H. Durability of Carbon-Fiber Composites

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Objective

- To develop experimentally-based, durability-driven design guidelines to ensure the long-term (15-year) integrity of representative carbon-fiber-based composite systems that can be used to produce large structural automotive components. Durability issues being considered include the potentially degrading effects of cyclic and sustained loadings, exposure to automotive fluids, temperature extremes, and low-energy impacts from such events as tool drops and kick-ups of roadway debris on structural strength, stiffness, and dimensional stability.

Approach

- Characterize and model the durability behavior of a progression of three representative carbon-fiber composites, each with the same thermoset urethane matrix but having a different reinforcement preform: (1) continuous fiber, ±45° crossply; (2) continuous fiber, quasi-isotropic; and (3) random chopped fiber.
- Replicate on-road conditions in laboratory tests of each composite to generate durability data and models.
- Subsequently shift focus to suitable thermoplastic composites, for which durability issues are generally more significant.
- Develop and publish durability-based design criteria for each composite.

Accomplishments

- Published and distributed a report that reviews measurement and development of crystallinity and its relationship to properties of neat Poly (Phenylene Sulfide) (PPS) and its fiber-reinforced composites (ORNL/TM-2004/304).1
- Published journal article on effect of thermal cycling on carbon-fiber-reinforced PPS composites. 2
- Completed baseline testing (tension, compression, shear, and flexural properties) for all plaques.
- Completed testing to determine effect of strain rate on tensile properties.
- Completed testing to determine effect of sequential loading on stiffness.
- Completed testing to determine effect of prolonged thermal exposure (i.e., up to 1000 hours) on tensile properties.
- Completed testing to evaluate effect of preconditioning temperature on flexural and shear strength.

- Completed environmental screening tests (e.g., short-beam shear strength and weight gain) to establish which, if any, common automotive fluids may have a degrading effect on the properties of the PPS composite material.
- Completed testing to determine effect of prolonged exposure (i.e., 1000 hours) to distilled water or windshield washer fluid on tensile, compressive, and shear properties.
- Completed in-air, room-temperature and in-air elevated-temperature (i.e., 70˚, 90˚ or 120˚C), sustained-load tension tests (94 tests).
- Completed room-temperature, sustained-load tension tests on specimens preconditioned and maintained in either windshield washer fluid or distilled water during testing (43 tests).
- Completed room-temperature and elevated-temperature (120˚C), sustained-compression load testing (19 tests).
- Completed cyclic fatigue tests (88 tests) involving stress ranges from 10 to 90% ultimate tensile strength and test temperatures of room temperature, -40˚, 70˚, or 120˚C.
- Completed mean stress effects cyclic fatigue testing (52 tests).
- Completed uniaxial and biaxial flexural strength testing.
- Carbon-fiber composite data feeding directly into the planning and analysis for the Focal Project 3 carbon-fiber body-in-white.

Future Direction

- Complete durability assessment of carbon-fiber-reinforced PPS material.
- Publish durability-driven design criteria documents for representative thermoplastic composites suitable for automotive structural applications.
- Complete report outlining minimum test matrix for development of design criteria for carbon-fiber-reinforced thermoset and thermoplastic materials.

Introduction

Before composite structures will be widely used in automotive applications, their long-term durability must be assured. The Durability of Carbon-Fiber Composites Project at the Oak Ridge National Laboratory (ORNL) was established to develop the means for providing that assurance. Specifically, the project is developing and documenting experimentally-based, durability-driven design criteria and damage-tolerance assessment procedures for representative carbon-fiber composite systems to assure the long-term (15-year) integrity of composite automotive structures. Durability issues being considered include the potentially degrading effects of cyclic and sustained loads, exposures to automotive fluids, temperature extremes, and incidental impacts from such things as tool drops and kick-ups of roadway debris. Research to determine the effects that these environmental stressors and loadings have on structural strength, stiffness, and dimensional stability is being conducted. The project is carried out in close coordination with the Automotive Composites Consortium (ACC).

It is envisioned that about 15% of the Focal Project 3 (See report 4.D) carbon-fiber-composite body-in-white will utilize directed continuous-fiber reinforcement architectures, while the remainder will employ random chopped-fiber reinforcement. The approach to investigating durability has thus been to address a progression of thermoset composites, each of which has the same urethane matrix:

- reference $[\pm 45]_{3S}$ crossply composite,
- $[0/90/\pm 45]_S$ quasi-isotropic composite, and
- randomly-oriented, chopped-carbon-fiber composite.

Characterization of the first two continuous-fiber composites has been completed, and design criteria documents published. In mid-FY 2002, the focus turned to chopped-carbon-fiber composites. Characterization of the randomly-oriented, chopped-carbon-fiber composite was completed in FY 2003 and the durability-based design criteria report published. In FY 2003, investigation of carbon-fiber-reinforced thermoplastic materials for structural automotive applications was initiated. Recent activities associated with evaluation of the thermoplastic material have addressed thermoplastic material characterization, baseline property determination, strain-rate and prior-load tests, environmental effects tests, uniaxial and biaxial flexural strength evaluations, sustained-load tests (tension and compression), and cyclic fatigue tests.

Thermoplastic Material Characterization

The ACC has supplied 46 plaques, 510 mm by 610 mm by about 3-mm thick, for use in durability studies. Plaque reinforcement is symmetrical and consists of 16 plies of carbon-fiber unidirectional tape, $[0/90/\pm45]_{2S}$. PPS is the matrix material.

Processing conditions are very important because they affect the crystallinity of a semicrystalline polymer such as PPS. Crystallinity changes of thermoplastic materials can result in significant changes in the mechanical behavior of composites containing them, particularly with respect to matrix-dominated properties such as compressive strength and creep. For this reason, the ability to precisely characterize the polymer crystallinity in a thermoplastic material becomes an important requirement. Unfortunately, due to the proprietary nature of the material processing, only limited information has been provided by the material supplier on processing of the as-received material.

In addition to information presented previously (Automotive Lightweighting Materials FY 2004 Annual Progress Report) on differential scanning calorimetry (DSC) and x-ray diffraction (XRD) results, a review of literature and contacts with industry has been conducted. Results of this review have been provided in a report that was published and distributed.[1] The objective of this report was to broaden the understanding of low-cost, semi-crystalline thermoplastic resins and composites for use in potential future automotive applications. PPS has an excellent combination of attributes including good mechanical properties and thermal stability, high chemical resistance, low moisture absorption, good weathering resistance, high dimensional stability, low flammability, and excellent processability. Specific areas addressed in the report include: structure of PPS; techniques for measuring crystallinity; crystallinity as a function of prior treatment; crystallization kinetics and morphology; effect of variation of crystallinity on properties of PPS and its composites; environmental stability; unusual effects of cooling rates and degree of crystallinity on mechanical properties of AS4/PPS composites; recent PPS laminate data (Ten Cate Advanced Composites); and recommendations for future research.

Baseline Property Determination

In an attempt to enhance the as-received material crystallinity, tests to establish room-temperature tensile, compressive, and shear properties of as-received material as well as material that had been annealed at 230°C for 2 hours have been completed. Investigation of specimen orientation effects also has been completed.

Table 1 summarizes tensile, compressive, and shear properties obtained for the as-received and annealed materials. Tensile, compression, and shear results represent tests of specimens that were obtained from 36, 10, and 6 plaques, respectively.

Strain-Rate and Prior-Load Tests

Testing to determine the effect of strain rate on tensile properties of the PPS composite has been completed. Four specimens each were tested at testing machine nominal stroke rates of 0.0005, 0.005, 0.05, 0.5, 5.0, and 50.0 in/sec. At rates up to 5.0 in/sec, an averaging extensometer was utilized to obtain strain data; however, at the 50 in/sec rate, strain gages had to be utilized due to difficulties in keeping the extensometer attached to the specimen. Strain rate for each of the specimens was determined using the test text files and determining the slope of the strain versus time curves. Strain rates ranged from 4.21×10^{-05} to $5.11\ s^{-1}$. Figure 1 presents the ultimate tensile strength as a function of strain rate. These results indicate that the ultimate tensile strength of the material increased slightly (<10%) when the strain rate increased from lowest to maximum. The tensile modulus of elasticity was relatively unaffected by strain rate while the tensile failure strain tended to decrease with increasing strain rate.

Table 1. Baseline properties: as-received material.

Property	As-Received Material	Annealed Material
	Tension	
Strength, MPa	551	539
Modulus, GPa	36.45	37.38
Failure Strain, %	1.53	1.42
Number Tests	207	31
	Compression	
Strength, MPa	295	292
Modulus, GPa	34.26	35.09
Failure Strain, %	0.95	0.92
Number Tests	57	13
	Shear	
Strength, MPa	193	196
Modulus, GPa	13.4	13.60
Failure Strain, %	1.63	1.59
Number Tests	34	12

Specimens oriented in long direction of plaque.

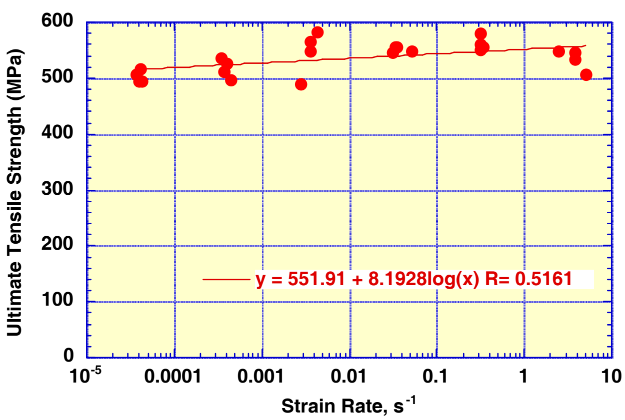

Figure 1. Effect of strain rate on ultimate tensile strength.

Testing to determine the effect of sequential loading on stiffness has been completed. After initial stiffness checks to establish baseline values, four tensile specimens each were subjected to initial loadings of either 20%, 40%, 60%, or 80% of the plaque average ultimate tensile strength (UTS). The specimens were then unloaded and reloaded with the load increased by 20% of the plaque average ultimate tensile strength. This procedure was repeated until the last load cycle in which the specimen was loaded to failure. Specimen modulus of elasticity was determined for each of the load applications. Figure 2 presents average change in

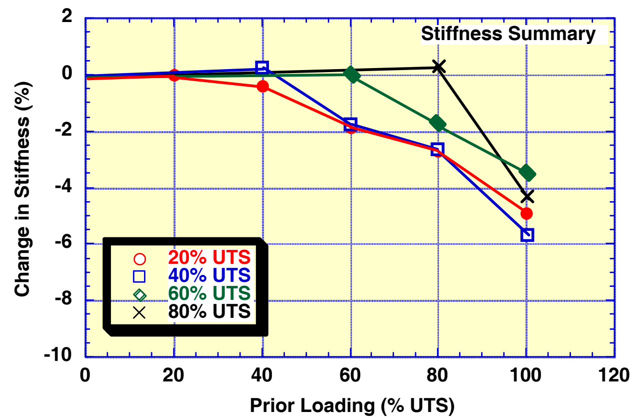

Figure 2. Effect of sequential loading on stiffness.

stiffness for each of the load applications. Results indicate that the first load increment did not produce a change in stiffness, but succeeding load increments produced increased reductions in the modulus of elasticity relative to the baseline values.

Environmental Effects Tests

Four series of tests were conducted that address environmental effects: prolonged thermal exposure on tensile properties, automotive fluids screening, and effect of exposure to distilled water and windshield washer fluid on tensile, compressive, and shear strengths.

Testing to evaluate the effect of prolonged thermal exposure on the ultimate tensile strength, tensile modulus of elasticity, and tensile failure strain has been completed. Either eleven or twelve specimens had been placed into ovens maintained at either 50°C, 70°C, 90° or 120°C. Two or three specimens were removed from each oven after thermal exposure periods of 100 h, 200 h, 500 h and 1000 h; placed into an insulated container and permitted to slowly return to room temperature; and tested to failure. Table 2 summarizes tensile strength results and indicates that although there was a 3 to 13% increase in ultimate tensile strength for specimens preconditioned at 120°C, there was no definite trend indicating significant effects of temperature level or periods of exposure on ultimate tensile strength. Tensile modulus of elasticity and tensile failure strain were unaffected by either the temperature level or the exposure period for the range of values investigated.

Table 2. Effect of elevated temperature exposure on ultimate tensile strength (MPa).

Preconditioning Time, hours	Preconditioning Temperature, °C				
	RT	50	70	90	120
0	594	-	-	-	-
100	-	581	637	632	610
200	-	588	569	573	620
500	-	599	552	572	670
1000	-	595	584	565	625

Environmental fluid screening tests to establish which, if any, common automotive fluids may have degrading effects on the carbon-fiber-reinforced PPS material have been completed. Nine automotive fluids were used in the screening (viz, antifreeze, battery acid, 5% NaCl solution, windshield washer fluid, brake fluid, distilled water, transmission fluid, gasoline, and motor oil). Twenty flexure specimens 12.7-mm-wide by 76.2-mm-long were submerged in each of the automotive fluids. Periodically, the specimens were removed from each of the fluids, measured, weighed, and returned to the appropriate fluid. After exposure periods of 100 h, 200 h, 500 h, 1000 h, and 2000 h, four specimens were tested to determine the effect of fluid exposure on the short-beam shear strength. Figures 3 and 4 present weight change and short-beam shear results obtained for each of the automotive fluids after 2000 hours exposure. Brake fluid, gasoline, and windshield washer fluid produced the largest percentage change in specimen weight; however, these changes are less than 0.7%. No significant change in specimen geometry occurred as a result of the fluid exposure. Battery acid, distilled water, and a 5% NaCl solution had the most effect on short-beam shear strength after 2000 hours exposure.

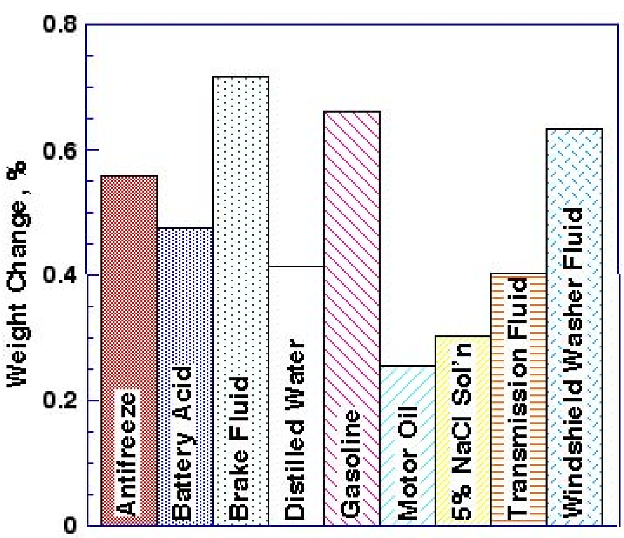

Figure 3. Weight change after 2000 hours exposure to typical automotive fluids.

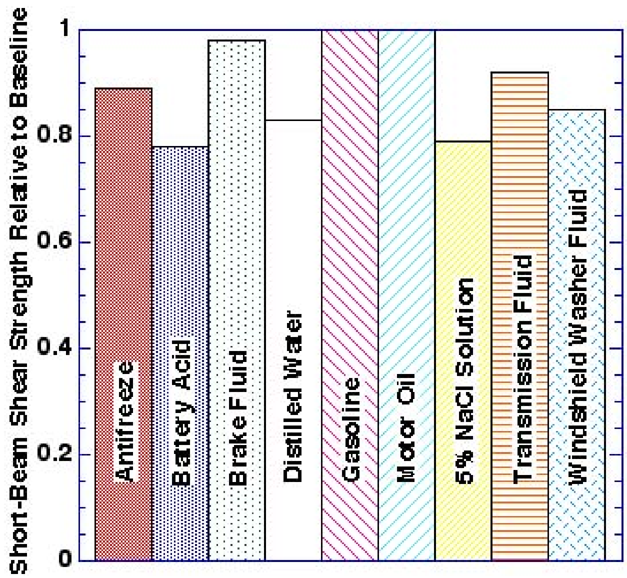

Figure 4. Short-beam shear strength after 2000 hours exposure to typical automotive fluids.

Tests to determine distilled-water and windshield-washer-fluid effects on tensile, compressive, and shear strength of specimens exposed to these fluids for periods up to 1000 h, have been completed. After 1000 hours exposure to distilled water and windshield washer fluid, the tensile strength decreased 6.8% and 6.3%, respectively; the compressive strength decreased 10.5% and 22.4%, respectively; and the shear strength decreased 34.9% and 31.3%, respectively, relative to the baseline strength. Compressive and shear properties, that tend to be more influenced by the matrix, were affected more significantly by 1000-hour exposure to distilled water and windshield washer fluid than was the tensile strength.

Uniaxial and Biaxial Flexural Strength Evaluations

Testing to determine the effect of thermal exposure on the uniaxial flexural strength and environmental effects on the biaxial flexural strength have been completed. Six specimens each, 76.2-mm long by 12.7-mm wide, were thermally preconditioned at either –40°C, 70°C, 90°C, or 120˚C for one hour prior to testing. Three specimens at each of these preconditioning temperatures were tested in three-point bending (50.8-mm major span) at temperature with the remaining three specimens permitted to return to room temperature prior to testing. Figure 5 summarizes flexural strength results for specimens tested at-temperature and specimens permitted to return to room temperature prior to testing. These results indicate that for specimens tested at-temperature, the flexural strength decreased as the preconditioning temperature increased. For specimens permitted to return to room temperature prior to testing, there was a slight trend for the flexural strength to increase as the preconditioning temperature increased. Results obtained from biaxial flexural tests in which a disk-shaped specimen supported at its edge is loaded by means of a load ring are summarized in Table 3. Results indicate that relative to the baseline value, the biaxial flexural strength was reduced by exposure to distilled water, windshield washer fluid, and elevated temperature.

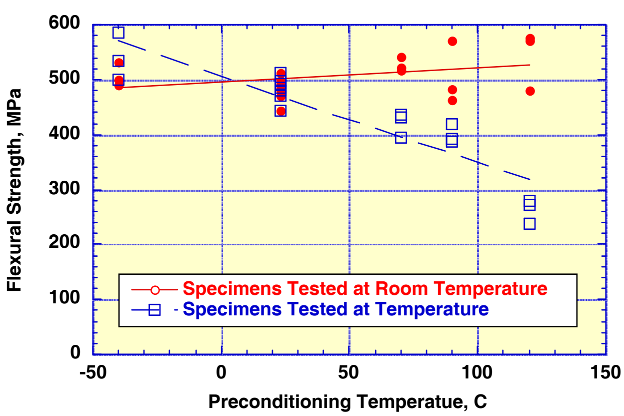

Figure 5. Effect of preconditioning temperature and test temperature on flexural strength.

Table 3. Biaxial flexural test result summary.

Preconditioning Environment	Maximum Load, kN	Displacement at Pmax, mm
Baseline	12.878	5.253
Distilled Water (1000 h Presoak)	9.697	5.011
Windshield Washer Fluid (100 h Presoak)	10.467	4.648
-40°C (1 hour)	14.497	5.672
70°C (1 hour)	10.849	5.296
90°C (1 hour)	10.422	4.920
120°C (1 hour)	6.770	4.590

Sustained-Load Tests

Sustained-load tests have been conducted as part of the overall assessment of the PPS composite material's ability to sustain constant loads for long-time periods. Sixty-one in-air room-temperature tests have been completed with sustained-load levels investigated ranging from 40 to 95% UTS. Thirty-three elevated temperature (70°, 90°, or 120°C) sustained-load tests have been completed with sustained-load levels investigated ranging from 40 to 91% UTS. Forty-three sustained-load tests in which the specimen was subjected to either room-temperature windshield washer fluid (1000 hour presoak) or distilled water (100 hour presoak) while under load have been completed investigating sustained-load levels ranging from 30 to 95% UTS. In addition, 19 compressive sustained-load tests have been completed in air at either room-temperature or 120°C. Figure 6 presents an example of total strain versus time plots for room temperature in-air tests of specimens subjected to sustained loads from 40.0 to 79.9% UTS.

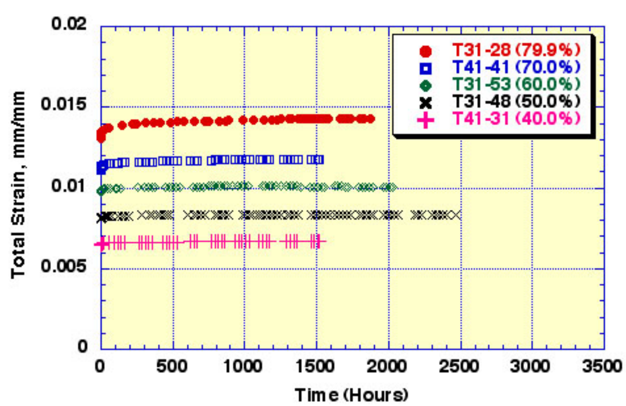

Figure 6. Examples of total strain results for room-temperature tensile creep tests.

Cyclic Fatigue Tests

Eighty-eight cyclic fatigue tests have been completed. Test parameters included the stress range (40 to 90% UTS, R = 0.1), test temperature (room temperature, –40°, 70° or 120°C), and effect of fluids (100-hour presoak in windshield washer fluid or 1000-hour presoak in distilled water). In addition, 52 tests were completed to examine the mean-stress effects (R = 0, R = -1, R = –∞, or 45% mean UTS). Figure 7 presents examples of stress versus cycles-to-failure results for tests involving different environmental exposures. Results such as these will be used to help establish design limits for cyclic loads for the PPS composite.

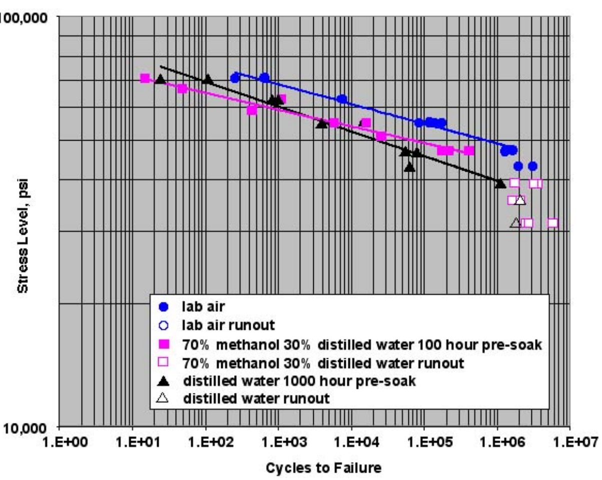

Figure 7. Stress versus number of cycles-to-failure results for various environmental exposures.

Summary and Conclusions

A quasi-isotropic carbon-fiber-reinforced PPS material is being investigated. This is the first thermoplastic material to be studied under the durability program. The ACC has supplied 46 plaques, 510 mm by 610 mm by about 3-mm thick, for use in durability studies. Plaque reinforcement is symmetrical and consists of 16 plies of carbon-fiber unidirectional tape, $[0/90/\pm45]_{2S}$.

Processing conditions for these plaques are very important because they affect the crystallinity of a semicrystalline polymer such as PPS, which can result in significant changes in the mechanical behavior of composites containing them. Because precise processing information on the plaques was not available due to the proprietary nature of the processing, the crystallinity of the material was investigated and a report prepared that presents data and information on the relationship between processing of PPS materials and crystallinity as well as the relationship between crystallinity and material properties.[1] Material characterization studies indicate that processing of the composite was fairly complete producing a crystallinity of about 85% of maximum achievable.
Tests to establish baseline room-temperature tensile, compressive, and shear properties of the PPS composite material have been completed. Additional tests (reported previously) established properties for material that had been annealed at 230°C for two hours in an attempt to increase crystallinity. Tensile, compressive, and shear strength properties of the as-received and annealed material were within 3% of each other tending to indicate that the material supplied possessed good crystallinity.

Strain-rate tests indicated that the material tensile strength increased somewhat (<10%) when the strain rate was increased from 4.21 x 10^{-05} to 5.11 s^{-1}.

Testing to determine the effect of sequential loading on stiffness indicates that the first load increment did not produce a change in stiffness, but succeeding load increments to higher load levels produced increased reductions in the modulus of elasticity relative to the baseline values. Sequential loading from 20 to 80% UTS did not have a significant effect on the ultimate tensile properties of the PPS material (last load cycle) as the tensile strength and tensile failure strain were relatively unaffected and the modulus of elasticity was reduced less than 10%.

Prolonged thermal exposures up to 120°C for periods up to 1000 hours produced a slight increase in tensile strength (3 to 13%); however, other exposure temperatures did not affect results. Tensile modulus of elasticity and strain at failure were not affected by either the exposure temperature or exposure period for the range of values investigated.

Environmental screening tests utilizing typical automotive fluids indicated that windshield washer fluid, gasoline, and brake fluid produced the largest weight gains due to exposure; however, the gains were less than 0.7%. Battery acid, distilled water, and a 5% NaCl solution had the most effect on short-beam shear strength. Exposure of 1000 hours to either distilled water or windshield washer fluid resulted in decreases in the tensile, compressive, and shear strengths, with the decreases greatest for properties that are more matrix dominated (i.e., compressive and shear).

Flexural results indicated a trend for the flexural strength to decrease as the preconditioning temperature increased when the specimens were tested at temperature; however, when permitted to return to room temperature prior to testing, the preconditioning temperature did not have much effect on the flexural strength.

Sixty-one in-air room-temperature creep tests have been completed with sustained-load levels investigated ranging from 40 to 95% UTS. Thirty-three elevated temperature (70°, 90°, or 120°C) sustained-load tests have been completed with sustained-load levels investigated ranging from 40 to 91% UTS. Forty-three sustained-load tests in which the specimen was subjected to either room-temperature windshield washer fluid (1000 hour presoak) or distilled water (100 hour presoak) while under load have been completed investigating sustained-load levels ranging from 30 to 95% UTS. In addition, 19 compressive sustained-load tests have been completed in air at either room temperature or 120°C.

Eighty-eight cyclic fatigue tests have been completed. Test parameters included the stress range (40 to 90% UTS, R = 0.1), test temperature (room temperature, –40°, 70° or 120°C), and effect of fluids (100-hour presoak in windshield washer fluid or 1000-hour presoak in distilled water). In addition, 52 tests were completed to examine the mean-stress effects (R = 0, R = -1, R = $-\infty$, or 45% mean UTS). Fatigue test results indicate that as the maximum applied stress level increased, the number of load cycles-to-failure decreased (R = 0.1). Also, exposure to either windshield washer fluid or distilled water resulted in a decrease in the number of load cycles-to-failure relative to in-air test results at the same maximum stress level (R = 0.1).

Results contained in this report will be utilized to develop durability-driven design criteria for the quasi-isotropic carbon-fiber-reinforced PPS composite.

References

1. J. E. Spruiell and C. J. Janke, “A Review of the Measurement and Development of Crystallinity and Its Relation to Properties in Neat Poly (Phenylene Sulfide) and Its Fiber Reinforced Composites,” ORNL/TM-2004/304, Oak Ridge National Laboratory, Oak Ridge, Tennessee (August 2004).
2. J. Cao and L. Chen, “Effect of Thermal Cycling on Carbon Fiber-Reinforced PPS Composite,” Proc. of SEM Annual Conference and Exposition on Experimental & Applied Mechanics, pp. 713-716, Portland, Oregon, 2005.