# CHARACTERIZATION AND PROCESS DEVELOPMENT OF CYANATE ESTER RESIN COMPOSITES

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# OBJECTIVES

- Investigate the effects of the cure cycle and process environment on cyanate ester resin and composite properties
- Develop a high-strength hoop-wound composite by the wet-filament winding method
  - Toray T1000G carbon fiber
  - YLA RS-14A (or RS-14) cyanate ester resin

# CYANATE ESTER RESINS

Cyanate esters are a family of monomers and prepolymers which contain reactive ring-forming cyanate (- O - C ≡N) functional groups

- Conversion, or curing, occurs via cyclotrimerization to form three-dimensional triazine ring connecting units
- Additive reaction
- Exothermic
- Thermoset polycyanurate plastics

# ADVANTAGES OF CYANATE ESTER RESINS

- Low outgassing
- Low moisture absorption
- High thermal stability
- Radiation resistant
- Tough/resistant to microcracking caused by thermal cycling
- Low dielectric constant and low dissipation factors
- “Zero” net volume change with cure
- Processing flexibility
  - Prepreg lamination
  - Wet-filament winding
  - Resin transfer molding

# CYANATE ESTER RESIN

- YLA RS-14A (or RS-14) resin
  - RS-14A and RS-14 resins are identical with the exception that the RS-14 resin contains minute quantities of zirconate coupling agent.
  - RS-14 product discontinued during course of this study and replaced with the RS-14A formulation.
- Low viscosity
  - 0.2 to 0.1 Pa•s between 70° to 85°C
  - Excellent wet-winding resin

# PROCESS VARIABLES

- Time-temperature profile (cure cycle)
- Thermal cycling
- Resin exposure to humidity during processing
- Resin exposure to air during cure

# CURE CYCLE VARIABLES

- Precure temperature
  - 138°C (~280°F)
  - 193°C (~380°F)
  - No precure step (ramp directly to postcure temperature)
- Postcure temperature
  - 250°C (~480°F)
  - 265°C (~510°F)
- Multiple precure and/or postcure cycles
  - Pertinent to fabrication of “thick” composite cylinders that are wound and cured in increments (“stages”)

# DSC ANALYSES

DSC analyses were conducted to determine the effects of ramp rate, precure and postcure temperature on the resin's ultimate $T_g$ and cure profile

- Cure Cycle
  - 138°C (~280°F) versus193°C (~380°F) precure step
  - No precure step (ramp directly to postcure temperature)
  - 250°C (~480°F) versus 265°C (~510°F) postcure step
- Ramp rate
  - 1°, 2°, and 4°C/min ramp rate to temperature
- Dwell times
  - 3 h precure
  - 4 h postcure

# DSC data for cyanate ester resin

| Resin | 135ºC | | 190ºC | | 250ºC | | 265ºC | | $T_g$ | Enthalpy |
|---|---|---|---|---|---|---|---|---|---|---|
| | Ramp ºC/min | Hold h | Ramp ºC/min | Hold h | Ramp ºC/min | Hold h | Ramp ºC/min | Hold h | ºC | J/g |
| RS-14 | | | | | | | 1 | 4 | 253 | -774 |
| | | | | | | | 2 | 4 | 256 | -624 |
| | | | | | | | 4 | 4 | 255 | -519 |
| | | | | | | | 4 | 4 | 253 | -539 |
| | | | | | 1 | 4 | | | 256 | -616 |
| | | | | | 2 | 4 | | | 254 | -536 |
| | | | | | 2 | 4 | | | 256 | -538 |
| | | | | | 4 | 4 | | | 255 | -472 |
| | 1 | 3 | | | | | 1 | 4 | 253 | - |
| | 1 | 3 | | | | | 1 | 4 | 255 | - |
| | 4 | 3 | | | | | 1 | 4 | 254 | - |
| | | | 1 | 3 | | | 1 | 4 | 254 | - |
| | | | 4 | 3 | | | 1 | 4 | 256 | - |
| | | | 4 | 3 | | | 1 | 4 | 256 | - |
| RS-14A | | | | | | | 2 | 4 | 270 | -570 |
| | | | | | | | 2 | 4 | 270 | -598 |

# DSC RESULTS

- $T_g$ the same for all cure cycles investigated
  - RS-14: 253° to 256°C
  - RS-14A: 270°C
- $T_g$ the same for samples postcured at 250°C or 265°C
  - long (4 h) dwell time enables cyclotrimerization to proceed to same degree of conversion for both postcure temperatures

# RESIN PANELS

Resin panels were fabricated and tested to determine effects of cure cycle and process environment on cyanate ester resin's properties

- Cure cycle
  - 138°C versus 193°C  precure step
  - No precure step (ramp directly to postcure temperature)
  - 250°C  versus 265°C  postcure step
- Process environment
  - air
  - inert (nitrogen)
- Thermal cycling to precure or postcure temperature
  - 3 to 4 cycles

# RESIN PANEL EVALUATION

- Tensile properties
  - strength
  - modulus
  - elongation
- $T_g$
  - DMA
  - Line-fit intercept method using storage modulus (G´) curve
- Density

# RESIN PANEL RESULTS

Comparable RS-14A and RS-14 resin properties were obtained for all of the process cycles conducted a single time (non-thermally cycled) and in a nitrogen environment

- Tensile properties
  - 82 to 90 MPa strength
  - 2.6 to 3.0 GPa modulus
  - 4.1 to 5.5% elongation
- $T_g$
  - RS-14 $T_g$: 242° to 255°C
  - RS-14A $T_g$: 262° to 263°C $T_g$
- Density
  - ~1.20 g/cm$^3$

# AIR VS INERT ($N_2$) CURE

- Panels exposed to air at elevated temperatures during cure had significantly **lower** tensile strengths and elongations than panels processed in nitrogen
  - Dark brown-black layer at panel surface
  - Dark layer hypothesized to act as flaw to promote premature tensile failure in specimens

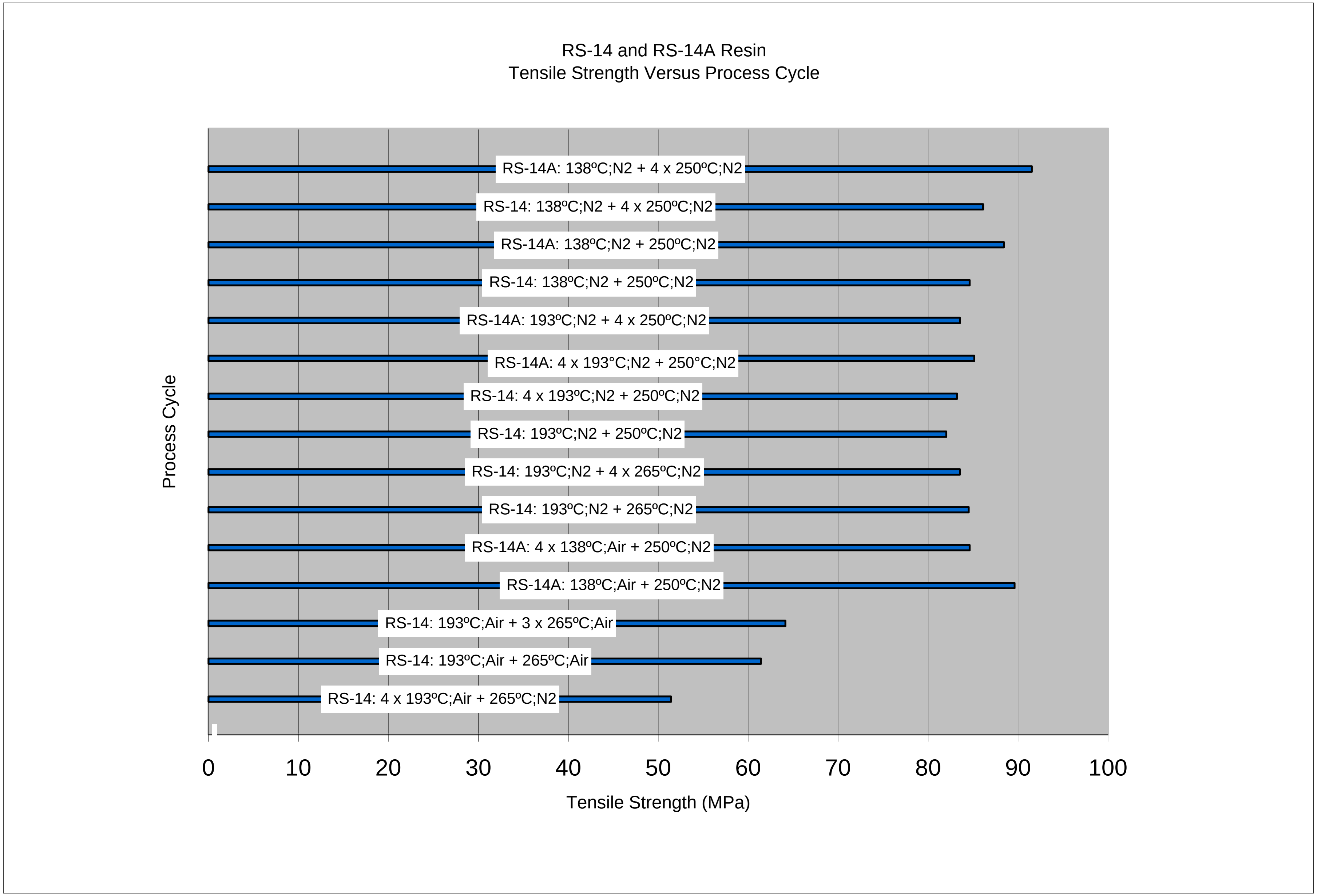
# AIR VS INERT ($N_2$) CURE (cont'd)

- Properties of panel thermally cycled to 193°C precure temperature in air similarly degraded even though later postcured in nitrogen
  - Slight darkening of panel surface with each thermal cycle
  - Reduced tensile strength and elongation
  - 10° to 20°C reduction in $T_g$
- Properties of panel thermally cycled to 138°C precure temperature in air unaffected
  - No surface reaction (coloration) evident

# THERMAL CYCLING

No significant change in resin properties with multiple precure and postcure cycles for panels that were maintained in a nitrogen environment

- Additional postcure cycles to either 250° or 265°C did not appreciably change resin $T_g$
- Multiple thermal cycles to 265°C postcure temperature in nitrogen significantly darkened resin with each cycle
  - Coloration visible throughout entire thickness of resin panel


RS-14 and RS-14A Resin
Tensile Strength Versus Process Cycle
RS-14A: 138ºC;N2 + 4 x 250ºC;N2
RS-14: 138ºC;N2 + 4 x 250ºC;N2
RS-14A: 138ºC;N2 + 250ºC;N2
RS-14: 138ºC;N2 + 250ºC;N2
RS-14A: 193ºC;N2 + 4 x 250ºC;N2
RS-14A: 4 x 193°C;N2 + 250°C;N2
RS-14: 4 x 193ºC;N2 + 250ºC;N2
RS-14: 193ºC;N2 + 250ºC;N2
RS-14: 193ºC;N2 + 4 x 265ºC;N2
RS-14: 193ºC;N2 + 265ºC;N2
RS-14A: 4 x 138ºC;Air + 250ºC;N2
RS-14A: 138ºC;Air + 250ºC;N2
RS-14: 193ºC;Air + 3 x 265ºC;Air
RS-14: 193ºC;Air + 265ºC;Air
RS-14: 4 x 193ºC;Air + 265ºC;N2
Process Cycle
0
10
20
30
40
50
60
70
80
90
100
Tensile Strength (MPa)

# HUMIDITY EXPOSURE

A study was conducted to characterize the effects of humidity (moisture) exposure during processing on the cured cyanate ester resin properties

- Simulate wet-filament winding environments
- Establish "thresholds" or limits at which the cyanate ester resin's properties are compromised by moisture exposure

# RESIN PRECONDITIONING

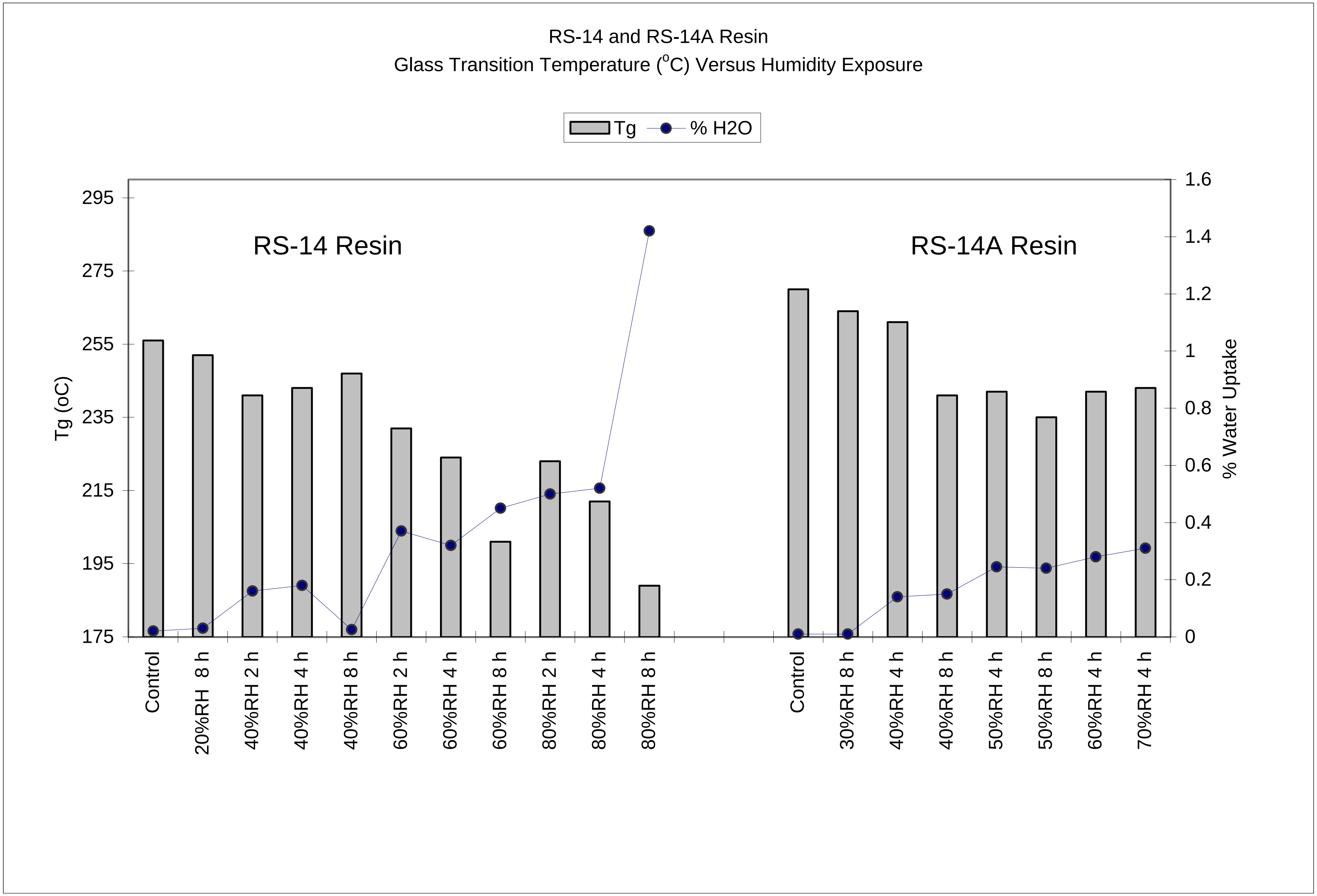
- Uncured resin samples exposed to a range of humidity levels in an environmental chamber
  - 80°C
  - 2, 4, and 8 h exposures
  - Continuous stirring
- Resin evaluation
  - Water content (Karl-Fischer titration)
  - $T_g$ (DSC)
  - Cured resin properties
    - Tensile strength, modulus and elongation
    - $T_g$ (DMA)

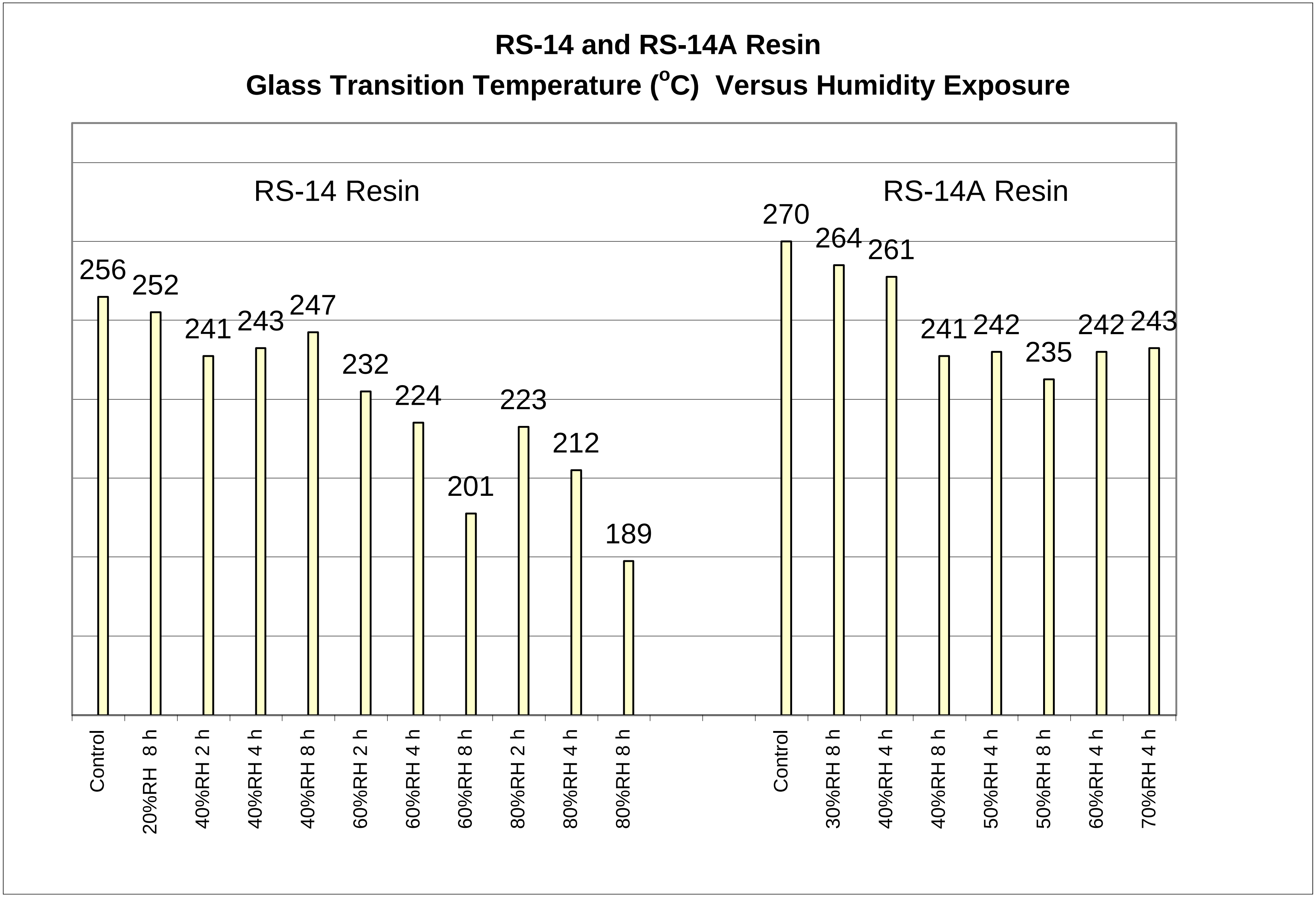
**Effects of humidity exposure (80ºC) on cyanate ester resin properties**

| Resin | Exposure | | Karl-Fischer | DSC | Tensile | | | DMA |
|---|---|---|---|---|---|---|---|---|
| | RH | Time | Water | Tg | Strength | Modulus | Elongation | $T_g$ |
| | % | h | % | ºC | MPa | GPa | % | ºC |
| **RS-14** | Control | | 0.02 | 256 | 89.8 | 2.7 | 5.8 | 252 |
| | 20 | 8 | 0.03 | 252 | 85.2 | 2.8 | 4.8 | 252 |
| | 40 | 2 | 0.16 | 241 | 91.4 | 2.7 | 5.9 | 243 |
| | 40 | 4 | 0.21/0.15 | 243 | 89.6 | 2.7 | 5.3 | 237 |
| | 40 | 8 | 0.03/0.02 | 247 | 90.4 | 2.8 | 5.5 | 248 |
| | 60 | 2 | 0.37 | 232 | 87.3 | 2.8 | 4.8 | 233 |
| | 60 | 4 | 0.38/0.26 | 224 | 83.9 | 2.8 | 4.4 | 227 |
| | 60 | 8 | 0.45 | 201 | (Extensive bubbles and voids in panel) | | | 206 |
| | 80 | 2 | 0.50 | 223 | 87.0 | 2.7 | 4.9 | 236 |
| | 80 | 4 | 0.52 | 212 | 88.7 | 2.8 | 5.0 | 231 |
| | 80 | 8 | 1.42 | 189 | (Extensive bubbles and voids in panel) | | | 199 |
| **RS-14A** | Control | | 0.01 | 270 | 88.4 | 2.6 | 5.5 | 262 |
| | 30 | 8 | 0.01 | 264 | 88.5 | 2.7 | 5.2 | 259 |
| | 40 | 4 | 0.14 | 261 | 86.4 | 2.7 | 5.1 | 258 |
| | 40 | 8 | 0.15 | 241 | 89.5 | 2.8 | 5.2 | 247 |
| | 50 | 4 | 0.21/0.28 | 242 | 91.1 | 2.7 | 5.3 | 251 |
| | 50 | 8 | 0.16/0.31 | 235 | 88.3 | 2.8 | 5.1 | 238 |
| | 60 | 4 | 0.28 | 242 | 93.2 | 2.8 | 5.1 | 240 |
| | 70 | 4 | 0.31 | 243 | (Extensive bubbles and cracks in panel) | | | 238 |

# HUMIDITY EFFECTS ON RESIN

- Significant $T_g$ reductions with increasing humidity exposure and water uptake
  - Slight $T_g$ reductions after 8 h at 30% RH
  - Greatest $T_g$ reductions with exposures greater than 40% RH
  - Water content increases from 0.01 to 0.02% (as-received) level to above 0.1% after 2 h at 40% RH
- Large bubbles in panels cast from resin preconditioned to 60% and 80% RH
- Tensile properties unaffected by high humidity exposures!


RS-14 and RS-14A Resin
Glass Transition Temperature (oC) Versus Humidity Exposure
Tg
% H2O
RS-14 Resin
RS-14A Resin
Tg (oC)
% Water Uptake
295
275
255
235
215
195
175
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Control
20%RH 8 h
40%RH 2 h
40%RH 4 h
40%RH 8 h
60%RH 2 h
60%RH 4 h
60%RH 8 h
80%RH 2 h
80%RH 4 h
80%RH 8 h
Control
30%RH 8 h
40%RH 4 h
40%RH 8 h
50%RH 4 h
50%RH 8 h
60%RH 4 h
70%RH 4 h


RS-14 and RS-14A Resin
Glass Transition Temperature (°C) Versus Humidity Exposure
RS-14 Resin
RS-14A Resin
256
252
241
243
247
232
224
201
223
212
189
270
264
261
241
242
235
242
243
Control
20%RH 8 h
40%RH 2 h
40%RH 4 h
40%RH 8 h
60%RH 2 h
60%RH 4 h
60%RH 8 h
80%RH 2 h
80%RH 4 h
80%RH 8 h
Control
30%RH 8 h
40%RH 4 h
40%RH 8 h
50%RH 4 h
50%RH 8 h
60%RH 4 h
70%RH 4 h

# CARBAMATE FORMATION

The degradation of thermal properties is attributed to the reaction of the cyanate function with water (hydrolysis) leading to the production of a carbamate species

- Carbamates decompose above 190°C, yielding an amine and $CO_2$
- $CO_2$ evolution can lead to bubbles and voids in resin and composite samples
- Triazine ring formation process interrupted
  - Reduced cyanate functionality due to carbamate formation
  - Amine resulting from carbamate decomposition can react with another cyanate group, leading to a linear species with reduced properties (lower $T_g$)

# COMPOSITE PROCESS TRIALS

Composite process trials were conducted to investigate the effects of cure cycle and process environment on composite mechanical properties

- Cure cycles (extension of resin process trials)
  - 138°C and 193°C precure step
  - No precure step (ramp directly to postcure temperature)
  - 260° or 265°C postcure step
  - 3 h precure & 4 h postcure
- Air versus inert atmosphere cure
- Thermal cycling (on mandrel) during manufacture
  - 3 to 4 cycles
  - Pertinent to fabrication of “thick” cylinders that are wound and cured in stages

# COMPOSITE CYLINDERS

- All-hoop wet-filament wound composite
- ~610 mm ID x 3.18 mm wall thickness
- T1000G carbon fiber
  - Single lot
  - 6,577 MPa (954 ksi) fiber strength
  - Lot average measured by ORNL
- YLA RS-14A or RS-14 resin

# CYLINDER EVALUATION

- Ring (hoop) tensile strength and modulus
  - “Split-D” method based on ASTM D2290
  - Extensometer-measured “D” separation (modulus)
- Interlaminar shear strength
  - ASTM D2344
- Transverse flexure strength
  - ASTM D790
  - OD surface in tension
- Composition
  - Calculated from composite density (ASTM D792) and weight percent resin and fiber contents (nitric acid digestion)

# Composite process trial results

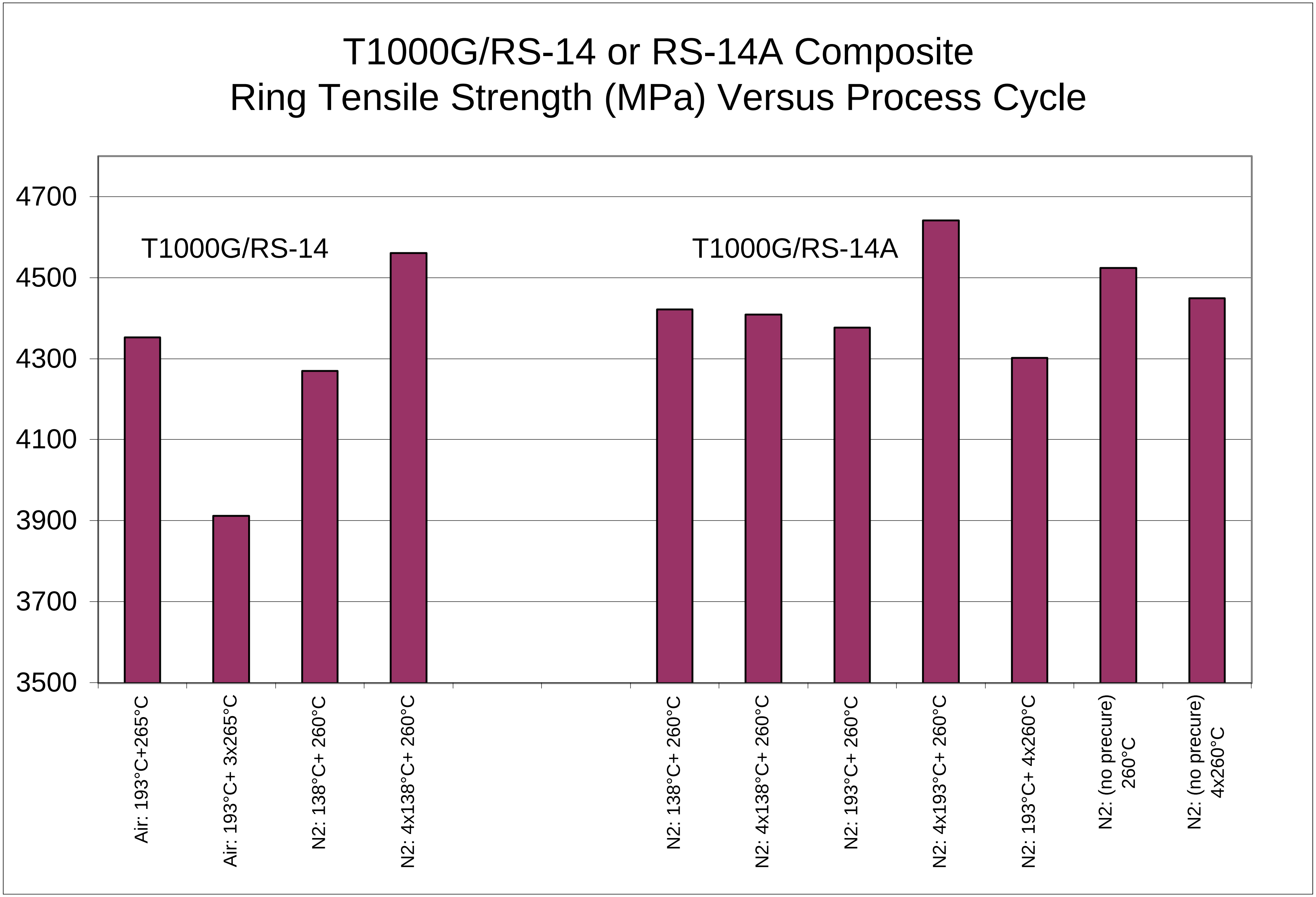
| Process Environment | Air | | Inert ($N_2$) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Precure<br>Postcure<br>Resin | 193ºC<br>265ºC<br>RS-14 | 193ºC<br>3 x 265ºC<br>RS-14 | 138ºC<br>260ºC<br>RS-14 | 4 x 138ºC<br>260ºC<br>RS-14 | 138ºC<br>260ºC<br>RS-14A | 4 x 138ºC<br>260ºC<br>RS-14A | 193ºC<br>260ºC<br>RS-14A | 4 x 193ºC<br>260ºC<br>RS-14A | 193ºC<br>4 x 260ºC<br>RS-14A | None<br>260ºC<br>RS-14A | None<br>4 x 260ºC<br>RS-14A |
| **Ring Tensile** | | | | | | | | | | | |
| Strength (MPa) | 4352.6 | 3911.4 | 4269.9 | 4560.8 | 4421.6 | 4409.2 | 4376.1 | 4640.8 | 4301.6 | 4524.3 | 4449.2 |
| Modulus (GPa) | 225.4 | 223.3 | 225.5 | 225.4 | 229.6 | 226.8 | 225.4 | 227.5 | 227.5 | 228.9 | 228.9 |
| **SBS Strength (MPa)** | 65.2 | 67.2 | 66.5 | 55.6 | 59.9 | 65.0 | 67.2 | 65.7 | 65.7 | 66.8 | 69.1 |
| **Transverse Flexure Strength (MPa)** | 97.1 | 86.9 | 74.4 | 68.9 | 71.6 | 71.4 | 80.3 | 74.0 | 81.9 | 78.9 | 73.1 |
| **Composition** | | | | | | | | | | | |
| Density (g/cm$^3$) | 1.6607 | 1.6667 | 1.6575 | 1.6569 | 1.6611 | 1.6646 | 1.6648 | 1.6658 | 1.6648 | 1.6663 | 1.6663 |
| Volume % Fiber | 78.4 | 79.6 | 78.4 | 78.3 | 78.6 | 78.7 | 79.2 | 79.0 | 79.2 | 79.5 | 79.5 |
| Volume % Resin | 21.5 | 20.1 | 21.1 | 21.3 | 21.2 | 21.4 | 20.6 | 21.0 | 20.6 | 20.3 | 20.3 |
| Volume % Voids | 0.1 | 0.3 | 0.5 | 0.4 | 0.2 | -0.1 | 0.2 | 0.0 | 0.2 | 0.2 | 0.2 |

**Notes:**
(1) Times at process temperature are 3 h for the precure segment and 4 h for the postcure segment.
(2) Cylinders that received additional precure or postcure cycles are indicated by the "number of cycles x" designation.

# THERMAL CYCLING IN AIR

Cylinder cycled to postcure temperature in air had significantly lower ring tensile strength than cylinders cycled in an inert atmosphere

- Black discoloration of OD surface resin for air-processed cylinders (versus amber-brown tint of $N_2$- processed cylinders)
- Ring tensile strength reduction attributed to reduction in cyanate ester resin tensile properties as a result of reaction with air and/or moisture at elevated temperature
- Comparable to results from resin panel study
- Increase in transverse flexural strength


T1000G/RS-14 or RS-14A Composite
Ring Tensile Strength (MPa) Versus Process Cycle
4700
4500
4300
4100
3900
3700
3500
T1000G/RS-14
T1000G/RS-14A
Air: 193°C+265°C
Air: 193°C+ 3x265°C
N2: 138°C+ 260°C
N2: 4x138°C+ 260°C
N2: 138°C+ 260°C
N2: 4x138°C+ 260°C
N2: 193°C+ 260°C
N2: 4x193°C+ 260°C
N2: 193°C+ 4x260°C
N2: (no precure) 260°C
N2: (no precure) 4x260°C

# PROCESS TRIAL RESULTS

There is a broad process envelope for processing composites that are wet-filament wound with RS-14 and RS-14A resin

- Comparable composite properties achieved for all process cycles conducted in an inert atmosphere
- No affect on composite properties from additional precure and postcure cycles when conducted in an inert atmosphere

# COMPOSITE COMPOSITION

The cylinders were wound reproducibly and have nominally the same compositions

- Density: ~1.66 g/cm$^3$
- Fiber content: 78.3 to 79.6 vol.%
- Voids: < 0.5 vol.%

# COMPOSITE PROPERTIES

- Ring tensile strength
  - 4270 to 4641 MPa
  - Individual ring strengths above 4826 MPa (***700 ksi***)
  - Highest fiber strength translations: ~89%
- Ring tensile modulus
  - 223 to 230 GPa

# COMPOSITE PROPERTIES (cont'd)

- Interlaminar shear strength
  - 56 to 69 MPa
- Transverse flexure strength
  - 69 to 82 MPa

# ELEVATED TEMPERATURE PROPERTIES

| Test Temperature<br>Stat 17 Result | 20°C<br>Average | <br>B-Basis* | 60°C<br>Average | <br>B-Basis* | 135°C<br>Average | <br>B-Basis* |
|---|---|---|---|---|---|---|
| **Ring Tensile** Strength (MPa) | - | - | 4508.4<br>(2.2) | 4232.7 | 4242.3<br>(1.4) | 4051.3 |
| Modulus (GPa) | - | - | 224.1 | - | 224.1 | - |
| **SBS Strength (MPa)** | 57.4<br>(4.7) | 51.0 | 56.7<br>(4.3) | 49.7 | 50.9<br>(4.4) | 44.7 |
| **Transverse Flex. Strength (MPa)** | 75.2<br>(5.3) | 62.9 | 69.4<br>(5.1) | 60.4 | 65.5<br>(6.0) | 55.2 |

* B-Basis value is from two-parameter Weibull calculation

( ) number in parenthesis is percent coefficient of variation

# SUMMARY

Process trials were conducted to determine the effects of the cure cycle and environment on cyanate ester resin and composite properties

- YLA RS-14A resin has a broad process envelope provided that the cure  is conducted in an inert atmosphere
- Exposure to air at elevated temperatures produces a black reaction layer that reduces resin tensile strength and elongation
- Exposure to moisture prior to cure reduces the resin’s glass transition temperature

# SUMMARY (cont'd)

High fiber fraction (78-80 vol.%) T1000G/RS-14A composite cylinders were wet-filament wound and cured in an inert ($N_2$) atmosphere

- Excellent ring tensile strengths
  - Highest average cylinder strength: 4641 MPa (673 ksi)
  - Highest individual ring strengths: 4826 MPa (700 ksi)
- Good transverse properties for such high fiber fraction composites
- Excellent strength retention at elevated temperatures

# APPLICATIONS

Potential applications for these materials include flywheel energy storage systems for space and satellite structures