4. POLYMER COMPOSITES R&D

A. Development of Manufacturing Methods for Fiber Preforms

Program Manager: Jeff Dahl
Ford Motor Company, Scientific Research Laboratory
P.O. Box 2053, MD 3135 SRL, Dearborn, MI 48121-2053
(313) 845-1039; fax: (313) 390-0514; e-mail: jdahl@ford.com

Project Manager: C. David Warren
Oak Ridge National Laboratory
P.O. Box 2009, Oak Ridge, TN 37831-8050
(865) 574-5069; fax: (865) 574-0740; e-mail: warrencd@ornl.gov

Technology Area Development Manager: Joseph A. Carpenter
(202) 586-1022; fax: (202) 586-1600; e-mail: Joseph.Carpenter@ee.doe.gov
Field Technical Manager: Philip S. Sklad
(865) 574-5069; fax: (865) 576-4963; e-mail: skladps@ornl.gov

Contractor: U.S. Automotive Materials Partnership
Contract No.: FC26-02OR22910

Objective

- Develop and demonstrate new fiber preforming processes to decrease cost, increase manufacturing rates, and improve reproducibility of large preforms for composite molding.
- Provide process development support to the Automotive Composites Consortium's (ACC's) Focal Project 3.

Approach

- Identify carbon fiber properties required to permit rapid processing and achieve desired performance levels.
- Investigate materials, process equipment, and tooling technology to further reduce the cost and enhance the quality of chopped fiber performs.
- Characterize chopped fiber preforms utilizing experimental carbon fiber rovings to determine important characteristics (permeability, light transmission, areal density distribution, etc.).

Accomplishments

- Obtained seven experimental rovings to investigate the effect of tow size on composite material performance; these were manufactured by Hexcel Carbon Fibers and delivered to the ACC.
  - Fabricated experimental light transmission analysis preforms using seven experimental carbon fiber rovings and sent them to Winona State University for analysis to determine the effect of tow size on material distribution.
  - Conducted preforming, molding, and mechanical testing using seven experimental carbon fiber rovings to determine the effect of bundle size on preforming, molding, and composite material performance.

- Established Fortafil carbon fiber roving development program, which is progressing with successful direct splitting of carbon fiber rovings.

Future Direction

- Evaluate experimental preforming and molding of mechanically split, low-filament-count, Fortafil carbon fiber rovings.
- Further characterize and investigate low-cost carbon fiber rovings with reduced individual bundle size.

Introduction

This project has focused on the development of the P4 process, a fully automated robotic preforming process. A prototype, two-station manufacturing cell was designed, fabricated, and installed at the National Composite Center (NCC) in Kettering, Ohio. This equipment is currently being utilized to support preforming and material development efforts within the Automotive Composites Consortium (ACC).

To obtain higher mass savings with composites relative to steel (50–70%), carbon fiber must be utilized as the reinforcing fiber. The extension of this technology to manufacture carbon fiber preforms is now in progress to support the development of ultra-lightweight vehicle structures. A major focus of this program is the development of a carbon fiber material suitable for chopped fiber processes; current production carbon fiber materials are not amenable. Advances in carbon fiber roving and preforming technology will be demonstrated in the structural automotive parts designed and prototyped as part of the ACC's Focal Project 3 (see 4.B).

Carbon Fiber Roving Development

To date, chopped carbon fiber preforming research and development has been limited due to material format and supply issues. To address fundamental material format issues present with current carbon fiber rovings, development programs have been initiated with two carbon fiber manufacturers (Hexcel and Fortafil) to expedite material research. The focus of these programs is to investigate the technology required to achieve a reduction in bundle size, to determine the effects of bundle size in the preforming/ molding processes and to ascertain the effect on composite material performance.

Hexcel Carbon Fibers

A carbon fiber roving development program to investigate the effect of individual bundle size on preforming, molding, and composite material performance is currently under way using Hexcel Carbon Fibers.

The development effort is focused on assessing the effect of individual bundle size on P4 preforming, structural reaction injection molding (SRIM), and the resultant composite material performance. It is theorized that a reduction in bundle size will improve material distribution in the preforming process and, therefore, positively impact the mechanical performance of molded structures. The rovings will be tested and assessed within the preforming process, and flat panel preforms will be manufactured for in-plane permeability testing, light transmission analysis, areal density distribution testing, flat panel molding trials, and mechanical characterization. To investigate the effect of individual carbon fiber bundle size, the program calls for manufacture of seven different combinations of carbon fiber rovings. The details of these rovings are shown in Table 1.

As highlighted, the overall carbon fiber roving was kept constant at 36,000 filaments (i.e., 36k); however, a wide range of total individual bundles,

Table 1. Carbon Fiber Roving Types

Roving ID	Precursor type	Roving construction
1	Pilot	0.5k × 72 bundles
2	Pilot	1.0k × 36 bundles
3	Pilot	1.5k × 24 bundles
4	Pilot	3.0k × 12 bundles
5	Production	3.0k × 12 bundles
6	Production	6.0k × 6 bundles
7	Production	12.0k × 3 bundles

from 3 to 72, and filament counts within these bundles, from 0.5k to 12k, comprise each roving to determine the effect of bundle size on processing and composite material performance. Also note that two 3.0k × 12 rovings were manufactured, one using precursor fabricated on Hexcel's pilot line and one using precursor fabricated on its production line. This would serve as a control to ascertain potential differences between pilot and production line precursor materials in the final carbon fiber roving.

Hexcel Carbon Fibers manufactured the aforementioned materials under a subcontract with Oak Ridge National Laboratory (ORNL) for the ACC. Carbon fiber roving manufacture was completed in January of 2004, and the material was shipped to the ACC for evaluation. Approximately 70 kg of each roving type was manufactured and received for experimental evaluation in this program.

Light transmission preforms were fabricated at 500 g/m^2 to determine the light transmission and coverage characteristics for each of the seven carbon fiber rovings. All preforming process parameters were held constant with the seven different carbon fiber rovings being the only variable. To minimize fiber filamentization that can cause erroneous preform light transmission results, two processing parameters were controlled. First, a section of the existing material delivery system was bypassed to minimize friction on the carbon fiber roving and subsequently reducing bundle filamentization. Second, input air pressure to the fiber ejectors on the chopper gun was reduced from 3.0 bar to 1.0 bar, thereby minimizing fiber filamentization caused within the chopper gun. A total of 21 flat panels, 3 panels with each carbon fiber roving type, were fabricated for light transmission testing.

These panels were shipped to Winona State University for image analysis to determine the light transmission characteristics of each carbon fiber roving tested. To conduct the analysis, digital images of the preform on a light table were obtained for each preform type in question. Each preform was divided into four quadrants and an image acquired for each quadrant. Using the 3 preforms of each type that were fabricated, a total of 12 images were obtained for each preform type. Following image acquisition, the digital images were imported into image analysis software to determine the amount of light transmission for each quadrant. In this analysis, a histogram distribution, comprised of the gray scale where zero represents black (i.e., complete coverage) and 255 represents white (i.e., zero coverage), was constructed for each image. The image analysis software was then used to calculate the percent of the image within each of the 256 ranges in the gray scale relative to the entire image. Results from the 12 quadrants were then averaged for each preform type to obtain the average light transmission. For this analysis, the range from 205–255 was assumed to be regions of zero fiber content and would be used to report the light transmission for a given preform type. A representative preform light transmission section is shown in Figure 1.

Upon examination of the experimental data, differences were noted between carbon fibers manufactured using pilot line precursor and those using production line precursor. After additional investigation, it was found that a slight variation in processing conditions existed, causing the bundles to be either relatively round (pilot line precursor) or relatively flat (production line precursor). This bundle geometry characteristic caused notable differences in the material following preforming and during light transmission testing. Based on this fact, data from the two groups of materials were treated as separate data sets.

As previously theorized, a reduction in individual carbon fiber bundle size subsequently

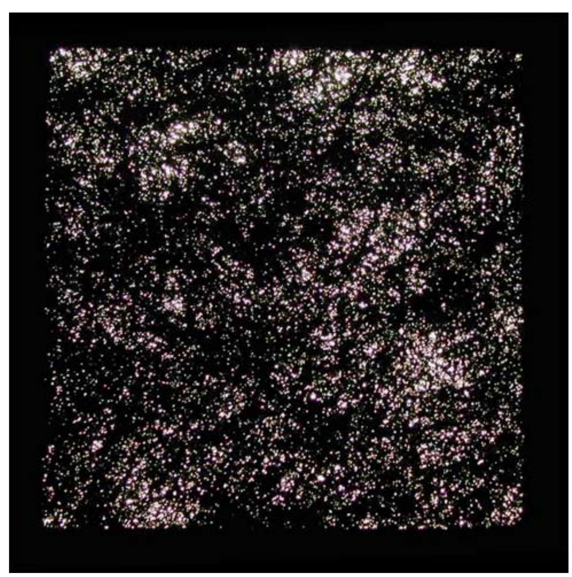

Figure 1. Representative preform light transmission image.

reduced the amount of light transmitted through a given preform. For example, the average light transmission for preforms manufactured using the 0.5k × 72 roving was 2.7 % vs 5.5% for preforms utilizing the 3.0k × 12 roving (Figure 2). In this instance, the reported light transmission is approximately two times, suggesting double the number of zero fiber content areas and higher areal density variability as a function of increasing bundle size. Because the quantity of light transmitted was reduced with smaller bundle sizes, the amount of zero fiber content regions were also reduced. This then suggests that a more uniform areal density distribution exists when utilizing carbon fiber rovings with smaller individual bundle sizes that should translate to more uniform mechanical properties. This same trend exists for both pilot and production line materials although the magnitude varies due to differences in the materials attributable to the carbon fiber manufacturing process.

To determine the effect of individual bundle size on composite material performance, flat panel preforms were manufactured and molded using SRIM. Following manufacture, the molded flat panels were mechanically tested to determine tensile and compressive properties.

Flat panels preforms were fabricated at 1260 g/m^2, corresponding to a fiber volume fraction of 35% for a 2.0-mm molded part thickness. All preforming and molding process parameters were kept constant throughout the trial with the only variable being the input carbon fiber roving. A total of 21 preforms were fabricated and molded using the seven Hexcel carbon fiber rovings

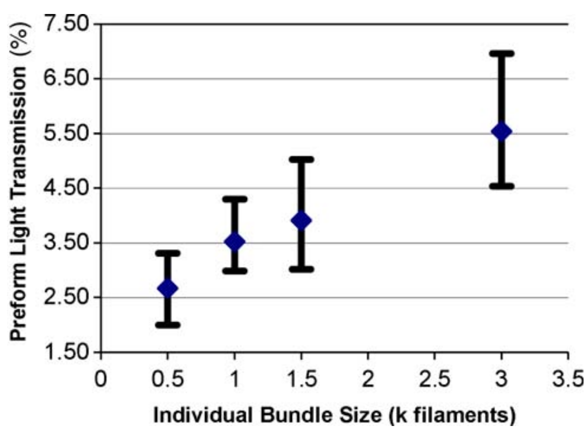

Figure 2. Light transmission vs bundle size.

(Table 1). Tensile samples were obtained from the molded panels and tested in accordance with American Society for Testing and Materials (ASTM) D-638. Eight samples from each panel were tested in both the 0° and 90° directions to determine tensile strength and modulus. A comparison of the 0° ultimate tensile strength for each of the seven carbon fiber rovings is shown in Figure 3.

The average 0° ultimate tensile strength for panels containing the 0.5k × 72 roving was nearly three times that of panels containing the 12k × 3 roving; 267 vs 90 MPa. Furthermore, the coefficient of variation (COV) was substantially reduced as a function of decreasing individual bundle size (Figure 4). The COV of 0° ultimate tensile strength for panels fabricated with the 12k × 3 carbon fiber roving was four times that of panels fabricated with the 0.5k × 72 carbon fiber roving (44 vs 11%). Average 0° tensile modulus was also higher in panels with the smallest individual bundles, but not nearly as significant as tensile

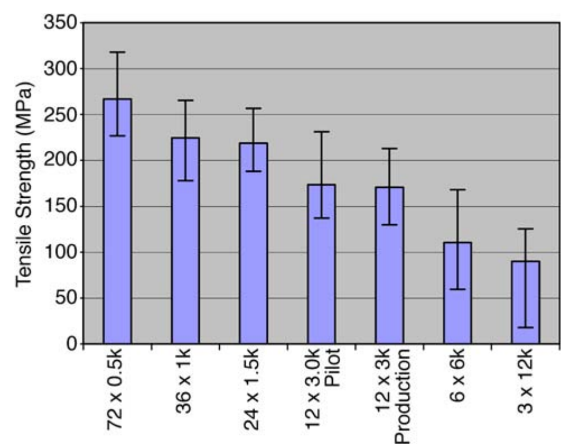

Figure 3. 0° ultimate tensile strength.

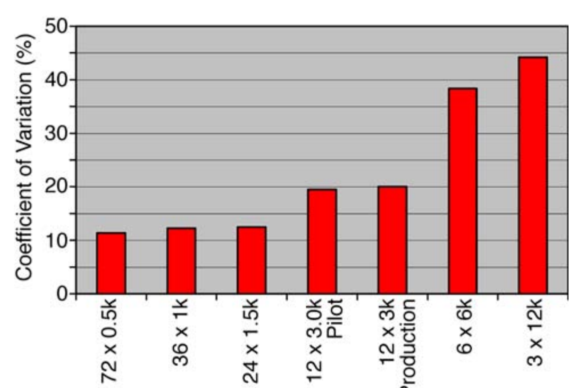

Figure 4. 0° ultimate tensile strength COV.

strength. For example, the average 0° tensile modulus was 27 GPa for the 0.5k × 72 fibers vs 22 GPa for the 12k × 3 fibers. However, the COV for tensile modulus was markedly different as a function of the particular carbon fiber roving. As shown in Figure 5, the COV for tensile modulus with panels containing 0.5k × 72 fibers and 12k × 3 carbon fiber rovings was 9% vs 33%, respectively.

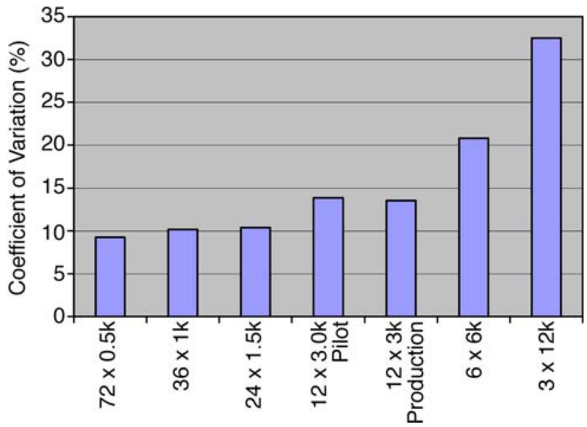

Figure 5. 0° tensile modulus COV.

As previously theorized and as the light transmission testing suggested, superior mechanical performance, both tensile strength and modulus, was evident in panels containing the smallest individual bundle sizes. In addition, the variability of these properties is also reduced with a reduction in bundle size. To be sure, a nearly identical trend was evident in the 90° tensile testing results. Furthermore, similar trends existed in both 0° and 90° ultimate compressive strength testing. Despite notable differences in the light transmission preforms between the control, 3.0k × 12 pilot and production line precursor/carbon fiber, no differences were evident in the mechanical properties as shown by the nearly identical tensile strength of both 3.0k × 12 carbon fiber rovings.

Based on the mechanical test data from this study, it can be stated that a reduction in individual bundle size both increases the magnitude of mechanical properties and reduces the variability of these properties within a panel. The data suggest that a reduction in bundle size within a carbon fiber roving will increase the mechanical performance of composite materials fabricated using chopped carbon fiber.

Fortafil Carbon Fibers

A research program to develop carbon fiber rovings more amenable to the P4 preforming process has been developed and initiated with Fortafil Fibers (now Teijin/Toho/Tenax). This program focuses on developing cost-effective methods to reduce the individual carbon fiber bundle sizes within a roving. A carbon fiber roving specification was developed jointly between the ACC and Fortafil as the target material for this program. The overall program is comprised of five phases and has an anticipated completion date of September 1, 2005.

The first phase of the program was to investigate whether splitting the precursor could give a final carbonized tow with fiber bundles of the desired dimensions. The initial technical efforts focused on methods to produce a stranded roving through modifications made to standard acrylic precursor. The work was carried out at the Acordis acrylic fiber production facility in Grimsby (United Kingdom). Technical resources were initially devoted to two major objectives. Firstly, the evaluation of mechanical techniques to introduce micro-splits in the precursor. And secondly, the identification and acquisition of candidate finishes to make splits in the acrylic strands permanent and able to survive the subsequent conversion to carbon fiber.

To address mechnical precursor splitting, stainless steel splitter bars to introduce the appropriate number of splits in the precursor were dimensioned to increment a subtow containing 80k filaments into 1k strands based on an operating subtow width of 9 in. Acordis concurrently identified candidate finishes with the properties necessary to hold the individual strands together while, at the same time, providing enough cohesion to maintain the integrity of the larger subtow during the crimping and packaging operations.

The first trials to produce stranded precursor were conducted in mid-October of 2004 using an 80k subtow. The splitter bar was evaluated at several locations, and a position immediately prior to the crimper hot plates proved to be the most effective. Split precursor samples were produced at the Acordis Grimsby site using a splitter bar to increment an 80k tow into approximately 2k filament strands and then “set” the strands by applying sizings developed specifically for this purpose. Several samples of mechanically split precursor were fabricated and the most promising candidates were shipped to Fortafil in Rockwood, Tennessee (U.S.A.) for oxidation and carbonization. The first precursor samples containing mechanically introduced strands were evaluated in November. The two samples processed through the pilot line were designated as PT288 and PT290 (Figures 6 and 7).

In the carbon fiber pilot line trials, the high finish level on both samples caused interfilament sticking to occur in the first oxidation oven. Although a cold water wash applied to the tows prior to their entering the oven was effective in removing enough finish to eliminate the sticking, a loss of strand definition was observed in the downstream oxidation. Thus, the sizings alone do not appear to be adequate to preserve the strand character during subsequent processing. Due to these limitations, this pariticular approach was deemed to be unfeasible at this time.

Figure 6. PT288 split precursor.

Figure 7. PT290 split precursor.

Upon completion of the mechanical bar slitting trials, work initiated on an air entanglement approach. The method adopted used compressed air, in conjunction with a splitter bar, to create strands within a tow by direct intermingling or entangling of the individual filaments. A first-generation “air splitter” device was fabricated in December of 2004 (Figure 8). Air entanglement produced by using dual splitters provided a precursor that was of sufficient quality to evaluate through carbonization. However, the splits were not sufficiently maintained through the carbonization step to warrant further work in this direction.

An alternative approach to producing a stranded roving involves first making a number of small strands and then ganging the strands to form a roving. Using readily available technology and a novel production approach, individual strands with filament counts as low as 500 were produced. The strands were then packaged into a roving containing 30 ends and shipped to the ACC for a P4 preforming trial. The trial showed specific directions for development and was overall very positive. However, cost analysis indicated that the developed material could exceed $10/lb, which was far enough over the cost target that it was decided to abandon this direction.

A fourth method of providing a split tow precursor is still under investigation. This involves spinning the precursor into split tows by manipulating the outlet hole pattern on the spinneret. Precursor strands have been fabricated that exhibit

Figure 8. Prototype air entanglement device.

appropriate splits. At the end of FY 2004, these samples were sent to Fortafil (Rockwood, Tennessee) and are awaiting carbonization.

The second phase of the program is to investigate techniques for direct creation of strands in a large carbon tow. This phase was initiated in April of 2004. Development efforts to date have concentrated on evaluating various machine geometries to obtain the cleanest and most scalable process to achieve the desired outcome. A preferred technology has been identified, and the optimum processing conditions are currently being established. The latest trials have generated promising results with rovings containing up to 30 ends. Quantities of stranded roving sufficient for evaluation in the P4 preforming process are expected by the second quarter of FY 2005. Figure 9 shows a sample of the stranded roving produced on the prototype development line.

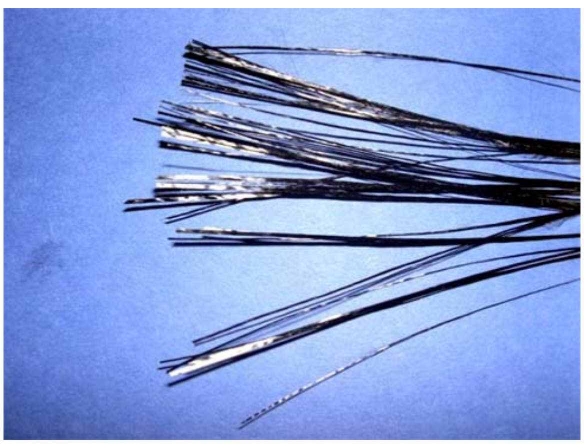

Figure 9. Stranded carbon roving produced on prototype development line.

Phase 3 is the development of appropriate fiber sizings for improved handling and fiber/matrix interface with a polyurethane resin system. This has been initiated in conjunction with the processing studies on the fiber slitting line.

The fourth phase is acquisition of a pilot line for fiber production, and the fifth phase is optimization of the pilot line, production of fibers for ACC evaluation, and assessment of manufacturing costs. Upon development of candidate carbon fiber rovings within this program, preforming and molding evaluations will be conducted by the ACC to determine the performance of these materials.

Conclusions

Carbon fiber roving manufacture for the development program with Hexcel Carbon Fibers was completed in January of 2004, and the material was shipped to the ACC for evaluation. Evaluation of the carbon fiber rovings is nearly complete with only preform permeability remaining. The experimental data generated to date clearly show increased mechanical performance with a decrease in the individual carbon fiber bundle sizes as previously theorized.

The first and second phases of the carbon fiber roving development program with Fortafil Fibers are under way. Progress has been made with regard to both precursor and carbon fiber mechanical splitting techniques along with fabrication of spun yarn rovings. Upon fabrication of prototype material in suitable test quantities, preforming and molding evaluation within the ACC will be conducted.