Advanced Material Technologies for Hydrogen Delivery and Storage

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Long Beach, CA

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About Me…

- Andrea Haight, Ph.D.
- Composite Technology Development, Inc.
- Chief Technology Officer
- Specializing in materials for challenging environments
- Over 25 years experience
  - Resin formulation (epoxy, cyanate ester, benzoxazine, light curing systems)
  - Fiber sizing and finishes
  - Polymer and raw material synthesis

CTD History

1988

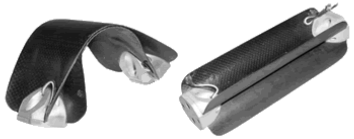
Insulation Materials

- Electrical – focus on superconducting magnets
- Radiation Resistant
- Thermal (Cryogenic & High Temperature)

1990

Cryogenic Testing

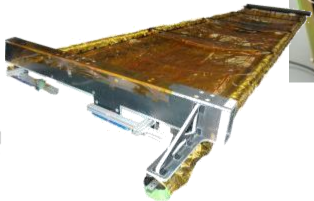
- Developed for Insulation
- Mechanical and electrical
- Test as low as 4K



1995

High Strain Materials

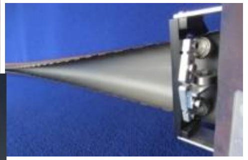
- Shape Memory Polymers
- Cryogenic applications
- Tough wear resistance



2000

Composite Components & Structures

- Lightweight deployable space structures
- Liner-less(Type V) Composite Tanks
- Deployable Solar Arrays & Antennas



2010

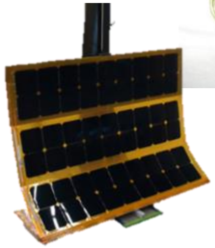
Integrated Systems and Products

- Deployable terrestrial and space solar arrays
- Aircraft & marine structures
- Polymer bearings
- Vibration and thermal isolators
- Pressure vessels & tanks

2020

Material Enabled Solutions

- Deployables
- Pressure Vessels
- Specialty Composites
- Engineered Materials
- New Space
- Clean Energy
- Next Generation Fusion



CTD Engineered Polymers

NANUQ® Electrical Insulation

- Used in the highest-performing magnets in the world
- Epoxy and cyanate ester-based systems
- Used in fusion, high energy physics, and MRI / medical accelerator magnets
- US Patents: 6,407,339 and 7,892,597

CryoCoat™ Thermal Insulation

- Excellent thermal and mechanical properties
- Tailorable formulations
- Processing flexibility
- Qualified for use on launch vehicles and the International Space Station

TEMBO® Shape Memory Polymers

- Replaces traditional, massive mechanisms
- Enables highest stowage efficiency
- Deployment provides motive force and accurate return to as-manufactured shape (low creep)
- Over 20 US Patents

KIBOKO® Structural Resins

- Optimal properties at ambient to cryogenic temperatures
- Versatile resin systems with wide applicability, including pressure vessels, high strain parts and advanced electronics
- US Patent: 8,074,826

Why Microcrack Resistant Resins?

- Ensure long-term structural performance of the composite
  - Microcracking of the composite resulting from repeated fill/drain cycles degrade performance over time
  - Loss of structural integrity in the composite can lead to fatigue cracking in the liner for CcH2 pressure vessels
- Improved cryogenic compatibility (CcH2, LH2)

CTD-7.1 Microcrack Resistant Resin

- Developed to enable Type V tanks at low pressure
- Wet winding resin
  - Working life ~ 4 hours
  - Room temperature gel
  - Cured at 50-70°C to achieve full properties

2.2-liter Type V propane tank

CTD-7.1 Resin & Composite Properties

Neat Resin Properties (at room temperature)

T_g (°C)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Ultimate Strain (%)
80-90	3102.6	51.0	7.1

Unidirectional Laminate Properties

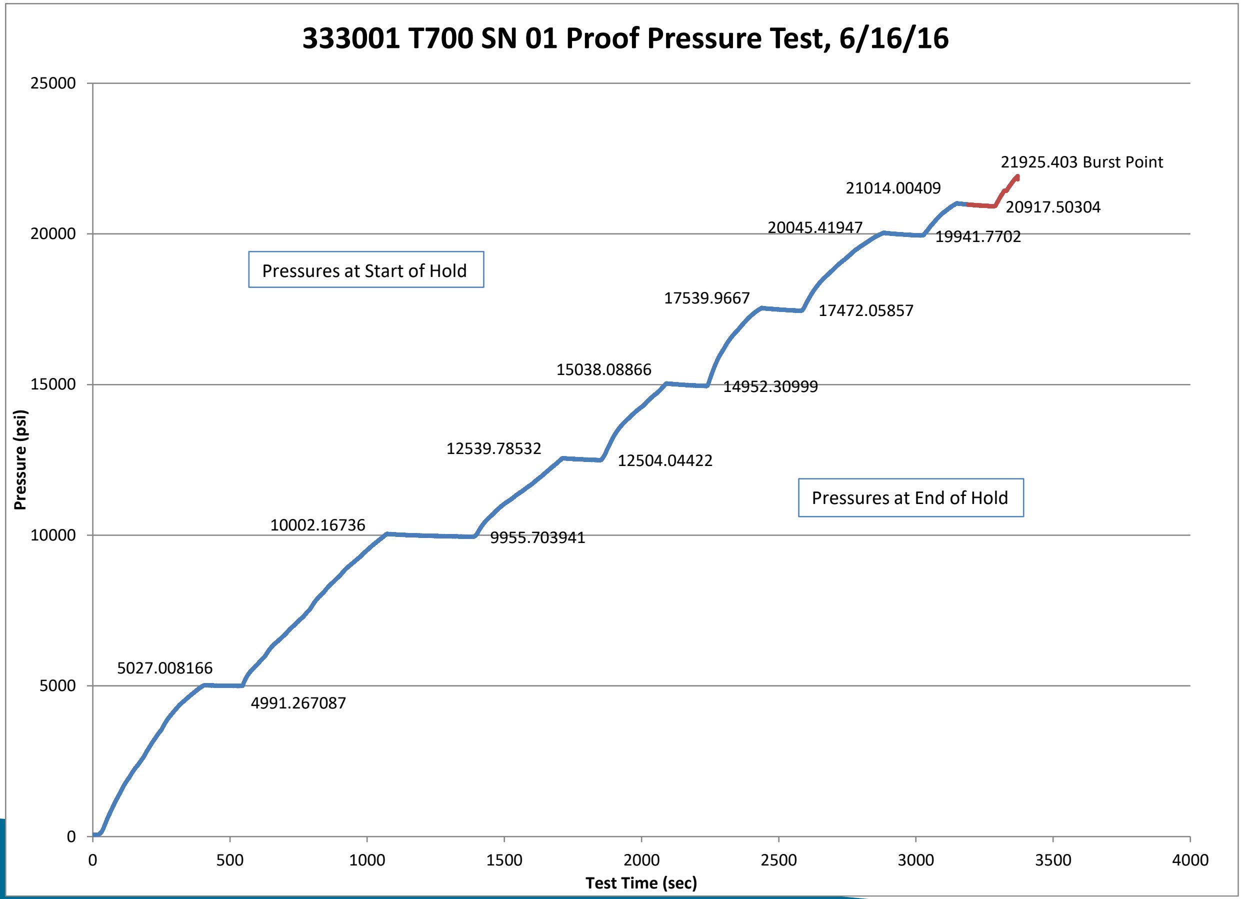
Material	Tensile Modulus (GPa)	Tensile Strength (MPa)	Ultimate Strain (%)	Test Temperature (K)
T700S/CTD-7.1 (0°)	108.3	2240.8	1.84	293
T700S/CTD-7.1 (90°)	8.89	41.8	0.46	293
T700S/CTD-7.1 (0°)	135.8	2440.7	1.60	77
T700S/CTD-7.1 (90°)	11.72	81.7	0.68	77
T1000/CTD-7.1 (0°)	161.3	2951.0	1.77	293
T1000/CTD-7.1 (0°)	156.5	3033.7		77

Fatigue Cycling CTD-7.1 Composites

	Specimen #	Cycles Completed	Material	Max Stress at failure after Fatigue (ksi)	% of Average Tensile Strength above non cycled samples	% Over OP during Fatigue testing	Ply Orientaion
1	133142-7	30000	Panex 35	137.60	101.6%	30.0%	zero
2	133142-8	30000	Panex 35	137.60	101.9%	30.0%	zero
3	133142-9	30000	Panex 35	172.60	84.3%	63.0%	zero
4	133142-10	30000	Panex 35	172.60	92.2%	63.0%	zero
5	133144-7	30000	T700 and Panex 35	108.9	91.3%	2.0%	zero
6	133144-8	30000	T700 and Panex 35	98.9	99.4%	-7.0%	zero
7	133144-9	30000	T700 and Panex 35	133.4	83.0%	28.0%	zero
8	133144-14	30000	T700 and Panex 35	99.5	101.0%	18.0%	zero
9	133144-15	30000	T700 and Panex 35	116.0	88.5%	12.0%	zero
10	133144-16	30000	T700 and Panex 35	118.3	100.8%	11.0%	zero
11	133144-17	30000	T700 and Panex 35	97.8	95.2%	-8.0%	zero
12	133146-7	30001	T700 and Panex 35	127.7	88.3%	23.0%	zero
13	133146-10	30000	T700 and Panex 35	147.3	91.3%	15.0%	zero
14	133149-1	30000	Panex 35	134.1	109.8%	63.0%	0/90
15	133149-2	30000	Panex 35	126.0	103.2%	63.0%	0/90
16	133150-1	30000	T700	209.7	99.9%	63.0%	0/90
17	133150-2	30000	T700	177.1	84.3%	63.0%	0/90

- Part of DOE SBIR program investigating graded carbon fiber structure for 700 bar GH2 storage
- Fatigue stress selected to represent ~50% over MEOP
- 30,000 cycles conducted (daily fill over 30 years is ~11,000 cycles
- Failure stress after 30,000 cycles at or above initial failure stress

Pressure Test of 700 bar Type IV COPV with T700/CTD-7.1



Burst Pressure ~1512 bar (21,925 psi)

CTD-133 Development

- Driving application is lightweight cryotanks for heavy lift vehicles
  - *linerless* composite tanks for cyrogenic H_2 storage
    - 50% weight savings over metal tanks
    - 15% weight savings over metal-lined, composite-overwrapped tanks
- Requirements guided by NASA's Composite Cryotank Technology Demonstration (CCTD) Program
- Key challenges
  - Performance at cryogenic temperatures
  - Structural requirements
  - Leak and/or permeation requirements
  - Processing requirements

Material Requirements

	Requirement	Units	Value
	System Level Requirements		
1.1	**Environmental**		
1.1.1	Temperature Range	K (°C)	20 (-253) to 373 (100)
1.2	**Permeation**		
1.2.1	Permeation rate	scc/sec/in^2	≤ 10^{-3}
	AFP Tank Fabrication		
2.1	**Handling**		
2.1.1	Tack	Pass	TBD
2.1.2	Tack Life	Days	> 20
2.1.3	Drape	Pass	TBD
2.2	**Stability**		
2.2.1	Minimum Out Life	Days	> 30
2.2.2	Moisture Sensitivity		<5% variability in properties
2.2.3	Viscosity at Room Temp	cPs	TBD
2.3	**Flow**		
2.3.1	Viscosity During AFP Consolidation	cPs	TBD
2.3.2	Viscosity During Cure	cPs	TBD
	Composite Laminate and Ply		
3.1	**Mechanical**		
3.1.1	0° Tensile Modulus	Msi	22
3.1.2	90° Tensile Modulus	Msi	1.4
3.1.3	Minimum 0° Tensile Strength	ksi	370
3.1.4	Minimum 90° Tensile Strength	ksi	12
3.1.5	0° ε	microstrain	7500
3.1.6	90° ε	microstrain	7500
3.1.7	0° CTE	10^{-6} m/m K	TBD
3.1.8	90° CTE	10^{-6} m/m K	TBD
3.1.9	Flexural Strength	ksi	
3.2	**Physical - Laminate**		
3.2.1	Void Content	Volume %	< 2
3.2.2	Fiber Content	Volume %	> 58

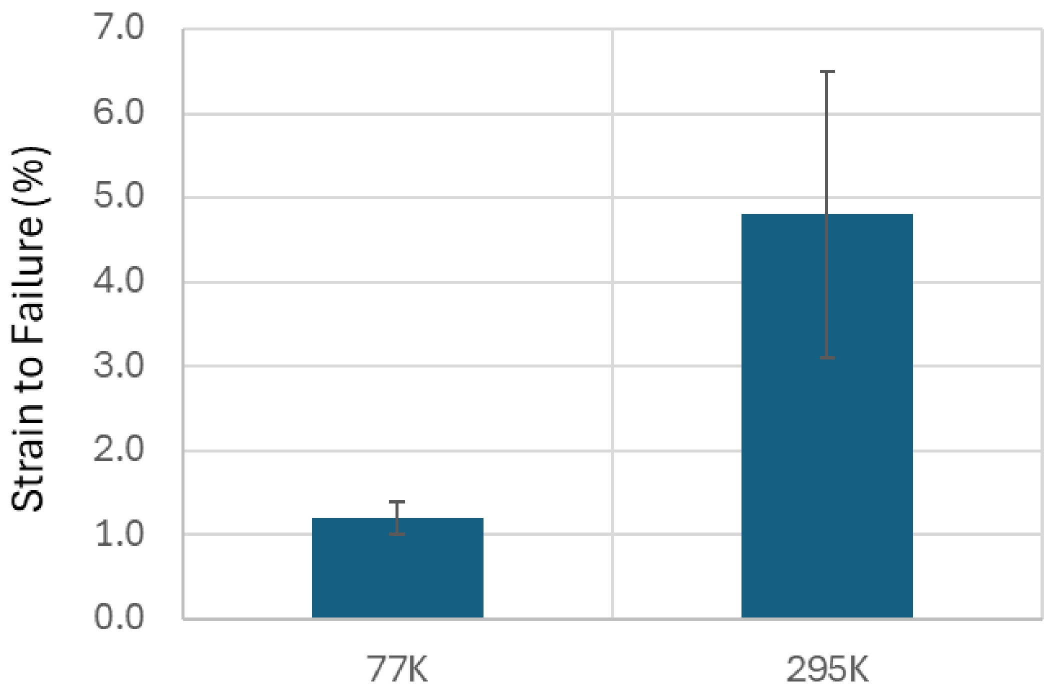
	Requirement	Units	Value
	Prepreg Process Requirements		
4.1	**Processing**		
4.1.1	Hot-melt Processing	—	Compliant
4.1.2	Polymer processing viscosity	cPs	<14,000
4.1.3	Volatile Content	%	<2
4.2	**Physical - Ply/Tow**		
4.2.1	Reinforcements	—	IM carbon fiber (70 or 145 gsm)
4.2.2	Typical Ply Thickness	inch	0.005 or 0.0025
4.2.3	Resin Content	wt%	< 34%
4.2.4	Tow Width	inch	0.125 to 0.3
4.2.5	Areal Weight	gsm	104 or 216 ± 2%

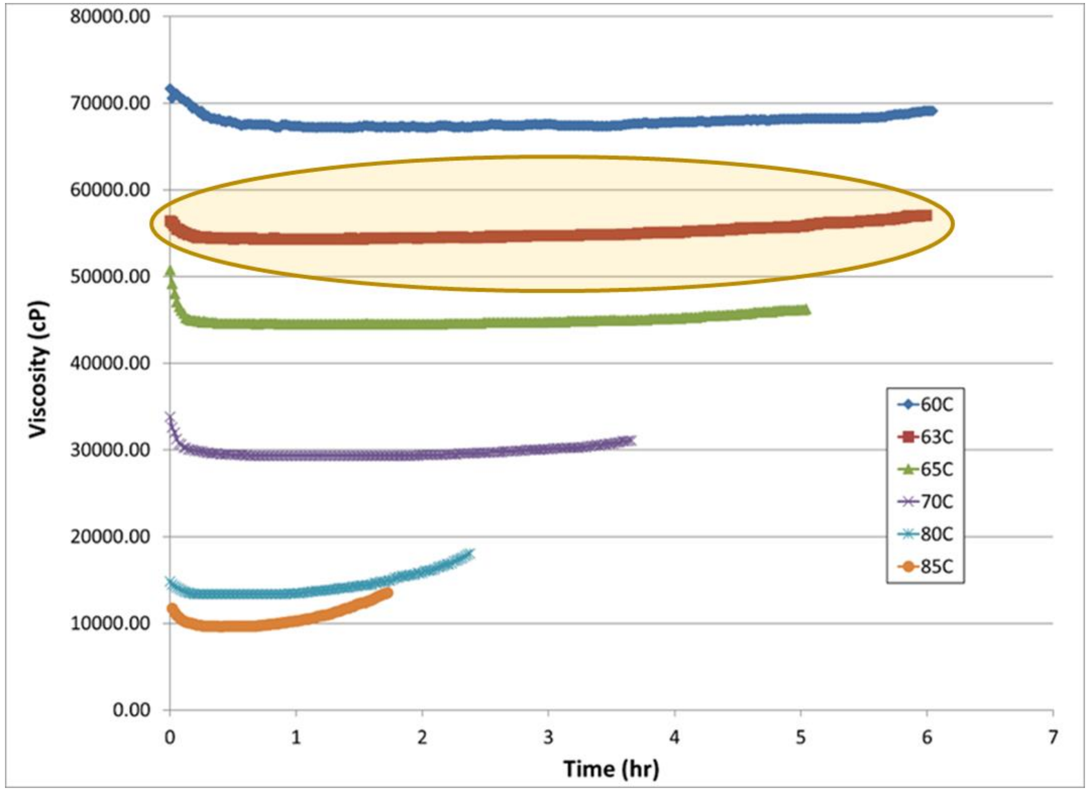
Key resin features:

- Microcrack resistance (high strain tolerance) at cryogenic temperatures
    - 0.75% (7500 $\mu\varepsilon$) requirement determined using FEA models developed for tank design
- Suitable for automated fiber placement (AFP)
    - Prepreg format
    - Long working times and extended room temperature out life

CTD-133 Neat Resin Properties

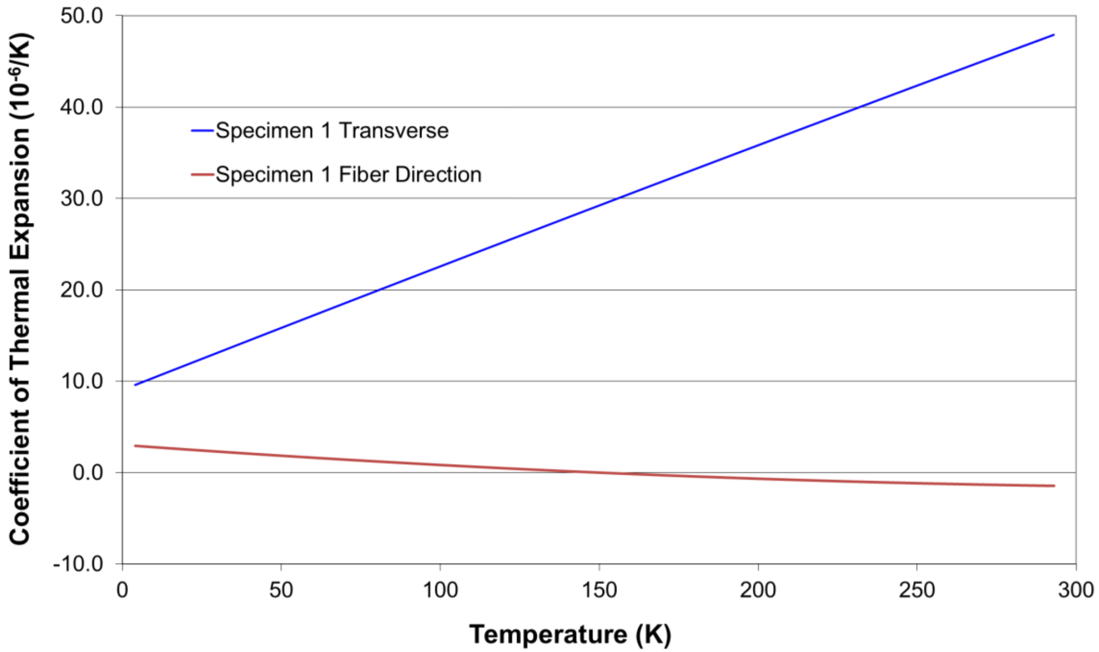
- T_g ~105°C (DMA, E')
- High strain to failure
- Optimal prepregging at 63°C

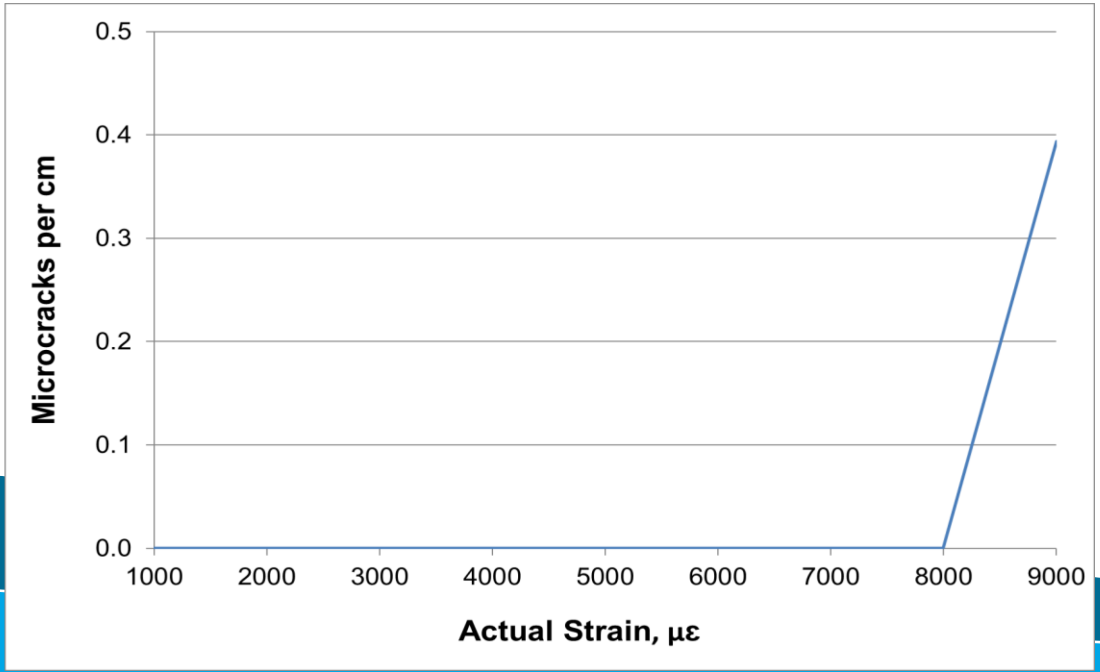




AFP Panels

Description	Dimensions	Quantity	Testing
0° Unidirectional	30 cm x 30 cm x 0.08 cm	2	Transverse Tension, Strain to Failure
0° Unidirectional	30 cm x 30 cm x 0.25 cm	2	Longitudinal Tension, Shear, CTE
$[0/90]_s$ Cross-Ply	30 cm x 30 cm x 0.05 cm	1	Microcrack Fracture Toughness
$[45/0\text{-}45/90]_s$ Quasi Isotropic	30 cm x 30 cm x 0.13 cm	3	Hydrogen Permeation



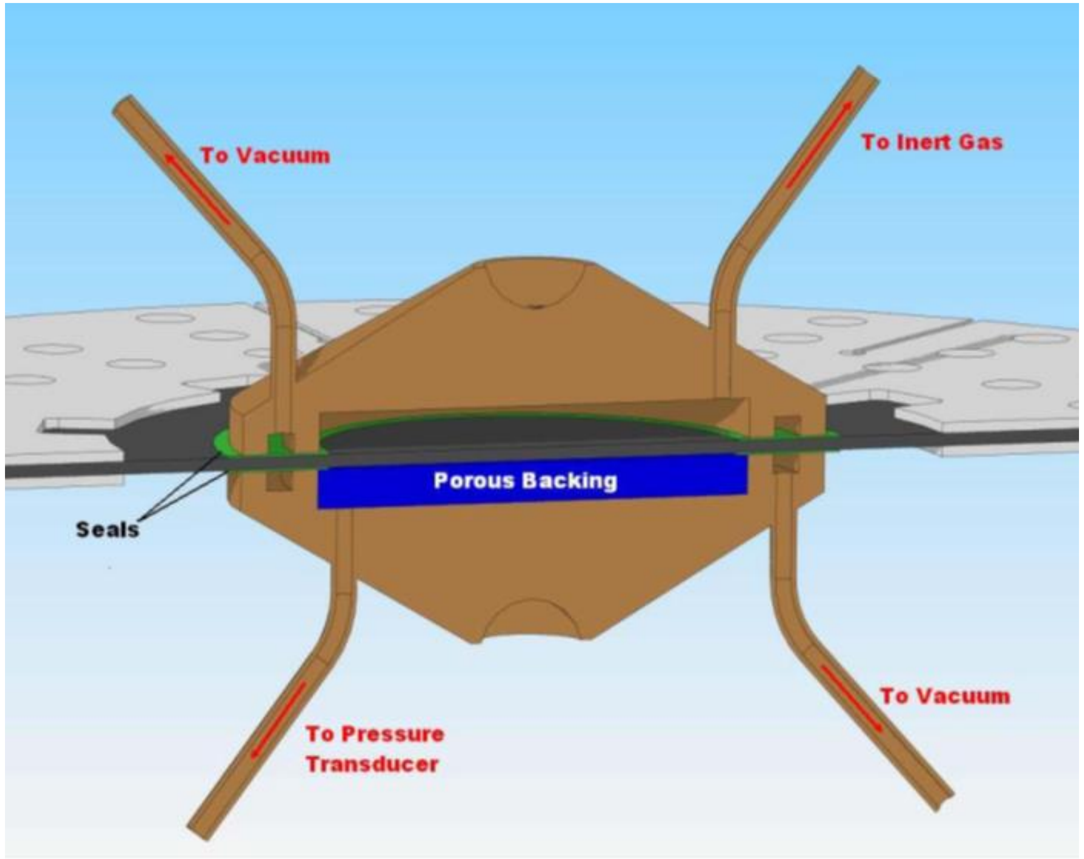


AFP Panel Testing

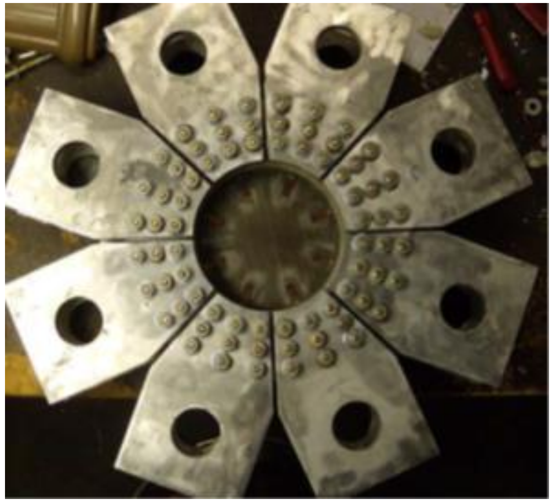
Evaluation Parameter	Measured Result	Requirement
0° Tension Modulus	155.8 ± 3.5 GPa (77K)	151.7 GPa
90° Tension Modulus	12.55 ± 0.11 GPa (77K)	9.65 GPa
0° Tension Strength	2575 ± 185.5 MPa (77K)	2551 MPa
90° Tension Strength	86.5 ± 6.14 MPa (77K)	82.7 MPa
Strain to Failure*	0.69 ± 0.06% (77K)	0.75%
Avg Fiber Volume Fraction	52.4%	> 58%
Avg Void Content	1.9%	< 2%

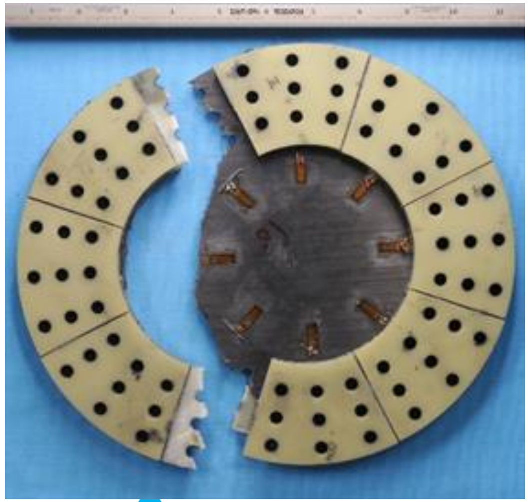
* Most specimens failed > 0.75% strain

Hydrogen Permeation



- Permeability measured through-thickness to mimic pressure vessel use case
- Testing conditions
  - Ambient (297K) and cryogenic (21K)
  - Different strain conditions, up to 0.75%

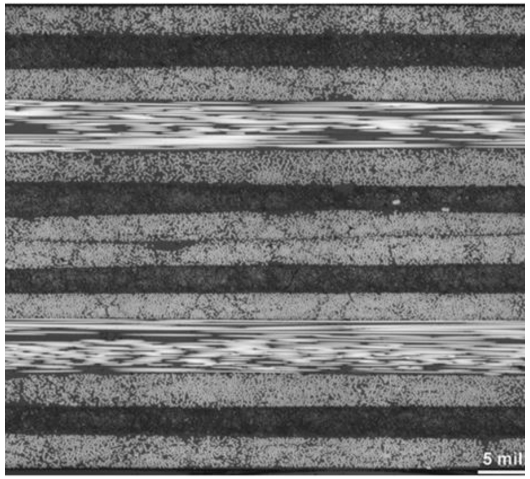


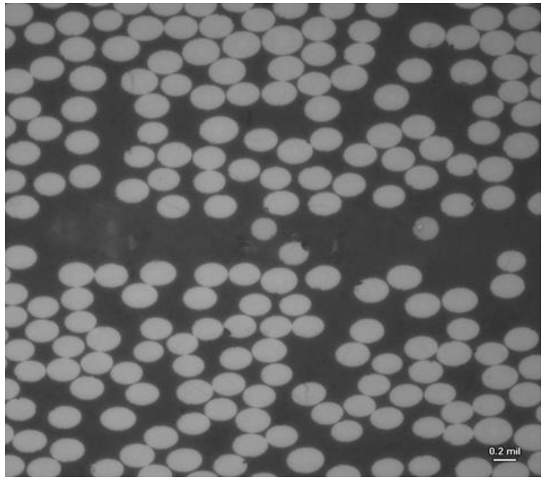


Hydrogen Permeation Results

Test Temperature	Strain State	Permeation Rate	Hydrogen Permeability
(K)	(μstrain)	($scc/sec/cm^2$)	(mol/s*Pa*m)
297	0	4.01×10^{-6}	2.76×10^{-17}
	1500	3.95×10^{-6}	2.74×10^{-17}
	3000	4.51×10^{-6}	3.03×10^{-17}
	4500	4.86×10^{-6}	3.33×10^{-17}
	5000	4.99×10^{-6}	3.40×10^{-17}
	5500	5.02×10^{-6}	3.42×10^{-17}
	6000	5.30×10^{-6}	3.63×10^{-17}
	6500	x	X
20	0	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	1500	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	3000	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	4500	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	5000	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	5500	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	6000	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	6500	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	7000	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
	7500	$< 1.55 \times 10^{-5}$	$<1 \times 10^{-16}$
297	0	2.81×10^{-6}	3.40×10^{-17}

- Permeation rate well below requirement ($\leq 1.5 \times 10^{-2}$ $scc/sec/cm^2$)
- Permeability below cryogenic detectable limit (1×10^{-16} mol/s·Pa·m)
- No microcracking
  - Verified by final unrestrained RT test
  - Observed via microscopy





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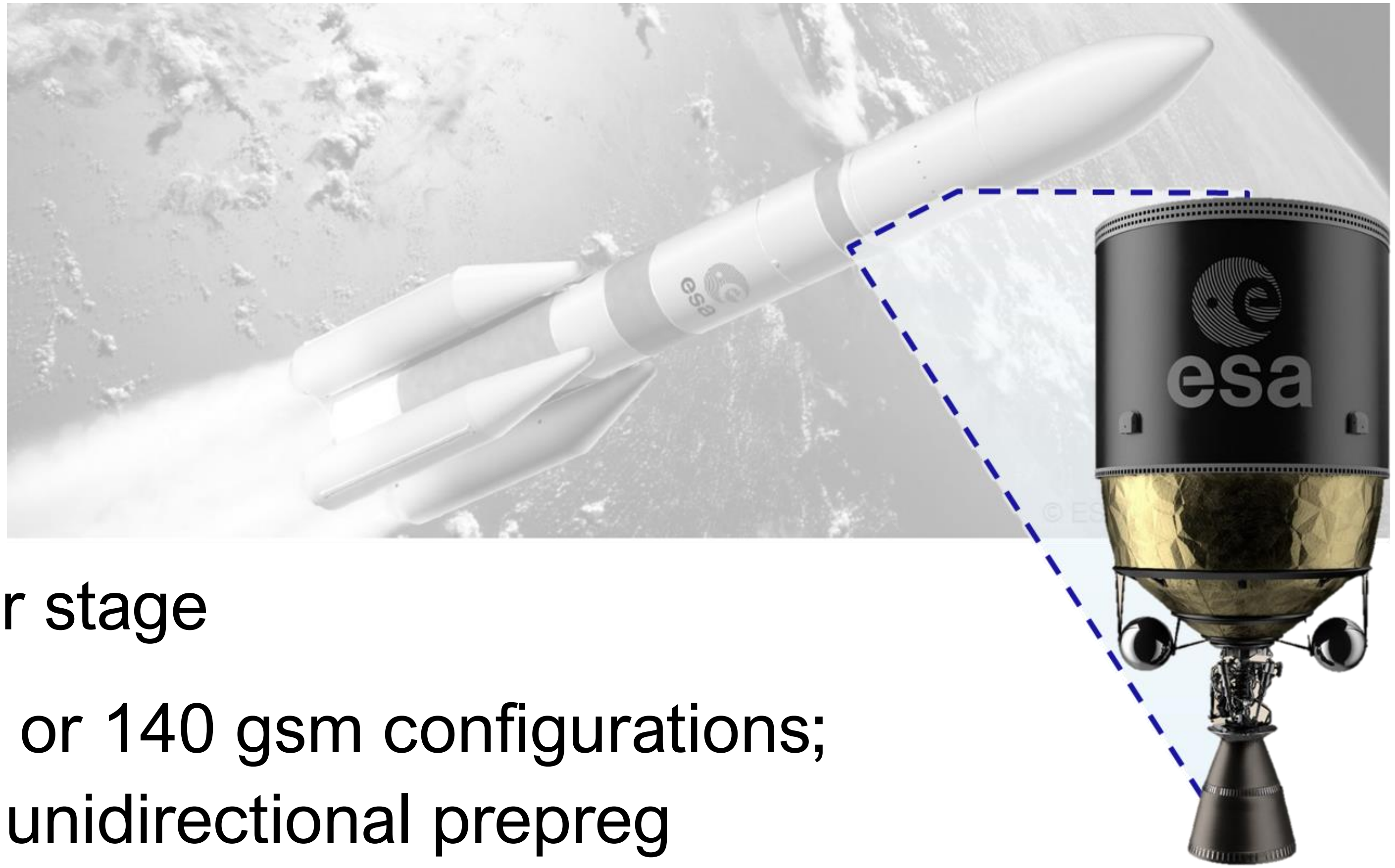
CTD Structural Composite Tank

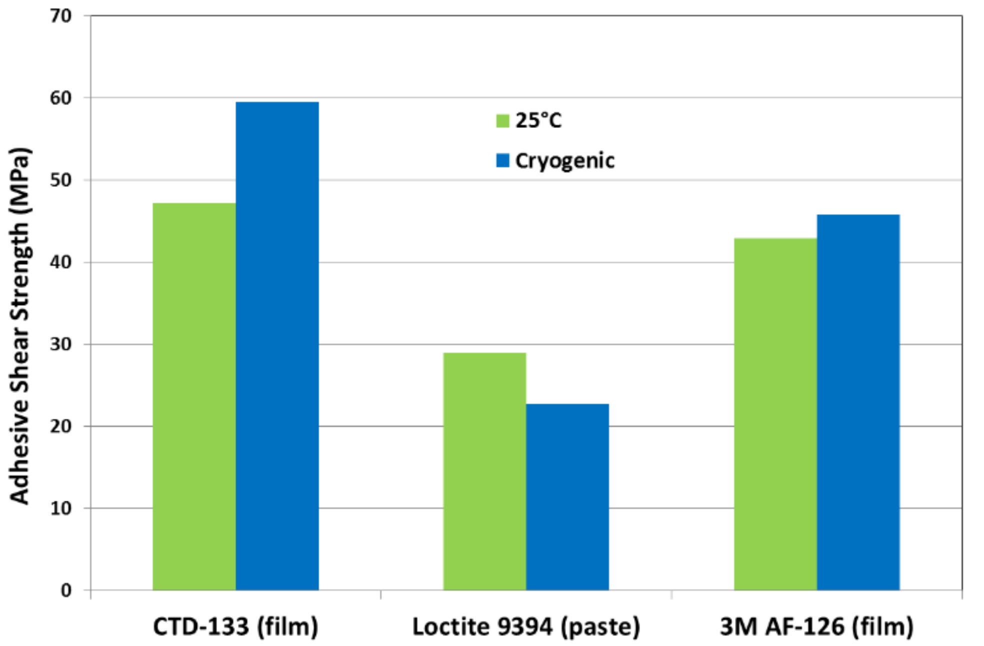
Liquid Oxygen, Liquid Hydrogen, & other Cryogenic Fuels

- Lightweight, microcrack-resistant, high strength epoxy prepreg
- Undergoing qualification for European Space Agency all-composite cryogenic upper stage
- Fiber Aerial Weight of 70 gsm or 140 gsm configurations; Widths: ¼” slit tape up to 12” unidirectional prepreg

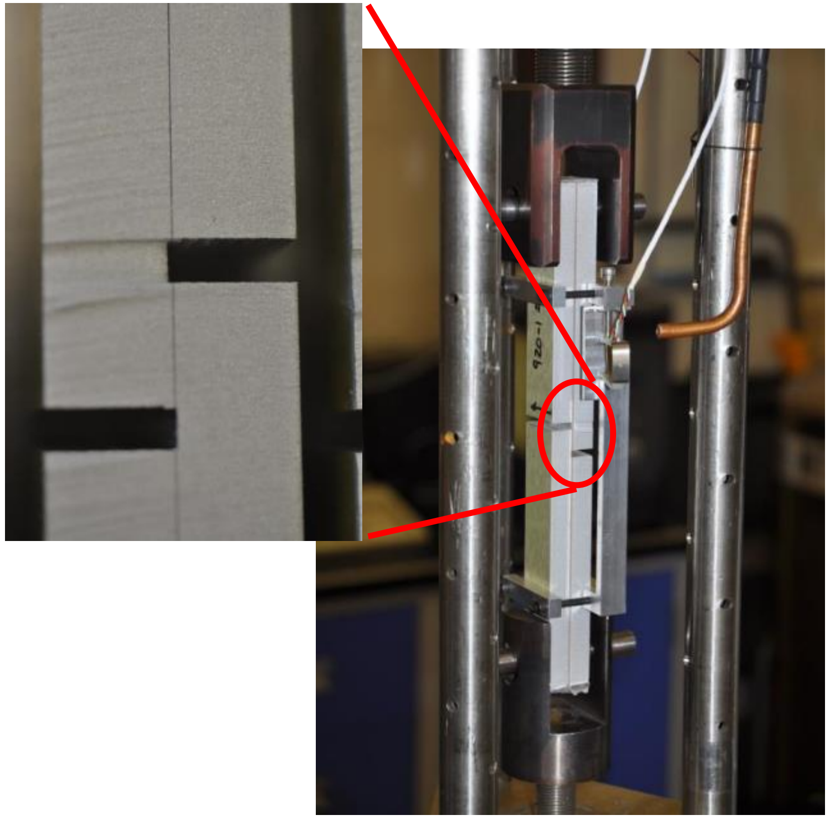


CTD-133 Film Adhesive

- 300 gsm film adhesive, 10 gsm polyester carrier cloth, Nominal 0.15 mm (0.006 in.) bondline
- Film thickness, carrier cloth, and bondline are tailorable to the application
- Excellent room temperature and cryogenic temperature adhesion properties



All data shown is for lap shear tests using primed and etched 2024 Aluminum



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Conclusions

- Microcrack resistant resin systems have been formulated that meet basic requirements for hydrogen storage applications
- Reduces risk of fatigue damage in all types of pressure vessels
- Low helium permeability has been demonstrated for Type V pressure vessels based on these systems at both ambient and cryogenic temperatures
- CTD-133 prepreg system has a long out-life that enables large structure manufacturing
- Continued development of systems with improved cost, performance and multiple formats is ongoing