NOVEL TOUGHENED EPOXY SYSTEMS FOR DAMAGE TOLERANT COMPOSITE PRESSURE VESSELS

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Olin™

Presentation Outline

Olin

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Filament Winding

Composite Pressure Vessels

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Summary

Olin History

OLIN INDUSTRIES

1892: Founded in East Alton, IL providing blasting powder to Midwestern coal mines

1898: Form Western Cartridge Company to manufacture small arms ammunition

1931: Acquire Winchester Repeating Arms

1940s - 1950s: Acquire cellophane, paper, lumber & powder-actuated tools businesses

1954: Merge to create the Olin Mathieson Chemical Corporation

1950s - 1960s: Enter into phosphates, aluminum, urethanes, TDI, skis, camping equipment and homebuilding businesses; expand paper and forestry businesses

2007: Acquire Pioneer Americas LLC and sell the Metals business, resulting in a company similar in businesses to that which existed in the late 1890s

2015: Acquire The Dow Chemical Company's U.S. Chlor Alkali and Vinyl, Global Chlorinated Organics and Global Epoxy businesses; now world's number one chlorine leader

1909: Introduce first commercial production of liquefied chlorine

1896: Build first Chlor Alkali plant in U.S.

MATHIESON CHEMICAL CORP.

1892: Founded in Saltville, VA to produce soda ash

1940s - 1950s: Build plants in Lake Charles, LA, and McIntosh, AL; buy Squibb

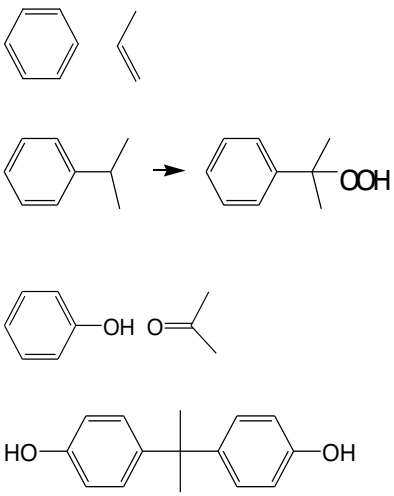
1970s - 2000: Consolidate back to core businesses; spin offs include forest products (Olinkraft), military ordnance (Primex) and specialty chemicals (Arch); sell aluminum, TDI, urethanes and Squibb businesses

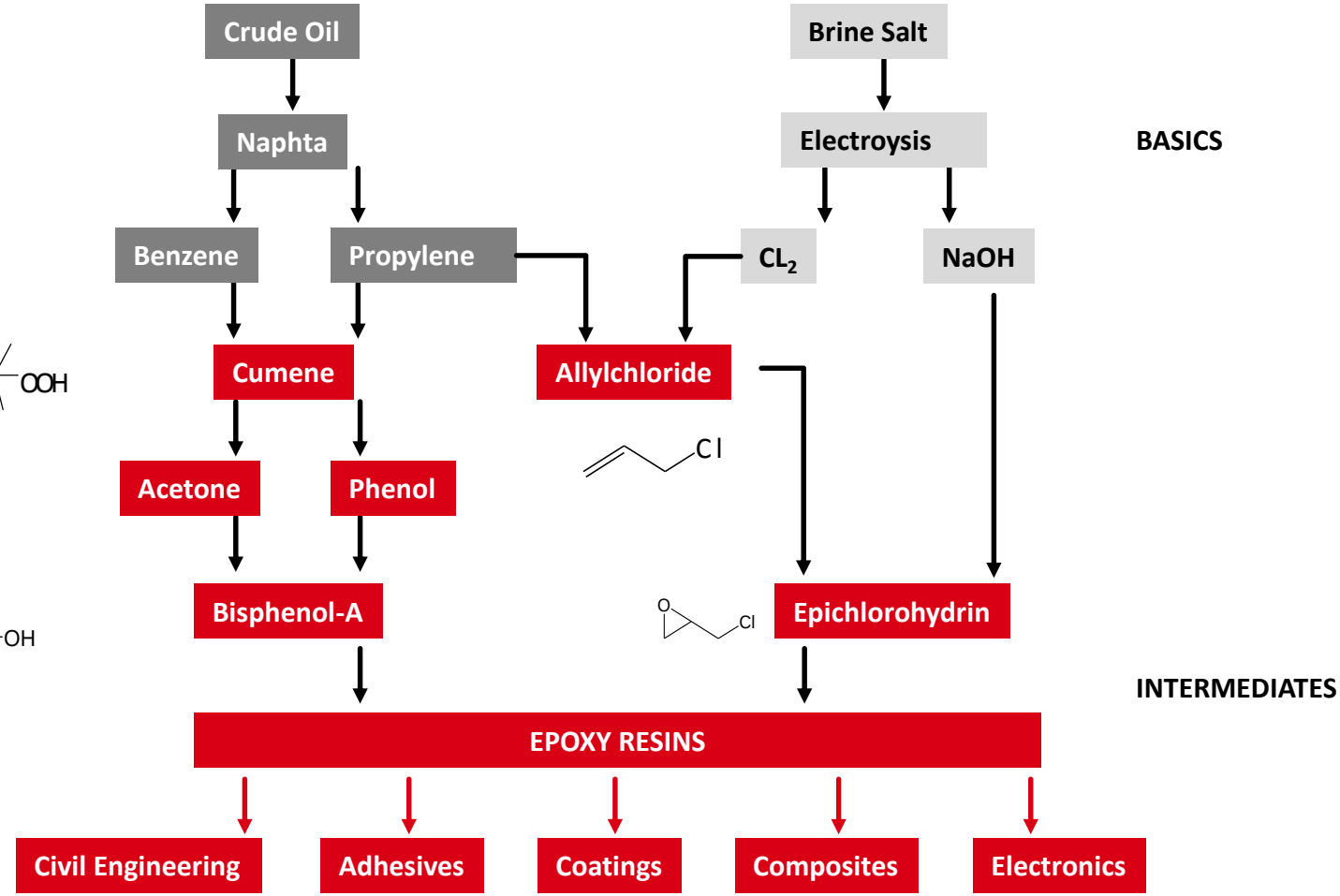
2012: Acquire K.A. Steel Chemicals, distributor of caustic soda and the largest manufacturer of bleach in the Midwest

The World's Chlorine Leader

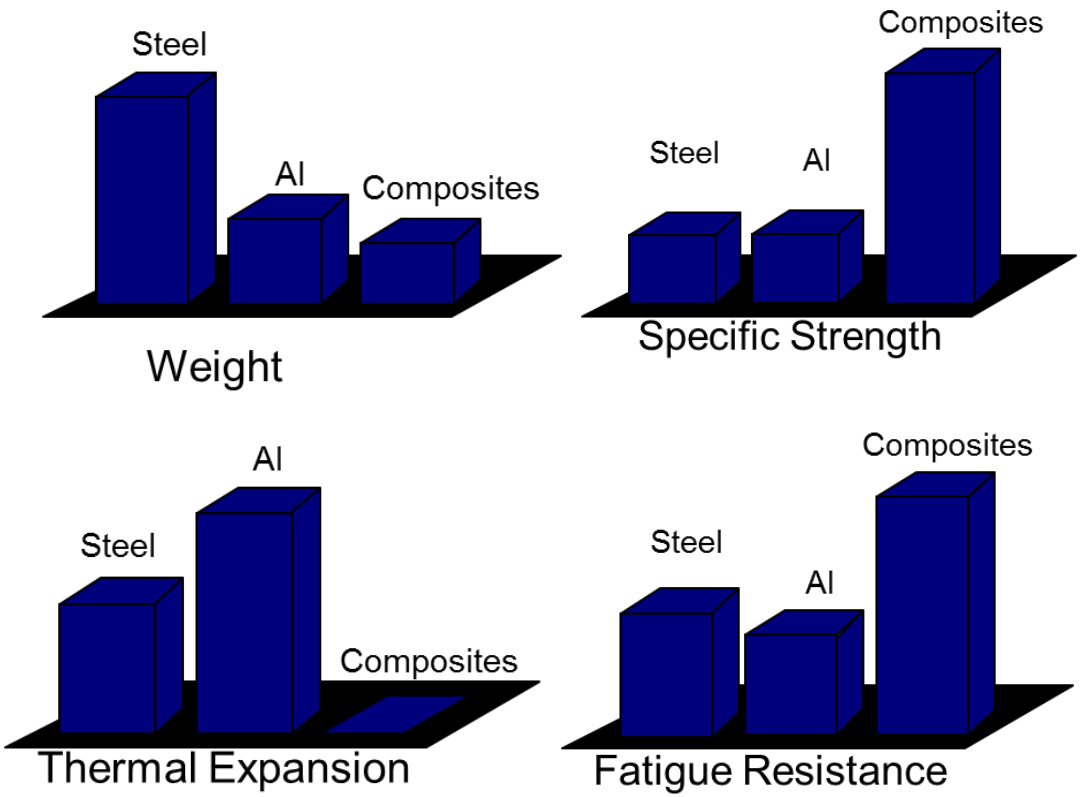
THE WORLD'S LEADING PRODUCER OF CHLOR ALKALI PRODUCTS

Unique Back Integration





Composites – An Overview



Fiber Reinforced Polymer (FRP) composites are increasingly employed as metal replacements

Composite Pressure Vessels

Type 1
- All Metal Pressure Vessels
- Inexpensive but heavy and prone to corrosion

Type 2
- Predominantly metal partially wrapped with steel wire or composite
- Slight weight reduction (30-40 %) compared to Type 1 but still prone to corrosion

Type3
- Thin metal liner completely wrapped with carbon fiber composite shell
- 70 % lighter than Type 1 cylinders and higher storage capacity . Higher cost.

Type 4
- Plastic liner completely wrapped with carbon fiber composite shell
- 80 % lighter than Type 1 and higher capacity than Type 3 . Higher cost than Type 1-3.

Type 5
- Liner-less all composite tank.
- Still in development but projected to offer 16-20 % higher storage capacity than Type 4.

Composite pressure vessels represent a safe and efficient option to store and transport cleaner energy sources

Pros and Cons of Composite Pressure Vessels

Composites World Magazine (2017) "**Going forward, demand for all metal CNG tanks will be outstripped by tanks that incorporate composites**"

Benefits of Composite-based tanks vs. all metal

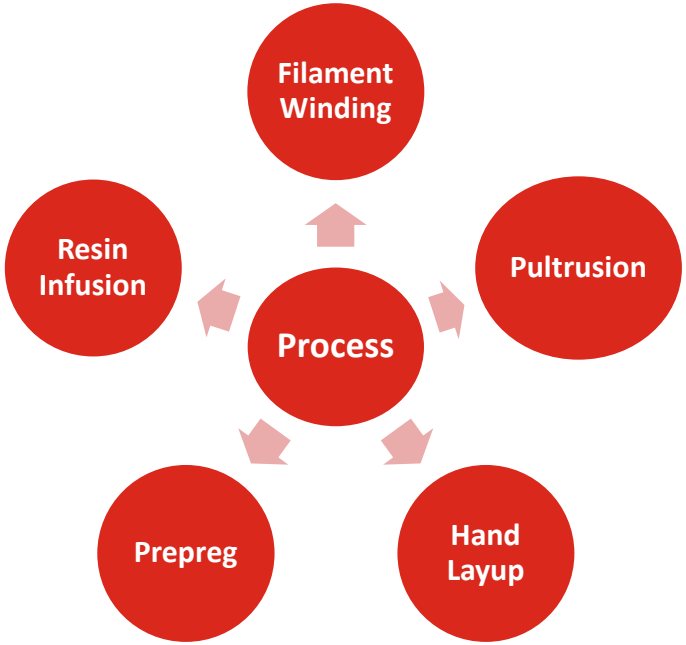
- Corrosion and fatigue resistant
  - ✓ Enhanced service lifetimes (up to 30 years vs. 15 years)
- Lightweight
  - ✓ 0.75 to 1 lb/L vs. 3 lb/L
- Improved energy storage density
  - ✓ Extended containment pressures (e.g 5000 psi and higher with a practical structure weight)

Downside of Composite-based tanks vs. all metal

- Cost
  - ✓ Fabrication and material costs can be nearly double that of metal tanks

http://www.compositesworld.com/articles/the-outlook-for-composite-pressure-vessels

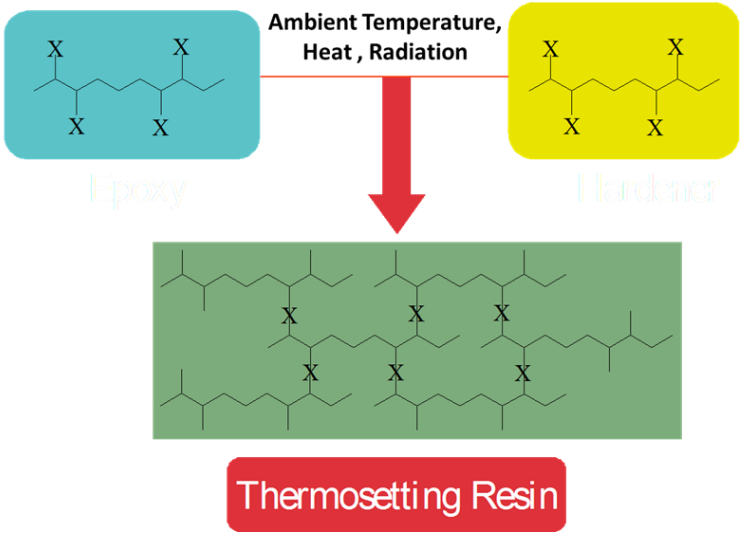
Composites Processing



Composites can be produced in unique sizes and shapes

Liquid Epoxy Resins – An Overview

- ✓ Ease of Processing
- ✓ Extremely good corrosion resistance
- ✓ Extremely good resistance against a wide range of chemicals (acids, base, solvents)
- ✓ Good adhesion to metals and fibers
- ✓ Versatile curing chemistry (wide variety of hardeners and catalysts)
- X Typical Epoxy matrices are rigid and brittle after cure and prone to impact damage

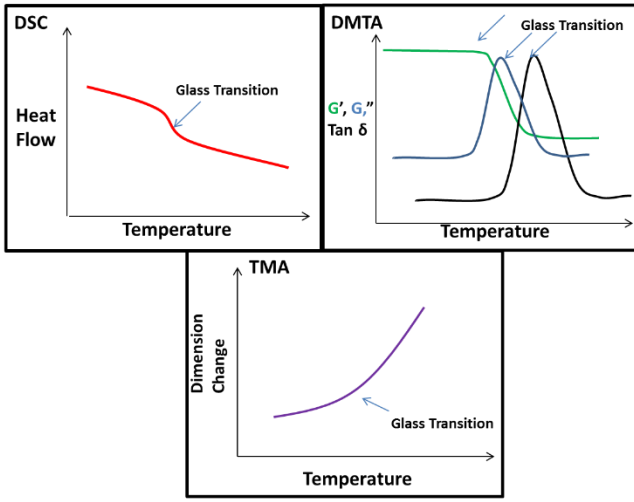


Improving the toughness and damage tolerance of cured Epoxy Thermoset remains a major unmet need in the composites pressure vessel industry

Thermoset Resin Requirements for Composites

Processing (Before/During cure)	Performance (After cure)
Viscosity (Fiber wetting)	Thermal (Tg, CTE, etc.)
Potlife (Working time)	Mechanical (Modulus, Strength, Toughness, etc.)
Reactivity (productivity)	Physical (Water uptake, solvent resistance, etc)

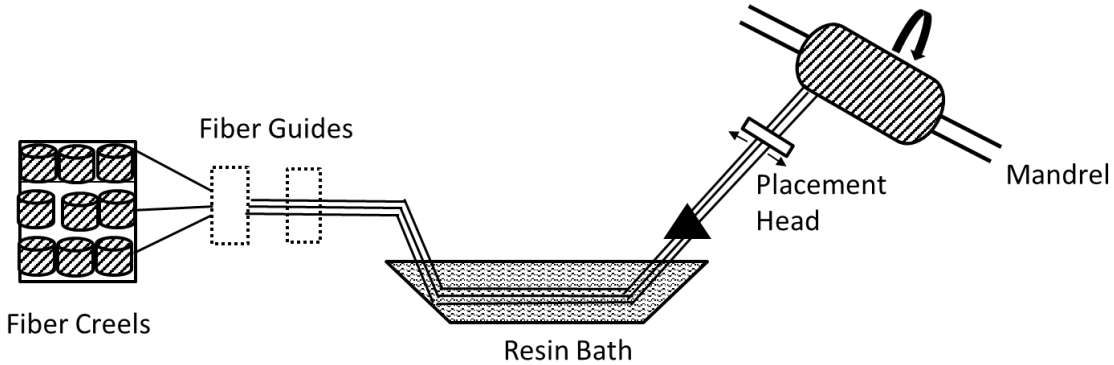
Resin Requirements



Epoxy systems offer a good balance of processing ease and performance

Filament Winding Composite Pressure Vessels

- Process involves wrapping resin-impregnated reinforcement fibers around a mandrel or a liner in a specified orientation; then transferring the part for curing in an oven to achieve final properties
- For composite pressure vessels, liner may be metal (Type 3) or plastic (Type 4)
- Carbon fibers are the typical reinforcements for compressed gas storage

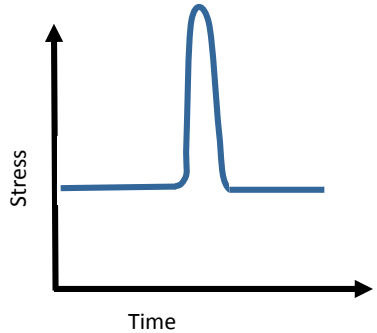


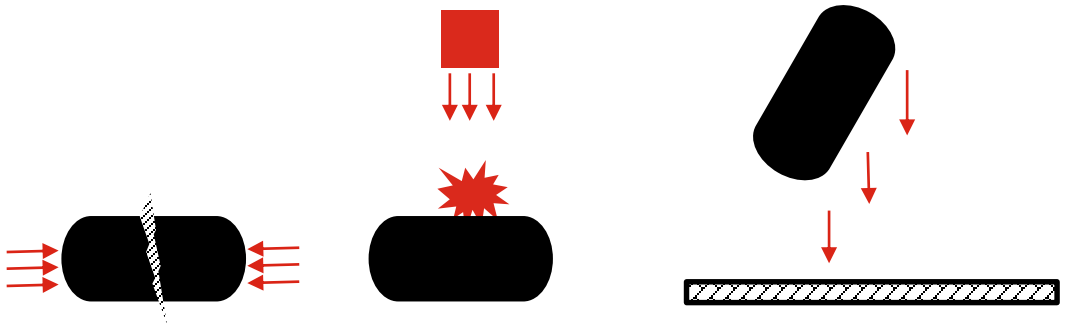
Broad Resin Requirements

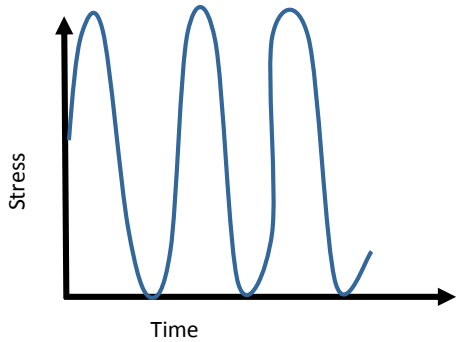
- Appropriate viscosity-temperature profile for fiber wetting
- Adequate stability and reactivity
- Thermal stability and mechanical performance after cure

Why Toughening ?

- The matrix can play a role in maximizing delivered fiber strength of a composite
- Composite Pressure Vessels often employ additional composite layers to meet stringent impact requirements, adding both weight and cost



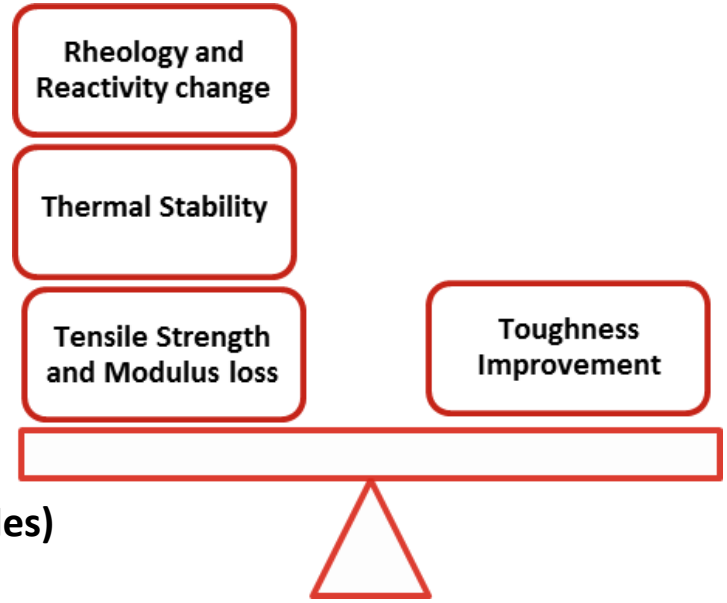




Epoxy Toughening can ENABLE more reliable, durable composite parts

Effects of Typical Toughening Agents

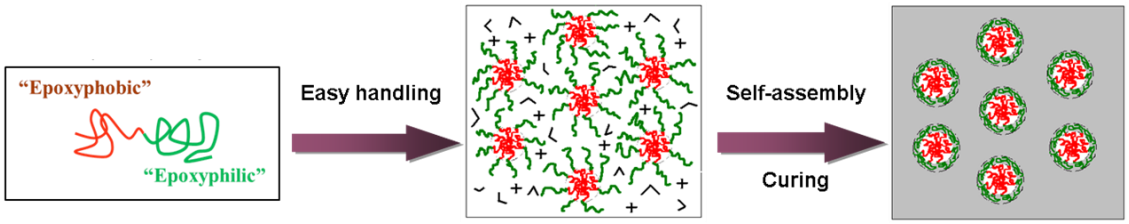
- **Fracture Toughness (K_{IC}, G_{IC}) increases**
  - Improved damage tolerance
- **Viscosity increases (rubbers or rigid fillers)**
  - Processing becomes a major challenge
- **Reactivity changes (inorganic fillers)**
  - Needs process modification
- **Tensile Modulus Tensile Strength decreases (soft particles)**
  - Reduces durability
- **Change in T_g (plasticizer)**
  - Impact on Service temperature

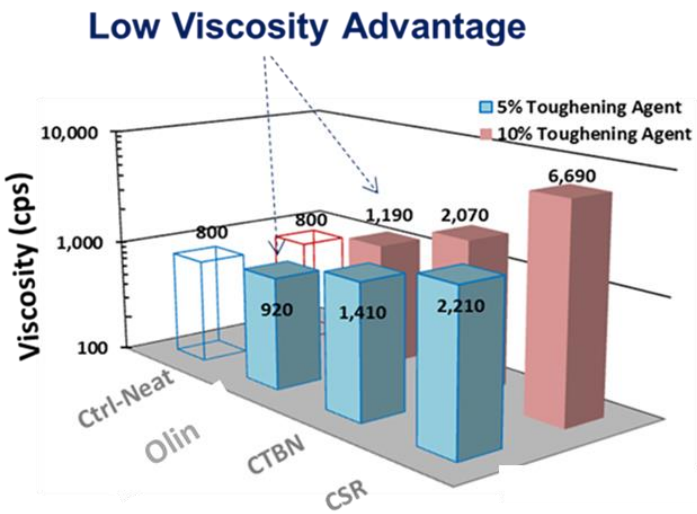


Balance is key for composite systems

Improving damage tolerance at the expense of other critical parameters could affect performance and/or processing

Olin Toughening Technology





Low viscosity toughening approach for drastic enhancement in toughness

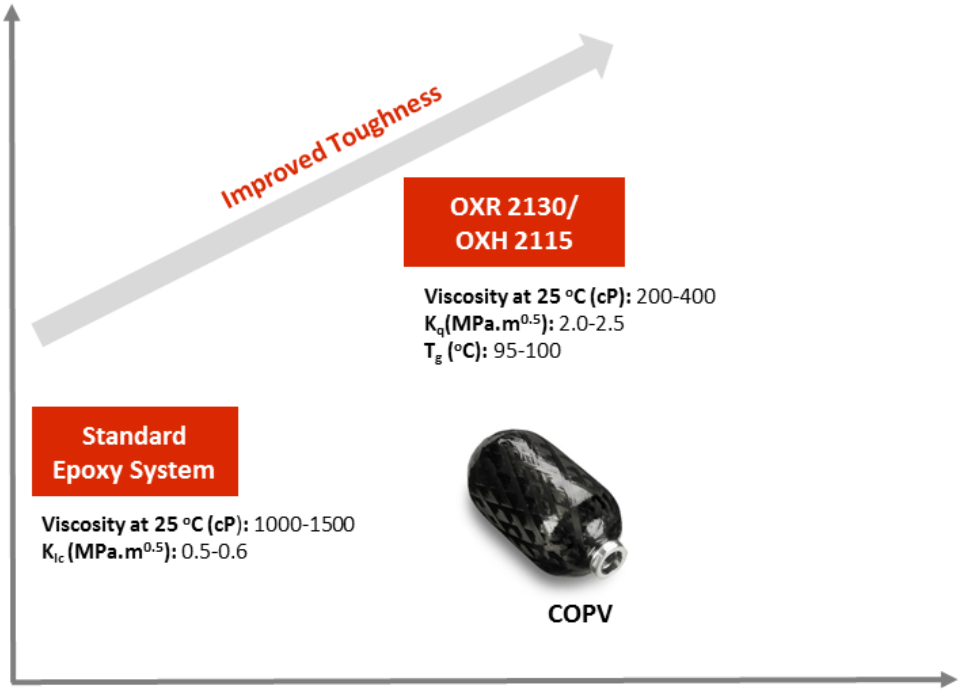
Low-Viscosity Toughened Epoxy-Amine Systems

THE BIG DEAL

- Low viscosity for fiber wet out
- Long pot life
- Enhanced fracture toughness for damage tolerance

Applications

- Pressure Vessels (Type 4), Cryo Cylinders, Sporting Goods



Motivation and Objectives

The objective of this work was to examine the effect of a drastic enhancement in matrix fracture toughness on the damage tolerance of subscale Type 4 Composite Pressure Vessels

- Formulate Epoxy system with drastic enhancement in fracture toughness when compared to a standard Epoxy Anhydride system without toughening
- Fabricate subscale Composite Pressure Vessel to examine the relationship between resin matrix fracture toughness and composite scale properties
- Develop an impact test protocol to measure the residual burst pressure of the subscale vessel following a controlled impact
- Conduct preliminary evaluation on effect of enhanced matrix toughness on cryo performance of Type 3 subscale vessels

Materials

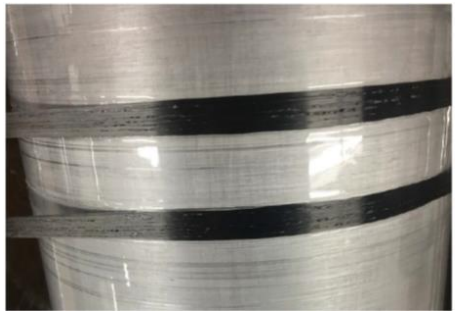
Property	Standard	Toughened	Fiber Properties[1]
Viscosity at 25 °C (cP)	400-500	200-400	
Tg (°C)	110-115	95-100	
Fracture Toughness, K1c /Kq (MPa. $m^{0.5}$) ASTM D5045	0.50 ±0.1	2.50 ± 0.05 (Kq)	
Tensile Modulus GPa	3.0 ±0.1	2.8 ±0.1	255
Tensile Strength MPa	84 ± 7	66 ± 2.0	5520
% Elongation	6.0 ± 2.0	6.7 ± 0.6	2.1

[1] Grafil 37-800WD 30K from Mitsubishi Rayon Company

Toughened system has ~ 5x fracture toughness vs. standard system

Subscale Vessel Fabrication

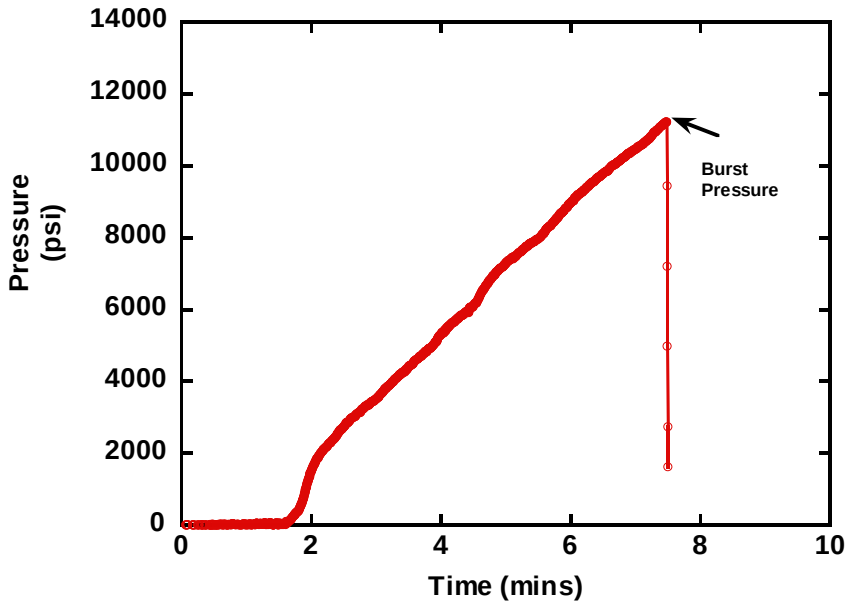
- The subscale (7.5 L volume) vessels were fabricated by wet filament winding
- Epoxy resin impregnated carbon fiber composite shell was wrapped over a HDPE liner
- Initial winding was conducted in the hoop direction followed by helical winding at a winding speed of 30”/sec to produce a composite shell with a thickness of 0.25-0.3”
- The fiber volume fraction in the composite shell is close to 65 vol. %
- Following winding, the vessels were cured in an oven with the cure schedule, which involved an initial cure at 90 ^{o}C for 1h followed by a post cure at 110 ^{o}C for up to 5h

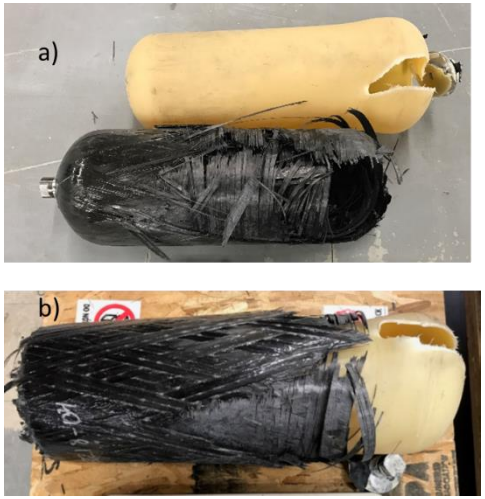


Low viscosity of the toughened system ensures uniform resin wet-out

Burst Test

Hydro burst testing was conducted by circulating high pressure water through the vessels until failure

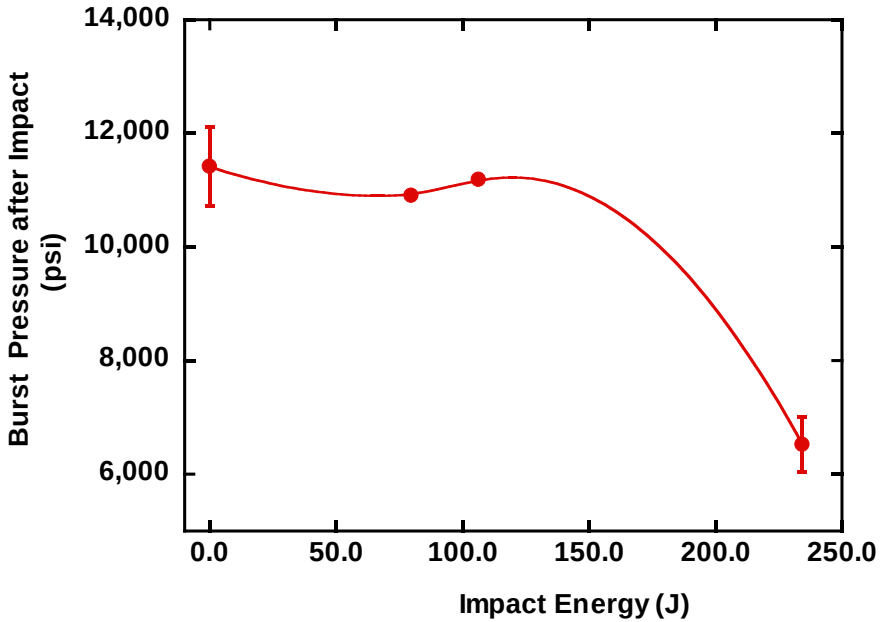




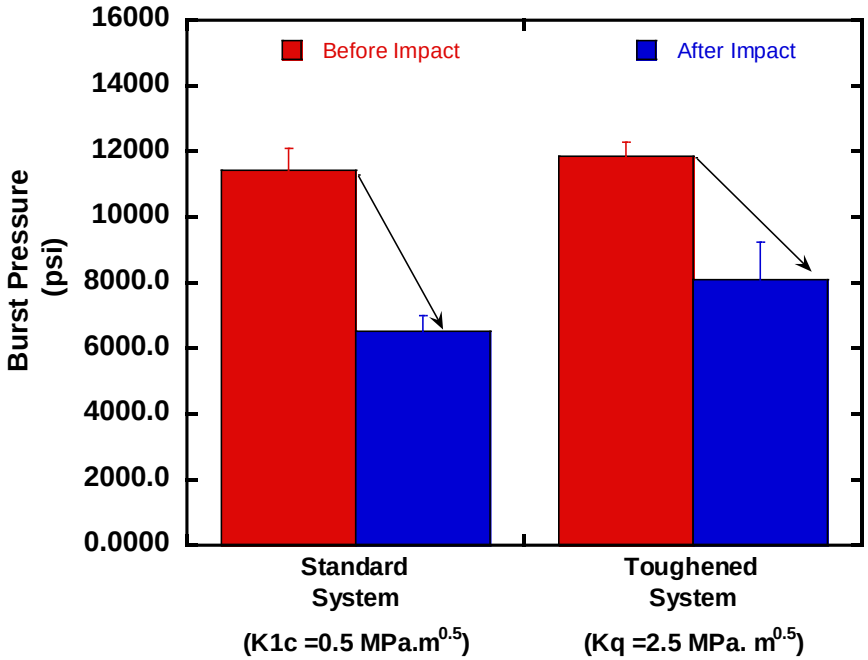
Failure point resulting in abrupt pressure drop is denoted as burst pressure

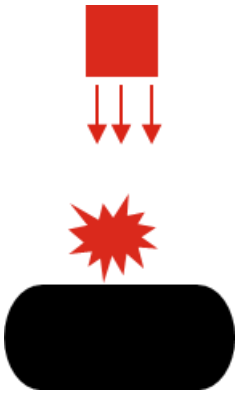
Impact Test

Impact energy required to reduce burst pressure outside of measurement variability was selected as 237.7J



Type 4 Subscale Damage Tolerance

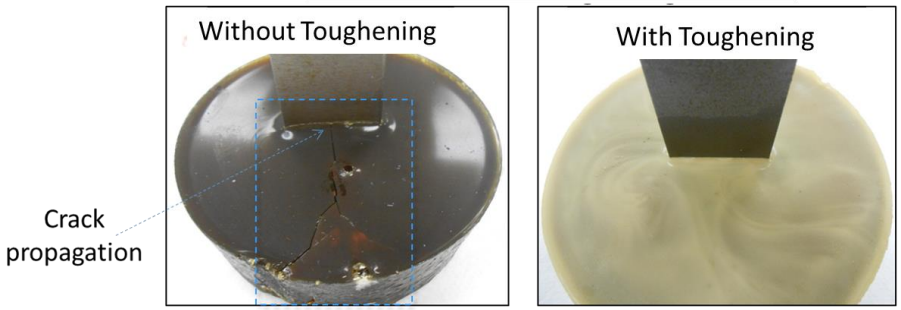




Toughened epoxy systems show 24% improvement in burst pressure following impact damage

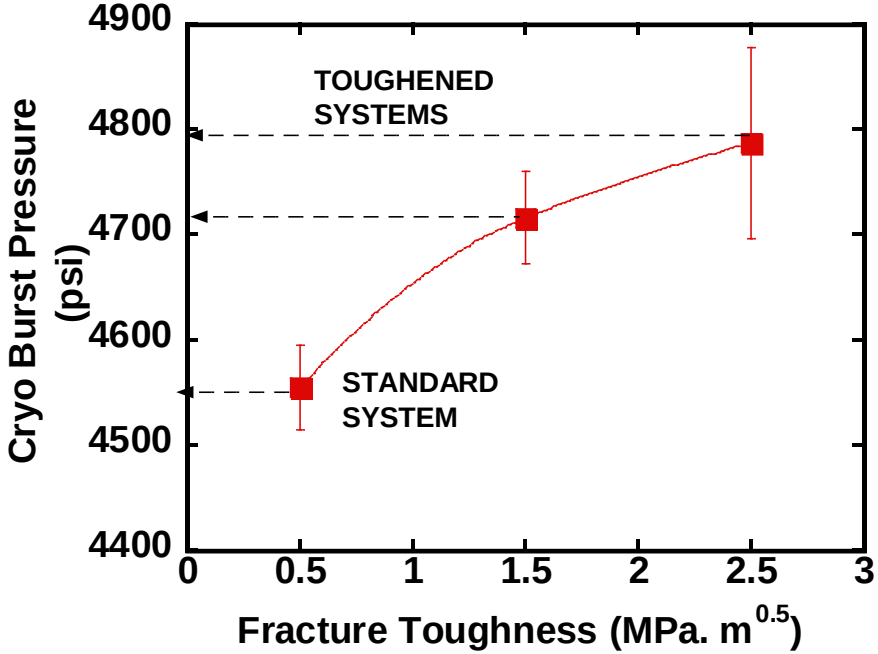
Matrix Toughening Effect on Performance

- Fiber properties are crucial for composite performance, while the resin matrix can ensure that the tensile properties of the fibers are delivered at the composite scale
- Enhancement in fracture toughness could minimize the internal propagation of the cracks and crazing through the matrix, following an impact
- During failure such as those experienced in a burst test following an impact where fiber breaks start to occur, the presence of the more damage tolerant matrix could potentially improve the bridging effect
- The presence of a matrix with enhanced fracture toughness may also deliver additional benefits
  - improved tolerance cyclic fatigue during service
  - reduction of thermally-induced residually stress cracking during curing.



* -20°C to 80°C, 10 cycles

Type 3 Subscale Cryo Burst Testing



Toughened epoxy systems exhibit up to 6% higher cryo burst pressure

Summary

- In this study, an Epoxy system with a drastic enhancement in fracture toughness was developed
- A test protocol was developed to measure the residual burst pressure of the subscale Type 4 vessels following a controlled impact on the vessel surface
- The retention of burst pressure following impact was improved by 23% for the subscale Type 4 vessels manufactured using toughened resins
- The cryo burst performance of subscale Type 3 vessels was also improved and found to be 6% higher
- The enhanced matrix fracture toughness reduces rate of crack propagation and may provide a fiber bridging effect during failure
- Additional benefits of matrix toughening will be investigated in future work
  - improved tolerance of cyclic fatigue during service
  - reduction of thermally induced residual stress cracking during curing

LITESTONE™
Systems for Composites

Resins	Hardeners	Hand-/Wet-Layup	Resin Infusion	Resin Transfer Molding	Filament Winding	Pultrusion	Mold Building	T_g	Remarks
LITESTONE™ 1100E	LITESTONE 1101H	•••			•			~75 °C	Hand-/Wet-layup epoxy system
	LITESTONE 1103H	•••			••			~75 °C	
LITESTONE 1500E	LITESTONE 1501H	•	•••	••	•			~80 °C	Standard resin infusion epoxy system
	LITESTONE 1503H	•	•••	••	••			~80 °C	
LITESTONE 1550E	LITESTONE 1553H	•	•••	••	••			~75 °C	Advanced resin infusion epoxy system; especially recommended for carbon fiber infusion
LITESTONE 1900E	LITESTONE 1901H		••	••	••	•	•••	~145 °C	Mold building/tooling system
	LITESTONE 1903H		••	••	••	•	•••	~145 °C	
LITESTONE 2100E	LITESTONE 2102H		••	••	•••	••		~120 °C	Toughened anhydride curing system
	LITESTONE 2105H	••	•	•	•••			~100 °C	Amine curing system; long pot life
	LITESTONE 2107H	••	•	•	•••			~100 °C	Amine curing system; long pot life and low exotherm
LITESTONE 2120E	LITESTONE 2122H		••	••	•••	••		~110 °C	Toughened Anhydride curing system; suitable for type 4 pressure vessels
LITESTONE 2130E	LITESTONE 2131H		••	••	•••	••		~115 °C	Anhydride curing system
	LITESTONE 2142H		••	••	•••	••		~115 °C	Toughened anhydride curing system; suitable for type 4 pressure vessels
LITESTONE 2210E	LITESTONE 2212H		••	••	•••	••		~220 °C	Toughened anhydride curing system
LITESTONE 3100E	LITESTONE 3102H		•	•	••	•••		~120 °C	Anhydride curing system
	LITESTONE 3103H		•	•	••	•••		~120 °C	
	LITESTONE 3122H		•	•	•	•••		~150 °C	Anhydride curing system
LITESTONE 3170E	LITESTONE 3172H		•	•	•	•••		~190 °C	Anhydride curing system

••• Target application
•• Suitable for application
• Suitable for application under certain requirements

THANK YOU!