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Ceramic Foams from Pre-ceramic Polymer Routes for Reusable Acreage Thermal Protection System Applications

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Outline

- Motivation
- Advantages of preceramic-polymer-derived ceramic foams
- Experimental approach
- Results
  - Sacrificial materials
    - Sacrificial blowing agent (Polyurethane)
    - Sacrificial fillers
  - Comparison of foam microstructures
  - Phase evolution and properties
    - Phase evolution
    - Oxidation behavior
    - Mechanical properties
    - Aerothermal performance
- Conclusions

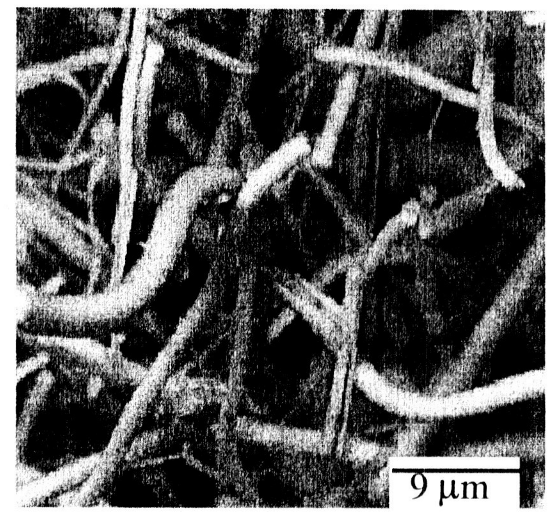
TPS

Motivation

- Current light weight insulation (acreage TPS)
  - used to protect the aluminum sub-structure of the shuttle.
  - High purity silica, aluminoborosilicate, and alumina fibers
    - (LI-900, FRCI-12, AETB-8)
  - Open porous structure
- Capabilities of current system:
  - Limited temperature capability
    - tile improvements in-process
  - Difficult to tailor scale of porosity
    - affects heat transfer
    - can be done by adding matrix

Foams can potentially be used in:

- acreage TPS
- tile leading edge applications
- on orbit repair technology



Microstructure of LI-900
(current tile material)

Ceramic Foam Research

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Objective:

Develop low density ceramic foams using preceramic polymers for Thermal Protection Systems (TPS) and other applications

Approach:

- Rigid insulation materials
- Different compositions
  - (Si-O-C, Si-C, Si-O-C-N, Si-O, Si-N, other)
- Investigate both unfilled and filled polymer systems
  - Fillers may enhance certain properties
    - Increased oxidation resistance (e.g. B)
    - Increased temperature capability
    - Change emissivity
    - Near net shape fabrication

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Potential Advantages of Ceramic Foams Derived from Polymeric Precursors

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- Tailor foam microstructures:
  - Pore size
  - Pore architecture (open vs. closed porosity)
  - Density
  - Composition
  - Near net shape processing
- High temperature capabilities
- Formation of functionally graded foams
  - In terms of
    - Composition
    - Density
    - Pore size

Advantages of processing with pre-ceramic polymers:

- Can aid machinability of green parts
- Low fabrication temperatures for ceramic materials (amorphous)
- Able to tailor microstructure and composition - formation of high purity materials

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Foam Processing Routes

- Foams processed using:
  (1) sacrificial blowing agent (polyurethane)
  (2) sacrificial fillers

Addition of fillers (reactive or inert):
- improves oxidation resistance
- retains amorphous structure to higher temps
- leads to reduced shrinkage during pyrolysis
- change emissivity properties

Can vary the ceramic foam density and cell size by
- Using different density polyurethane foams
  - 0.042 g/cc (2.6 lb/ft^3) to 0.24 g/cc (15 lb/ft^3)
- Using appropriate surfactants
- Using appropriate sacrificial fillers

- Preceramic polymer
- Processing aids
  - Surfactant
- Blowing agent/filler
  - Polyurethane foam
  - Sacrificial filler

- Mix required constituents
- Controlled foaming conditions
  - Atmosphere, pressure
- Controlled pyrolysis conditions
  - Atmosphere
  - Heating rate

Foam Processing using Sacrificial Blowing Agent Polyurethane (PU) Configuration

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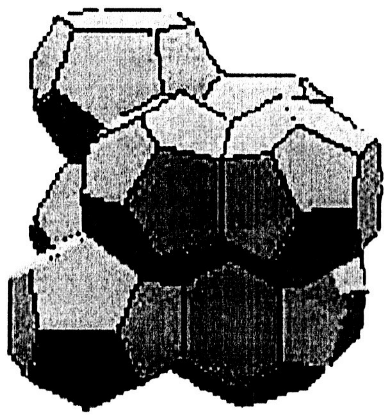
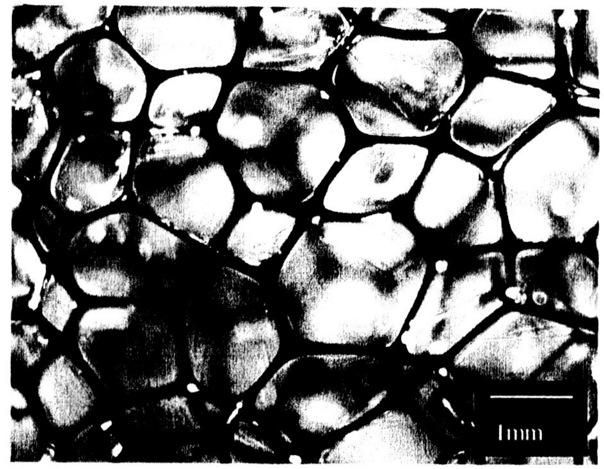
- In general, polyurethane foams form cells with a polygonal-dodecahedron configuration
- This configuration is retained in the final ceramic foam cell configuration

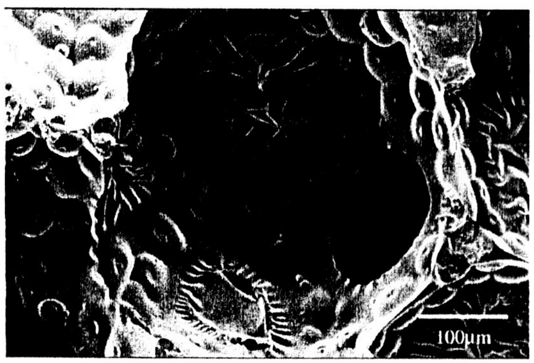


Polygonal-dodecahedron

→



Microstructure of SiOC foam after pyrolysis



Microstructure of SiC foam after pyrolysis

- Approach leads to open macrocellular foams (min cell size ~ 50μm)
- Conducive to making large parts and complex shapes
- Can easily incorporate fillers (reactive or inert)
- Density and cell size are tailorable

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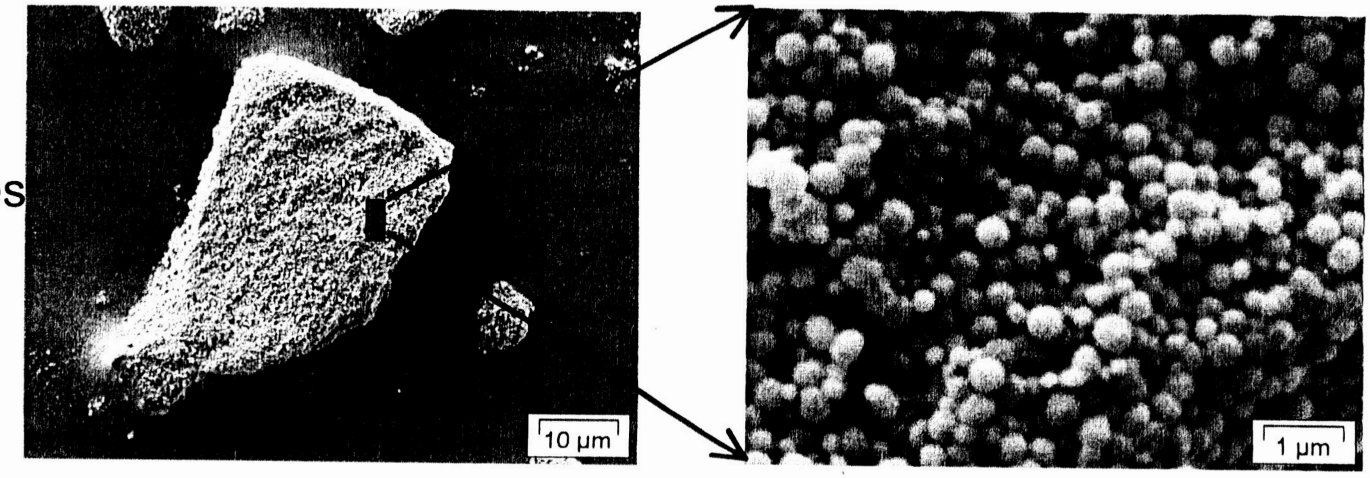
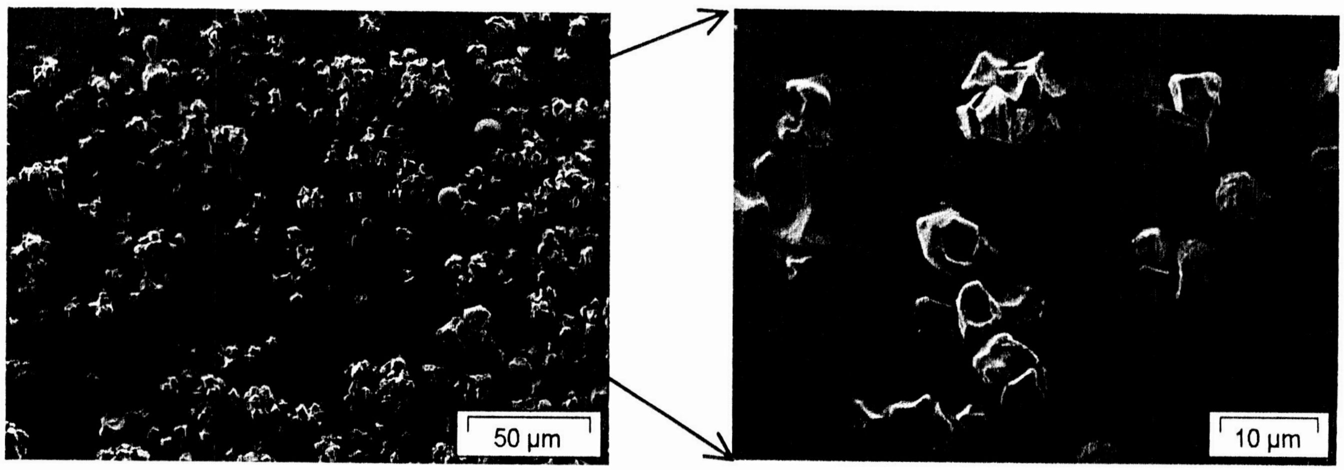
Foam Processing using Sacrificial Fillers (Sacrificial Filler: Polymers or Starches)

- PMMA or other polymer
- Sub micron particles
- Agglomerates



- Particle size ranges from 5µm to 50µm depending on starch type
- Irregular or spherical shape



Foam Processing using Sacrificial Fillers (Sacrificial Filler Burn Out Characteristics)

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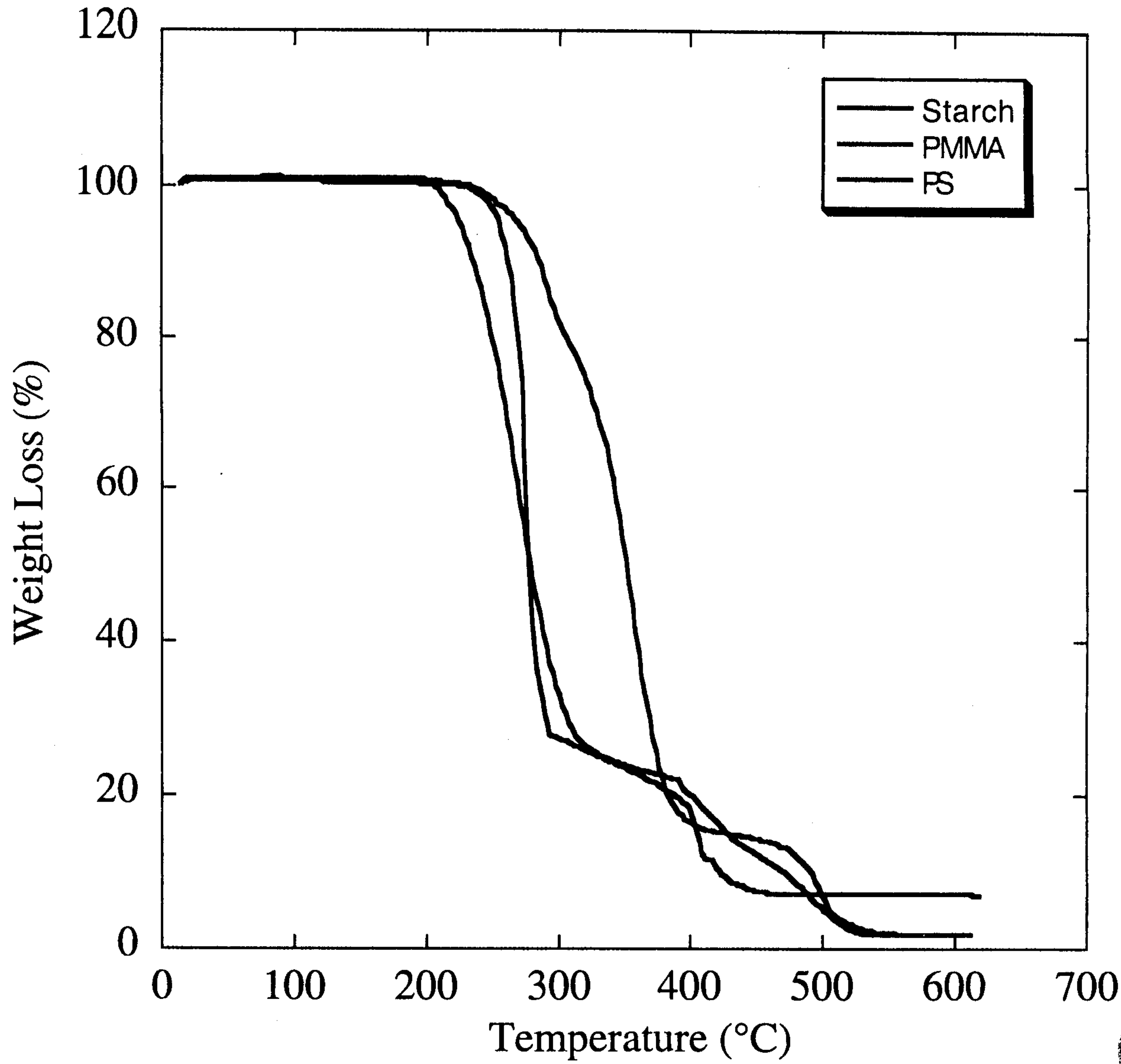
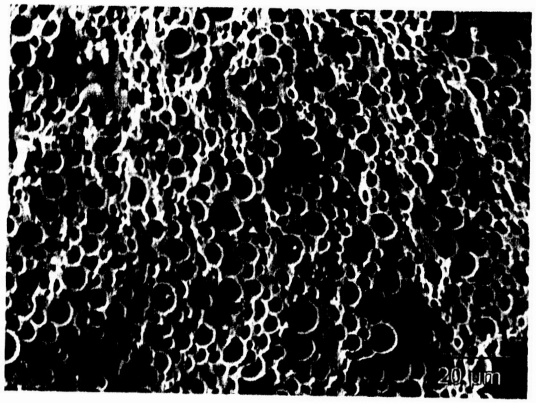
TGA run in Ar to evaluate filler removal

- All fillers start to decompose at T > 200°C
- Polymer fillers are fully decomposed at ~ 500°C
- A residual 'ash' remains after burn out of starches

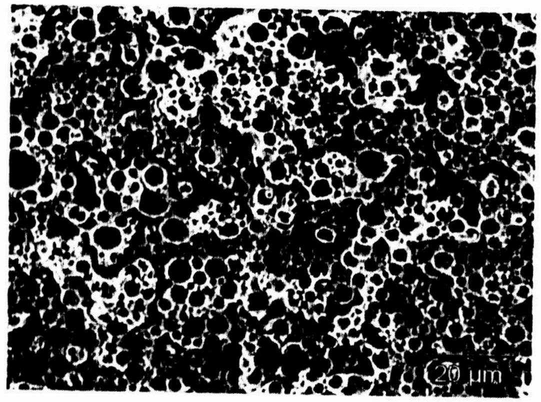


Foam Processing using Sacrificial Fillers (Sacrificial Filler: Polymers or Starches)

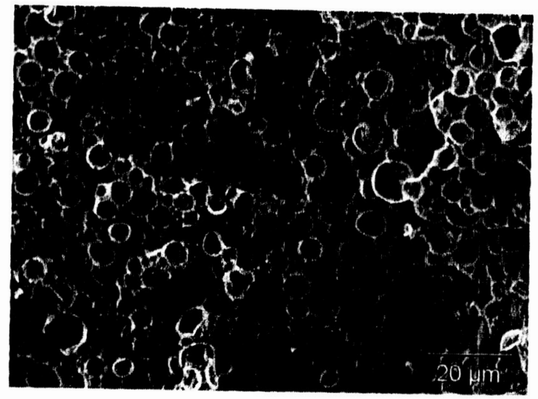
- Foams of various densities processed using PMMA sacrificial fillers
- Foam cell size is comparable in all cases
- Foam composition is comparable



ρ - 0.93g/cc



ρ - 0.72g/cc

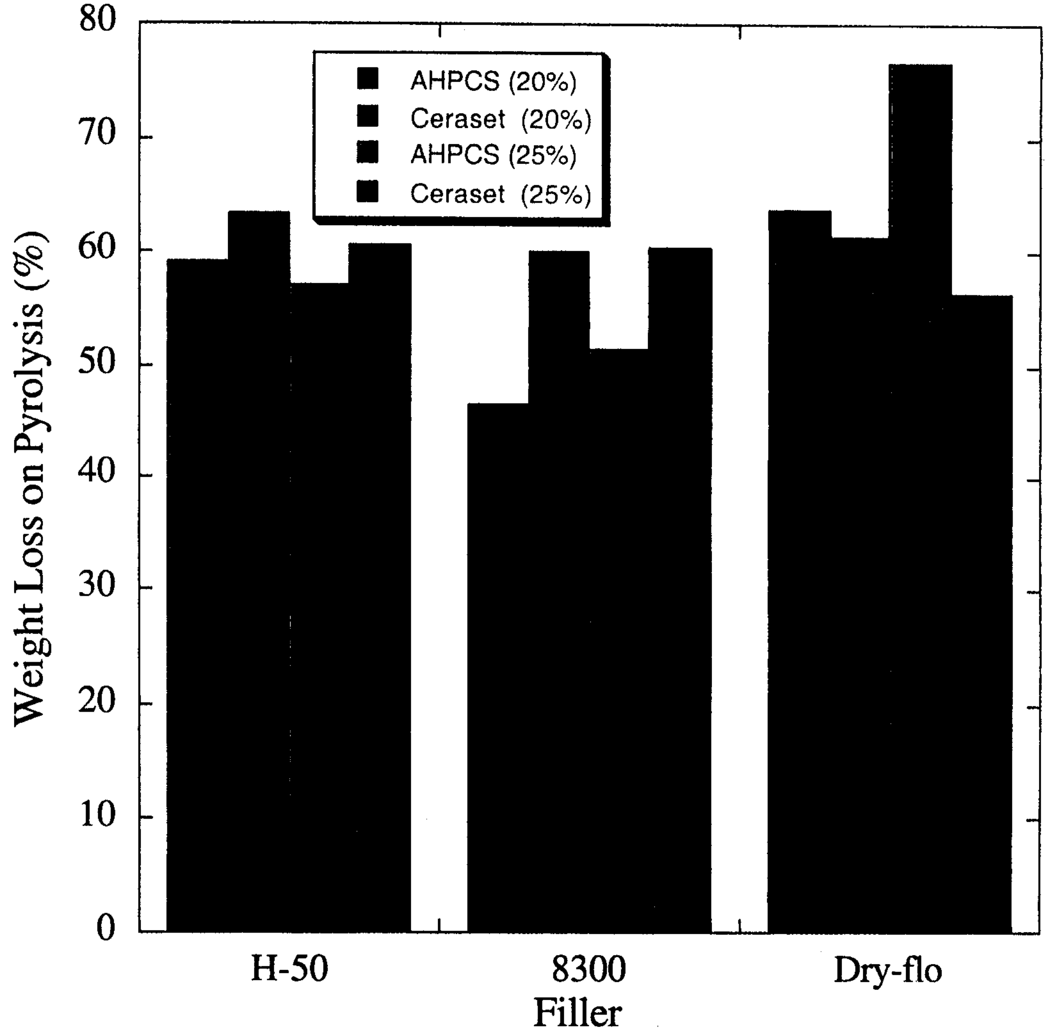


ρ - 0.56g/cc

- Approach leads to open microcellular foams (cell size ~ 10µm or less)
- Can easily incorporate fillers (reactive or inert)
- Density and cell size are tailorable

Foam Processing using Sacrificial Fillers
Yield of Pyrolysis Products Obtained

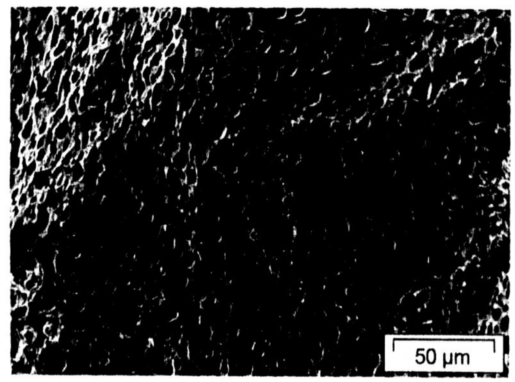
- Polycarbosilane and polysilazane with modified starch sacrificial filler
- All samples experience weight loss (50 to 70%) due to filler removal and loss of volatiles from preceramic polymer during pyrolysis
  - Leads to large shrinkages on pyrolysis



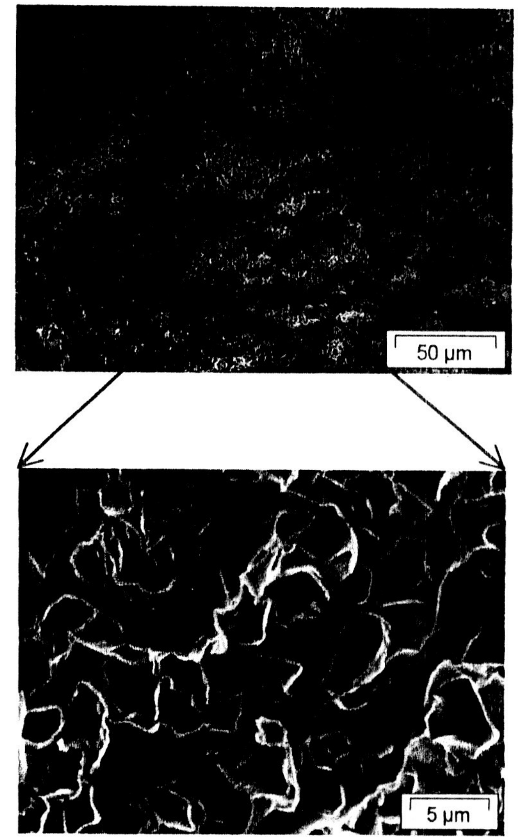
Scale of Microstructures Obtained

PU blowing agent

Starch filler



Starch filler



- Order of magnitude variation in cell size possible
- Foam density is comparable in all cases
- Foam composition is comparable
- Strut size is much larger in PU processed systems

Phase Evolution of Pyrolysis Products

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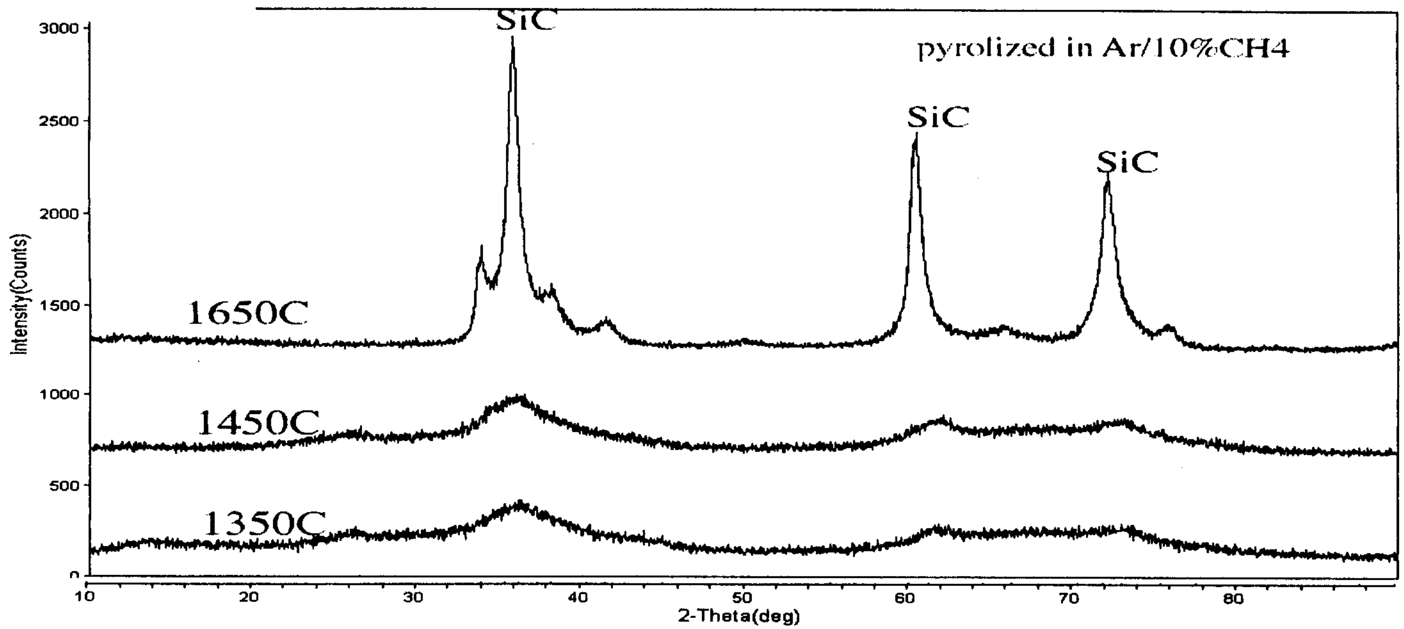
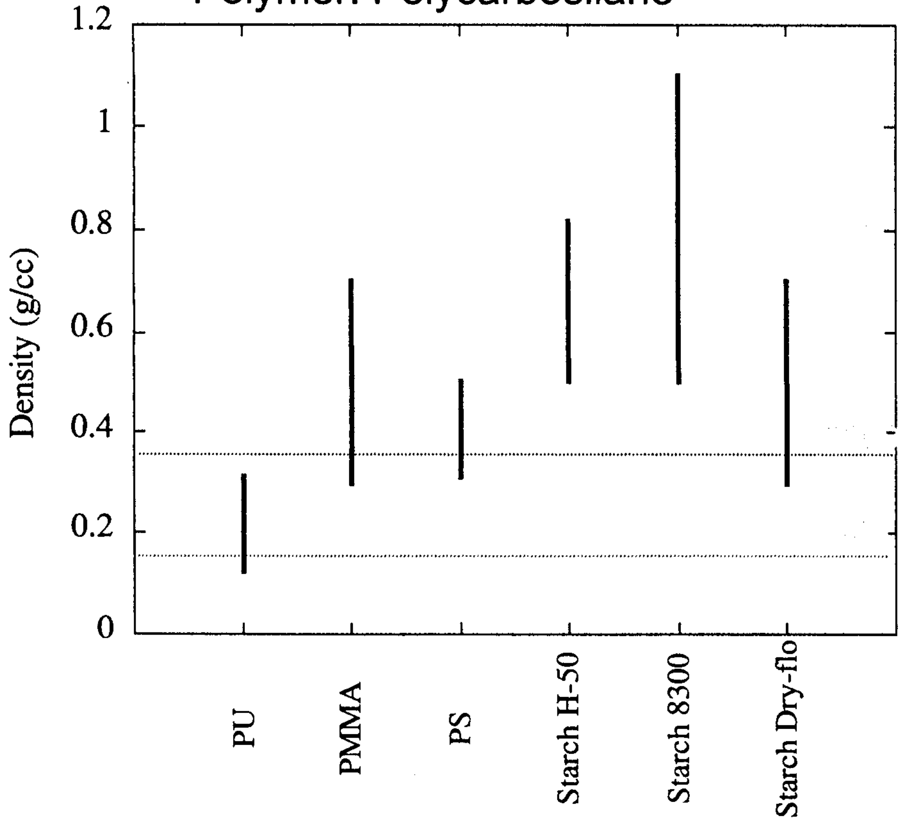


Phase evolution of SiC/Si_3N_4 yielding polymer

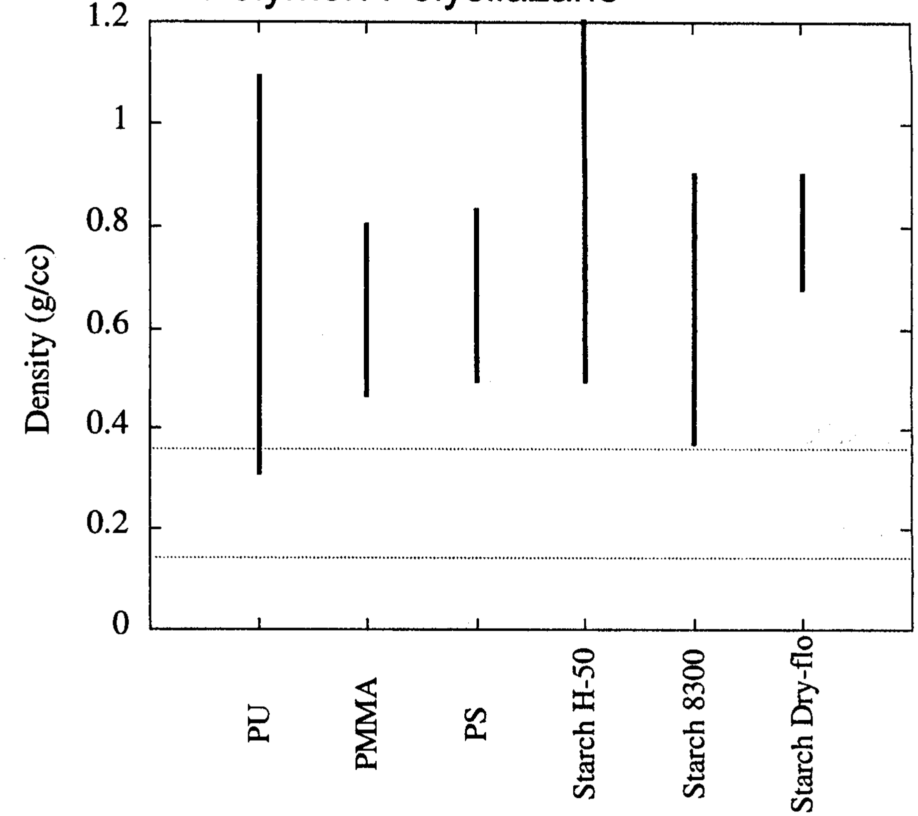
- Pyrolysis product is amorphous or nanocrystalline at lower processing temperatures (< 1500˚C) for all preceramic polymers
- Crystalline at higher processing temperatures

Density of Ceramic Foams

Polymer: Polycarbosilane



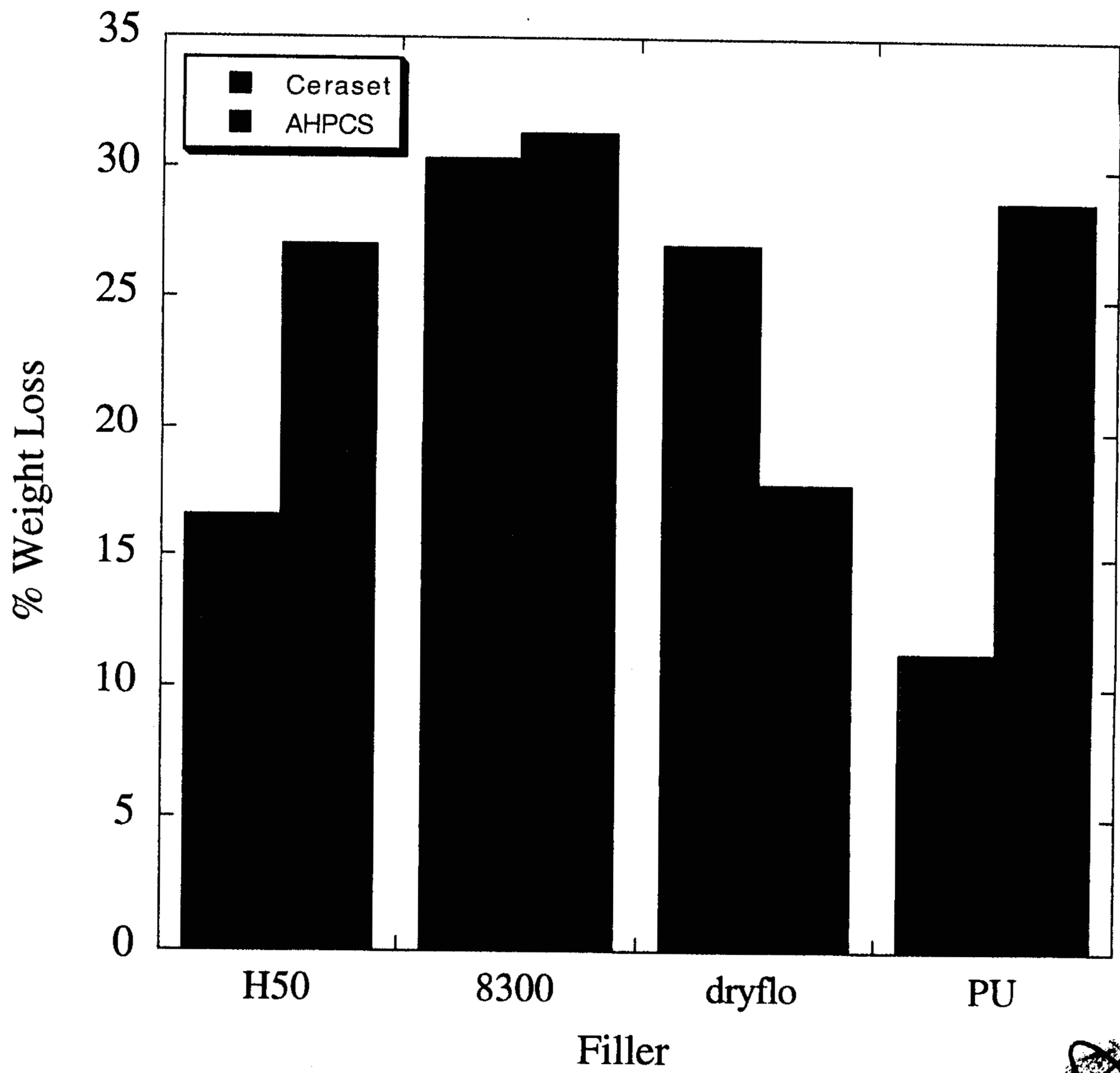
Polymer: Polysilazane



- Possible to process foams of varying densities in both the polycarbosilane and polysilazane systems
- Cell size is constant for a given filler at varying densities, however strut thickness changes with density

Oxidation Behavior of Foams

- All samples experience weight loss (15 to 30%) due to residual carbon removal after oxidation at 1000°C in air for 1 hr
- Residual carbon present from both pyrolysis product and filler decomposition product
- Similar carbon content present in foams from modified starch sacrificial filler and PU sacrificial blowing agent



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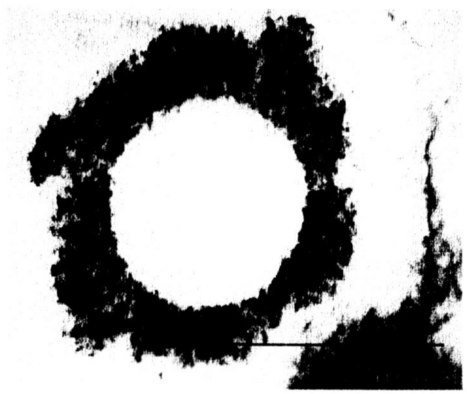
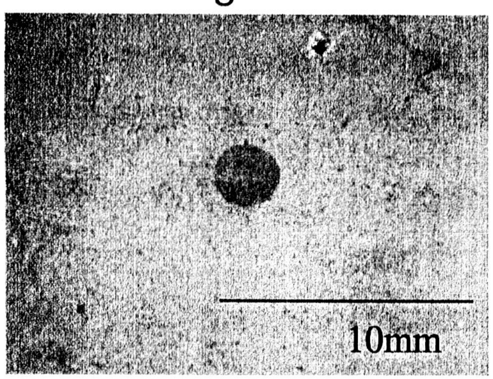
Impact Damage of Microcellular Foams

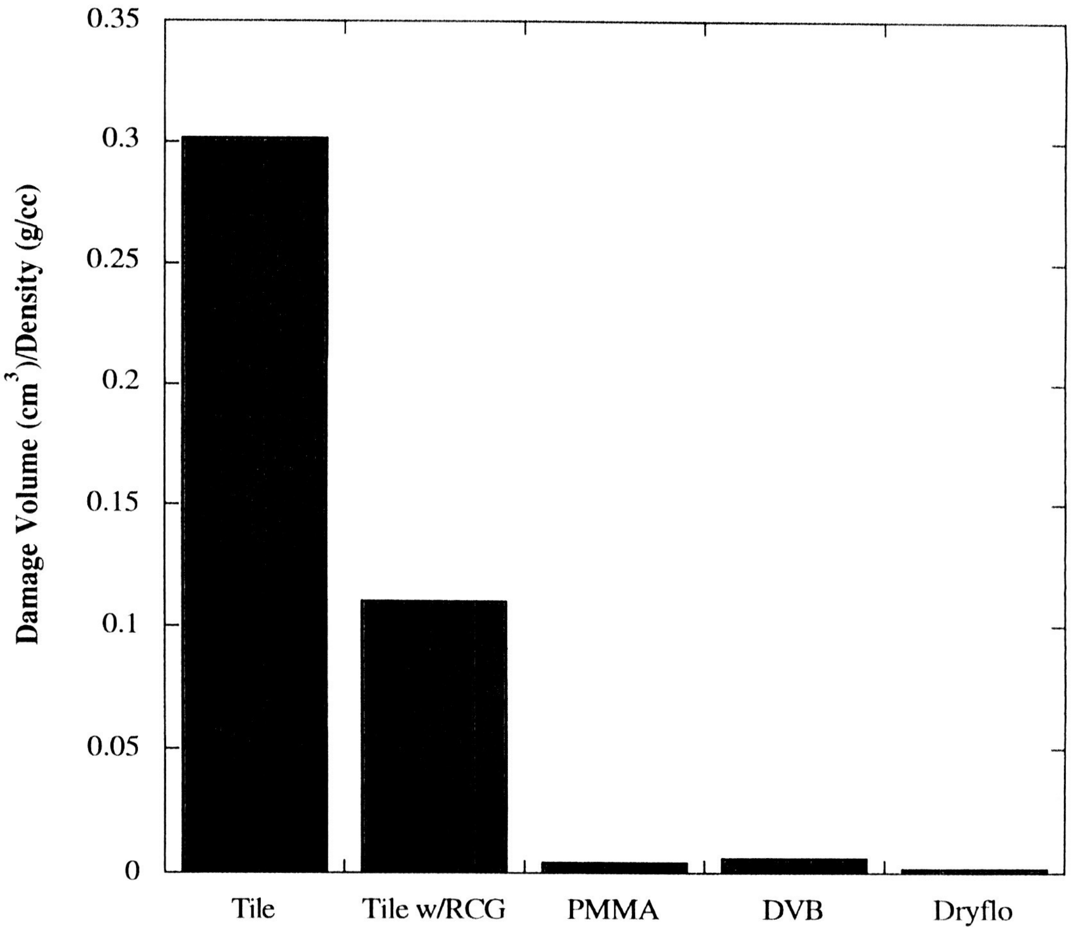
Foam samples impacted using drop test with cone shaped indenter



Tile damage area



Foam with PMMA sacrificial filler damage area



- Preliminary results indicate that foams have encouraging impact damage resistance

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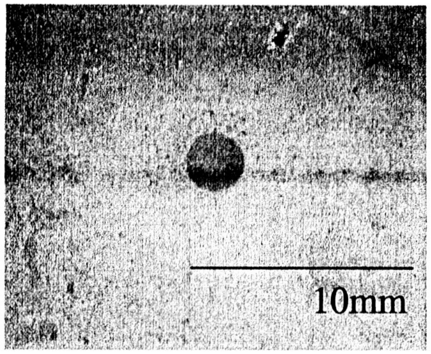
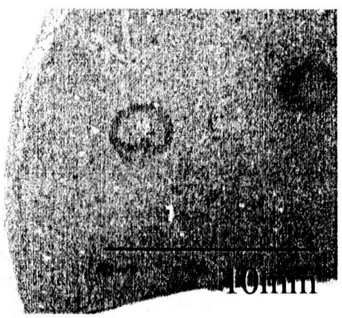
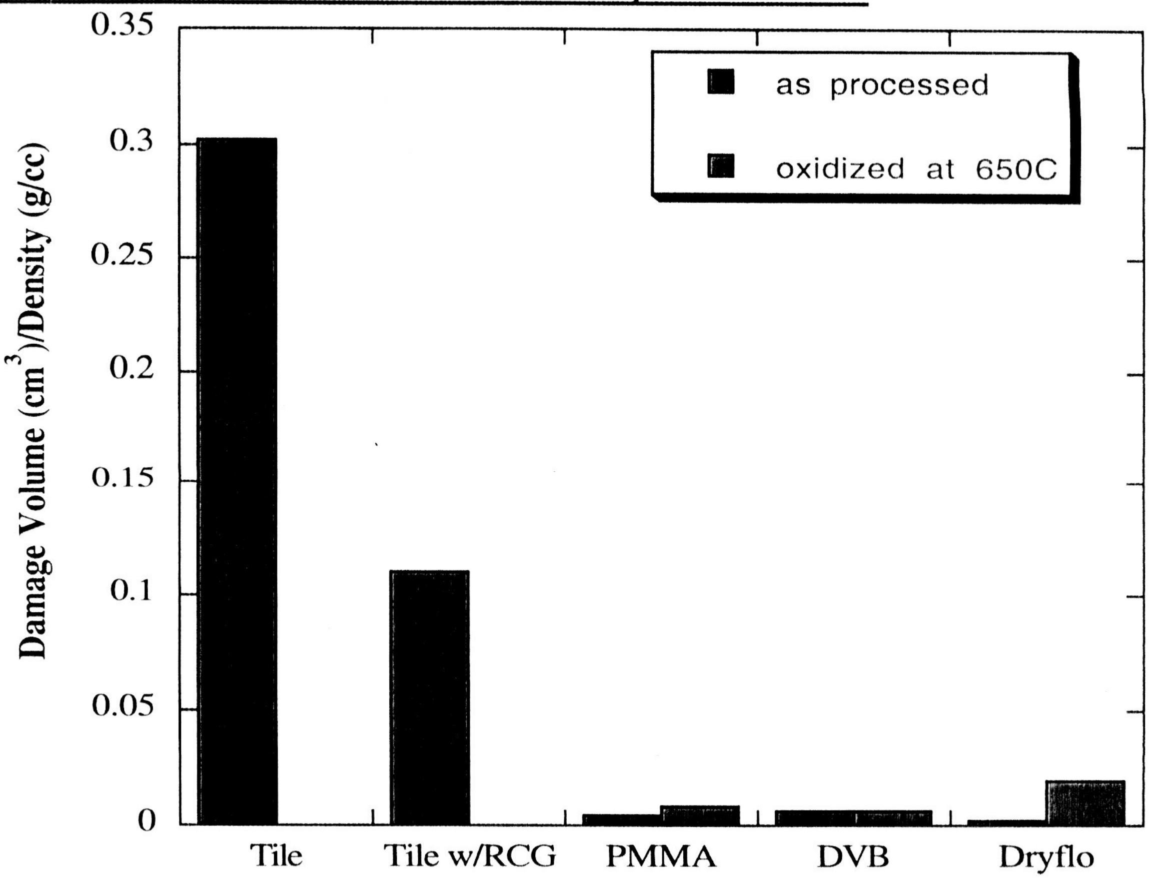
Impact Damage of Microcellular Foams (Post Oxidation Behavior)



As processed PMMA

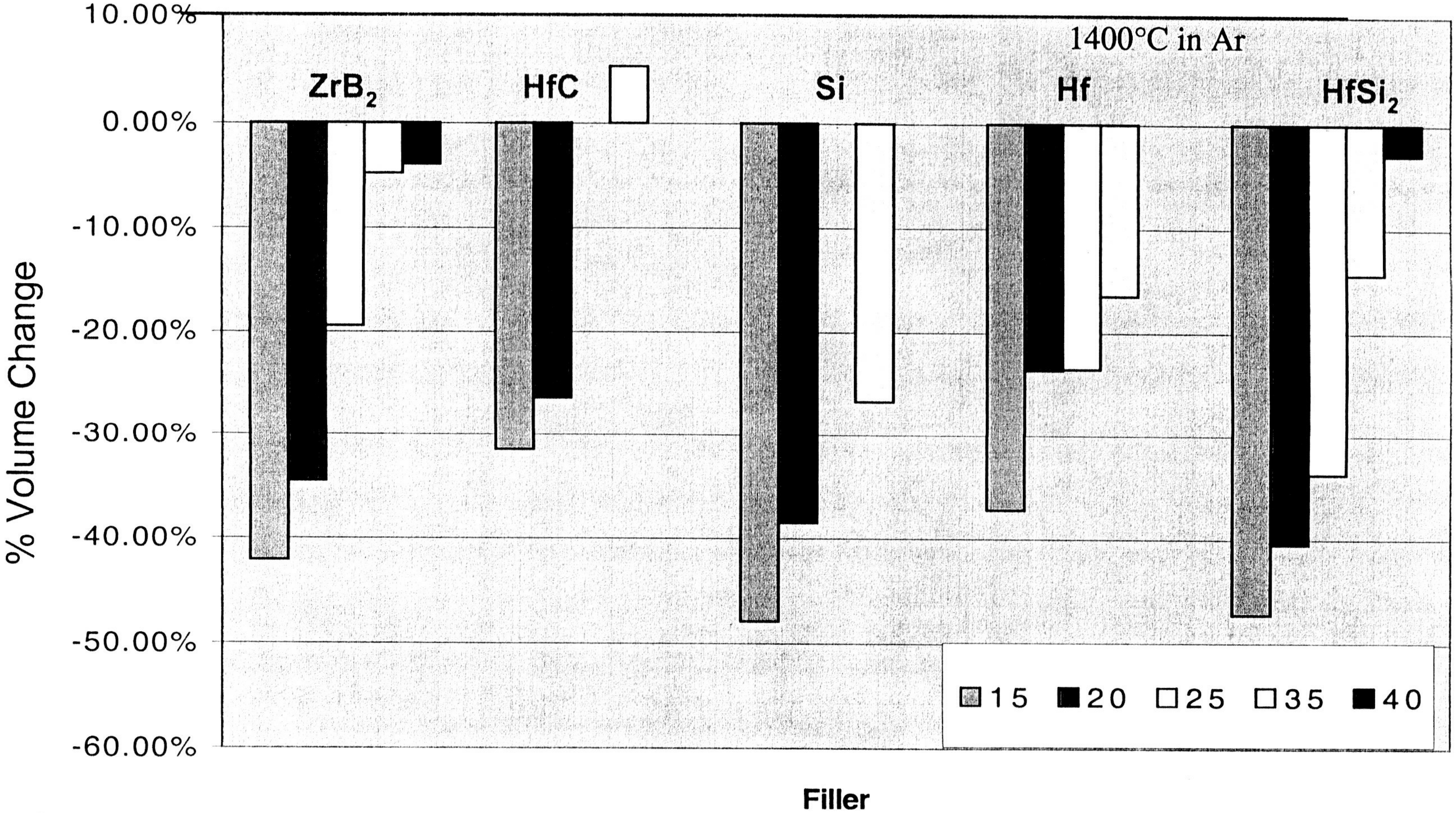


Post oxidized PMMA



- Residual carbon present in foams from both pyrolysis product and filler decomposition product
- All samples experience weight loss (15 to 30%) due to residual carbon removal after oxidation
- Slight decrease in impact damage volume after removal of residual carbon

Near Net Shape Processing of Macrocellular Foams



- Incorporation of reactive or inert fillers substantially reduce shrinkage during pyrolysis
- Can approach zero shrinkage with appropriate filler addition
- Reactive atmospheres lead to increased conversion of reactive fillers

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Summary of Foam Properties

Pre-ceramic Polymer System	Sacrificial Blowing Agent or Filler	Foam Density (g/cc)	Average Cell Size (µm)	Strength (MPa)
SiC precursor	Polyurethane	0.124 to 0.836	140 to 460	1.7 to 4.9
Si_3N_4 precursor	Polyurethane	0.186 to 1.063	60 to 500	2.4 to 6
SiO_2 precursor	Polyurethane	0.192 to 0.273	TBD	TBD
SiC precursor	PMMA, PS	0.3 to 1.3	< 20	1.4 to 3
SiC precursor	Rice starch	0.4 to 1.2	< 5	2.6

Foams are isotropic in behavior

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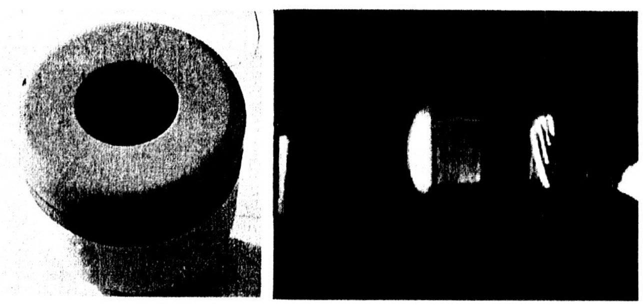
Aerothermal Performance of Foams

Ames arc jet facilities are used to simulate typical aerothermal environments observed during atmospheric re-entry.

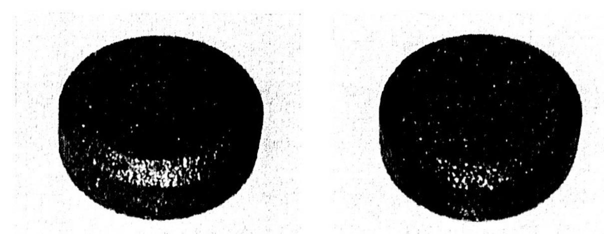
- HETC surface treatment was applied to the beveled ceramic foam disks prior to testing.
  - HETC provides high emissivity, low catalycity, and increased durability.
  - SiC foam substrate
- Samples were placed in SiC-coated graphite model holder. Test conditions were:

Heat Flux (W/cm^2)	Temperature (K)	Emittance
74	1950	0.9

- No observable degradation in foam substrate; however, the HETC material blackened as expected.
- Future work will consider longer duration exposure, larger samples, and additional foam formulations.



Arc jet model before and during testing.



Pre-test and post-test images of sample of foam (90-sec arc jet exposure at 3040°F).

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Conclusions

- Ceramic foams can be processed from preceramic polymers with the addition of sacrificial foaming agents or sacrificial fillers
- Obtained foams with different architectures and compositions by varying process and starting materials
- Current process allows for tailoring of the microstructure in terms of density, cell size, composition
- Preliminary samples show encouraging properties
- This work provides the basic groundwork for long-term projects on understanding the processing and properties of these new materials
- Potential for use in TPS and other applications e.g. filters and catalyst carriers