E. Low-Cost Carbon-Fiber Manufacturing Using Microwave Energy

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Objective

- Investigate and develop a microwave-assisted technical alternative to carbonize and graphitize polyacrylonitrile (PAN) based precursor.
- Prove that carbon fiber with properties suitable for use by the automotive industry can be produced inexpensively using microwave-assisted plasma (MAP) processing.
- Demonstrate that MAP processing can produce acceptably uniform properties over the length of the fiber tow.
- Show that for specified microwave input parameters, fibers with specific properties may be controllably and predictably manufactured using microwave furnaces.
- Demonstrate the economic feasibility for producing approximately 30-Msi modulus fibers at a significant cost reduction relative to those produced conventionally.

Approach

- Demonstrate the ability to deliver high fiber mass throughput by increasing line speed and tow count.
- Conduct parametric studies on the continuous carbon-fiber processing pilot unit to continually improve the system design, process parameters, and fiber properties.
- Characterize MAP-processed carbon fibers to confirm that they satisfy program requirements.
- Continually evaluate, develop, and characterize “spin-off” technology, hardware, and ideas that improve upstream or downstream processing, or facilitate more efficient utilization of fiber.

Accomplishments

- Completed MAP relocation and re-assembly of equipment.
- Restarted MAP carbonization line after relocation and re-assembly.
- Validated improved energy distribution in reactor.
- Carbonized three large tows, satisfying property requirements and a major milestone, at > 1 m/min line speed.

Future Direction

- Integrate into advanced technology, subscale carbon-fiber pilot conversion line and address remaining technical issues.
- Develop partnership(s) to commercialize the technology.

Introduction

The purpose of this project is to investigate and develop a microwave-assisted technical alternative to carbonize and partially graphitize PAN precursor. The project is to prove that carbon fiber with properties suitable for use by the automotive industry can be produced inexpensively using MAP processing. It is to be demonstrated that MAP processing can produce acceptably uniform properties over the length of the fiber tow. The project is also to show that, for specified microwave input parameters, fibers with specific properties may be controllably and predictably manufactured using microwave furnaces. Lastly, but most importantly, this project is to demonstrate the economic feasibility for producing fibers with tensile modulus ≥ 25 Msi and ultimate tensile strain ≥ 1.0% at a significant cost reduction below those produced conventionally.

Project Deliverables

At the end of this project, a continuous, multiple-tow, scalable, high-line-speed, MAP carbon-fiber prototype unit will have been developed, constructed, and tested. The MAP hardware will subsequently be integrated into an advanced-technology pilot line. Appropriate industry briefings will be conducted to facilitate commercialization of this economically-enabling technology.

Facility Relocation

In fiscal year (FY) 2005, the carbon-fiber conversion laboratory and associated equipment was moved from the Y-12 site to the ORNL main campus. Completion of equipment reassembly, installation, and checkout was completed in early FY 2006.

Processing

Changes were made to the reactor to improve its reliability and power distribution, and decrease reflected power. The improved power distribution yielded a 4X increase in the plasma volume in the reactor, enabling substantially higher line speed. Figure 1 shows the MAP system during operation, with the glow indicating good local power density along the entire reactor length. Experimental operations resumed and operational testing was performed in the first half of FY 2006. At the request of the Automotive Composites Consortium (ACC), two one-lb. spools of pre-oxidized, 50k tow were single-tow MAP carbonized and short sample lengths were delivered to ACC researchers for characterization. ORNL also characterized samples of this fiber. Physical and mechanical properties are shown in Table 1. Wide angle x-ray scattering morphology data are shown in Figure 2, and include data for Zoltek's Panex® 33 fiber, indicating that MAP-carbonized fiber morphology compares favorably with that of commercial-grade fibers.

The latter half of FY 2006 was principally dedicated to experimental operations targeted toward achieving 3-tow operation at a line speed ≥ 1 m/min. The first experiments were conducted with one tow to perform system debugging during carbonization. Then we began to push toward the milestone. We experienced several process and equipment failures as we extended the limits of our operational experience. Some of these failures, such as broken

Figure 1. Latest version of MAP reactor during operation.

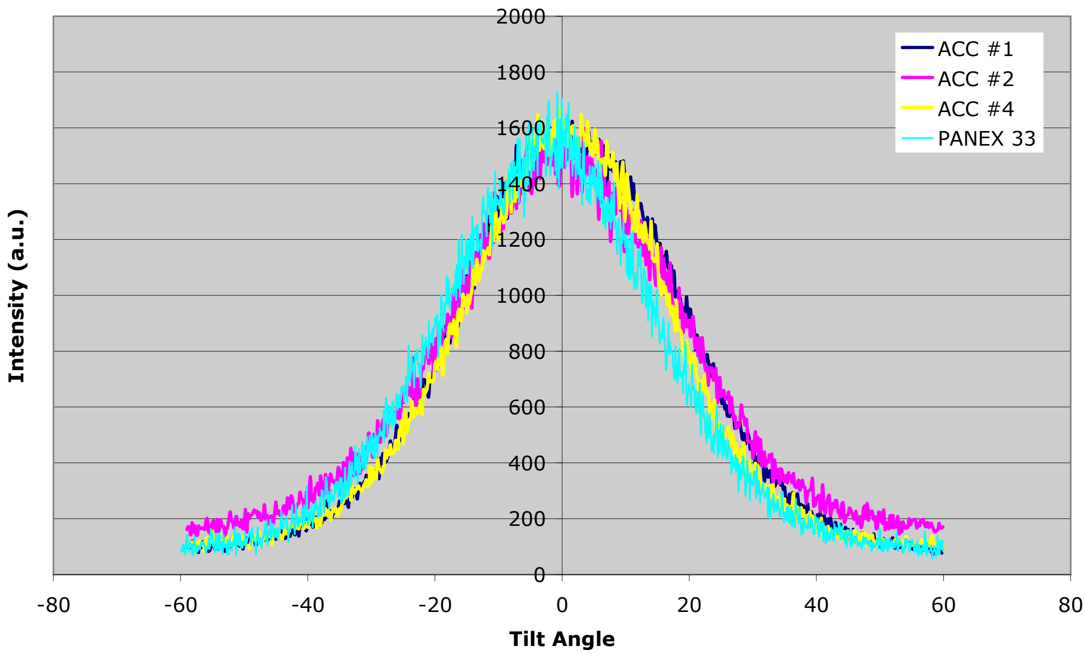

Figure 2. Crystal tilt angle in fibers delivered to ACC.

reactor tubes, caused considerable delays. Nevertheless, we were able to resolve all of the problems and ran the system with three large tows, at ~ 1.1 m/min, for a period of about one hour, in August 2006.

Mechanical properties of the finished fibers from the milestone run are shown in Table 2. These data were measured using untreated, unsized, large tows made into 50k broom straws. There is a clear pattern of changing properties from tow to tow; this is because the tows are not equidistant from the microwave inlet. This is easily resolvable by a simple geometrical reconfiguration. Otherwise, the mean properties are quite satisfactory, especially considering that the absence of surface treatment and sizing should slightly reduce the strength and strain properties. The high variability is expected at this point in the development program. Reducing the variability will be a necessary part of future work.

The current estimated status against established metrics is shown in Figure 3. These metrics are based on limited experience operating the new reactor design, and should improve with further experimentation and increased operational experience.

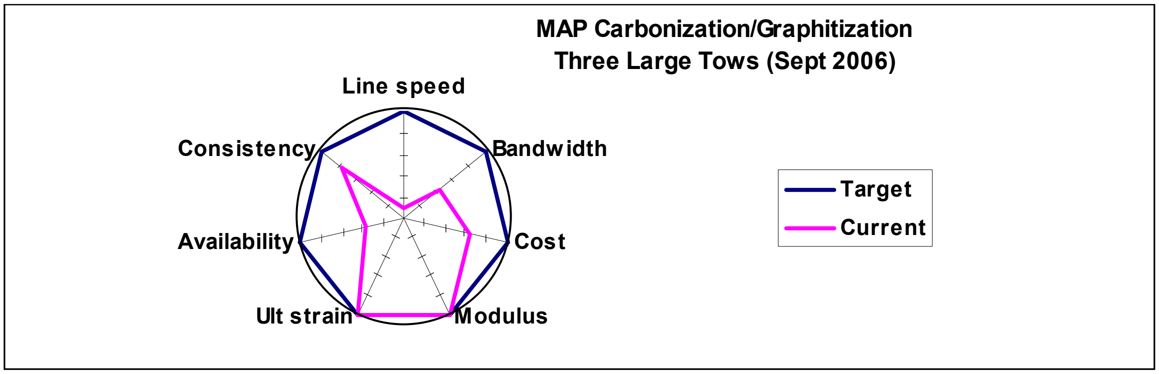

Figure 3. "Spider chart" showing estimated current status vs. metrics.

Future Direction

Remaining technical issues that need to be addressed include improved reactor sealing methods and/or atmospheric-pressure operation, reactor materials, reduced variability of finished fiber properties, as well as continued scale-up of both tow count and line speed, and integration with other conversion modules.

Patents and Publications

Patent application # 11/270,065, co-invented by T.S. Bigelow, F.L. Paulauskas, and T.L. White, and entitled "System to Continuously Produce Carbon Fiber via Microwave-Assisted Plasma Processing," was filed in November 2005. It describes the design details of the MAP carbonization system.

A paper by F.L. Paulauskas, T.L. White, and J.E. Spruiell, entitled "Structure and Properties of Carbon Fibers Produced Using Microwave-Assisted Plasma Technology, Part 2," was presented at the spring SAMPE conference in Long Beach, CA.

Education

The materials characterization has been conducted in partnership with the University of Tennessee's Materials Science Department. Graduate students provided characterization support to the project under the guidance of Professors Roberto Benson and Joseph Spruiell.

Conclusions

After relocation of the MAP carbonization system to ORNL's main campus in late FY 2005, it was re-assembled and operationally tested in early FY 2006. Checkout tests indicated a much improved power distribution and plasma volume. At their request, fiber samples were provided to ACC for evaluation. Fiber conversion experiments were conducted in the last half of FY 2006. Experiments culminated in 3-tow operation at 1 m/min line speed to produce mechanically-competent fibers. This satisfied the project's end-of-year milestone. Future work includes scale-up and resolution of a small number of key technical issues.

Table 1. Physical and mechanical properties of fibers provided to ACC.

	Production Date	Approx. Production Line Speed	Final Density (pycnom.)	Calculated Tow Area	Calculated Filament Diameter	Tow Linear Electrical Resistance	Electrical Resistivity	Mechanical Properties (based on single filament tests) Modulus	Ultimate Tensile Strength	Elongation at Break	Comments
		in/min	g/cm^3	10^{-2}cm^2	μm	Ω/ft (10^{-2} Ω/cm)	10^{-3} Ω-cm	Msi	Ksi	%	
ACC #1	5/4/2006	36	1.8472	2.376	7.77	7.0 (22.966)	5.46	22.4	437	1.70	
ACC #2	5/9/2006	36	1.7912	2.342	7.72	4.5 (14.764)	3.46	26.0	410	1.46	
ACC #3	5/11/2006	36	1.8244	2.335	7.71	7.5 (24.606)	5.75				Due to the similarities to ACC #1, no mechanical evaluations w ere performed.
ACC #4	5/11/2006	36	1.7884	2.323	7.69	3.4 (11.158)	2.59	28.2	382	1.28	

Table 2. Mechanical properties of 50k tows that were MAP carbonized in 3-tow, 1 m/min milestone run.

	3 Tow MAP Single Filament Test *Broom Straw Test ** Tow 1	**Tow 2**	**Tow 3**	**CONVENTIONAL Zoltek Panex 33**	**Fortafil F3(C)**	**Program Goals**
Production Line Speed (in/min)	44	44	44	-	-	**-**
Modulus** (x 10^6 lb/in^2)	28.5 ***27.7 ± 0.6***	25.2 ***25.2 ± 1.5***	24.5 ***23.0 ± 0.7***	26.1	31.1	**25**
Ultimate Strength (x 10^3 lb/in^2)	432 ***303 ± 27***	448 ***280 ± 33***	375 ***272 ± 30***	408	485	**250**
Elongation at Break (%)	1.44 ***1.08 ± 0.10***	1.59 ***1.10 ± 0.12***	1.44 ***1.16 ± 0.14***	1.5	1.5	**1.0**
Production date:	08/17/06					

* 50k broom straw without fiber surface treatment or sizing

** modulus increases with applied load for broom-straw tests, measurements reported at ε = 0.2 – 0.6 %