CHARACTERIZATION AND PROCESS DEVELOPMENT OF CYANATE ESTER RESIN COMPOSITES

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ABSTRACT

Cyanate ester resins offer advantages as composite matrices because of their high thermal stability, low outgassing, low water absorption, and radiation resistance. This paper describes the results of a processing study to develop a high-strength hoop-wound composite by the wet-filament winding method using Toray T1000G carbon fiber and YLA RS-14A cyanate ester resin as the constituent materials. The study shows that the cyanate ester resin has a broad process envelope but that an inert-atmosphere cure is essential for obtaining optimum resin and composite properties. Minimizing moisture exposure prior to and during cure is also crucial as it affects the glass transition temperature of the resin and composite. Composite cylinders wound and cured with these methods yielded excellent ring tensile strengths both at room and elevated temperature. A summary of the measured mechanical and thermal property data for these composites is presented. Potential applications for these materials include flywheel energy storage systems for space and satellite structures.

KEY WORDS: Advanced Composites, Cyanate Ester Resin, Filament Winding

1. INTRODUCTION

The Oak Ridge National Laboratory (ORNL) is involved in the development of affordable composite structures for military, aerospace, and transportation applications. As part of this continuing activity, ORNL evaluates new materials and combinations of materials for use in such applications as pressure vessels, flywheel energy storage systems, and aerospace. The determination of the thermomechanical properties of the composite is a key factor in the successful design of composite hardware for high performance applications.

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Cyanate ester resins offer advantages as composite matrices because of their high thermal stability, low outgassing, low water absorption, and radiation resistance. For these reasons, cyanate ester resins are finding increasing acceptance in the aerospace industries. Depending on their physical properties, cyanate ester resins also have a good potential for composite applications fabricated by the wet-filament winding method.

The work presented here documents the results of a processing study to develop a high-strength hoop-wound composite by the wet-filament winding method using Toray T1000G carbon fiber and YLA RS-14A cyanate ester resin as the constituent materials. In previous work conducted and reported by ORNL [1-2], material characterization and process trials suggested that the properties of the cyanate ester resin were sensitive to factors that included the process environment and cure profile. In this study, process trials, tests, and analyses were conducted in order to gain insight into factors that can affect final properties of the cured cyanate ester resin and its composites. A description of these investigations and the results are presented.

2. RESIN CHARACTERIZATION

The objective of this study was to investigate the cyanate ester resin's properties as a function of cure cycle and the processing environment. Specifically, the process variables studied included (1) the time-temperature profile (cure cycle) used to convert the prepolymer resin to the polycyanurate via cyclotrimerization; (2) resin exposure to air during cure; (3) thermal cycling during the cyclotrimerization or cure process; and (4) resin exposure to humidity prior to cure.

The resin investigations were conducted with YLA RS-14A or RS-14 cyanate ester resin. RS-14 and RS-14A resin are identical formulations with the exception that the RS-14 resin contains minute quantities of a zirconate coupling agent. The RS-14 product was discontinued by YLA during the course of this study and replaced by the RS-14A resin formulation.

The cure process variables studied were: (1) a 138°C (~280°F) versus a 193°C (~380°F) precure step prior to postcure; (2) a cure cycle with no precure step that ramps directly to the postcure temperature; and (3) a 250°C (~480°F) versus a 265°C (~510°F) postcure temperature. The dwell times at process temperature for these studies were maintained at 3 h for the precure segment and 4 h for the postcure segment of the cure cycle.

The 138°C precure temperature was investigated because previous studies [2] indicated that this is the minimum temperature required to effectively gel the RS-14 cyanate ester resin. The 193°C temperature has also been used successfully at ORNL to precure composite cylinders and was initially recommended by YLA. Eliminating the precure step is of potential benefit for a production scenario because it represents a significant time saving to the cure process.

Similarly, the 250°C postcure temperature was selected for study based on YLA's recommendations and because preliminary DSC studies suggested that RS-14 resin postcured at this temperature would achieve the same T_g as resin postcured at higher temperatures. Previous ORNL composite cylinders have been postcured at 265°C in an effort to maximize the resin and composite T_g, and so this process temperature was also investigated.

2.1 DSC Analyses Differential Scanning Calorimeter (DSC) analyses were conducted with uncured RS-14 and RS-14A resin to investigate the effects of ramp rate, precure temperature, and postcure temperature on the resin cure profile and ultimate T_g. Table 1 summarizes the results for 10 cure cycles. Ramp rates to the precure temperature were evaluated at 1° and 4°C/min; ramp rate to the postcure temperature was evaluated at 1°, 2°, and 4°C/min. After postcure all of the samples were cooled to 25°C and then ramped at 5°C/min to 300°C to determine the resin T_g.

Table 1. DSC data for cyanate ester resin.

Resin	135°C		190°C		250°C		265°C		T_g °C	Enthalpy J/g
	Ramp °C/min	Hold h	Ramp °C/min	Hold h	Ramp °C/min	Hold h	Ramp °C/min	Hold h		
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

The DSC analyses showed that the T_g obtained with all cure cycles was essentially the same and in the range of 253° to 256°C for the RS-14 resin samples. The data indicate that the precure temperature (or lack of a precure step) as well as the resin heat up rate have no effect on the RS-14 resin's ultimate T_g.

There was also no difference in the T_g for resin samples postcured at 250° and 265°C. It is speculated that the long (4 h) soak at the 250°C postcure temperature is the factor that enabled the cyclotrimerization reaction to proceed to the same degree of conversion as the samples postcured at 265°C.

The T_g of the RS-14A resin is significantly higher than that of the RS-14 resin and is 270°C. It is not known whether this difference is due to the normal batch-to-batch variability for these resins or if it is because the RS-14 came from an older lot of resin.

Based on literature values [3], enthalpies of –100 to –110 kJ/cyanate equivalence are typical for cyanate ester resins. YLA calculates the cyanate equivalent weight for the RS-14 and RS-14A resin to be on the order of 178 g/equivalence, which suggests that the measured enthalpy should be between –561 to –618 J/g. These calculated enthalpy values are in the proximity of the enthalpy data summarized in Table 1.

2.2 Cured Resin Properties Process trials were conducted to determine the effects of the cure cycle and environment on the cyanate ester resin's physical, mechanical (tensile), and thermal properties. The RS-14 and RS-14A resins were poured into steel molds and cured to the specified conditions to produce nominal 3.18 mm thick resin panels for characterization.

Thermal cycling trials were conducted as part of this study to determine the effects of multiple precure and postcure cycles on the cyanate ester resin's final properties. This information is pertinent to the fabrication of "thick" composite cylinders that may be wound and cured in increments, and is to determine the effects of multiple cure cycles on neat resin properties. Ramp rates to the precure and postcure temperatures were maintained at nominally 1° to 2°C/min. The times at process temperature were 3 h for the precure segment and 4 h for the postcure segment of the cure cycle. These trials were conducted in both air and inert (nitrogen) atmosphere to determine the effects of the processing environment on resin properties.

All curing and thermal cycling was accomplished in an autoclave. To achieve an inert atmosphere, the autoclave chamber was purged for ~1 h at room temperature with 2 to 3 psi dry nitrogen. The autoclave vent was cracked slightly during purging so that the nitrogen would eventually displace the air in the autoclave chamber. After purging, the cure cycle was initiated. Panels designated for cure and thermal cycling in air were processed similarly with the exception that the autoclave was not purged with nitrogen during the process cycle(s).

Panels designated for multiple precure cycles were precured once in the mold to a partially cured condition. They were then removed from the mold and laid flat on a metal plate before being subjected to the additional precure cycles. At the end of the last precure cycle, the panels were ramped to the postcure temperature to fully cure the resin. Panels designated for multiple postcure cycles were precured only once during the initial cure in the mold. The panels were then removed from the mold and laid flat on a metal plate. All subsequent thermal cycling of the panels was performed from room temperature directly to the postcure temperature.

The cured resin panels were evaluated for tensile properties (ASTM D638) and density (ASTM D792). The glass transition temperature of the panels was measured by Dynamic Mechanical Analysis (DMA). The T_g data presented are calculated by extrapolating the straight-line portions before and after the "knee" in the storage modulus (G') versus temperature curve and interpreting T_g as the point on the temperature axis where the two lines intersect.

The measured resin properties are presented in Table 2. The data show that for resin panels receiving a single process cycle (non-thermally cycled) in nitrogen, there is no significant difference in mechanical, physical, and thermal properties. The average tensile strength for the RS-14 and RS-14A resin system is on the order of 82 to 90 MPa. The ultimate elongation ranges from 4.1 to 5.5% and the modulus is 2.6 to 3.0 GPa. The nominal resin density for all of the panels is on the order of 1.20 g/cm^3.

The glass transition temperature of the RS-14 resin panels cured in nitrogen ranges from 242° to 255°C. The RS-14A resin panel glass transition temperatures are higher and on the order of 262° to 263°C. The data also show that there is no significant difference in T_g for panels that were postcured at 250° and 265°C. It is believed that the long (4 h) soak at

Table 2. Effect of cure cycle and environment on cyanate ester resin properties.

Sample Processing[1,2]	Resin	Density g/cm^3	Tensile Properties Strength MPa	Modulus GPa	Elongation %	DMA T_g ºC
193ºC;N_2 + 265ºC;N_2	RS-14	1.200	84.5	2.8	5.1	253
193ºC;Air + 265ºC;Air	RS-14	1.205	61.4	2.9	2.6	235
4 x 193ºC;Air + 265ºC;N_2	RS-14	1.209	51.4	3.0	1.9	234
193ºC;N_2 + 4 x 265ºC;N_2	RS-14	1.210	83.5	3.1	3.4	242
193ºC;Air + 3 x 265ºC;Air	RS-14	1.208	64.1	3.0	2.5	237
193ºC;N_2 + 250ºC;N_2	RS-14	1.203	82.0	2.7	4.1	248
4 x 193ºC;N_2 + 250ºC;N_2	RS-14	1.205	83.2	2.8	4.1	243
4 x 193ºC;N_2 + 250ºC;N_2	RS-14A	1.199	85.1	2.6	4.7	263
193ºC;N_2 + 4 x 250ºC;N_2	RS-14A	1.199	83.5	2.6	4.6	263
138ºC;N_2 + 250ºC;N_2	RS-14	1.200	84.6	2.6	4.8	255
138ºC;N_2 + 250ºC;N_2	RS-14A	1.198	88.4	2.6	5.5	262
138ºC;Air + 250ºC;N_2	RS-14A	1.200	89.6	2.6	5.2	262
4 x 138ºC;Air + 250ºC;N_2	RS-14A	1.201	84.6	2.7	4.4	257
138ºC;N_2 + 4 x 250ºC;N_2	RS-14	1.209	86.1	2.9	3.9	246
138ºC;N_2 + 4 x 250ºC;N_2	RS-14A	1.205	91.5	2.7	4.9	263

Notes:

[1] Sample processing is designated as "precure temperature;precure environment + postcure temperature; postcure environment." Times at process temperature are 3 h for the precure segment and 4 h for the postcure segment.

[2] Additional precure or postcure cycles that a sample received are indicated by the "number of total cycles x" designation.

the 250°C postcure temperature is the factor that enabled cyclotrimerization to proceed to the same degree of conversion as for samples postcured at 265°C. These results are consistent with the DSC data presented in the preceding section.

The most striking result of the thermal cycling trials is the degradation of tensile properties for the RS-14 cyanate ester resin panels exposed to air at elevated temperatures. Panels postcured in air had significantly lower tensile strengths and ultimate elongations (61 to 64 MPa and 2.5 to 2.6%, respectively) than their counterparts that were postcured in nitrogen. The outer surface of these panels turned a dark brownish-black color and it is believed that this layer acted as a series of flaws to promote premature failure in the tensile specimens. Light sanding of the surface removed the dark layer, revealing the normal light tan color of the RS-14 resin beneath. This surface layer was not produced in resin panels cycled to the postcure temperature in nitrogen. This suggests that a reaction occurs between the cyanate ester resin and ambient oxygen and/or humidity at elevated temperature.

Similarly, cycling partially cured RS-14 resin to the 193°C precure temperature in air yielded a significantly lower tensile strength (51 MPa) and elongation (1.9%) in the cured panel. This panel, too, exhibited a slight darkening of the surface, which is attributed to reaction of the resin with the ambient air and/or humidity at the precure temperature. The T_g is roughly 10° to 20°C lower than those of the other panels. This degradation is apparently irreversible and still evident after the sample is postcured in a nitrogen environment.

The tensile strength and elongation of the RS-14A panel cycled to the 138°C precure temperature in air prior to postcure were not substantially different than those of the non-cycled panels or the panels processed in nitrogen. The T_g (257°C) was only slightly reduced from those of the RS-14A panels cycled in an inert atmosphere and no discoloration was visible at the panel's surface. The surface resin reaction either does not occur at this low a temperature or occurs at too slow a rate to be significant for these exposure times.

The remainder of the data shows no significant change in resin properties with multiple precure and postcure cycles for resin panels that are maintained in a nitrogen environment. Multiple cycles to the 265°C postcure temperature in nitrogen tended to produce a significant darkening or discoloration of the RS-14 resin with each cycle that was visible through the entire panel thickness. This color change was not as pronounced as for the panels cycled to 250°C. Additional postcure cycles to either 250° or 265°C did not appreciably change the resin's T_g.

2.3 Cyanate Ester Resin Properties with Humidity Exposure The objective of this study was to characterize the impact of humidity (moisture) exposure during processing on the cured cyanate ester resin properties. These data make it possible to establish "thresholds" or limits at which the cyanate ester resin properties are compromised by moisture exposure. Emphasis was placed on characterizing the resin's moisture tolerance at 80°C because this is a key process temperature for wet-winding with RS-14A resin.

The humidity exposures were conducted in a Tenney Benchmaster Environmental Chamber. Nominal 450 g resin samples were poured into a 150 x 75 glass crystallizing dish, which was placed inside the chamber. A stirring attachment was positioned with the blades beneath the resin's surface near the center of the dish. The chamber was sealed and brought to the specified temperature and humidity set points. The stirrer motor was turned on and the resin was stirred continuously for the test duration to maximize the resin surface area exposed to the humidity. After the specified time had elapsed, the stirrer motor was turned off and the resin was transferred to a sealed container and stored in a refrigerator until further testing could take place.

A portion of each conditioned resin sample was evaluated for moisture content by the Karl-Fischer titration technique. Other samples of the conditioned resin were heated in a DSC from 25° to 265°C at 2°C/min and held at the upper temperature for 4 h to cure the resin. These samples were then cooled and rescanned to obtain the resin T_g. The remainder of the conditioned resin sample was poured in a mold and cured for 3 h at 138°C and 4 h at 250°C in a nitrogen environment. The resin panel properties were evaluated for T_g (by DMA) and for tensile properties.

Table 3 is a summary of the cyanate ester resin properties as a function of humidity exposure. The Karl-Fischer data show that the water content of the as received RS-14 and RS-14A resin is very low and on the order of 0.01 to 0.02%. The conditioned samples show that the water content increases significantly to above 0.1% at 40% relative humidity (RH) with as little as 2 h exposure.

The greatest impact to resin properties from exposure to moisture, as determined by DSC and DMA, is the reduction in resin T_g. A slight T_g reduction is evident after 8 h exposures at 30% RH. The largest reductions occur after exposures of greater than 40% RH.

The degradation of thermal properties is attributed to the reaction of the cyanate function with water leading to the production of a carbamate [4-5]. Above 190°C, the carbamate function decomposes, giving rise to an amine and evolving CO_2. The resulting amine can react with another cyanate group leading to a linear junction [5].

The significance of carbamate formation to cyanate ester resin and composite properties is two-fold. The evolution of CO_2 gas at elevated temperatures can lead to bubbles and voids in resin and composite samples. Indeed, some of the resin panels conditioned with 60 and 80% RH contained so many large bubbles that they could not be tested for tensile properties. The second consequence is that the amine resulting from carbamate decomposition can interrupt the triazine ring formation process by reacting with available cyanate groups. The resulting linear species may have less desirable properties (such as a lower T_g) than the triazine ring structure, impacting the material's ultimate performance.

The data in Table 3 do show that the tensile properties of RS-14 and RS-14A resin are remarkably insensitive to moisture exposure. Even panels that developed some bubbles and voids during cure and/or cracked in the mold (exposures of 60% RH and greater) had excellent tensile properties in the sections remaining that were large enough to test.

Table 3. Effects of humidity exposure (80ºC) on cyanate ester resin properties.

Resin	Exposure		Karl-Fischer	DSC[1]	Tensile			DMA[2]
	RH	Time	Water	T_g	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

Notes:

[1] Conditioned resin cured in DSC. 2°C/min ramp to 265°C and hold for 4 h. Return to room temperature and rescan at 5°C/min for T_g.

[2] Conditioned resin poured in mold and cured 3 h at 138ºC and 4 h at 250ºC in inert (nitrogen) environment. Cured panels tested for tensile properties and T_g (DMA).

3. COMPOSITE PROCESS TRIALS

Composite process trials were conducted to investigate the effects of the cure cycle and environment on composite mechanical properties. All-hoop composite cylinders (nominally 610 mm diameter x 3.18 mm thick) were wet-filament wound on a steel mandrel with a single lot of Toray T1000G carbon fiber and RS-14 or RS-14A cyanate ester resin. The average fiber strength for the lot of T1000G carbon fiber used for these studies was 6,577 MPa (954 ksi), as determined by ORNL strand tensile tests [2].

The major process variables studied parallel those conducted with the neat resin. They included (1) a 138°C versus a 193°C precure step prior to postcure; and (2) a cure cycle with no precure step that ramps directly to the postcure temperature. All composite cylinders were postcured at either 260° or 265°C. The dwell times at process temperature were maintained at 3 h for the precure segment and 4 h for the postcure segment of the cure cycle. Ramp rates to temperature were held nominally 0.5° to 1°C/min.

The process environments investigated were ambient air and inert (nitrogen) atmosphere during the cure cycle. Cylinders processed in air were cured in a standard convection oven. For inert atmosphere cures, the composite and mandrel were first sealed within a metal enclosure (canopy) before being placed in the oven. This was then purged with nitrogen gas to displace the air within prior to initiating the cure cycle. Monitoring indicated that the oxygen levels within the canopy were maintained at nominally 2% or less with this procedure.

Selected cylinders were thermally cycled on the mandrel at either the precure or postcure temperature to determine the effects on ultimate composite properties. This information is pertinent to the fabrication of “thick” cylinders that may be wound and cured in increments (“stages”). Processing options for thick cylinders can include fully curing each stage to the postcure temperature prior to winding the next increment or, instead, precuring each stage prior to winding the next increment and postcuring the entire cylinder wall thickness at the end of the fabrication. In either case, the inner composite layers receive multiple thermal cycles, the effect of which on composite properties requires verification.

Composite cylinders receiving multiple precure cycles were ramped from ambient temperature to the precure temperature for the requisite number of times. After the last precure cycle, the composite was ramped to the postcure temperature to complete curing. Cylinders receiving multiple postcure cycles were given an initial precure/postcure treatment and then ramped on the mandrel from ambient to the postcure temperature for the specified number of cycles.

The composite cylinders were cut into specimens and tested for ring (hoop) tensile strength and modulus, interlaminar (short beam) shear strength, and transverse flexure strength. Each data set for each of the process trials and test methods was comprised of a minimum of 8 to 10 specimens. All testing was conducted at room temperature.

The ring tensile properties were obtained using a “Split-D” tensile test based on the ASTM D2290 standard test method, but for a larger (610 mm) diameter ring. The specimens were loaded to failure and the break loads in conjunction with the cross-sectional area of the ring were used to calculate the apparent ring tensile strength for the composite. An extensometer was used to measure deflection at the opening of the Ds.

The measured load and deflection data were used to calculate the composite ring (fiber direction) modulus in the initial 1000 to 6000 microstrain range.

The interlaminar shear test is based on ASTM D2344 with the fiber direction being parallel to the beam axis. Testing was accomplished with a nominal 4:1 span-to-depth ratio. The transverse flexure test is based on ASTM D790 and uses a beam specimen loaded in 4-point bending in the rz-plane. The axis of the beam (z-axis) is parallel to the axis of the composite cylinder. Testing was performed with the concave surface of the cylinder's radius of curvature on the compression side of the beam (or the OD surface of the cylinder in tension).

Composition data was calculated from the measured density of the composite (ASTM D792) and the weight percent fiber and resin contents (determined from nitric acid digestion of the composite). The RS-14 and RS-14A resin densities used in the calculation are an average of the data in Table 2, and the T1000G fiber density was provided by Toray.

The composite cylinder properties are presented in Table 4. The data show that the cylinders were wound reproducibly and have nominally the same compositions. The composite densities are on the order of 1.66 g/cm^3 and the fiber contents range from 78.3 to 79.6 vol.%. The void levels are extremely low and less than 0.5 vol.%. There is good agreement between the ring tensile modulus values for all of the cylinders, which range between 223 to 230 GPa. This is as expected because the ring tensile modulus is dominated by the carbon fiber modulus and the cylinders have virtually the same fiber contents.

Visual examination of the cylinders processed in air showed that the resin at the OD turned a dark black color while the OD resin of cylinders cured in nitrogen retained a lighter amber-brown tint. The ring tensile strength of the RS-14 cylinder cycled three times in air to the postcure temperature (3911 MPa) was significantly lower than the strength of the cylinder postcured a single time in air as well as the cylinders that were cured or thermally cycled in nitrogen. The ring tensile strength reduction for the air-processed cylinder is attributed to degradation of the exposed resin's tensile strength and elongation as a result of reaction with ambient oxygen and/or moisture at elevated temperature. It is similar to the effects encountered during the thermal cycling trials conducted with neat resin panels and that were described in the preceding section.

Excluding the air-processed cylinders, the average ring tensile strengths range between 4270 to 4641 MPa. The 4641 MPa (673 ksi) average tensile strength is the highest tensile strength measured by ORNL to-date for a set of ten hoop-wound composite rings. (It also comes from a cylinder that received *four* precure cycles on the mandrel prior to postcure.) This set had three rings that broke with individual ring tensile strengths that measured over 4826 MPa (700 ksi). These measured ring tensile strengths are considered conservative and may actually be lower than the true material strength of the cylinder because of the additional bending stresses that the split-D fixtures impose on the ring during loading.

The fiber strength translation is obtained by dividing the measured ring tensile strength by the product of the fiber strength and the fiber fraction in the composite. It is therefore a measure of the efficiency of the carbon fiber in transferring its tensile strength to the composite. Based on this method and using the 6577 MPa fiber average lot tensile strength, the highest fiber strength translations achieved were ~89% for all-hoop T1000G/RS-14A composite cylinders.

Table 4. Composite process trial results.

Process Environment	**Air**		**Inert (N_2)**								
Precure[1,2]	**193ºC**	**193ºC**	**138ºC**	**4 x 138ºC**	**138ºC**	**4 x 138ºC**	**193ºC**	**4 x 193ºC**	**193ºC**	**None**	**None**
Postcure[1,2]	**265ºC**	**3 x 265ºC**	**260ºC**	**260ºC**	**260ºC**	**260ºC**	**260ºC**	**260ºC**	**4 x 260ºC**	**260ºC**	**4 x 260ºC**
Resin	**RS-14**	**RS-14**	**RS-14**	**RS-14**	**RS-14A**	**RS-14A**	**RS-14A**	**RS-14A**	**RS-14A**	**RS-14A**	**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)	1.661	1.667	1.658	1.657	1.661	1.665	1.665	1.666	1.665	1.666	1.666
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.

The interlaminar shear strengths of all of the cylinders range from 56 to 69 MPa. The lowest shear strength (56 MPa) is from a RS-14 cylinder that was cycled four times to the 138°C precure temperature prior to postcure. The low(er) shear strength may be the result of damage incurred to the composite by thermal cycling undercured composite on the mandrel. This result is inconclusive, however, because this cylinder also had one of the highest recorded tensile strengths (4561 MPa) in the study. A RS-14A cylinder that was also cycled four times to the 138°C precure temperature prior to postcure had a significantly higher shear strength (65 MPa), which is equivalent to the shear strengths of the other cylinders.

The transverse flexure strengths of the cylinders processed in nitrogen are between 69 to 82 MPa. Ironically, the cylinder receiving multiple postcure cycles in air had the highest transverse flexure strength (97 MPa). It is speculated that the blackened outer resin layer (which is loaded in tension in this test configuration) has a somewhat higher modulus than the nitrogen-processed cyanate ester resin. This blackened reacted resin layer may have had an artificially high impact on the strength by biasing the measured break loads upward.

The combination of composite data show there is a broad process envelope for curing composites with RS-14 and RS-14A resin. Comparable ring tensile strengths and moduli, interlaminar shear strengths and transverse flexure strengths were achieved for all process cycles conducted in an inert atmosphere. Similarly, additional precure and postcure cycles conducted in nitrogen did not affect the ultimate composite properties. The shear and transverse flexure strengths are considered excellent for such high (~78 to 80 vol.%) fiber content composites.

4. ELEVATED TEMPERATURE PROPERTIES OF T1000G/RS-14A COMPOSITE

The elevated temperature and B-basis mechanical properties were determined for a T1000G/RS-14A hoop-wound composite cylinder. The cylinder was wet-filament wound with RS-14A resin and with the same Toray T1000G fiber lot and procedures used to fabricate the process trial cylinders. The composite was cured 3 h at 193°C and 4 h at 260°C in an inert (nitrogen) atmosphere.

The cured cylinder was cut into specimens and tested for ring tensile strength and modulus, interlaminar shear strength, and transverse flexure strength using the procedures and test methods described in Section 3. Testing was conducted at 60° and 135°C. Interlaminar and transverse flexure testing was also done at ambient temperature (20°C) for comparative purposes. A minimum of 10 specimens were tested for each condition with the exception of the ring tensile modulus measurement, which is based on the test data from 3 to 4 rings.

The data are summarized in Table 5. Averages and B-basis values were calculated using the Statistical Analysis Program for MIL-HDBK-17 (STAT 17, Revision 3.1, 1992). The B-basis values are from the two-parameter Weibull calculation.

Table 5. Elevated temperature properties of T1000G/RS-14A composite cylinder.

Test Temperature Stat17 Result	20°C Average	 B-Basis*	60°C Average	 B-Basis*	135°C Average	 B-Basis*
Ring Tensile Strength (MPa)	-	-	4508.4 (2.2)	4232.7	4242.3 (1.4)	4051.3
Modulus (GPa)	-	-	224.1	-	224.1	-
SBS Strength (MPa)	57.4 (4.7)	51.0	56.7 (4.3)	49.7	50.9 (4.4)	44.7
Transverse Flex. Strength (MPa)	75.2 (5.3)	62.9	69.4 (5.1)	60.4	65.5 (6.0)	55.2
Composition						
Density (g/cm^3)	1.657					
Volume % Fiber	78.6					
Volume % Resin	20.9					
Volume % Voids	0.5					

Number of specimens is 10 minimum for ring tensile strength, interlaminar (SBS) shear strength and transverse flexure strength. Number of specimens is 3-4 for ring tensile modulus.

*B-basis value is from two-parameter Weibull calculation.
( ) number in parentheses is percent coefficient of variation.

Overall, the ring tensile strength data scatter is extremely low for this cylinder. The average ring tensile strength at 60°C is 4508 MPa (654 ksi) with only a 2.2% coefficient of variation, and is comparable to the room temperature ring tensile strengths measured for the process trial cylinders. The B-basis value for this set is 4233 MPa. At 135°C, the average ring tensile strength decreases by 6% to 4242 MPa with only a 1.4% coefficient of variation and the B-basis value is 4051 MPa. As expected, the ring tensile modulus does not change with temperature because it is a fiber dominated property.

At 60°C, the short beam shear or interlaminar shear strength is statistically unchanged from its room temperature value, and is reduced by 11% at 135^{o}C. At 60° and 135°C, the transverse flexure strength reductions are 8% and 13%, respectively, from ambient temperature.

5. SUMMARY

Process trials were conducted to determine the effects of the cure cycle and environment on the physical, mechanical, and thermal properties of cyanate ester resin and composite. The study shows that the YLA RS-14A cyanate ester resin has a broad process envelope but that an inert-atmosphere cure is essential for obtaining optimum resin and composite properties. Exposure of the cyanate ester resin to air at elevated temperatures produces a black reaction layer at the surface that reduces its tensile strength and elongation. Minimizing moisture exposure prior to and during cure is also crucial as it can significantly reduce the glass transition temperature of the cured resin.

High fiber fraction (78-80 vol.%) composite cylinders were wet-filament wound with Toray T1000G carbon fiber and YLA RS-14A cyanate ester resin and cured in an inert (nitrogen) atmosphere. These cylinders yielded excellent ring tensile strengths both at room and elevated temperature. The highest average ring tensile strength was 4641 MPa

(673 ksi) and with individual ring tensile strengths that measured over 4826 MPa (700 ksi). The measured transverse properties were also exceptional for such high fiber fraction composites.

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7. REFERENCES

1. B. J. Frame and J. M. Starbuck, "Preliminary Investigation of Polycyanate Resins for Wet-Filament Wound High-Strength Composites," 41st International SAMPE Symposium, (1996).

2. B. J. Frame, "Process Study of Polycyanate Resin for Wet-Filament Wound High-Strength Composites," ORNL/TM-13387, Oak Ridge, Tennessee, (1997).

3. A. W. Snow, "The Synthesis, Manufacture and Characterization of Cyanate Ester Monomers," in I. Hamerton, ed., Chemistry and Technology of Cyanate Ester Resins, Chapman, & Hall, New York, 1994, pp. 26-28.

4. D. A. Shimp and W. J. Ising, "Moisture Effects and Their Control in the Curing of Polycyanate Resins," ASC National Meeting PMSE Division, San Francisco, (1992).

5. J. P. Pascault, J. Galy and F. Mechin, "Additives and Modifiers," in I. Hamerton, ed., Chemistry and Technology of Cyanate Ester Resins, Chapman, & Hall, New York, 1994, pp. 116-117.

8. BIOGRAPHY

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