

C. Advanced Stabilization of PAN Fiber Precursor

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Objectives

- Develop an improved technique for stabilizing carbon-fiber precursor with increased line speed and reduced carbon-fiber cost.
- Verify that finished fiber properties satisfy automotive and heavy-vehicle manufacturers' requirements.
- Conduct a preliminary evaluation of the cost impact of the new stabilization technique.
- Integrate the stabilization module into an advanced technology pilot-line.

Approach

- Investigate thermochemical, ultraviolet, and electron-beam processing stabilization routes.
- Select one of the aforementioned stabilization routes for detailed equipment and process development.
- Develop fiber-handling protocols for continuous processing.
- Conduct parametric studies to correlate processing parameters and fiber properties.
- Characterize fibers to confirm that they satisfy program requirements.

- Develop equipment and process specifications for a prototypical stabilization module to be implemented in a subscale, advanced-technology pilot-line.

Accomplishments

- Demonstrated that thermochemically-stabilized fibers can be plasma oxidized.
- Demonstrated that electron-beam-stabilized fibers can be plasma oxidized.
- Discovered that ultraviolet irradiation of polyacrylonitrile (PAN) precursor fibers produces relatively high gel fraction in < 2 minute residence time.
- Preliminary cost estimate completed for electron-beam stabilization.

Future Direction

- Complete feasibility investigation of ultraviolet stabilization route.
- Sufficiently investigate all routes to establish reasonable basis for evaluation of metrics including throughput and cost estimates.
- Select one stabilization route for detailed development.
- Conduct parametric studies and fiber characterization to better understand process effects and the processing window and to quantify fiber properties.
- Design an advanced stabilization module for an advanced-technology pilot-line.

Introduction

The purpose of this project is to investigate and develop a technique to rapidly and inexpensively stabilize a PAN precursor. New processing techniques are being developed for the purpose of reducing the cost of carbon-fiber conversion. Previous and ongoing research at ORNL has demonstrated that plasma processing shows great promise for inexpensively and rapidly oxidizing, carbonizing, and graphitizing polymer precursors to convert them to carbon fibers. However, the precursor needs to be lightly stabilized, or cross-linked, before it is exposed to plasma-generated oxidative species. Stabilization and oxidation together are estimated to represent ~ 18% of the cost of commercial-grade carbon fiber¹. A rapid, inexpensive, and robust stabilization technique is needed to complement the aforementioned advanced process modules, and enable the development of an integrated advanced-technology conversion line that converts polymer precursor fibers into carbon fibers at significantly lower cost than conventional conversion technology.

This project therefore intends to develop an advanced stabilization module that integrates with other advanced fiber-processing modules to produce

inexpensive carbon fiber with properties suitable for use by the automotive industry. Critical technical criteria include (1) ≥ 25 Msi tensile modulus and $\geq 1.0\%$ ultimate strain in the finished fiber; (2) uniform properties along the length of the fiber tow; (3) repeatable and controllable processing; (4) and significant unit cost reduction compared with conventional processing.

Project Deliverable

At the end of this project, the project team will have demonstrated satisfactory PAN precursor-fiber stabilization with line speed exceeding (or residence time less than) that typical of conventional carbon-fiber conversion lines. The project deliverable is a process specification from which advanced stabilization equipment can be scaled to develop an operational stabilization module for a subscale, multiple- large-tow, advanced-technology pilot-line.

Technical Approach

The researchers are investigating three prospective PAN-precursor-fiber stabilization routes: electron-beam processing, thermochemical processing, and ultraviolet processing. All three routes are based on discoveries previously made in other carbon-fiber

projects, and each appears to offer certain advantages. After initial feasibility studies, the researchers will select the most promising route for detailed process development, with the principal criteria for selection being mechanical properties and finished fiber cost. The preferred route will then undergo detailed parametric studies to characterize the process and develop the processing recipe.

Progress

Electron-Beam Processing

Initial electron-irradiation experiments were conducted at the Radiation Dynamics Inc. Long Island facility in late 2005. Several precursor tows are shown in Figure 1. The precursors on the glass frame were electron irradiated followed by brief heat treatment at a temperature below conventional stabilization temperature. The top precursor was not irradiated, but was heat treated at the same condition as the others. In all cases of irradiation, significant darkening is observed, suggesting that cross-linking has occurred during irradiation.

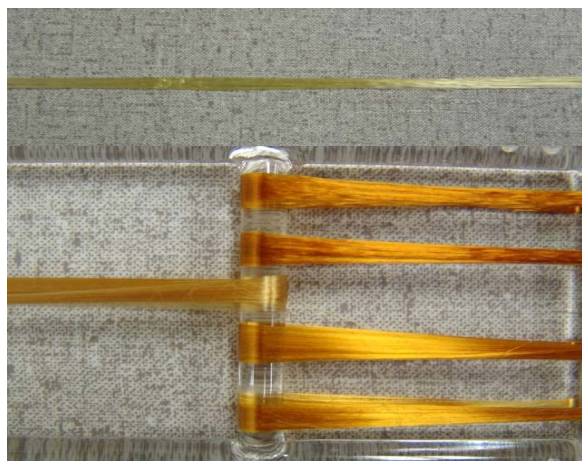


Figure 1. Lower 5 tows were irradiated followed by brief heat soak. Top tow was not irradiated but subjected to identical heat soak.

The precursor density increases only negligibly during electron irradiation, but advances rapidly thereafter upon brief post-treatment at the right conditions.

Differential scanning calorimetry (DSC) results, an example of which is shown in Figure 2, indicate that electron irradiation lowered and spread the exothermic peak, and moved the curve slightly to

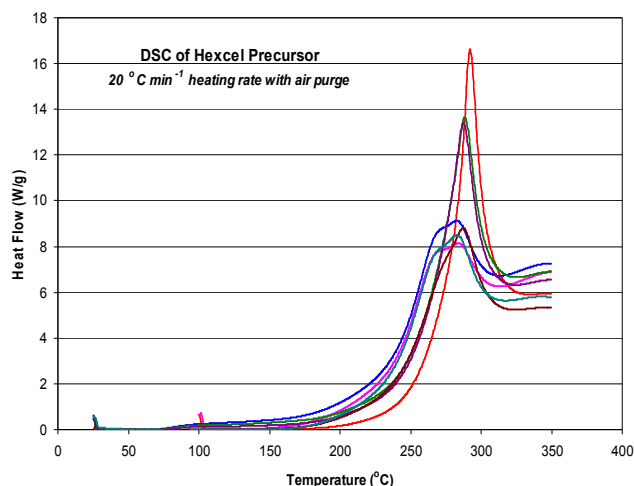


Figure 2. DSC results for electron-irradiated PAN precursor. Highest peak is virgin precursor; others are after irradiation at various conditions.

the left. This was expected to lower the onset of exothermic reaction and to cause greater heat generation at temperatures below the baseline curve, but overall to make the reaction more controllable by reducing the impact of the narrow and steep exothermic peak. However, electron-irradiated precursor could not be processed using the oxidation conditions established for conventionally-stabilized precursor. A parametric investigation of oxidation parameters was initiated and acceptable operating parameters have been identified, but considerably more work is needed in this area. Electron-beam-stabilized fibers were subsequently plasma oxidized, satisfying a mid-year project milestone. In the last half of fiscal year (FY) 2006, initial DSC characterization was repeated and many more DSC runs were made using new equipment at ORNL's Center for Nanophase Materials Sciences. The project team planned and prepared for a new set of irradiation experiments scheduled in October 2006.

Electron-beam-stabilized precursor has been converted to finished fibers by a range of process combinations, and the results compared in Figure 3.

All of the conversions, even by fully-conventional means, were conducted at low carbonization temperature and without the benefit of fiber tensioning, tow spreading, or controlled stretching in any of the conversion stages; hence, the fiber mechanicals are expected to be low compared to those of corresponding commercial fibers. In fact,

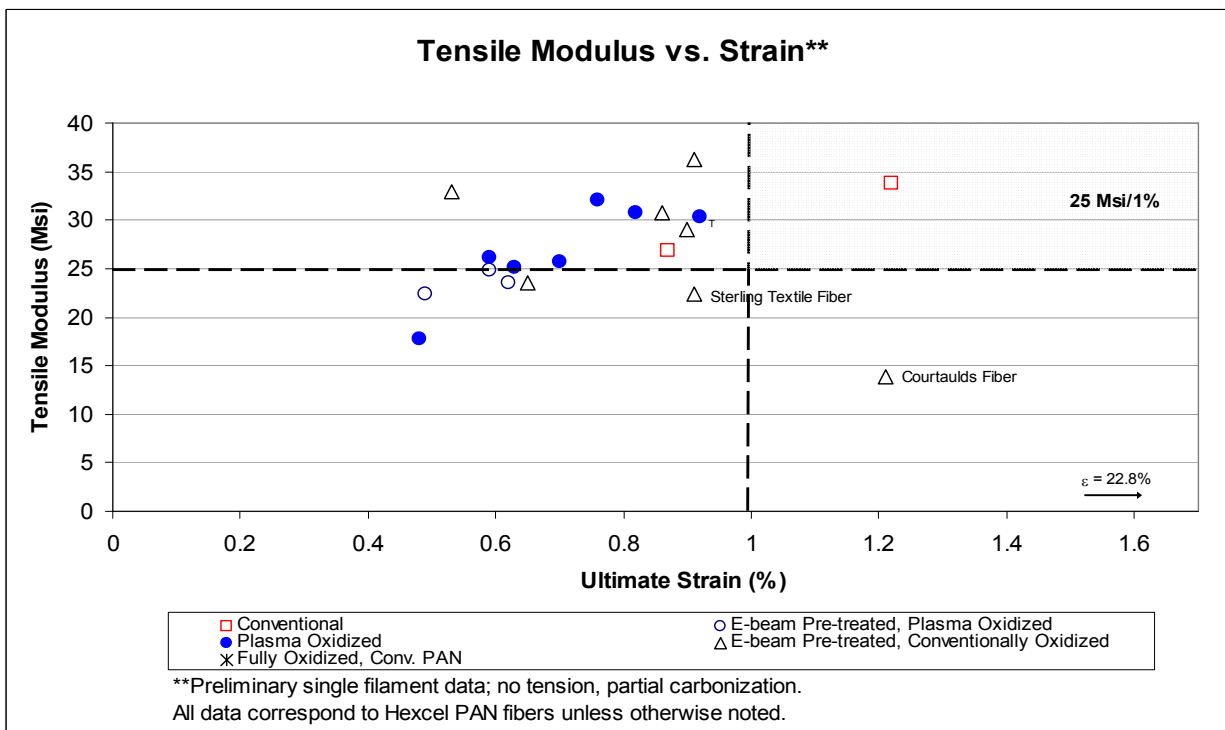
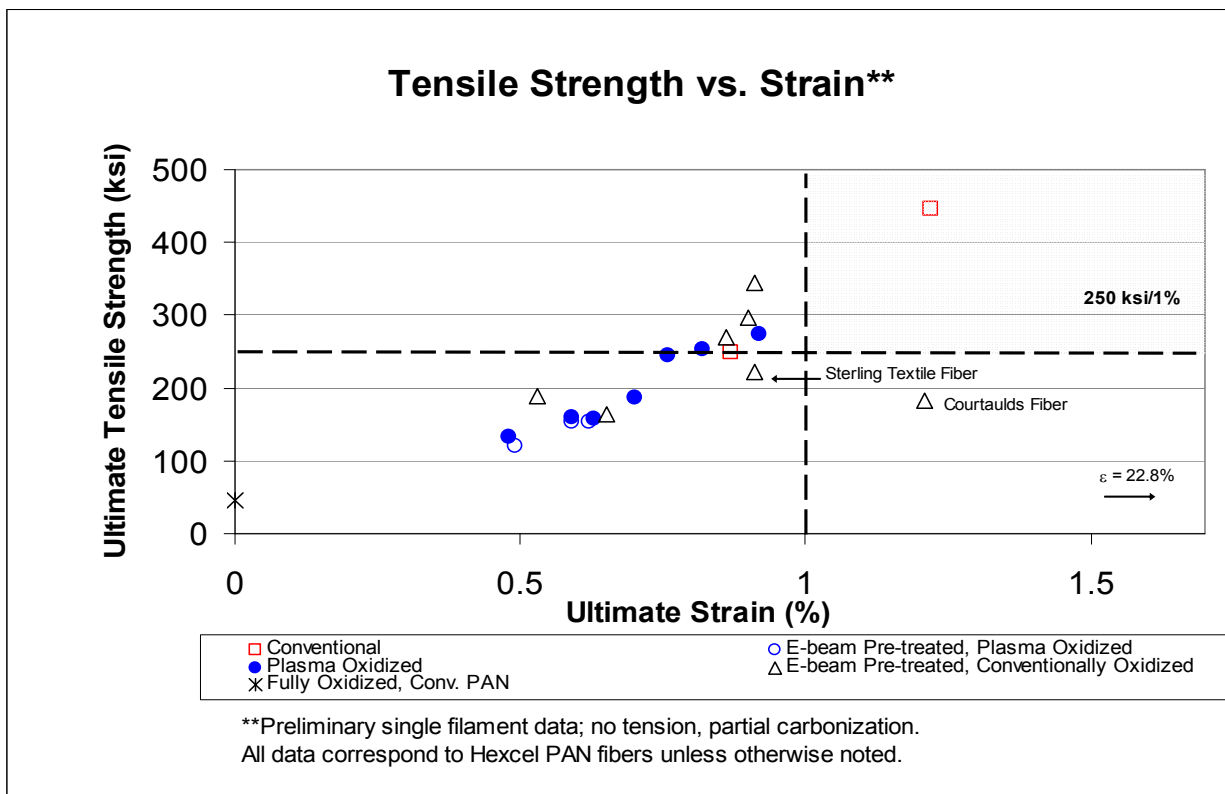


Figure 3. Mechanical properties of first electron-beam-stabilized fiber specimens (tested by single-filament tensile-strength method). Conventional data points were thermally shocked and thermally ramped, respectively.

several of the advanced-technology specimens exhibit a tensile modulus exceeding the 25 Msi requirement. The strain is generally somewhat below the 1% requirement. It is noteworthy that the electron-beam-stabilized samples, even those that were subsequently plasma oxidized, exhibit mechanicals that are not far below those of the thermally-converted fibers. This gives us confidence that the property targets are well within reach. Electron-beam-stabilized fibers will be carbonized at correct temperature and tension after commissioning a high-temperature tube furnace in the second quarter of FY 2007.

Electron-beam irradiation equipment and protocols are relatively mature in other industries, with high reliability and throughputs. One can extrapolate from a well-established experience base to estimate parameters such as availability, throughput, and cost per unit of dose delivered to the product. The major challenges appear to be the interfacing of electron-beam-stabilization and plasma-oxidation processes, and the high capital cost of electron beams. The unit capital cost drops precipitously with increasing scale, and a single high-power beam may be able to serve several production lines. But this will make it necessary to provide “surge capacity” that isolates the beam from downstream processes so that a single-point failure will not disrupt the operation of several fiber production lines. Early analysis suggests that electron-beam stabilization will not be cost-effective for low-production-volume conversion factories, but if system-compatibility issues can be successfully resolved, it is likely to be very attractive for high-volume factories. It may be preferable to electron-beam stabilize at the precursor factory, immediately after precursor spinning, rather than in-line at the conversion factory. This could potentially address the scaling economics. Current metrics are shown in “spider chart” format in Figure 4.

Thermochemical Processing

Stabilization was found to be needed before plasma oxidation because virgin precursor could not withstand the reactive oxidative species generated by plasma. When virgin precursor is exposed to the plasma-generated chemistry, significant exothermic heating occurs fairly rapidly, resulting in interfilamentary adhesion and tow rigidity.

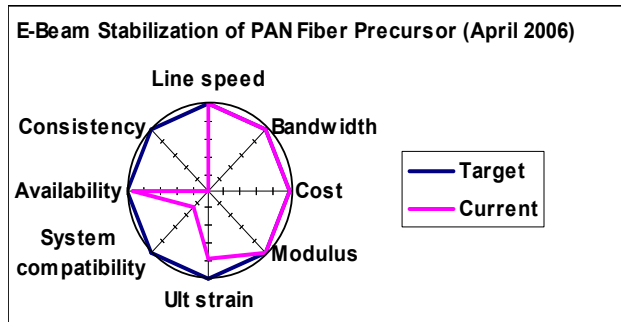


Figure 4. “Spider chart” showing current estimates of electron-beam-stabilization metrics.

Thermochemical stabilization, using some modification of thermal and/or chemical conditions experienced in plasma oxidation, appears to potentially offer a rapid stabilization route.

Thermochemical stabilization was investigated and shown to be technically viable. Virgin precursor was thermochemically treated in the oxidation reactor. The researchers demonstrated the capability to thermochemically stabilize virgin precursor in about 30% less residence time than that required for conventional stabilization. Thermochemically-stabilized fiber was subsequently plasma oxidized, satisfying a mid-year milestone. The researchers are continuing to investigate thermochemical-stabilization parameters with the hope of further reducing the residence time. It is currently too early in the thermochemical stabilization investigation to estimate cost or other metrics.

Other (non-plasma) thermochemical stabilization routes will be conceived and/or reviewed in early FY 2007, and further investigated if they are deemed to offer sufficient merit.

Ultraviolet Processing

Ultraviolet processing potentially offers the combination of high line speeds with low capital cost. The chemistry is generally similar to that of electron-beam processing, but very often ultraviolet requires a photoinitiator that would not be needed for electron-beam cross-linking. One of the major challenges is whether ultraviolet irradiation can deliver uniform cross-linking throughout the tow, with acceptable residence time.

The ultraviolet processing development is being conducted at Clemson University with ORNL providing technical consultation and direction. Clemson's experimental ultraviolet equipment is shown in Figure 5. It utilizes a mercury lamp, with a conveying system to move the material through the temperature-controlled irradiation zone.



Figure 5. Experimental ultraviolet equipment.

Virgin precursor and ultraviolet-irradiated precursor (absent photoinitiator) are shown side-by-side in Figure 6. As shown, a few minutes of ultraviolet irradiation can produce significant color change.

The gel fraction (fraction of material remaining solid in dimethyl sulphoxide solvent) of ultraviolet-irradiated material was measured to be ~41%, compared to ~1% for virgin precursor, >90% for oxidized PAN fiber, and >99% for finished carbon-fiber. DSC results, shown in Figure 7, show reduction and a slight broadening of the exothermic peak ("UV + thermal" trace). The sample is irradiated at elevated temperature. The purely thermal stabilization, i.e., the stabilization that would occur due only to heat at the temperature in the ultraviolet chamber, is shown by the "thermal" trace in Figure 7. The "thermal" trace approximately duplicates the "as received" trace, suggesting that there is virtually no thermal stabilization component at the irradiation conditions. This indicates that the thermal component alone is insufficient, i.e., the ultraviolet irradiation component is needed to achieve the "UV + thermal" results.

To evaluate the uniformity of cross-linking, DSC measurements were made on different parts of the tow. Figure 8 shows the DSC results, indicating that



Figure 6. Virgin PAN precursor fibers, at left, exposed to increasing ultraviolet dose, at right.

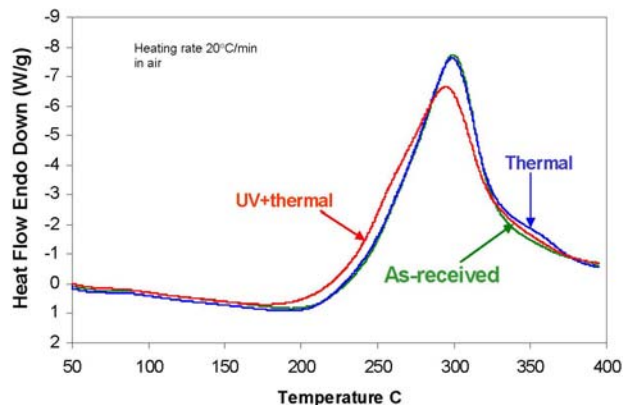


Figure 7. Ultraviolet stabilization DSC (in air) results for Courtaulds precursor.

there is significant cross-linking variability across the tow. The fiber surfaces are damaged by soaking in a 50% solution of sulfuric acid. Figure 9 shows micrographs showing the damage.

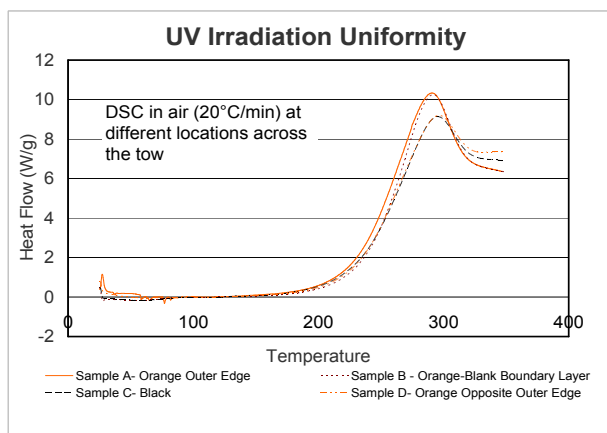


Figure 8. DSC scans of UV-stabilized fibers taken from different locations across the tow.

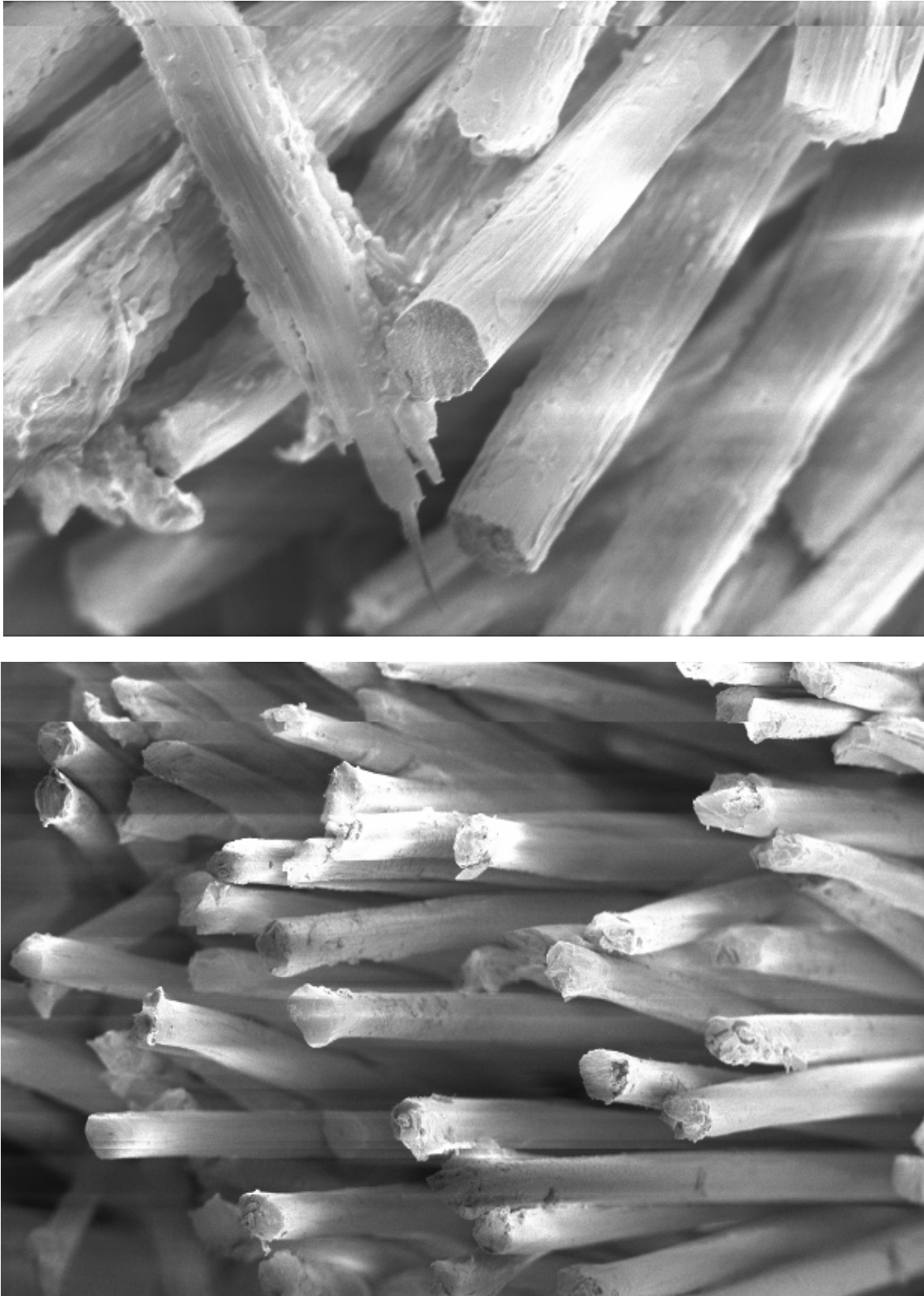


Figure 9. Micrographs of UV-irradiated fibers after acid soak. Top – nominal dose; bottom – 3X nominal dose.

This damage indicates that surface cross-linking is inadequate to protect the underlying polymer from the acid. The low level and variability of cross-linking cause concern, but it is not presently known how dense or uniform the cross-linking must be. Clearly there is some effect of cross-linking, as virgin precursor, when subjected to the same acid treatment, will show significant damage in just minutes. Light cross-linking at the fiber's surface may be sufficient to prepare the fiber for plasma oxidation, and some low nonuniformity is probably acceptable. The fibers must be tested in the oxidation reactor to determine whether they are sufficiently cross-linked.

To date, there has been no attempt to plasma oxidize ultraviolet-stabilized fibers. This will be done in FY 2007. Ultraviolet-stabilization metrics also have not yet been evaluated. The results to date have raised issues of concern, but on the whole have been encouraging. Considerably more work is needed to determine whether ultraviolet processing is a viable stabilization route.

Future Direction

Early FY 2007 will be devoted to continuing parallel studies of the proposed stabilization routes, with down-selection to a single route in mid to late 2007.

Patents and Publications

Two patents were filed, as follows:
F.L. Paulauskas, T.L. White, and D.M. Sherman, "Apparatus and method for oxidation and stabilization of polymeric materials," application # 11/344,573, filed January 2006; and

F.L. Paulauskas and D.M. Sherman, "Apparatus and method for stabilization or oxidation of polymeric materials," application # 11/391,615, filed March 2006.

A paper by S.M. White, J.E. Spruiell, and F.L. Paulauskas, entitled "Fundamental Studies of Stabilization of Polyacrylonitrile Precursor, Part 1: Effects of Thermal and Environmental Treatment," was presented at the spring SAMPE conference in Long Beach, CA.

Education

Educational institutions participating in this project include Clemson University and the University of Tennessee (UT). A Clemson post-doctoral researcher is conducting ultraviolet-processing studies under the direction of Professor Amod Ogale. UT materials-science graduate students are providing characterization support to the project under the guidance of Professor Roberto Benson.

Partners

ORNL gratefully acknowledges the following partners that have made valuable contributions to this project:

- Atmospheric Glow Technologies – plasma equipment design and processing (subcontract)
- Automotive Composites Consortium – programmatic and technical direction (complimentary)
- Clemson University – ultraviolet process development (subcontract)
- Hexcel Corporation – raw materials and technical consultation (complimentary)
- Radiation Dynamics Inc. – irradiation analysis, protocols, and beam time (complimentary)
- TohoTenax America – raw materials and technical consultation (complimentary)
- University of Tennessee – characterization (subcontract).

Conclusions

Three prospective processing routes to lightly stabilize polymer precursors in an advanced carbon-fiber conversion line are under investigation. Electron-beam processing and thermochemical processing have been shown to be technically feasible, and the early results from ultraviolet processing are surprisingly good. It appears likely that there will be multiple good options from which to choose an advanced stabilization route. Down-selection is scheduled in mid- or late-FY 2007.

¹ S.M. Cohn and S. Das, "A Cost Assessment of Conventional PAN Carbon-fiber Production Technology." Energy Division, Oak Ridge National Laboratory, TN (1998)