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Evaluation of Large Tow-Size Carbon Fiber for Reducing the Cost of CNG Storage Tanks

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ABSTRACT

The performance of large tow-size carbon fiber was evaluated to determine any design impacts that would prohibit their introduction into the fabrication process of compressed natural gas (CNG) storage tanks. The evaluation was based on manufacturing process trials and mechanical property tests. The tests consisted of impregnated strand, composite ring, and composite sub-scale cylinder tests for static strength, fatigue, and stress rupture. Modifications required in the wet-filament winding process are documented as well as the development of test methodologies required for testing large tow-size impregnated strands.

INTRODUCTION

Compressed natural gas (CNG) is an alternative vehicle fuel that is stored under high pressure on the vehicle. The storage tanks are classified into four types depending on the type of materials used in the design. Type 1 tanks are all metal, Type 2 tanks are metal with a composite over-wrapped in the cylindrical part of the tank, Type 3 tanks are metal-lined, fully over-wrapped with composite, and Type 4 tanks are plastic-lined, fully over-wrapped with composite. For weight critical vehicle applications the Type 3 and Type 4 tanks are more commonly in use today. The Type 4 tank is a very lightweight design where the liner material is used for preventing gas permeation and the composite over-wrap is designed to carry the entire pressure loading. The reinforcement used in over-wrapping a tank is typically a carbon fiber, a glass fiber, or a hybridization of these two fibers with an epoxy resin as the binding material.

The use of CNG as an alternative fuel in automotive applications is not widespread primarily because of the high cost and limited durability of the Type 4 composite storage tanks. Carbon fiber composite cylinders are desirable in weight critical passenger vehicles because of the low density of carbon fiber. The high strength of carbon fiber further reduces the weight because thinner wall designs are possible that still withstand the internal pressure loads. However, carbon fiber composites are relatively expensive because of the raw material cost of the carbon fiber, which accounts for approximately 40% of the total tank cost (1). By introducing large tow-size carbon fiber in the tank design there is the potential for a tremendous cost savings. The cost of large tow-size carbon fiber is approximately one-half the cost of conventional tow-size carbon fiber. However, not all of this savings is realized in the final overall tank cost because of the lower fiber strength and lower strength translation that has been demonstrated in large tow-size carbon fiber composite structures.

CNG storage tanks are manufactured to specific design and safety standards. Tanks in use today are either designed to DOT-RSPA, U.S. DOT NHTSA FMVSS No. 304, or ANSI/AGA NGV2-1992 standards. Rigorous design qualification tests are required and include pressure cycling, environmental exposure, hydrostatic burst, bonfire test, drop test, penetration test, permeation test, and accelerated stress rupture (2). CNG tanks are designed for a nominal service pressure of 24,820 kPa (3600 psi) with a safety factor of 2.25 for carbon fiber and 3.5 for glass fiber reinforcements. The tanks have a design life of 20 years with 750 filling cycles/year (15,000 cycles). To evaluate the cost reduction that can be achieved by utilizing large tow-size carbon fiber for the over-wrap material and still meet these design requirements, manufacturing process trials and durability testing were conducted.

MANUFACTURING PROCESS TRIALS

Composite CNG tanks are typically fabricated using the wet-filament winding process. This is a process where the fiber tow is passed through a resin bath to impregnate the tow and then wrapped around a mandrel prior to curing at elevated temperature in an oven. Process parameters include mandrel temperature, fiber tension, and bandwidth. The bandwidth is the amount of tow advance per one revolution of the mandrel. These parameters affect the composition of the cured composite material in terms of the fiber, resin, and void content. The type of compaction used can also affect the composition data. The Akzo Fortafil 3C large tow-size carbon fiber was selected for evaluation based on the vendor reported impregnated strand tensile strength and the fiber's handling characteristics. This fiber has a nominal filament count of 50,000 (commonly referred to as a 50K tow) compared to a standard tow-size carbon fiber having 12,000 filaments (12K tow).

COMPOSITION DATA

Process trials were completed to quantify the effects of fiber tension, bandwidth, and type of compaction on the composite material's composition. To accommodate the larger cross-sectional area of the 50K tow-size carbon fiber, wider pulleys were utilized throughout the process. Nominal 20-cm diameter cylinders were fabricated using an epoxy resin, Union Carbide ERL-2258/mPDA. The temperatures for the resin pot and mandrel were maintained at 52°C. The cylinders were cured at 175°C and then sectioned for composition. The fiber, resin, and void volume fractions were calculated based on the measured composite density and the sample fiber weight determined by the acid digestion method.

The parameters for each of the eleven different process trials are shown in Table 1 and the composition data are presented in Table 2. The bandwidth varied between 1.118 and 1.123 cm and the fiber tension varied between 9.1 and 15.9 kg. The type of compaction was either double roller (DSS) or single roller (SSS) with either a 9.1 or 18.1 kg weight. The results showed the highest fiber volume fraction was achieved with the smallest bandwidth. However, the small bandwidth resulted in a washboard surface on the outer diameter of the cylinder that was a result of the tows overlapping. A bandwidth of 1.123 cm minimized the tow overlap and also produced minimal gaps between the tows. The lowest void content corresponded to the highest compaction weight and the highest fiber tension but this fabrication had the lowest fiber content. The winding tension of 9.1 kg was determined to be insufficient for proper consolidation because this process trial had the highest void content.

In general, the composition data did not indicate any conclusive trends that could be used to determine the optimum processing parameters. Based on the observations stated in the above paragraph, cylinder fabrications for machining the ring specimens were completed using the processing parameters of 12-13 kg fiber tension, 9.1-kg compaction weight, and a 1.123-cm bandwidth. It is recommended that additional process studies be completed to determine if the high fiber content (75-80%) and low void content (<1%) that are achievable with the standard tow-size carbon fiber are possible with the large tow fiber.

Table 1. Process trial conditions.

Process Number	Tension (kg)	Compaction (kg/type)	Bandwidth (cm)
1	11.3	9.1/DSS	1.079
2	11.3	9.1/DSS	1.105
3	11.3	9.1/DSS	1.118
4	9.1	9.1/DSS	1.123
5	13.6	9.1/DSS	1.123
6	13.6	9.1/SSS	1.123
7	11.3	18.1/DSS	1.118
8	11.3	18.1/DSS	1.123
9	13.6	18.1/DSS	1.123
10	15.9	18.1/DSS	1.123
11	13.6	9.1/DSS	1.123

Table 2. Composition data.

Process Number	Density (g/cc)	Fiber content (%)	Resin content (%)	Void content (%)
1	1.5920	69.30	27.79	2.91
2	1.5834	69.17	27.29	3.54
3	1.5786	68.10	28.45	3.45
4	1.5575	66.05	29.72	4.23
5	1.5780	68.98	27.13	3.89
6	1.5772	68.50	27.75	3.74
7	1.5844	67.05	30.44	2.51
8	1.5629	65.06	31.60	3.34
9	1.5728	67.05	29.50	3.44
10	1.5636	63.16	34.42	2.42
11	1.5756	66.14	31.05	2.80

DURABILITY TESTING

Performance of the Akzo 50K tow-size carbon fiber was evaluated to determine any design impacts that would prohibit their introduction into the fabrication process of CNG storage tanks. The evaluation was based on conducting a durability test matrix for static strength, fatigue, and stress rupture. The static strength data was needed to ensure that the design safety factor of 2.25 on burst pressure was met, whereas the fatigue and stress rupture data was used to estimate reliability over the life of the tank for refueling cycles and time under constant pressure loads. Size effects were addressed by testing impregnated strands, sub-scale composite rings, and sub-scale composite pressure vessels.

IMPREGNATED STRANDS

Impregnated strand tensile specimens were fabricated by running a continuous tow of fiber through an epoxy resin bath and then through an orifice to remove the excess resin. The resin-impregnated tow was then wrapped around two wooden blocks such that a straight specimen having a nominal 25-cm gage length was produced. The specimens were cured at 175°C and then cut to length.

Test Development

Relative to the standard tow-size carbon fiber, modifications were needed to the orifice size and to the tabbing method when fabricating and testing large tow-size impregnated strands. Naturally, due to the cross-sectional area of the 50K-tow carbon fiber, a larger orifice was required. The correct orifice size is needed to have a resin content that will transfer the load between filaments and a value of 50% by weight is typically used. A different tabbing method from the standard cardboard or aluminum foil was required because of the higher tensile loads needed to fail the specimens and because of the physical size of the specimens.

Tensile strengths were measured on different specimen configurations to determine the correct orifice size and best tab arrangement. The tabbing materials used in this study were foil, fiberglass, and epoxy. When foil was used, the tabs were co-cured during fabrication of the impregnated strands and rubber-faced air-pressurized grips were used in the tests. The fiberglass tabs were hand-laid using a ±45° stacking sequence and then bonded to the strands using an adhesive film. Two different epoxy systems were used, Epoxy A and Epoxy B, where Epoxy B was a higher elongation system than Epoxy A. The epoxy tabs were fabricated by potting the ends of the cured strands using glass test tubes as molds. Self-tightening mechanical grips were used with the fiberglass and epoxy tabs, where the serrated grip faces were flat and notched, respectively.

Static Strength

The results for the Akzo 50K-tow impregnated strand tensile strength are shown in Figure 1 as a function of the orifice size and tabbing method. The average strengths are plotted along with standard deviation error bars. The highest average tensile strength was obtained by using the 2.9-mm (114-mils) orifice size and the fiberglass tabs. A Weibull analysis of this data set, having a sample population equal to 18, determined a characteristic strength (scale parameter) of 3735 MPa with a shape parameter of 20.0. This shape parameter is consistent with previous strand data on 12K-tow carbon fiber. The average strength was 3634 Mpa which compares favorably to the vendor reported tensile strength of 3792 MPa that is measured by splitting the 50K tow into smaller sub-tows.

Fatigue

Tension-tension fatigue tests were conducted at different stress levels corresponding to different percentages of the characteristic strength. Based on the results from the static tensile tests, fiberglass tabs were used for the initial fatigue tests. In using this method, tab failures consistently occurred after a limited number of load cycles. The specimens simply pulled out of the tab material due to a poor bond-line produced by the irregular surface of the cured strand. To consistently produce gage section failures it was found that the Epoxy B potting compound was the most reliable method for producing tabs.

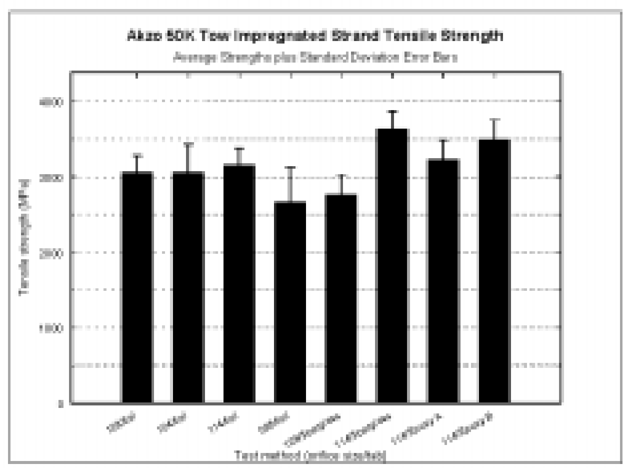

Figure 1. Impregnated strand tensile strength

The results for the impregnated strand tension-tension fatigue tests using the Epoxy B tabs are shown in Figure 2. The tests were run under ambient temperature conditions at R=0.1 and a frequency of 4 Hz. Shown in the plot are the cycles-to-failure at three different percentages (81%, 85%, and 89%) of the characteristic strength measured from the static strength tests. A short duration test program was planned so high stress levels were needed. The actual operating stress level is much less than this with a safety factor of 2.25 on the composite tank's designed burst pressure. The trends in the data appear reasonable with a decade increase in cycles-to-failure for a 4% reduction in stress level.

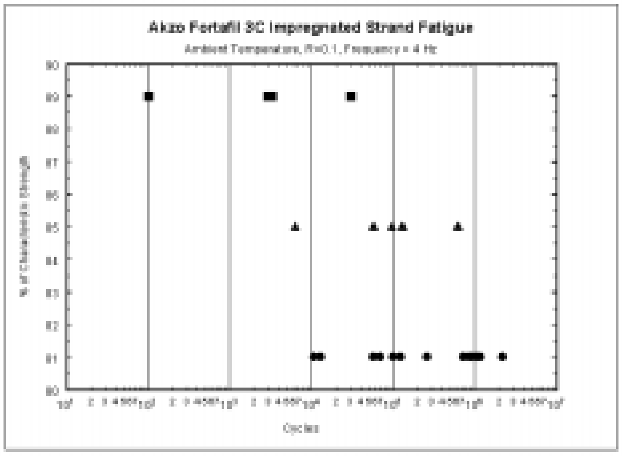

Figure 2. Impregnated strand tension-tension fatigue

<u>Stress Rupture</u>

The fiberglass tabs proved to be an acceptable method for the stress rupture tests. The results for the strand stress rupture tests at ambient temperature are shown in Figure 3. The data points for prompt failure, i.e., specimens that failed during loading, are not shown in the plot but the number of prompt failures at each of the three different stress levels are indicated. Similar to the strand fatigue testing, high percentages of the characteristic strength were applied to the specimens. One observable trend in the data is that as the applied stress level was reduced there were fewer prompt failures. Additional data points are needed at lower stress levels to better estimate the probability of failure due to stress rupture.

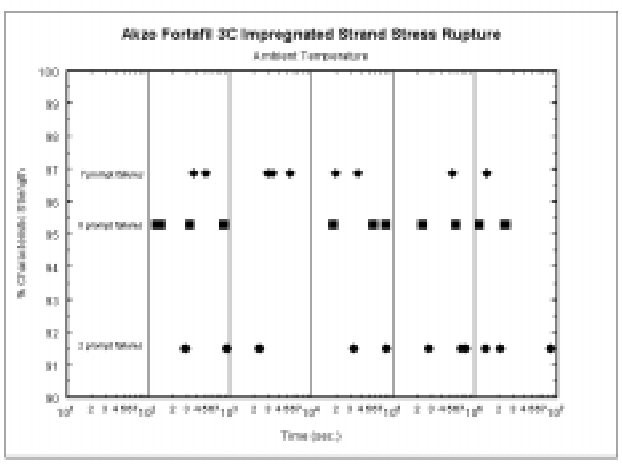

Figure 3. Impregnated strand stress rupture

COMPOSITE RINGS

<u>Test Development</u>

In the characterization of filament-wound advanced composite materials, rings are typically fabricated as test specimens for measuring the material's performance. One of these performance parameters is the in-plane tensile strength of the composite ring in the hoop direction. Composite ring hoop strengths are commonly determined by using the split-disk or U.S. Naval Ordnance Laboratory (NOL) method as described by the ASTM D2290-76 standard test method. The NOL method results in a non-uniform stress distribution and significant bending stresses can occur due to the straightening of the ring at the opening between the split-disk fixtures. Increasing the radius-to-thickness ratio of the ring can reduce these bending stresses but this usually means having to test very large diameter rings or very thin rings that are not representative test articles. Friction can also be a contributing factor to the validity of the NOL method, but placing Teflon tape on the inner diameter of the ring can reduce this effect.

Both the bending stresses and the friction become even more critical when extending this method from a static strength test to a tension-tension fatigue test. Prior experience has shown that the Teflon tape wears out during fatigue testing and the composite rings fail prematurely due to stress concentrations. Loading the ring hydraulically using a hydro-burst test fixture can eliminate the bending stresses associated with the NOL method and minimize friction. However, the design of such a fixture can result in seal drag and may have a limited test capability due to the maximum hydraulic pressure and seal design.

A new test fixture for conducting 15.2-cm diameter ring hoop tensile strength and tension-tension fatigue was designed and fabricated. The fixture was designed to test ring specimens that were 15.2 cm in diameter with a 0.635-cm axial height and having a radial thickness that would produce burst failures within a pressure capability of 55 MPa. A cross-sectional drawing of the test fixture is shown in Figure 4.

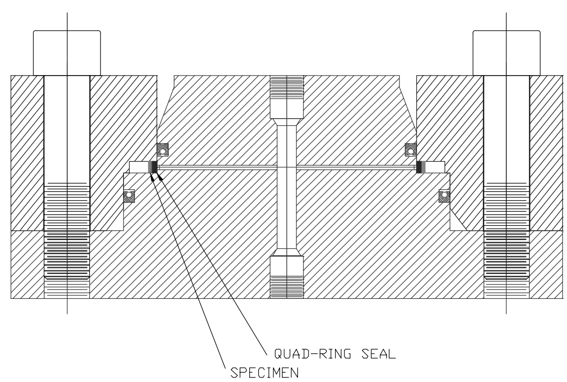

Figure 4. Schematic of hydro-burst ring test fixture

The operation of the test fixture was verified by pressurizing a steel ring that was instrumented with four bi-axial strain gages. The gages were bonded to the outer diameter of the ring at 90-degree intervals. Strain measurements were taken prior to assembly, after hand-tightening the bolts, and after torqueing the bolts to 30 ft-lbs. The results indicated that no axial pre-load was being introduced to the specimen by the test fixture. The ring was then pressurized to 34.5 MPa and the measured strains indicated a uniform pressure distribution on the inner diameter of the ring. A cyclic fatigue test was conducted by pressurizing the steel ring between 0 and 34.5 MPa at 1 Hz. The results (shown in Figure 5) are indicative of little or no seal drag.

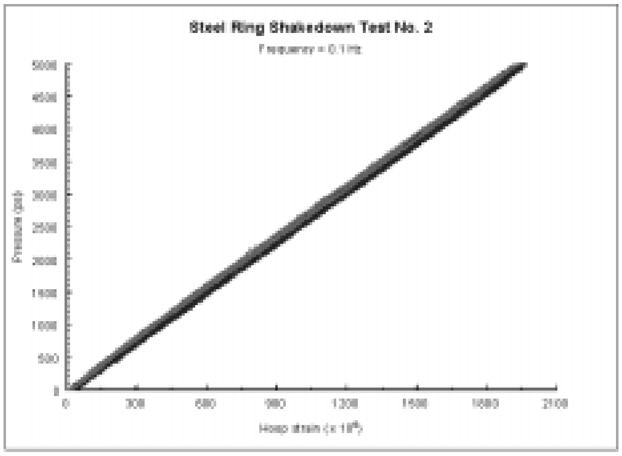

Figure 5. Hydroburst fatigue test of steel ring.

The preliminary shakedown tests on the composite rings indicated that a new seal was required to prevent excessive oil blow-by during the internal pressurization of the ring. This oil blow-by was a result of machining tolerances on the composite ring dimensions and the axial shrinkage of the ring due to Poisson's ratio effect when the ring is expanded in the hoop direction. A special acrylonitrile butadiene quad-ring was designed and fabricated by Minnesota Rubber for this purpose. Additional testing indicated some seal wear problems and the seal compound was replaced with a carboxilated nitrile.

Static Strength

Tests were conducted to measure the hoop tensile strength of unidirectional Akzo Fortfil 3C/Epoxy rings. Rings were tested using both the hydroburst test fixture and a conventional split-disk test fixture and the results compared. A sample population of 10 was used and the average hydroburst strength was 1248 MPa with a coefficient of variation of 5.76%. The measured results using the split-disk fixture corresponded to an average strength of 1206 MPa and a coefficient of variation of 6.17%. By eliminating the bending stress in the test method the measured hydroburst strength is higher than the split-d strength. However, the fiber strength translation is still much lower than what is typically measured in carbon fiber/epoxy filament wound composites. This is believed to be a result of the large tow-size and bandwidth of the Akzo fiber and testing rings that have a 0.635-cm axial height.

From Table 1, the bandwidth was shown to be equal to 1.123 cm. In machining the ring specimens, a single tow width of carbon fiber is actually being machined and this could have induced large amounts of free-edge damage. An improvement to the specimen geometry would be to test rings having a larger axial height. Despite the low fiber strength translation, the results from the static hydroburst tests were valid for determining the applied stress levels in the fatigue tests.

Fatigue

Fatigue tests using the hydroburst test fixture were conducted at three different stress levels corresponding to three different percentages of the characteristic strength. The Weibull scale parameter (characteristic strength) was calculated from the static tests to be 1282.5 MPa. The ring specimens were tested at 80.6%, 69.9%, and 64.5% of this strength value and the corresponding test pressures were 31.0 MPa, 26.9 MPa, and 24.8 MPa, respectively. The R-value was 0.1 and the test frequency was 1 Hz.

The test results for cycles to failure at each of the applied stress levels are plotted in Figure 6. A Weibull analysis of the fatigue data is shown in Figure 7, where the cumulative distribution function (CDF) is the probability of failure and eta and beta are the Weibull scale and shape parameters, respectively. For a 15,000 cycle-life the failure probabilities can be calculated for the different applied stress levels using the Weibull parameters given in Figure 7. For example, at 64.5% of the characteristic strength, the probability of failure after 15,000 cycles is 0.35. Assuming a linear relationship exists between the probability of failure and the applied stress level and a failure probability of 1 x 10^{-6} the applied stress would be 55.8% of the characteristic strength. Based on this limited set of test data and a design safety factor of 2.25 it does not appear that fatigue will be a critical failure mode.

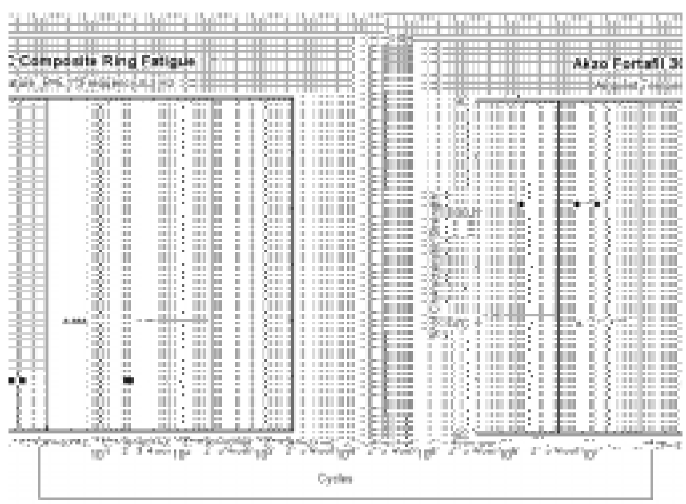

Figure 6. Fatigue results for composite rings.

SUBSCALE PRESSURE VESSELS

Sub-scale pressure vessel tests were conducted to evaluate the performance of large tow-size carbon fiber in a structural application. The test articles were 22.9-cm diameter Type 4 cylinders with a reduced wall thickness and a design failure pressure of 27.6 MPa. The cylinders were designed and fabricated by Lincoln Composites using the Grafil 34-600 carbon fiber in an epoxy matrix. The Grafil fiber is a 48,000-filament carbon fiber and has a higher tensile strength than the Akzo Fortafil 3C fiber. The measured tensile strength of the Grafil fiber using the test method documented above was 4000 MPa. This fiber also has excellent handling and wet-out characteristics. The Grafil fiber was not considered in the earlier impregnated strand and composite ring testing due to its unavailability during the time frame when the tests were being conducted.

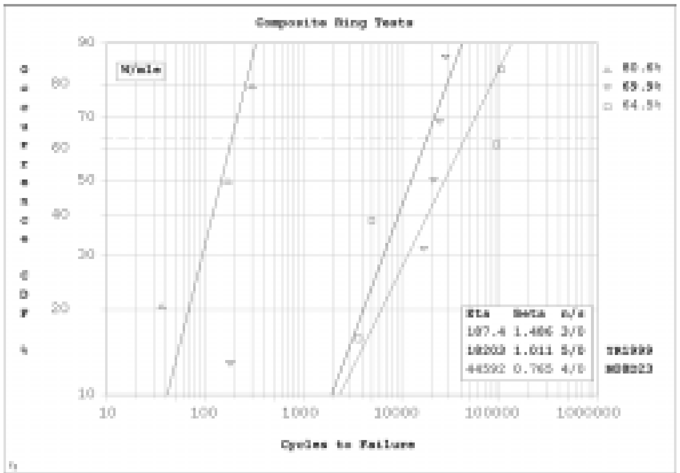

Figure 7. Weibull analysis of ring fatigue data.

Burst tests were conducted at both ambient temperature and 82°C. The cylinders were pressurized using hydraulic oil at a rate of 70-kPa/second. The elevated temperature test condition was achieved by heating the hydraulic oil to 82°C and circulating the fluid through the cylinder until thermal equilibrium was reached. The average burst pressure at ambient temperature was 25.9 MPa with a standard deviation of 1.1 MPa. At 82°C the average burst pressure was 26.5 MPa and the standard deviation was 1.0 MPa. The scatter in the data was very low and the results are in close agreement with the design burst pressure. Also, the results show that the elevated temperature test condition has an insignificant effect on the burst strength.

The results from the elevated temperature tests were used to define the pressures for stress rupture testing at 82°C. In the stress rupture tests, three cylinders were tested at each of the following pressures: 98%, 94%, and 90% of the burst pressure. Currently, the stress rupture tests are in progress and the results will be reported on in a future publication.

CONCLUSION

The cost and durability of Type 4 CNG storage tanks are major factors that have inhibited the growth of CNG as an alternative fuel in automotive applications. By introducing lower cost large tow-size carbon fiber in the tank design there is a potential for tremendous cost savings. A testing and evaluation program of the Akzo Fortafil 3C carbon fiber was conducted to determine what design impacts may result if this fiber was used in manufacturing CNG tanks.

Manufacturing process trials were completed using larger pulley widths, increased fiber tension, and larger bandwidths than conventional tow-size carbon fiber. Additional process trials are needed to optimize the process parameters to achieve lower void contents. Test development efforts resulted in a new test procedure for conducting impregnated strand tests on 50K tow-size carbon fiber. Also, a new hydroburst test fixture was designed and fabricated for conducting the composite ring strength and fatigue tests.

Impregnated strand, composite ring, and sub-scale composite pressure tests were completed to quantify the static strength performance of large tow-size carbon fiber composites. The measured strength data is critical in the design of CNG tanks to ensure the required safety factors on burst are achieved. The results from the impregnated strand and composite ring fatigue tests indicated that fatigue should not be a failure mode for the large tow-size carbon fiber under CNG operating conditions. Additional data is needed for determining the stress rupture probability of failure. To address this issue, data is currently being generated on sub-scale pressure vessels under stress rupture loading conditions.

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REFERENCES

1. Mark E. Richards, Christopher Blazek, Craig Webster, Joe Wong, and Livio Gambone, "Final Report – Compressed Natural Gas Storage Optimization for Natural Gas Vehicles", GRI-96/0364, Gas Research Institute, December 1996.

2. Norman L. Newhouse and Dale B. Tiller, "All-Composite Natural Gas Vehicle Fuel Container", Lincoln Composites, August 1997.