7. ENABLING TECHNOLOGIES

A. 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 kickups 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 report addressing mechanical response of randomly-reinforced, chopped-fiber composites (MABE03-1.0-CM, University of Tennessee, October 2003).
- Completed draft report assessing the effects of processing on poly(phenylene sulfide) (PPS) crystallinity and the relationship between crystallinity and properties (ORNL report, August 2004).
- Completed testing to determine baseline tensile and compressive properties and effect of specimen orientation and annealing on these properties.
- Completed testing to investigate effect of thermal exposure and thermal cycling on tensile and compressive properties.

- Completed in-air, room temperature, tensile creep-rupture testing.
- Completed impact testing (pendulum, air-gun, and brick drop tests) and compression- and tension-after-impact testing.
- Completed testing to evaluate damage tolerance to circular holes and cracks.
- Completed testing to evaluate effect of specimen width on tensile properties.
- Published report on the nonlinear response of quasi-isotropic laminates (*Composite Science and Technology*, Vol. 64, pp. 1577–1585, Elsevier, 2004).
- Published report on properties, failure, and aspects of material design for randomly-reinforced composites. (Report MABE04-3.0-CM, Mechanical, Aerospace and Biomedical Engineering Department, University of Tennessee, Knoxville, August 2004.)
- Input carbon-fiber composite data directly into the planning and analysis for the Focal Project III carbon-fiber body-in-white.

Future Direction

- Publish report on relationship between processing of PPS materials and crystallinity as well as relationship between crystallinity and material properties.
- Complete durability assessment of carbon-fiber-reinforced PPS material.
- Publish durability-driven design criteria documents for representative thermoplastic composites suitable for automotive structural applications.

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 effect 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 III (4.C) 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. Also in FY 2003, investigation of carbon-fiber-reinforced thermoplastic materials for structural automotive applications was initiated. Primary activities associated with evaluation of the thermoplastic material have addressed thermoplastic material characterization, baseline property determination, environmental and sustained-loading effects testing, and damage-tolerance assessments.

Thermoplastic Material Characterization

The ACC has supplied 43 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/±45]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.

Differential scanning calorimetry (DSC) results, over the temperature range from 40 to 320˚C, have been obtained from several samples of the quasi-isotropic material to investigate crystallinity of the as-received material. The first scan indicated that the degree of crystallization was less than optimum—about 85% of maximum crystallinity or about 32% crystallinity assuming a 40% resin content. The crystallization peak was not present during the second scan, indicating a higher degree of crystallinity due to the first scan test temperature. Additional ramp-and-hold experiments were run in which samples were either heated from 40 to 90°C at 20˚C/min, held at 90°C for 60 min and then permitted to return to room temperature; or heated to 120°C and held for 60 min prior to cooling to room temperature. After the 90°C ramp, the scan (sample ran at 40 to 320°C at 20°C/min) showed a T_g and crystallization peak signifying less than an optimum degree of crystallinity. The second scan exhibited a flat baseline indicating a high degree of crystallinity. Additional testing conducted by the University of Tennessee using X-ray diffraction produced crystallinity results in agreement with those obtained at ORNL.

A review of literature and contacts with industry has been conducted to provide data and information that addresses the relationship between processing of PPS materials and crystallinity as well as the relationship between crystallinity and material properties. Results of this review are provided in a report that has been prepared.[1]

Baseline Property Determination

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

Table 1 summarizes tensile and compressive properties obtained to date for the as-received material. Tensile results represent tests of 128 specimens that were obtained from 24 plaques. Compressive results represent tests of 46 specimens obtained from 8 plaques. Tensile and compressive properties for material that had been annealed at 230°C for 2 h are summarized in Table 2. Results for specimens tested at room temperature indicate that annealing produced little change in tensile or compressive properties compared to results from as-received material.

The effect of specimen orientation was investigated. Tensile and compressive test specimens were machined having their major axis

Table 1. Baseline properties: as received material

Property	Tension	Compression
Strength, MPa	540	294
Modulus, GPa	36.44	34.40
Failure Strain, %	1.51	0.94

Table 2. Baseline properties: annealed material

Property	Tension	Compression
Strength, MPa	539	292
Modulus, GPa	37.38	35.09
Failure strain, %	1.42	0.92

oriented either at 0°, 22.5°, 45°, or 90° relative to the long direction of the plaque. Test results are summarized in Table 3. Tensile strength results for each orientation were fairly consistent except for the 22.5° orientation, which is the only orientation that does not coincide with a carbon fiber direction. Compressive strength results were maximum at a specimen orientation of 45°. The carbon-fiber reinforcement tends to have the greatest influence on tensile properties, and the matrix material has added significance relative to compressive results. The tensile and compressive moduli of elasticity for both tensile and compressive testing did not exhibit an orientation effect. Tensile and compressive strains at failure exhibited similar trends to the tensile and compressive strength results. Tensile and compressive results obtained from annealed material exhibited similar trends to the as-received material.

Table 3. Effect of specimen orientation

Property	Orientation[a]			
	0°	22.5°	45°	90°
Tensile				
Strength, MPa	546	383	618	614
Modulus, GPa	37.3	36.7	37.0	40.0
Failure strain, %	1.43	1.07	1.65	1.48
Compression				
Strength, MPa	254	335	369	336
Modulus, GPa	33.8	34.9	34.6	36.5
Failure strain, %	0.83	1.07	1.23	0.98

[a] 0° is in long direction of the plaque.

Environmental and Sustained-Loading Effects Testing

Three series of tests were conducted that address environmental and sustained-loading effects: elevated temperature, thermal cycling, and creep rupture.

The effect of elevated temperature on tensile and compressive properties was evaluated by subjecting specimens to preconditioning temperatures of either –40, 70, 90, or 120°C for 1 h prior to testing. For each preconditioning temperature, half the specimens were tested at temperature with the other half permitted to return to room temperature prior to testing. This series of tests involved material in the as-received condition as well as material that had been annealed.* Figures 1 and 2 present tensile strength results as a function of preconditioning temperature for as-received and annealed materials that had been either permitted to return to room temperature prior to testing or tested at temperature, respectively. Similar results were provided for both the as-received and annealed materials because the tensile strength tended to increase slightly with preconditioning temperature for specimens permitted to return to room temperature prior to testing and decrease slightly when specimens were tested at temperature. Modulus of elasticity results for both materials were relatively unaffected by preconditioning temperature for specimens either permitted to return to room

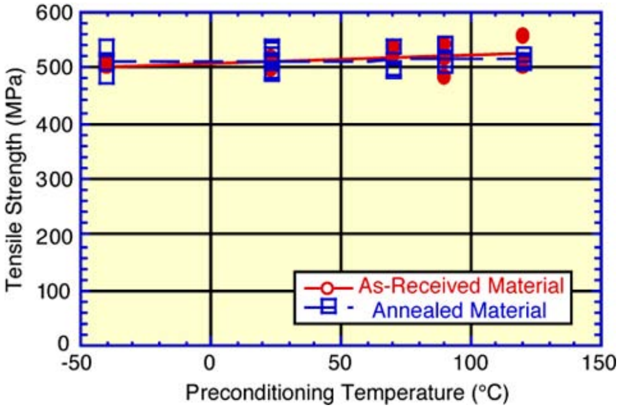

Figure 1. Effect of preconditioning temperature on tensile strength: room temperature tests.

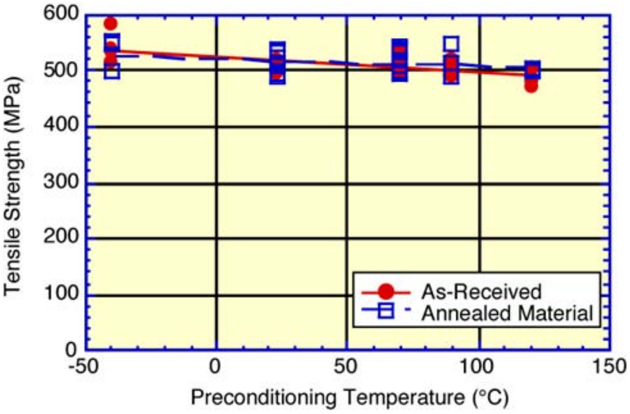

Figure 2. Effect of preconditioning temperature on tensile strength: tests at temperature.

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*Specimens were tested having major axis orientations of 0° and 22.5°. Only 0° orientation results are presented.

temperature prior to testing or tested at temperature. The effect of preconditioning temperature on compressive strength of as-received material tested either at temperature or permitted to return to room temperature prior to testing is presented in Figure 3. Results for both test environments were fairly consistent up to a preconditioning temperature of 70°C; however, at higher temperatures the compressive strength of specimens permitted to return to room temperature prior to testing was consistently higher than that obtained from specimens tested at temperature. Compressive modulus of elasticity was relatively unaffected by the preconditioning temperature and test environments (Figure 4). Compressive strength results for the annealed material tested at temperature also tended to decrease with increasing preconditioning temperature; however, the tensile strength results for the annealed material tested at room temperature exhibited a trend to increase slightly with preconditioning temperature.

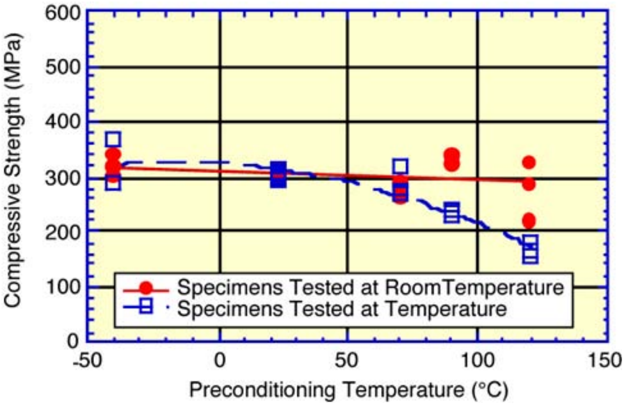

Figure 3. Effect of preconditioning temperature on compressive strength: as-received material.

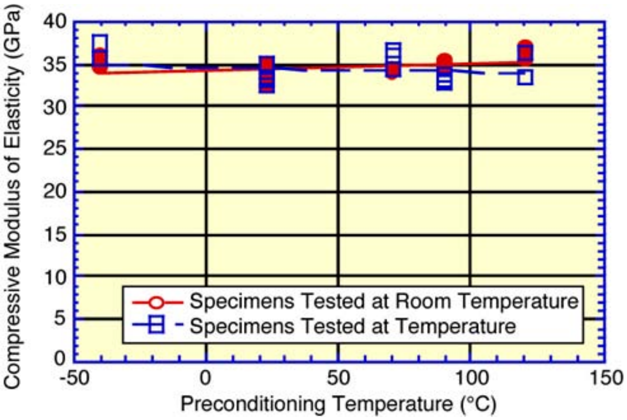

Figure 4. Effect of preconditioning temperature on compressive modulus: as-received material.

The effect of prior thermal cycling on tensile and compressive properties was also investigated. Prior to testing, specimens were subjected to either, 1, 5, 10, or 25 thermal cycles from 23°C to 120°C to –40°C to 23°C. Results, summarized in Table 4, indicate that for the temperature range and number of thermal cycles investigated, there was a slight increase in tensile strength resulting from the thermal exposure; however, little change in other tensile and compressive properties resulted relative to the baseline data.

Table 4. Effect of thermal cycling

Property	Number of thermal cycles				
	0	1	5	10	25
Tensile					
Strength, MPa	520	568	551	555	532
Modulus, GPa	36.3	35.9	36.1	35.3	35.1
Failure strain, %	1.37	1.47	1.48	1.45	1.42
Compression					
Strength, MPa	323	296	322	316	311
Modulus, GPa	34.6	39.1	34.4	33.4	33.7
Failure strain, %	1.05	0.83	1.04	1.03	1.02

Sustained-load tests (creep rupture) were conducted as part of an overall assessment of the PPS composite material's ability to sustain constant loads for long time periods. Twenty-three in-air room temperature tests were conducted in which tensile specimens were loaded to nominal values representing 80.0 to 95% of the material's ultimate tensile strength. The specimens remained under load until either they failed or the test was terminated. Failure times ranged from less than 2 h for specimens loaded to 95% ultimate tensile strength to 500 to 2000 h for specimens loaded to 86% ultimate tensile strength. No failures were observed for specimens loaded to ≤84% ultimate tensile strength. Seven in-air, elevated-temperature (120°C) creep rupture tests are under way.

Damage Tolerance Assessments

Damage tolerance assessments have addressed both damage resistance (impact tests) and damage tolerance (holes and cracks). Both of these aspects are important because it is desired that an automotive composite be resistant to formation of damage as well as tolerant of any damage or defect that is present.

Forty-two impact tests have been conducted as part of an assessment of the ability of the PPS composite material to continue to perform its function in the presence of damage. Air-gun and pendulum tests were performed both at room temperature and at low temperature (–40°C) (Figure 5). Also, a series of brick-drop tests was performed at room temperature. The impact tests were performed to address potential service-induced damage resulting from events such as kick-ups of roadway debris, tool drops, and events of interest to pickup truck boxes. The tests utilized material in the as-received condition as well as material that had been annealed prior to testing. Impact parameters (e.g., velocity or drop height) were selected to inflict damage ranging from slight to severe. Ultrasonic "C" scans of the specimens were used to determine the damage area in each of the specimens. Figure 6 presents time-of-flight results for an air-gun impact specimen tested at –40°C, indicating that damage occurred at different depths in the material thickness. After conduct of an impact test and assessment of the damage areas, each specimen was cut into three test specimens to be used for compressive or tensile tests: specimen containing impact damage, specimen for baseline testing, and specimen containing a circular hole having roughly the same area as the corresponding impact damage. Figure 7 presents damage area vs kinetic energy for the pendulum and air gun impact tests and compares it to a thermoset quasi-isotropic material tested previously (Note: quasi-isotropic thermoset is 2.2-mm thick vs 2.8-mm thickness of thermoplastic). Results indicate that the air gun produced larger damage areas than the pendulum for a given impactor energy. Compression-

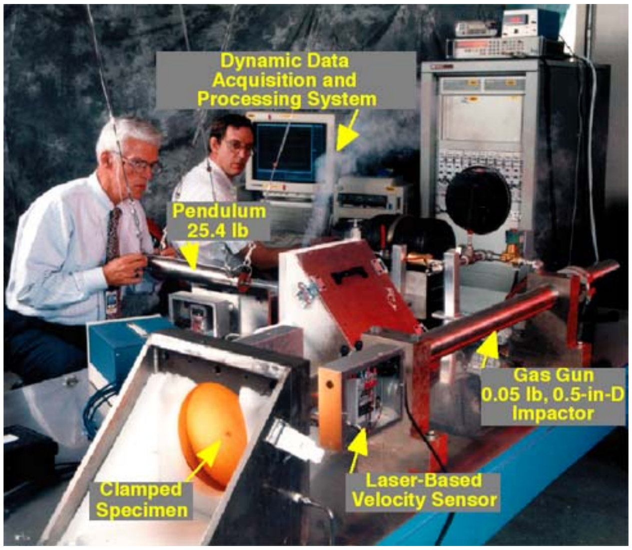

Figure 5. Air gun and pendulum impact test facility.

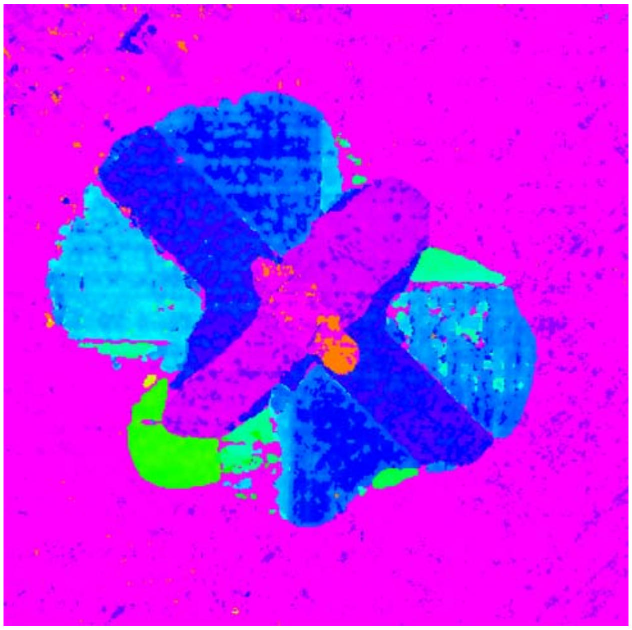

Figure 6. Time-of-flight ultrasonic results: Spec. T7-27.

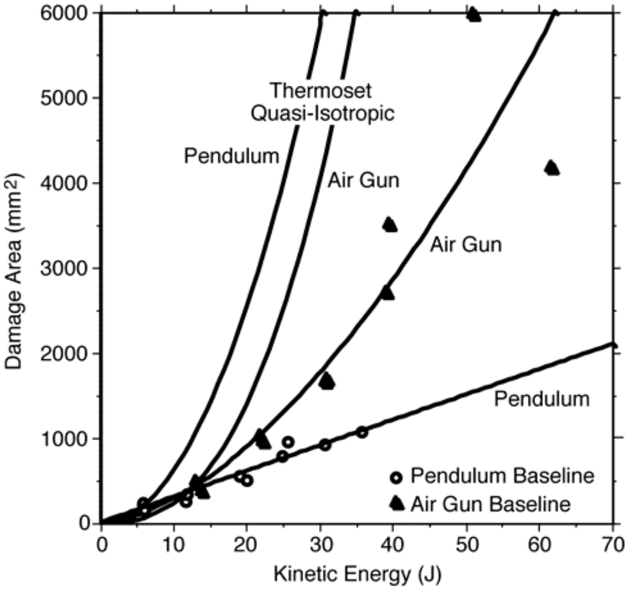

Figure 7. Impact test results: damage area vs kinetic energy.

and tension-after-impact tests indicate that compressive strength reduction was greater than tensile strength reduction.

Additional information on damage tolerance was provided by testing tensile specimens that contained center holes and cracks. Figure 8 presents notch strength (gross stress in an infinitely wide plate away from hole or crack) normalized for plaque ultimate tensile strength as a function of hole diameter or crack length. Crack results agree closely with those obtained from holes and tend to be in agreement with fracture-mechanics relationships.

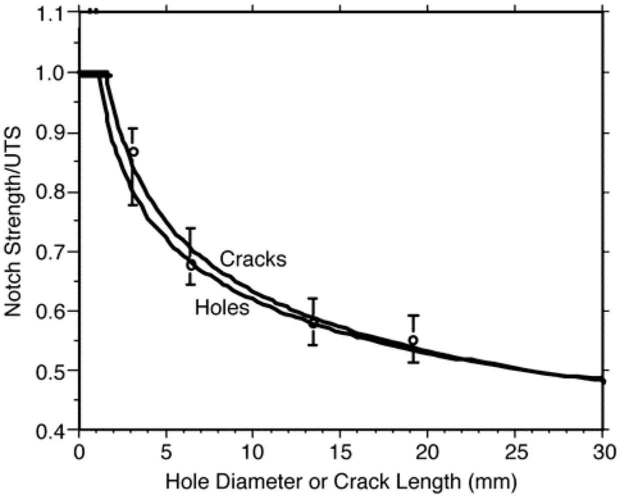

Figure 8. Impact test results: damage area vs kinetic energy.

Summary

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 43 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 is not available due to the proprietary nature of the processing, the crystallinity of the material was investigated. DSC and X-ray diffraction have been utilized to investigate the as-received material crystallinity, and results indicate that the material has a crystallinity that is about 85% of maximum. A report has been 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.

Tests to establish baseline room-temperature tensile and compressive properties of the PPS composite material have been completed. The effect on tensile and compressive properties of annealing at 230°C for 2 h to increase crystallinity of the as-received material has been investigated. Testing to evaluate specimen orientation effects for the as-received and annealed material has been completed. The effect of thermal exposure at temperatures up to 120°C for 1 h prior to testing on tensile and compressive properties has been evaluated. Testing to investigate the effect on tensile and compressive properties of applying up to 25 thermal cycles from room temperature to 120°C to –40°C to room temperature prior to testing has been completed. In-air, room-temperature sustained tensile loading (creep rupture) tests have been completed. Damage tolerance assessments have been completed that address both damage resistance (impact tests) and damage tolerance (presence of holes and cracks).

Results presented above in addition to subsequent testing to be conducted will be used to develop recommended durability-based design properties and criteria for the quasi-isotropic carbon-fiber-reinforced PPS composite for possible automotive structural applications. Durability issues being addressed include the effects on deformation, strength, and stiffness of cyclic and sustained loads, automotive fluid environments, and low-energy impacts. Guidance will be developed for design analysis, time-dependent allowable stresses, rules for cyclic loadings, and damage-tolerance design guidance.

Reference

1. J. E. Spruiell and Chris 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.