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Development of high char foam encapsulation

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Livermore, CA

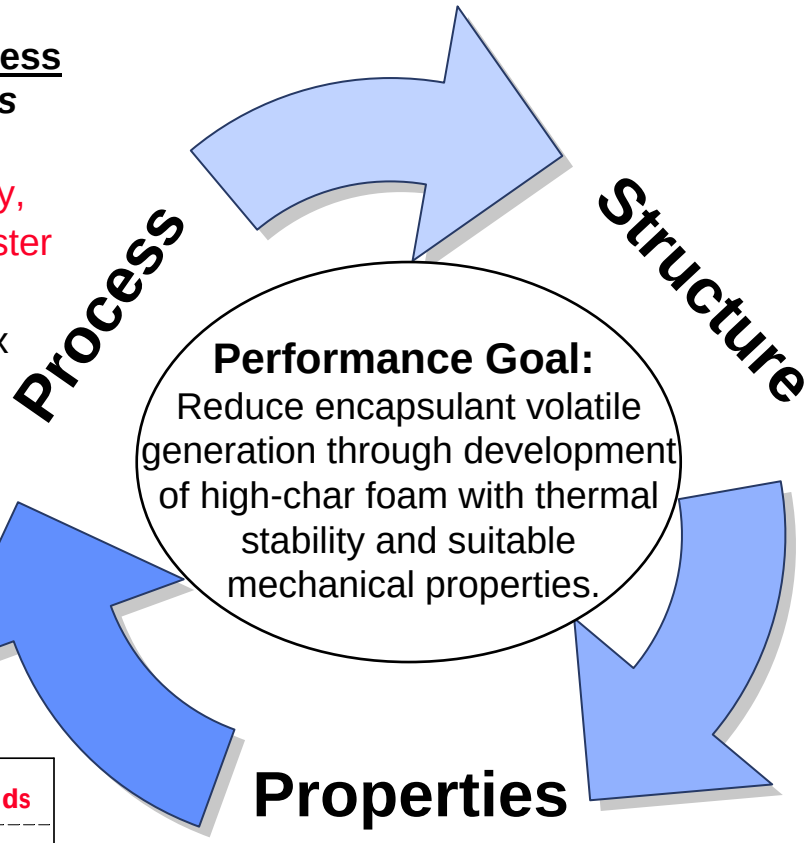
Sandia National Laboratories

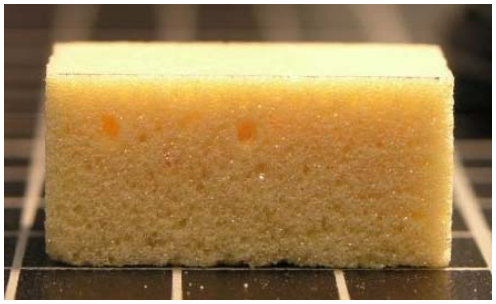
Issue: When encapsulant foam materials decompose under abnormal thermal conditions, gaseous volatiles are produced resulting in deleterious pressure increases

Encapsulant Synthesis Process

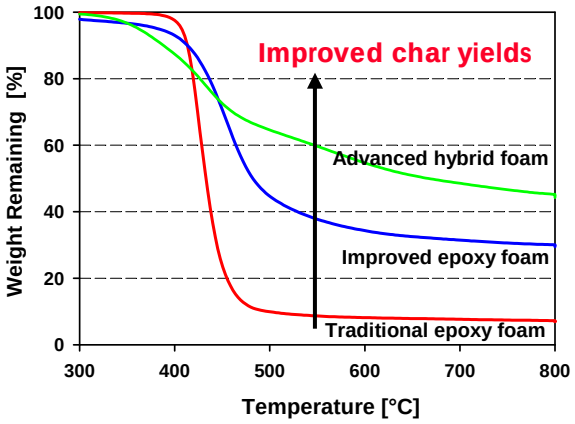
X + Y + Z resins + catalysis + surfactants:

- X,Y & Z: High char Epoxy, Urethane and Cyanate-ester reagents
- Hybrid chemistry/complex catalyzed cure
- Low defoaming action surfactants





New Hybrid Foam Encapsulant
(Prepared using curable system with CO_2 foaming agent)



Process produces high-char foam encapsulants with structural strength and good adhesion.

Current work focuses on optimized char, easy processing and foams with a range of densities

Impact: Through the selection of special resins, synergistic cure catalysis and non-traditional chemistry, we have developed a hybrid foam material that is CO_2 foamed and has considerably higher char than commercial foams.*

**Patent protection will be sought*

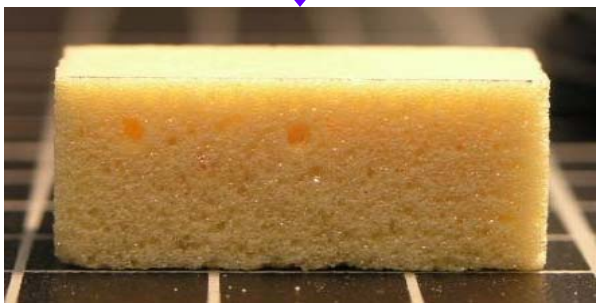
High char foams - requirements

- Char behavior depends on constituent chemistry and cure
- Physical additives are useful but affect viscosity and processing
- Need novel resin combinations
- Requires a systematic evaluation of foam and char chemistry

- Cure reactions
- Individual and hybrid

- Precursor resin
- Individual char
- Mw, Viscosity
- Functionality

- Catalyst
- Nucleophilic initiators
- Surfactants



Vol. and Temp vs. time

- Foaming reaction
- Chemical vs physical
- Isocyanate, anhydrides, BOC

- Cure kinetics
- Competitive kinetics
- Cell stabilization

Char yield
Quality demands
System needs

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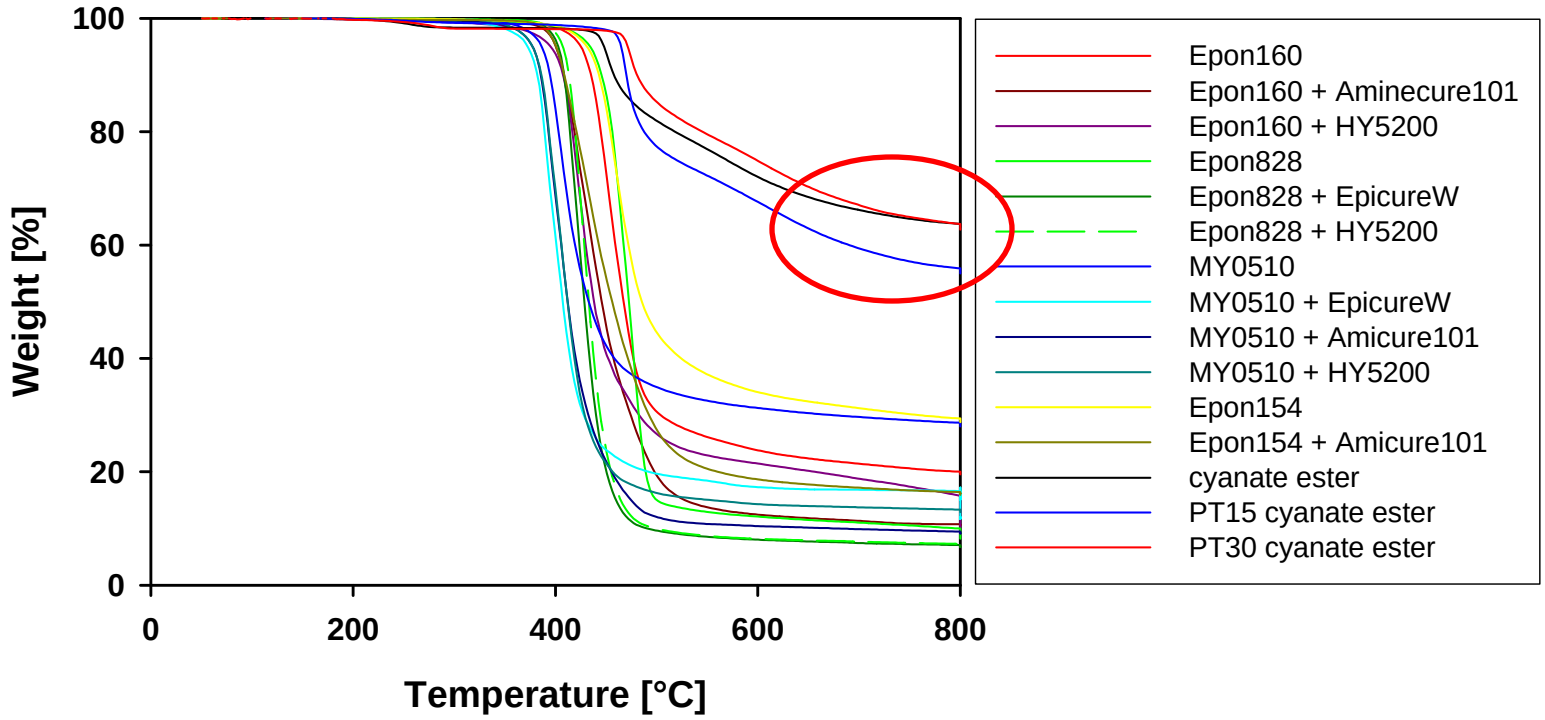
Traditional resins have low char

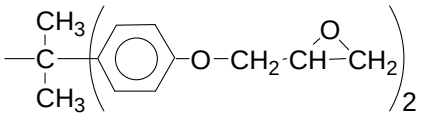
- TGA analysis under N2 up to 800°C
- Many epoxies and PU materials have low char (<20%) or liquefy
- Oxygen, nitrogen and weak aliphatic carbon bonds produce volatiles
- Some epoxies and aromatic amines may yield 30% char
- Acid anhydrides may also produce cured materials up to 30% char

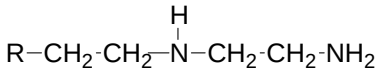


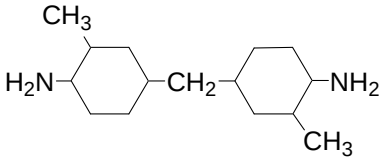
Alternative resins with high char behavior (>60%) exists

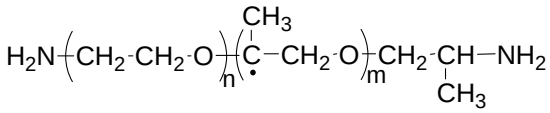
Primary resin selection issues-low char

DGEBA epoxies, cured with aliphatic amines, or polyol-amines

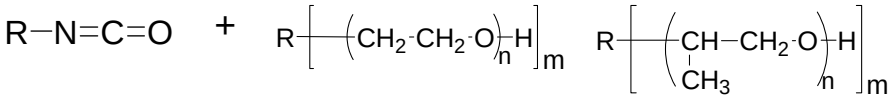


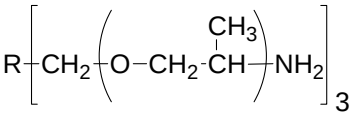




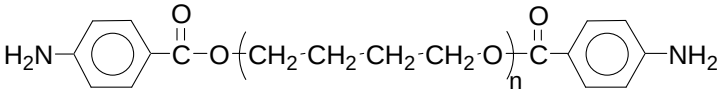


PU's cured with aliphatic polyols





poly-Ureas, isocyanates cured with aromatic polyol-ester-amines



Many traditional resins used for foams or structural composites will result in major volatiles, decomposition, and liquefaction

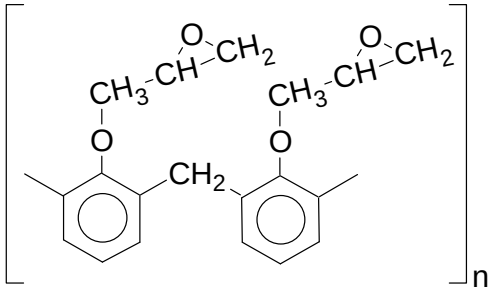
Aliphatic units generally result in low char

Traditional PU-foam: Evidence of significant liquefaction, fluid flow, and outgassing after thermal decomposition

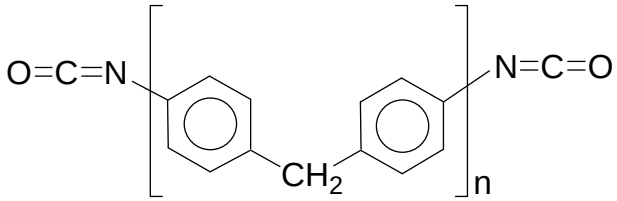
- **Good char formation related to build up of carbon structures**
- **Facilitated by aromatic structures and aromatization**

Primary resin selection issues-increased char

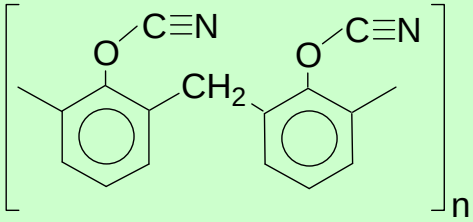
Aromatic based materials deliver higher char yields
Aromatic resins, amines, phthalic acid anhydrides, etc are better
p-MDI, novolac based epoxies, and cyanate esters
Trade-off: Higher viscosity, less chain mobility and alternative cure required



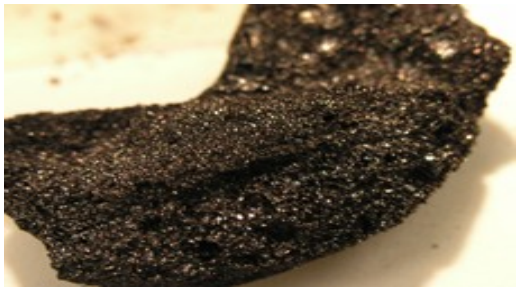
novolac based
epoxy, ~30% char



polymeric MDI
~ 30% char



cyanate ester resins
native char, up to 65% (800C)



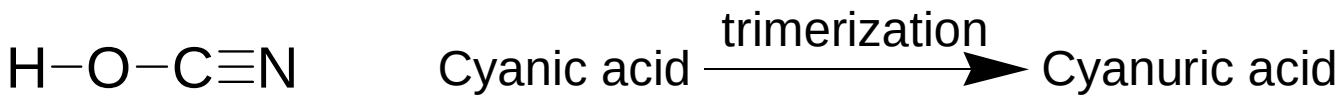
Pyrolysis will lead to a carbon foam at 800°C exposure

- **Aim: Utilize native high char resins**
- **Improve char yield further with synergists**
- **Additives: Potentially higher char with phosphates, borates, other fillers**

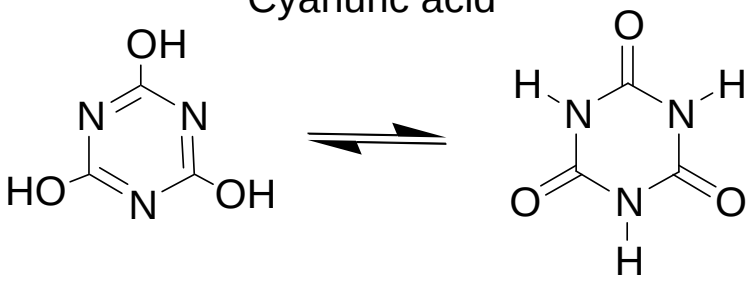
Cyanate ester resins

- **Aryl cyanate esters, specialty resin, derivatives of cyanic acid**
- **Reactions of phenol with cyanogen chloride, elimination of HCl**

- **Derived from dicyan (cyanogen), anhydride of oxamide**
- **Isomer of fulminate [ONC]-**
- **Carbon is electrophilic, hence amenable to nucleophilic initiation and cycloaddition reactions**
- **Cyanic acid**



Cyanuric acid

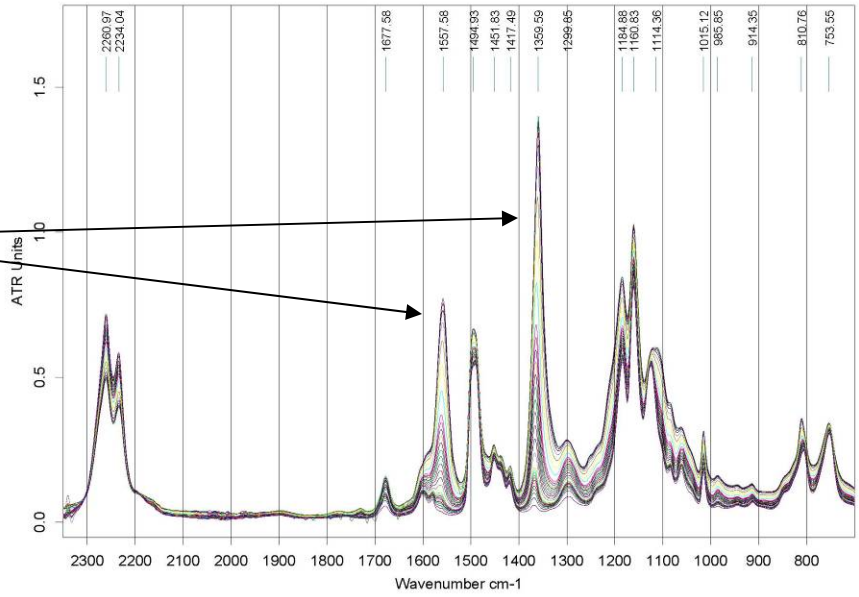


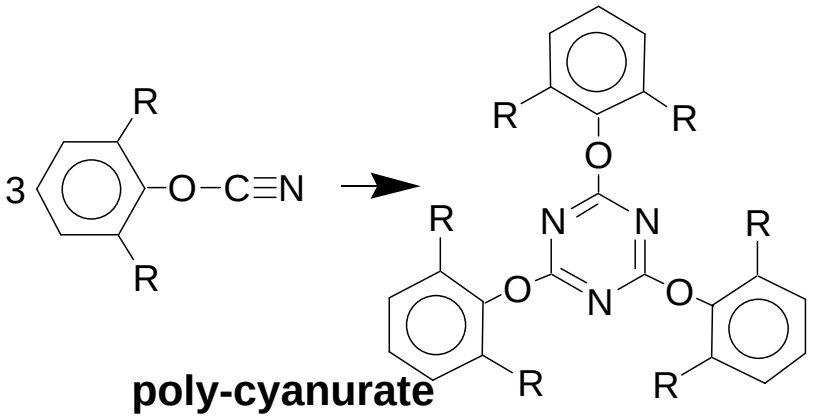
s-triazine-2,4,6 triol s-triazine-2,4,6 trione

Interesting cure chemistry, homopolymerization and additions

Curing of cyanate ester resins- trimerization

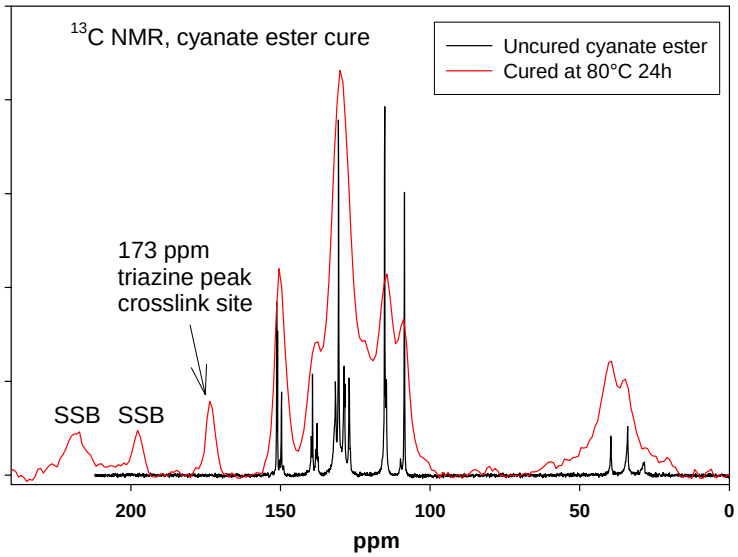
- **Triazine formation from cyanate ester**
- **Requires nucleophilic catalysis**
- **^{13}C NMR signal at 173ppm**
- **IR signature at 1360 and 1558 cm-1**
- **Precursor to condensed aromatic systems yielding high char**





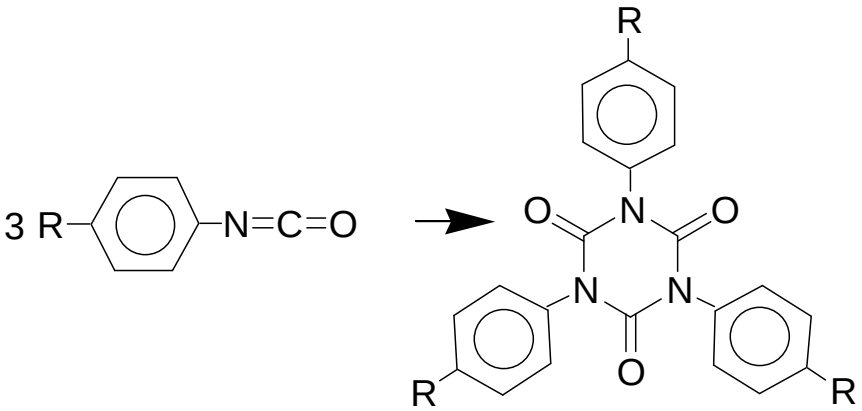
poly-cyanurate

- **Cyanate-ester trimerization difficult to catalyse, normally requires high T**
- **Managed to activate resin achieving substantial cure at 75C**
- **Co-cure approach in foam system**

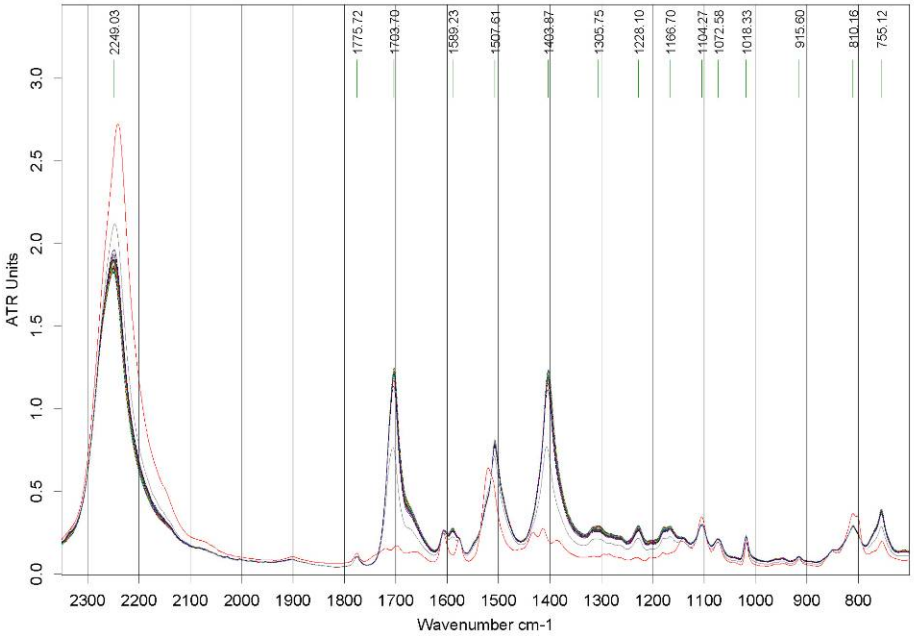


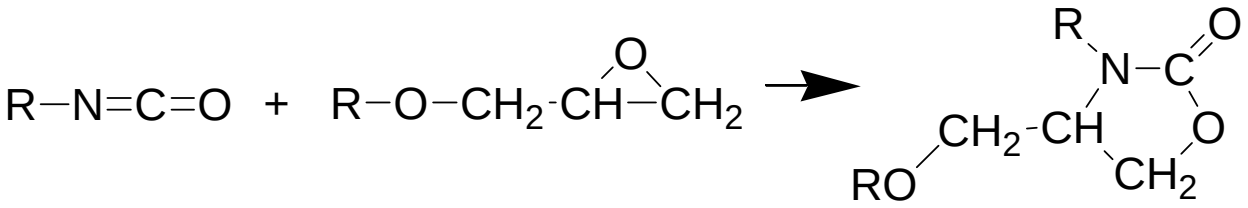
Homo-polymerization of pMDI and epoxy reaction

- Isocyanate trimerization to poly-isocyanurate
- Triphenyl-isocyanurate has absorbances at 1405,1495 and 1705 cm-1
- Observed at 1404, 1508, 1704 cm-1
- Plus secondary oxazolidone reaction (epoxy-isocyanate reaction)



poly-isocyanurate





oxazolidone

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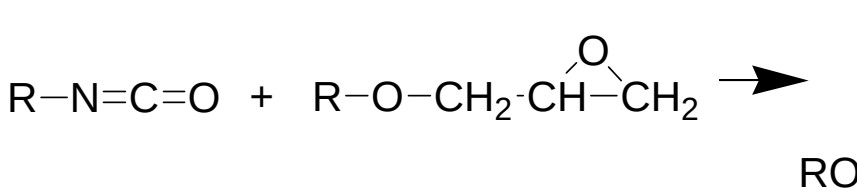
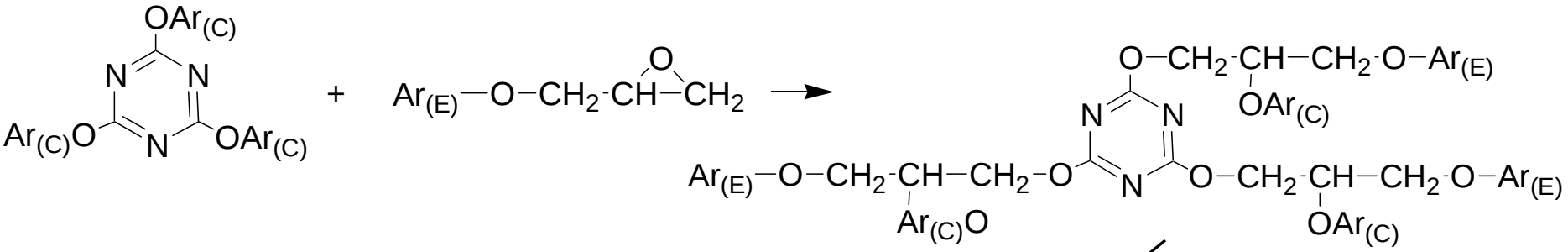
Hybrid chemistry – further reactions

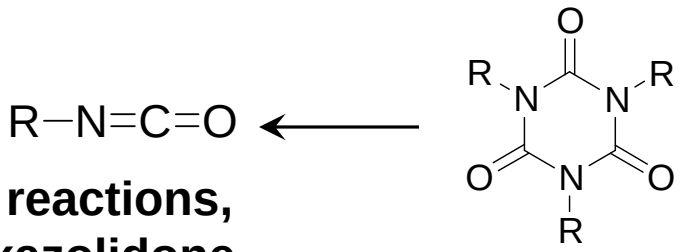
- **Secondary oxazolidone formation (epoxy-isocyanate reaction)**
- **Triazine plus epoxy reactions, further crosslinking**
- **Also, isomerization to alkyl substituted isocyanurates**
- **Reverse cleavage into isocyanates**
- **Simultaneous cyanurate and isocyanurate chemistry**



oxazolidone



isomerization



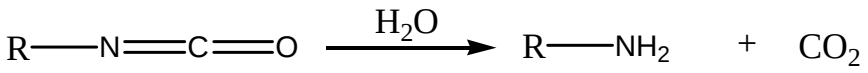
further addition reactions, with epoxy to oxazolidone

Foaming reactions

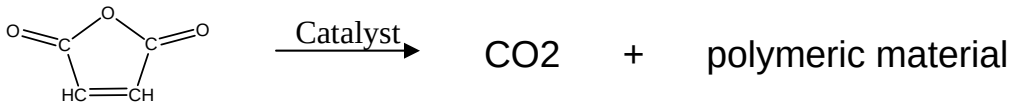
Needed reliable foaming reactions compatible with matrix cure and catalyst selection (nucleophilic initiation)

Three foaming approaches were initially explored:

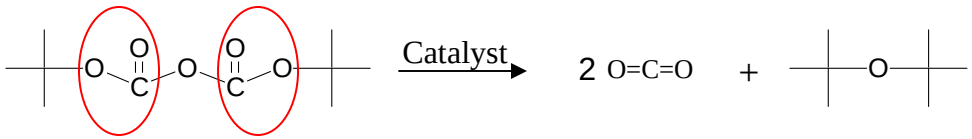
- **Traditional isocyanate to yield CO_2**



- **Maleic anhydride based foaming in non-reactive matrix**



- **Decomposition of t.butyl-dicarbonate to generate CO_2**



- **MA foaming initially very attractive, somewhat more brittle materials**
- **Decided to rely on pMDI isocyanate foaming**

A new high char foam (CHIC)

- Used combination of cyanate ester, epoxy and pMDI to generate CO_2
  1st generation of high char foam (native 50%, no physical additives)
- Tg 80-90°C, good mechanical properties and adhesion, easy foaming
- Different versions, density, toughness, some variations in char yield

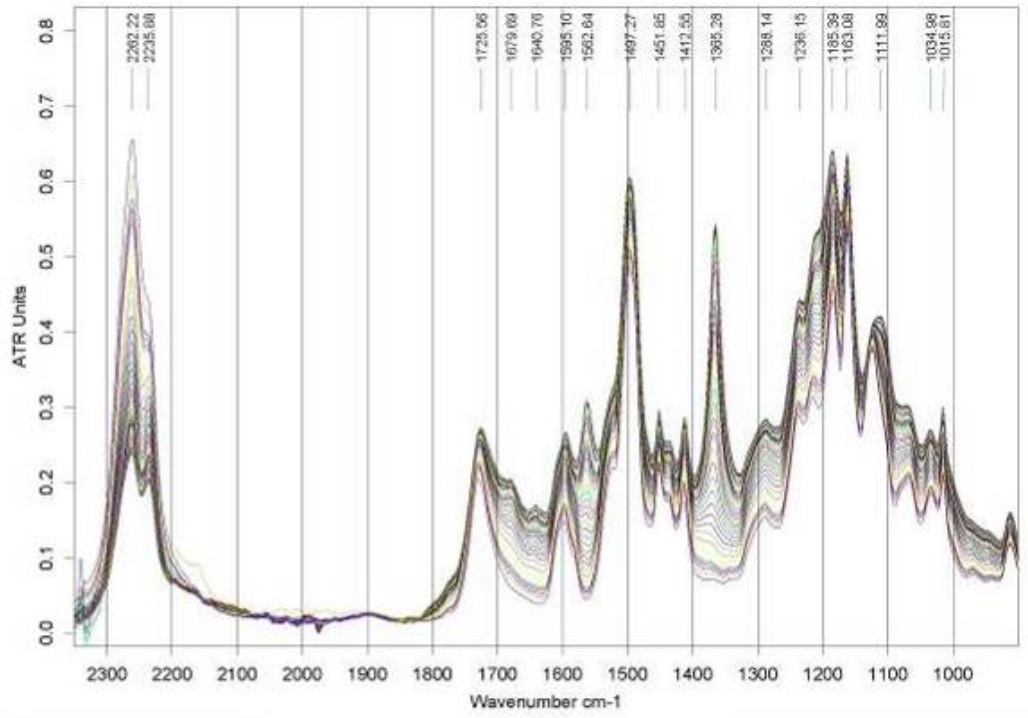
- Cyanate ester matrix resin
- Novolac epoxy resin reinforcement
- pMDI for foaming and hybrid cure
- Surfactant
- Catalysts facilitating foaming and cure

- Char: ~65% at 500°C,
  ~ 45-50% at 800°C

CHIC foam: Char Hybrid Isocyanate Cyanate-ester "chic" (french for style and fashion)

Cure of 0.2 g/cc foam system

- Cure chemistry monitored using IR
- Large cylinder cure at 75°C for 72 hours
- Dominant bands related to triazine formation
- Good conversion, foaming facilitates extra catalysis
- PU chemistry, urethanes, urea nitrogens act as additional nucleophils

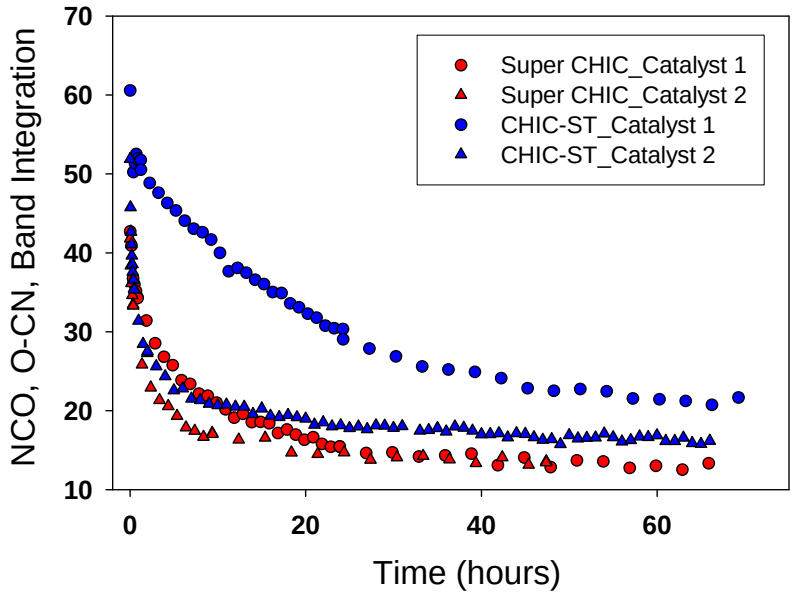


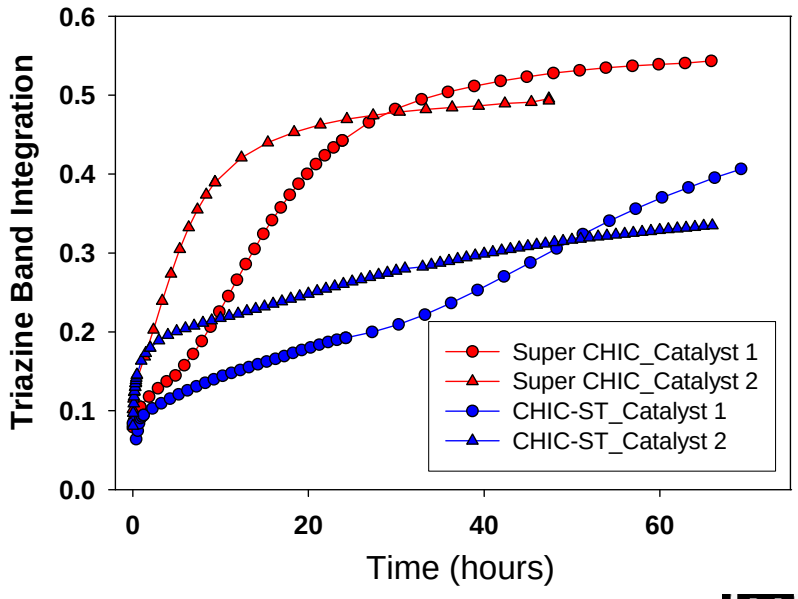
- CHIC foam cures nicely, some evidence for hybrid cure

Foam optimization-cure kinetics

- Fine cells depend on foaming and curing (locking in off structure)
- Cure is generally foaming first, followed by matrix solidification
- Cyanate ester trimerization slower but controllable with catalysts
- Use of IR to monitor consumption in combined R-C=N=O and R-O-CN
- Unique band at 1365cm-1 shows trimerization conversion

- 1st generation 0.1 and 0.2 g/cc foams (CHIC)
- 2nd generation kinetically optimized (finer cells and better mechanical properties (Super-CHIC)





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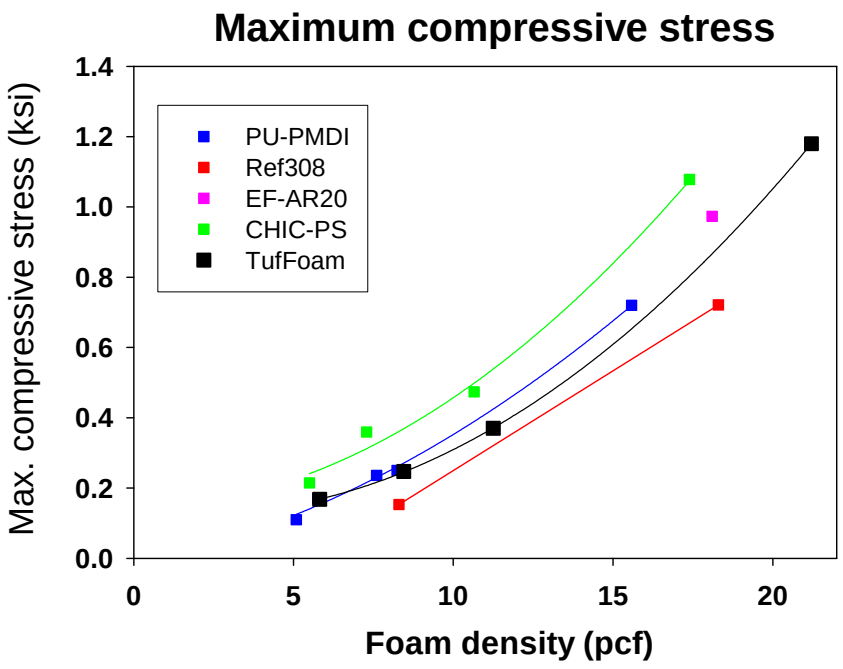
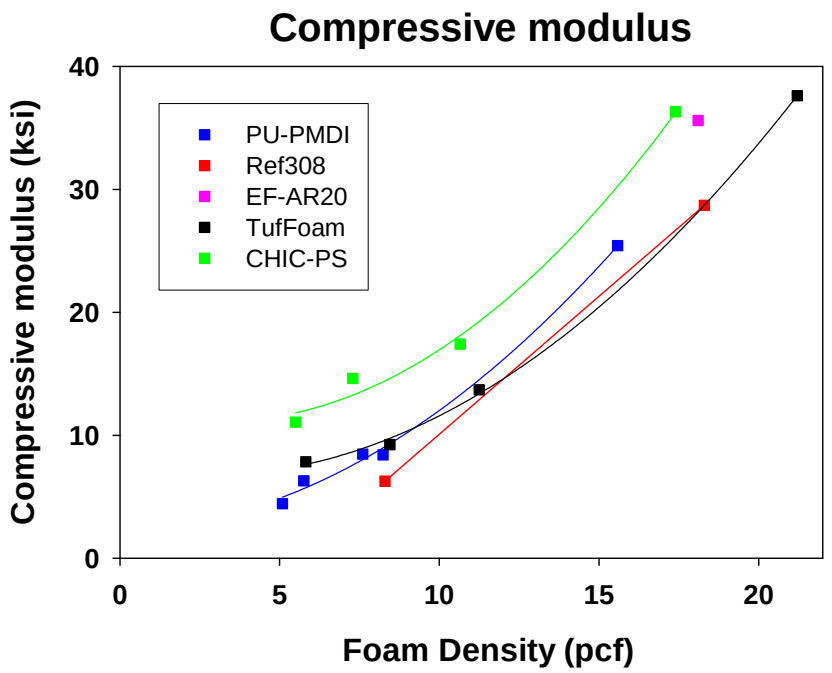
Mechanical property comparison

Compression testing on 1” cubes
Comparison of CHIC-PS, PU, TufFoam, Removable foam

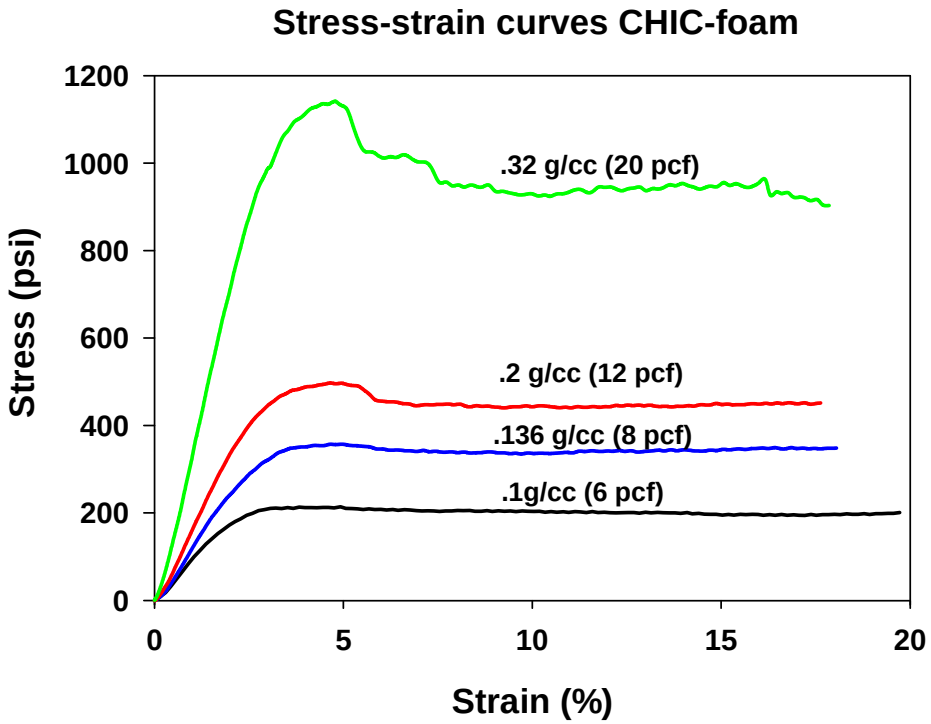




- **CHIC foam has good strength and robustness**

Mechanical property comparison

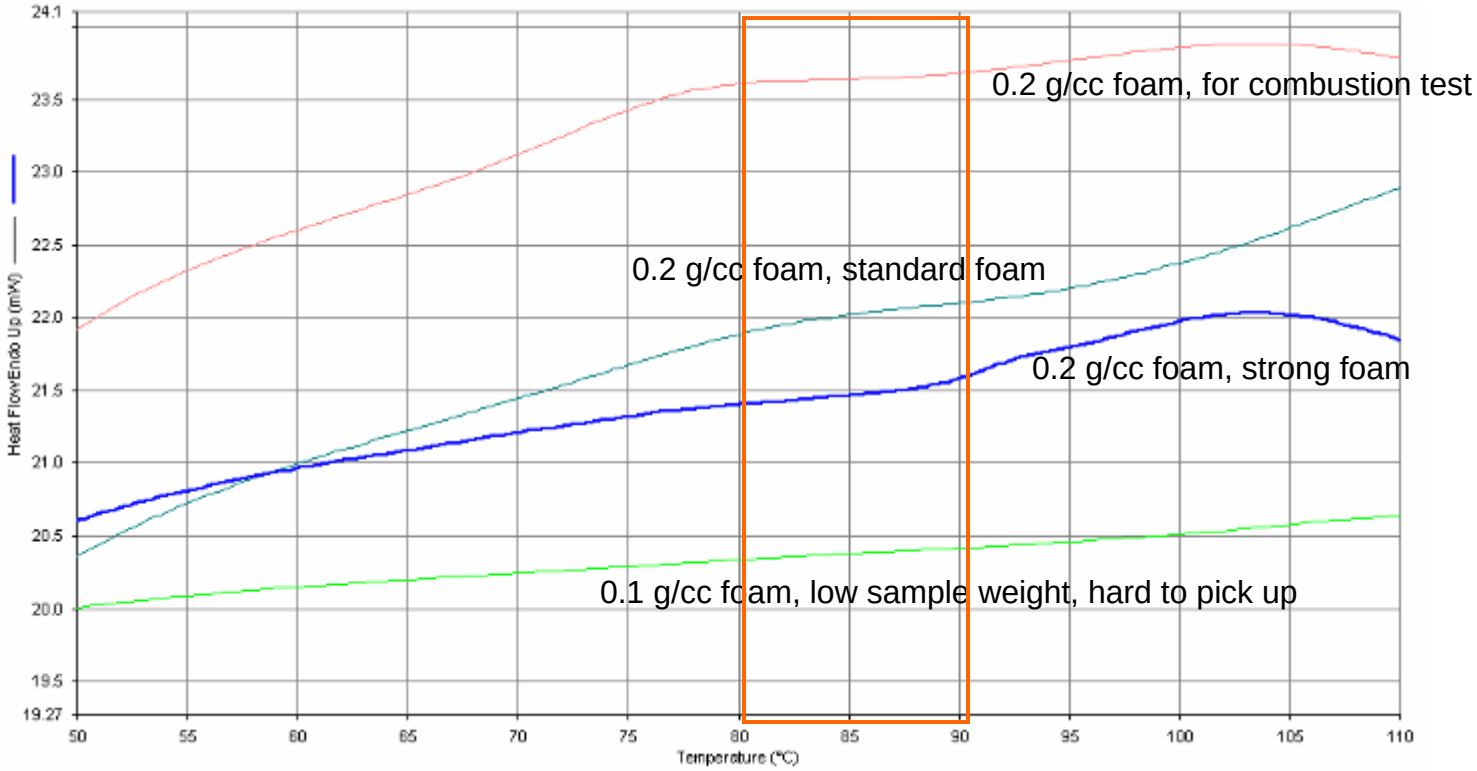
Stress- strain curves for 1” cubes from compression experiments
Note: Adhesive tests are pending, adhesion is generally very good



- **CHIC foam has good cohesive strength and can accommodate compression without immediate fragmentation**

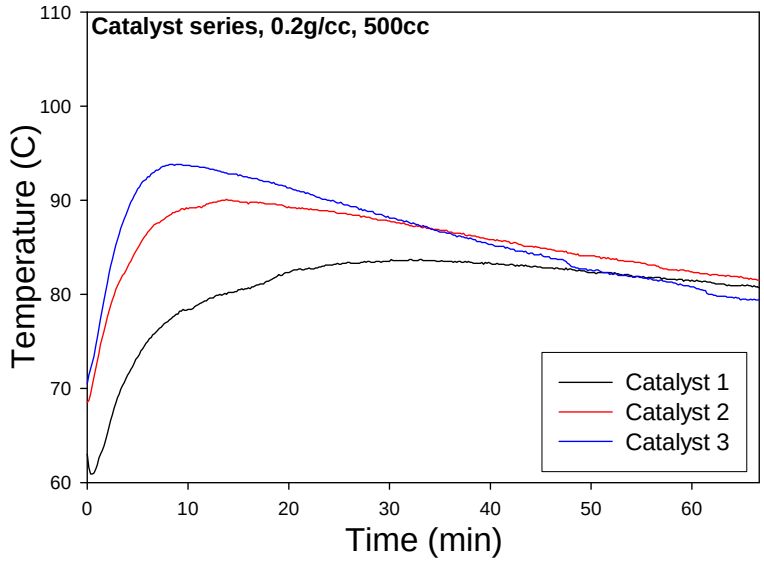
Glass-transition temperature

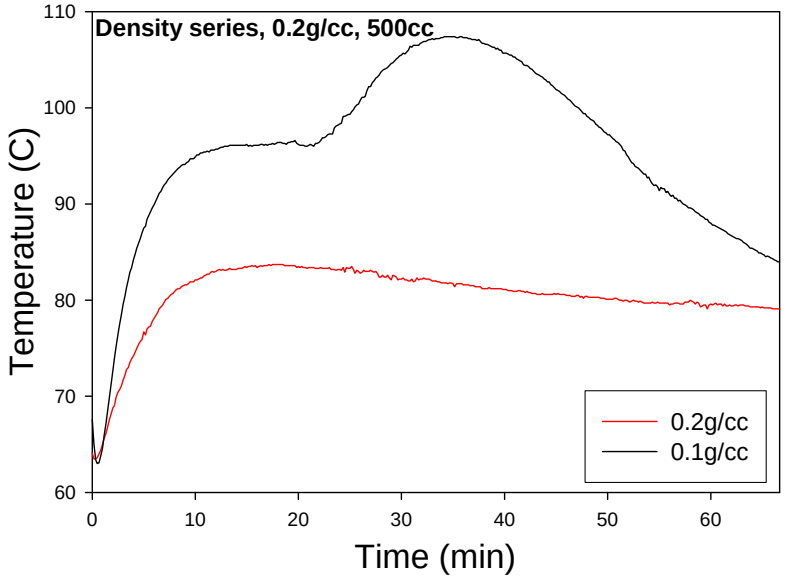
Overview: DSC scans used for determination of Tg



- **CHIC foam has Tg in the range of 85-90°C**

Exothermic cure properties





- Initial foaming reaction is exothermic, isocyanate reactions
- Cyanate ester cure is delayed
- Auto-catalysis in large volume foam can result in thermal runaway
- Thermal control via catalyst, resin and mold pre-warm temperature

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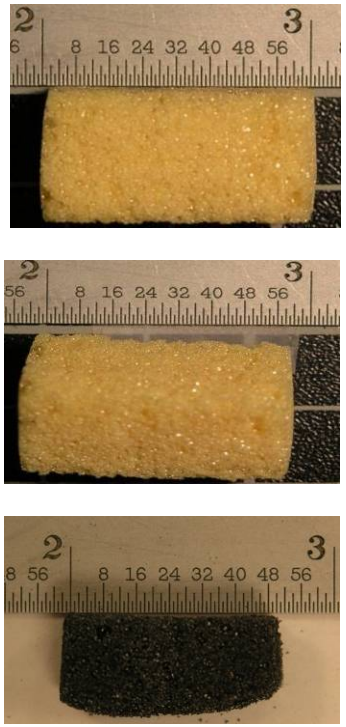
Char formation of hybrid foam

Worst case scenario, thermal runaway, immediate char in the mold
Highly exothermic potential, evidence for significant cure chemistry

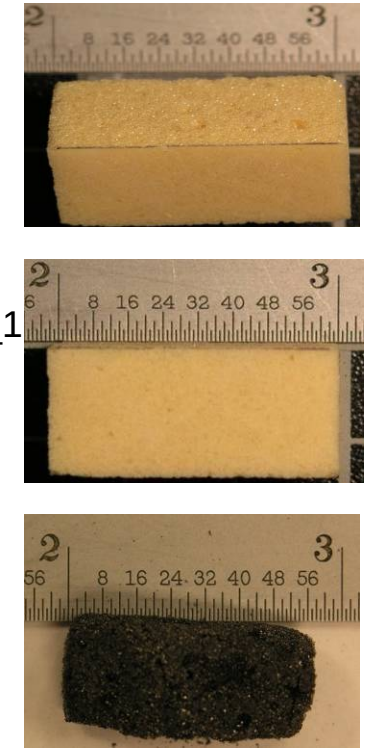
Char formation of hybrid foam

- Good volume and shape retention
- No liquefaction

CHIC_St



CHIC_PS_1



CHIC_PS_2

Sample	Vol_i (cc)	Vol_f (cc)	% Vol Retention
CHIC_St	4.32	2.05	47%
CHIC_PS_1	4.14	2.36	57%
CHIC_PS_2	7.63	4.57	60%

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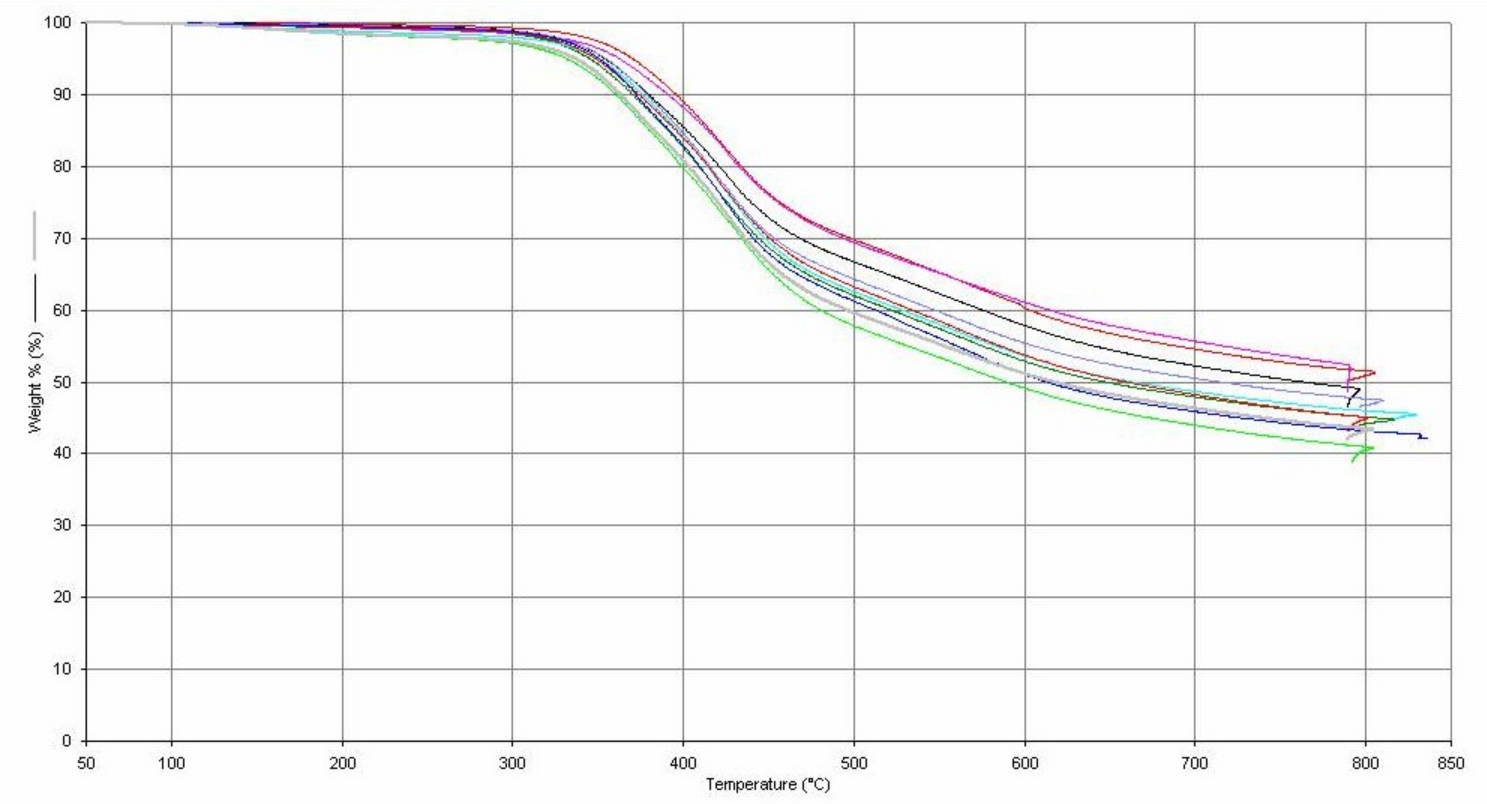
Char formation of hybrid foam

- **Char depends on foam density, mechanical property tuning and density**
- **Without inorganic additives, native char levels are around 50%**



Foam systems assessment and future directions

Triaxial compression experiments (Andy Kraynik):

- **Mid July 2008. Multiple samples for Wei-Yang Lu and Steve Bauer. Mechanical modeling parameters for 20 pcf structural support foam.**

Ken Erickson, Dept 1512:

Combine material synthesis, modeling, and simulation early into the definition of requirements for thermal, chemical, and mechanical properties of foam that fulfill system requirements and have substantial advantages in abnormal thermal environments.

- **Physical and thermal properties of initial foam and subsequent char**
  - **Density, specific heat, thermal conductivity, glass transition temperature, latent heats**
- **Thermal decomposition chemistry**
  - **Kinetics, heats of reaction, analyses of evolved gas/vapor species**
- **Mechanical response: yield properties under loads to determine properties in visco-plastic foam model**
  - **Uniaxial compression, hydrostatic compression, assorted tri-axial tests**
- **Adhesion and processing characteristics**
- **Component-scale experiments**
  - **Obtain data for development and validation of numerical models for heat transfer and pressure growth in sealed systems**
  - **Obtain data for impact and shock response (from CASA program)**
- **Model development and parameter evaluation (Complementary ASC project to develop radiation-conduction heat transfer models for homogeneous participating media)**

Some conclusions

- Cyanates ester resins were successfully used as a foam matrix material
- Resin mix allows for a hybrid system with multiple foam and cure mechanisms
- Foams have good mechanical and adhesive properties
- We understand the function of different catalysts
- Able to control processing and cure requirements
- Able to control exotherm behavior and foam density

- These systems will be further optimized as a function of viscosity, density, cure demands, mechanical robustness and char

- A new family of custom engineerable foams:

"Vivent longtemps Le CHIC"

Acknowledgements

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- **Ed Russick and Mark Stavig for some foam mechanical testing and reference data**
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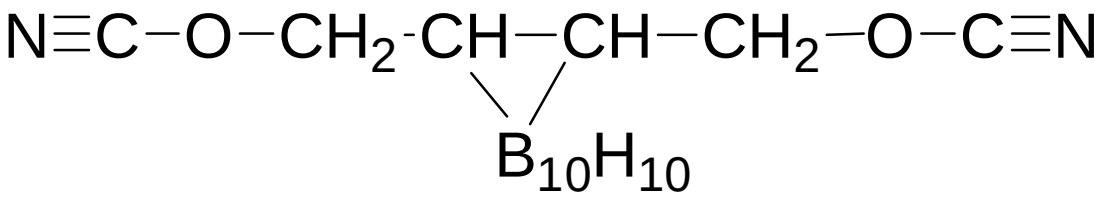
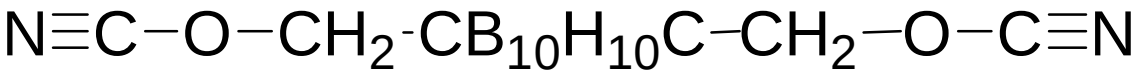
The ideal high char precursor?



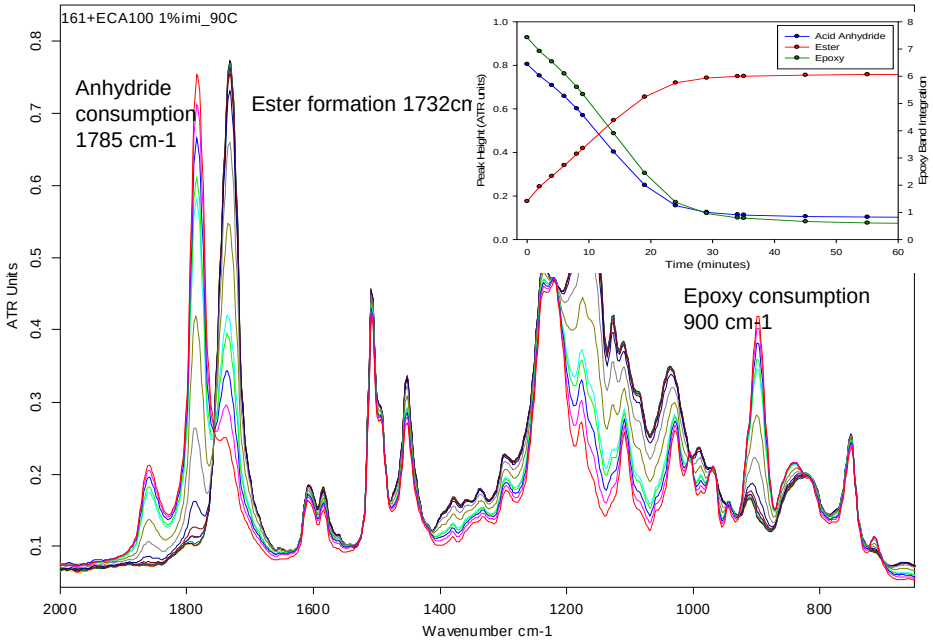


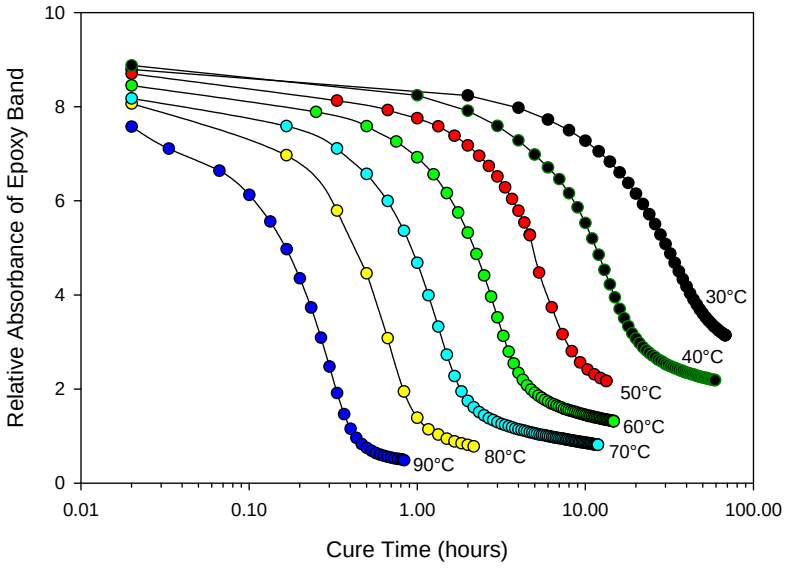
Cyanate ester carborane combination

Mat Celina, Dept. 1821

New capability in Dept.1821: Reaction kinetics of resin cure

- IR spectroscopic monitoring as a function of t,T
- State of the art efficient spectral acquisition
- Heated diamond ATR up to 210°C
- First spectroscopy attachment sold in the USA
- Software macros for band quantification/plotting





Example: Anhydride cured epoxy, t,T data yield $E_{act.}$ of 78 KJ/mol
Conversion at different T's shows how concentration of residual epoxy groups depends on T and associated glassification