3. Polymer Composites

A. Polymer Composite Development
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Executive Summary

This project consists of two tasks critical for the manufacture and implementation of composite materials in automotive structures. The tasks are the development of predictive models for long fiber thermoplastic (LFT) injection molding and the development of rapid, reliable joining methods for composites. These projects are aimed at developing methods for low cost manufacturing and design of composites in automotive structures. They include lower cost directed-fiber placement technologies, development of reliable models for LFT injection molding, and development of an understanding of the design of joints composed of composite materials.

LFT composites have attracted significant interest in the automotive industry as candidate materials for structural applications due to the high speed, low cost manufacturing processes that can be used. Predictive engineering capabilities are needed to assist in design of these materials and the molding process. This project takes an integrated approach, linking process to structural modeling using new fiber orientation and length distribution models, advanced property prediction models for linear and nonlinear responses, advanced microstructural characterization methods, and mechanical testing.

The focus application for the second project is the joining of a polymer matrix composite (PMC) underbody to the rest of the vehicle structure. This effort includes the development and validation of analytical models and tools capable of predicting multi-material joint performance and durability under multiple loading scenarios. It also includes the generation of an experimental database on a multi-material joint's performance and durability under various loading and environmental conditions to support and validate the modeling approach.

Activity and Developments

Engineering Property Prediction Tools for Tailored Polymer Composite Structures

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Accomplishments

- Two molding trials with large instrumented plaque mold were performed using 40% long glass-polypropylene (PP) and 40% long glass-PA6,6 [type 6,6 polyamide (nylon)] materials [Automotive Composites Consortium (ACC) plaques].
- Fiber length distribution, fiber orientation distribution, dispersion, and mechanical properties were evaluated for validation of property prediction tools.
- Autodesk Moldflow Insight (AMI) models were established and successfully run for the injection molding analyses of the ACC plaques to predict fiber orientation and length distributions. Model predictions captured quite well the through-thickness variations of fiber orientation at various regions with twenty-one of the twenty-four samples having fiber orientations measured within 15% of the predicted values and the average agreement for all twenty-four samples being 7.7%.
- ABAQUS–Eshelby-Mori-Tanaka– (EMTA) non-linear analysis (NLA) models were modified and used for tensile specimens cut from the ACC plaques along the flow and cross-flow directions. Preliminary analyses show that the models correctly predicted damage accumulation, failure location and stress-strain responses of the specimens up to failure within 10%.

Future Directions

- Mold three-dimensional complex geometry part with features including thickness variation, splitting flow, and flow direction change using 40% glass-PP and 40% glass-PA6,6 materials.
- Evaluate the microstructure and mechanical properties of a complex geometry part for validation of prediction tools.
- Further optimize the fiber orientation model parameters for the ACC plaques previously molded.
- Validate process and property model predictions, within 15%, against experimental data obtained for the complex geometry part.

Technology Assessment

- Target: Achieve a match of 15% between fiber orientation predictions and experimental data for the complex part.
- Gap: Fiber orientation models have not been validated for complex geometry parts involving thickness variation, splitting flow, and flow direction change.
- Gap: Property prediction tools have not been validated for complex geometry parts.

Introduction

Property prediction models and experimental methods have been developed for injection molded LFT composites. Process models involved a fiber orientation model, termed the anisotropic rotary diffusion–reduced strain closure (ARD-RSC) model (Phelps and Tucker, 2009), and a fiber length attrition model (Phelps, 2009) that captures fiber breakage in the mold during filling. These models were implemented in the University of Illinois ORIENT code and also in a research version of AMI. AMI is a finite element (FE) software package for injection molding analyses. Techniques for measurement of fiber length and fiber orientation distributions developed or refined at ORNL were used to develop these new process models.

Experiments on coupon size samples performed at ORNL were used to develop property prediction models, which were implemented at PNNL and named EMTA and EMTA-NLA. The property prediction models comprise a series of micromechanical models using the standard and improved EMTA approaches to capture the linear and nonlinear behaviors of LFTs (Nguyen, 2008; Nguyen 2009; and Nguyen and Kunc, 2010). While EMTA is stand-alone software for computation of thermoelastic properties, EMTA-NLA presents the capabilities implemented in the ABAQUS FE packages (via user subroutines) for nonlinear analyses of LFT structures.

This project task aimed at validating the process and basic property prediction models for molding trials was performed with large ACC plaques.

Approach

Model validation performed this year was conducted on 600 mm by 600 mm square plaques, 3 mm thick. Two gating options were used to achieve desired flow patterns: flow in edge-gated and center-gated plaques.

The experimental data were collected using methods and techniques developed in previous years of this project. The test matrix for the model validation was selected with input from industry experts. AMI was applied to simulate the injection molding of the ACC plaques to predict the fiber orientation and length distributions in these structures. The predicted results at selected locations were compared with the experimental data. Based on the advice of the industry experts, the validation is considered satisfactory if the averaged through-thickness values agree with the measured data within 15%. Next, to validate the property prediction models, tensile specimens cut from ACC plaques in the flow and cross-flow directions were analyzed by ABAQUS-EMTA-NLA to predict damage accumulations, failure locations, and stress-strain responses. EMTA-NLA mapped fiber orientation and length results for the specimens from AMI to ABAQUS. The predicted elastic moduli and strengths were compared to the experimental results within 15% accuracy to validate the models. Also, the predicted failure locations were checked to determine their agreement with the experimental cracks.

Results and Discussion

Plaques from the first molding trial with the ACC tool were provided to the team in August 2011. Because of equipment problems, the intended molding matrix was only partially completed. Additionally, initial x-ray experiments have shown leaks through the center gate during molding of edge-gated plaques and significant weld lines in portions of the plaques, as shown in Figure 1. This report does not cover results obtained from tests obtained on these plaques.

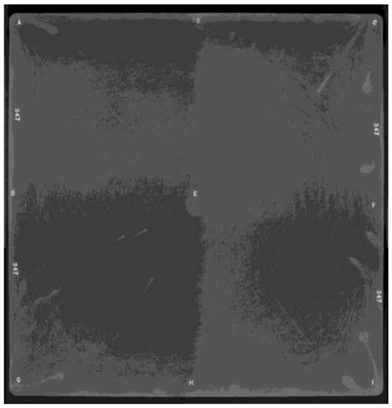


Figure 1. Center-gated sample from the first ACC molding trial exhibiting weld lines.

The second molding trial was performed at Injection Technologies, Windsor, Ontario, in March 2011. The three parameters varied during the molding trial are summarized in Table 1. A 2,200 ton injection machine was used with the lowest possible back pressure setting to achieve maximum retention of fiber length.

Table 1. Molding variables for March 2011 trials.

Parameter	Condition 1	Condition 2
Gating	Edge gate	Center gate
Fill speed	Slow	Fast
Material	40% glass-PP	40% glass-PA6,6

Based on x-ray dispersion analyses performed on three plaques of each type, sampling locations were selected. Location A is near the injection point, location B is about mid-flow in the sample, and location C is near the end of the flow yet not within the region influenced by the presence of the plaque edge. All tensile bar samples are centered over location B. This information is summarized in Figure 2.

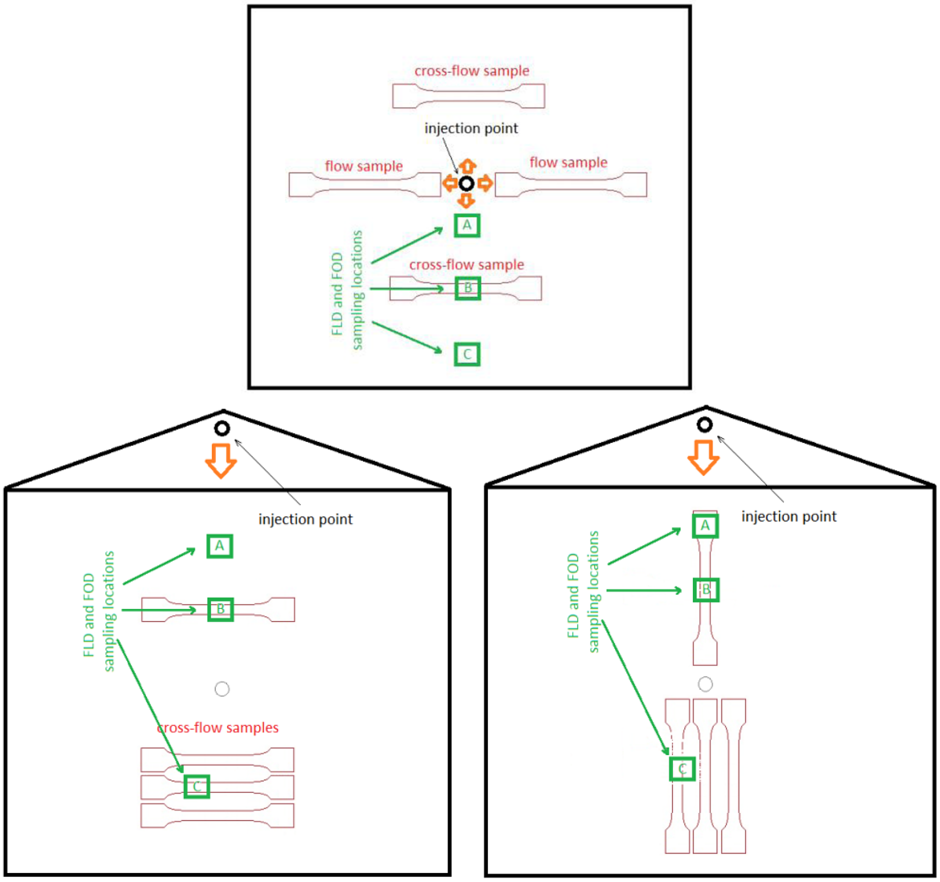


Figure 2. Sampling locations for center-gated plaques (top), and edge-gated plaques (bottom).

Figure 3 shows fiber length distributions measured at location B for all parameter combinations. The data indicate that a large portion of the material consists of fibers of 2 mm or less in length and that variations in process parameters do not qualitatively influence fiber length distribution. It is therefore likely that fiber attrition occurred before or at the entry to the mold cavity.

Despite the apparently large number of short fibers, the samples contained a network of entangled fibers. Figure 4 shows orientation components A11 and A22 for a 40% glass-PP center-gated sample with slow fill. Samples molded with these parameters should experience severe fiber length attrition, yet the plot of fiber orientation indicates

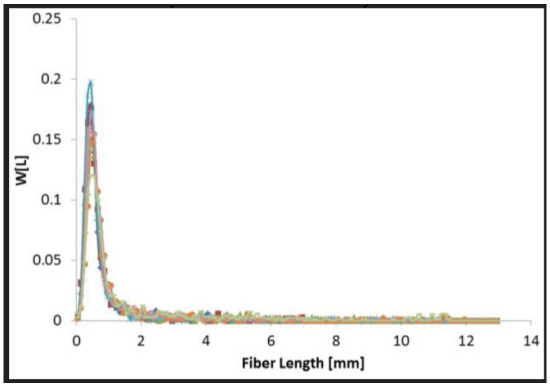


Figure 3. Fiber length distribution at location B for all samples.

a rather wide core, which significantly differs from observations made for short fiber LFTs. The presence of the entangled fiber network was also qualitatively observed after matrix burn-off. Figure 4 also shows narrowing of the core along the flow length, which is consistent with previous observations.

Experimental data measured for the second molding trial with ACC plaques point to consistent material properties, which include appropriate dispersion, lack of weld lines in sample regions, and an entangled fiber network with a relatively wide core. Therefore, test data obtained from these plaques are well suited for validation of the ARD-RSC flow model and EMTA-NLA property prediction software.

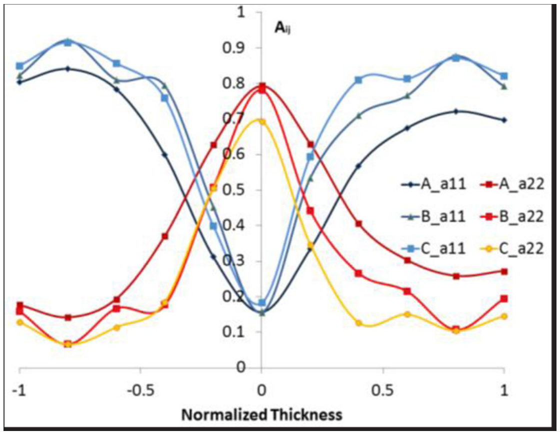


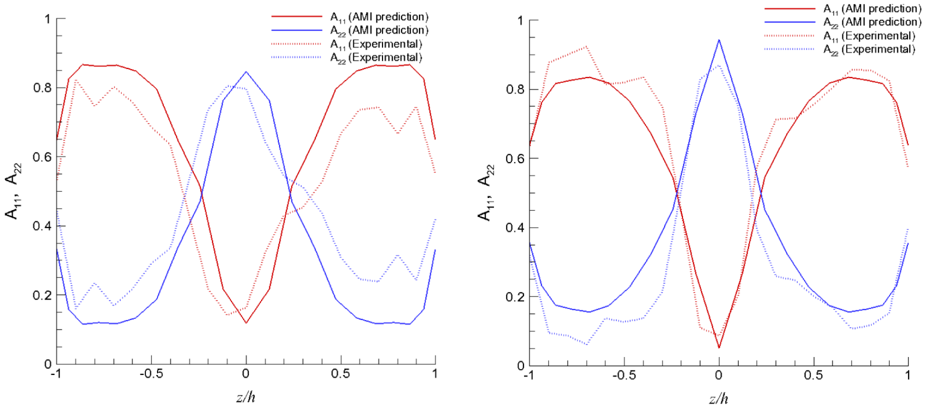
Figure 4. Fiber orientation tensor components A11 and A22 for 40% glass-PP center-gated sample with slow fill.

Experimentally obtained fiber orientation results were compared to ARD-RSC model predictions. These predictions were performed using AMI with a single set of model parameters for each material. The goal for this project was to achieve agreement between predicted and experimental results within 15% for all but three of the samples. The difference between experimental and predicted average orientation for tensor component A11 is shown in Table 2 for all the molded plaques. The target for this project was reached for 21 of 24 validation cases.

Table 2. Relative errors between predicted and experimental average orientation for component A11 at locations A, B, and C for all the molded plaques. Data above the 15% threshold is in bold.

Molding condition and geometry	Location A	Location B	Location C
Slow-fill glass-PP edge-gated plaque	2%	4.2%	8%
Slow-fill glass-PP center-gated plaque	**21.5%**	11.1%	**16%**
Fast-fill glass-PP edge-gated plaque	12.6%	9.4%	13.5%
Fast-fill glass-PP center-gated plaque	**18%**	9.1%	3.2%
Slow-fill glass-PA6,6 edge-gated plaque	6.6%	3.1%	4.8%
Slow-fill glass-PA6,6 center-gated plaque	2.8%	1%	11%
Fast-fill glass-PA6,6 edge-gated plaque	1.3%	13.3%	3.9%
Fast-fill glass-PA6,6 center-gated plaque	1.2%	1%	7.3%

Figures 5(a) and (b) show fiber orientation results for the worst case, with a 21.5% mismatch, and for one of the best cases, with a 1% deviation. These results are for the slow-fill glass-PP center-gated plaque location A and the fast-fill glass-PA6,6 center-gated plaque location B, respectively. While the prediction shown in Figure 5(a) does not capture the average orientation result within 15% accuracy, qualitatively, it captures the through-thickness variations of A11 and A22 quite well. Investigations into these deviations may be part of any follow-on activities in future years.



(a) (b)

Figure 5. Comparisons of the experimental and predicted fiber orientation results for (a) the 40% slow-fill glass-PP center-gated plaque at location A, and (b) the 40% fast-fill glass-PA6,6 center-gated plaque at location B.

Preliminary analyses of the specimens cut from the ACC plaques were performed using ABAQUS-EMTA-NLA to predict the stress-strain responses and damage accumulations up to failure. Figures 6(a) and 6(b) show the predicted and experimental failure locations in the flow-direction specimens cut from slow-fill glass-PP center-gated plaques. The predicted failure location agrees with the experimental observation.

(a) (b)

Figure 6. (a) Predicted failure and (b) experimental failure for the flow-direction specimens cut from the 40% glass-PP center-gated plaques

Conclusions

A consistent set of large ACC plaques was molded for model validation. A full matrix of x-ray, fiber length distribution, fiber orientation, and mechanical tests was completed. A set of model runs was performed and model predictions were compared to experiments. The results of this comparison indicate a globally good agreement between predicted and measured data. The target of matching results for orientation within 15% was achieved for 21 of 24 test cases. Preliminary analyses of tensile specimens cut from ACC plaques were performed that show good agreement on the damage and fracture patterns with the experimental results. This work will be pursued to assess the stress-strain responses up to failure after improvement needed for fiber orientation predictions for all the study cases.

Composite Underbody Attachment

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Accomplishments

- Completed modifications of super lap shear specimen geometry and test methods to enable evaluation of joint durability via cantilever bending and torsion test methods. These test methods enable bend and torsion durability data to be generated for joint model validation and development efforts.

- Conducted quasi-static torsion and torsion fatigue tests with composite-to-steel joint specimens fabricated with and without spot welds. Results showed that the weld bonded joints are more robust and sustain higher levels of torsional loading and rotational displacement than the adhesively bonded specimens.

- Torsion fatigue tests revealed several potential failure mechanisms in composite-to-steel joint specimens including cracks in the vicinity of spot welds of weld bonded joint specimens. Torsional loading provides for the case of combination peel-and-shear stress loading of the joint.

- Conducted analyses in which quasi-static torsion coupon tests were simulated for the purpose of test analysis correlation and modeling method development (Multimatic Inc.).

Future Directions

- Move from developing test methods for two-dimensional parts to developing test methods for three-dimensional (3D) parts. This effort will include design of specimens, tests, fixtures, and equipment for evaluating multi-material joint durability in 3D composite parts.
- Advance methods for material joining by completing modifications of super lap shear specimen geometry and test method to enable evaluation of joint durability via peel loading in support of the underbody project. Test method will provide for higher levels of peel load than were attainable using the cantilever bend test method and will be based on a modified coach peel test.

Technology Assessment

- Target: Develop and validate a method (analytical tools and test methods) capable of predicting the durability of automotive composite/adhesive/metal joints under combined environmental and mechanical loading.
- Gap: Generic tools for predicting the performance of composite-to-metal joints do not exist and must be developed (or adapted) for the specific automotive application.
- Gap: Usable material property databases and the relevant test methods must similarly be developed for the specific automotive application.

Introduction

This project is a collaborative effort of the Composite Underbody project (Focal Project 4) between ACC, Multimatic Inc., and ORNL. The objective of this project is to develop a method to predict the effects of environmental exposures and mechanical loadings on the durability of a composite-adhesive-metal joint. The focus application is joining a PMC underbody to an automotive body structure and validating the assembly’s long-term durability and performance.

Approach

This project has six key elements to accomplish the goals: (1) design of the multi-material joint tests, (2) material characterization, (3) test article manufacture, (4) mechanical performance of joint specimens for durability, (5) synergistic durability from multiple environmental stressors, and (6) computer aided engineering (CAE) model validation and development. Test program specifics are determined based on an analysis of an underbody design project.

The underbody geometry was simplified to allow extraction of test data representative of the performance of this type of multi-material joint, and a method for coupon-level testing of combined environmental and mechanical loading on the joint will be developed. The validity of existing automotive CAE durability tools for this application is being evaluated. Inputs for model validation and development are based on test results obtained as part of this project and previous research on similar materials.

As part of this approach, experimental durability test data derived from tensile, bending, and torsional coupon tests, along with appropriate material durability data, are being generated by ORNL and ACC and are being used by Multimatic Inc. to develop the appropriate modeling techniques for this project. This, followed by testing and correlation using data derived from a larger 3D structural specimen subjected to two unique loading conditions that produce different types of stress concentrations in the joint, will provide a high level of confidence in the validity of the models.

Contributions from the project team include the following.

- ORNL: Project lead, test method development, durability testing, dynamic tension testing on the ORNL testing machine for automotive composites.
- ACC: Technical consultation regarding automotive industry needs and requirements, material characterization, test specimen fabrication.
- Multimatic Inc.: Joint FE analyses, CAE model validation and development.

Deliverables include a composite-to- steel joint coupon-testing protocol, test data, CAE model validation results, and final report. Recommendations to improve the method (testing and analytical) will be proposed as deemed appropriate.

Results and Discussion

Test equipment and fixtures to evaluate joint specimens via torsional loading were prepared, and quasi static and cyclic fatigue tests with specimens prepared with weld bonded and adhesively bonded joint configurations were conducted. Torsional loading provides for the case of combination peel-and-shear stress loading of the joint. Figure 7 shows photographs and a description of the composite-to-steel weld bonded torsion test specimen. Figure 8 shows the ORNL MTS (MTS Systems Corporation) axial-torsion test machine with test fixtures installed.


(a) (b)

Figure 7. Composite-to-steel weld bonded joint specimen: (a) front and (b) back

- Combination of adhesive bonding and spot welding
- Steel doubler strip enables spot welding to steel structure
  - Compatible with OEM assembly processes
  - Mitigates peel stresses

Composite adherend: 7-ply quasi-quasi isotropic laminate; 63% glass by weight

Figure 8. MTS axial-torsion test machine and test fixtures for torsional loading of composite-to-steel joint specimens.

Quasi-static torsion tests have shown that the weld bonded joints are more robust and able to sustain higher torsional loads and rotational displacements than the adhesively bonded specimens. Plots of torque versus rotational displacement for both types of joint specimens are provided in Figure 9. Photographs of an adhesively bonded and a weld bonded torsion test specimen after failure are shown in Figure 10(a) and (b). The adhesively bonded specimens typically failed via delamination of the composite adherend. The spot welds and steel doubler strip of the weld bonded specimens hold the composite together longer and reinforce the joint so that higher torsional loads can be sustained.

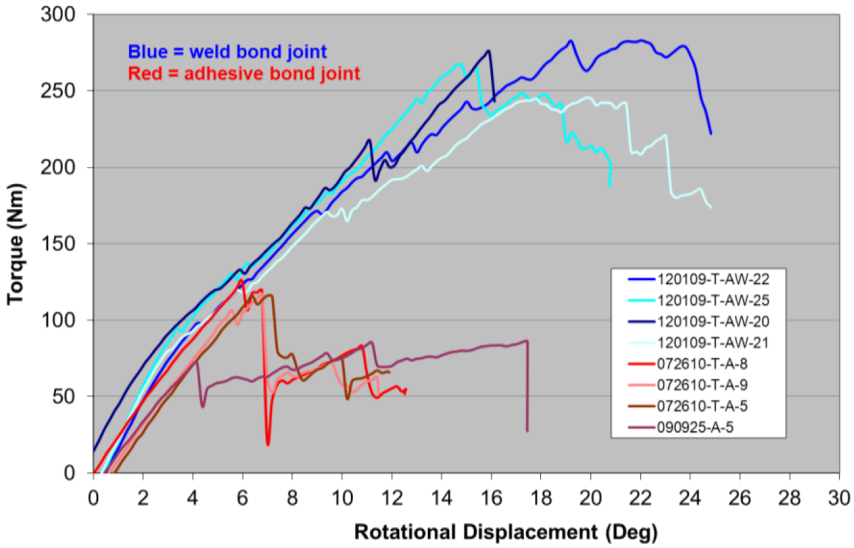
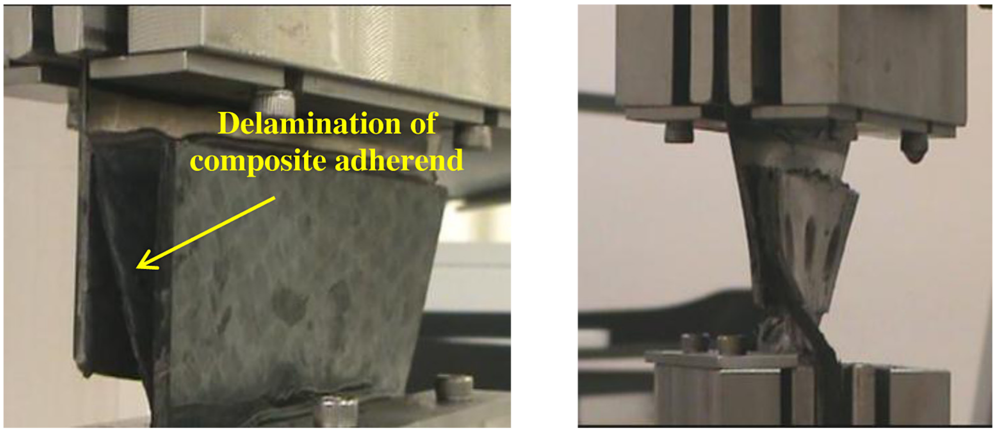


Figure 9. Quasi-static torsion test results for weld bonded and adhesively bonded joint specimens.



(a) (b)

Figure 10. Composite-to-steel joint specimens after quasi-static torsion test: (a) adhesively bonded joint and (b) weld bonded joint.

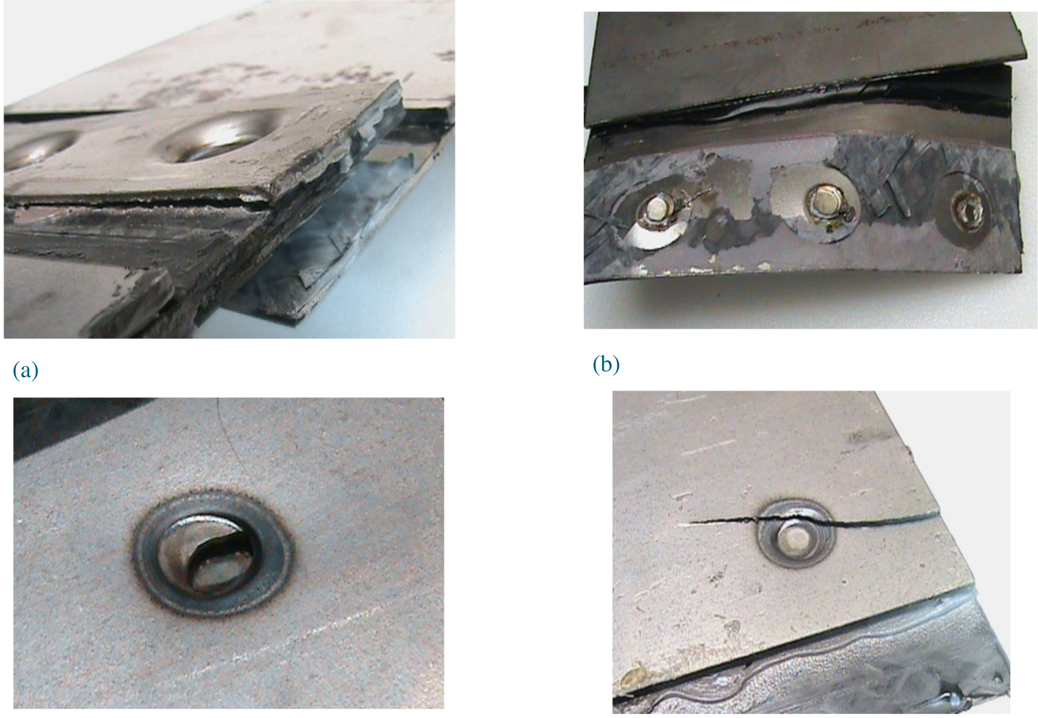
Cyclic torsion fatigue tests were conducted under both rotational displacement control and torque control conditions. Both adhesively bonded and weld bonded specimens were evaluated using these two different cyclic fatigue methods. Joint loading in most cases was defined to be fixed plus-and-minus rotational displacement (or torque) set points. That is, the specimen is rotated first in one direction from a neutral (unloaded) position to the defined set point. Rotational direction is then reversed to bring the specimen back to the neutral position and then beyond that position until it reached the same magnitude set point in the opposite direction.

Under conditions of rotational displacement control, specimens register a progressive loss of stiffness with increasing cycle number, indicating damage accumulation over time. In these tests, torque continues to decline with cycle until the test is terminated.

Under conditions of torque control, damage accumulation and loss of stiffness are compensated for by increased rotational displacement to maintain the specified torque level. Specimens accumulate increasing levels of damage until either the specimen fails and/or the test is terminated.

The initial cyclic torsion fatigue tests were conducted at frequencies of up to 3 Hz. However, large rotational displacements make controlling the hydraulic test machine difficult at this frequency. Better control was achieved when the cyclic fatigue frequency was reduced to 1 Hz. Numbers of cycles collected prior to specimen failure and/or test termination range from hundreds of cycles to more than a million cycles (defined as run-out) depending on test conditions for adhesively bonded and weld bonded specimens.

Cyclic torsion fatigue results with composite-to-steel weld bonded and adhesively bonded joint specimens indicate that this is a subassembly type test, with progressive damage occurring in multiple locations of the specimen (joint, steel adherend, composite adherend, and spot welds). Photographs of various failed weld bonded specimens are shown in Figure 11. Composite delamination and adhesive failure have been observed in previous testing (quasi-static tensile, cyclic tension-tension fatigue) conducted with these specimens. Cracks originating in the vicinity of the spot welds have not previously been observed and are believed to be associated with the combination shear-and-peel load cases associated with this test method.



(a)

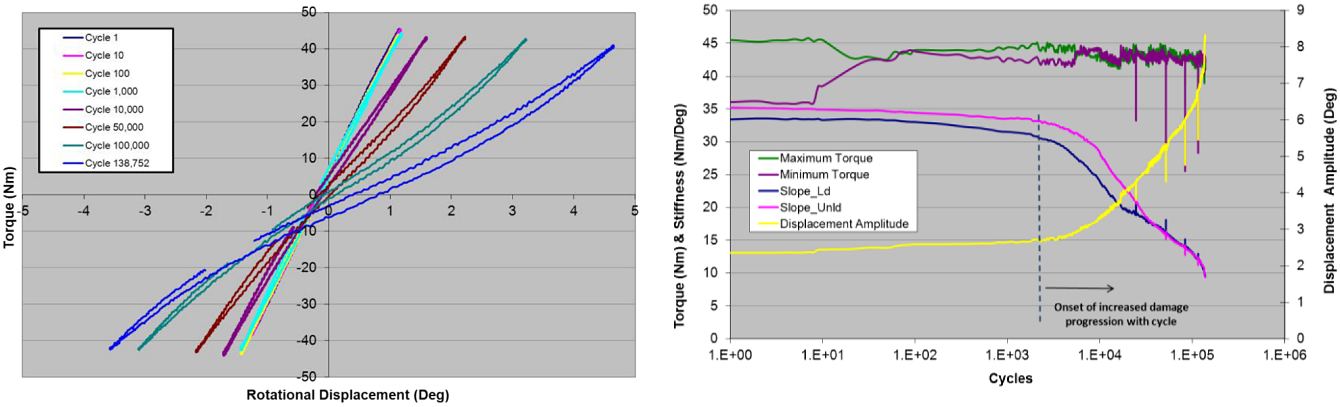
(b)

(c)

(d)

Figure 11. Cyclic torsion fatigue failures observed with composite-to-steel weld bonded joint specimens: (a) composite delamination, (b) combination delamination-adhesive failure, (c) spot weld, and (d) crack in the vicinity of a spot weld..

Examples of types of cyclic torsion fatigue data collected during testing are provided in Figure 12. Plots of rotational displacement, torque, stiffness, and displacement amplitude versus cycle aid in monitoring damage progression in the specimen prior to failure and/or test termination.



(a)

(b)

Figure 12. Cyclic torsion fatigue data collected for composite-to-steel weld bond specimen (± 42.4 Nm, 1 Hz): (a) rotational displacement versus cycle and (b) torque, stiffness, and displacement amplitude versus cycle.

Low amplitude cantilever bend fatigue tests have been demonstrated with composite-to-steel weld bonded specimens for millions of cycles. The maximum fatigue loads were set below the predicted fatigue threshold for steel, and none of the specimens showed detectable signs of peel or other damage at the weld bonded joint. Application of higher levels of peel loading was not possible with the provided composite-to-steel specimens because the steel adherend is too thin and plastically deforms (bends) before transmitting the peel load to the joint. Plans are to characterize and evaluate the effects of peel loading on weld bonded and adhesively bonded specimens using a modified coach peel test and specimens assembled by ORNL.

Multimatic Inc. conducted analyses in which the quasi-static structural torsion test data were simulated for test analysis correlation and modeling method development. Analyses included the cases for weld bonded composite-to-steel joint specimens and comparative specimens made of steel and aluminum (Al).

Composite underbody prototypes were laid up and molded by the ACC and assembled for destructive testing and model validation by the ACC and Multimatic, Inc. These composite underbody prototypes have been proposed for the purpose of providing the 3D composite joint specimens for this project once destructive testing is completed.

Plans are to assess the condition and potential of the composite underbody sections that remain following these destructive tests. If suitable, an appropriate durability test method will be selected, test fixtures will be designed and fabricated, and durability testing will proceed.

Conclusions

Test equipment and fixtures to evaluate joint specimens via torsional loading were prepared, and quasi static and cyclic fatigue tests with specimens prepared with weld bonded and adhesively bonded joint configurations were conducted. Quasi-static torsion tests have shown that the weld bonded joints are more robust and able to sustain higher torsional loads and rotational displacements than the adhesively bonded specimens. Cyclic torsion fatigue results indicate that this is a subassembly type test, with progressive damage occurring in multiple locations on the specimen (joint, steel adherend, composite adherend, and spot welds). Cyclic torsion fatigue data collected during testing aid in monitoring damage progression in the specimen prior to failure and/or test termination.

Multimatic Inc. conducted analyses in which the quasi-static structural torsion test data were simulated for test analysis correlation and modeling method development.

Application of peel loading is not possible with the provided composite-to-steel specimens using the cantilever bend test method because the steel adherend is too thin and plastically deforms (bends) before transmitting the peel load to the joint. Plans are to characterize and evaluate the effects of peel loading on weld bonded and adhesively bonded specimens using a modified coach peel test.

Composite underbody prototypes laid up and molded by the ACC and assembled for destructive testing have been proposed to provide 3D composite joint specimens for durability testing. Plans are to assess their condition and potential following these destructive tests, and if suitable, an appropriate durability test method will be selected, test fixtures will be designed and fabricated, and durability testing will proceed.

Conclusions

The predictive modeling of PMCs project has resulted in the development of a model for predicting the fiber placement, fiber orientation, resulting properties, failure loads, and failure location for direct injected LFT composites. The model was validated within 15% accuracy for 21 of the 24 samples tested and has been integrated into Moldflow. This work will be extended to make the same predictions for a 3D part. The effort to develop composite joining techniques has developed a unique “super lap-shear” specimen geometry which has been subjected to torsional loading for both quasi-static and dynamic fatigue tests. This was done for both adhesively bonded and weld bonded samples. The tests have shown that the weld bonded specimens were the superior design. Durability testing of these samples is beginning. The information from the joining effort has fed into the ACC Focal Project 4 design for an all composite underbody subsystem. All milestones on both projects were successfully met.

Presentations/Publications/Papers

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Executive Summary

The cost of producing carbon fiber (CF) is the single largest obstacle to its incorporation in future automotive systems. Fifty-one percent of the cost of producing CF is attributable to the cost of the precursor; therefore, a significant share of effort is being expended on developing lower cost precursors. The precursor development tasks include development of lignin based CF precursors, commercialization of a previously developed lower cost textile based polyacrylonitrile (PAN) precursor, and development of lower cost polyolefin precursors. Thirty-nine percent of the cost of producing CF is attributable to the cost of conversion of the precursor into CF; therefore, significant effort is being expended on developing lower cost, higher rate production technologies. Conversion work includes development of a higher speed, lower cost oxidative stabilization process and development of a microwave assisted plasma process method, which is funded under a separate program. While surface treatment and sizing account for only 4% of the cost of manufacturing CF, appropriate surface treatments and sizings targeted at automotive (not epoxy) resin systems are critical for the production of high quality automotive components. Therefore, one task is aimed at the development of CF surface treatments and sizing specifically targeted at resin systems of interest to the automotive industry.

The first task under this project addresses the cost of CF by demonstrating the use of lignin, a sustainable resource, as a new precursor material. The project is evaluating the use of low cost, high volume lignin feedstocks that have the potential to meet the demand requirements and product performance needs of the automotive market. The task goal is to demonstrate that one or more lignin based precursor formulations can be expected to produce commodity grade CFs at a selling price around \$5–\$7 per pound, with a modulus of at least 25 Msi, and with strength of at least 250 Ksi. The end of year milestone for achieving 150 Ksi strength and 15 Msi modulus was not met so this task will not be continued.

In the second task, a collaborative international program led by ORNL and Fibras Sinteticas de Portugal S.A. (FISIPE) is working to render textile based PAN suitable for conversion into CF on a commercial scale. Use of textile fiber, which sells for half the cost of conventional CF precursors, would result in a savings of more than \$2.00 per pound for finished CF.

The third task is aimed at developing the technology for the production of low cost CF (LCCF) from melt spun polyolefin precursor fibers. Polyolefin based fibers are industrially produced in the United States and are very low cost commodity plastic fibers (\$0.50–\$0.70 per pound). The cost of precursor fibers from polyolefin is projected to be less than half of that of the PAN based precursor fibers, yet the carbon yield will be significantly higher than with PAN precursors. The combination of lower raw material cost, higher material yield, and process savings from melt spinning of the precursor makes the polyolefin precursor the most cost advantageous alternative.

The fourth task is aimed at developing a plasma processing technique to rapidly and inexpensively oxidize PAN precursor fibers. Conventional oxidation is a slow thermal process that typically consumes more than 80% of the processing time in a conventional CF conversion line. A rapid oxidation process could dramatically increase the conversion line throughput

and appreciably lower the fiber cost. A related project has already demonstrated the potential for significantly accelerating carbonization. To supply developmental quantities of fiber, a significant upgrade to the ORNL CF pilot line is being conducted as the fifth project.

The quality of the fiber-matrix interface is often a critical factor in determining composite mechanical properties and durability. CFs are typically surface treated and sized to make them compatible with aerospace resin systems. The final task under this project is aimed at developing surface treatments and fiber sizings that will make CFs compatible with vinyl ester and nylon. Research at ORNL is targeting the control of surface functional groups, the creation of highly energetic surfaces, and the development of appropriate sizings.

Figure 1 shows a breakdown of CF production costs and the range that each of these tasks affects in the production process.

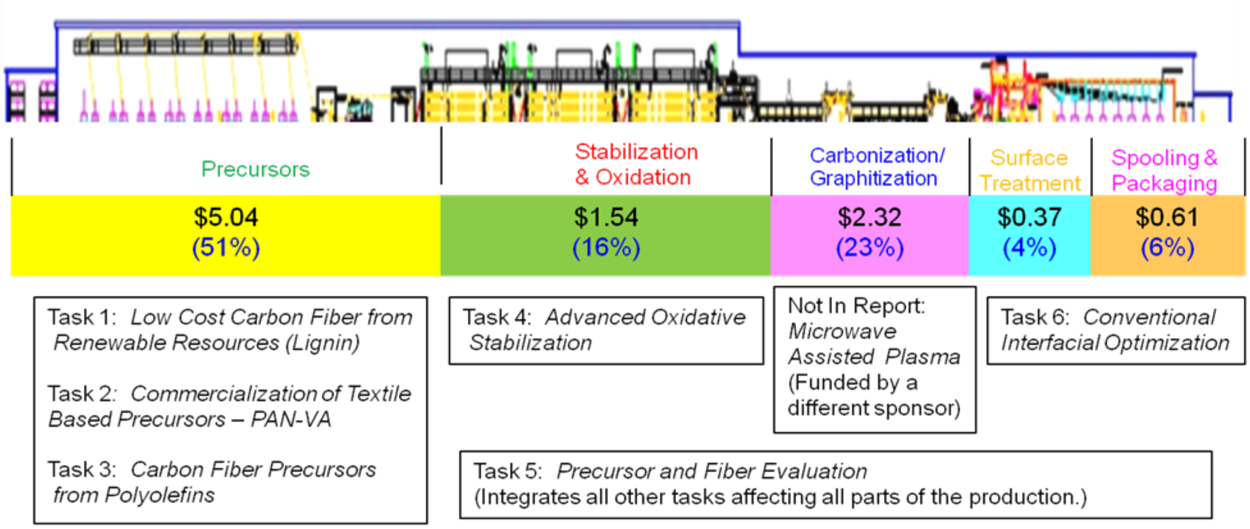

Figure 1. Role of LCCF development program tasks in the CF production process. (Base diagram courtesy of Harper International.)

The strategy for transitioning each of these technologies to industry is to involve industry as early in the development process as is practical from the risk-benefit standpoint. It is realized that trying to incorporate multiple technologies into production lines simultaneously would be a very high risk for industries; therefore, the project teams seek to involve industry in each of the tasks as the particular technologies involved become sufficiently mature to be of interest for commercialization. Textile precursors, for example, have reached that level of development, and thus, both precursor manufacturers and CF manufacturers are now involved. The lignin and polyolefin precursor development efforts are premature for precursor and carbon manufacturers but are far enough along for raw material suppliers [lignin and polyethylene (PE)] to be involved. The advanced oxidation task is nearing a maturity stage to involve oxidation oven manufacturers and the surface treatment and sizing development efforts. This effort also has automotive suppliers involved.

Low Cost Carbon Fiber from Renewable Resources

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Partners: Kruger Wayagamack, Innventia, Metso Corporation, Lignol Innovations

Accomplishments

- Determined the mechanisms and relationships that make lignins melt spinnable and cross-linkable.
- Reduced the oxidative stabilization time of lignins from days down to 15 minutes.
- Determined the carbonization protocol for converting lignin precursors into CF.

Future Plans

- This project will not be continued under the Lightweighting Materials program due to missing the end of year mechanical property milestone metric.
- ORNL has other related work toward developing lignin based precursors.

Technology Assessment

- Target: Develop low cost, melt spinnable CF from lignin, a renewable resource that is less expensive than other CF precursors and meets program mechanical property goals.
- Gap: CF is too expensive for many automotive applications, and the cost of the precursor contributes 51% of the CF cost.
- Gap: Current CF precursors are from petroleum based sources and a precursor from a renewable resource is needed.

Introduction

This project sought to reduce the cost of CF by demonstrating the use of lignin, a sustainable resource, as a new precursor material. The project evaluated the use of a low cost, high volume lignin feedstock that has the potential to meet the demand requirements and product performance needs of the automotive market. The project goal was to demonstrate that one or more lignin based precursor formulations can produce commodity grade CFs at a selling price of around $5–$7 per pound with a corresponding modulus of at least 25 Msi and strength of at least 250 Ksi.

Approach

The development of lignin based precursors must first be accomplished using laboratory-scale equipment and pilot-scale melt spinning and CF production lines. The project proposed constructing the technical database necessary to facilitate commercial production of lignin based CF, including knowledge of (1) isolation and purification of lignin to obtain appropriate precursor properties for CF production; (2) melt spinning technology, including compounding/pelletization of precursor feed material, extruder and spinneret configuration, spinning conditions, copolymers, and plasticizing agents; (3) thermal processing of precursor fiber into CF; (4) advanced processing of lignin based CF; (5) mechanical properties of lignin based CFs; and (6) surface treatment and sizing for relevant resin systems, and, finally, developing process flow sheets and economics for lignin based CF production for presentation to companies considering entering the business of lower cost CF production.

This task sought to develop materials and methods for the manufacture of lignin based CFs. Industrial partners and collaborators included Lignol Innovations (Vancouver, British Columbia, Canada); Kruger Wayagamack (Trois-Rivières, Quebec, Canada); INNVENTIA, formerly STFI Packforsk (Stockholm, Sweden); University of Tennessee (Knoxville); and the Institute of Paper Science and Technology at the Georgia Institute of Technology (Atlanta).

Results and Discussion

Influence of Lignin Chemistry on Spinnability and Precursor Fiber Stabilization

Lignins comprise three distinct monomers, methoxylated to different degrees, in various combinations: coniferyl alcohol, p coumaryl alcohol, and synapyl alcohol. Softwood lignins comprise predominantly coniferyl alcohol (90%), with the lowest degree of methoxylation, and the balance p-coumaryl alcohol; in contrast, hardwood lignins (HWLs) comprise a mixture of coniferyl alcohol and synapyl alcohol in various proportions. Figure 2 shows representative structures of softwood (G-type) and hardwood (S-type) lignins with a broad generalization on how the different types influence melt spinnability on one hand and stabilization (cross-linking) of the fiber on the other hand. In summary, the additional methoxy group present in the syringyl phenylpropanoid of HWL apparently renders the lignin readily melt spinnable (exhibits well defined melting point); on the other hand, it also inhibits intermolecular cross-linking of the lignin. The challenge regarding the tailoring of lignin chemistry is to obtain, in a single lignin material, the positive characteristics of hardwood and softwood lignins.

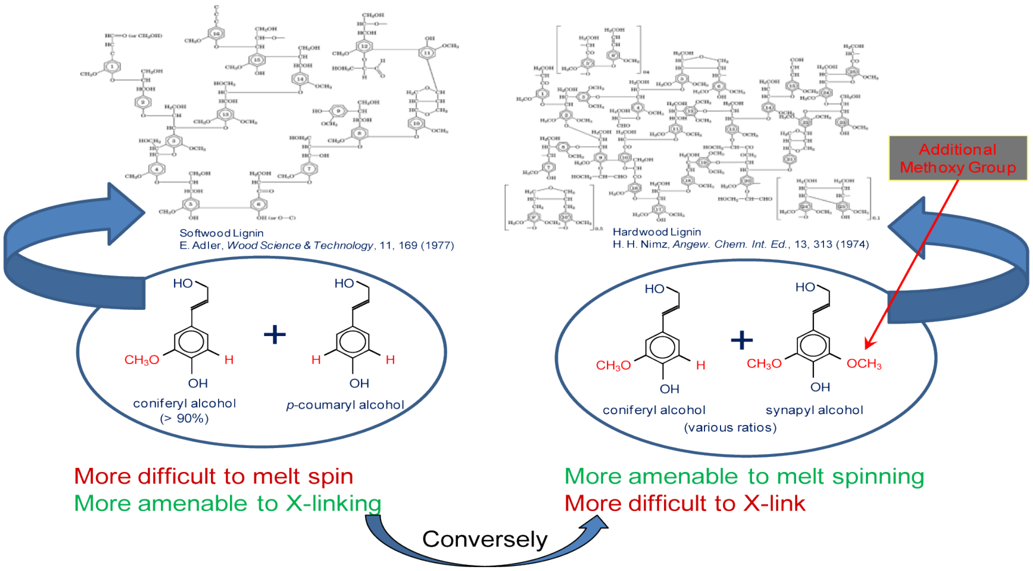

Figure 2. Influence of lignin chemistry on spinnability (broad generalization).

Influence of Fiber Stabilization Heating Rate on Carbonization of Lignin Fiber

Extensive studies of the influence of various process parameters on the subsequent carbonization of lignin precursor fibers were made. To illustrate the dependency of subsequent steps of CF production on preceding steps, data for the yield of carbon from two lignin materials are shown in Figure 3 as a qualitative function of the rate of heating for the stabilization step (the specific heating rates used for the construction of this figure have been deleted to comply with Export Control regulations). The data are expressed as the yield of carbon, at 1000°C, based on the "green" (as spun) fiber.

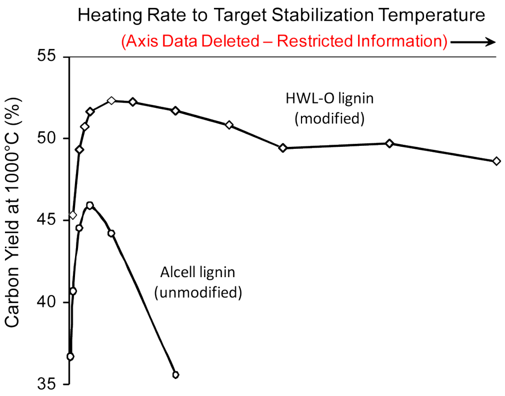

Figure 3. Carbon yield as a function of stabilization heating rate.

It is clear from Figure 3 that, for a constant set of carbonization conditions, the yield of CF from either lignin precursor fiber was significantly influenced by the rate of heating during the stabilization of the precursor fiber, most notably for the (unmodified) Alcell lignin. Carbon yield from the Alcell precursor fiber reached a maximum of about 46% at some relatively low heating rate during the stabilization step, thereafter falling off rapidly. Organically purified HWL (HWL-O) not only exhibited significantly higher carbon yields, reaching a maximum of almost 53%, but more importantly the fiber form was retained throughout the range of stabilization heating rates evaluated. The stabilization time for HWL fibers was reduced from almost 2 days to less than 15 minutes for the modified HWL-O material ramped at the fastest heating rate.

Influence of Fiber Carbonization Heating Rate on Carbon Fiber Structure (Texture)

The scanning electron microscope (SEM) images shown in Figure 4 provide an indication of how thermal processing conditions in batch-type furnaces impact the structural integrity of lignin based CFs and thereby the mechanical properties of the fibers. When the precursor fiber was carbonized relatively quickly, structurally sound CFs were obtained (left hand SEM image); in marked contrast, when the precursor was carbonized relatively slowly, many defects were introduced into the CF (right hand SEM image), which was reflected by lower mechanical properties. On one hand, this finding appears to be counterintuitive because the more slowly one ramps up the temperature of the stabilized precursor fiber, the greater is the time for diffusion of the volatile by products of carbonization through the bulk of the emerging CF. On the other hand, though, the more slowly one ramps up the temperature, the greater the time and temperature range over which the CF is exposed to gasification conditions (i.e., to volatile by-products that are oxidative in nature such as H_2O and CO_2, which burn away carbon to create the detrimental porosity seen in the fiber in the right hand SEM image in Figure 3).

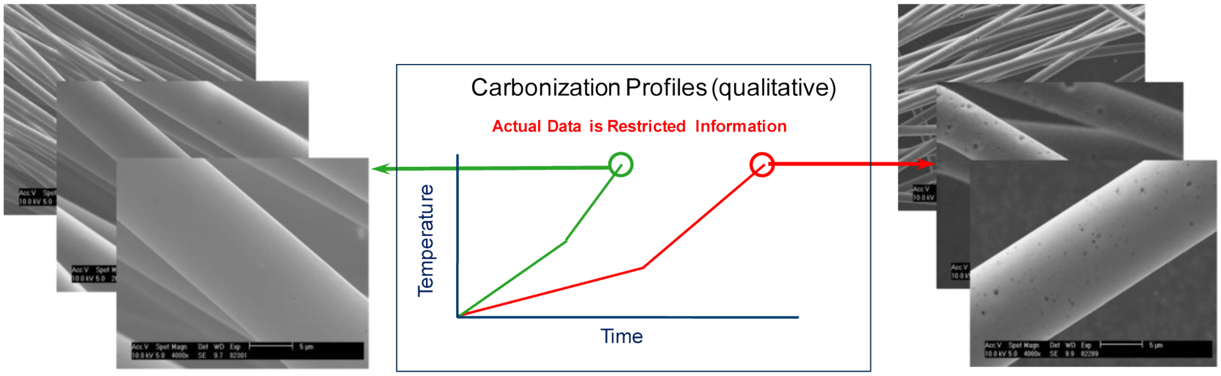

Figure 4. Influence of carbonization heating rate on structure of CF.

Graphitization of Lignin Based Carbon Fiber

Recent x-ray diffraction (XRD) studies in which axial and radial scans of lignin- and PAN-based CFs were made revealed the root cause of the lack of relationship between degree of fiber graphicity and modulus. An example of the axial and radial XRD data obtained on a lignin based CF heat-treated to 2,700°C is shown in Figure 5.

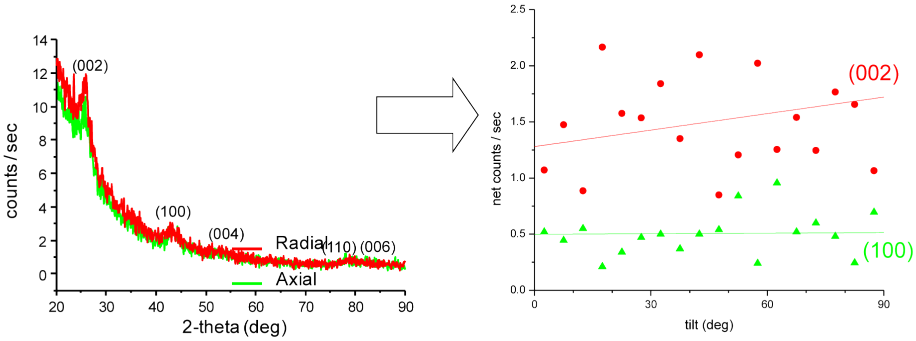

Figure 5. Axial and radial XRD patterns for lignin based CF.

The diffraction patterns in Figure 5 indicate that there was a low degree of preferential orientation of the graphite crystallites along the axis of the CF. The corresponding XRD data for the commercial T300 PAN based CF, shown in Figure 6 for comparison purposes, clearly show the preferential alignment of the graphitic structure, which is critical for attainment of good modulus.

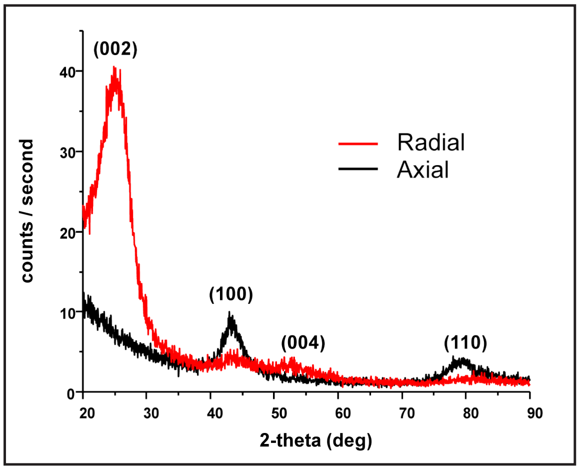

Figure 6. Axial and radial XRD patterns for PAN based CF.

Thus, even though a highly graphitic structure is created in a lignin based CF heat-treated at high temperature, and more than a commercial PAN based CF that meets the target mechanical properties for automotive applications, preferential alignment of the graphite crystallites along the lignin CF axis is not being obtained.

Mechanical Properties of Lignin Based Carbon Fiber

The average tensile strength and tensile modulus of lignin based CF produced to date are 155 Ksi and 12 Msi, respectively. This summary information is based on measurements of the mechanical properties of 25 single fiber specimens of a given batch of CF. In a few instances, tensile strengths of individual single fiber specimens approached 175 Ksi. The highest values were obtained with softwood lignins.

A proposed path forward to overcome these processing obstacles was presented to the DOE Vehicle Technologies Program (VTP); however, the project will not be continued.

Conclusions

Lignin sources have been identified which meet the purity qualifications required for making CF. Barriers to making a satisfactory lignin CF precursor are primarily related to maintaining the positive attributes of hardwood and softwood lignins while minimizing the negative attributes of each (melt spinnability and cross-linkability). Rapid stabilization methods have been developed and carbonization protocols determined. To obtain the molecular alignment necessary to develop elevated properties, significant work still remains. This work will not be continuing under the Lightweighting Materials program.

Scale-Up of Textile Based Precursors—Textile Polyacrylonitrile–Vinyl Acetate

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Accomplishments

- Completed validation of full-scale development of a textile PAN precursor with FISIPE. Supported efforts to improve tow-splitting technology of textile precursors for reducing tow sizes in the precursor plant.
- Validated that fiber being produced on the production line had achieved program targets. Achieved fiber properties for strengths of 540 Ksi on full-scale tows of carbonized textile PAN precursors (program requirement is 250 Ksi). Achieved modulus property values of 38 Msi, which are well above the program goal of 25 Msi.
- Consulted with the multiple partner companies on the applicability of FISIPE precursors in their manufacturing systems, and provided small samples to several companies to assist in their evaluations of FISIPE precursor potential.
- Working with FISIPE, developed methods for air-gap spinning of its precursor to provide rounder fibers which will have greater compressive stress strength.
- Provided assistance in scale-up of production facilities to commercially produce textile based CF precursor and aid current and future CF producers in the incorporation of new textile precursors into manufacturing plants.

Future Directions

- Produce product development quantities of carbonized fiber from the FISIPE precursor as part of the ORNL Carbon Fiber Technology Facility (CFTF) validation.
- Integrate the textile precursor into the Advanced Oxidation project to get the combined cost savings of using both a lower cost precursor and a lower cost conversion method.
- Pursue commercialization of lower cost textile based precursors with current industrial CF suppliers and potential future CF suppliers to high volume industries.

Technology Assessment

- Target: Scale to production quantities the lower cost precursor that has been developed in this task.
- Gap: Production of sufficient quantities of material to enable product development by commercial companies.

Introduction

Over the past few years, the DOE Lightweighting Materials program has been developing technologies for the production of lower cost CF for use in body and chassis applications in automobiles. Program requirements target materials that have tensile strengths in excess of 250 Ksi and moduli of at least 25 Msi. Past work included the development of alternate lower cost precursors and alternate lower cost methods for manufacturing precursors into finished CF. The purpose of this project is to take one precursor technology, textile based PAN, from the technical feasibility stage and scale up to high volume manufacturability on a large volume textile line. The technology being pursued for the textile based precursor is the chemical modification of textile PAN containing vinyl acetate (VA) using a proprietary solution bath while the fiber is still in the uncollapsed state.

This project has resulted in the determination of the optimum concentration-temperature-exposure profiles to render the fiber carbonizable by conventional processes and also readily and inexpensively manufactured in existing textile PAN plants. Successful completion of this project will result in a manufacturer being ready to sell precursors to CF converters and ORNL providing specific instructions for precursor conversion to those producers, subject to export control limitations. Deliverables include spools of partially or fully carbonized CF and verification of mechanical properties.

Approach

Previously, under a separate contract as part of the Automotive Lightweighting Materials program, Hexcel Corporation developed the basic science necessary to render textile based PAN polymers carbonizable. That science included subjecting the textile precursor to a chemical pretreatment bath while the fiber was still in the uncollapsed state. That work was conducted offline from the textile fiber manufacturing. Fiber samples were split off from the line by hand, packaged, and processed in Hexcel's laboratory. Hexcel obtained satisfactory samples but under only one set of processing conditions and with one specific textile fiber. Certain issues needed to incorporate the technology into manufacturing plants were not addressed but are being addressed for VA containing precursors in this project.

Results and Discussion

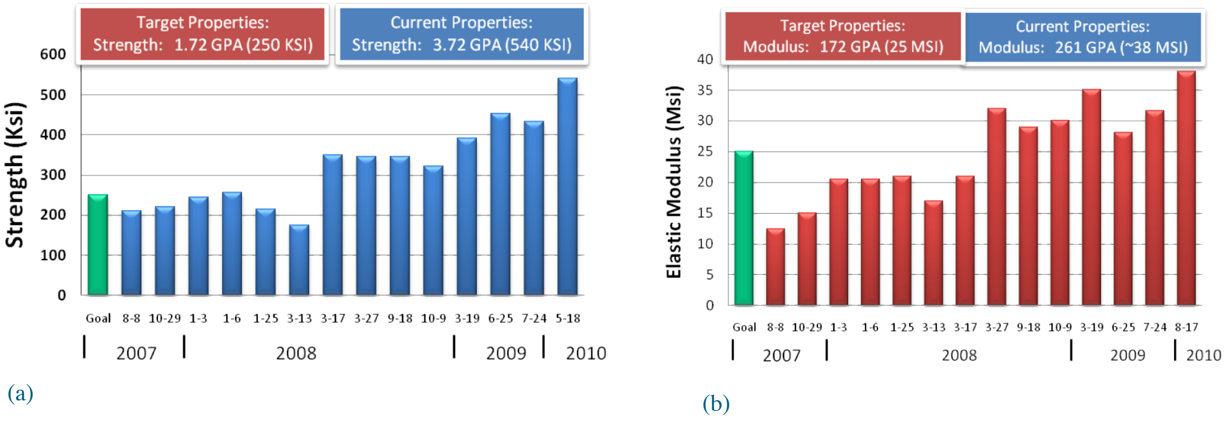
ORNL has established a partnership with a Portuguese textile fiber manufacturer, FISIPE, which produces VA-comonomered PAN for textile applications. FISIPE is a high volume manufacturer that produces a commodity fiber that is roughly one-half the cost of conventional acrylic CF precursors. Our efforts are aimed at developing a chemical pretreatment to be added in their manufacturing line to render one of their textile formulations oxidizable, carbonizable, and satisfactory as a CF precursor.

During this reporting period, FISIPE has formulated and spun production quantities of precursor fiber variants (examples shown in Figure 7) and provided extensive samples to ORNL for conversion and evaluation. FISIPE also processed (Figure 8) and evaluated larger size tows internally as part of its scale-up efforts. Note the golden color of this precursor fiber, which differs from the traditional white color of typical CF-grade PAN. The color is indicative of the specialized pretreatment that was developed and implemented by ORNL and FISIPE and is key to the success of this alternative product.

Figure 7. Textile tow precursor as produced by FISIPE and supplied to ORNL on spools for evaluation.

Figure 8. Textile tow precursor as produced by FISIPE and evaluated internally.

ORNL previously used both the precursor and fiber evaluation line and the pilot line to determine time-temperature-tension processing profiles for the FISIPE precursor. Program requirements are to develop fibers with strengths of at least 250 Ksi and moduli of at least 25 Msi. Figure 9 shows the evolution of the strength and modulus during development of processing conditions over time. We have currently reached strengths of 540 Ksi, which exceed program goals, and a modulus value of 38 Msi, which is well above program goals. Property levels have varied, and significant effort is being devoted both to achieving these property levels consistently at the small scale and to establishing robust processes capable of reproducing these properties as the process is scaled up for production.



(a)

(b)

Figure 9. Strength (a) and modulus (b) data from FISIPE precursor converted and tested at ORNL showing substantial improvement trends.

The capabilities and approach developed and demonstrated in this project can be applied to facilitate both the industrial scale-up and the commercialization of the FISIPE precursor and of other precursors.

Conclusions

The development of VA-PAN textile precursors has been a success. Strength values (540 Ksi) exceed program requirements (250 Ksi), and modulus values (38 Msi) are above program requirements (25 Msi). The chemical pretreatment equipment has been installed in the production facility and final verification of production-quality material has occurred. FISIPE is pursuing additional support for its ongoing commercialization efforts.

Carbon Fiber Precursors from Polyolefins

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Accomplishments

- Produced a polyolefin based CF with a maximum tensile strength of 201 Ksi and a modulus of 21.6 MSI (targets for this year were 200 Ksi strength and 20 Msi modulus).
- Successfully resolved the issue of incomplete functionalization of the fiber core and interfilament bonding during thermal treatment identified in FY 2010.
- Completely eliminated the problem of interfilament bonding for >10 μm diameter filaments.

Future Directions

- Discern the effect of the precursor molecular orientation (i.e., fiber draw ratio) on the mechanical properties of the resulting CF. This approach, along with generation of stronger precursor fibers, will enable the team to completely meet the milestone (200 Ksi, 20 Msi) within the coming months.

Technology Assessment

- Target: Produce a polyolefin based CF with a tensile strength of 250 Ksi and a tensile modulus of 25 Msi at 1% ultimate strain or above by the end of FY 2012 that will be lower cost than PAN precursors.
- Gap: Application of tension during carbonization is limited by knots tied at the ends of spliced-in samples and not the inherent strength of the fiber. Production of stronger precursor fibers with less deterioration in properties, after functionalization, and process parameter optimization for fibers with anisotropy will be required to address this gap.
- Gap: CF precursors contributed to half of the cost of CF. Lower cost precursors are needed.

Introduction

The goal of this project is to develop the technology for the production of LCCF from melt spun polyolefin precursor fibers. At present, industrial CFs are produced from PAN based precursors. PAN based textile precursors are a potential candidate for LCCFs, with projected cost savings of about $2.00 per pound for finished CF. Currently, however, there are no domestic producers of textile PAN and supply and price stability could become an issue. Textile fibers are solution spun and the manufacturing process involves multiple unit operations to produce the precursors. Also, in solution spinning the mass throughput rate is significantly less than that of the relatively simpler conventional melt spinning process. Polyolefin based fibers (PE and polypropylene) are industrially produced in the United States and are very low cost commodity plastic fibers ($0.75 per pound). Polyolefin fibers have carbon fiber yields of 68% compared to polyacrylonitrile fibers which have 48% yields. The higher yield further increases the cost savings potential of polyolefin based precursors. The cost of precursor fibers from polyolefins is projected to be less than half that of the PAN based textile precursor fibers. Because polyolefin fibers are thermoplastic, a stabilization route involving crosslinking of the polymer need to be developed to render the precursor fibers infusible prior to carbonization. In subsequent carbonization steps, optimal processing parameters need to be identified to develop the desired CF morphology and properties.

Approach

The technical approach in developing carbonized filaments from a melt-processable precursor involves modification of the filaments by a chemical reaction to render them infusible. In the case of PAN based fiber, thermal oxidation (incorporation of oxygen heteroatoms in the polymer) cross-links the fiber and increases the glass transition temperature above its pyrolysis temperature. For polyolefin fibers, chemical functionalization is required after melt spinning to form a thermoset plastic. This may be achieved either by modifying the polyolefin resin before spinning without affecting its melt rheology (spinnability) or by modifying the fibers after spinning.

An accelerated functionalization method is being developed to meet the above objective. A chemical reactor was constructed for continuous functionalization of the precursor fibers. The target functionalization time is 1 h or less because the residence time inside the reactor is important for high volume viability of this technology.

Carbonization trials under various operating conditions and optimization of processing parameters are under way to tailor the fiber morphology and properties. Tensile properties of the filaments have been measured and thermal analyses, in addition to analyses by electron micrographs, have been conducted at each fiber processing step to understand thermochemical changes in the filaments. Critical technical criteria of this technology include achieving ≥25 Msi tensile modulus, ≥250 Ksi breaking strength, and ≥1.0% ultimate strain in the finished fiber by the end of FY 2012.

Results and Discussion

Functionalization of polyolefin fibers is a key step for stabilization prior to pyrolysis. Multiple parameters in this step affect final CF properties. In FY 2010, a gradient heteroatom (S) concentration across the filament radius resulted in a mixture of solid and hollow CFs, and the issue of incomplete functionalization of the fiber core was identified as one of two major obstacles. To understand and overcome this issue, the reaction kinetics of functionalizing polyolefins as a function of temperature and reagent concentration were investigated using proper analysis tools.

The degree of functionalization and carbon yield were readily determined by analyzing a piece of the fiber using thermogravimetric analysis (TGA). TGA curves of representative partially functionalized PE fiber and completely functionalized PE fiber are shown in Figure 10 and Figure 11. Initial loss where the derivative peak ranges from 160°C to 175°C corresponds to the loss of functional groups on PE fiber, and the second weight loss at the derivative peak for 450°C–480°C corresponds to degradation of PE, which was confirmed with TGA. If the degradation of PE around 450°C–480°C was not observed in TGA (Figure 11), the functionalized fiber would have been fully stabilized. The weight loss up to 400°C was assigned as a weight fraction of functional groups and used to calculate the degree of functionalization. The degree of modification of precursor was represented as a weight ratio of functional group/PE (wt/wt) repeat unit. Kinetic plots for one representative PE are depicted as sulfonate/PE (wt/wt) and char yield (%) in Figure 12.

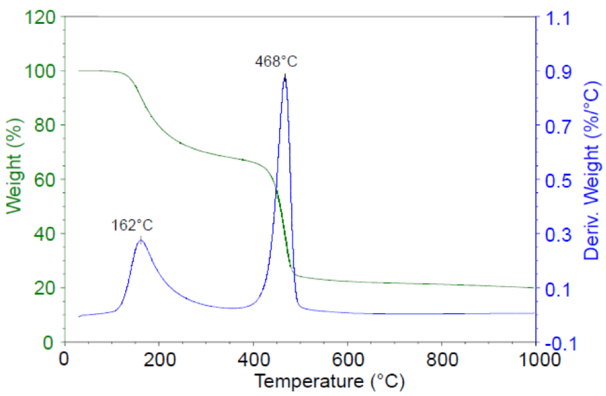


Figure 10. TGA of partially functionalized PE fiber.

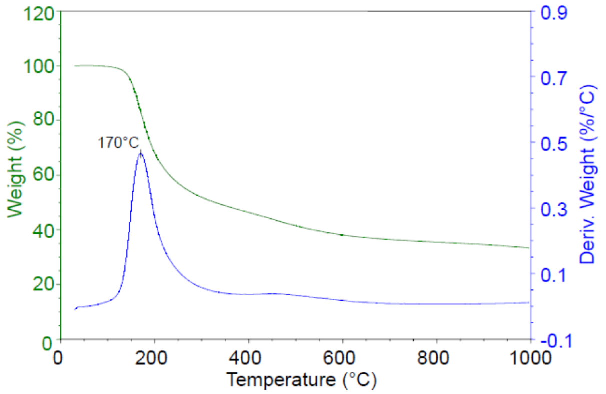
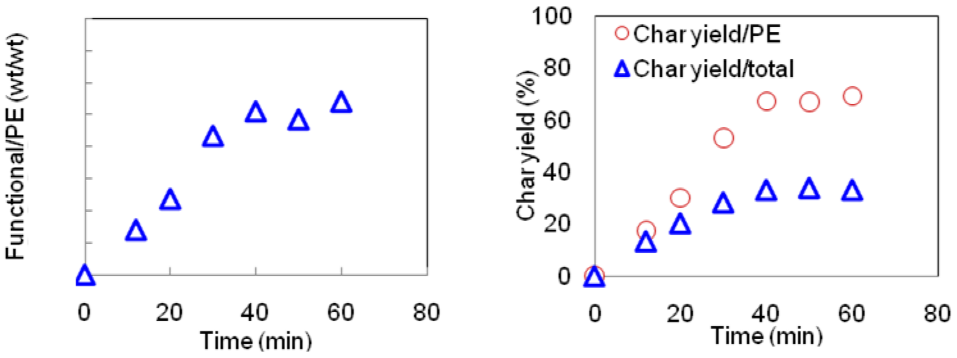


Figure 11. TGA of fully functionalized PE fiber.



(a)

(b)

Figure 12. Functionalization of PE fibers in wt/wt basis (arbitrary scale) (a), and char yield data (b) as a function of reaction time at undisclosed conditions.

Functionalization of any type of PE fibers with various degrees of crystallinity reaches very similar degrees of functionalization at the end. When all PE in the fiber from surface to core is functionalized (typical TGA profile in Figure 11), functionalization is complete. Partially functionalized PE fiber correlates well with diffusion of the reactant, which has been confirmed by elemental mapping and the resulting hollow CFs (annual report for FY 2010). In addition, the char yield of functionalized fibers in TGA agrees very well with the kinetic plot, which confirms that functionalized PE yielded carbon char and unfunctionalized PE was burnt off. When fully functionalized PE fibers are carbonized, the formation of hollow CFs was eliminated.

As reported in the annual report for FY 2010, functionalized polyolefin fibers showed inconsistent functionalization mainly due to failure to control reagent concentration. Functionalization kinetics decrease significantly as reagent concentration decreases. An accurate method for determination of reagent concentration was developed and used to determine reagent concentration in each functionalization reaction. The reactor design was adjusted to provide better control of reagent concentration (Figure 13). (For proprietary reasons, detailed descriptions are not given here.) The new reactor design; monitoring reagent concentration; and functionalization kinetic study as a function of time, temperature, and reagent concentration enabled the production of fully functionalized polyolefin fibers in a continuous manner. Thus, developing a method for controlled reaction of the precursor is one of the major accomplishments of FY 2011. Based on functionalization kinetic studies with various sources of PE fibers it was concluded that morphology of PE significantly alters the kinetics.

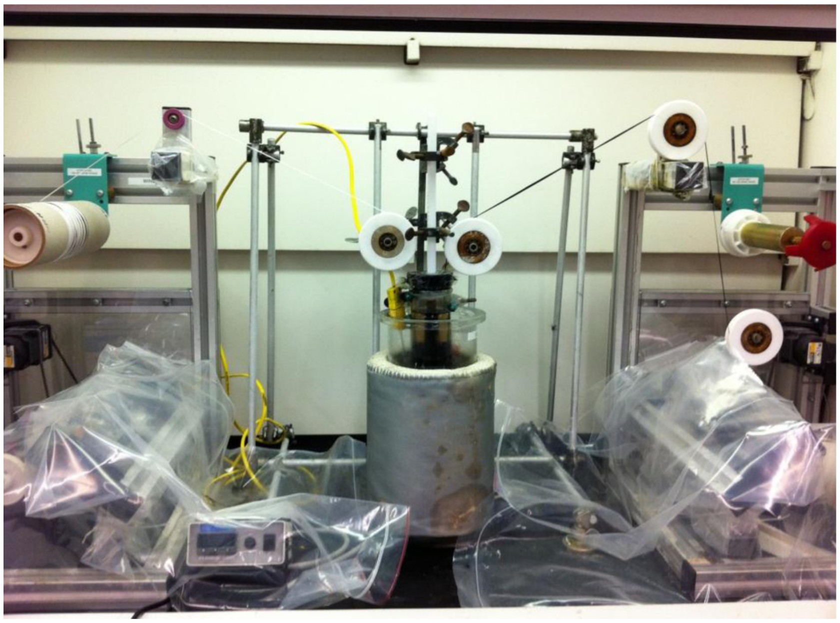


Figure 13. Continuous functionalization reactor assembly. White fiber is polyolefin fiber and black fiber exiting the reactor is functionalized polyolefin fiber.

The issue of interfilament bonding during thermal treatment was identified as one of two major obstacles in FY 2010. This is particularly true of filaments with smaller filament diameters, which impose increased hydrogen bonding and subsequent interfilament bonding during thermal treatment. To overcome this issue, various methods prior to carbonization were investigated. After undertaking numerous studies, optimized fiber treatments were identified and interfilament bonding, even with small diameter fibers, has been eliminated. Successfully prepared functionalized fibers without bonding between filaments can survive higher tension during carbonization, and the load applied to the bundle of fibers is distributed evenly.

Applied tension in each step strongly influences final CF properties. Tension during functionalization and post treatment prior to carbonization were varied. Due to the reactor modification, significant tension could be applied during functionalization of PE fibers, while almost no tension could be applied in previous reactor designs in FY 2010. Thermomechanical analysis (TMA) has been used to analyze how much tension it takes during heat treatment before carbonization of larger quantities in a furnace. The thermal response of functionalized polyolefin fibers under tension in TMA corresponded very well with the thermal degradation profile obtained from TGA. Tension, temperature, residence time, processing method, and reagent concentration have been varied to obtain optimum conditions to produce CFs with high mechanical strength, and investigation of each parameter affecting final CF properties will continue in FY 2012.

The tensile properties of the precursor filaments at various stages are summarized in Table 1. The tensile properties of melt spun fibers can be tailored by altering draw-down ratios during melt spinning. As-spun filaments (spun drawn) were hot drawn in a continuous fashion to increase filament orientation and mechanical properties. Three different precursor fibers with different thermomechanical properties were studied. Upon functionalization of precursors A and B, carbonization trials were carried out under specific processing conditions. Tensile properties were tested using a single-filament test method. Carbonized filaments with 237 Ksi tensile strength, 11.5 Msi modulus, and 2.05% ultimate elongation were produced. (To comply with export control regulations, processing parameters are not disclosed in this report.) Another sample with a modulus of 17.2 Msi was obtained with precursor C, which has a larger diameter than the other precursors (Table 1). Work is currently under way to enhance the mechanical properties beyond what has been achieved so far.

Table 1. Mechanical properties of precursor and carbon fiber samples at room temperature.

Sample	Source	Diameter (µm)	Maximum filament stress (Ksi)	Maximum filament modulus (Msi)	Ultimate elongation (%)
Precursor A	-	9.4	2.0	0.013	>200
Precursor B	-	9.1	1.5	0.013	>200
Precursor C	-	18	22	0.15	100
Carbon fiber 1	Precursor A	12.6	91.3	4.4	2.0
Carbon fiber 2	Precursor A	10.6	86.7	6.1	1.4
Carbon fiber 3	Precursor A	11.0	97.7	8.3	1.2
Carbon fiber 4	Precursor B	10.7	121	5.3	2.4
Carbon fiber 5	Precursor B	9.3	237	11.5	2.1
Carbon fiber 6	Precursor C	15.8	129	17.2	0.76

Figure 14 shows scanning electron micrographs of CFs from precursor C. These fibers are solid as a result of complete functionalization.

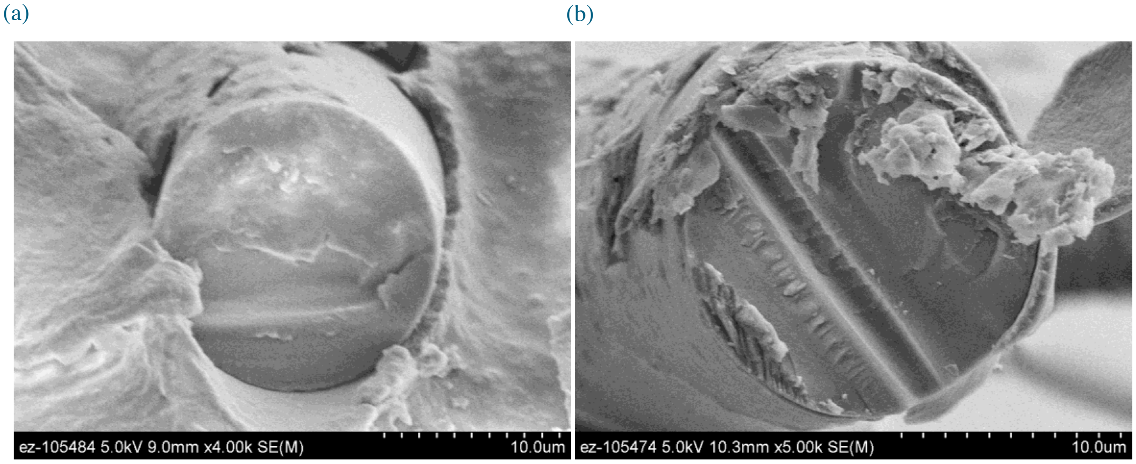


Figure 14. Scanning electron micrographs of fracture surfaces of CFs carbonized under (a) low and (b) high tension.

Conclusions

During FY 2011 significant progress was made toward the production of LCCFs from PE precursors. The effects of tension, temperature, residence time, processing method, reagent concentration to control functionalization kinetics, and tensile properties of both functionalized fibers and final CFs are partly understood. PE fibers were made infusible through continuous processing in less than 1 h, and processing parameters were optimized and will continue to be optimized to form CFs with high mechanical properties. Previously identified issues (FY 2010) of incomplete functionalization of the fiber core and interfilament bonding during thermal treatment were successfully resolved via investigation of reaction kinetics with varied temperature and reagent concentration and careful tuning of post treatment conditions. A polyolefin based CF was produced with a maximum tensile strength of 237 Ksi, while a different sample yielded a modulus of 17.2 Msi. The modulus can be improved by carbonizing long samples to avoid knots that concentrate stress at the sample ends.

Advanced Oxidative Stabilization of Carbon Fiber Precursors

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Accomplishments

- Developed new plasma based processing technique resulting in oxidation time of as little as 20 minutes for aerospace grade PAN, compared to 90–120 minutes for conventional processing, while surpassing the automotive and programmatic mechanical property requirements of 250 Ksi tensile strength, 25 Msi modulus, and 1% strain. Minimal fiber damage detected.
- Developed a new technique that is simpler in design, uses no exotic feedstocks, is easier to scale, and is safer than before.
- Successfully processed first textile grade PAN samples with new advanced oxidation technique to required density levels in 45 minutes. Mechanical property requirements met except for modulus (5% under minimum).
- Completed exhaustive fiber damage analysis in conjunction with mechanical properties analyses of aerospace grade PAN processed with the advanced oxidation process.
- Applied for two new patents involving advanced oxidation processes.

Future Directions

- Continue refining and scaling the plasma reactor design and processing protocols to achieve high speed, multiple large tow, semi-continuous (multiple pass) plasma oxidation process.
- Conduct rate-effect studies and update cost analysis.
- Incorporate alternative precursor into the newly designed system.
- Scale the process and equipment to ORNL small pilot line scale.
- Develop pre-industrial-scale oxidation oven technical specifications for integration into Carbon Fiber Technology Facility.

Technology Assessment

- Target: Develop higher rate, lower cost methods for oxidation of CF precursors.
- Gap: Conventional oxidation methods require 80–120 minutes thus limiting CF production rates.
- Gap: Conventional oxidation methods contribute significantly to CF costs and must be reduced.

Introduction

The purpose of this project is to develop a plasma processing technique to rapidly and inexpensively oxidize PAN precursor fibers. Conventional oxidation is a slow thermal process that typically consumes more than 80% of the processing time in a conventional CF conversion line. A rapid oxidation process could dramatically increase the conversion line throughput and appreciably lower the fiber cost. A related project has already demonstrated the potential for significantly accelerating carbonization. The oxidation time must be greatly reduced to effect fast conversion. This project will develop a plasma oxidation technology that integrates with other advanced fiber conversion processes to produce LCCF with properties suitable for use by the automotive industry. Critical technical criteria include (1) tensile modulus ≥25 Msi, tensile strength > 250 Ksi, and ultimate elongation in the finished fiber ≥1.0% (DOE programmatic goals); (2) uniform properties over the length of the fiber tow; (3) repeatable and controllable processing; and (4) significant unit cost reduction compared with conventional processing. This effort is aimed at further developing those technologies to be able to continuously process tows of fiber and achieve properties equivalent to industrial grades of CF. The goals also include significantly reducing the time required for oxidative stabilization (conventionally 90–120 minutes), which will permit greater fiber production rates and improved economics.

Approach

Task researchers are investigating PAN precursor fiber oxidation using nonthermal plasma at atmospheric pressure. As illustrated in Figure 15, conventional oxidative stabilization produces "core-shell" geometry with a distinct interphase between the (slowly growing) fully oxidized shell and the (shrinking) stabilized inner core. Plasma processing enhances oxygen diffusion and chemistry in the PAN oxidation process, accelerating the oxidized layer growth rate and oxidizing the fiber more uniformly, with a considerably less pronounced interface between the two regions. Previous work has shown this approach can reduce the required residence time for complete oxidation.

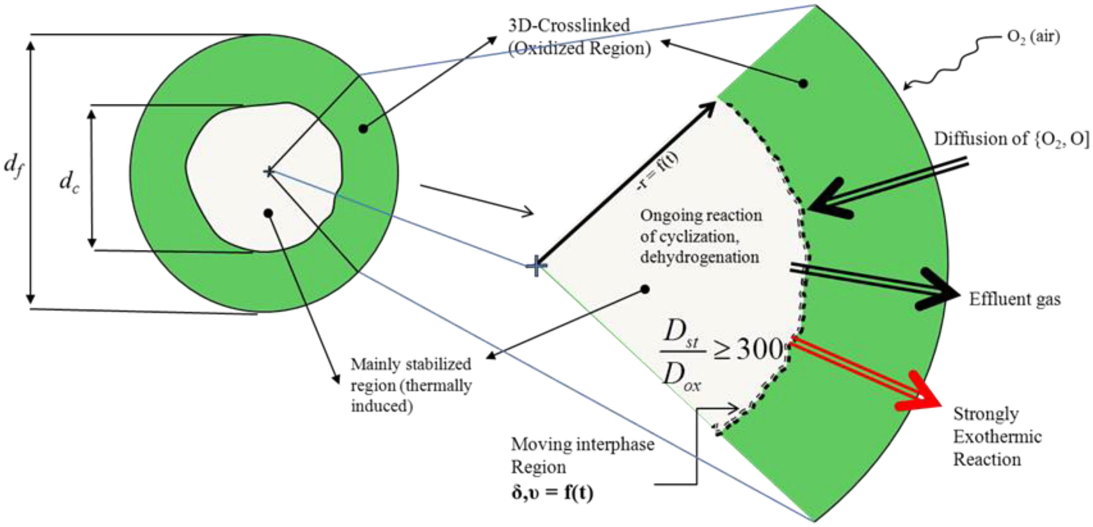

Figure 15. Single filament cross section during conventional oxidative stabilization process.

Results and Discussion

During the ongoing aerospace PAN testing in the Multiple Tow Reactor 1 (MTR1) it became evident that certain processing conditions that produced high density results at the lower residence times were also resulting in damage to the oxidized fiber. Therefore, an exhaustive study was launched to examine the cause and effect relationships of this damage. During the course of this study it was discovered that, under certain conditions, the nature of the damage being done was very unique, producing physical properties that could be beneficial for certain applications but detrimental to others. A systematic testing procedure was established to isolate the cause, and it was subsequently determined that a combination of issues was to blame for the inadequate results. During this investigation, which ran from mid-FY 2010 into early FY 2011, it was decided to try a new technique that had the potential to address the shortcomings of the MTR1 design.

Early in FY 2011, the research took a dramatic leap forward with the implementation of a new plasma based processing technique that takes advantage of thermal, chemical, aerodynamic, and geometrical properties of a different discharge method. This change resulted in the thermal environment of the furnace and the chemical environment of the plasma being integrated. Processing time so far has been reduced from 75 minutes in the MTR1 to as little as 20 minutes with the new technique for aerospace grade PAN and 45 minutes for the first samples of a textile grade PAN. All work with this new technique was accomplished using single tow processing.

Up until late in FY 2011, 3k (filaments) aerospace grade PAN was primarily used in project research to eliminate the uncertainties that are associated with 26k textile grade PAN. However, the research has now reached a point where textile PAN can be integrated to facilitate further cost reductions in the overall CF conversion process. Using textile grade PAN introduces new challenges which will be addressed going into FY 2012.

Mechanical Analysis

All oxidized PAN fibers (OPFs) of sufficient density were delivered to ORNL for mechanical characterization. ORNL performed single filament testing on part of the OPF sample, conventionally carbonized the remaining OPF, and performed further single filament testing on the carbonized samples. For reference purposes, Table 2 contains the mechanical properties of the various types of PAN based precursors used in this research. The two textile fibers in the last two rows (stretched and relaxed) have the same chemical composition. The difference lies in the stretching during the generation process, which affects the final mechanical properties.

Table 2. Mechanical properties of various grades of PAN precursor.[a]

Type[b]	Fiber diameter (µm)	Peak stress (Ksi)	Modulus (Msi)	Strain at break (%)
Aerospace	12.3	76.9	1.8	9.93
Commodity (range)	11.7–13.5	36.5–73.5	1.5–1.5	11.2–24.0
Textile (stretched)	13.0[c]	65.6	1.0	12.17
Textile (relaxed)	15.6[c]	36.7	0.6	14.02

[a] All results are from single tow processing.

[b] Aerospace grade represents a high quality fiber. Commodity grade is accepted as a medium grade fiber. Textile grade represents the range of low cost fibers.

[c] The wet spinning filament generation process of textile grade PAN results in a precursor with a kidney shaped cross section. The resulting diameter is dependent on the measurement technique used.

Table 3 highlights test results for some of the more than 160 evaluated samples of aerospace grade PAN processed using the new method and represents the bulk of the research team’s work in FY 2011. Typically, an average of 16 filaments were measured and averaged per sample.

Table 3. Mechanical properties of select samples of 3k aerospace grade PAN.[a]

Test identifier[b]	Oxidized fibers: Res. time (min)	Oxidized fibers: Fiber dia. (µm)	Oxidized fibers: Peak stress (Ksi)	Oxidized fibers: Modulus (Msi)	Oxidized fibers: Strain at break (%)	Carbonized fibers: Fiber dia. (µm)	Carbonized fibers: Peak stress (Ksi)	Carbonized fibers: Modulus (Msi)	Carbonized fibers: Strain at break (%)
ORNL aero.	75–120	13.1	42.7	1.0	14.7	7.9	359.8	29.6	1.17
Aero.	75–120	11.8	43.7	1.4	13.0	7.4	427.2	25.9	1.58
Com.	75–120	12.6	37.8	1.2	20.4	7.2	543.9	30.7	1.60
494	20	11.6	60.4	1.4	15.4	6.9	379.6	29.4	1.20
498	30	12.2	38.4	1.3	11.4	6.9	436.7	32.9	1.23
499	30	11.9	37.1	0.9	9.4	7.1	371.5	31.6	1.10
500	30	11.4	36.0	1.5	7.7	6.6	394.0	34.4	1.08
502	30	11.9	39.9	0.7	12.1	6.6	449.9	34.0	1.21
504	30	12.6	35.9	1.2	12.8	7.3	338.4	30.8	1.03
505	30	11.2	39.9	1.3	13.0	5.9	415.3	36.8	1.05

[a] All results are from single tow processing. Data highlighted in brown are for conventional processing and are displayed for comparison. Yellow highlights are the best properties achieved.

[b] Aerospace grade (Aero./aero.) represents a high quality fiber. Commodity grade (Com.) is accepted as a medium grade fiber.

Table 4 represents the most recent thrust of the research into textile grade PAN fiber, the results of which are only preliminary in nature. Three significant differences exist between aerospace grade PAN and textile grade PAN. The first is in the size of the tow. The typical aerospace grade PAN used in the research is a tow consisting of 3,000 filaments, while textile PAN tows typically comprise 26,000 filaments. The second difference lies in the chemical purity. While aerospace grade PAN is typically more than 99% pure, textile grade PAN purity is much lower. The third difference lies in the physical structure, with textile PAN having a higher percentage of morphological defects than aerospace PAN. These differences introduce additional challenges in the oxidation of textile PAN that require significant effort to overcome. The research team is in the midst of this effort, which will continue into FY 2012. The OPF mechanical properties in Table 4 indicate that the research is on the right track to achieve optimal oxidation of textile PAN.

Table 4. Mechanical properties of select samples of 26k textile grade PAN (initial trials). [a]

Test identifier[b]	Oxidized fibers: Res. time (min)	Oxidized fibers: Fiber dia. (µm)	Oxidized fibers: Peak stress (Ksi)	Oxidized fibers: Modulus (Msi)	Oxidized fibers: Strain at break (%)	Carbonized fibers: Fiber dia. (µm)	Carbonized fibers: Peak stress (Ksi)	Carbonized fibers: Modulus (Msi)	Carbonized fibers: Strain at break (%)
Com.	75–120	12.6	37.8	1.2	20.4	7.2	543.9	30.7	1.60
Text.	75–120	10.3	38.8	0.5	20.6	5.3	381.9	26.2	1.33
468[c]	45	10.1	29.3	0.9	16.6	5.3	294.7	22.6	1.17
530	45	7.0	49.4	1.2	13.5	6.1	165.0	12.0	1.33
531	45	5.97	56.2	1.4	12.9	too brittle			
532	45	8.50	36.5	1.3	9.8	too brittle			
536	45	8.81	34.3	1.0	21.9	*…Broke during carbonization (8/30/11)…*			

[a] All results are from single tow processing. Data highlighted in brown are for conventional processing and are displayed for comparison.

[b] Commodity grade (Com.) is accepted as a medium grade fiber. Textile grade (Text.) represents the range of low cost fibers.

[c] This textile grade PAN was the relaxed type, while the remaining samples were the stretched type.

Chemical Analysis

In mid FY 2011, a spectroscopic study was begun on the correlation between the chemical, physical, and mechanical properties of OPF. A review of the literature confirmed the abilty to directly relate FTIR measurements to the tensile strength, modulus, and density of OPF. The challenge of this technique lies in the capture of properties of the full cross section of the OPF filaments, not just the outer skin. A variety of measurement techniques were investigated. Preliminary relationships between various chemical bonds in the OPF and density, tensile strength, and modulus were established, but further work is necessary to verify these results.

Thermal Analysis

With the added thermal requirements of textile grade PAN, differential scanning calorimetry (DSC) is being used to characterize the degree of thermosetting of the OPF from its initial thermoplastic PAN precursor state. The results are shown in Figures 16 and 17. Figure 16 shows reference curves for the conventional oxidation of textile PAN, while Figure 17 gives a comparison of conventional to advanced oxidation. Already, in the early stage of processing textile PAN, we are achieving nearly the same degree of thermosetting in half the time of conventional processing.

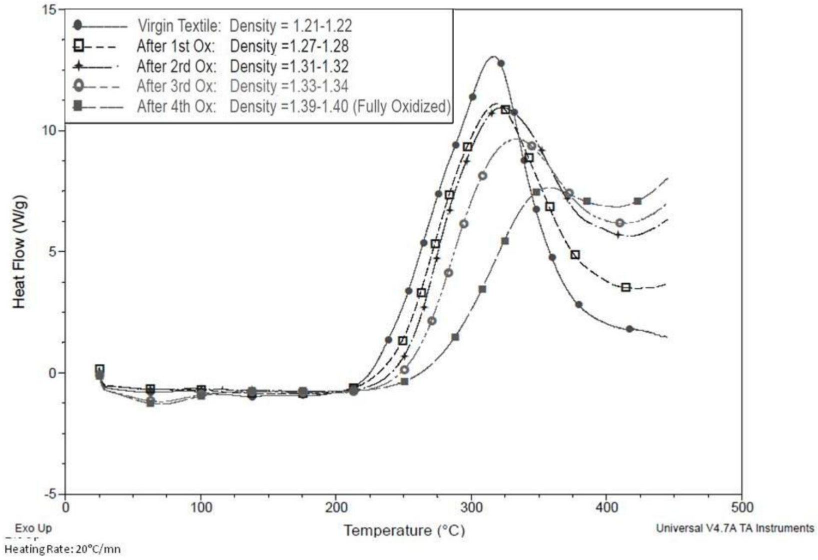

Figure 16. DSC plots of various stages of conventional oxidation for textile grade PAN. Density in grams per cubic centimeter for each stage is noted in the legend.

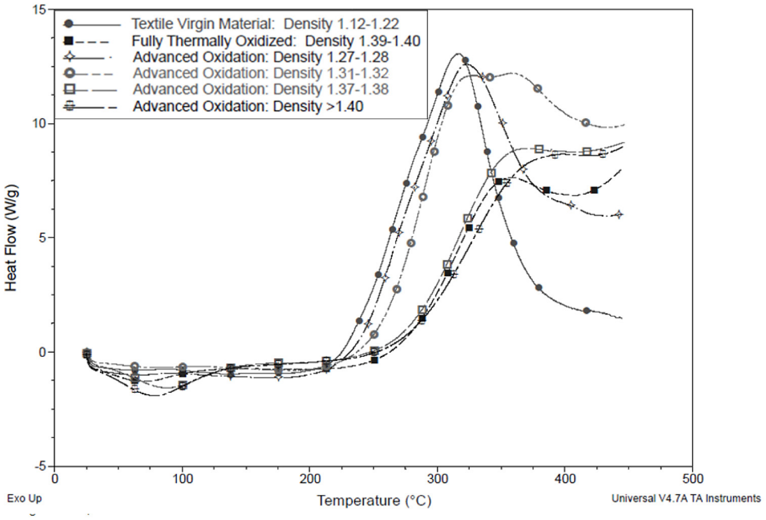

Figure 17. DSC plot comparison of conventional to advanced oxidized textile grade PAN fibers.Density in grams per cubic centimeter for each stage is noted in the legend. Note the advanced fiber with density 1.36–1.37 is considered an anomaly.

Current Status

Currently the research team is focused on optimizing the new technique for textile grade fibers. In addition, design work is currently being conducted on MTR2. This device will represent a significant scale-up from the current level of processing and will involve a minimum capability of processing 4 × 26k tows. Four serial modules will make up MTR2. The fiber handling system has already been designed and is under construction by the vendor, Izumi International. This system consists of three independent winders with encoders for constant line speed capabilities. The system is very compact to accomodate the space limitations in the laboratory.

Conclusions

This fiscal year was perhaps the most significant of this project's history. With the accomplishments of surpassing the program's mechanical property requirements while dramatically reducing the required residence time, Phase I of this project is coming to a close. During Phase II, which will begin in FY 2012, the research team will investigate the scaling requirements of this new technique while continuing to optimize the process.

At the conclusion of Phase II of this project, the researchers will be positioned to procure, install, test, and operate a pilot-scale plasma oxidation module in an advanced technology pilot line. The follow-on of this project will be the design and construction of the advanced technology pilot line that will then be installed in CFTF. It will be used to validate system performance and scalability and to produce the required quantities of advanced technology CFs to support the Lightweighting Materials program's advanced development activities.

Pilot Line Upgrade

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Accomplishments

- Procured a three zone high temperature carbonization furnace and an oxidation furnace with multiple independent stretching zones for integration with the Precursor Evaluation System to improve CF processing capabilities.
- Completed preliminary engineering for a major upgrade to the ORNL pilot line to enhance throughput, controls, flexibility, and other capabilities; contractual work for completing the upgrade is in progress. The upgrade will double the material throughput and allow for the production of higher volumes of finished carbon fiber to support Vehicle Technologies Program projects. The current line can run two tows while holding appropriate tension producing two pounds of carbon fiber per day. The upgrade will double the line speed and allow tensioning of six tows increasing the daily production possible to 12 pounds per day.

Future Directions

- Pilot line upgrade will be completed in mid-2012 enabling ORNL to demonstrate fully integrated precursor conversion with flexibility in stretching and to facilitate ORNL capability to increase production capacity from two to twelve pounds per day.
- The pilot line upgrade will allow for more precise tensioning of precursors during oxidative stabilization which will allow the achievement of higher tensile strength. Precursors that typically processed to 400 Ksi strength carbon fiber will be able to be converted to more than 500 Ksi strength, matching what is produced in the precursor evaluation line.
- The Precursor Evaluation System will continue to be used as workhorse equipment in day-to-day development of alternative precursors.

Technology Assessment

- Target: Increase the material through put of the pilot line to provide needed quantities of material to the Vehicle Technologies Program.
- Target: Increase the tensile strength of fiber produced on the pilot line to match properties that are achievable with the precursor and fiber evaluation line.
- Gap: The current pilot line is not capable of providing the quantities of carbon fiber that is needed by the Vehicle Technologies Program.
- Gap: The current pilot line does not produce carbon fiber with properties equal to that achievable on smaller lines due to a lack of precise tensioning in the oxidative stabilization ovens.

Introduction

The Carbon Fiber Pilot Line facilitates the evaluation of materials and processes for the LCCF project. This line plays a key role in advancing technology development and providing critical information necessary for planning and executing production scale-up. The use of this facility includes evaluation of alternate precursor convertibility and production of fibers for evaluation by automotive composites manufacturers and other interested parties, and new concept evaluations. This task is to upgrade the output of carbon fiber from two to twelve pounds per day and to increase the tensioning control allowing for the production of higher strength carbon fiber.

Approach

ORNL's conventional pilot line enables the production of order 1–10 lb/day of 50k tow. Therefore, it is useful for making small quantities of fiber for tow and composite evaluations. It can also be used to conventionally oxidize or carbonize tows that are partially converted by advanced processes. Minimum material requirements for evaluation on the pilot line are hundreds of feet of ≥ 3K tow, and startup time for the high temperature carbonization furnace is ≥ 10 hours. A significant upgrade to this system is currently being conducted. The upgrade will double the line speed from eight inches per minute to sixteen inches per minute and provide tensioning for six tows rather than the two tows for which it is currently designed. It will also allow for more precise tensioning control which will allow for a 100+ Ksi increase in the strength of carbon fiber from textile based precursors.

Results and Discussion

Better understanding of the Precursor Evaluation System and its capabilities has facilitated minor upgrades this year, including a three zone high temperature carbonization furnace (Figure 18) capable of reaching temperatures over 1,500°C. This unit has a longer heating zone and much better capability to tailor the heating progression than the single zone furnace we are currently using. A second improvement is the addition of an oxidation oven with fully integrated, but independently controlled, tensioning sections (Figure 19). These upgrades allowed for the development of higher strength fiber from textile precursors but could not be mimicked in the pilot line due to the low level of tension control available in the pilot line. The upgrade will allow for production of fiber achieving the same mechanical property values in the pilot line and in volumes that will allow for composite evaluation.

Figure 18. Three-zone high temperature carbonization furnace.

Figure 19. Oxidation oven with fully integrated tension controls, shown at right.

The Precursor Evaluation System transitions development from laboratory scale [individual process stages (e.g., each of four stages of oxidation and two or more stages of carbonization) and working at the few grams and single or few filaments to single tow levels] closer to pre-production demonstration scale, with multiple tow and fully integrated process development via the conventional pilot line. Although the pilot line has itself proven to be a useful tool, it has limitations that we are working to address, including the following which are part of the upgrade.

- The pretreatment system is based on a simplistic system designed specifically to eliminate crimp, so current processing is nonuniform, without the capability for progressive, controlled stretching.
- The oxidation stages lack capabilities for progressive, controlled stretching to enhance overall properties via molecular orientation or provide tension compensation for heat induced relaxation.
- The overall tension controls are marginal and not very flexible, and the fiber transport system is low speed and antiquated, without the capacity to increase speed, number of passes, or bypass potentially superfluous processes.
- With the exception of oven temperatures, no monitoring of process parameters (tension, speed, stretching, etc.) capabilities and no automated data acquisition system to capture and analyze data are present on the current system.

ORNL has been working extensively with a well-established company specializing in fiber movement features to design and implement a major pilot line upgrade. The upgraded system, scheduled for completion in mid-FY 2012, will be capable of implementing the individual and collective process steps as developed on the Precursor Evaluation System. The following items are part of the upgrade:

- 4 ea. Gruenberg Model No. MO65H106 Oxidation Ovens with associated fiber rolls, support structure, insulated end seals, and end seal cubicles
- 1 ea. Thermcraft Model #6-30-5ZH Low Carbonizing Furnace rated up to 1,010˚C, with 5 individually controlled zones
- 1 ea. Thermcraft Model #36-28-3ZH High Carbonizing Furnace rated up to 1,500˚C, with 3 individually controlled zones
- 1 ea. Thermcraft Control Cabinet Assembly with controls for both the Model #6-30-5ZH and Model #36-28-3ZH Furnaces
- End Seals for Both Furnaces
- 1 ea. Step Down Transformer for the Thermcraft Model #36-28-3ZH Graphitizing Furnace
- 1 ea. Set of Mounted Nitrogen Furnace Flow Meters
- Modular Control Room for Drive and Furnace Controls
- 1 ea. Fiber Tow Positioning and Tensioning Stand

- 5 ea. Fenner Contrex M-Drives (calibrated for 0.5 ipm minimum and 18 ipm maximum line speeds) for the following rolls:
    - 1 ea. Set (2 Drives) for Feed and Stretch Godets with Steam Conditioning Chamber Mounted Between the Independently Driven Sets of Godets.
    - 1 ea. Oxidizer Exit Nip Roll Stand Drive
    - 1 ea. Carbonizer Exit Nip Roll Stand Drive
    - 1 ea. Size Bath Exit nip Roll Stand Drive
    - 1 ea. Drive Control Panel as Supplied by Landon Electric

The upgraded system will then be able to produce six time the quantities of CF (from two to twelve pounds per day) for mechanical property testing. It will also be capable of producing fiber with mechanical properties that match those developed in the precursor and fiber evaluation laboratory with the same precursor. This line is a critical link in scaling technologies from the precursor and fiber evaluation to the 25-ton-per-year CFTF, scheduled for completion in FY 2013.

Conclusions

The pilot line continues to function as an essential tool for the validation of new precursor technologies, having been used for the textile PAN precursor. Important upgrades to the pilot line are scheduled for near-term implementation to provide higher speed capability, additional stretching capability, enhanced surface treatment and sizing capabilities, and enhanced controls and data acquisition systems. The line speed will be increased from eight to sixteen inches per minute. The number of tows that can be simultaneously processed will be increased from two to six and the amount of tension control on each tow will be significantly enhanced allowing for the production of carbon fibers matching those available in the smaller precursor and fiber evaluation laboratory.

Conventional Interfacial Optimization of Reinforcement Fibers for Polymeric Systems

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Accomplishments

- Developed a CF sizing with industrial partners that yields 14 Ksi short beam shear strength (SBSS) from unidirectional composites made of vinyl ester resin. The fiber-matrix interface bond strength is improved ~60% compared with commercially sized CFs.
- Developed a highly effective surface treatment method. Using oxygen treatment, the project developed a surface treatment resulting in a nearly threefold increase in surface atomic oxygen concentration when compared with conventional surface treatments. This accomplishment demonstrates the potential to dramatically improve upon the traditional sizing methods used in industry.

- Scaled up a laboratory-scale continuous-process surface treatment method. The new surface treatment applicator is capable of surface treating CFs in about 90 s at a line speed of up to 70 in. /min. More than a thousand feet of single large tow (50,000 filaments) CF was continuously surface treated using ORNL's advanced techniques. This demonstrated the scalability and industrial feasibility of the technology.

- Achieved surface treatment uniformity in between filaments and along fiber tows and confirmed by x-ray photoelectron spectroscopy measurements.

Future Directions

- Surface treatments and sizings will be modified for short cycle composite manufacturing resin systems and processes such as sheet molding compounds and resin transfer molding. Sizings will also be optimized for optimum processability and handleability. This task will be executed with a high level of contributions from project industrial partners.

- The knowledge obtained will be used to develop surface treatments and sizings for thermoplastics that are of interest to the automotive industry and emerging energy applications. The bonding mechanism is different with thermoplastics so development of different types of surface treatments and high temperature sizings that stay effective after high temperature thermoplastic composite processing is required.

Technology Assessment

- Target: Produce commercially acceptable, low cost composites from the next generation LCCFs. Develop CF surface treatment and sizing technologies that will deliver 15 Ksi or greater SBSS in composites made from lower cost resins and short cycle processes. The goal of this research is to remove the barrier to the manufacture of low cost composites.

- Gap: The quality of the fiber-matrix interface and processability of commercially available CF is poor. Traditional surface treatment and sizing materials will not provide sufficient bonding between fibers and the new generation matrix polymers.

Introduction

CF composites are attractive materials for automotive structures because of the opportunity to realize substantial weight savings and fuel economy. LCCFs are currently being developed at ORNL for automotive applications. Those fibers are likely to be combined with low cost, high volume resins such as vinyl esters, polyesters, and nylons as the matrix materials for automotive applications.

The quality of the fiber-matrix interface is often a critical factor in determining composite mechanical properties and durability. It has been observed that the interface in commercially available carbon-vinyl ester composites is poor (see Figure 20). It is likely that the interface will be of low quality with the lower cost CFs as well. Conventional CFs are too expensive to be used in large volume applications, yet their superior properties would enable lightweighting in current glass-fiber-based industrial composite applications. Because of this cost barrier, CF producers have not developed their products for large volume processes such as sheet mold compounding and injection molding. Thus, the goal of this research is to remove the barrier to the use of LCCFs with automotive resins due to the lack of fiber-matrix compatibility.

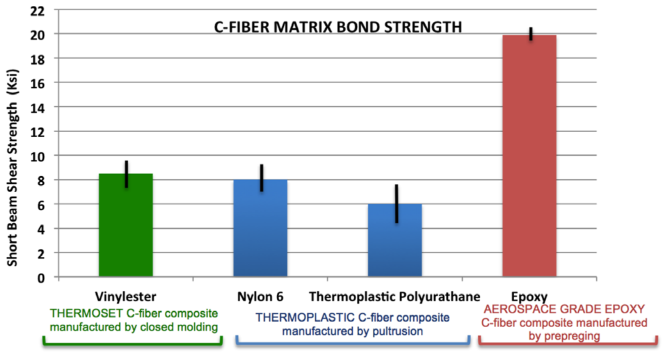


Figure 20. Comparison of relative interfacial bond strength of commercial epoxy sized CFs (C-fiber in the figure) with different resins using SBSS measurements. Industrial standard epoxy based sized CFs were used for all resins and processes.

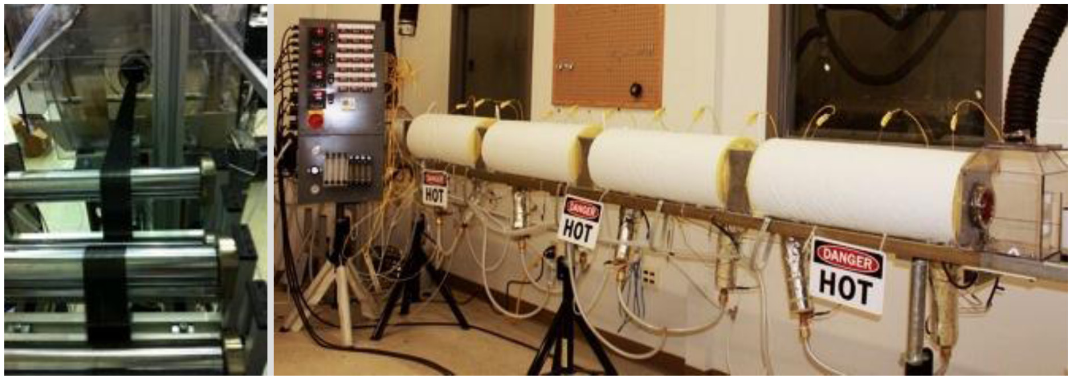
Approach

Novel gaseous surface treatments and sizing materials are being developed at ORNL to use in CF production to address the need for large volume, low cost composites. Present common practice is to surface treat CFs in an electro-oxidative bath. After surface treatment, the fibers are sized with a waterborne polymer (usually epoxy) by immersion in a sizing bath. Electro-oxidative treatments form a wide range of acidic and basic oxygen containing moieties on carbon surfaces including ethers, hydroxyls, lactones, ketones, carboxylic acids, and carbonates at crystallite edges and defects [Fitzer et al., 1987 and Ishitani, 1981]. The electro-oxidative process cannot be controlled to emphasize only a particular surface species. For this reason, it cannot be tailored for forming acid/base or chemical bonds with vinyl esters. Research at ORNL is targeting the control of surface functional groups and the creation of highly energetic surfaces that not only change the type of surface treatment used, but also present different requirements for sizing techniques that diverge from the traditional approach. CF surfaces can be functionalized with narrow distributions of moieties centered on desired groups by properly choosing source gases and application parameters. The flexibility of the surface treatment method that is being developed at ORNL permits the use of a variety of sizing chemistries and components. It also will allow an array of surface functionality designs to be used with various reactive coupling agents, film forming polymers, radical inhibitors, and surfactants. Traditional surface treatment and sizing materials will not provide sufficient bonding between fibers and the high volume commodity polymers.

Results and Discussion

The SBSS of commercially available CFs with vinyl ester, nylon 6, thermoplastic polyurethane, and epoxy matrices is shown in Figure 20. Baseline data have been generated from composites made from commercial grade CFs with standard commercial surface treatment and sizing. The SBSS of commercial CF coupled with vinyl ester resins is measured in the range of 7.5 to 9.5 Ksi. Results indicated that CF and vinyl ester adhesion was significantly lower when traditional surface treatment and sizing were used compared with aerospace grade CF-epoxy composites, whose SBSS usually ranges between 14 and 20 Ksi. We measured 19.9 Ksi SBSS from composites made of CF epoxy. A similar trend has been observed with CF thermoplastic composites manufactured by pultrusion. ORNL and industrial project partners addressed this significant technology gap in the areas of surface treatment and sizing for the next generation of lower cost CFs and high volume manufacturing processes. The objective of this project is to fully develop and demonstrate novel atmospheric plasma surface treatment technologies and compatible sizings for current and future lower cost CFs that (a) address the shortcomings listed above, (b) are optimized for low cost polymer matrices, and (c) permit short process cycle manufacturing systems that are of interest to high volume industries. The project is being geared toward the use of high volume, lower cost CFs and composite manufacturing technologies.

ORNL's surface treatment system is capable of efficiently treating tows up to 50,000 filaments [Figure 21(a)]. The current surface treatment method is the processing of a continuous single tow at a residence time of about 90 s. A scaled-up continuous thermochemical surface treatment applicator is shown in Figure 21(b). Up to 30% atomic oxygen content has been achieved at laboratory scale by continuous treatment with an ability to focus around the combination of desired functional groups. Raman spectroscopy results (not shown) indicated that the weak layers and debris left from the carbonization furnace had been partially removed from the surface using this method.



(a) (b)

Figure 21. ORNL surface treatment system: (a) delivery of continuous 50,000 filament CF using spreading bars and (b) developed and scaled-up experimental ORNL thermochemical surface treatment applicator.

$$\ln \sigma = \frac{-1}{m} \ln l + ln \left[\sigma_0 \Gamma \left(1 + \frac{1}{m} \right) \right]$$

The average tensile strength of the fiber, σ, is related to the gauge length, l, according to the following equation, with m and σ_0 being the Weibull modulus and the scale parameter, respectively, and Γ being the gamma function.

The value of the Weibull modulus, m, and the ultimate tensile strength, σ_0, can be easily determined when plotted against each other in log scale (Figure 22). The method was shown to be more appropriate than a regular two or three parameter Weibull analysis because the latter gave values of the Weibull modulus and the scale parameter that were dependent on the gauge length.

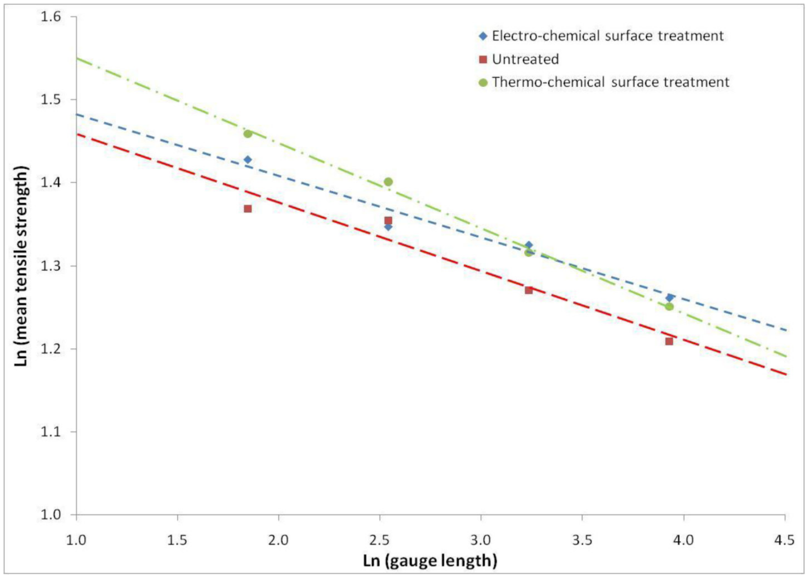


Figure 22. Determination of the Weibull modulus and the scaling parameter.

The fibers that were electrochemically surface treated appeared to be the less sensitive to the gauge length (higher value of the Weibull modulus), which can be explained by a higher density of flaws. Their ultimate tensile strength was similar to that of untreated fibers. The nature of the flaws was different though, and the breaking of the fibers might not follow the same mechanism. Oxidative surface treatments create defects (pits) in the first graphitic layers but also remove the weak boundary layers of graphitic material produced by the graphitization step during the manufacturing of the fiber. That may explain why the tensile strength of untreated fibers was generally lower than the tensile strength of electrochemically surface treated fibers. The lowest value of the Weibull modulus and the highest ultimate strength were obtained with the thermochemical surface treatment. As shown in Figure 22, the thermo-oxidative surface treatment presented here, within the experimental conditions that were used, induced a healing of the CF surface by removing the surface imperfections without creating new flaws. The atomic force microscopy (AFM) images presented earlier showed that the electrochemical surface treatment generated a rougher surface, inducing a higher density of surface flaws (and eventually more stress at the tip of those flaws), which may have made up for the gain obtained with the removal of the weak boundary layers originally present at the surface of the fibers. The benefit of removing the weak boundary layers reached its full potential with the thermochemical surface treatment, as the subsequent etching of the surface was smoother. Therefore, while the developed surface treatment method functionalizes the surface twofold or more compared with industrial practice, it also cleans the imperfections on the surface and improves the tensile strength of CFs.

One micron by one micron images of the surface of the fibers before and after surface treatment were taken. The characteristic features of the surfaces are shown in Figure 23. Three-dimensional equivalents of the two-dimensional images are given to better represent the shape and depth of the features. The surface of the non-surface-treated fibers was made of 200–400 nm thick grooves that were oriented along the fiber axis. The depth of these grooves was about 30 nm. After both surface treatments, the surface became rougher. Indeed, the surface was made of grooves with similar thickness but deeper (Figure 23). The depth of the grooves was around 100–120 nm in the case of the electrochemical surface treatment and 60–90 nm in the case of the thermochemical surface treatment. Moreover, a secondary structure made of smaller pits and grooves (50–100 nm) was superimposed on the main grooves in the case of the electrochemical surface treatment. It is already known that electrochemical surface treatments create microporosity at the surface of CFs, and these pores may diminish fiber strength and initiate failure. The grooves created by the thermochemical surface treatment appeared to be rather smooth in comparison. Although the surface area is lower for thermochemical surface treatment and expected to contribute less to mechanical interlocking due to high functionality of the surface, thermochemical surface treatment delivers significantly higher interfacial bond strength.

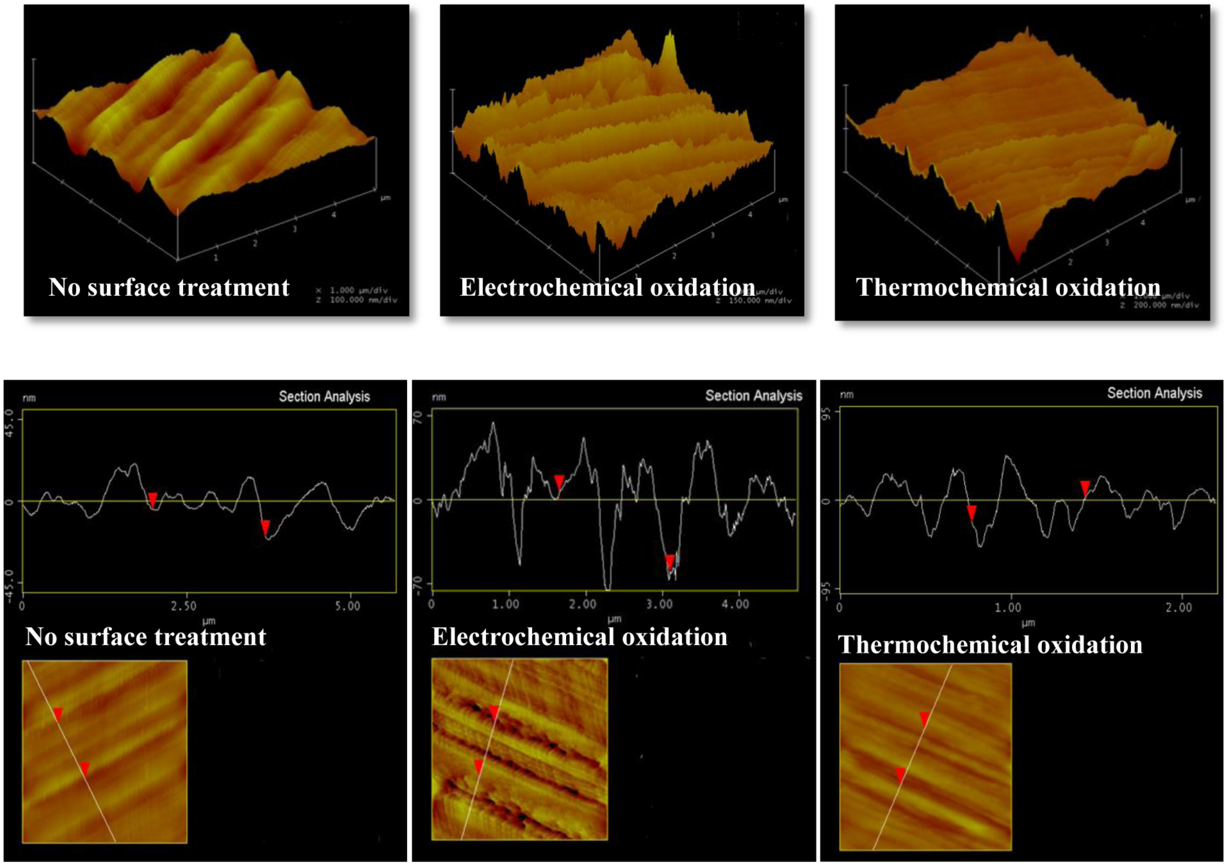


Figure 23. AFM imaging of the surface of the fibers showing roughness of the surface of the fibers perpendicular to the fiber axis.

To understand the interfacial bonding mechanism, several approaches to a vinyl ester compatible sizing were systematically considered at ORNL, among them thermoplastic sizing, film-forming polymers with vinyl functional silanes, coupling agents, specialty surface modification (functionalization), application of reactive finishes, and various combinations of the different approaches. Approaches that reduce the residual stresses at the interface region due to resin shrinkage were also taken into consideration (vinyl esters typically shrink 2–3 times more than epoxies). The fiber-matrix bond strength has been screened using SBSS measurements and 90° flexural tests to compare the performance of industrial and ORNL sizings. SBSS test results are given in Figure 24. This project led to the development of sizings (reactive finish) that yielded 14 Ksi SBSS. This is an almost 60% improvement compared with conventional industrial sizings.

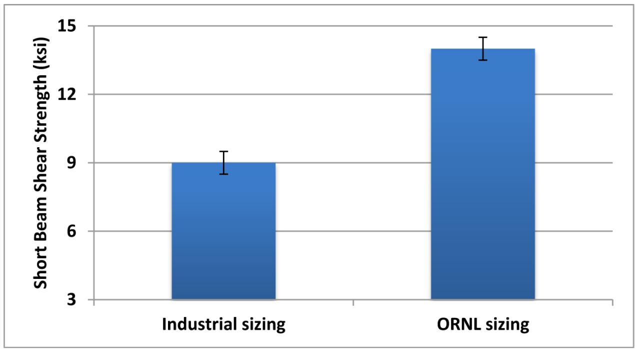


Figure 24. SBSS of CF-vinyl ester matrix composites made from industrial CF and ORNL sized CF.

Conclusions

A new thermochemical method of surface treating CFs was developed and tested during this fiscal year. In just a short time, the concept has been proven and scaled up and significant progress has been made in increasing the oxygen content on the surface of CFs (from 6% to ~30%), which improves the adhesion of CF to low cost vinyl resins used in industry. Mechanical testing of the SBSS of composites manufactured from ORNL surface treated CF confirmed the improvement. One of the advantages of the new surface treatment is the ability to clean the fiber surface (surface imperfections and defects) and improve the tensile strength of CFs. Next generation commodity grade CFs are expected to be lower cost but at the expense of mechanical properties. Improvements in tensile strength of CFs after surface treatment with the thermochemical surface treatment developed during this project suggest that it can be used effectively to improve the performance of next generation CFs. The developed sizing delivers around 60% better bond strength with vinyl ester compared with industrial epoxy based sizing. However, the processability of CF with the new sizing has not been investigated yet.

Conclusions

This project comprises six separate tasks that are aimed at developing technologies to lower the cost of CFs, making them more attractive to the automotive industry. The fibers must have a minimum strength of 250 Ksi and a minimum modulus of 25 Msi and be compatible with automotive grade resin systems. Three alternative precursors are being developed, two alternative production methods are under development (one by a sister DOE program), and one surface compatibility project is being developed.

In the development of a lignin based precursor, lignin sources have been identified which meet the purity levels required for making CF. Work toward identifying and producing precursor fiber with appropriate plasticizers is continuing. The mechanical properties achieved to date do not meet the required program minimums.

The second precursor development project involves the modification of textile grade PAN to render it as a suitable CF precursor. This task is nearing completion and has been a success. Strength values (540 Ksi) exceed program requirements (250 Ksi), and modulus values (38 Msi) are above program requirements (25 Msi). The chemical pretreatment equipment has been installed in the production facility, and final verification of production-quality material has validated that the production equipment produces the same quality of fiber as was obtainable with laboratory-scale equipment. Commercialization plans are in development.

During FY 2010, significant progress was made toward the production of LCCFs from polyolefin precursors. The effects of draw ratio and degree of functionalization on fiber crystallinity and tensile properties are understood. PE fibers were made infusible through continuous processing in less than 1 hour and processing parameters were optimized to form carbonized filaments exhibiting tensile strength of 160 Ksi, modulus of 15 Msi, and 1.1% elongation. However, issues of interfilament bonding during thermal treatment and incomplete sulfonation of the fiber core were identified as major obstacles to be addressed in FY 2011 to achieve the targeted CF properties. The team met the milestones of FY 2010. Polyolefin precursors are the lowest cost potential precursors due to their low raw material cost, low production cost (melt spinning), and inherently high carbon content, which gives greater production yield.

Important upgrades to the pilot line are scheduled for implementation during the next year which will include a six fold increase in carbon fiber production capability. It will also include improved tow tensioning during oxidative stabilization allowing for fiber production matching the properties achievable in the precursor and fiber evaluation line with the same precursor.

In the development of a more rapid oxidative stabilization process, several important objectives were met that produced valuable knowledge on the scaled-up advanced oxidation process. We are now completing the work necessary to design a pilot-scale unit under that task. At the conclusion of this project, the researchers will be positioned to procure, install, test, and operate a pilot-scale plasma oxidation module in an advanced technology pilot line.

A new thermochemical method of surface treating CFs was developed and tested during this fiscal year. In just a short time, the concept has been proven and significant progress has been made in increasing the oxygen content on the surface of CFs (from 6% to over 22%), which improves the adhesion of CF to low cost vinyl resins used in industry. Mechanical testing of the SBSS of composites manufactured from ORNL surface treated CF confirmed the significant improvement. Nylon resin systems will be considered in future work.

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Contract No.: DE-AC05-00OR22725

Executive Summary

The largest ORNL carbon fiber processing facility is the Carbon Fiber Technology Facility (CFTF). The CFTF is designed to be readily accessible to domestic industry and universities for the development and commercialization of carbon fiber technologies. ORNL has developed and worked with an extensive network from industry, academia, and the federal government to develop vertically integrated teams for commercialization of carbon fiber technologies. The CFTF is intended to spur the development and growth of U.S. carbon fiber manufacturers and help them capture significant market share from foreign competitors. The facility is also intended to be a development center for lower cost carbon fiber technologies and provide a test bed for full commercialization of those technologies.

Activity and Developments

Carbon Fiber Technology Facility

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Deputy Principal Investigator: Robert E. Norris, Jr.; ORNL
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Accomplishments

- Received DOE approval of Alternative Selection and Cost Range [change directive- (CD-1)].
- Established and received DOE approval of Performance Baseline (CD-2).
- Received DOE approval for Start of Construction/Procurement (CD-3).
- Signed contracts for procurement of melt spinning and carbon fiber semi-production lines.
- Finalized overall equipment architecture.

- Completed preliminary design of major baseline equipment.
- Commenced fabrication of carbon fiber semi-production equipment.
- Signed building lease, private building owner commenced construction, and significant progress toward completion has been made.

Future Directions

- Complete procurement, construction, manufacturing, installation, and commissioning of building and equipment.
- Commence operations by mid-February 2013.

Technology Assessment

- Target: Develop a carbon fiber facility to aid in the commercialization of lower cost carbon fiber technologies that demonstrates continuous equipment operation and provides product development quantities of material to industry.
- Gap: No test bed currently exists in the United States for scaling up lower cost precursors or new carbon fiber conversion technologies.
- Gap: Product development quantities of material are not available for product development to create an industry pull for lower cost carbon fiber technologies.

Introduction

DOE has awarded ORNL $34.7 million to design and construct the CFTF. The award was funded under the DOE Office of Energy Efficiency and Renewable Energy's 2009 Lab Call for Facilities and Equipment (Lab Call 09 002) (American Recovery and Reinvestment Act funds). According to the mission need statement that authorized this project,

> *Low-cost carbon fiber will likely have different mechanical properties than the carbon fiber grades currently produced for the aerospace industry. End-use industries are unlikely to commit to using lower cost carbon fiber without significant efforts to validate that low-cost carbon fiber meets their needs while fiber manufacturers are unlikely to commit to investing in large scale manufacturing technologies without purchasing commitments. . . . In order to address these issues, it is necessary to acquire a flexible capability for advanced research, development, and demonstration of carbon fiber to achieve EERE's long-term program goals. This capability combines the ability to handle various feedstock materials, the integration of advanced energy efficient conversion technologies, and the ability to produce sufficient quantities of finished fiber to supply end-users for validation trials. . . . The successful completion of this activity will remove the obstacles for accelerated adoption of this light-weight, enhanced performance material in multiple high volume industries.*

The primary tasks to be undertaken in this effort are as follows.

- Lease a suitable general purpose building at a former government site that is being reindustrialized.
- Deploy a highly flexible carbon fiber semi-production line (CFSL) designed to handle all low cost carbon fiber (LCCF) precursor chemistries and material formats with capacity to carbonize 25 tons/year of polyacrylonitrile (PAN) fibers in 24k tow format.
- Deploy a melt spun precursor fiber semi-production line (PFSL) for producing melt spun low cost precursor fibers in both tow and web forms with production capacity matched to the carbon fiber line throughput.
- Make space and utility provisions for the future deployment of semi-production scale advanced conversion technologies.

Approach

To satisfy this mission need, ORNL is designing and constructing the CFTF to be a highly flexible, highly instrumented LCCF technology facility for demonstrating and evaluating new low cost manufacturing processes and technologies at semi-production scale. The CFTF will promote successful commercialization of LCCF technologies. A new, general-purpose industrial building is under construction (by a private owner/lessor) to house a thermal (conventional) conversion line and a melt spinning precursor fiber line. It will provide the capabilities to

- demonstrate the scalability of LCCF;
- produce and make available up to 25 tons/year of conventionally converted fibers, made from low cost precursors, for large scale material and process evaluations;
- accommodate the future deployment of advanced conversion technologies;
- produce precursor fibers made from a variety of precursor materials (e.g., lignin and polyolefin) on a melt spinning line in sufficient quantity to feed the conversion lines;
- foster industrial collaborations for LCCF technology development and transition; and
- host workforce training for LCCF implementation.

Previous and ongoing LCCF developments must be demonstrated in the CFTF to achieve successful transfer of these technologies to industry, as illustrated in Figure 1. The CFTF will serve as a bridge from research to commercialization

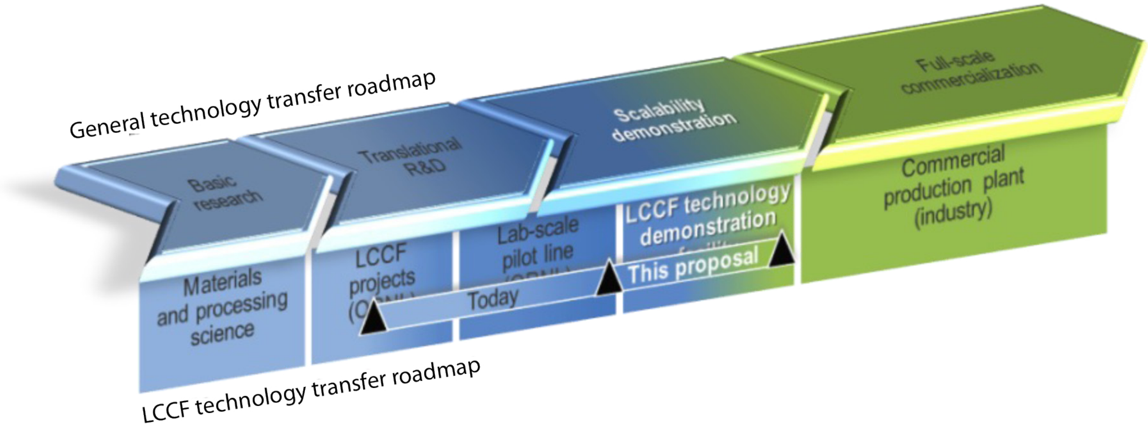

Figure 1. Roadmap for technology transfer and commercialization.

The CFTF is designed to be readily accessible to domestic industry and universities. It will be located at the Horizon Center industrial park, a former government site that is now being industrialized and has available space where industry partners can locate leveraging facilities.

The CFTF technical scope includes the specification, procurement, and commissioning of (1) a CFSL; (2) a melt spun PFSL, and (3) a building to house these lines plus an advanced technology CFSL that will be deployed in the future. The facility should be able to produce various carbon fiber grades including standard modulus commercial grades, intermediate modulus aerospace grades, and fiber grades that are in development at both ends of the cost and performance spectrum.

The CFSL will be a highly instrumented conventional conversion line capable of processing several kinds of precursor fibers including those based on PAN, pitches, lignin, and polyethylene (also upgradeable for rayon) in tow or web form. The CFSL will have an output of up to 25 tons per year of standard modulus carbon fibers made from PAN precursor. This is sufficient capacity to provide the estimated material needs for large scale material and process evaluations for several applications including automotive [1–2 total tons for each, separate, original equipment manufacturer (OEM)], wind energy (5–10 total tons for each OEM), and oil and gas (1–5 total tons for each new application). The PFSL will be capable of melt spinning filaments from lignin, polyolefins, and pitches, with capacity matched to that of the CFSL. The CFSL and PFSL are both designed to produce materials in tow and web forms. While both the CFSL and PFSL are based on conventional technology, each has flexibility (and therefore complexity) that considerably exceeds the current state-of-the-art. When the advanced conversion processes that are presently in development become sufficiently mature, they will also be scaled up and deployed in CFTF as advanced technology conversion semi-production lines with scales similar to that of the CFSL. Figure 2 is a schematic showing the equipment and floor plan of the facility. The primary deliverable of this project is an operational facility capable of manufacturing up to 25 tons per year of carbon fibers made from PAN, lignin, or polyolefin precursor materials.

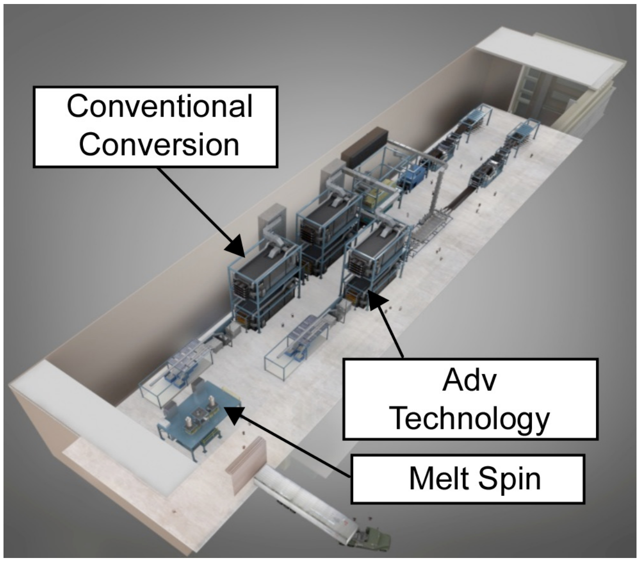

Figure 2. Schematic of the CFTF and equipment.

Results and Discussion

The building lease was signed in October 2010, the preliminary building design was developed in the first half of FY 2011, and construction commenced in April 2011. The building will have about 42,000 gross square feet, including support spaces, plus a high bay with nearly 29,000 square feet of usable area. The process equipment will be housed in the high bay. Figure 3 shows the building status in late July 2011 as seen from Tennessee State Highway 58. Figure 4 is a closer view of the building structure.

Figure 3. View of CFTF building structure in late July 2011.

Figure 4. View of CFTF building structure looking southwest in late July 2011

The major equipment procurement is being conducted in accordance with the DOE Acquisition Management System as prescribed in DOE O 413.3. This defines a rigorous stage-gated process for project execution with critical decision approvals required to proceed through each gate. The process was tailored for this project by combining major gates 1–3 into a single review. These gates are (1) Alternative Selection and Cost Range, (2) Performance Baseline, and (3) Start of Construction. Approval of critical decision 3, which was required before the major equipment procurement contracts could be signed, was received in March 2011, and the contracts for procurement of both the CFSL and PFSL were signed in March.

A significant change to the overall system architecture was evaluated and incorporated in FY 2011. Recent research and development results led to concerns about whether certain fibers could be melt spun, packaged, and then fed into the carbon fiber line. After evaluation, it was determined that the melt spinning line could be positioned in-line with the carbon fiber line to enable continuous in-line spinning and heat treatment of fibers produced in web forms. This change has been made to the system architecture, and the current baseline is in-line, continuous spinning, and heat treatment of fibers produced in web format. This architecture still allows high-speed melt spinning of spooled tows, which are then mounted to the creel and heat treated at normal CFSL speed. The current system layout is shown in Figure 5.

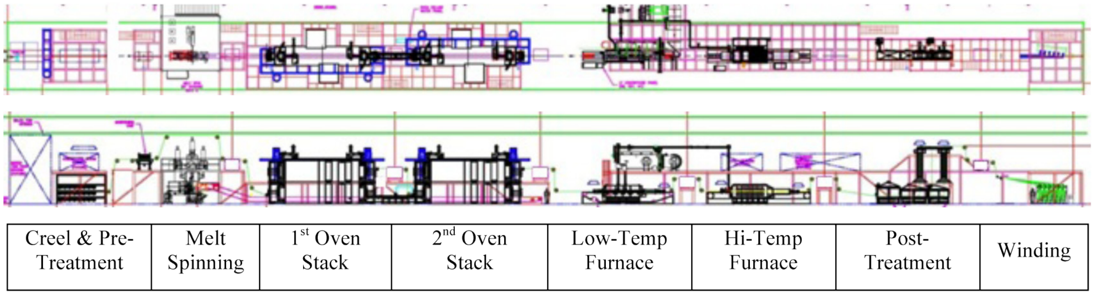

Figure 5. Equipment layout plan and elevation views.

Equipment preliminary design is essentially complete and detailed design is well under way for most unit operations. In some cases, equipment fabrication has begun. For example, the first of eight oxidation oven end seal assemblies has been fabricated.

In FY 2012, the primary activities will be completion of construction and manufacturing. The building is on schedule for completion in the third quarter of FY 2012 and most of the equipment is scheduled to arrive at the site in the third quarter. Equipment installation will occur in the last half of FY 2012 with commissioning continuing into FY 2013.

Conclusions

ORNL was awarded $34.7M in November 2009 to design, construct, and operate the CFTF. The building lease and major equipment contracts were signed in the first half of FY 2011. The building construction is well under way and on schedule for completion in the third quarter of FY 2012. Detailed equipment design is well under way and equipment fabrication has begun. The project is on schedule for equipment installation in the second half of FY 2012 followed by commencement of operations in FY 2013.

Conclusions

The CFTF has passed all critical design phases and is currently being built. The equipment is on order. ORNL has formed a carbon fiber consortium composed of companies who will be the users of the facility. The facility will begin operation in FY 2013.