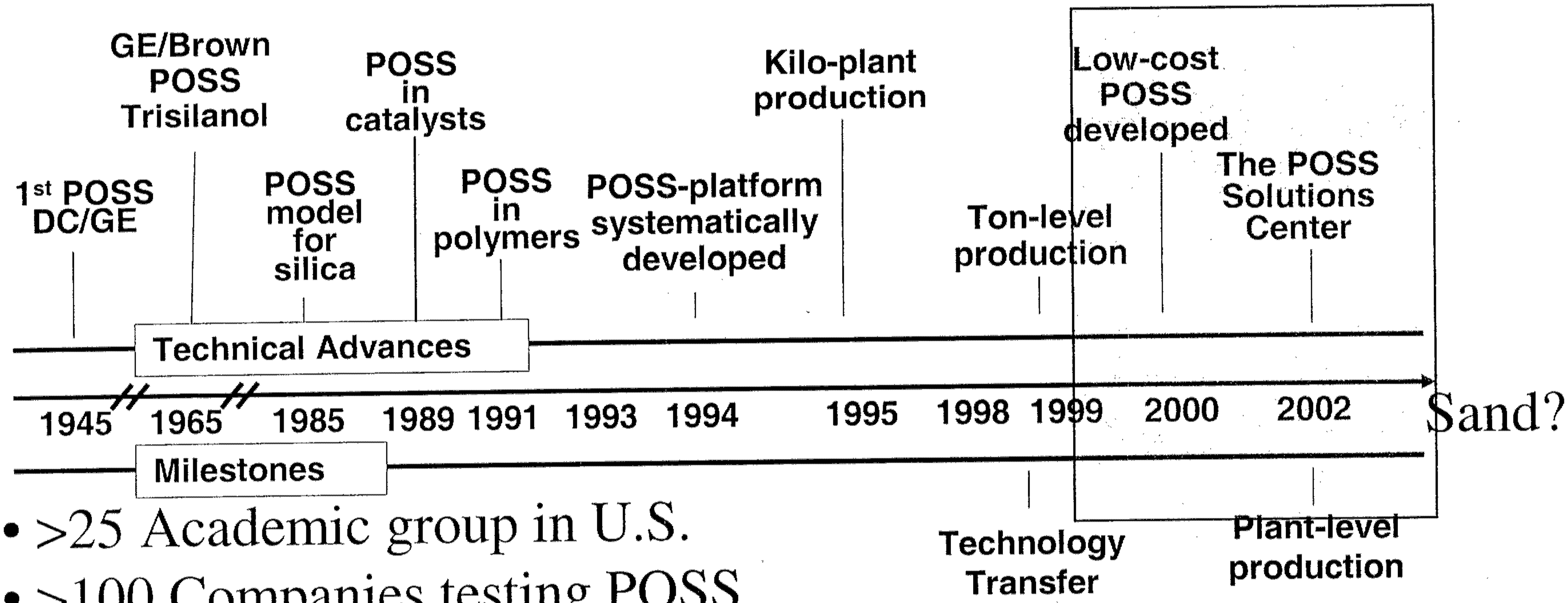


Hybrid Plastics™

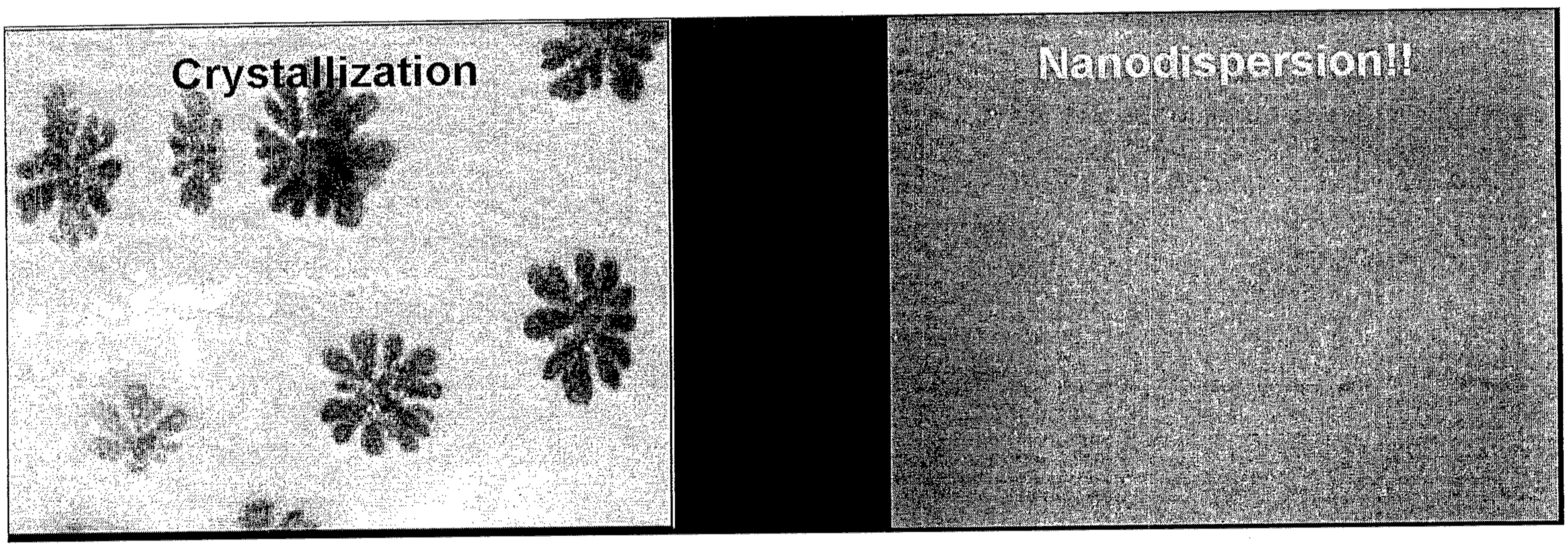
Combined Material & Labor Costs Relative to Volume



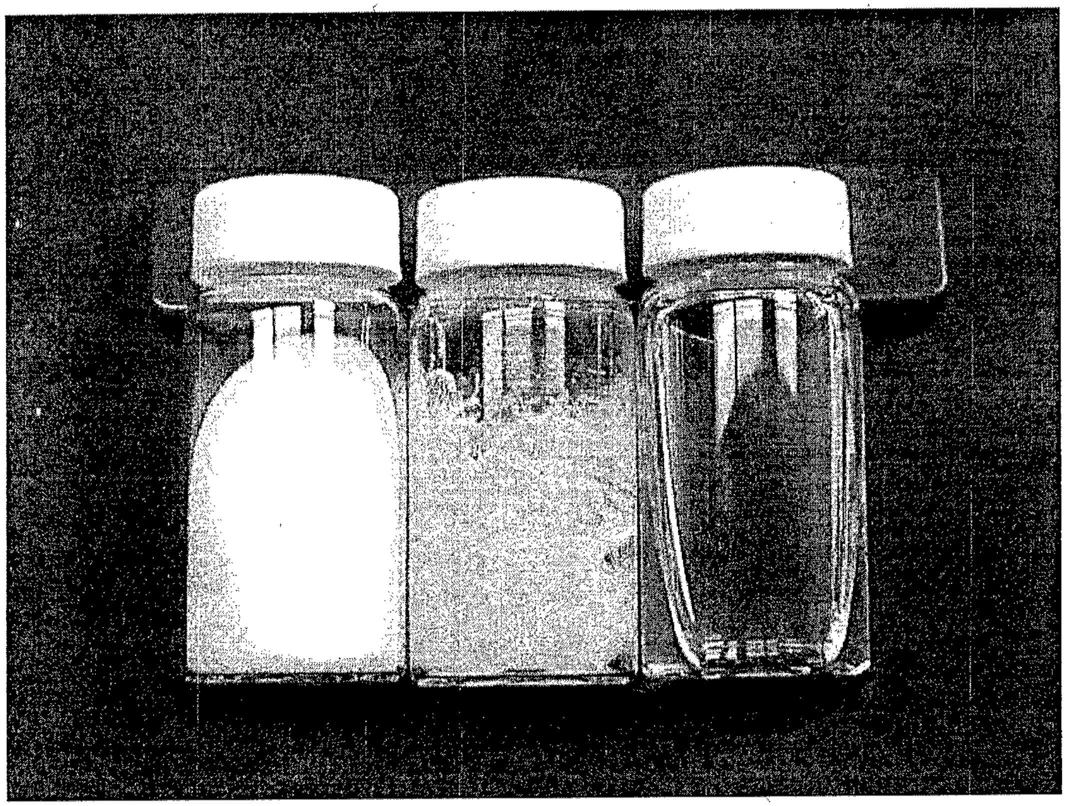
Regression analysis for POSS™ manufacturing process.



- >25 Academic group in U.S.
- >100 Companies testing POSS



Nanostructured™ POSS Chemicals Physical Form of Products

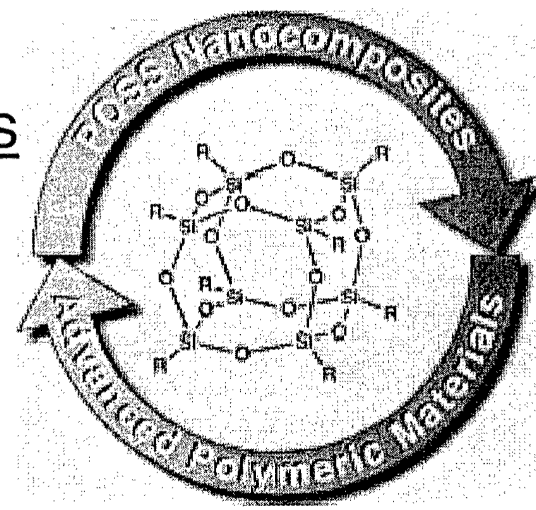


Crystalline Solids	Waxes	Liquids & Oils
Wide melting range 24°C to 400°C+		Wide viscosity range 40cSt. to 400cSt

Hybrid Plastics™

POSS™ Applications: Now Leveraged Primarily by Tech Transfer Company

R&D Through Market Development



R&D Chemicals and Nanotechnology Markets

Aldrich Chemical Co.
Gelest Inc.
Hybrid Plastics

Monomers & Polymers

Aerospace
Electronics
Medical
Composites
Packaging

Blendable Agents

Viscosity Modifiers
Processing Aids
Fire Retardants
Performance Additives
Corrosion Resistance

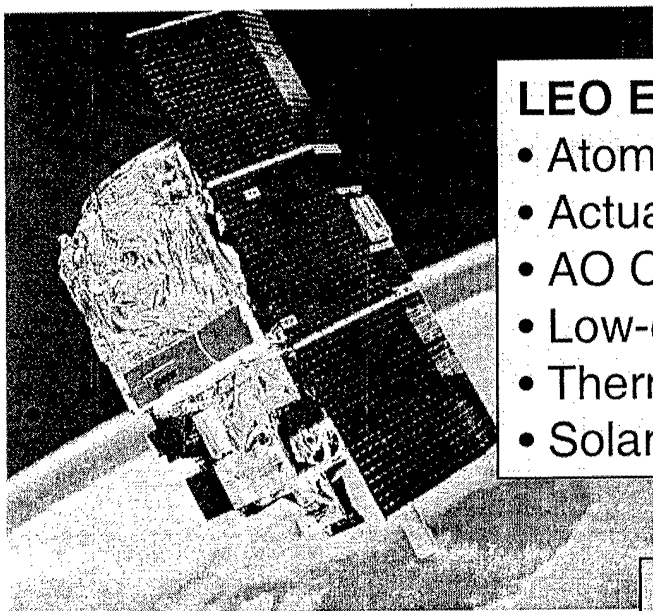
Catalysis

Metathesis
Epoxidation
Ligands
Supports

Biology & Agriculture

Drug Delivery
Medical Prosthetics
Pharmaceuticals
Antifungal Agents

Space-Survivable Polymers



Satellites & Space Systems

LEO Environment (Altitudes of 200 to 1500 km)

- Atomic Oxygen (AO): ~10^8 atoms/cm^3
- Actual AO flux on spacecraft ~10^{15} atoms/$cm^2 \cdot s$
- AO Collision energy ~ **5eV**
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar VUV and UV radiation (~ 150 – 400 nm).

Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
Si-O	8.3	150	Nanocomposite

Objectives

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

Tri-collaborative Effort for Proposed High-Risk, High-Payoff Program (Industry, Academia & Government)

Hybrid Plastics™

POSS-Aniline Synthesis.
Scale up and Validation.

DARPA

UNIVERSITY OF FLORIDA / **MONTANA STATE UNIVERSITY** BOZEMAN

Space Survivability Testing:
Includes erosion yields, surface Topographical, and in-situ analysis of POSS polymers following atomic oxygen and vacuum ultraviolet radiation exposure .

Michigan State University

Thermal, mechanical, and dielectric Properties of POSS-polyimides.

AIR FORCE RESEARCH LABORATORY

POSS-Polymeric Materials Group
Materials Application Branch
AFRL, Edwards AFB

Efficient cost effective POSS-Aniline Monomer and POSS-Polyimide Synthesis.
Development, characterization, and testing of POSS-Polyimide composite materials with high temperature stability and space survivability.

tsi TRITON SYSTEMS INC

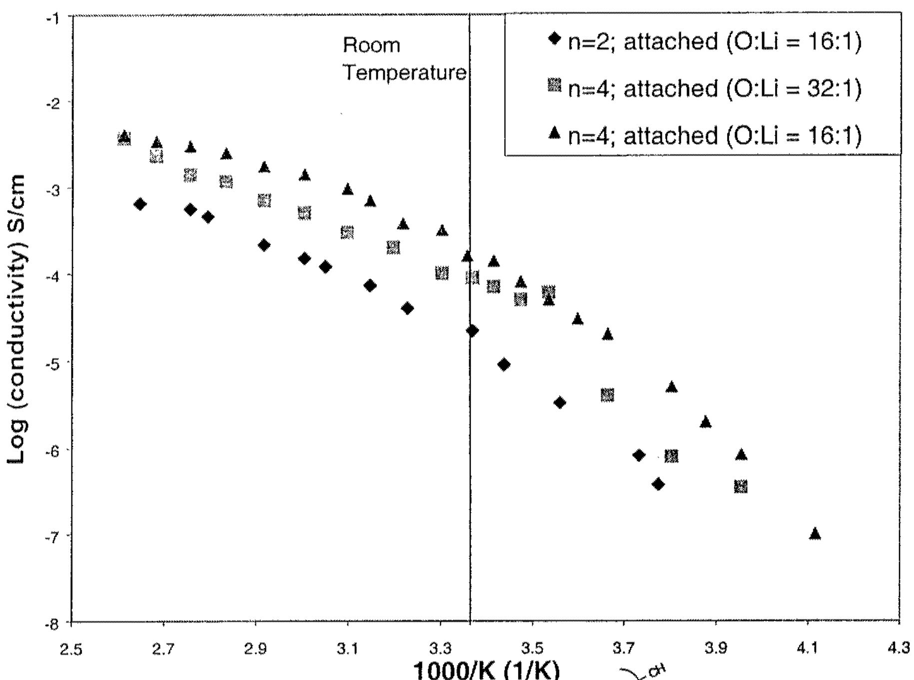
POSS Incorporation in Triton's High Performance Polyimide Resins: Triton RTM PMR polyimides and NASA and Triton's co-developed Phosphine Oxide Polyimides.
Scale up and Validation.

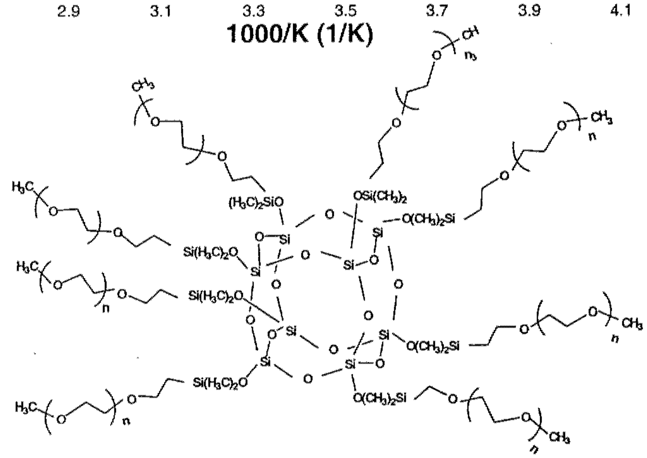
THE AEROSPACE CORPORATION

Space Survivability Testing:
Includes simulated GEO exposure and mechanical property testing prior to and following exposure.

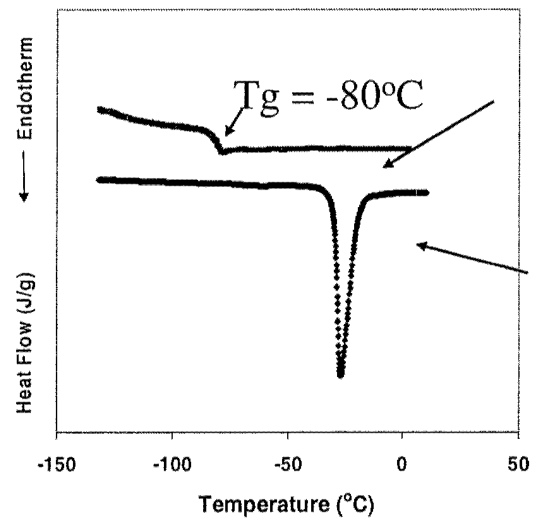
Stephanie Wunder-POSS Based PEO Electrolytes for Li Ion Batteries

Conductivity of $Q_8M_8^{PEO(n)}$ and $LiClO_2$





DSC Data: Crystallinity completely suppressed on attachment of PEO(n=4)



σ of PEO at RT is ~ 10^{-5}

σ goal for PEO-based solid polymer electrolytes is 10^{-3}

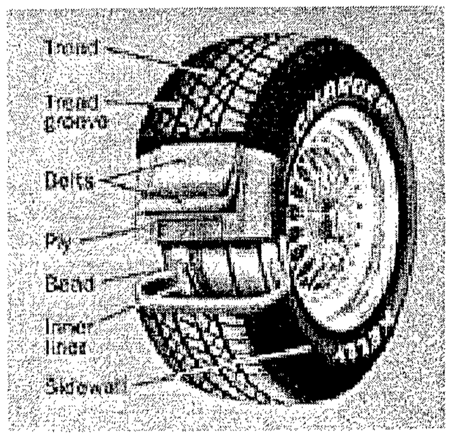
POSS Conference 2002

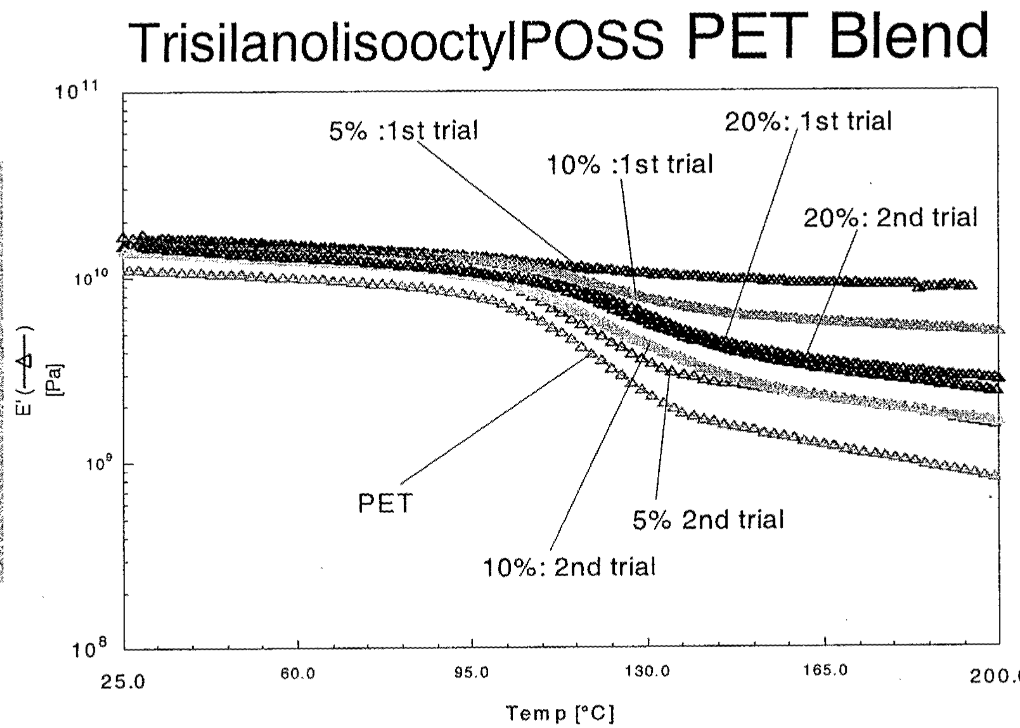
Dave Scheraldi: POSS PET

Tires are typically Reinforced with PET Fabrics

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

Internal Tire Temperature
~ 120° C





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

Masanori Ikeda: Flame resistant POSS PPE

Asahi-KASEI Corporation: Hybrid Plastics Asian Distributor

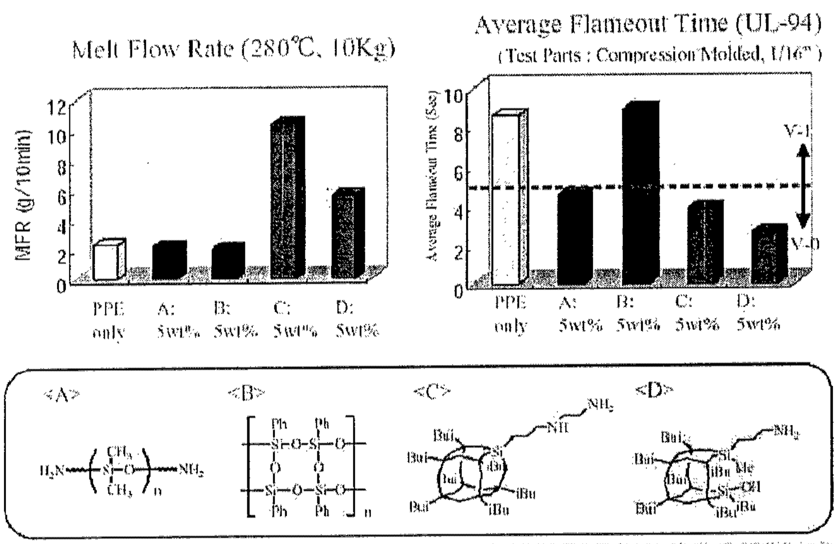


Figure 8. Effects of Additives on MFR and Anti-Flammability

(UL-94 Test).

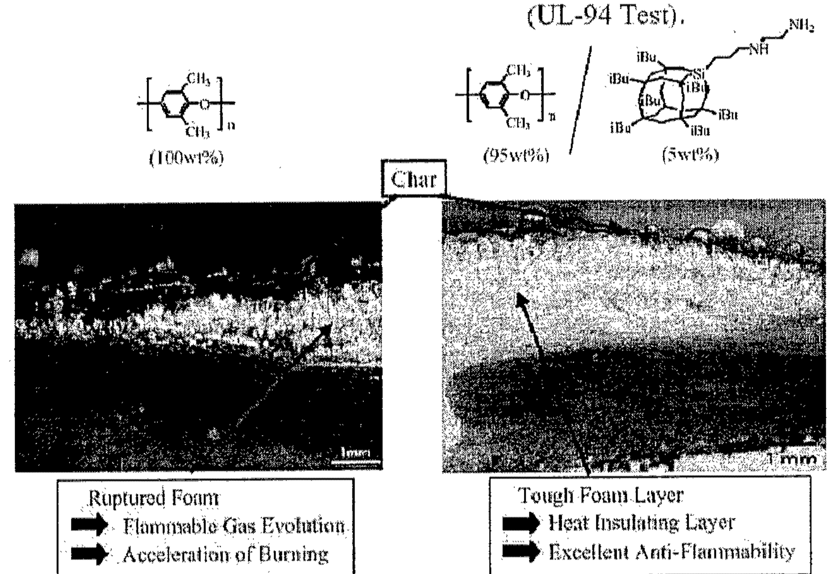
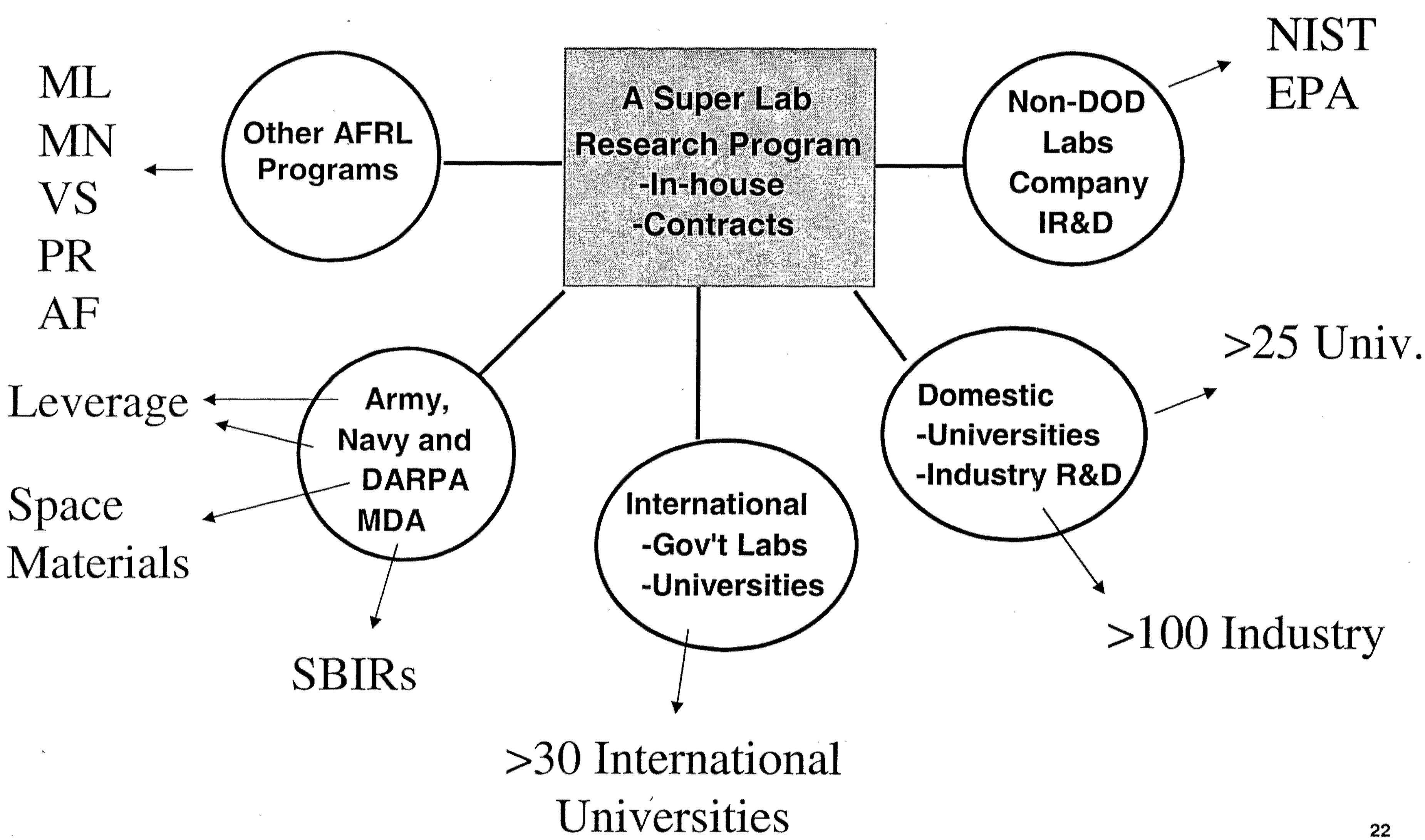


Figure 10. Cross Section Photograph of Burned Test Piece

Isobutyl POSS cage in PPE gives:
superior flame retardance
imparts superb processability
excellent HDT is maintained

POSS Conference 2002

A Super Lab Created from the Ground Up



Collaboration Tools Employed

- Cooperative Research and Development Agreements
- Research and Agreements
- Small Business Development Centers
- Memorandum Agreements
- Confidentiality Agreements
- Contractual and Subcontractual Agreements
- Termsheets
- Option Agreements
- Assignment, Patent, and Licensing Agreements

Keys to Success for the POSS™-Team

(1) Committed Team - shared interests

(2) Talented People - persistent and skilled

(3) Clear Common Goals - cost & simplicity

(4) Communication - weekly

(5) Flexibility - find and reinforce success

(6) Resources - finances and facility

(7) We all had something to gain!!!

What did the Air Force Gain?

- **Sustainment of technology for DoD**
- Increased leverage of 6.1/6.2 IR&D funding
- Additional external customer funding
- Increased technical competency

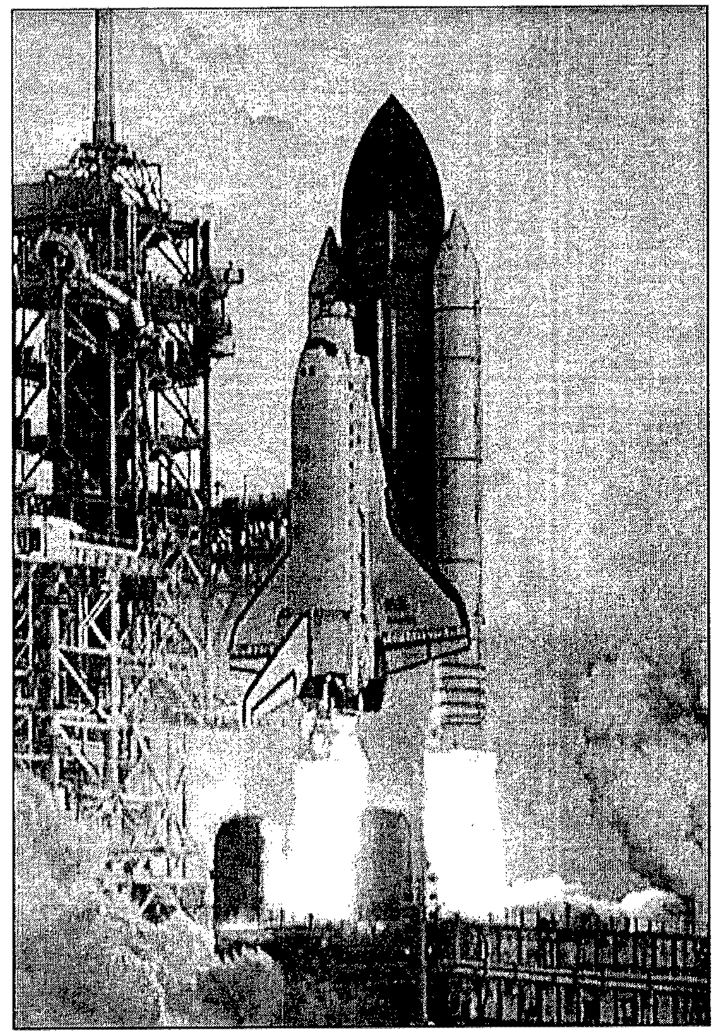
Events Facilitating the Collaboration

1991-1998: Collaboration history between UCI and the Air Force
1996: Assignment of initial POSS patents to UDRI
1996: Execution of a conduit (third party client) CRADA to UDRI
1997: Significant increase of commercial interest in POSS
1998: Creation of a commercial spin-off (Hybrid Plastics)
1998: Award of $2M NIST ATP grant to Hybrid Plastics
1998: Execution of a conduit CRADA between AFRL and HP
1999: WTN completes commercialization report
2000: POSS™ receives FLC Technology Transfer Award
2000: POSS™ receives R&D Top 100 Award
2001/2: POSS-Team receives Council of Chemical Research Award

Rapid Densification of Carbon-Carbon: A Similar Story

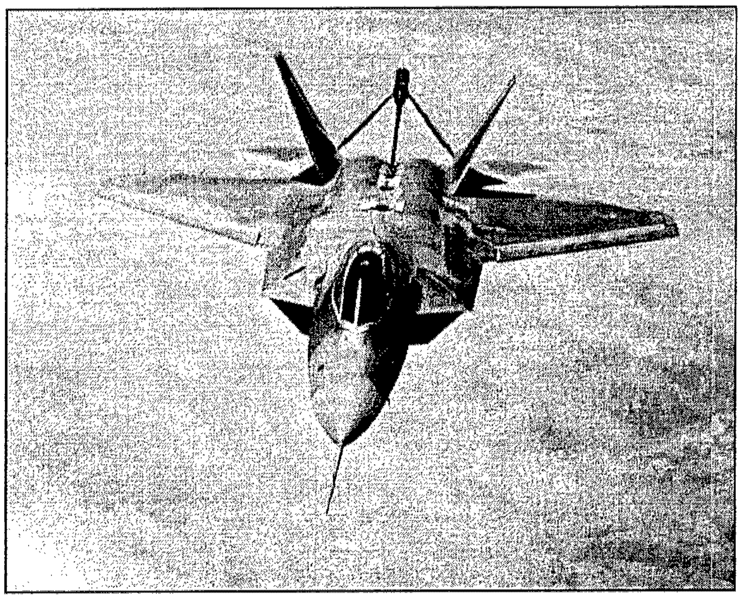
2001 FLC Technology Transfer Award!

- Carbon-Carbon Advantages
  - Excellent High Temperature Structural Material
  - Very Reliable in Rocket Nozzles, Exit Cones, Nosetips, and Leading Edges As Well As Aircraft Brakes
- Drawbacks to Carbon-Carbon
  - SOTA Production of Carbon-Carbon Is Very Expensive
  - Carbon-Carbon Oxidizes at High Temperature in the Presence of Oxidizers

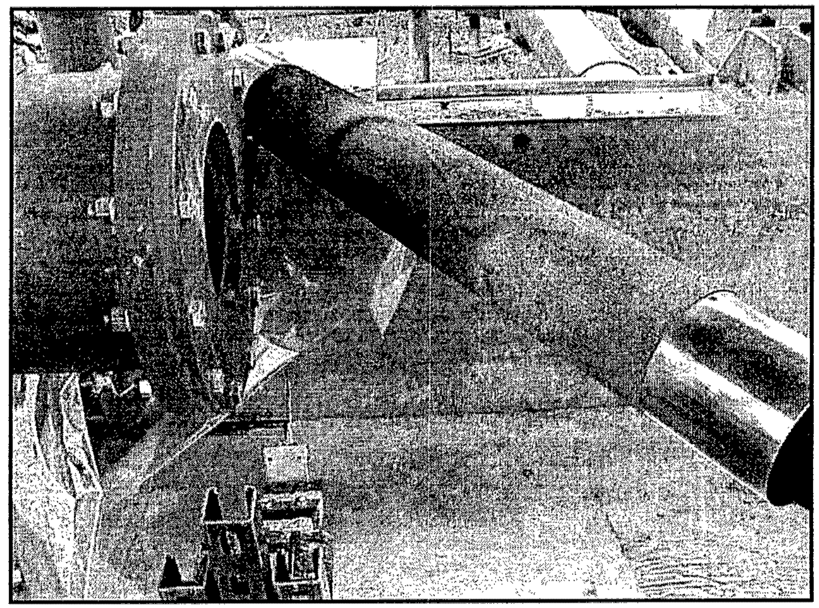


Objectives

- Decrease the processing time of Carbon-Carbon composites from many months to less than two weeks.
- Cut the densification cost in half.



F-22



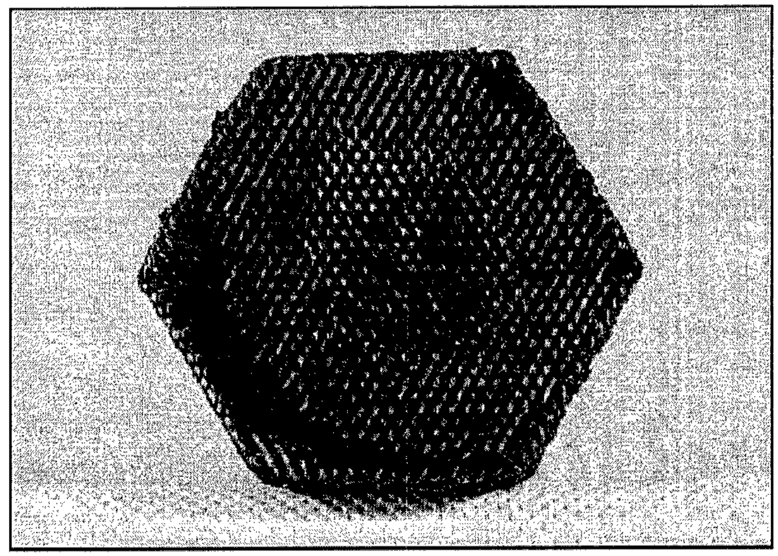
Protective Sleeve for Spin-arrest Parachute

Rapid Densification of Carbon-Carbon

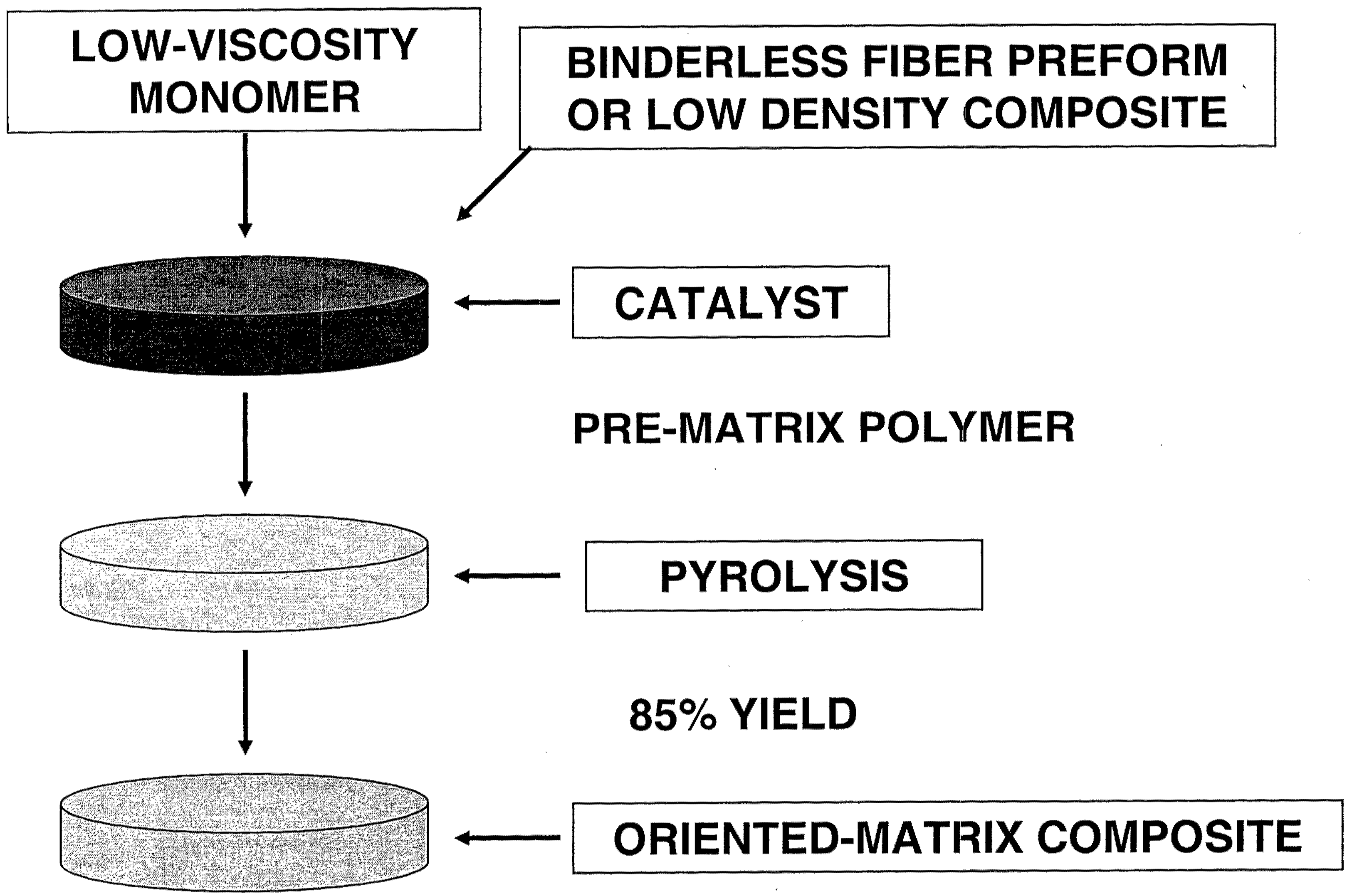
<u>Technical Challenge:</u>

- With Conventional Liquid Phase Processes There Is Incomplete Penetration of the Liquids Due To:
  - a.) High Viscosity
  - b.) High Surface Tension
  - c.) Gassing of Precursor

- With Gas Phase Processes There Is Incomplete Penetration of the Gases Due to Their Decomposition on the Outer Surface

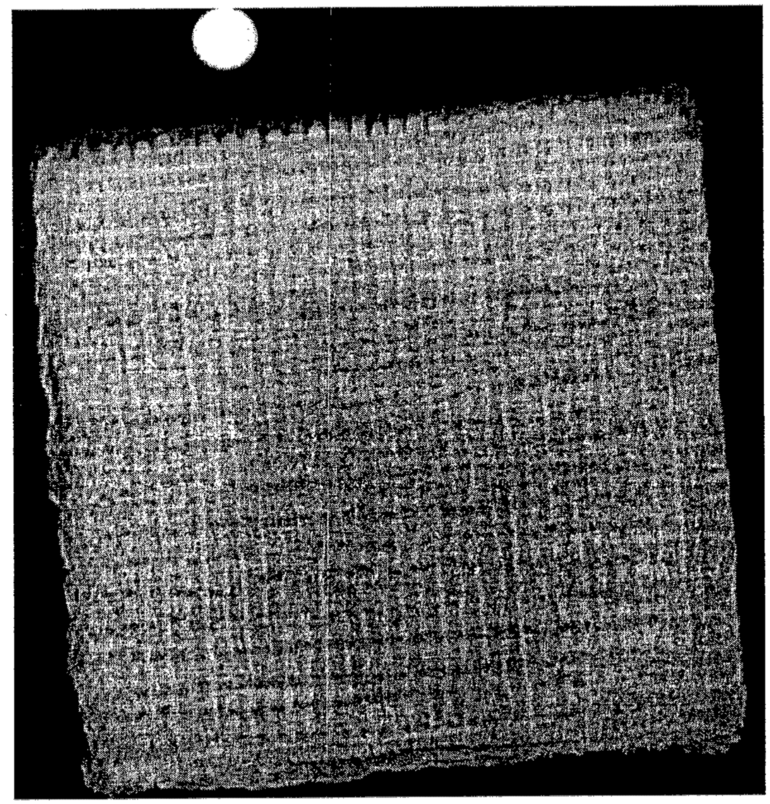


In-Situ Formation of Carbon and Ceramic Matrices



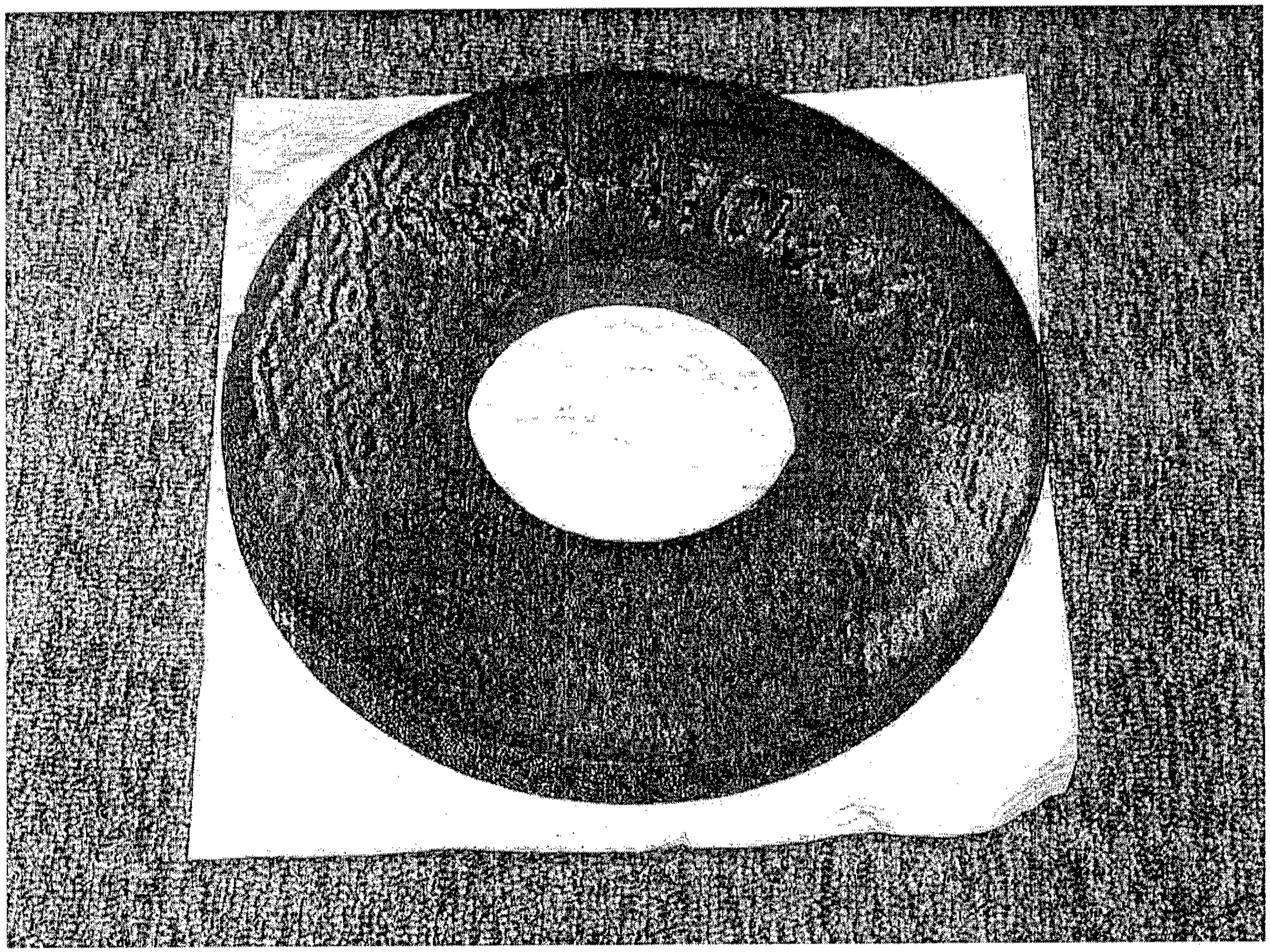
Process Advantages & Recent Success

- Very Uniform Density
- Can Densify Thick Composite
- Complex Geometries
- No Need to Graphitize
- No Need to Machine Outside of Billet



•This is a CAT Scan of the middle of a 10" cubic block of carbon-carbon for the PBCS that has been densified with two In Situ cycles. Density variation is ± 2%

In Situ Densification Accomplishments (F-16 Brake)



70% of World C-C brake market is being worked with!

Does all this hard work pay off?

- 2 Generation Leap for U.S. Propulsion
- Numerous programs to aid the Warfighter
- Dramatic reduction in cost due to commercialization
- Royalties for the researchers!!!!