Characterization of New TPS Resins

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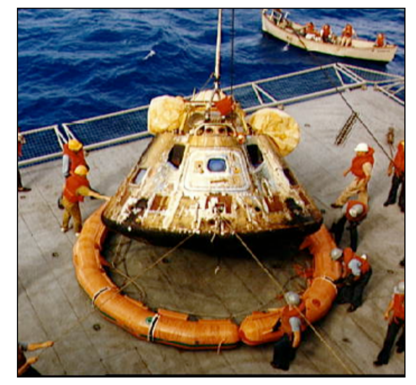
Background – Thermal Protection Systems



- The thermal protection system (TPS) is a barrier that protects the space vehicle from heating during high speed atmospheric entry
- Heritage TPS that protected astronauts from entry heating when returning from the moon (Apollo) & from space station (Shuttle) may not be adequate for missions returning from asteroids or Mars due to higher reentry speeds
- Current TPS materials do not lend themselves to optimization for a particular mission thereby resulting in higher masses or increased risk
- Lack of NASA applications drives costs of maintaining capabilities or incurring high risks of material restart

Potential Capabilities of Current Foreboby Ablative TPS Materials

Density	TPS Material	Supplier	Flight Qual or TRL	Potential Limit: Heat flux, W/cm²	Potential Limit: Pressure, atm	Entry velocity, km/s: < 13	Entry velocity, km/s: > 13	Other Potential Missions
FOREBODY HEAT SHIELD								
Low-Mid	PICA	FMI	Stardust	~ 1200	< 1	Fully capable	Potentially capable, qual needed	SR, CEV, Mars
	Avcoat	Textron	Apollo	~ 1000	~ 1	Fully capable	Not capable	Venus (aerocapture)
	ACC	LMA/C-Cat	Genesis	> 2000*	> 1	Potentially capable, qual needed	Potentially capable, qual needed	SR, CEV, Mars
	BPA	Boeing	TRL 3-4	~ 1000*	~ 1	Potentially capable, qual needed	Not capable	Venus (aerocapture)
	PhenCarb family	ARA	TRL 5-6	~ 2,000-4000*	> 1	Potentially capable, qual needed	Potentially capable, qual needed	MSR, CEV, Venus, Earth
High	3DQP	Textron	DOD (TRL 4)	~ 5000	> 1	Capable but heavy	Capable but heavy	SR, Venus
	Heritage Carbon Phenolic	Several capable, none active	Venus, Jupiter	10,000-30,000	>> 1	Capable but heavy	Capable but heavy	MSR, Venus, Jupiter, Saturn, Neptune

● Fully capable ● Potentially capable, qual needed ● Capable but heavy ● Not capable

* Never Demonstrated

Objective/Motivation

- Phenolic has been used extensively since the 1960s as an ablative resin system for composites. However, phenolic resin has disadvantages such as:
  - The processing of phenolic resin using resin transfer molding is not easy, often resulting in parts that have high defect rates and unacceptable amounts of porosity
  - Condensation reaction happens during curing which influence the final properties
  - Brittleness and porous parts leading to poor mechanical performance
  - Low char yield
  - Low decomposition onset temperature
  - Low glass transition temperature

Our goal is to introduce a new generation of ablative resin systems for NASA's future missions and improve on some of the challenges with phenolic leading to resins that are:

- Suitable for processing using resin transfer molding
- Have improved mechanical properties
- Have increased char yield and higher decomposition onset temperature
- Have increase glass transition temperature

Approach

- In this study the glass transition temperature (Tg) and mechanical properties of two resin systems were evaluated and compared with heritage phenolic resin (SC1008):
  - Cyanate Ester (CE)
  - Polybenzoxazine (PBZ)
- Char yield of additional high temperature resins were evaluated and compared with heritage phenolic resin (SC1008):
  - PBI (polyimidazole)
  - Polyimide
- All the characterization was performed on cured resins without any matrix and compared to heritage phenolic resin.

Resins Preparation/Processing

A series of cylindrical samples were processed. Care was taken to ensure the porosity in all samples was minimized. The resins were cured in the oven at a specified curing temperature for the given resin. After curing the resins were sectioned and characterized.

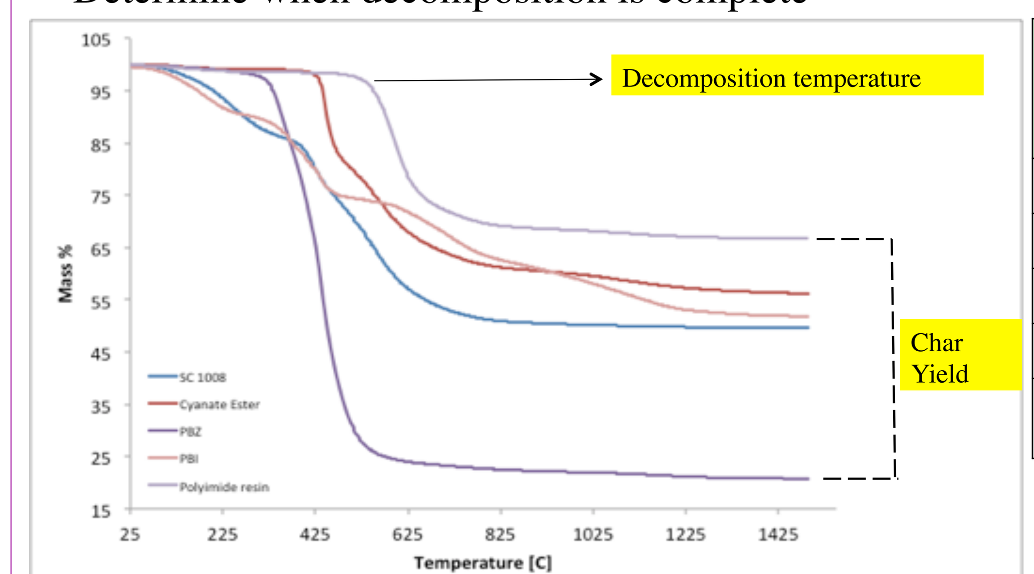
Phenolic resin Cyanate ester Polybenzoxazine

Resin	Density (g/cc)
Phenolic resin	1.21
Polybenzoxazine (PBZ)	1.12
Cyanate ester	1.25

Thermal Gravimetric Analysis (TGA)

TGA measures the mass change of a material as a function of temperature and can give very useful information such as:

- Characterize ablative behavior if the TGA is directly in line with a mass spectrometer or FTIR
- Determine decomposition onset temperature and char yield
- Determine when decomposition is complete



Resin	Decomposition Temperature (°C)	Char Yield (%)
SC1008	375	49
PBZ	294	20
PBI	298	52
Polyimide	529	67
Cyanate Ester	417	56

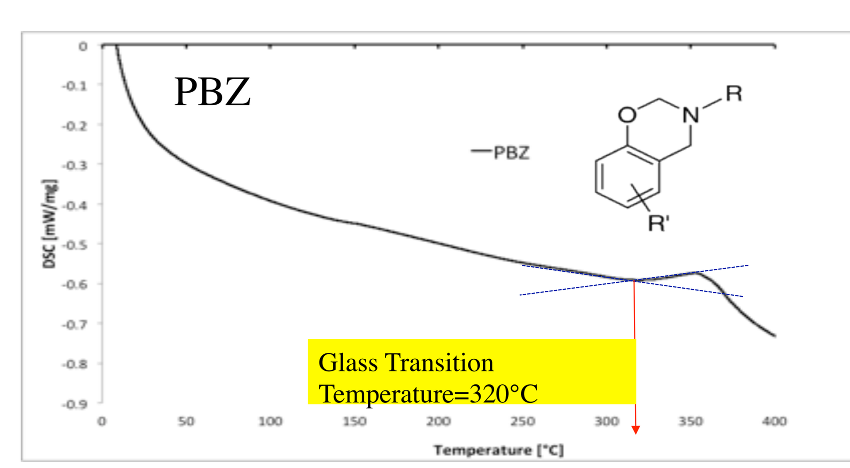
Result:

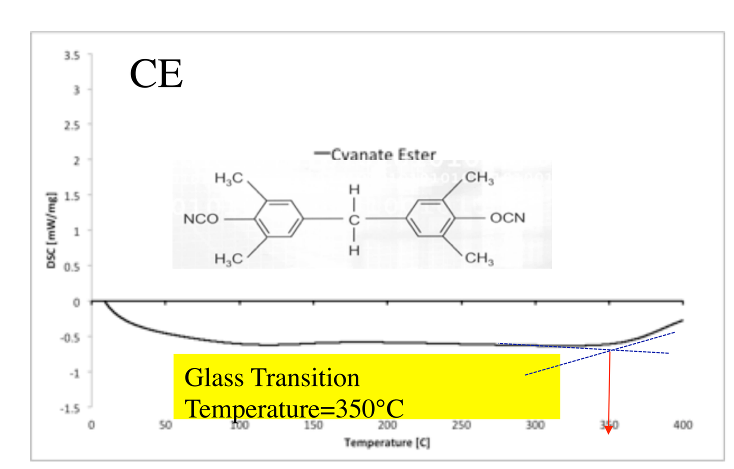
- TGA was run on all resins and compared with phenolic. All samples were run in inert gas, with the heating rate of 10°C/min. The results indicate polyimide and CE have higher decomposition onset temperatures than phenolic resin. CE, polyimide and PBI have higher char yields than phenolic – a higher char yield results in a more robust char

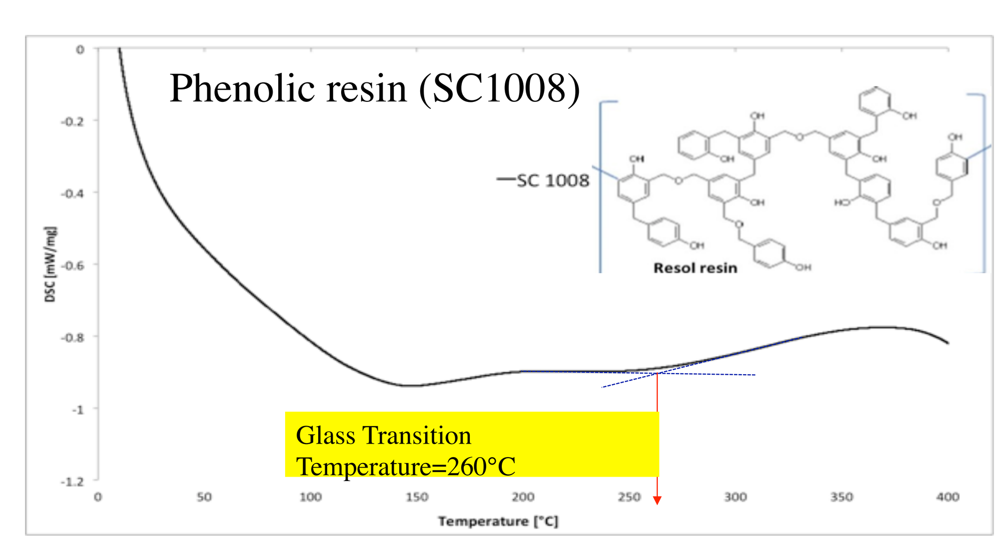
DSC: Differential Scanning Calorimetry

DSC is very useful technique to measure a number of characteristic polymer :

- Glass transition temperature (Tg) – the temperature range where a polymer changes from a hard, rigid or "glassy "state to a more pliable, compliant or "rubbery" state
- Crystallization temperature - The percent crystalline content of a polymer can be estimated from the crystallization/melting peaks of the DSC graphs
- Melting temperature
- Determining thermal degradation of a polymer using oxidative onset temperature







Result:

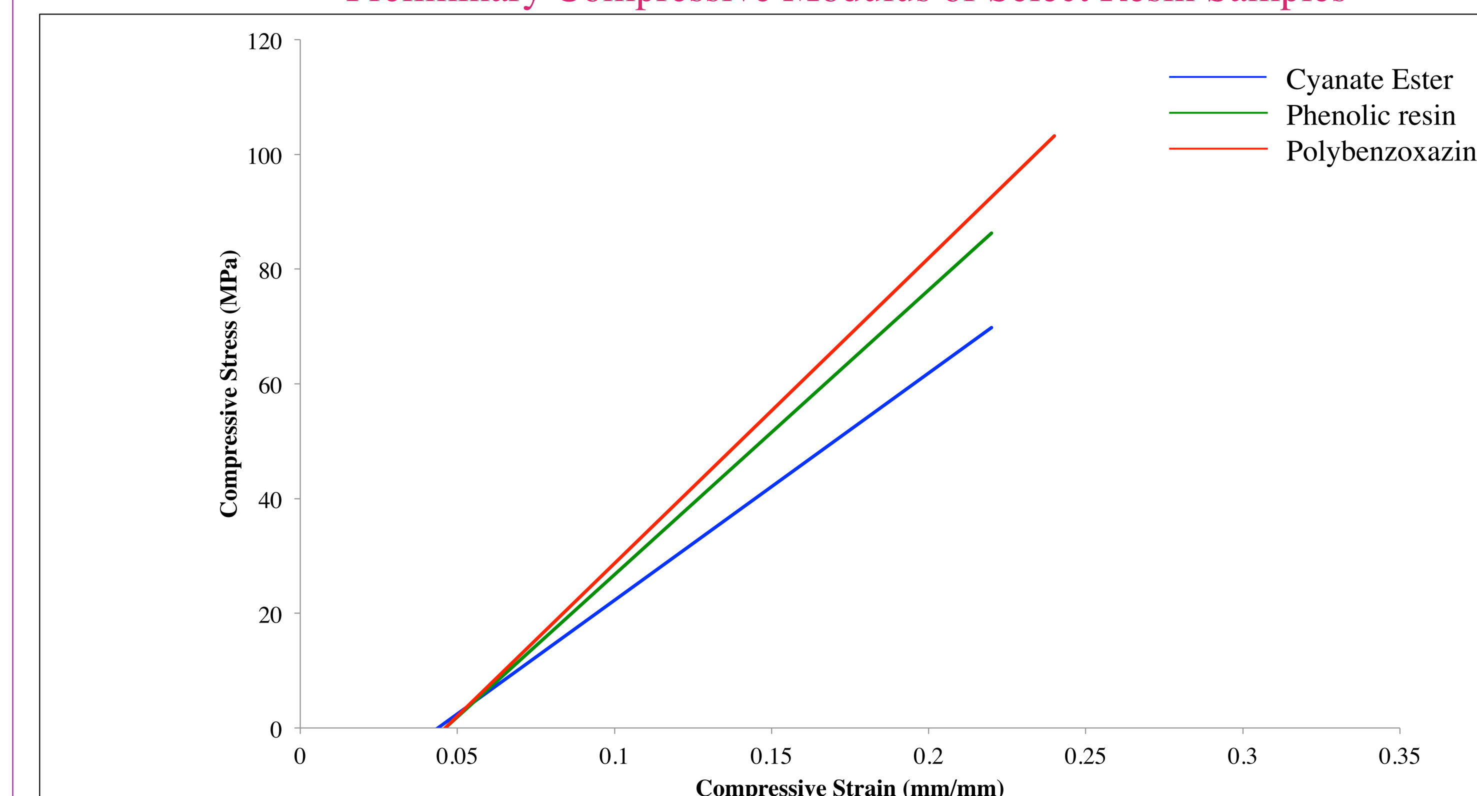
Phenolic resin has lower glass transition temperature than PBZ and CE resins. A lower glass transition temperature results in matrix softening at lower temperature and a drop off in mechanical properties

Compression Testing

Benefit Of Compression Tests

- Easy sample preparation of known cross sectional area and thickness of macroscopically homogenous sample
- Reproducible results with options for comparing values across variation in geometry
- Tailorable to different material types

Preliminary Compressive Modulus of Select Resin Samples



Result:

- Compression testing completed on CE and PBZ
- In order to quickly assess the mechanical properties of small polymer samples a compression test coupon is easier to manufacture and allows for smaller samples and gives consistent test results with high reproducibility.

	Modulus (E)	Compressive Stress (σ)	Stiffness (ϰ)
	[MPa]	[MPa]	[MPa/mm]
PBZ	718.7	113.7	371
Cyanate Ester	668.8	82.9	458
Phenolic	814	101.9	430.3
All values were at peak load (near load limit of 50 kN load cell)			

- All samples evaluated have comparable compression properties. A limited quantity of test coupons was evaluated.

Summary

- Alternative ablation resins (PBZ, CE, PBI, Polyimide) were evaluated and compared with heritage phenolic resin.
- The resins were characterized by TGA and DSC and their data were compared with heritage phenolic resin. Mechanical properties were also evaluated.
- Based on the TGA, DSC, and mechanical test PBI, polyimide and CE have higher char yield, higher glass transition temperature and comparable mechanical properties to phenolic resin and will be further evaluated
- Based on TGA, the PBZ resin has a very low char yield compared with all evaluated resins and phenolic. This resin is not downselected for further evaluation.

Future Work

- NASA is evaluating a series of different substrate materials that would be suitable as the reinforcement phase for ablative composites. The reinforcement architectures include rigid fibrous substrates, felt and woven based substrates. Future work will focus on infusing the most promising alternative resins into select substrates and evaluating the composite properties
- PBI, polyimide, and CE resins will be further evaluated by infusing into substrates and characterizing properties.

Acknowledgements

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