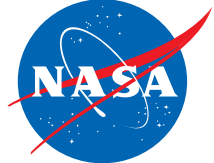


Alternative high performance polymers for ablative thermal protection systems

Ablative thermal protection systems are commonly used as protection from the intense heat during re-entry of a space vehicle and have been used successfully on many missions including Stardust and Mars Science Laboratory both of which used PICA – a phenolic based ablator. Historically, phenolic resin has served as the ablative polymer for many TPS systems. However, it has limitations in both processing and properties such as char yield, glass transition temperature and char stability. Therefore alternative high performance polymers are being considered **including** cyanate ester resin, polyimide, and polybenzoxazine. Thermal and mechanical properties of these resin systems were characterized and compared with phenolic resin.

Authors:

Tane Boghuzian
Maired Stackpoole
Greg Gonzales



Alternative High Performance Polymers for Ablative Thermal Protection Systems

Tane Boghuzian

ERC Inc. at NASA Ames Research Center

Mairead Stackpoole

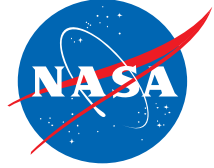
NASA Ames Research Center

Greg Gonzales

ERC Inc. at NASA Ames Research Center

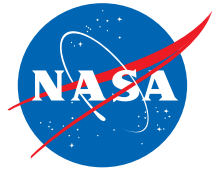
Joe Wong

University Space Research Association



Outline

- Introduction
- Objective
- Ablation– the concept
- Testing on mechanical performance
 - Resin systems
 - Cyanate ester resin(CE)
 - Polyimide resin
 - Polybenzoxazine (PBZ)
 - Polybenzimidazole(PBI)
 - Characterization results
 - Summary and future efforts



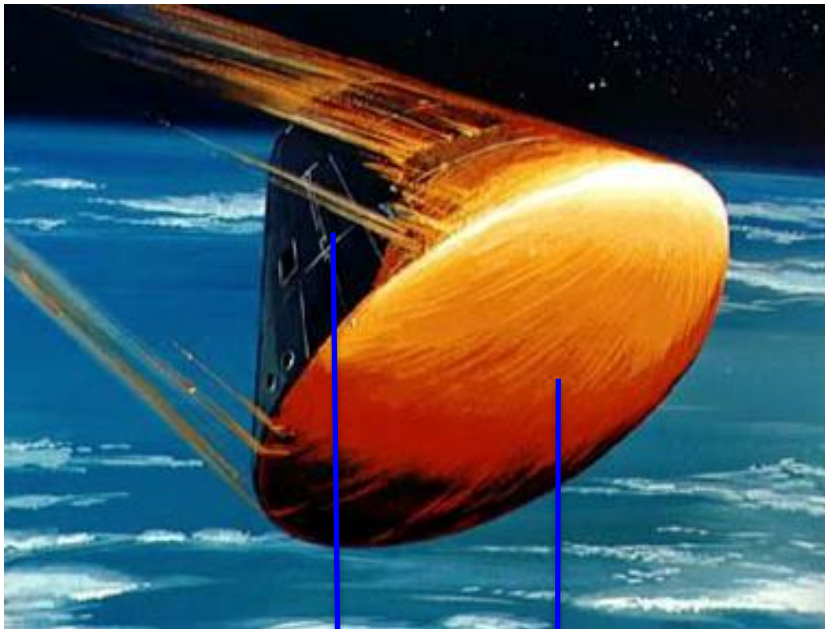
Introduction On TPS Materials

What is a Thermal Protection System (TPS)?

- TPS are required to protect aerospace vehicle systems against the hostile environment in which the temperature can reach up to 2000°C
- TPS is made of a polymer system and carbon matrix (ablative materials)

TPS materials can be classified as:

- High heat flux condition use which called ablators such as PICA (phenolic impregnated carbon ablator) used in MSL(Mars science laboratory)
- Low heat flux condition TPS such as those used in the space shuttle orbiter

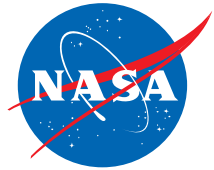


Vehicle structure

TPS



PICA Heat shield in Mars Science Lab



Objective

Goal of this research:

Characterize alternative resins to improve/tailor the performance of ablative TPS

Phenolic is the baseline resin but it has some processing and property issues, such as:

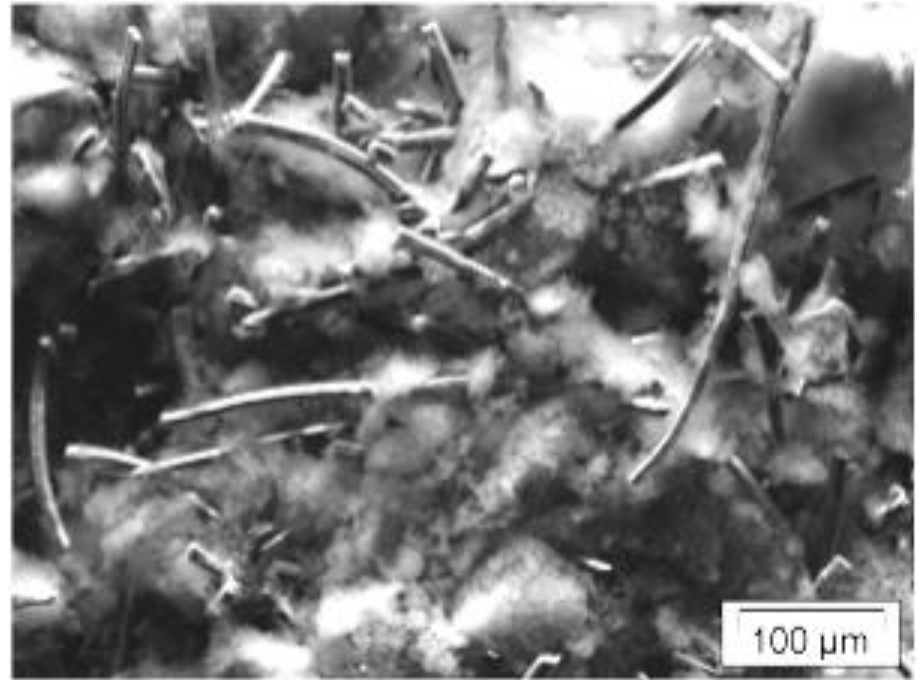
- Many defects from processing
- Poor shelf life
- Brittleness /Low mechanical performance
- Low char yield

Alternative resin systems investigated:

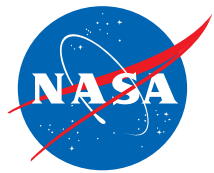
- Polyimide resin
- Polybenzimidazole(PBI)
- Cyanate Ester resin(CE)
- Polybenzoxazine (PBZ)

Characterization of critical properties:

- Char yield (high)
- Thermal conductivity (low)
- Glass transition temperature (high)
- Mechanical property (high)



SEM image of PICA



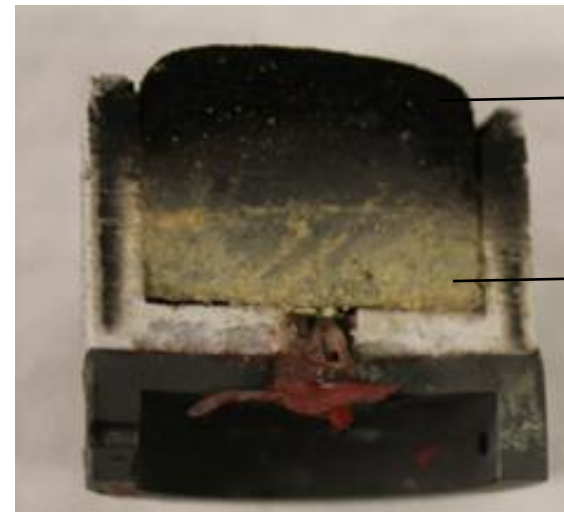
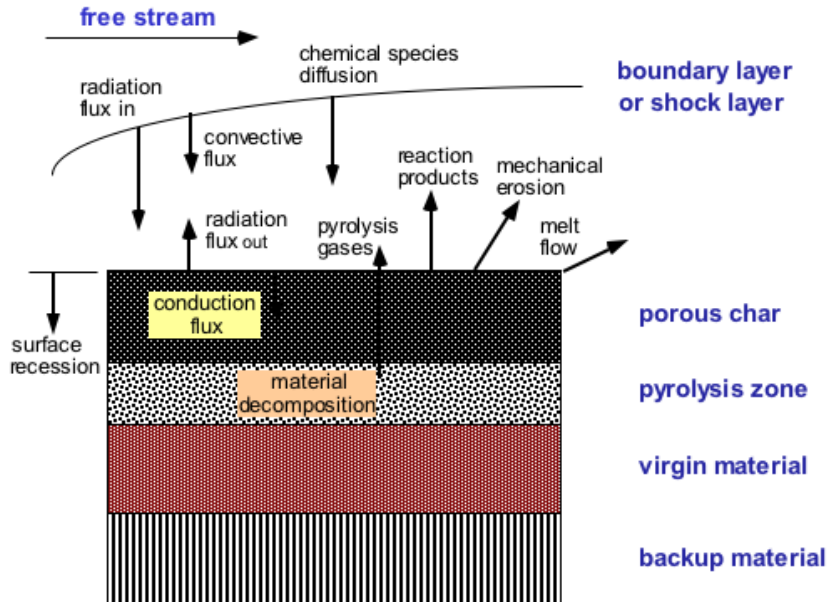
Ablation Process

Ablation:

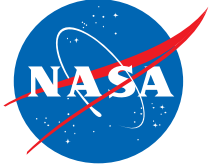
Energy management through material consumption

Ablation process:

- Heat is dissipated through a decomposition of the ablating materials
- Charring occurs
- Pyrolysis gases flow through the porous char
- A carbon char can be further oxidized
- Recession of the surface materials



High temperature post test sample



Techniques to Characterize and Identify Polymer Structure

The followings are the techniques we used to evaluate the best polymer system for TPS.

1- Thermal gravimetric analysis (TGA)

Provides information on the thermal stability of materials, along with degradation temperatures and char yield

2- Differential scanning calorimeter (DSC)

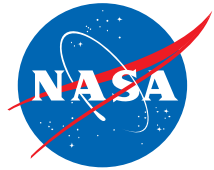
Identifies the glass transition as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state

3- Laser flash analysis (LFA)

LFA is a technique which measures the thermal diffusivity of materials

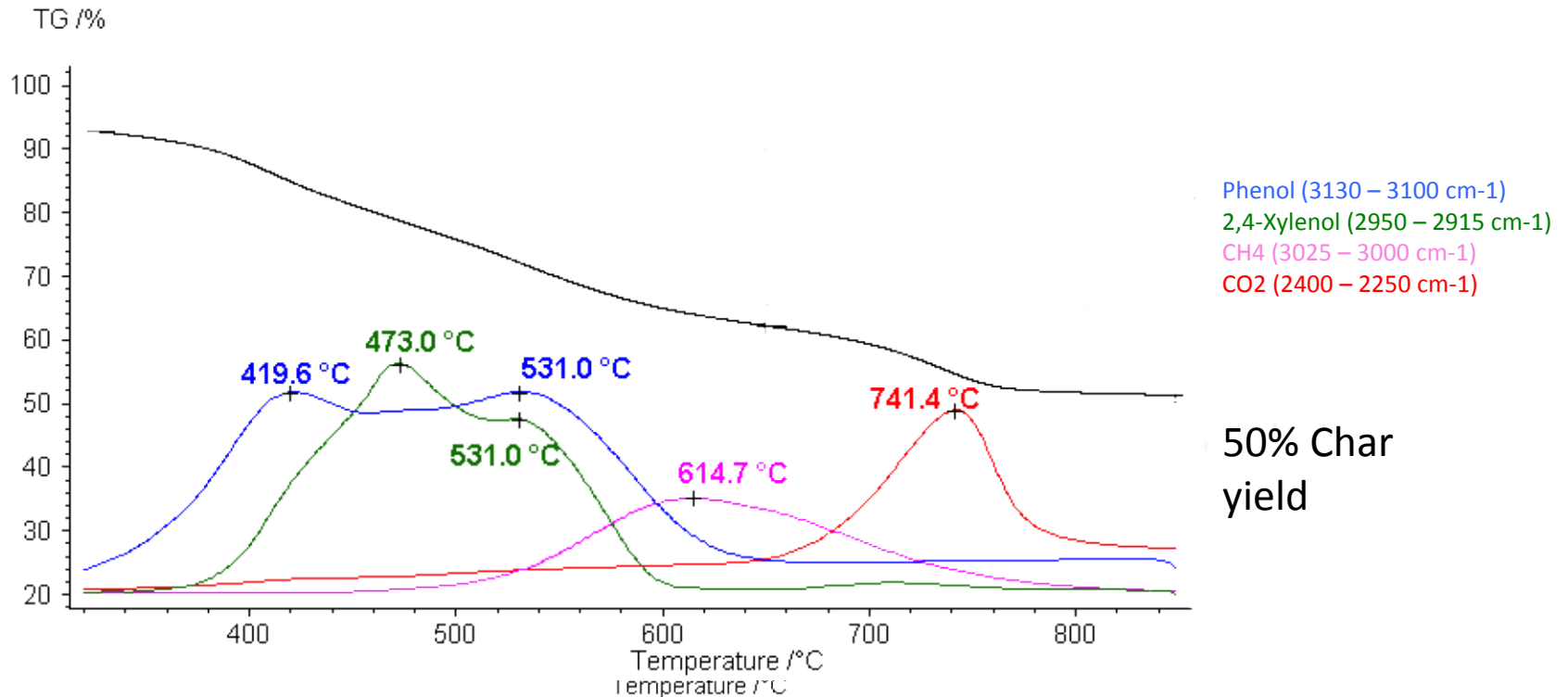
4- Mechanical testing

Determines the compressive strength and stiffness of a material



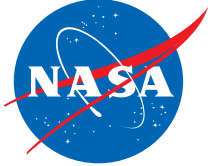
TGA (Char Yield)

- TGA measures mass change as a function of temperature
- If the TGA is connected to a mass spectrometer or FTIR it can characterize the decomposition products of an ablative composite
- For ablative polymers the remaining mass fraction is the char yield



Phenolic resin in TGA connected to mass spectrometry

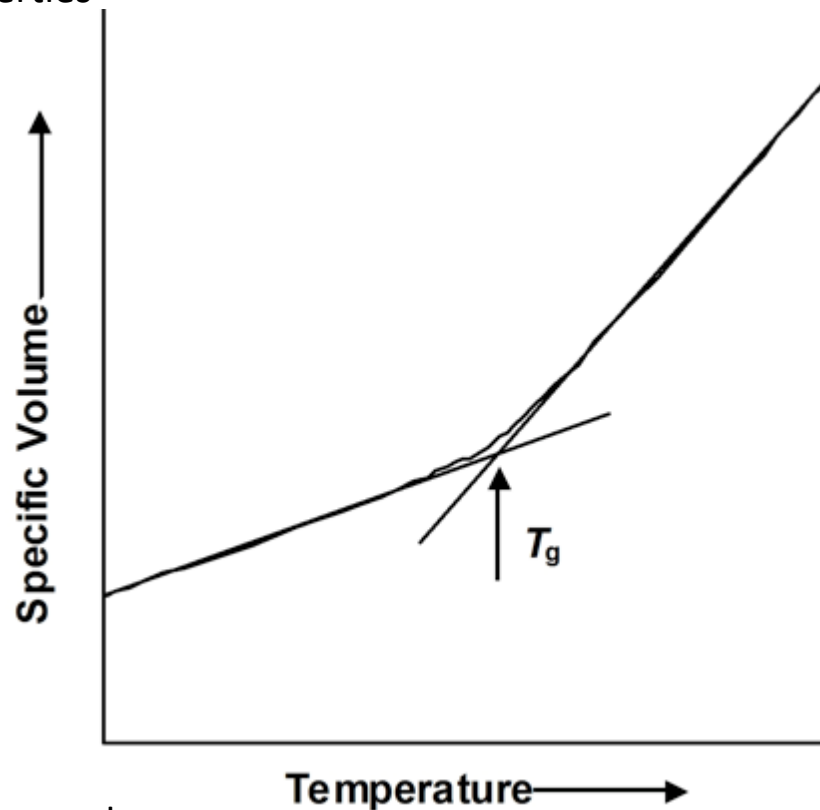
www.Netzsch.com



DSC (Glass Transition Temperature)

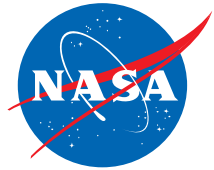
Glass transition temperature (T_g):

- Glass transition occurs as the temperature of an amorphous solid is increased
- Sample undergoes a change in heat capacity
- Higher glass transition temperatures are desirable because materials will have better mechanical properties



Can also obtain:

- Crystallization temperature
- Melting temperature
- Curing temperature

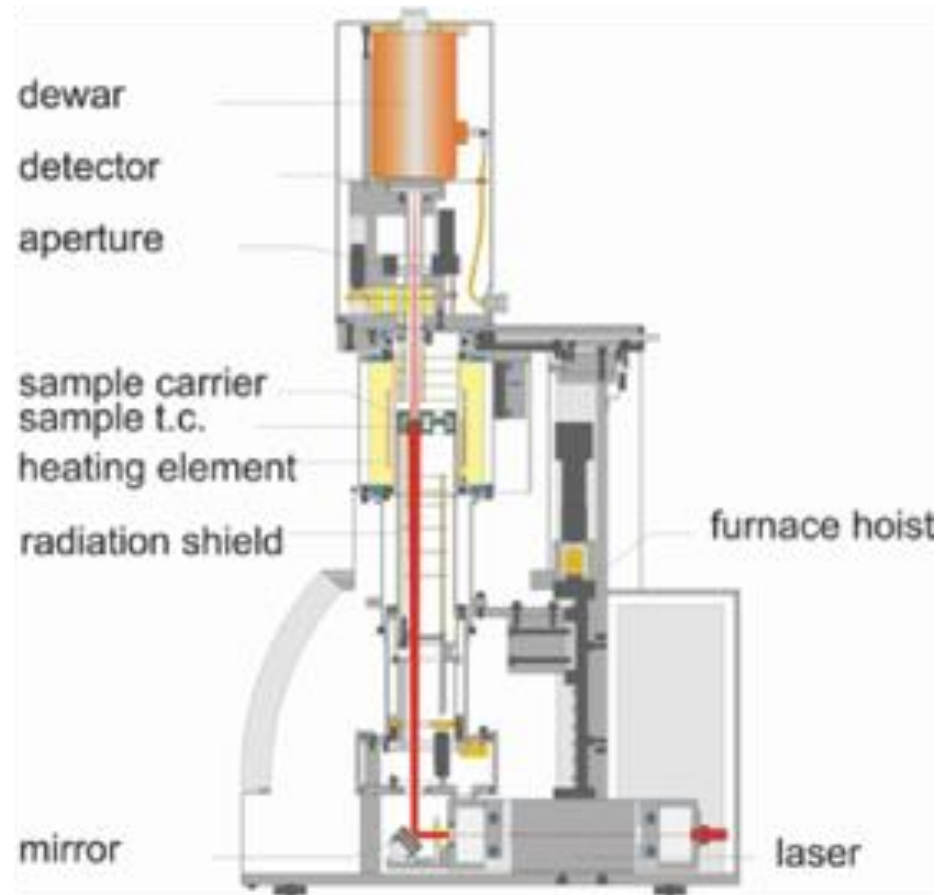


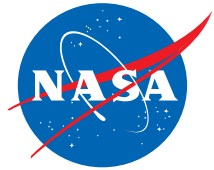
LFA (Thermal Diffusivity)

- The front side of a plane-parallel sample is heated by a short laser pulse
- The absorbed heat propagates through the sample and causes a temperature increase on the rear surface
- The temperature rise is measured as a function of time using an infrared detector
- If the material density is known the thermal conductivity can then be determined

$$\kappa(T) = C(T)\rho(T)\alpha(T)$$

- κ is the thermal conductivity (W/(mK))
- C is the material heat capacity (j/Kg)
- ρ is the density of the material (g/m³)
- α is the thermal diffusivity (m²/s)

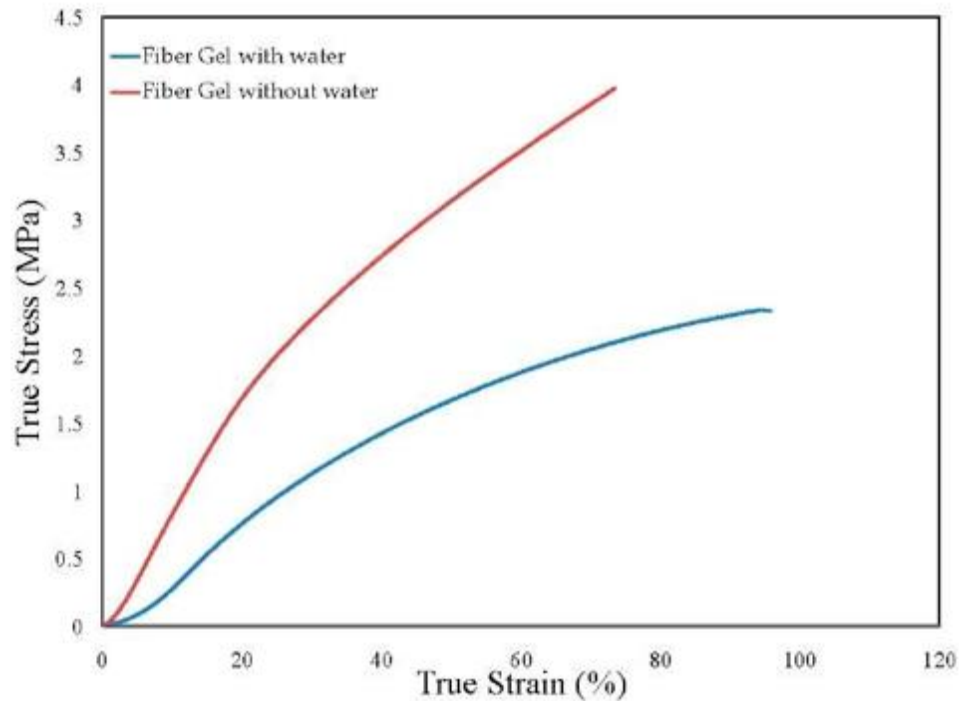


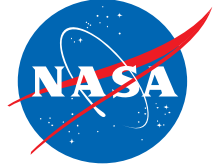


Mechanical Testing

Benefit of compression tests

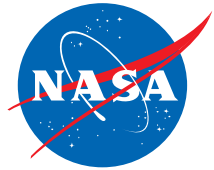
- Easy sample preparation
- Reproducible results from sample to sample
- Suitable to different material types



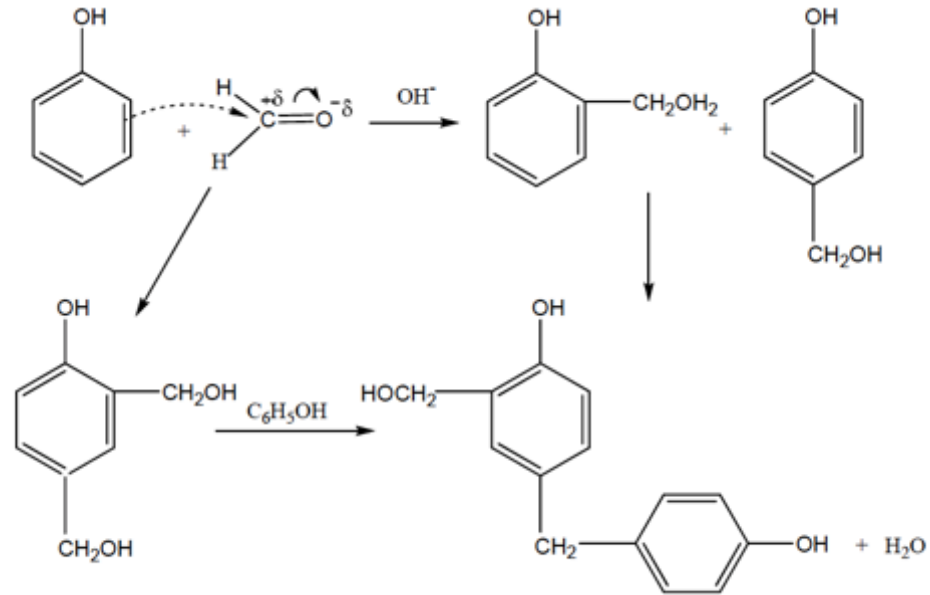


Outline

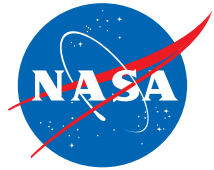
- Introduction
- Objective
- Ablation– The Concept
- Testing on mechanical performance
- Resin systems
 - Cyanate ester resin(CE)
 - Polyimide resin
 - Polybenzoxazine (PBZ)
 - Polybenzimidazole(PBI)
- Characterization results
- Summary and future efforts



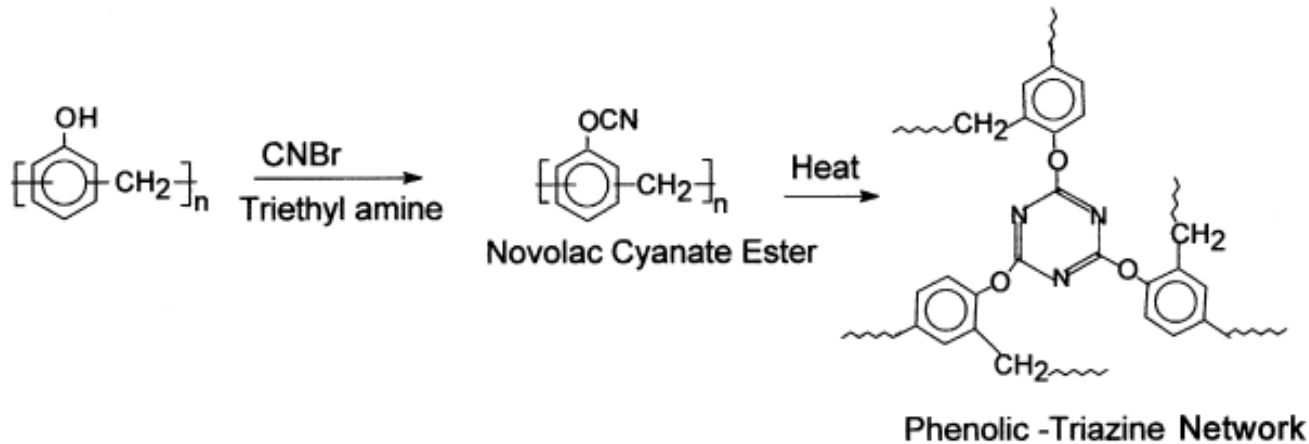
Phenolic Resin



- About 52% char yield
- Very brittle
- Reacts with oxygen



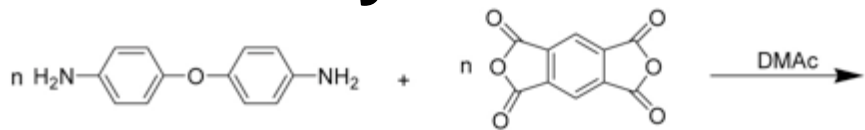
Cyanate Ester Resin(CE)



- High glass transition temperature
- High char yield
- Synthesized by reacting phenols with cyanogen halide
- Radially available
- High thermal stability
- Less harmful outgassing
- Low water absorption
- Radiation resistance

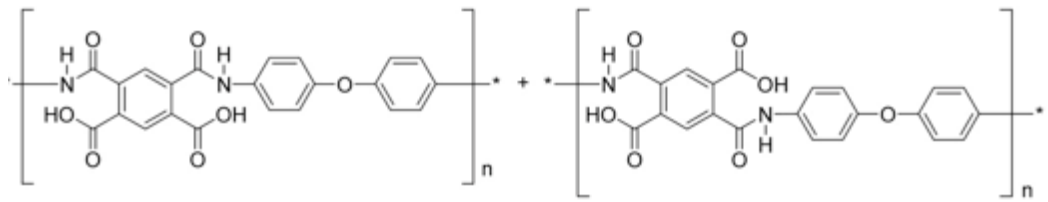


Polyimide Resin



ODA (4,4'-oxydianiline)

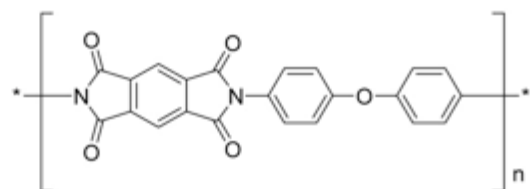
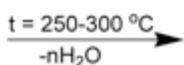
PMDA (pyromellitic dianhydride)



m-

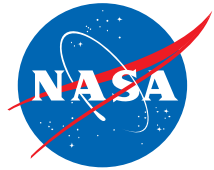
p-

PAA (Poly(amic) acid)

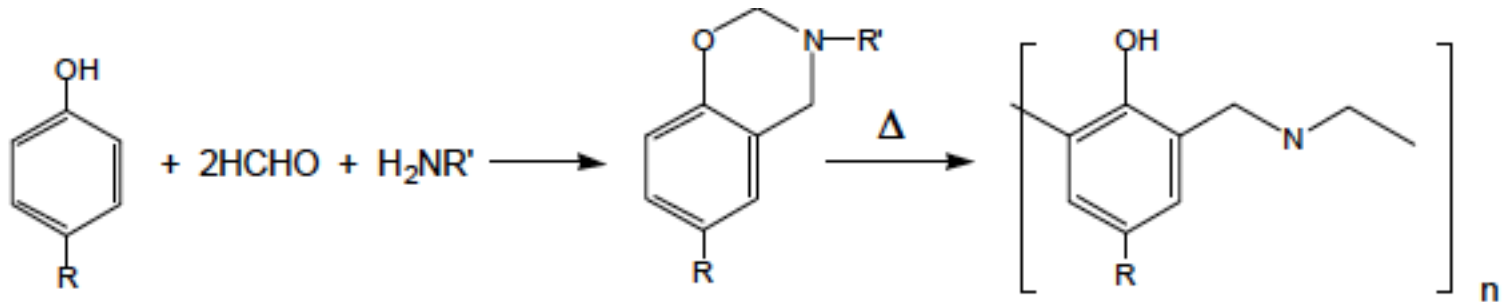


PI (Polyimide)

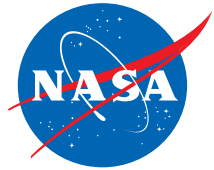
- High thermal and thermal-oxidative stability up to 400°C
- Excellent mechanical properties, both at room temperature and elevated temperature
- High glass transition temperature
- High char yield.



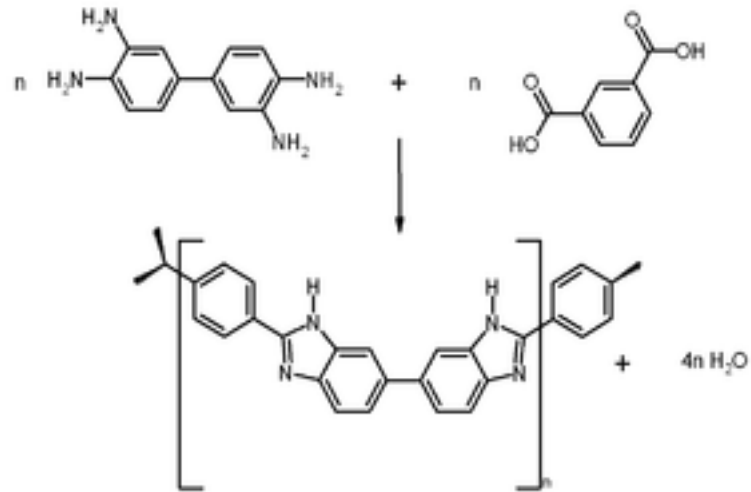
Polybenzoxazine Resin



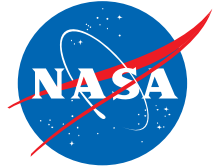
- High glass transition temperature
- Low char yield
- Low shrinkage
- Low thermal expansion
- Moisture resistance



Polybenzamidazole Resin

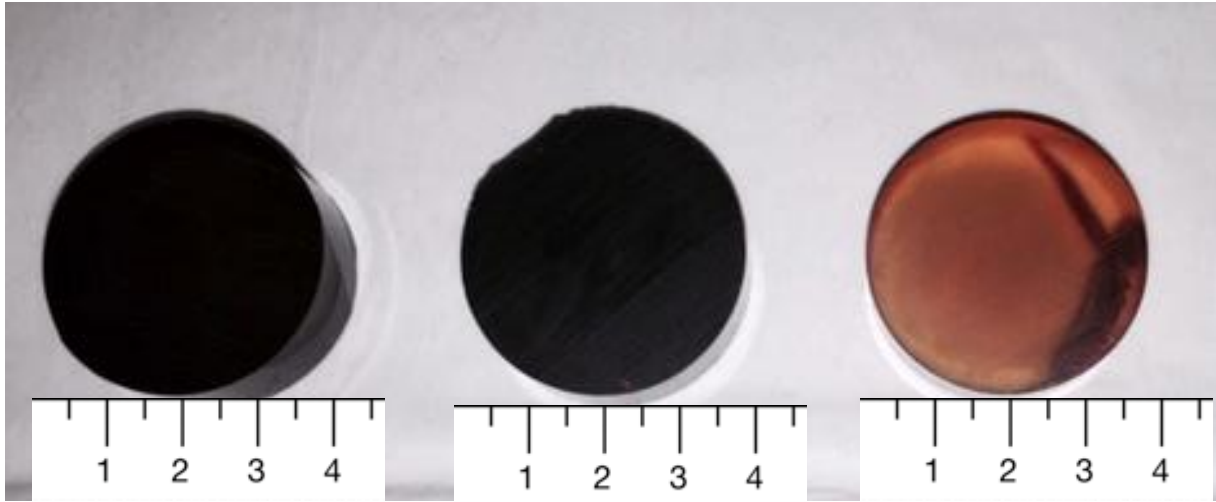


- High char yield
- Good mechanical properties
- Low thermal conductivity
- Has highly organized char structure with minimum shrinkage
- Good physical integrity
- No oxygen bearing functional groups to interact with the char and cause internal oxidation



Processed Samples

PBI and Polyimide resins did not yield dense test coupons

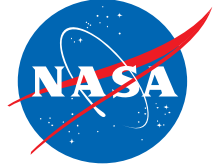


Polybenzoxazine resin

Cyanate ester

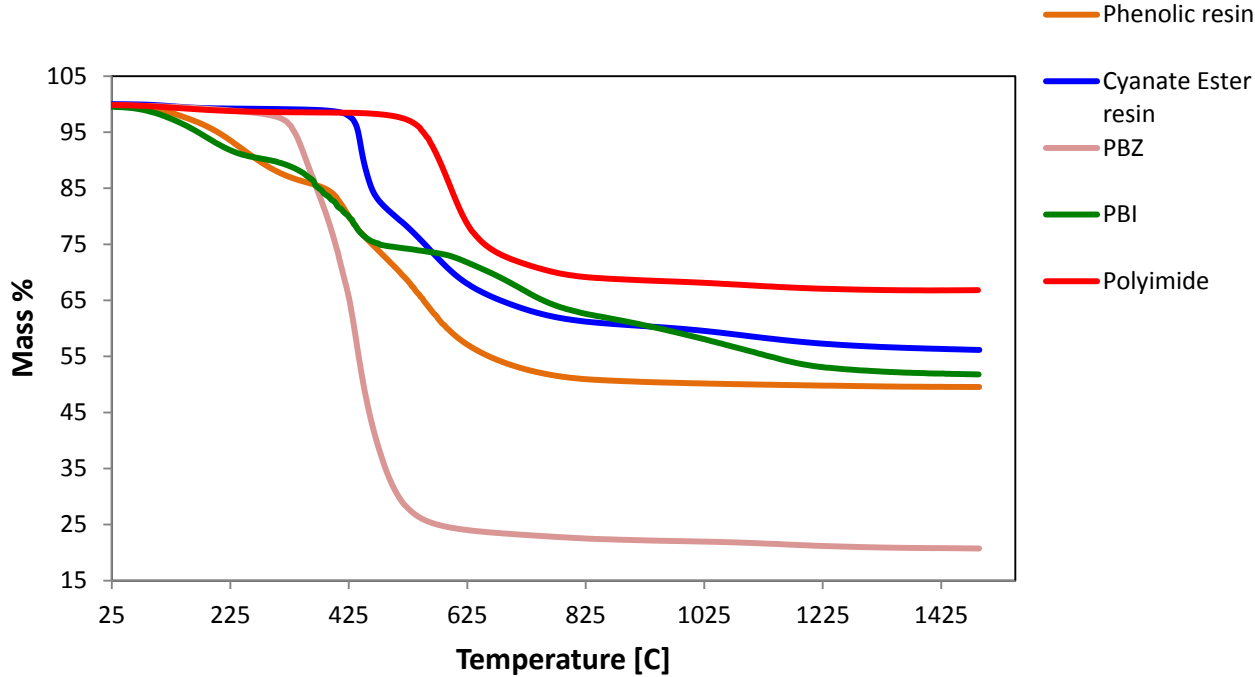
Phenolic resin

Resin system	Density (g/cm ²)
Polybenzoxazine	1.12
Cyanate ester	1.13
Phenolic resin	1.3

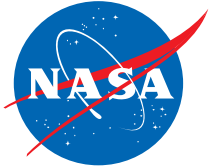


Comparison of TGA data

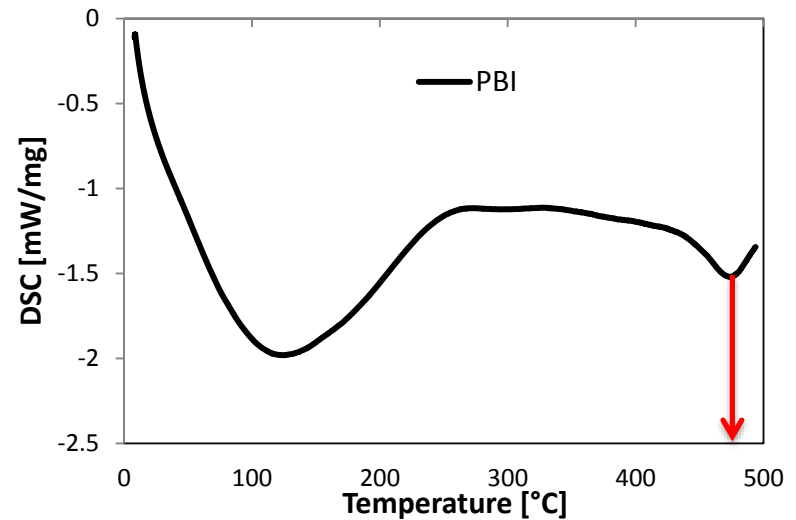
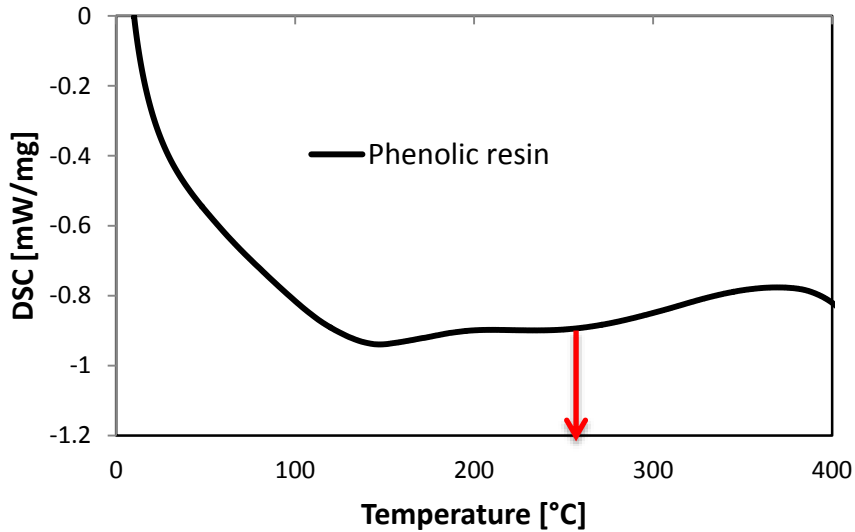
- Polyimide resin starts to decompose at very high temperature (529°C)
- Has a very high char yield (67%)



Resin	Decomposition Temperature (°C)	Char Yield (%)
Polyimide	529	67
Cyanat Ester	417	56
PBI	298	52
Phenolic	375	49
PBZ	294	20

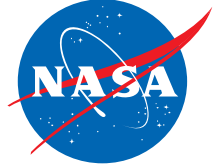


Differential Scanning Calorimetric (DSC)



Resin	Glass transition temperature (°C)
PBI	470
Polyimide resin	430
Cyanate ester	352
PBZ	320
Phenolic resin	260

Polyimide resin has the highest glass transition temperature and therefore should have better high temperature mechanical properties

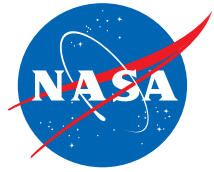


Thermal Diffusivity

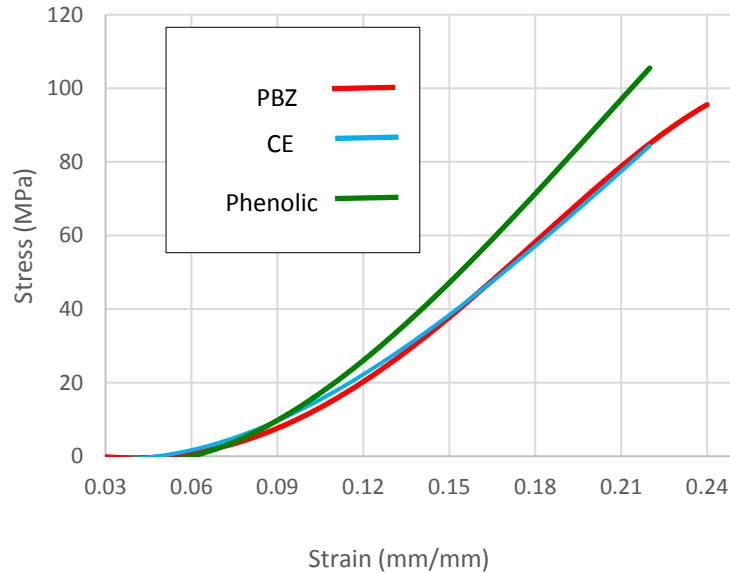
- Thermal diffusivity of phenolic resin and cyanate ester were compared.
- Cyanate ester has lower thermal diffusivity and thermal conductivity compared with phenolic resin.

$$\kappa(T) = C(T)\rho(T)\alpha(T)$$

Resin system	Density (g/cm²)	Thermal diffusivity (mm²/s)
Phenolic resin	1.13	0.19
Cyanate Ester	1.2	0.13

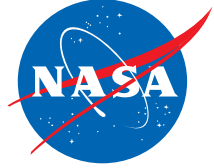


Approximate Compressive Modulus of Select Resin Samples



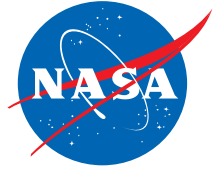
	Modulus (E)	Thickness	Density
	[MPa]	[mm]	[g/cc]
PBZ	684.1	8.6	1
Cyanate Ester	668.8	6.9	1.2
Phenolic	814	8.5	1.2
All values were at peak load (near load limit of 50 kN load cell)			

Phenolic resin has highest modulus compared with cyanate ester and PBZ. Therefore it is more brittle.



Summary

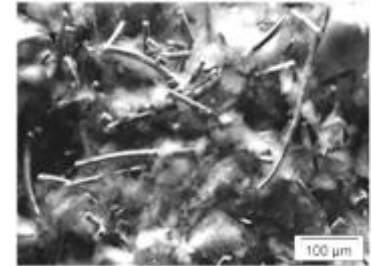
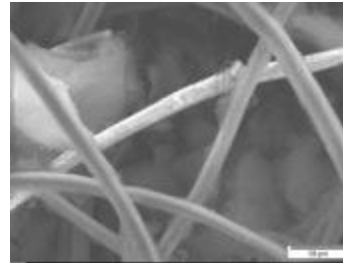
- Four resins (PBI, PBZ, Cyanate ester and polyimide) were evaluated and compared with phenolic resin
- Techniques used to characterize the resins include LFA, TGA, DSC, and compression test.
- TGA and DSC work indicate that polyimide and cyanate ester resins might be good alternatives to phenolic resin, because they have high char yields and high glass transition temperatures



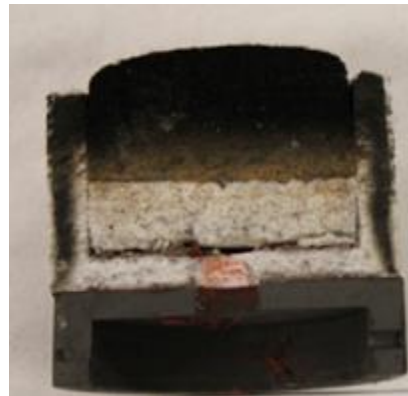
Future Work

- Continue evaluating thermal conductivity and mechanical properties of high dense PBI and polyimide resins
- Make lower density version of the mentioned resins
- Infused the resins into a carbon matrix such as carbon fiber and carbon felt
- Test the materials in more flight representative environments

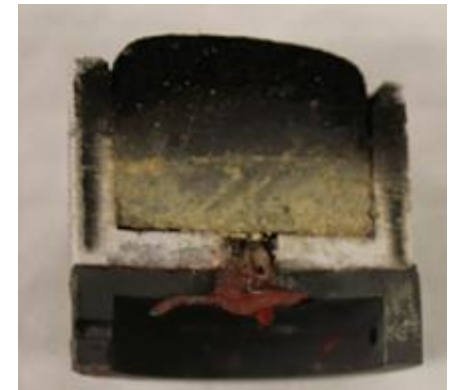
Example:



Pre-test



Cyanate ester



Phenolic resin

Cross section Post-test

Low density Cyanate ester infused into carbon fiber substrate