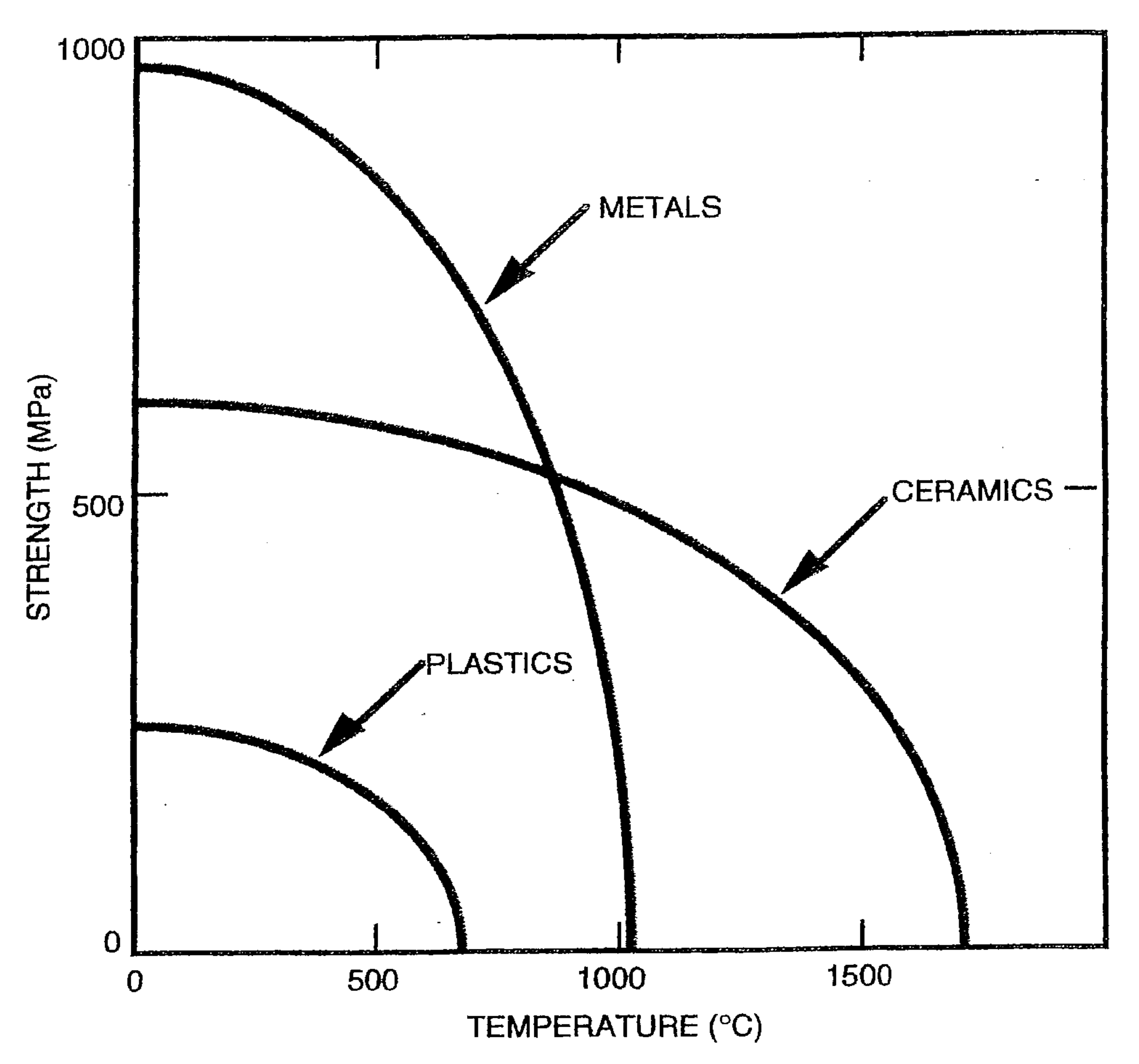
Introduction to Preceramic Polymers

Alexander Lukacs

Approximate Ranges of Usefulness for Structural Materials



Why use Preceramic Polymers?

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- **Traditional ceramic processing methods (Powder) are shape-limiting and not amenable to CMC fabrication**
- **Tough, non-crystalline ceramic compositions are possible**
- **Homogeneous, nanoscale ceramic compositions can be achieve that demonstrate ultra-high temperature durability**

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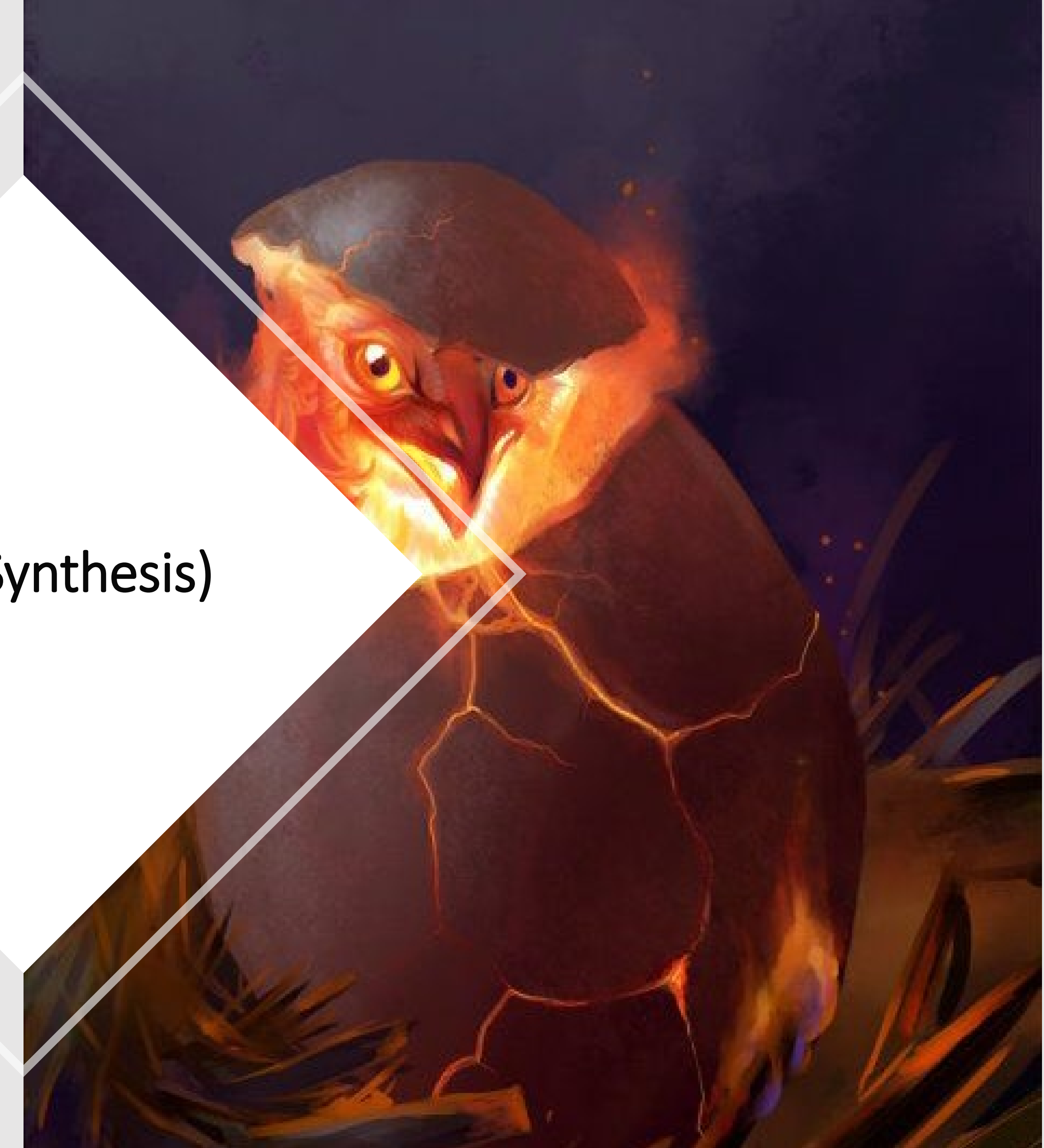
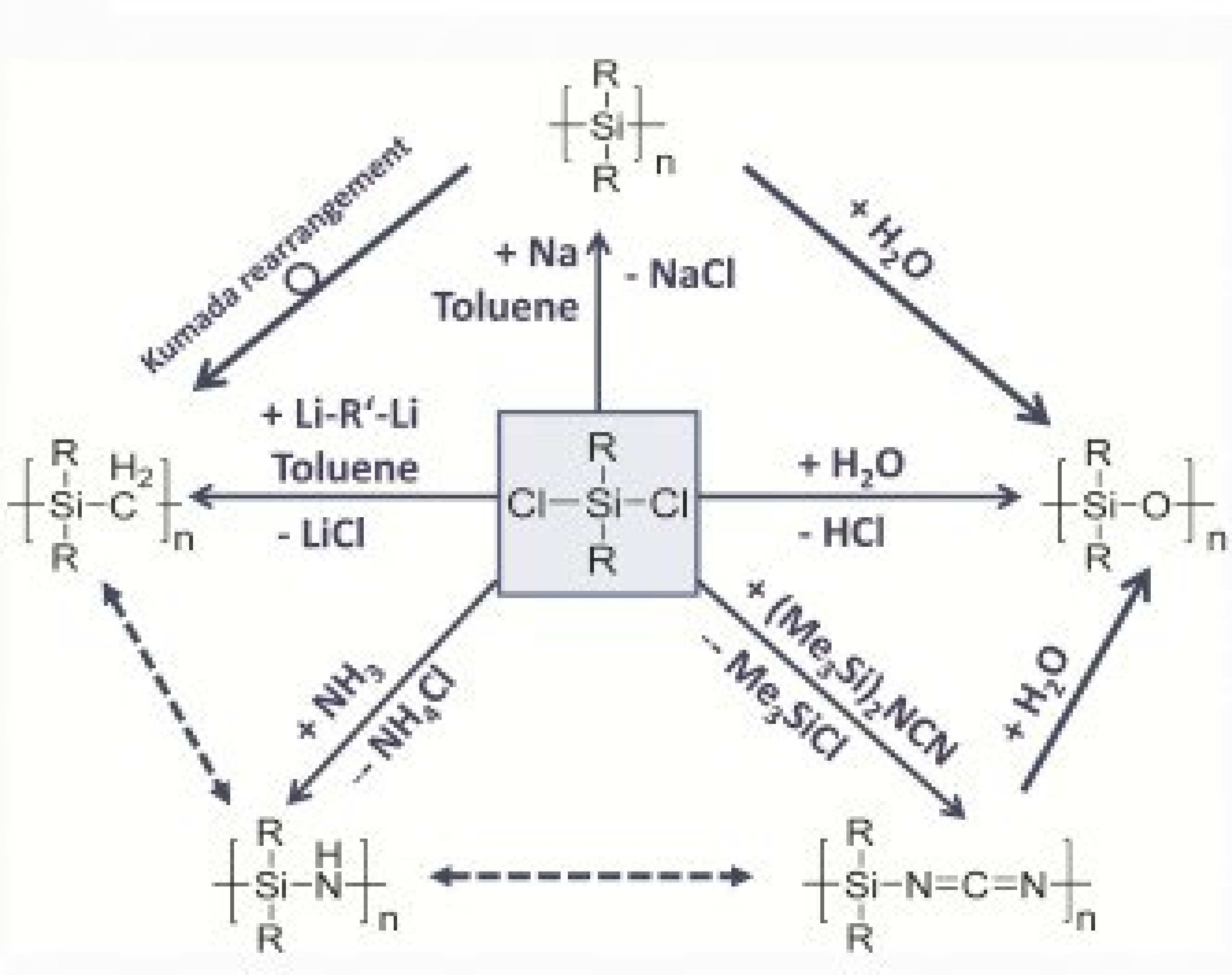
Birth (Synthesis)



Synthesis of Most Commonly Used Silicon-Based Preceramic Polymers



Preceramic Polymer Requirements

- Sufficiently HIGH MOLECULAR WEIGHT – minimizes volatilization during pyrolysis (2,000 – 10,000 daltons)
- Polymeric structure containing CAGES or RINGS – minimizes volatilization during pyrolysis
- Suitable RHEOLOGICAL PROPERTIES and SOLUBILITY (for solid polymers) – to enable shaping processes

Preceramic Polymer Requirements (cont.)

- LATENT REACTIVITY – to enable thermoset or cure prior to pyrolysis
- For CMC Fabrication, SOLVENTLESS LIQUID PRECURSORS are desirable – to enable Polymer Infiltration Pyrolysis processing
- For NON-OXIDE ceramics, all but the most exotic preceramic polymers are SILICON-BASED

Utility of Ceramics Derived from Si-Based Preceramic Polymers

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Ceramic Compositions	General Applications
SiOC	Cost-Sensitive and Moderate Temperature Applications
SiCN, SiC	High Temperature Applications

DEATH (Pyrolysis)

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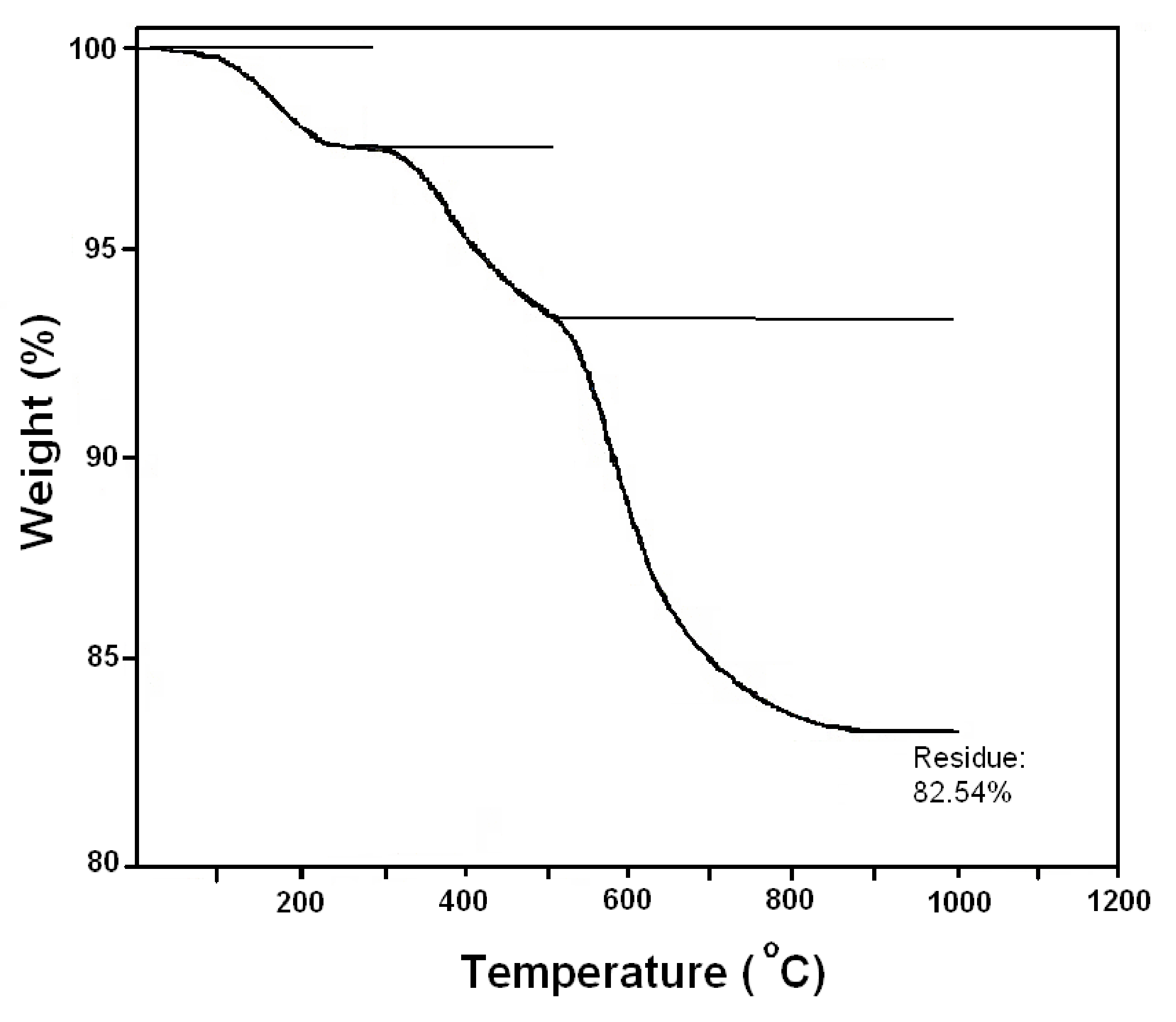
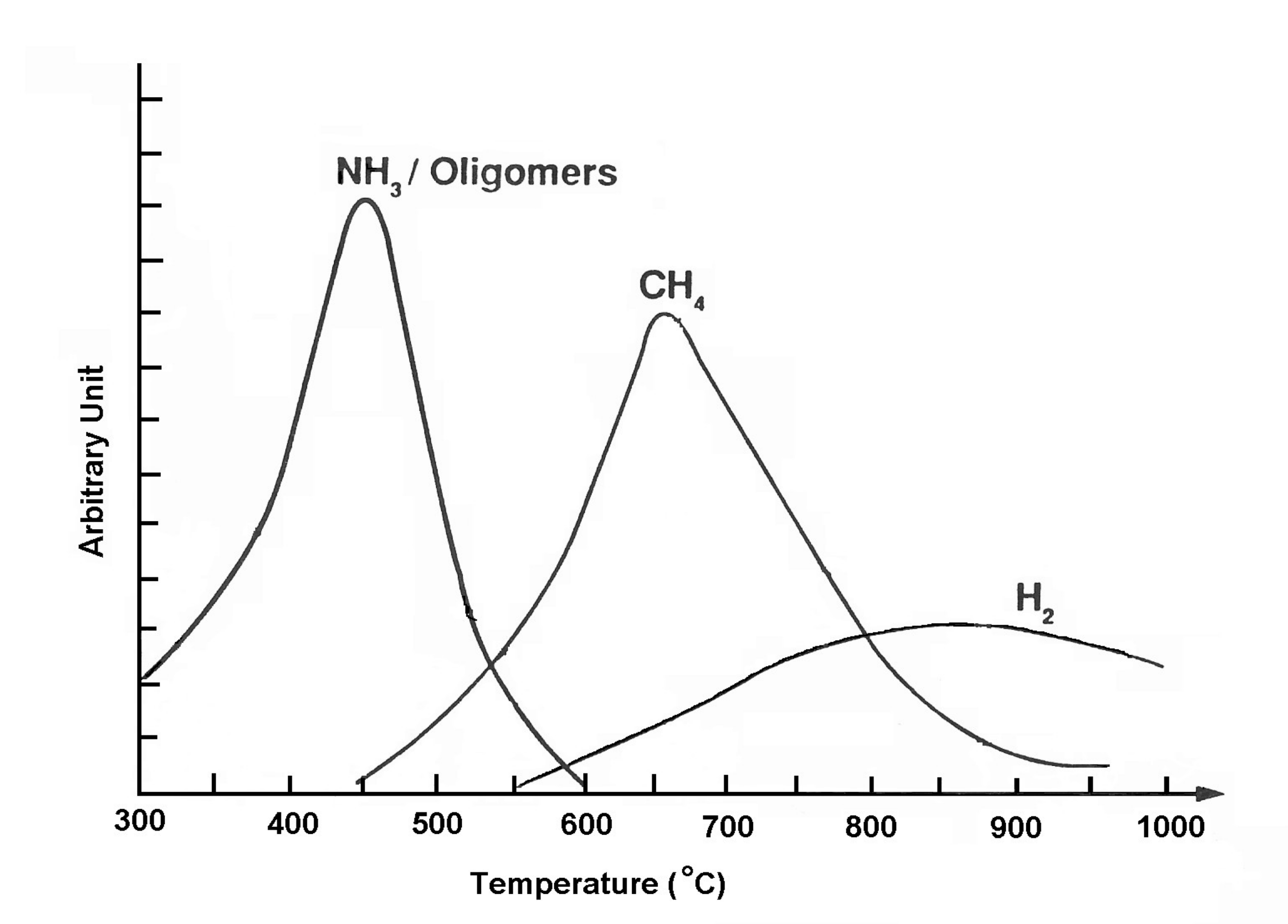
For Example: POLYSILAZANES

TGA Curve for Polysilazane Polymer

1. Oligomers – 2.447% Mass Loss
2. Ammonia – 3.757% Mass Loss
3. Ceramization (Methane and Hydrogen) – 10.22% Mass Loss

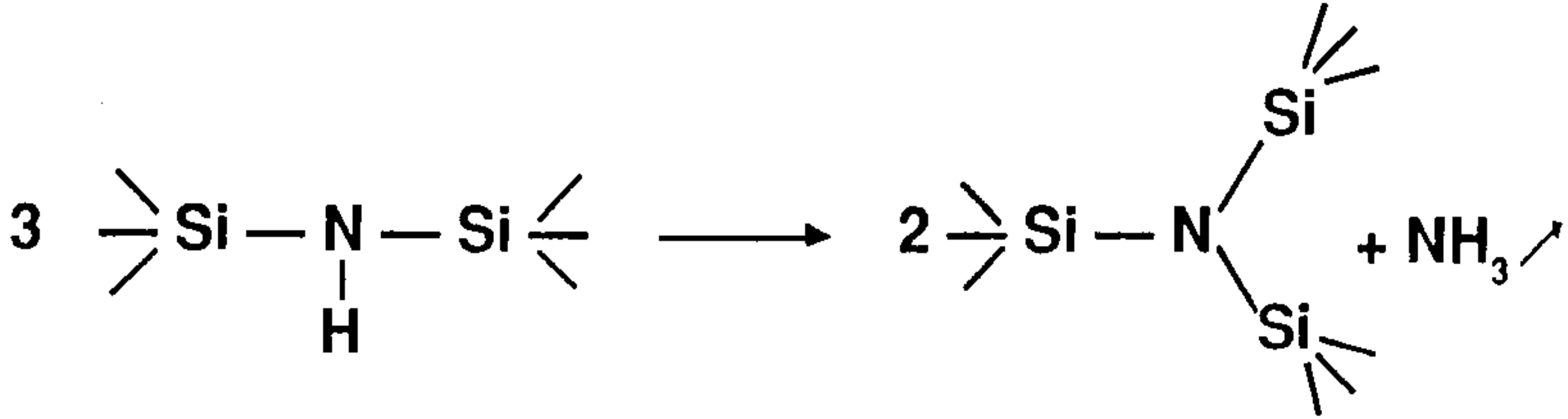


Polysilazane Evolved Gases During Pyrolysis



FIRST STEP : (150 to 450°C)

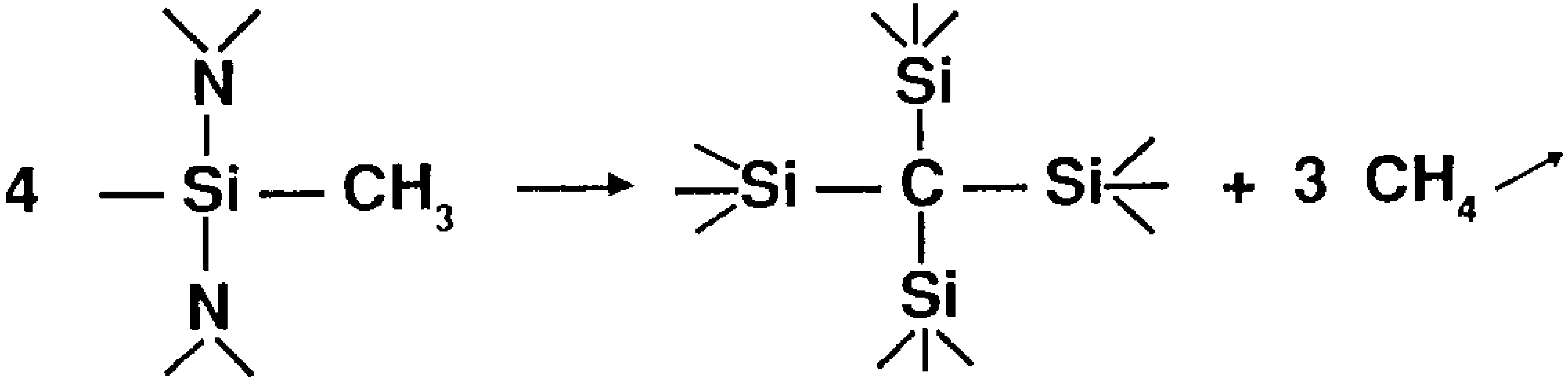
Ammonia and oligomers emission



⇨ CONSOLIDATION OF THE NETWORK

SECOND STEP : (> 500°C)

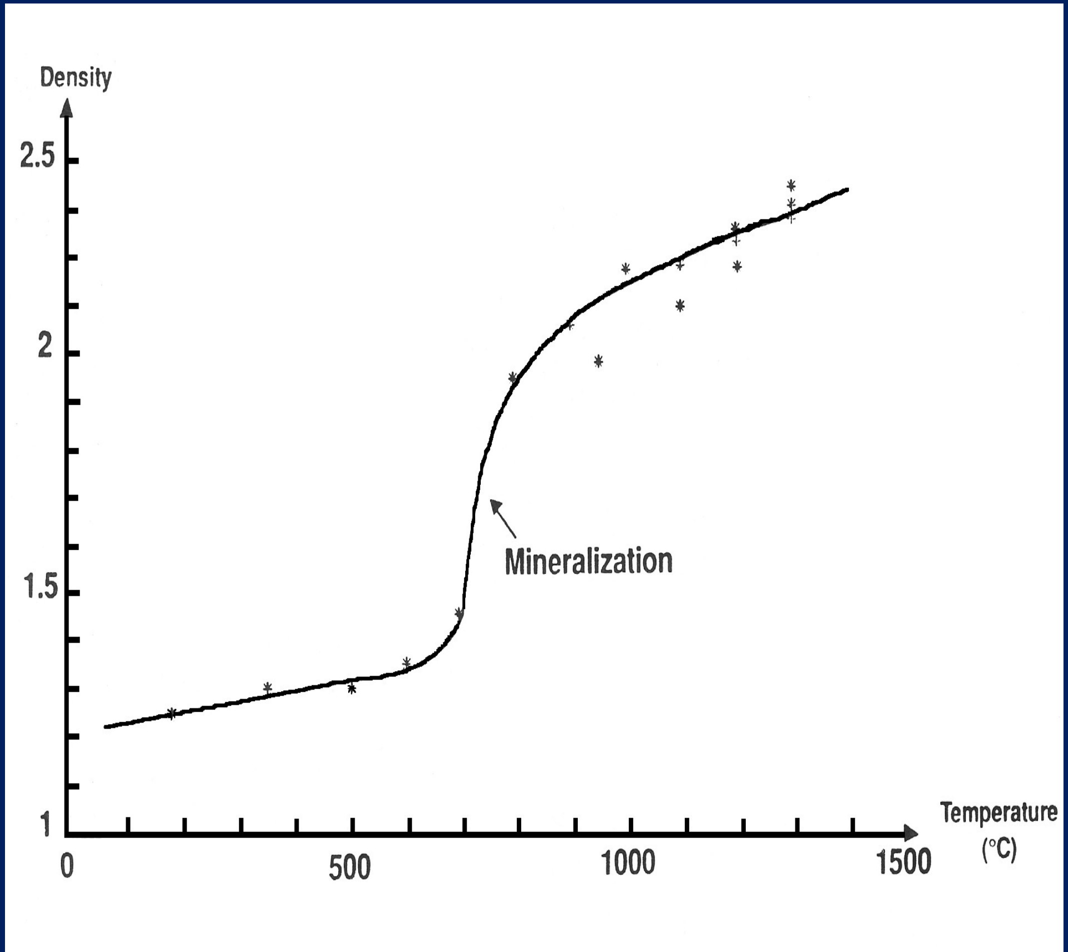
Methane and hydrogen emission



$$CH_4 \longrightarrow [C] + H_2 \nearrow$$

TRANSITION FROM ORGANIC TO INORGANIC MATERIAL

Density Change with Temperature

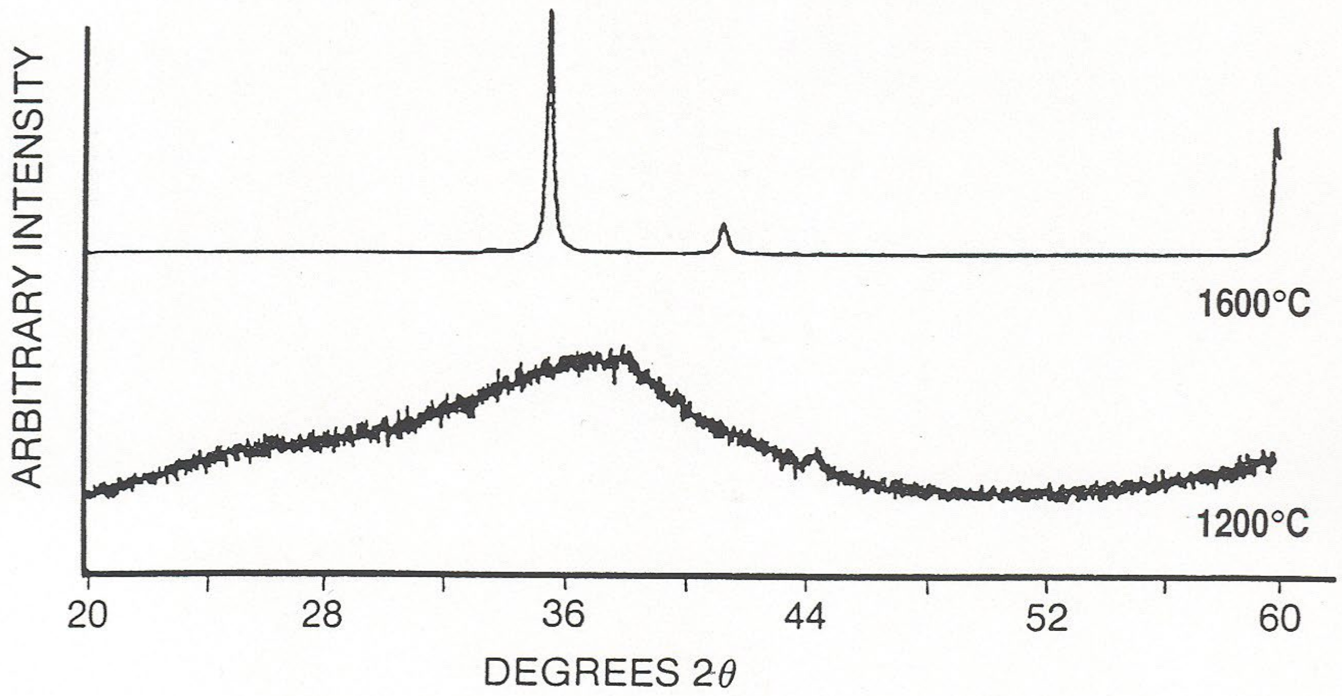


Polymer → X-linked Polymer → Preceramic Network → Amorphous Ceramic → Crystalline Ceramic

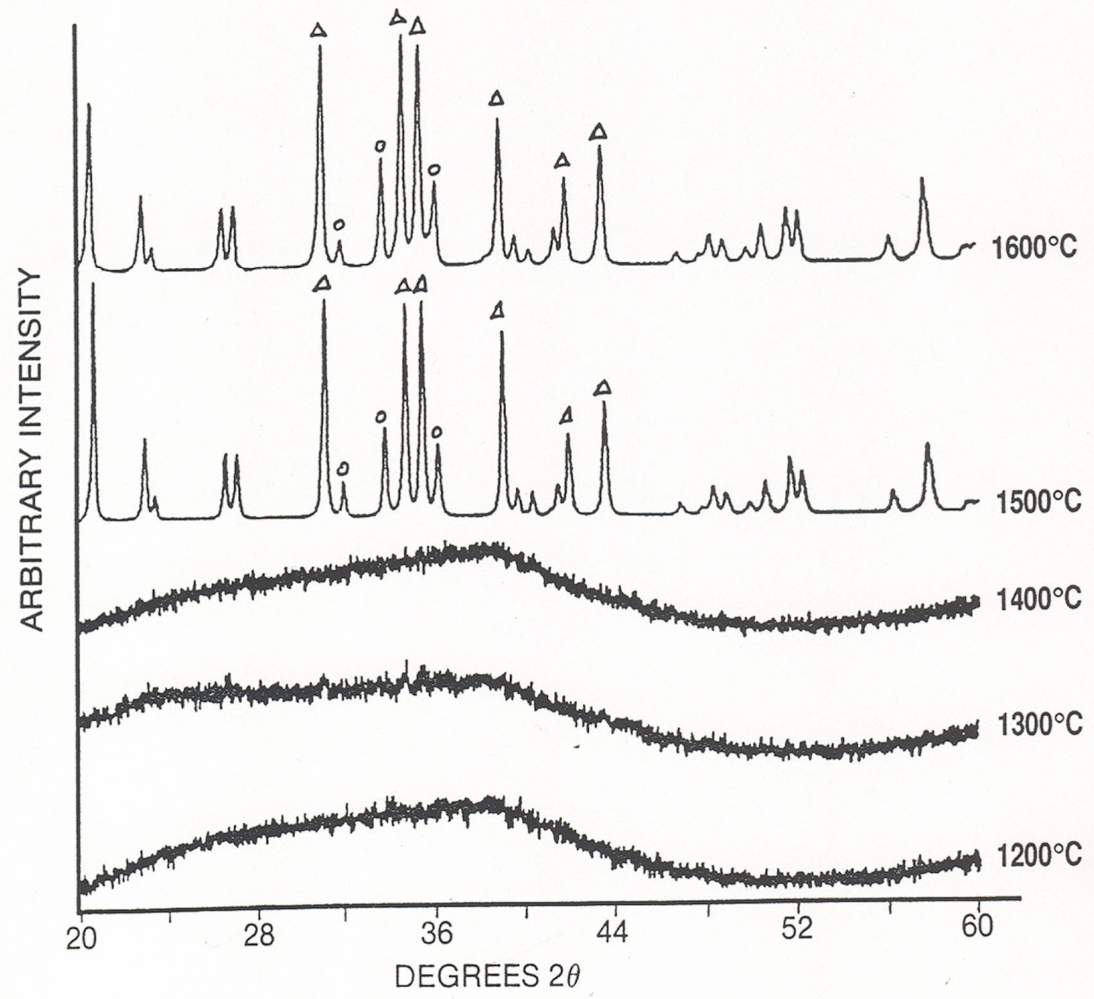
Influence of Pyrolysis Atmosphere on High Temperature (1500 °C) SiCN Crystallization

Pyrolysis Atmosphere	Composition	Crystalline Phases
Argon	SiC	b-SiC
Nitrogen	SiC/Si3N4	a-Si3N4 b-Si3N4
Ammonia	Si3N4	a-Si3N4 b-Si3N4
Air	SiCxNyOz/SiO2	a-SiO2 a-Si3N4

Development of Crystalline Silicon Carbide
Argon Pyrolysis Atmosphere



Development of Crystalline Silicon Nitride Nitrogen Pyrolysis Atmosphere



Comparative Properties of SiCN, SiC, and Si3N4 Ceramics

Property	SiCN	SiC	Si3N4
Density (g/cm^3)	2.35	3.17	3.19
E modulus (Gpa)	80-225	405	314
Poisson’s ratio	0.17	0.14	0.24
CTE (X10^6/K)	~3	3.8	2.5
Hardness (Gpa)	25	30	28
Strength (Mpa)	500-1200	418	700
Toughness (Mpa m^1/2)	3.5	4-6	5-8
Thermal Shock FOM*	1100-5000	270	890

Transfiguration (Part Manufacture)

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Ceramic Part Fabrication from Preceramic Polymers

- Ceramic Monoliths can be produced by “Warm Pressing” Techniques

- CMCs can be produced by Vacuum Bag, Resin Transfer Molding, and Polymer Infiltration Pyrolysis (PIP) using liquid compositions

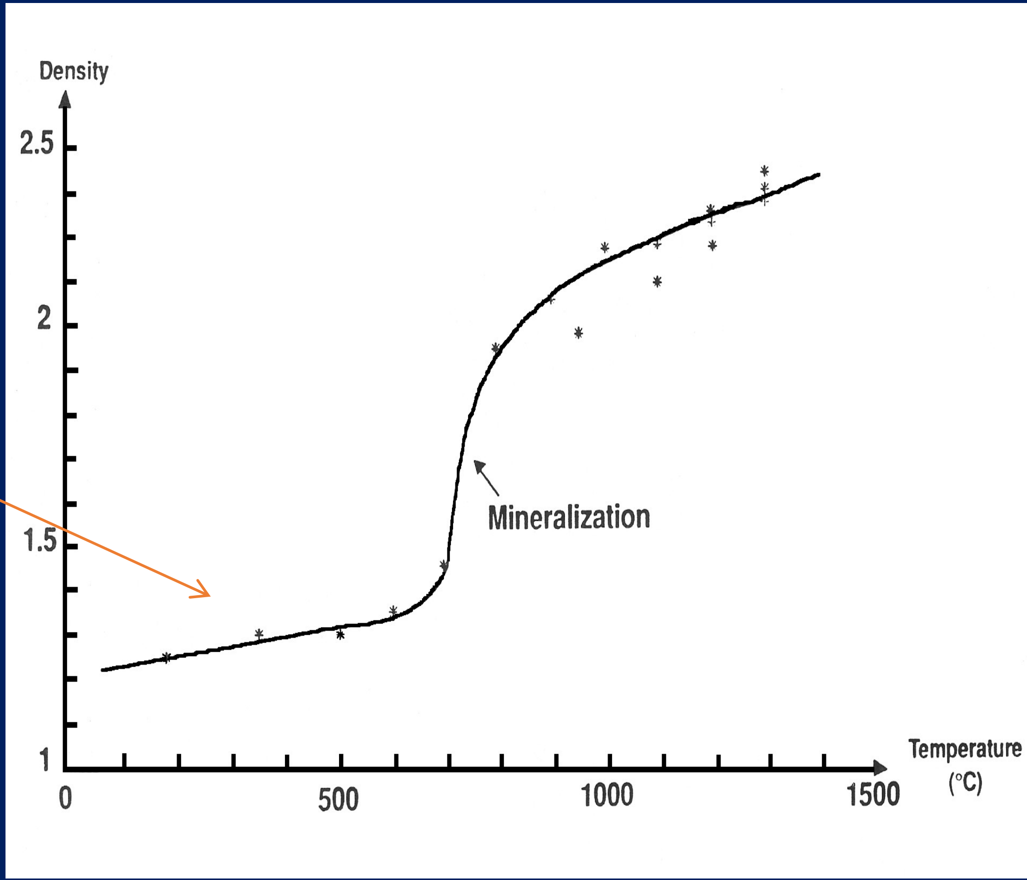
  -Solid Polymer in Solvent

  -Solventless Liquid Polymer

- Applications include: aerospace, automotive, missiles, military, electronics, etc.

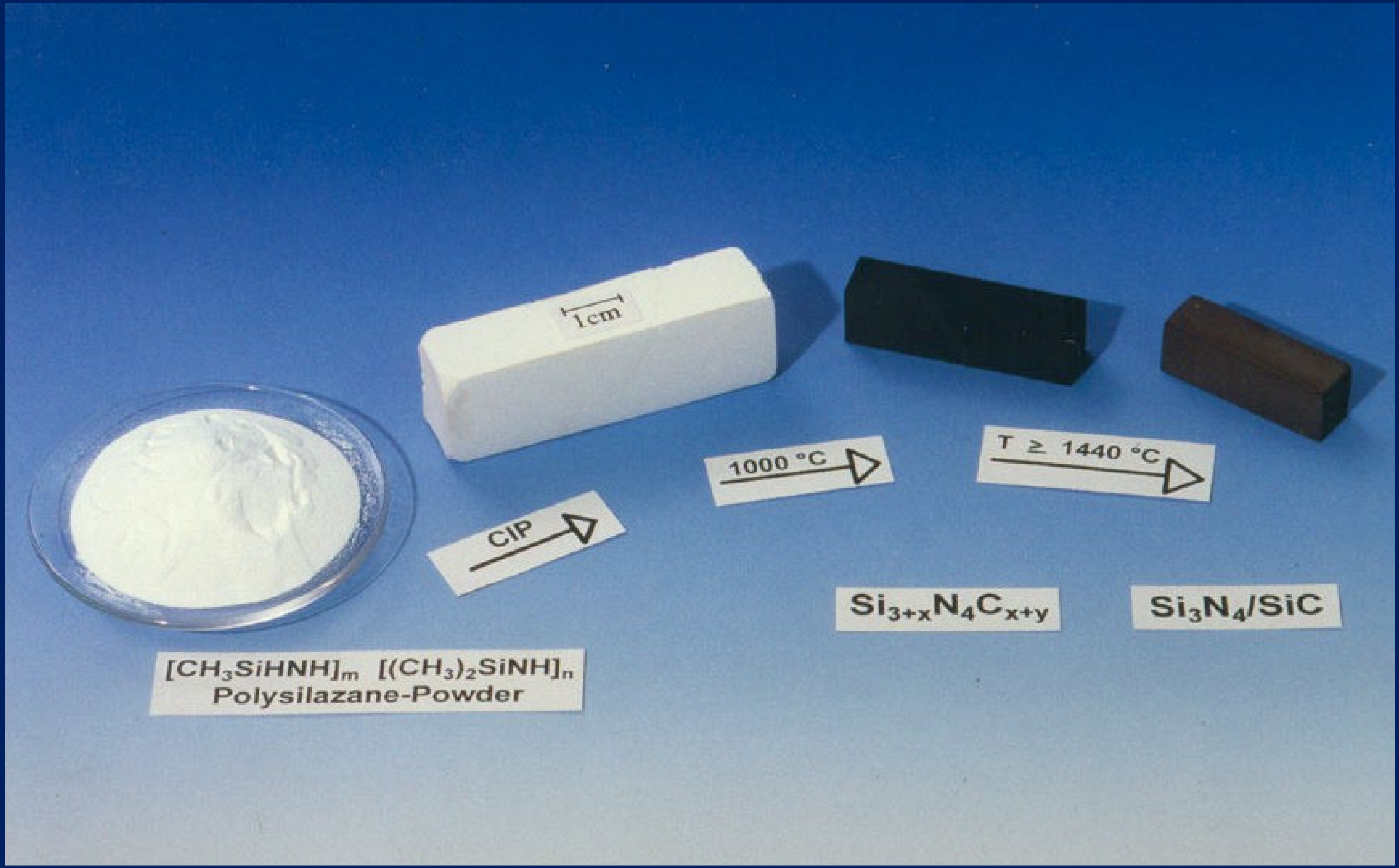
Ceramic Monolith Fabrication Powder "Warm Pressing" Technique

Partially X-linked Polymer Powder



Polymer → X-linked Polymer → Preceramic Network → Amorphous Ceramic → Crystalline Ceramic

Ceramic Monolith Fabrication Powder "Warm Pressing" Technique



Ceramic Matrix Composite (CMC) Fabrication

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- Typically made by Polymer Infilitration Pyrolysis (PIP)
- Infusion of Liquid Preceramic Polymer into continuous fiber preform
- Polymer cure followed by Pyrolysis to Ceramic
- Process is repeated until desired Matrix Density is achieved (typically 6-10 cycles)

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Current Ceramic Applications

a. Ceramic Matrix Composites (CMCs)

b. Ceramic MEMS (Microelectromechanical Systems)

c. Ceramic Coatings

a.Ceramic Matrix Composites (CMCs)

SiOC CMC Applications

- Diesel Particulate Filters
- VOC Remediation/Incineration
- Environmental Monitoring Filters (EPA)
- Structural Insulation for Industrial Processing
- Commercial Airframe Structural Materials
- Radiant Burners

SiCN and SiC CMC Applications

- Aircraft Engine Components

-Defense

-Commercial Aerospace

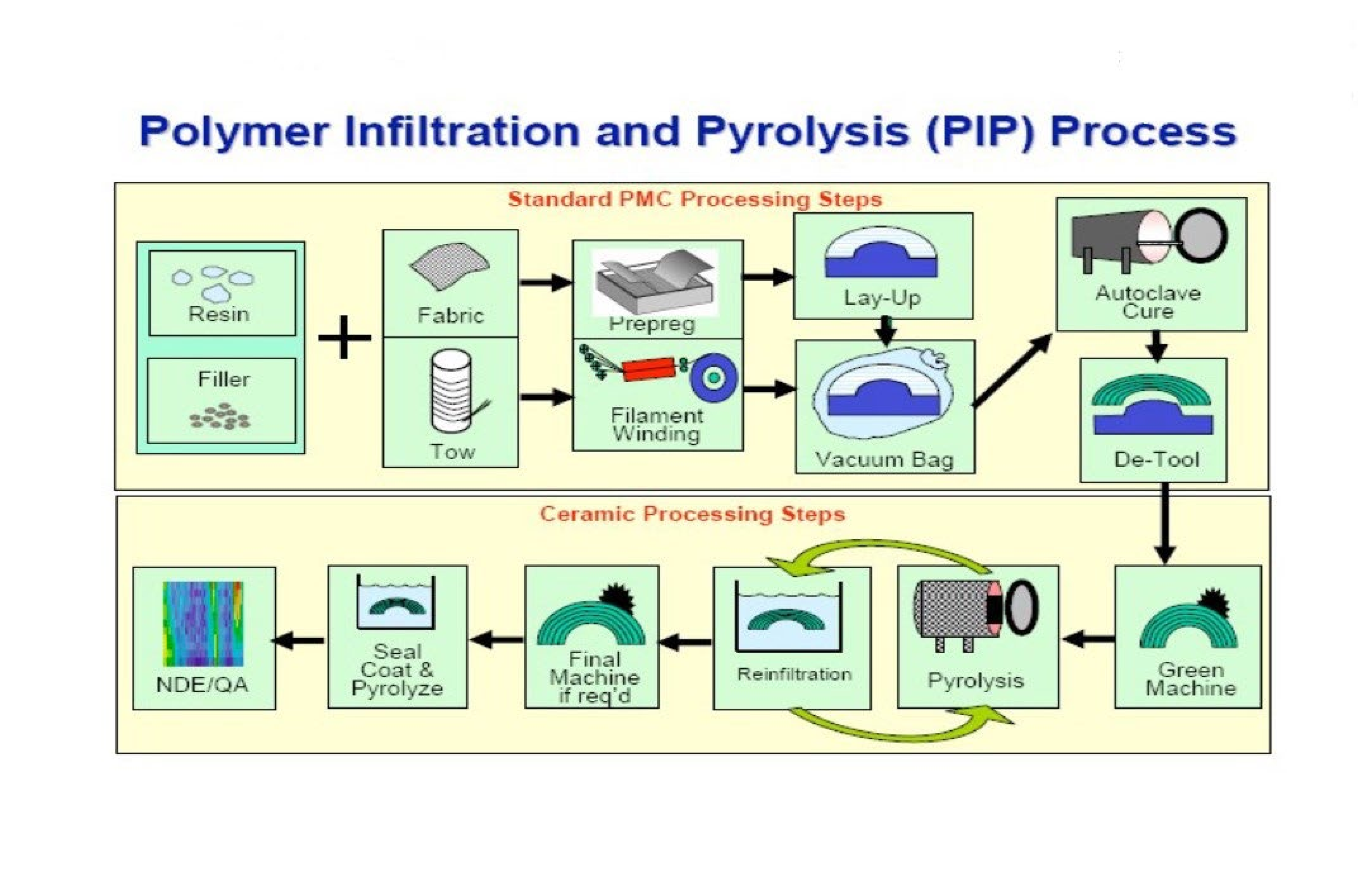
- Aircraft & Automotive Brakes
- Stationary Gas Turbines

-Commercial Power Generation

- Semiconductor Processing

-Fixtures & Heating Elements

Polymer Infiltration and Pyrolysis (PIP) Process



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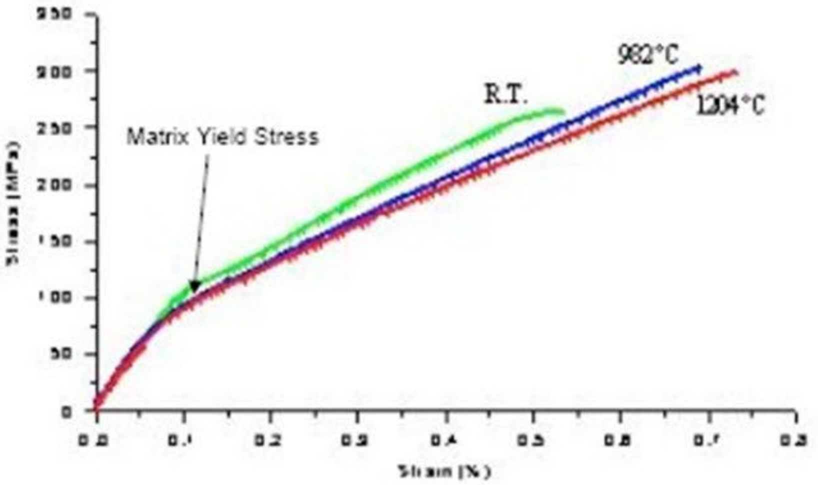
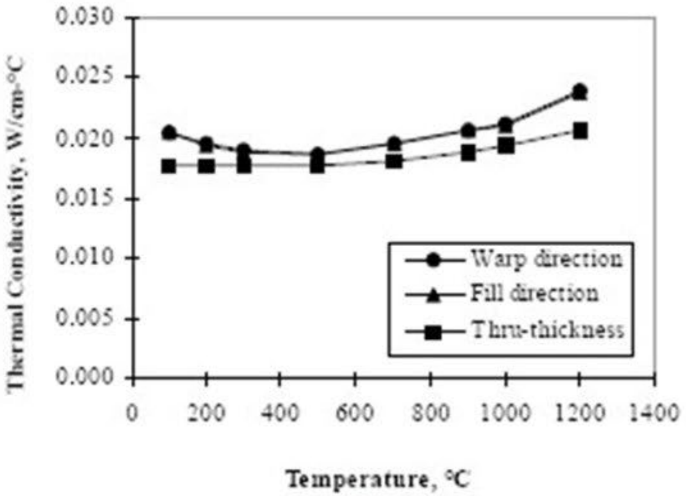
Properties of S200 CMC





	Tensile Strength, MPa (ksi)	Shear Strength, MPa (ksi)	Flexure Strength, MPa (ksi)	Compressive Strength, MPa (ksi)
20°C	262 (38)	38 (5.5)	379 (55)	434 (63)
1000°C	300 (43)	24 (3.5)	414 (60)	NA

	Tensile Modulus, MPa (ksi)	Proportional Limit, MPa (ksi)	Proportional Strain, %	Strain-to-Failure, %
20°C	96 (14)	96 (14)	0.09	0.5
1000°C	90 (13)	90 (13)	0.08	0.7

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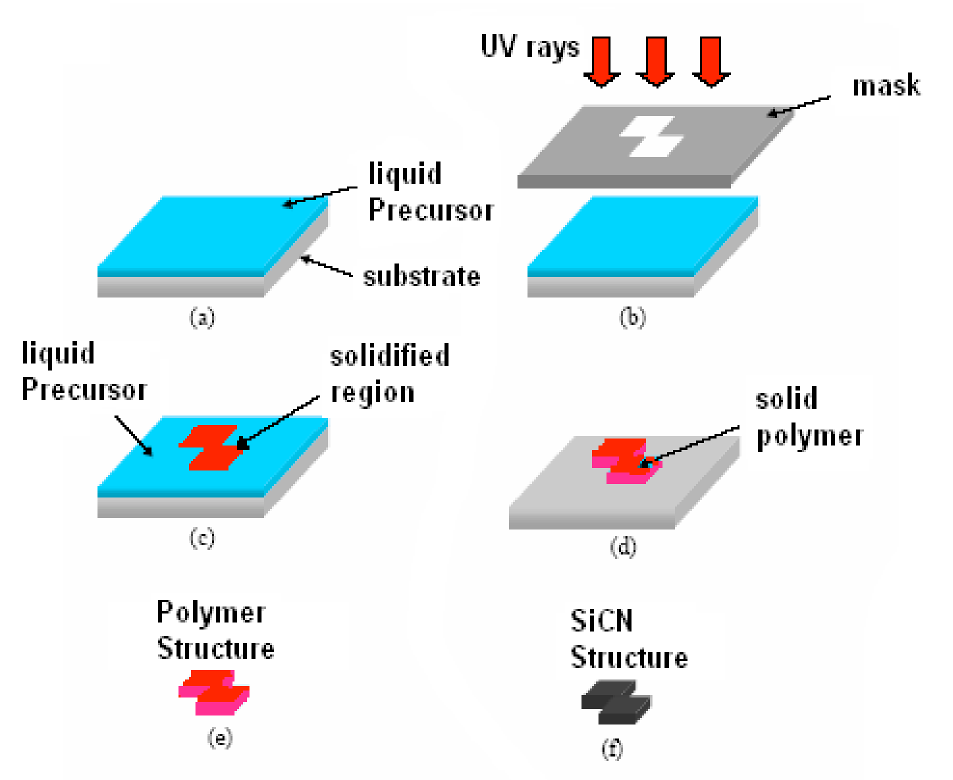
b. Ceramic MEMS

Polysilazane Derived MEMS

- High temperature SiCN ceramic devices
- Easy, low cast fabrication
- Microcasting, Photopolymerization, etc.
- Uses include sensors for gas turbine engines, micro-mirrors for lasers, micro-machines, actuators, etc.

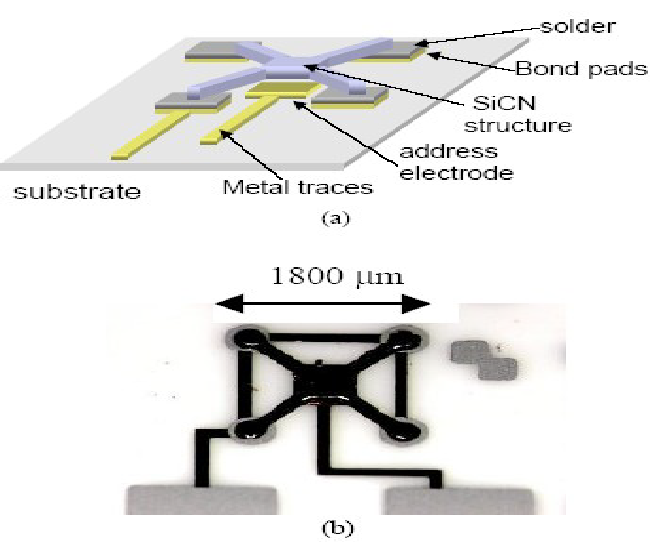
Fabrication of SiCN MEMS by Photo-polymerization of Polysilazane



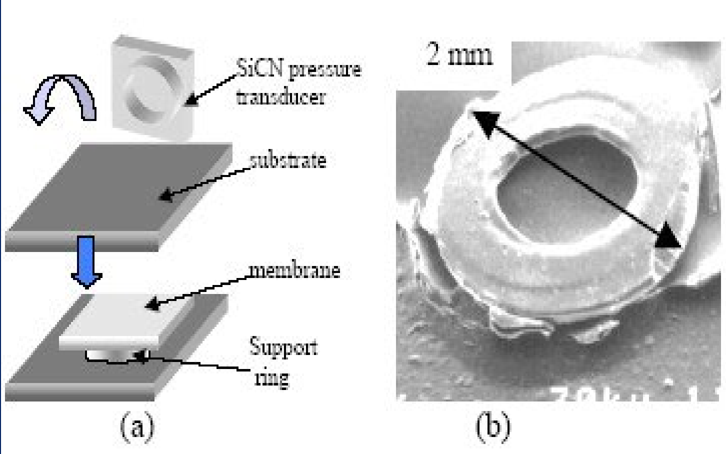
- Fewer processing steps
- Obtain free-standing polymer structures for crosslinking
- Thin, membrane-like layers can be made

L. A. Liew, et al, "Fabrication of Multi-Layered SiCN Ceramic MEMS Using Photo-Polymerization of Precursor," Proceedings of the 2001 IEEE International Conference on Microelectromechanical Systems, Interlaken, Switzerland, January 21-25, 2001

SiCN MEMS Devices Fabricated with Polysilazane

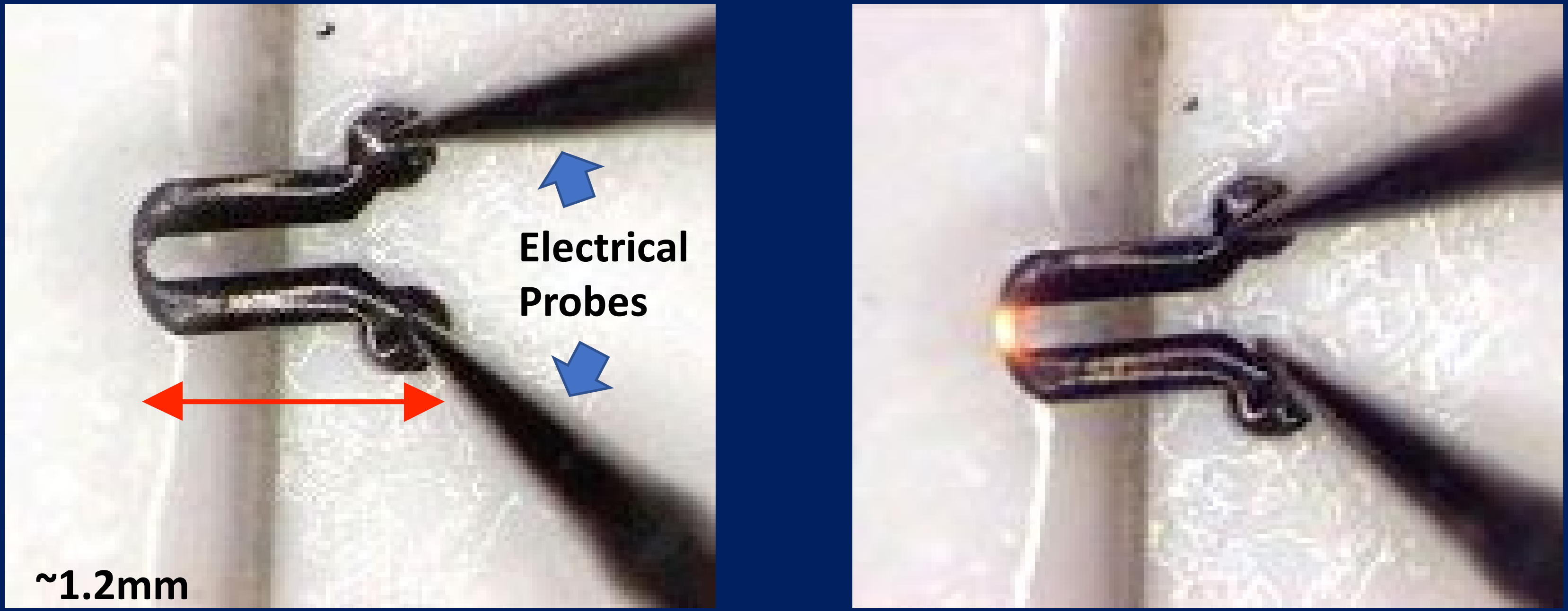


(a) Schematic and (b) fabricated electrostatic actuator



(a) Schematic and (b) SEM pressure sensor

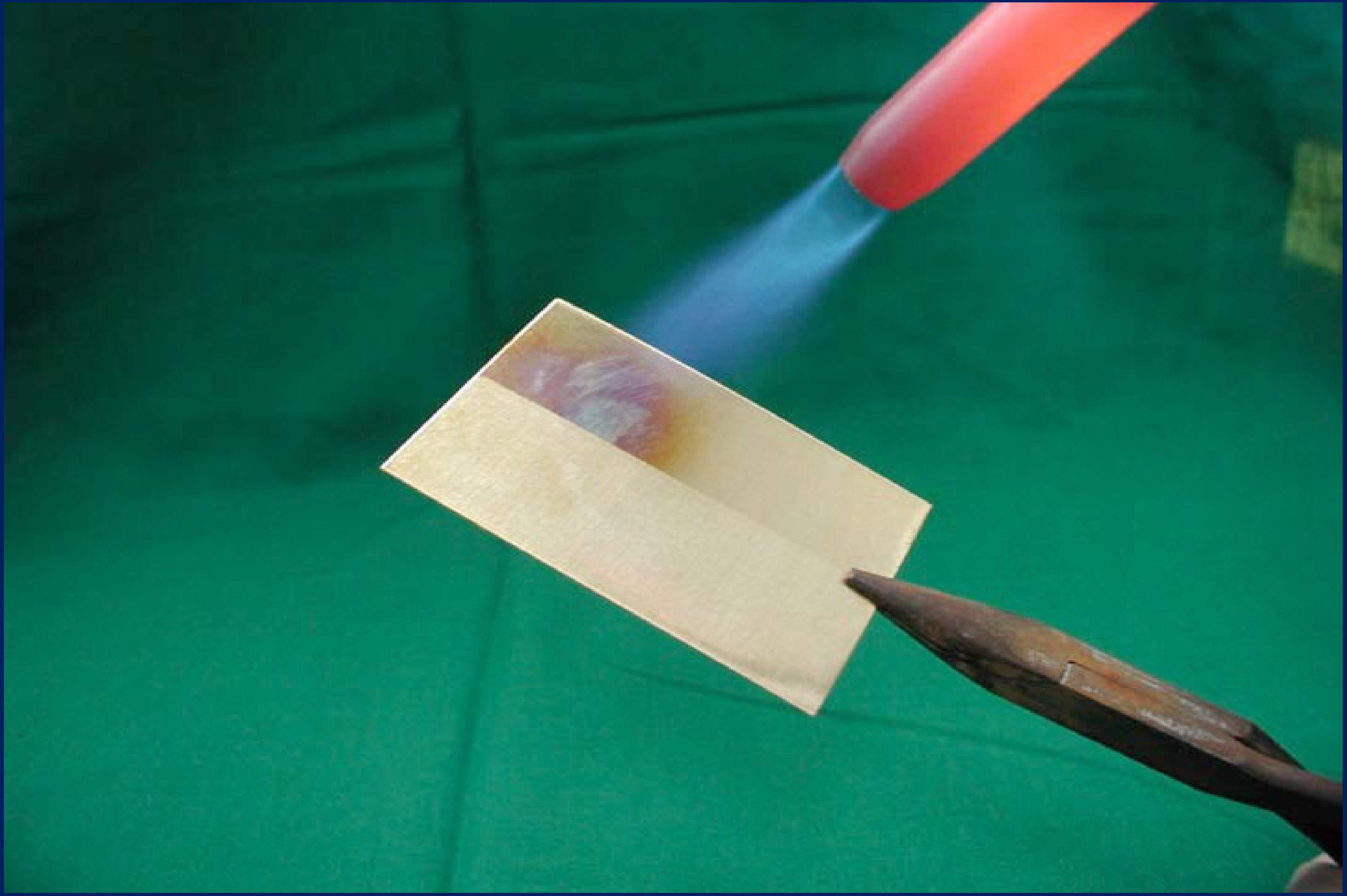
SiCN Microigniter Fabricated with Polysilazane



SiCN Microigniter ("off" & "on" modes) fabricated from a Polysilazane at the University of Colorado, Boulder, Research Laboratories of Prof. Rishi Raj

c. Ceramic Coatings on Metals

Brass Coupon Coated with Polysilazane Clear Coat
(0.1 mil thick PSZ coating on ½ of Brass Coupon)



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Pigmented High Temperature Ceramic Coatings from Polysilazanes

- Electro-Sprayable
- No Delamination from Metal substrates
- Thermal & Corrosion Resistant to 1,000 oC
- Can be Pigmented / “Signature Color”
- Uses include engines, exhaust components, heat exchangers, etc.

Exhaust System and Engine Coatings

- Provide thermal protection against high temperature oxidation
- Provide thermal insulation
- Stable in extreme high temperatures (900 oC)
- Non-Fouling
- Increase horsepower

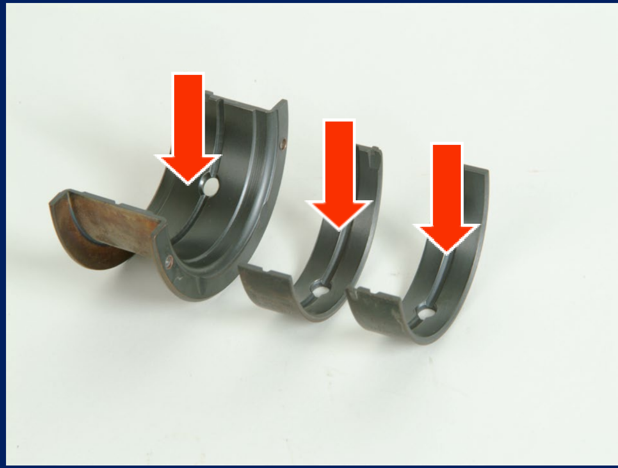
Basic Formulation

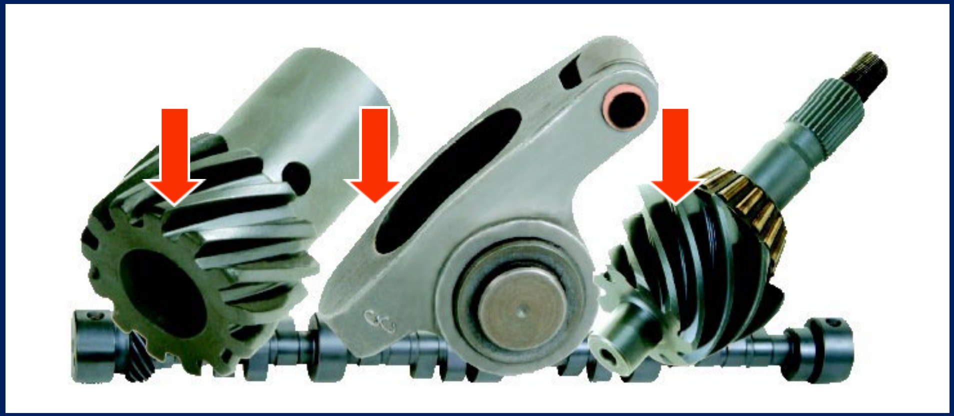
Exhaust Manifold Coating
(Based on KDT HTT 1800 Polysilazane)

Material	% by weight
KDT HTT 1800	26.0
Xylenes	6.9
Zirconium Ocide (0.7 micron)	62.0
Boron Carbide (0.5)	4.6
Dicumyl Peroxide (cure catalyst)	0.5
Total	100%

Dry Film Lubricant Coatings

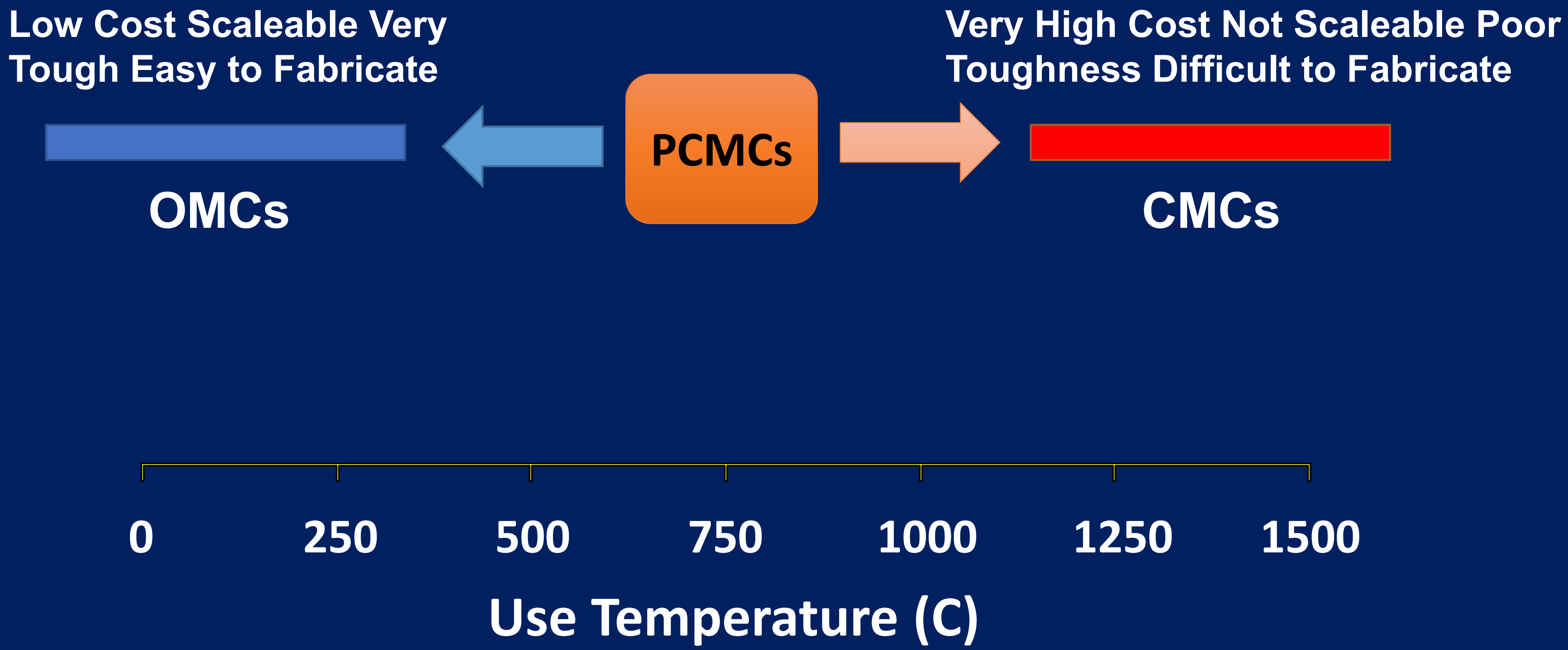
Reduces friction Reduces heat build-up Boosts performance





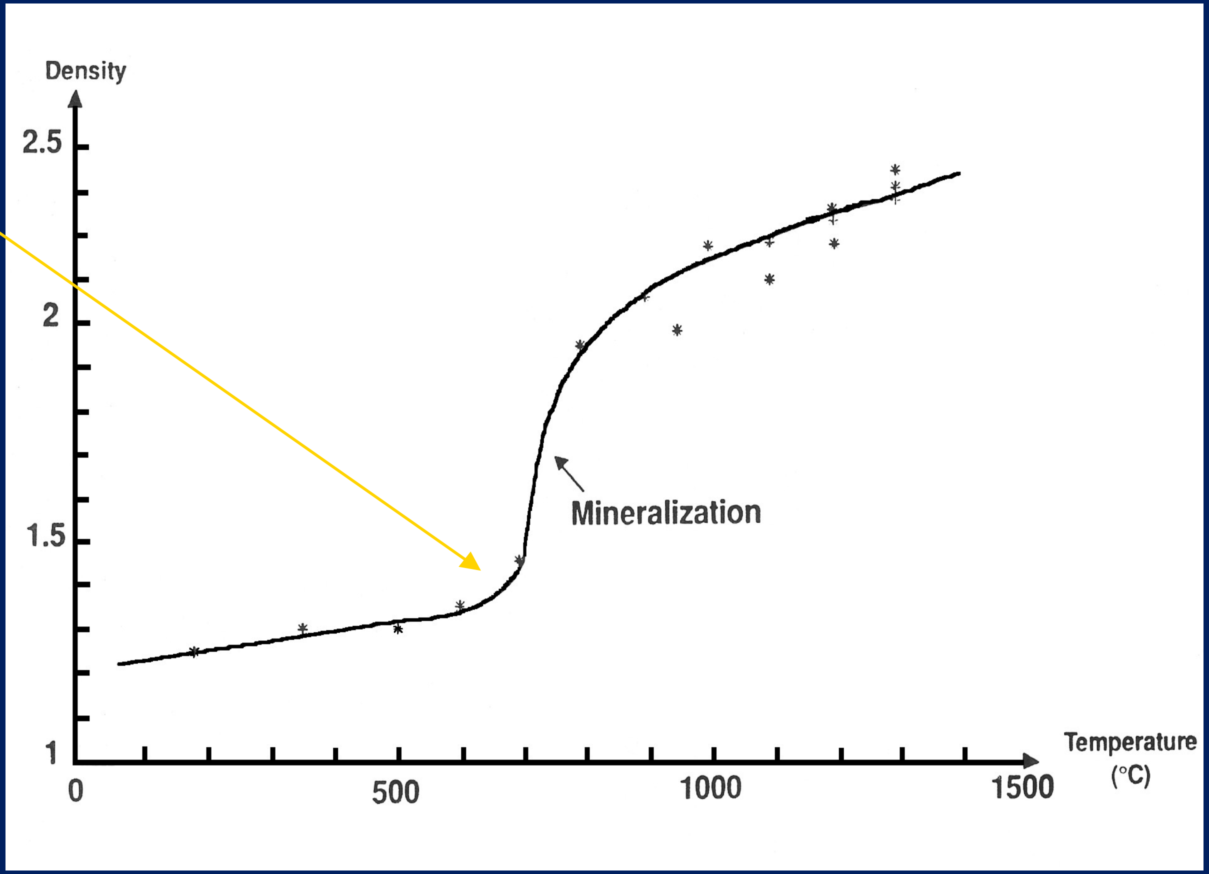
II. Polyceramics and Polyceramic Matrix Composites (PCMCs)

Window of Opportunity for Polyceramic Matrix Composites



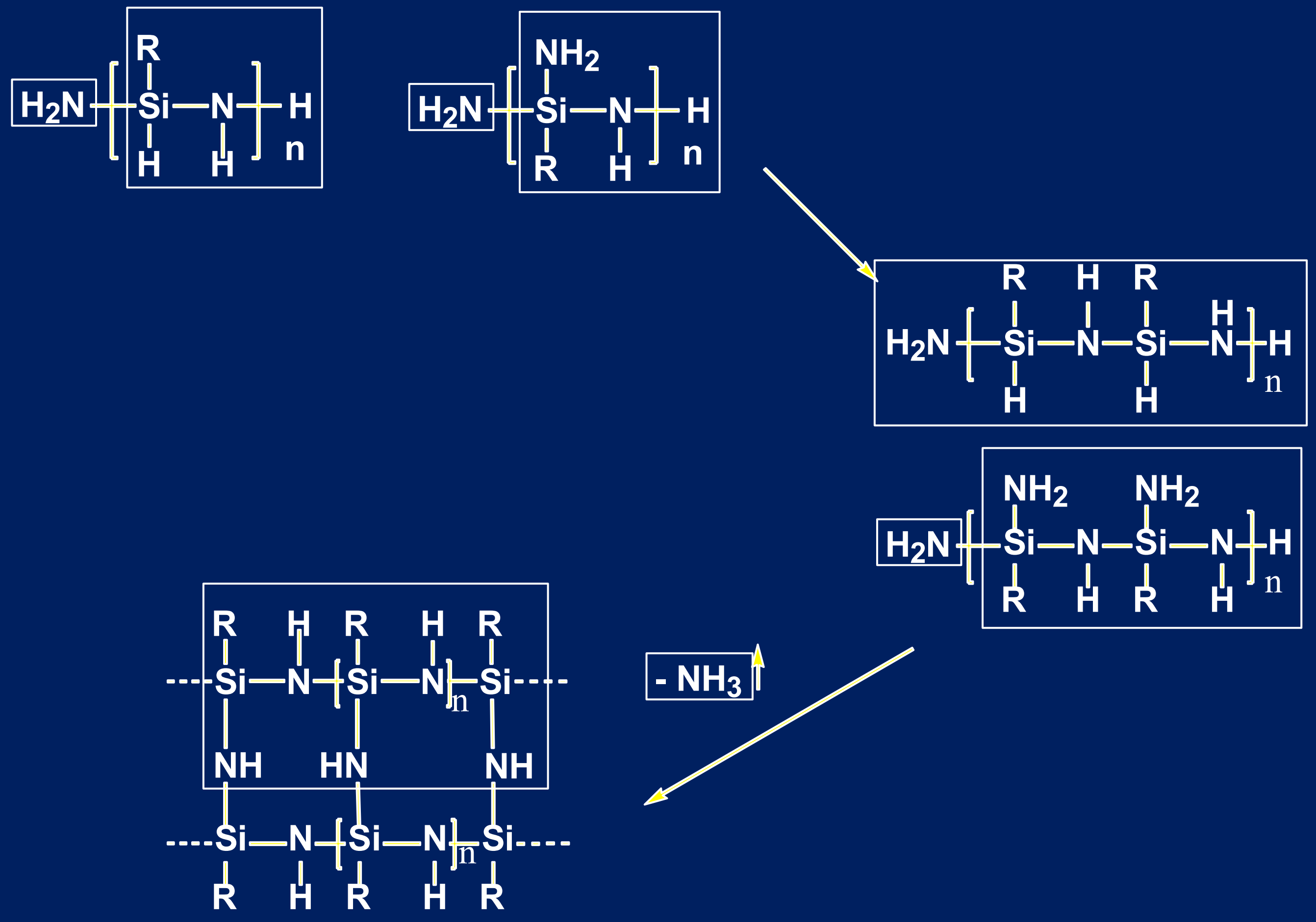
Density Change with Temperature

Fully X-linked Polymer



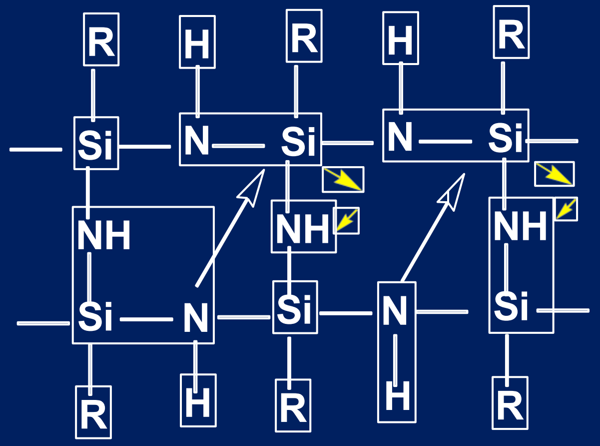
Polymer → X-linked Polymer → Preceramic Network → Amorphous Ceramic → Crystalline Ceramic

Thermal Condensation of Polysilazanes

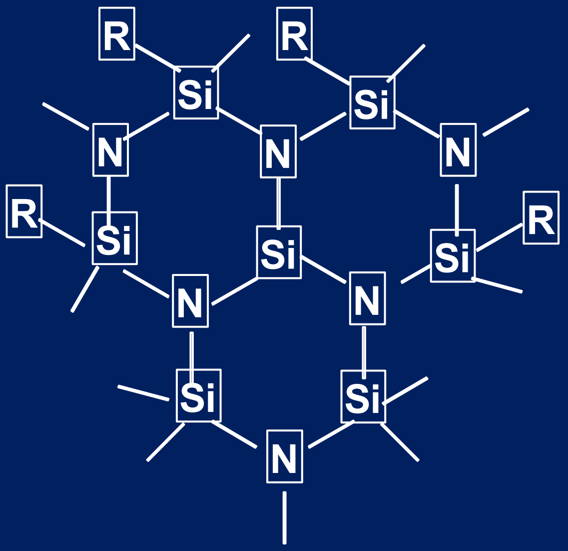


Thermal Condensation of Polysilazanes

LADDER



FUSED CYCLIC



Comparison of Temperature Limits of Organic Matrices Titanium, and Condensed DI-200 Polysilazane

Material	Actual Temperature Limit (°F)	Claimed Temperature Limit (°F)
Epoxies	250	350
Bismaliimides	350	450
Typical Polyamides	550	700
AFRB 4 Polyimide	~600	
Titanium metal	700	
DI 200	~1800	

Polysilazane / Quartz Fiber Composites

- High thermal stability (600 °C) and thermal shock resistance
- High Mechanical Strength and Toughness
- Low, stable dielectric constant at high temperatures
- Suitable Material for Radomes & Antenna Windows

Typical PSZ / Quartz Fiber Composite Mechanical Properties

Material	Quartz Fabric/ DI-200 Resin
Ultimate Tensile Strength (psi)	35,500 @ -35°F 39,000 @ RT; 19,500 @ 1000°F
Youngs Modulus (msi)	2.6 @ -35°F 2.6 @ RT 2.9 @ 1000°F
Compressive Stress (psi) at Maximum load	10.6 @ -35°F 9,200 @ RT 9.600 @ 1000°F
Flexture Strength (psi)	26,000
Flexture at Modulus (msi)	3.32
Shear Strength Isopecscu, psi	2,700 @ RT 4,270 @ 1000°F
Thermal Conductivity BTU-in/hr-sq.ft.-°F	2.8

Electrical Properties: PSZ / Quartz Fiber Composite

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Electrical Property	Value	Stability
Dielectric Constant (25 °C to 1,100 °C)	3.0	Stable vs. Temperature
Dielectric Constant (0.03 GHz to 30 GHz)	3.0	Stable vs. Frequency
Loss Tangent (25 °C to 1,100 °C)	0.003	Stable vs. Temperature
Loss Tangent (0.03 GHz to 30 GHz)	0.003	Stable vs. Frequency

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III. Organic / Inorganic Hybrid Materials

Organic / Inorganic Copolymers from Polysilazanes

- Urethanes
- Epoxies
- Cyanate Esters
- Phenolics

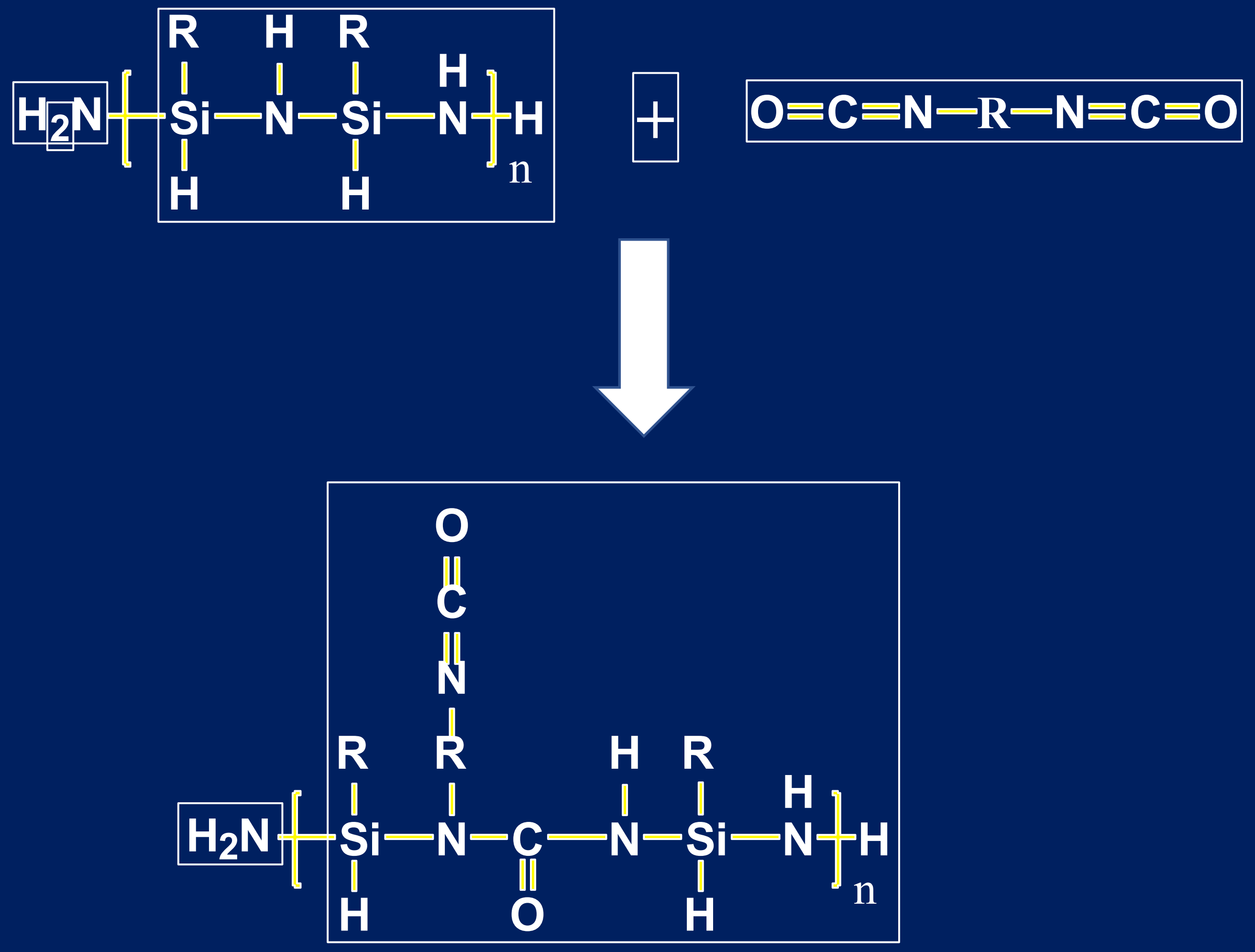
Benefits of Organic / Inorganic Copolymers

Exceptional
Thermal Stability

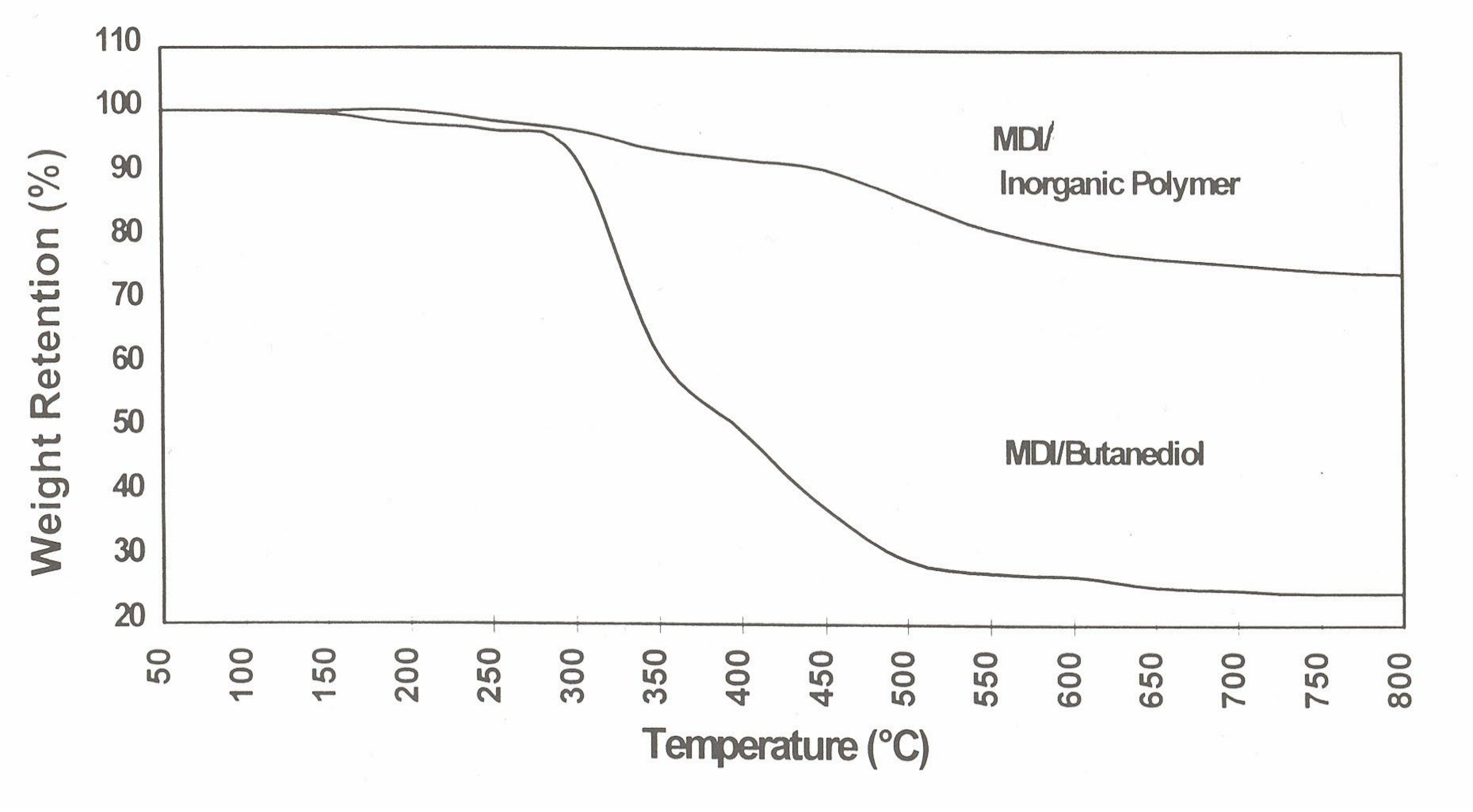
High Char

Excellent Adhesion
(Fibers, Fillers, etc..)

Urethane Copolymer Formation



Urethane Copolymer TGA Trace



Urethane Copolymer Composite Characteristics

- High Durability
- Non-Burning
- No Smoke Generation
- UV Stable
- Cost Effective (High Filler Loading)

Urethane Copolymer / Glass Fiber Composites
HDI Trimer / Polysilazane (7 glass plies in 0/90 lay-up)

Property	E-Glass	S-Glass
Tensile Strength, MPa	384	584
Tensile Modulus, Gpa	20.3	28.3
Strain to Failure, %	2.1	2.1
Flexural Strength, MPa	402	572

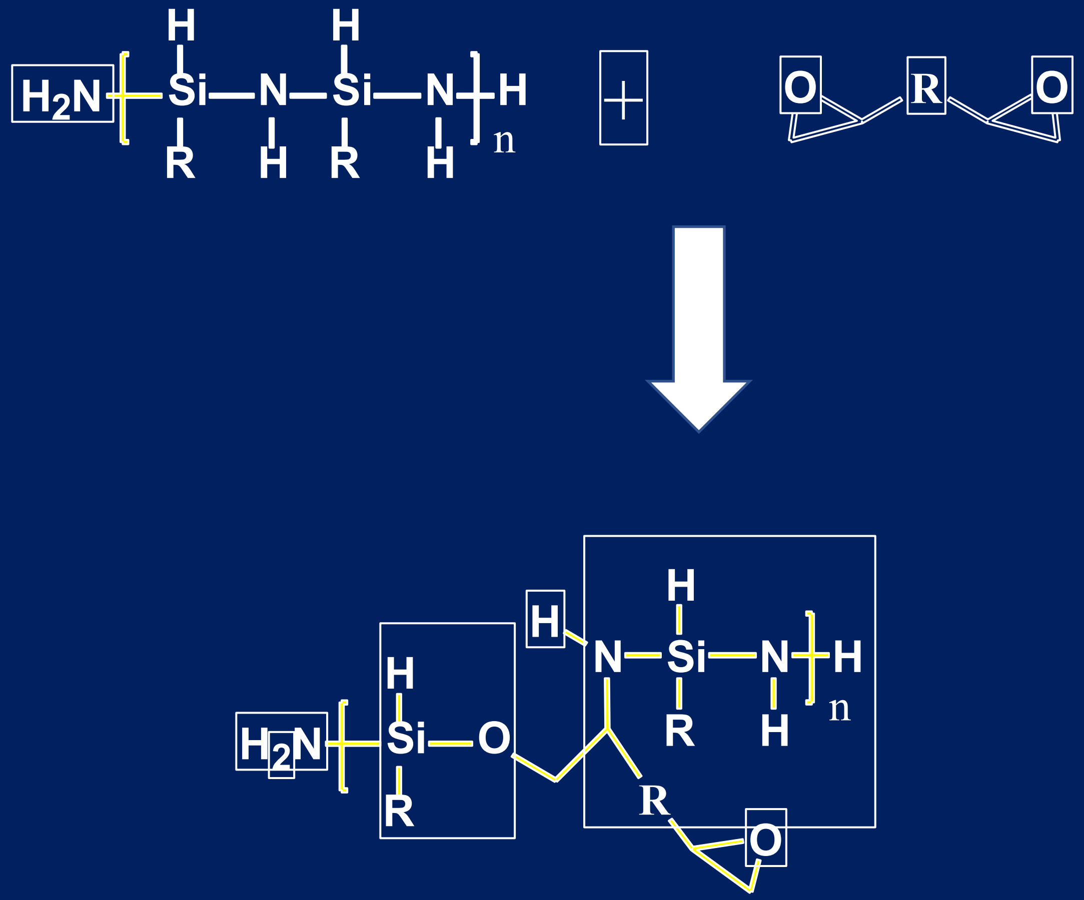
Urethane Copolymer Trackside Warning Tile

Property	Nominal Value	Test Method	Result
Accelerated Weathering	No deterioration (200 hours)	ASTM G-23	None
Chemical Resistance	No Dissolution	ASTM D-1308	None
Flexural Strength	15,000 psi	ASTM C-293	26,000
Freeze/Thaw/Heat At 5 (cycles)	No disintegration	ASTM C-1026	None
Impact Resistance	No Cracks @ ambient Temperature	ASTM D-3029	No Cracks
Flame Spread Index	<25 (Class A)	ASTM E-84	20
Smoke Generated	<450 (Class A)	ASTM E-84	105
Wear Resistance	<0.03 inches	ASTM D-658	0.0058 inches

Trackside Warning Tile

Grand Central Station, New York, New York

Epoxy Copolymer Formation



Carbon Fiber / Epoxy Hybrid Composite Properties

Identical # of Piles and Layup

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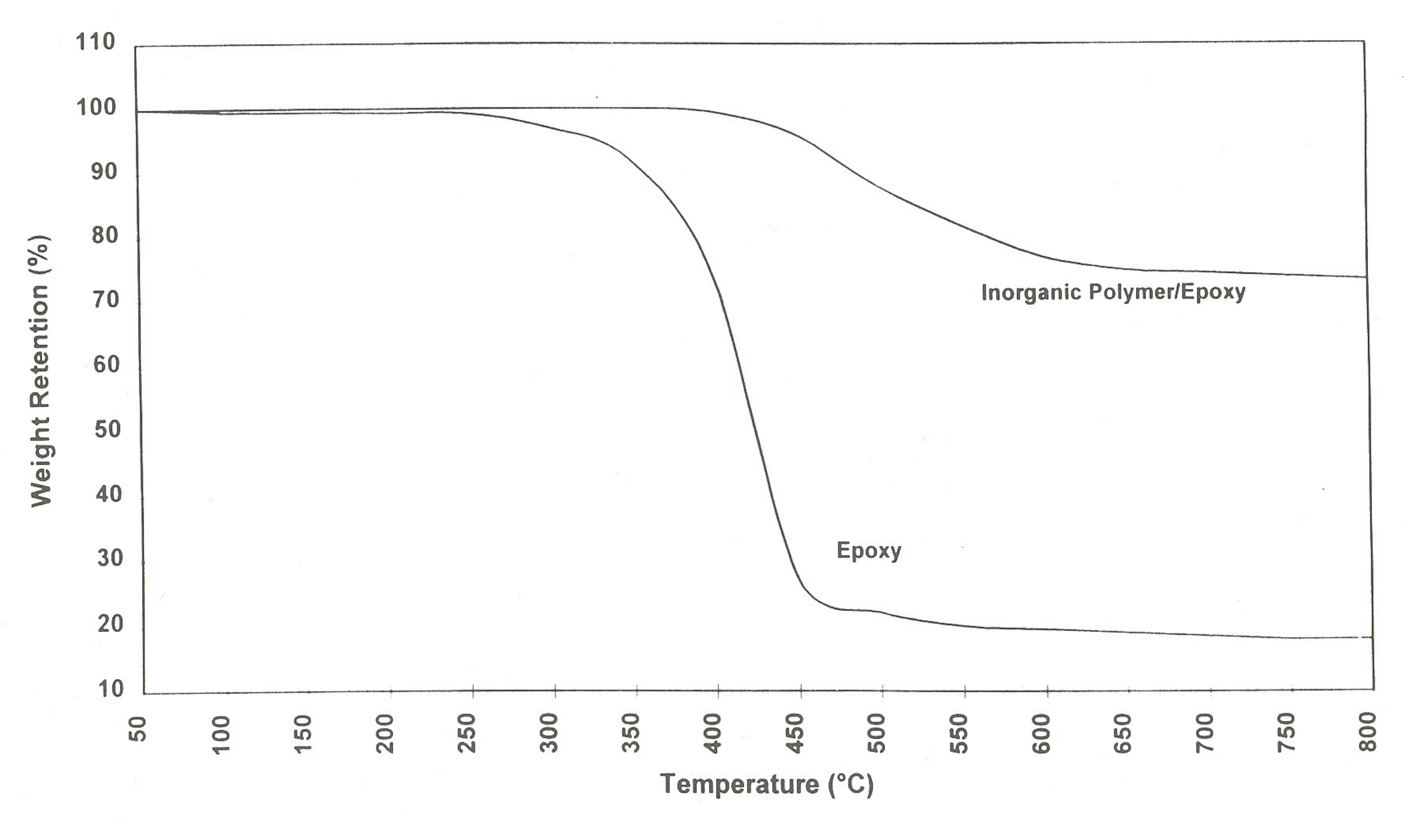
Tensile Strength

Fiber	Fiber Vol.	Epoxy Matrix (published values)	Hybrid Resin Matrix
AS4 / 12K	62%	225 ksi (1550 MPa)	192 ksi (1323 Mpa)
AS4 / 3K	62%	225 ksi (1550 MPa)	167 ksi (1151 Mpa)
AS4 / 8H	62%	120 ksi (827 MPa)	94 ksi (648 Mpa)

Epoxy Hybrid TGA Trace



Carbon Fiber / Epoxy Hybrid Composite Properties

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AS4 / 3K Hybrid Composite

	20°C (Room Temperature)	300°C	400°C	600°C
Tensile Strength	138 ksi	123 ksi	107 ksi	35 ksi

Organic / Inorganic Hybrid Clear Coats also in Commercialization

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- Low Surface Energy
- Anti-Fouling
- Anti-Graffiti

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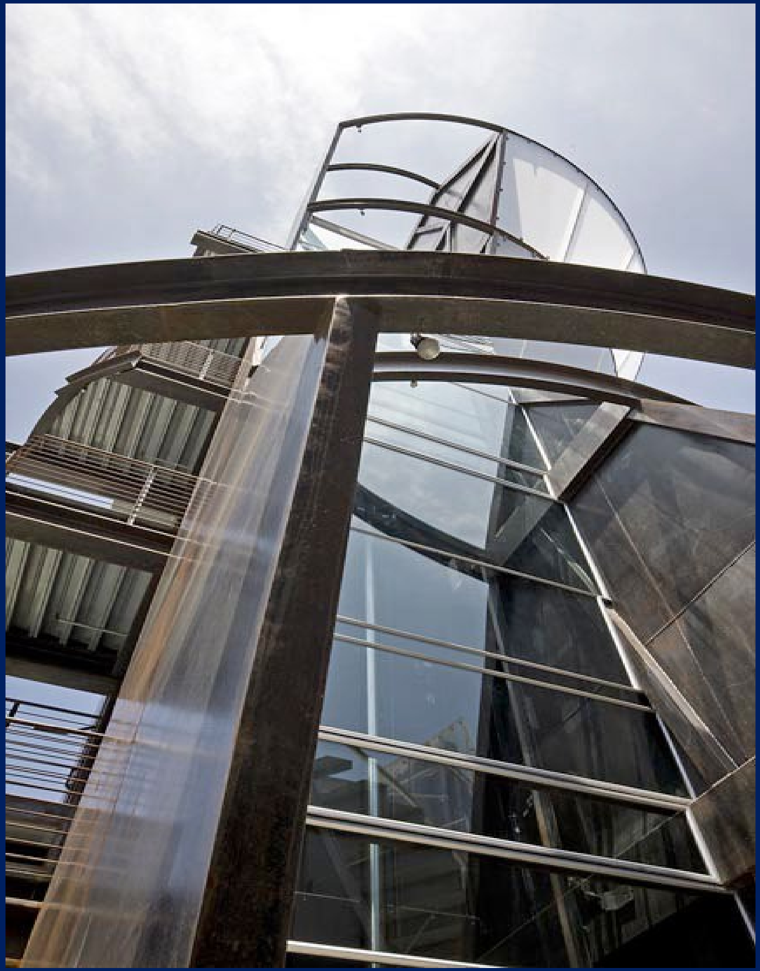
Anti-Graffiti Coatings

- Clear coat for painted surfaces, metals Interior and exterior application
- Reduces adhesion of a wide range of paints and markers
- Only thin layers necessary

  (ca. 10 µm)
- Highly transparent
- Very durable (light and weather resistant)

Polysilazane Façade Coating for Anti-Fouling / Anti-Graffiti

Eric Owen Moss Arts Tower / Los Angeles, CA



Summary

- Preceramic Polymers provide a versatile tool in the manufacture of ceramic objects that cannot be made using conventional ceramic forming techniques.

- Preceramic Polymers can be used in the preparation of ceramic coatings, monoliths, and composites.

- Preceramic Polymers can be useful as high temperature-stable materials in-and-of-themselves without full conversion to ceramic.

- Preceramic polymers can be used as co-reactants with organic polymers to provide for organic / inorganic hybrid materials that have enhanced thermal stabilities versus their wholly organic counterparts and which can demonstrate non-burning characteristics or low surface energies.

References & Recommended Literature

GENERAL INFORMATION

- New Structural Materials Technologies – Opportunities for the use of Advanced Ceramics and Composites; Congress of the United States Office of Technology Assessment, U.S. Gov. Printing Office; September, 1986.

- Polymer-Derived Ceramics – From Nano-Structure to Applications; P. Colombo, Editor; DEStech Publications, Inc., September 28, 2009.

- Polymer-Derived Ceramics: 40 Years of Research and Innovation in Advanced Ceramics; Paolo Colombo et al; J. Am. Ceram. Soc., 93 [7] 1805-1837 (2010).

- PRECERAMIC POLYMERS

- From Molecules to Ceramics – Synthesis of Organosilicon Polymers as Precursors for Ceramic Materials; Markus Weinmann; Max Planck Institute for Metal Science; Stuttgart, 2010.

- Modern Trends in Advanced Ceramics; R. Riedel et al; Ceramics Science and Technology, Vol. 1: Structures, pp 3-37 (2008).

- **Polysilazane Precursors to Advanced Ceramics; Alexander Lukacs; American Ceramic Society Bulletin, Vol. 86, No. 1, pp 9301-9306 (2008).**
- **<u>CERAMIC MONOLITHS & CERAMIC MATRIX COMPOSITES (CMCs)</u>**
- **Dense Silicon Carbonitride Ceramics by Pyrolysis of Cross-linked and Warm Pressed Polysilazane Powders; Ralf Riedel et al; J. Eur. Ceram. Soc. 19 (1999), pp 2789-2796.**
- **Mechanical Properties of a Fully Dense Polymer Derived Ceramic made by a Novel Pressure Casting Process; Rishi Raj et al; Acta Materialia 50 (2002), pp 2093-4103.**
- **Fabrication and Characterization of Fully Dense Si-C-N Ceramics from a Poly(ureamethylvinyl)silazane Precursor; Fritz Aldinger et al; J. Eur. Ceram. Soc. (2009), pp 163-173.**
- **CMCs for Navy Air Vehicles; G.Y. Richardson; MATECH/GSM Ceramic Fibers & Composite Workshop, September 21-22, 2004 High Temperature Matrices for Filament Wound Composites; Rock A. Rushing; 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; July 10-13, 2005; Tucson, Arizona.**

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- The Use of Starfire Preceramic Polymers in Friction Applications; Stan Hemstad et al; 30th International Conference & Expo on Advanced Ceramics and Composites; January 27, 2006.

- <u>CERAMIC MEMS</u>

- Ceramic MEMS – New Materials, Innovative Processing and Future Applications; American Ceramic Society Bulletin, Vol. 80, No. 5, pp 25-30.

- Fabrication of SiCN MEMS by Photopolymerization of Pre-ceramic Polymer; Sensors and Actuators A, 95 (2002), pp 120-134.

- Fabrication of SiC-Based Ceramic Microstructures from Preceramic Polymers with Sacrificial Templates and Lithographic Techniques – A Review; Journal of the Ceramic Society of Japan, 114 [6], pp 473-479 (2006).

- Fabrication of Novel Polysilazane MEMS Structures by Microcasting; Proceedings of 2001 ASME International Mechanical Engineering Congress and Exposition, November 11-16, 2001, pp 1-8.

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- Novel Polymer Derived Ceramic-High Temperature Heat Flux Sensor for Gas Turbine Environment; Journal of Physics: Conference Series 34 (2006), pp 458-463 [International MEMS Conference 2006].

- A Novel Design and Analysis of a MEMS Ceramic Hot-Wire Anemometer for High Temperature Applications; Journal of Physics: Conference Series 34 (2006), pp 277-282 [Interntional MEMS Conference 2006].

- POLYCERAMIC MATRIX COMPOSITES

- Radomes Based on Novel Inorganic Polymer Composites; David W. Marshall; SAMPE Journal, Vol. 37, No. 5, September/October 2001.

- ORGANIC / INORGANIC HYBRID POLYMERS

- KiON Defense Technologies Website; www.kiondefense.com; Technical Bulletins: TB3 – Polysilazanes – Reactivity with Isocyanates, TB4 – Polysilazanes – Reactivity with Phenolic Resins, TB5 – Polysilazanes – Reactivity with Epoxy Resins

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LLC

- High Char Yield Silazane-Modified Phenolic Resins; Ronald E. Myers; U.S. Patent 5,089,552; February 18, 1992.
- High Temperature Matrices for Filament Wound Composites; Rock A. Rushing; 41st AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit; July 10-13, 2005.
- <u>PIGMENTED CERAMIC COATINGS</u>
- Heat Resistant Coating Compositions, Coated Articles, and Methods; Carl L. Cavallin; U.S. Patent Application 2008/0096024; April 24, 2008.
- <u>CLEAR COATS</u>
- Hydrophobic and Scratch-Resistant Paints for Metal Surfaces and Brake Dust-Repelling Wheel Coatings; H. Krannich et al; U.S. Patent Application 2010/0075057; March 25, 2010.
- Self Cleaning Aluminum Alloy Substrates; Albert L. Askin et al; U.S. Patent Application 2008/0241573; October 2, 2008.

Corrosion Resistant Aluminum Alloy Substrates and Methods of Producing the Same; T. L. Levendusky; U.S. Patent Application 2009/0061216; March 5, 2009.

Corrosion Resistant Aluminum Alloy Substrates and Methods of Producing the Same; T. L. Levendusky; U.S. Patent Application 2010/0200415; August 12, 2010.