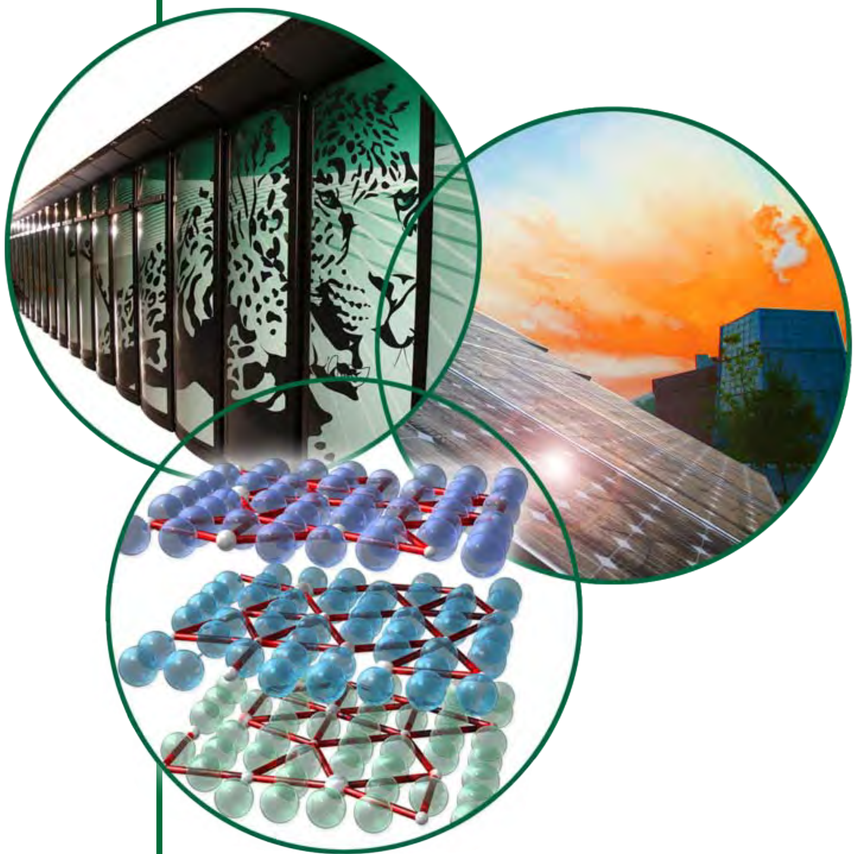
Materials Characterization Capabilities at the High Temperature Materials Laboratory: Focus on Carbon Fiber and Composites

Project ID: LM027



DOE 2011 Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

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Washington, DC
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U.S. DEPARTMENT OF ENERGY

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The HTML User Program: Background

- The High Temperature Materials Laboratory is a National User Facility that supports the missions of DOE, EERE and the Vehicle Technologies Program in particular, by working with industry, universities, and other national laboratories to develop energy-efficient technologies that will enable the U.S. to use less petroleum. The HTML is organized into six user centers, which are clusters of highly skilled staff and sophisticated, often one-of-a-kind instruments for materials characterization.
- Access to the HTML User Program is provided through the HTML User Program proposal process. Research proposals are reviewed by a committee and approved based on scientific merit, relevance of the proposed research to the mission of DOE's Vehicle Technologies Program, feasibility, and non-competition with the private sector. Projects have a well-defined scope, and research is completed within 24 months and often involves multiple user visits to the HTML.
- Both nonproprietary and proprietary research is conducted within the HTML User Program. There are generally no charges for nonproprietary research projects, and users conducting nonproprietary research must agree to submit research results for publication in the open, refereed literature. A nonproprietary project is complete when research ends, accompanied by the required publication in the open literature and/or presentation at a professional conference. For proprietary research, the user owns the research data, and all costs at the HTML are paid by the user based on DOE guidelines for ORNL cost recovery.

The HTML User Program – FY2010 Activity

During FY2010, the HTML User Program collaborated with 18 companies, 25 universities, and 6 national laboratories on 68 user projects addressing critical technical barriers to achieving the goals of DOE's Vehicle Technologies Program. There were 96 researchers, 63% of them first-time users, who visited the HTML for a total of 716 research days.

The HTML User Program FY2010 budget was $5,312,400 and allocated as follows:

- Capital equipment: $881,959
- Operations: $4,430,441

Users cost-share their HTML user projects through:

1) direct involvement with HTML staff members during the development of the user project;
2) funding their time and travel to the HTML to perform research;
3) cost of materials provided by the user or the research performed prior to the user project;
4) collaboration with HTML staff members to analyze the data and publish the results.

The HTML also supports the education and preparation of the next generation of scientists and engineers. During FY2010, students and professors from 25 universities participated in the HTML User Program. Five of those students earned their Ph.D. degree and one earned her M.S. degree based in part on research they conducted through the HTML User Program.

Relevance to the VT Program

- The Vehicle Technologies Program funds the operation of the HTML User Program to maintain world-class expertise and instrumentation capabilities for materials characterization to work with industry, universities and national laboratories toward the goals of the Vehicle Technologies Program. The HTML User Program capabilities at the Oak Ridge National Laboratory support the activities of the Vehicle Technologies Program's subprograms in Lightweight Materials, Propulsion Materials, Energy Storage, Solid State Energy Conversion, Combustion & Emissions Controls, Power Electronics & Electric Motors, and Non-Petroleum Fuels.

- During FY2010, the HTML User Program managed **17** characterization projects in Lightweight Materials, and this presentation highlights ***one*** of them. This presentation discusses the user project with the Polymer Matrix Composites Group at Oak Ridge National Laboratory. The focus of this project is characterization of carbon fibers in order to address technical challenges and barriers in cost and manufacturability to achieving the goals of the Vehicle Technologies Program.

Polymer Matrix Composites Group User Project: Milestones

- One of the FY2011 milestones for the HTML User Program is to complete three user projects dealing with the characterization of lightweight materials, including carbon fibers and carbon fiber-reinforced polymer matrix composites, by September 30, 2011.

Project ID	Organization	Project	Status
2010-018	Atriax Components Inc.	Characterizing heavy vehicle compressor components: Mg and Al castings and Al-MMC cylinder liner interface	Completed ✓
2010-027	Virginia Commonwealth University	Characterization of lightweight materials for automotive applications	Completed ✓
2010-028	University of Alabama-Birmingham	Effect of chemistry on the transformation characteristics of metastable austenite in intercritically austempered ductile iron for automotive applications	Completed ✓

Project ID	Organization	Project	Due Date
2010-017	Polymer Matrix Composites, ORNL	Development of next generation low-cost carbon fibers: Surface and microstructure analysis	December 2011

"Development of next generation low-cost carbon fibers: Surface and microstructure analysis"

Timeline

- Start date: 2/1/2010
- End date: 12/30/2011
- % complete: 65%

Barriers

- Cost
- Design Data and Modeling Tools
- Manufacturability

Budget

- Included in the user center allocations from the annual budget of the HTML User Program; users cost-share as noted on slide #3.

Collaborators

- **Users:** Polymer Matrix Composites Group Soydan Ozcan, Felix Paulauskas, Amit Kumar, Rebecca Brown
- **HTML Staff:**
  XRD: Melanie Kirkham, Andrew Payzant
  Raman Spectroscopy: Michael Lance
  XPS: Harry M. Meyer III

Collaborations

As a DOE User Facility, the HTML User Program is collaborative in nature. Potential users are assisted with the proposal submission process as necessary, and all research is hands-on with direct involvement from both user and HTML User Program staff researchers. The DOE-required publication of results for non-proprietary projects is also a collaborative effort.

Collaborators on the user project reported in this presentation:

Polymer Matrix Composites Group, Oak Ridge National Laboratory

Felix Paulauskas, Distinguished Scientist
Soydan Ozcan and Amit Kumar, R&D Staff Members
Rebecca Brown, postdoctoral associate

HTML Staff

Melanie Kirkham, Andrew Payzant, Michael Lance, Harry Meyer

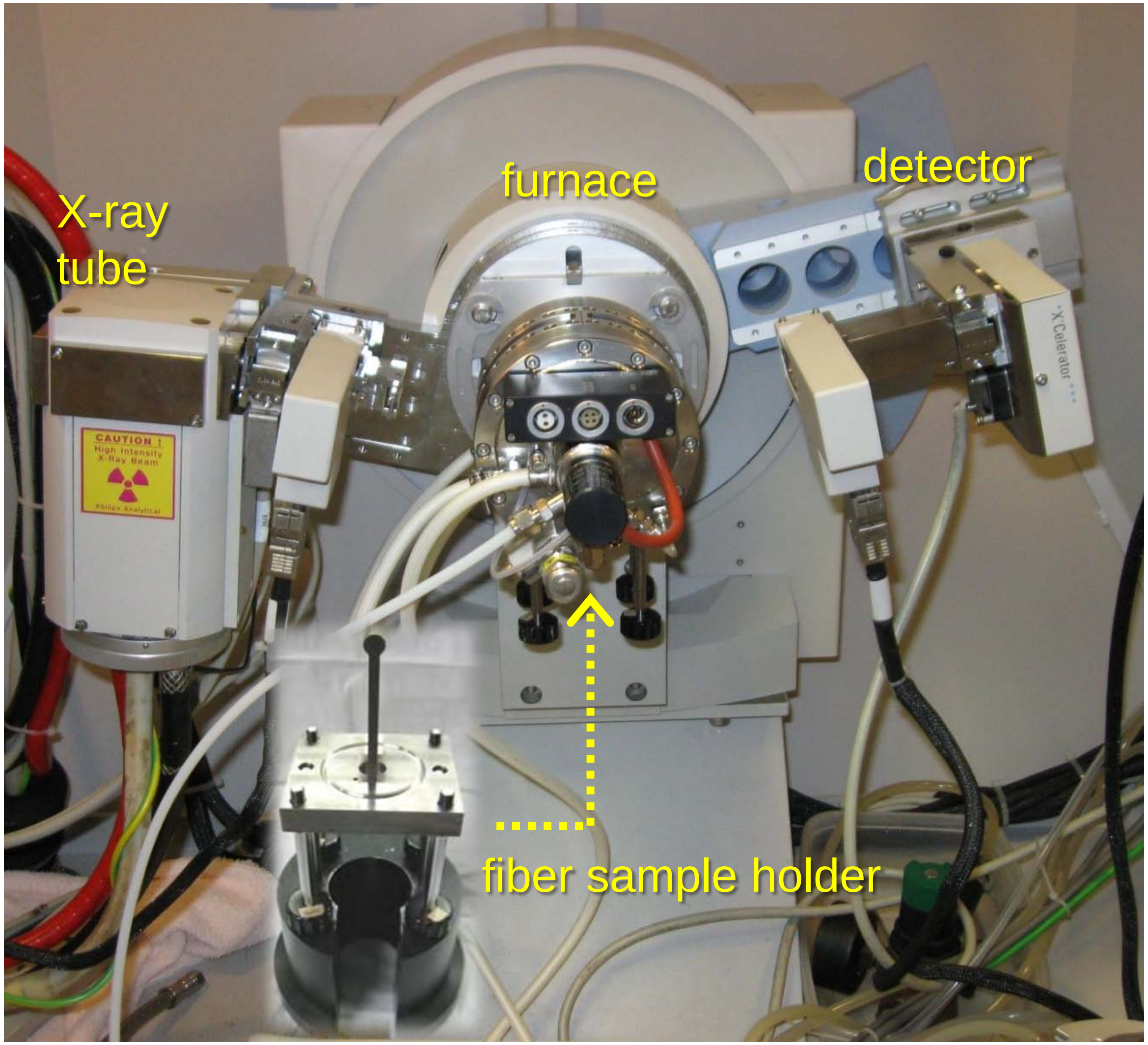
Technical Approach: X-ray diffraction (XRD) and Raman spectroscopy

Research problem: To use new classes of precursor feedstock for fibers and provide the tools for precursor scale up. If successfully developed, these precursors will displace current reliance on pitch and polyacrylonitrile (PAN) precursors that carry an initial cost premium. Processing methods will be developed for significantly reducing the cost of producing carbon fiber include microwave carbonization, radiation stabilization, plasma oxidation, and improvements in line speed and reduction in production downtime.

The optimum processing conditions are not well understood. *In situ* x-ray diffraction (XRD) has been selected as a suitable probe for characterization of the high-temperature oxidation/carburization process, in order to provide additional insights into the nature of the structural evolution from textile fiber to carbon fiber.

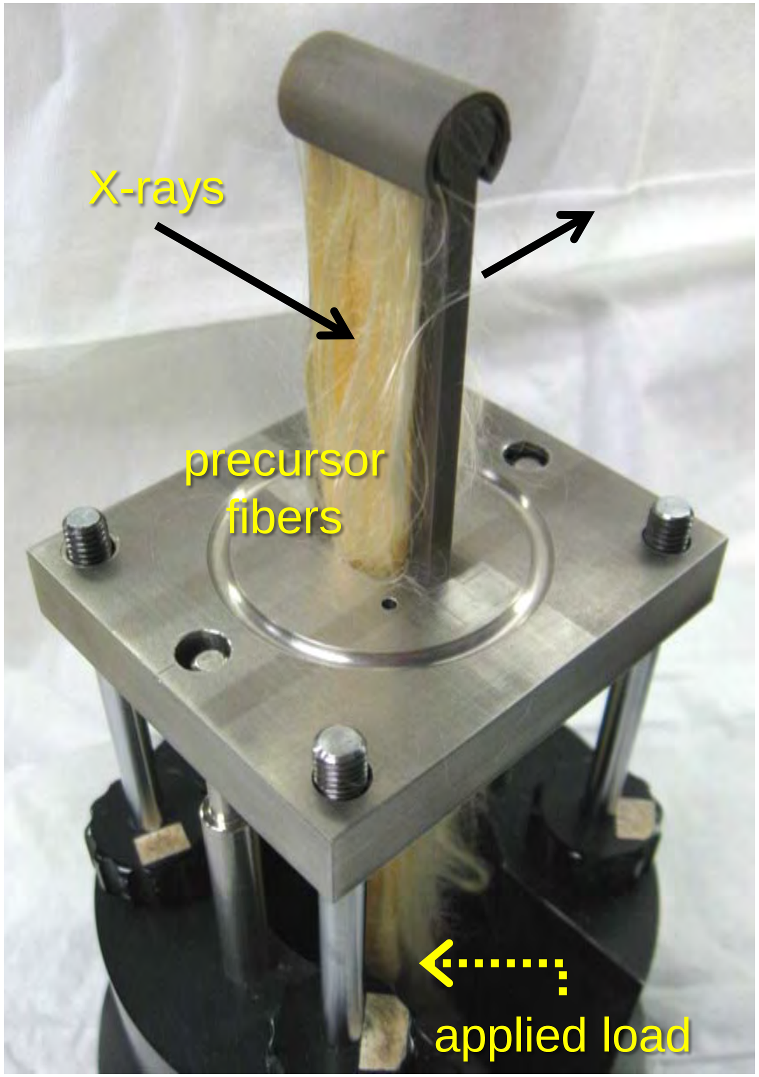
Raman spectroscopy enables a study of the nature of the carbon structure at the fiber surface, and can distinguish between different allotropes of carbon in individual fibers.

"Development of next generation low-cost carbon fibers: Surface and microstructure analysis"



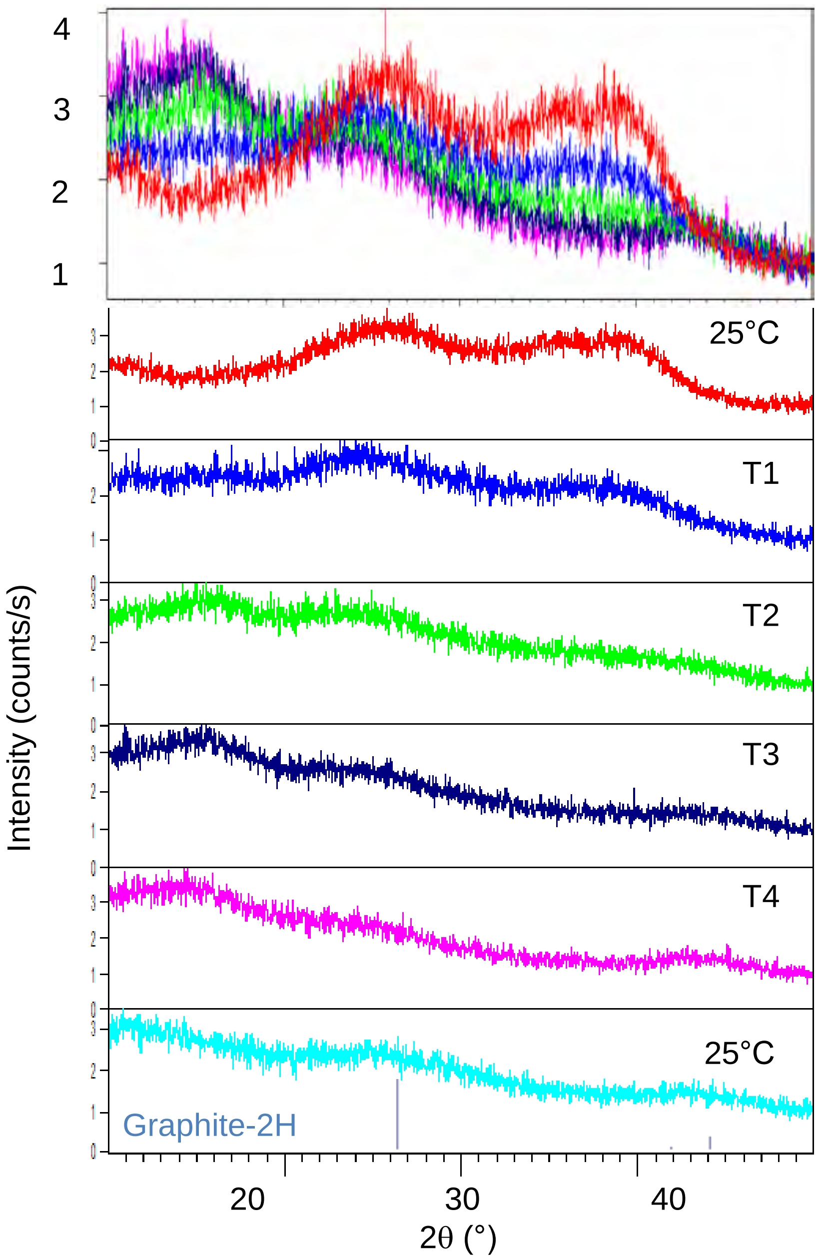
In Situ XRD Platform

- The HTML provides User access to modern x-ray diffractometers with programmable slits, fast position-sensitive detectors, and a variety of specialized sample chambers.
- A commercial X-ray furnace (Anton Paar XRK900) was modified for this project to enable *in-situ* XRD analysis of fibers under mechanical loading, controlled temperature, and atmosphere.



Fiber Sample Holder

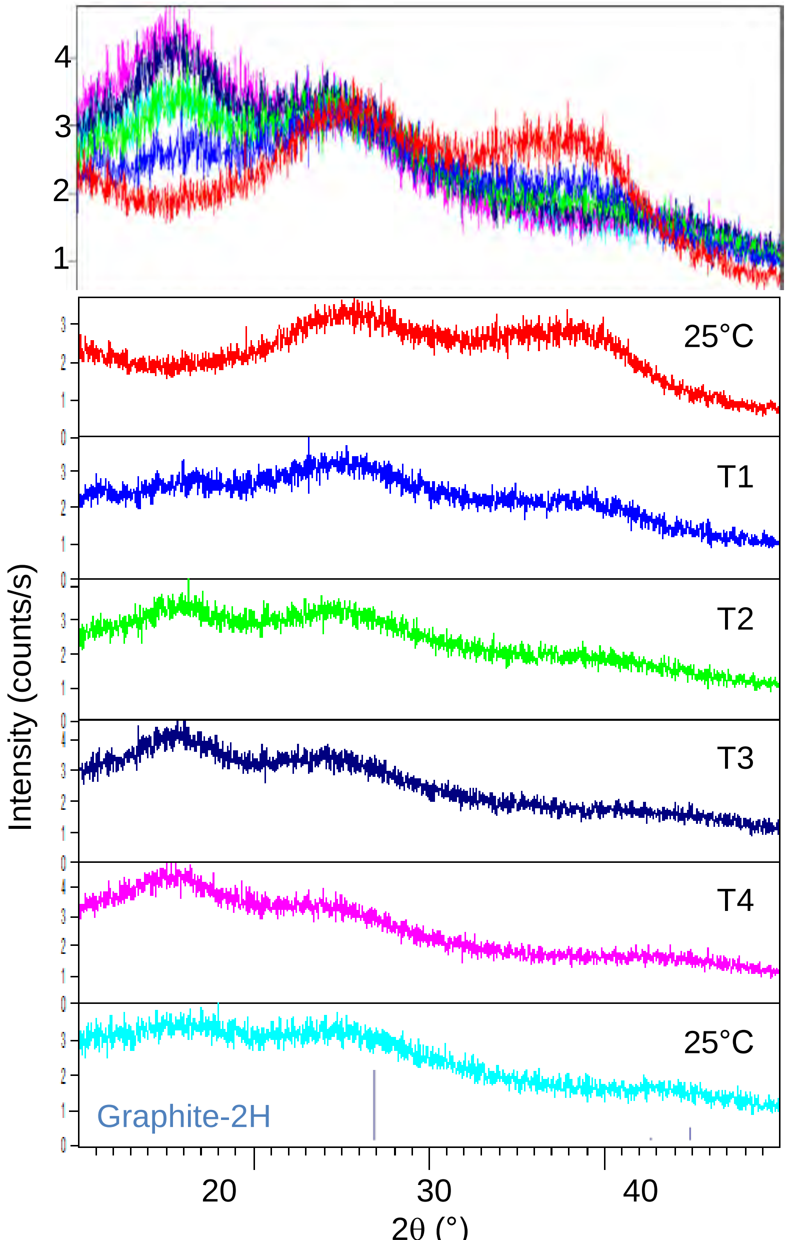
- A sample holder was designed and built to enable the desired in-situ XRD studies
- Fibers are looped over a refractory metal bar and routed through a hole in the bottom of the sample holder, where weights can be attached to provide adjustable tensile loading.
- X-rays pass through the fibers (transmission geometry) which enables characterization of the structure along the fiber axis
- The temperature is controlled using a thermocouple adjacent to the sample.



F1237 fiber – Step 1a under applied load

- X-ray diffraction was used to determine changes in the structural changes during the 2-step thermal treatments developed empirically by the ORNL Carbon Fiber Program for converting textile-based fibers into carbon fibers.
- Details of the thermal treatments are not disclosed herein, in accordance with Export Control regulations.
- During Step 1 as the sample is heated, the structure of the original precursor fiber is lost, while an intermediate structure grows, as evidenced by the peak around 16 2θ (~5.6 Å d-spacing). Additionally, features of the graphite-2H structure begin to appear.

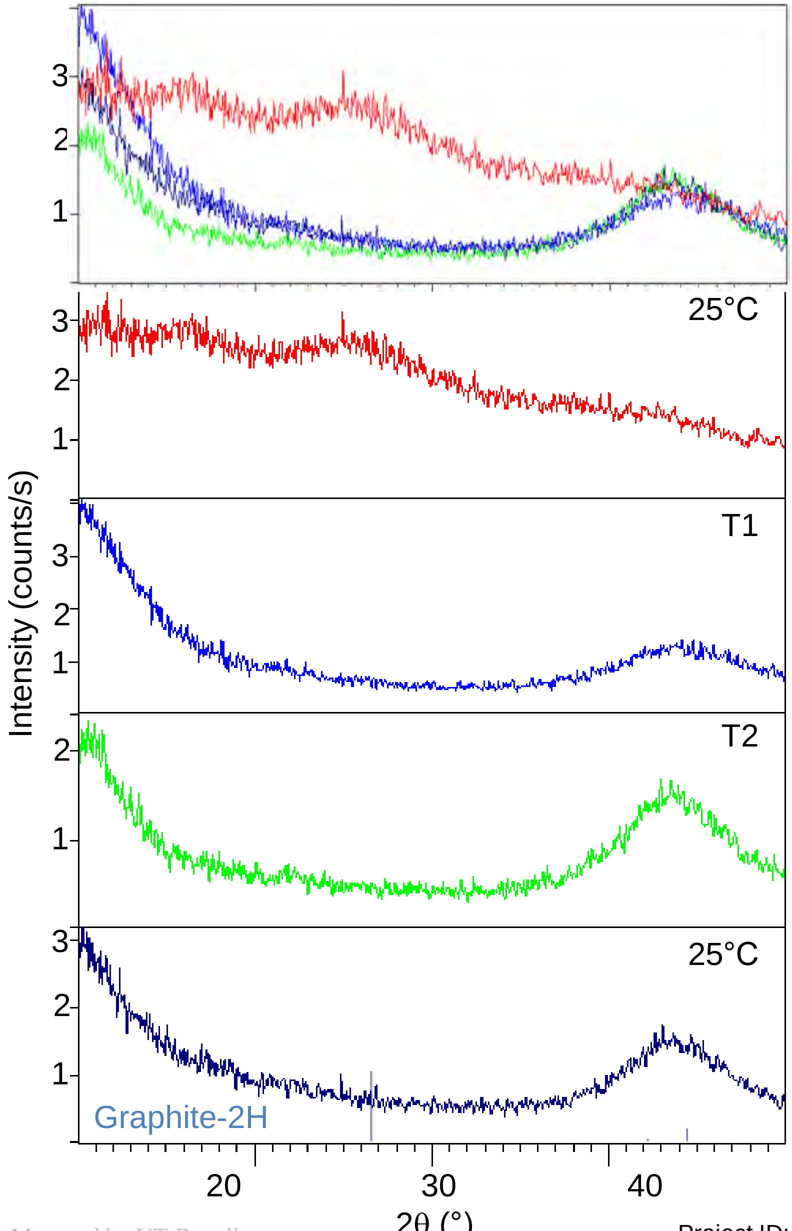
ORNL Polymer Matrix Composites Group User Project: Technical Approach



F1237 fiber – Step 1b no applied load

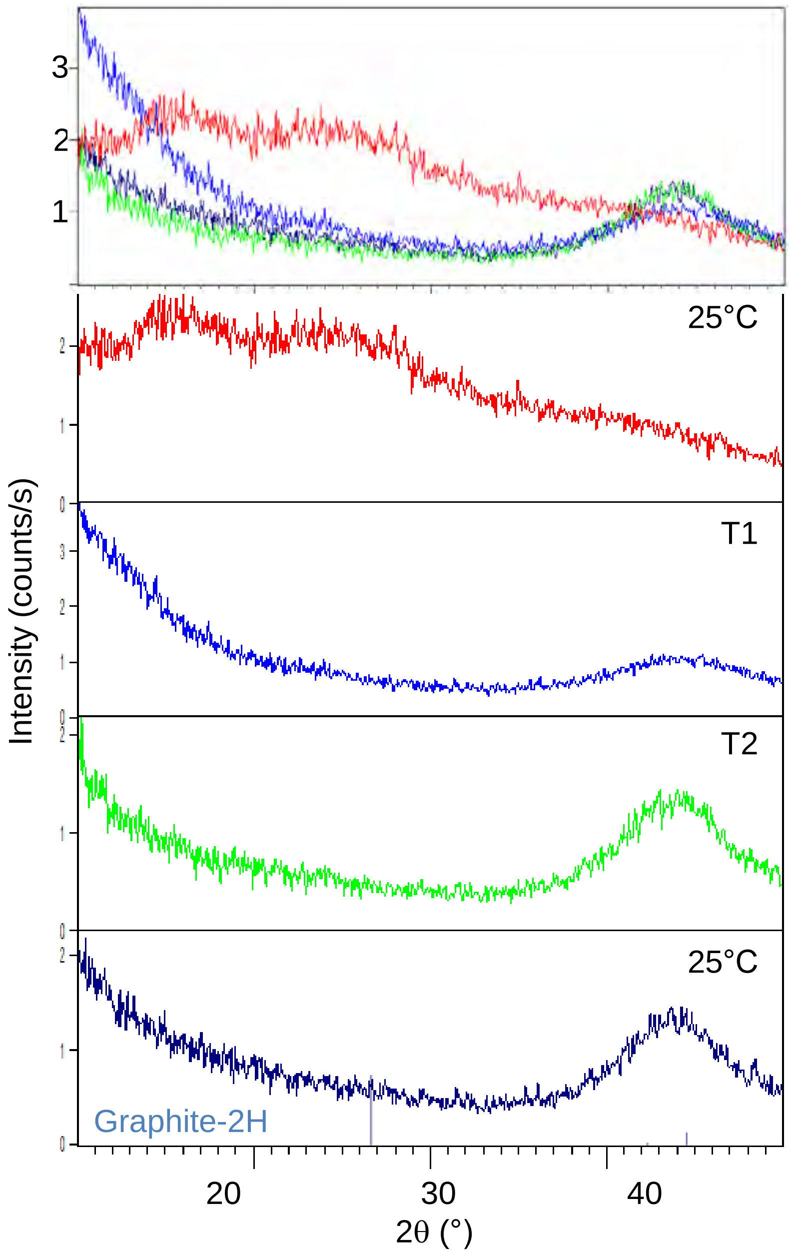
The only major difference between the “under load” (preceding slide) and “no load” conditions is that the intermediate structure is slightly less intense under load.

From a crystal structure and crystalline phase perspective, there is little difference between Step 1 applied load and Step 1 no applied load thermal processing.



F1237 fiber – Step 2b under applied load

During the second thermal treatment step, as the sample is heated, the intermediate structure disappears and is replaced by carbon – the graphite become more highly oriented as the treatment continues.



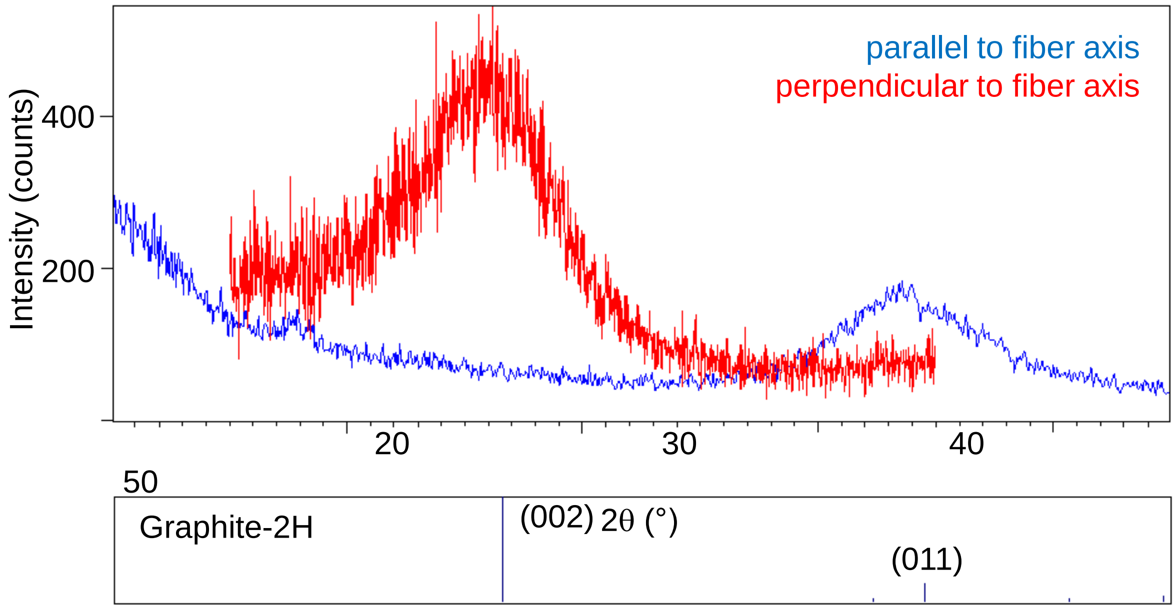
ORNL Polymer Matrix Composites Group User Project: Technical Approach

F1237 fiber – Step 2b no applied load

During the second step, as the sample is heated, the intermediate structure disappears, and is replaced by carbon including highly oriented graphite.

Based on *in situ* XRD, there is very little difference between the loaded and unloaded thermal treatment. The loading of a sample during heat treatment steps does <u>not</u> impact the crystallinity, crystal structure, or degree of preferred orientation.

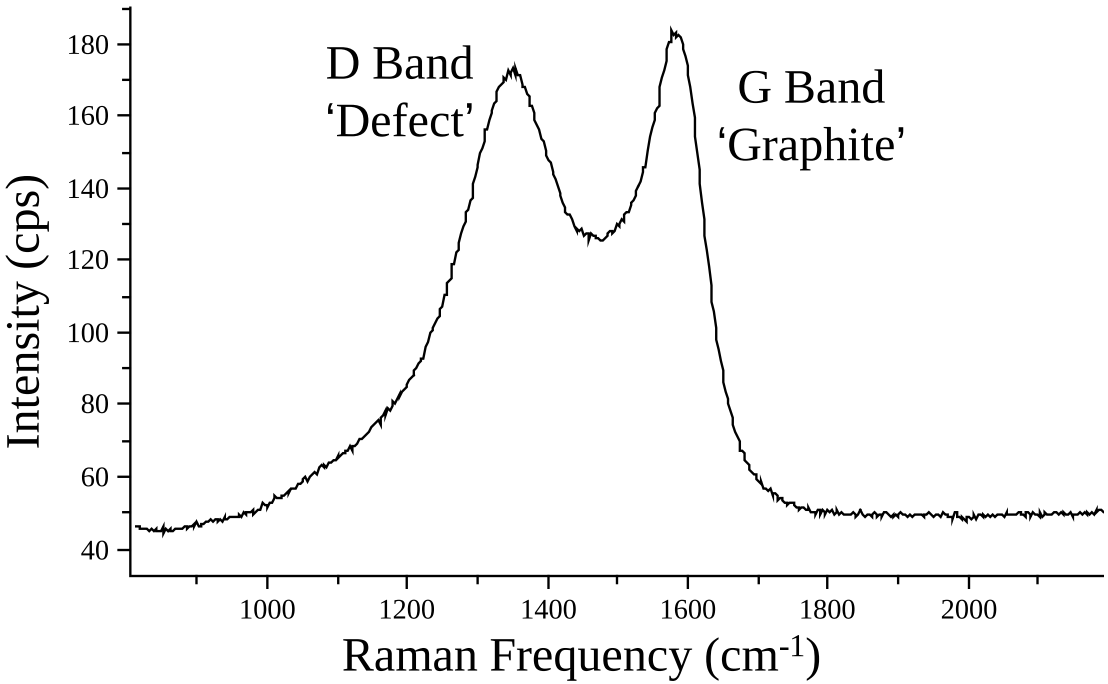
Final fibers show a highly oriented graphite phase

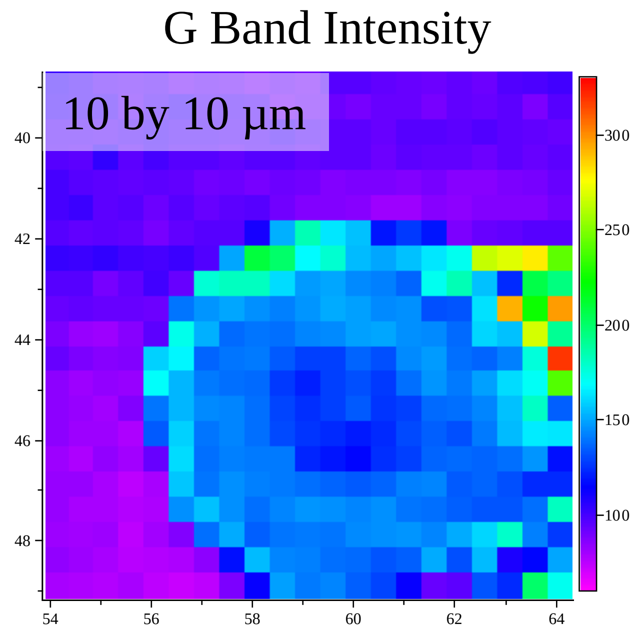


The final fibers exhibit a highly-oriented graphitic structure, with the (002) plane normals perpendicular to the fiber axis and the (011) plane normals parallel to the fiber axis. Alignment of the crystallographic c-axis normal to the fiber axis is essential to obtaining a high-strength carbon fiber.

However, *in situ* XRD gives a bulk average structure and is not sensitive to non-crystalline phases, so Raman spectroscopy was used to spatially resolve the degree of graphitization.

Raman Spectroscopy Reveals Structural Details in Hexcel-based Fibers





- Raman spectroscopy is sensitive to the degree of graphitic bonding in carbon.
- Raman micro-Spectroscopy was used to measure changes from the center of an 8- µm diameter Hexcel fiber to the edge with high spatial resolution (~1 µm), .
- This fiber appears to have more ordered or graphitic binding near the surface which compares well to nano-indentation results.

Technical Approach: X-ray photo electron spectroscopy (XPS)

Research problem: As described in the MYPP for Polymer Composite Research and Development, Phase 3: "Develop fiber surface treatments and polymer modifications to optimize fiber/resin compatibility in carbon fiber reinforced composite systems."

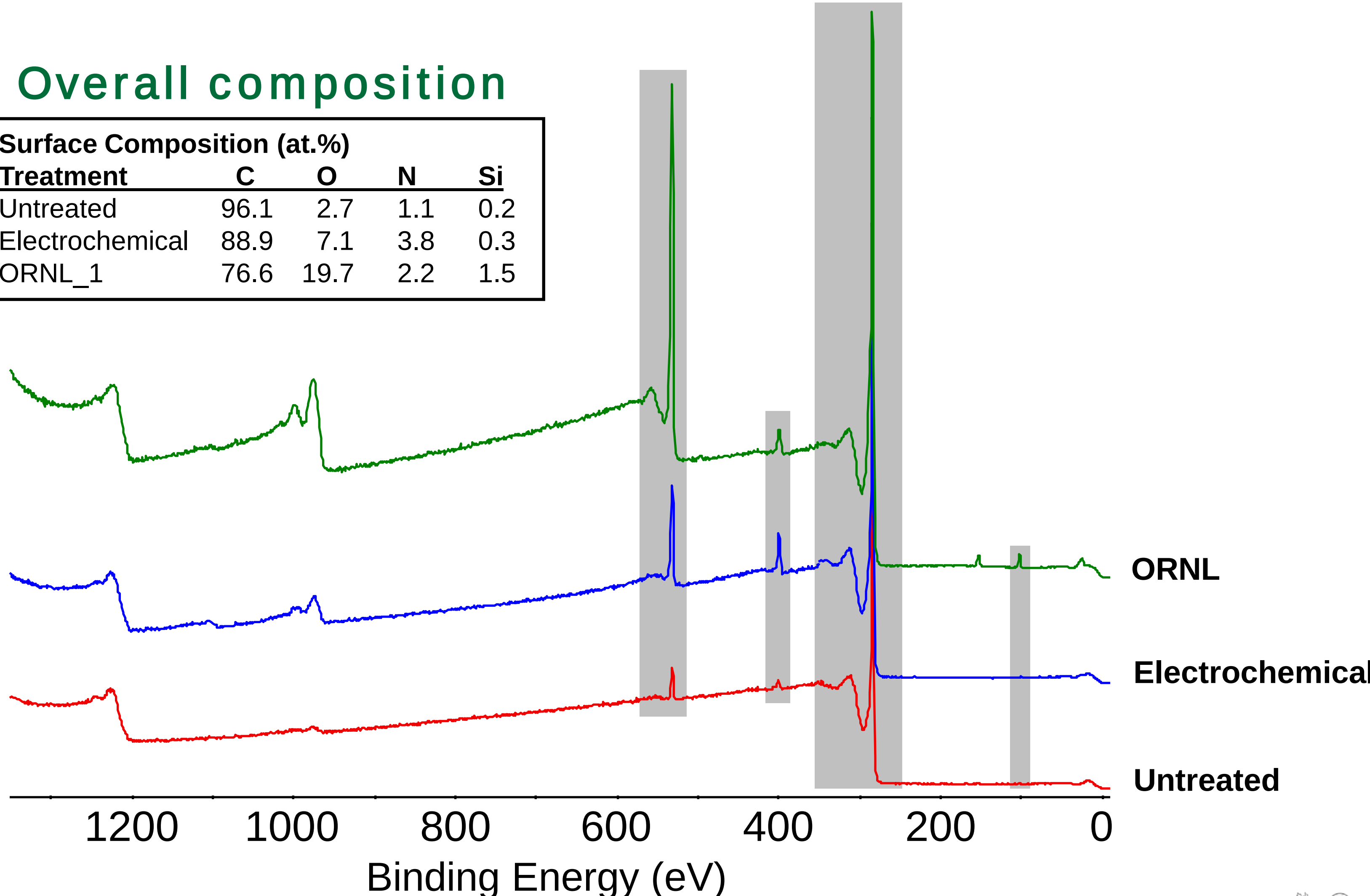
Surface chemical properties of carbon fibers dictate how well they work as the reinforcing phase in composites. Determining the chemical properties of carbon fibers requires the use of very surface-sensitive analytical techniques.

X-ray photoelectron spectroscopy (XPS) is the standard for assessing the chemical nature of the surface of carbon materials. The HTML User Program recently added a high-performance XPS instrument to its array of materials characterization tools. This instrument has been used extensively by the ORNL Carbon Fiber Program to assess the quality of surface treatment processes.

Polymer Matrix Composites Group User Project: XPS comparison of surface treatments

Overall composition

Surface Composition (at.%)				
Treatment	**C**	**O**	**N**	**Si**
Untreated	96.1	2.7	1.1	0.2
Electrochemical	88.9	7.1	3.8	0.3
ORNL_1	76.6	19.7	2.2	1.5



Project ID: LM027_Payzant_2011_o

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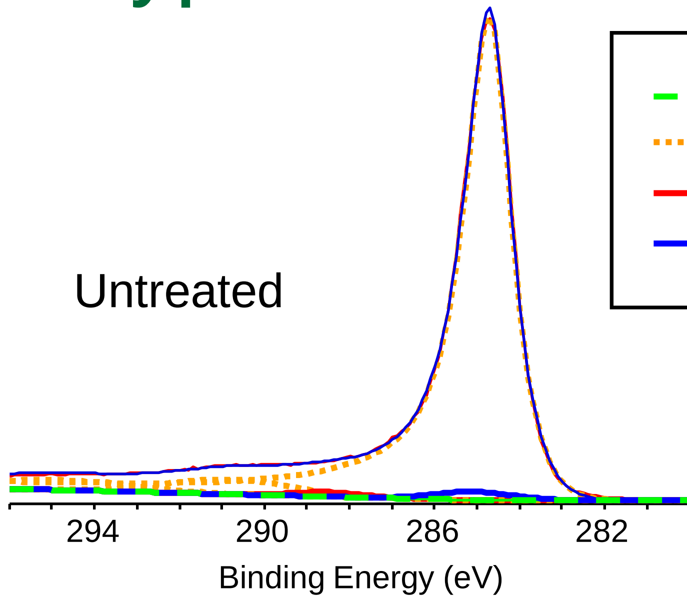
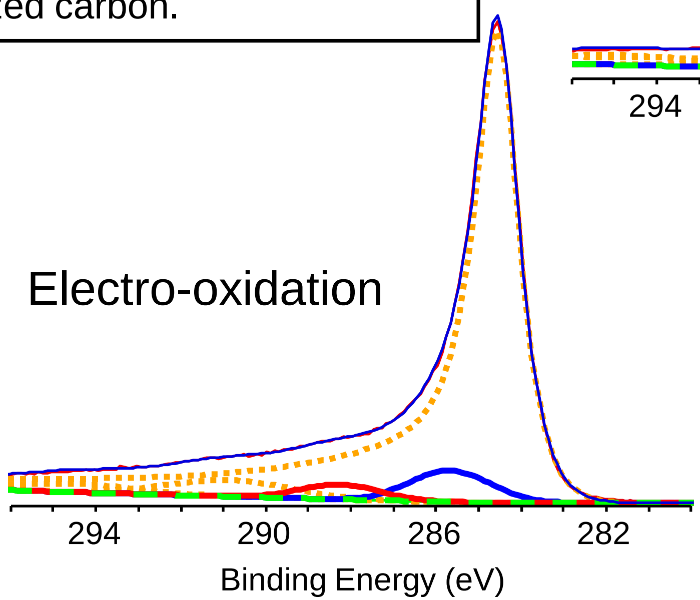
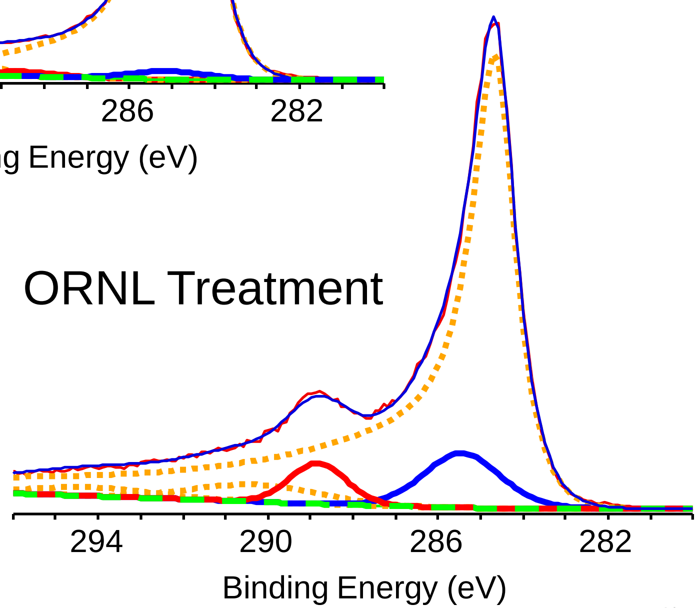
Amount and Type of Oxidation

C 1s Core Level Spectra

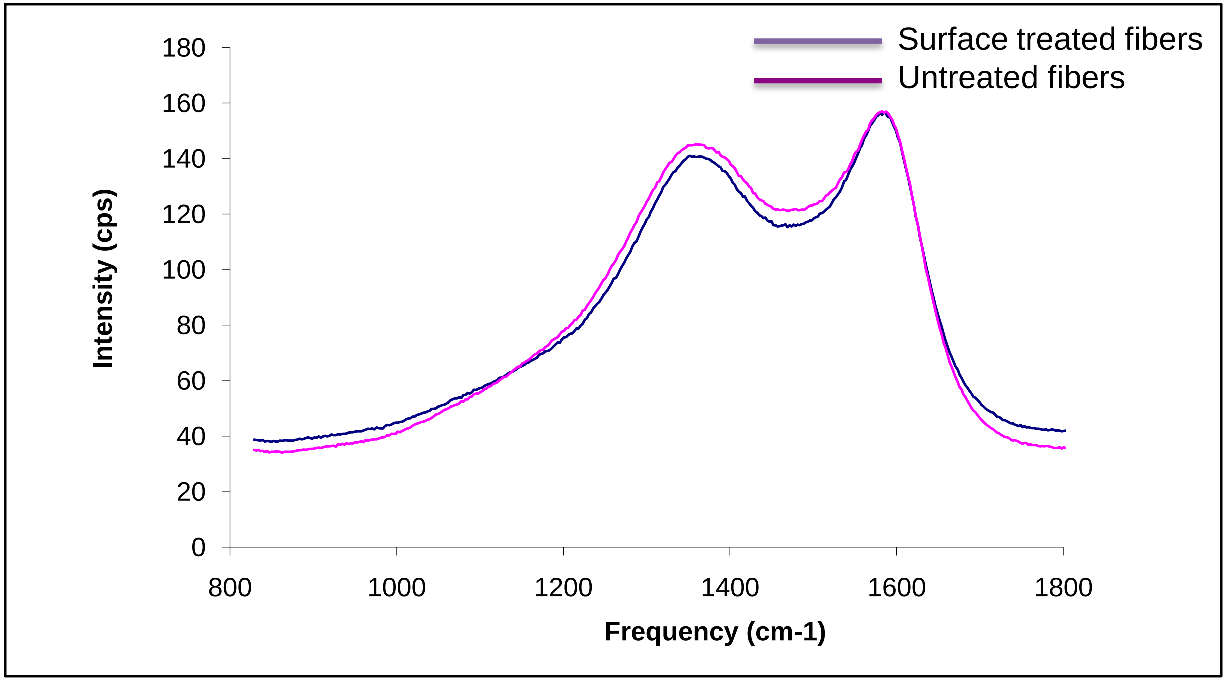
Untreated shows >95% graphite. The electro-oxidation sample shows enhanced C-O and C=O species comprising ~6-8% of the signal. ORNL surface treatment more than doubles the amount of oxidized carbon.







Raman micro-spectroscopy characterizes structural changes on surface-treated fibers



- ORNL surface treatment partially removes weakly bonded surface debris and weak amorphous carbon, but not the graphite.

Summary

- By having rapid, on-site access to the wide array of unique materials characterization capabilities and expertise available through the HTML User Program, the Polymer Matrix Composites Group was able to quickly incorporate research results into their process development.
- The results from this investigation play a critical role in the process of producing new carbon fibers with improved properties.
  - *In situ* XRD was used to better understand the thermal and mechanical processes through which low-cost textile fibers are converted to carbon fibers.
  - Raman micro-spectroscopy and XPS were used to study the carbon chemistry at the fiber surface, control of which could improve bonding with polymer matrix.

Future Work

- Advanced characterization drives development of improved processing methods.
- The characterization work illustrated in this presentation continues into FY2011. Results will be included in development activities for improved materials, which will then be characterized at the HTML.

Technical Back-Up

Supplementary XPS Background

Novel gaseous surface treatment are being developed at ORNL to use in carbon fiber production addressing large-volume, low-cost composites. Present common practice is to surface treat carbon fibers in an electro-oxidative bath. Electro-oxidative treatments can 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. The present electro-oxidative processes cannot be controlled to emphasize only a particular surface species and therefore 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.

Slide 18 compares the overall surface composition for three fibers, (1) untreated, (2) treated by “standard” electro-oxidation, and (3) treated using an ORNL process.

Slide 19 shows the amount and type of oxidation of carbon atoms on the variously treated fiber surfaces.