U.S. Department
Of Transportation
Federal Transit
Administration

Low Cost Carbon Fiber Technology Development for Carbon Fiber Composite Applications

Phase I

Final Report

January 4, 2008

REPORT DOCUMENTATION PAGE		Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	January 4, 2008	**August 10, 2005 - May 31, 2007**

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Low Cost Carbon Fiber Technology Development for Carbon Fiber Composite Applications	**TN-26-7028**
6. AUTHOR(S) Ahmad Vakili, Zhongren Yue, Youqing Fei	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The University of Tennessee Space Institute 411 B. H. Goethert Parkway Tullahoma, TN 37388-9700	8. PERFORMING ORGANIZATION REPORT NUMBER **FTA-TN-26-7028-2007.1**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Federal Transit Administration U.S. Department of Transportation Washington, DC 20590 Website URL [www.fta.dot.gov]	10. SPONSORING/MONITORING AGENCY REPORT NUMBER **FTA-TN-26-7028-2007.1**
Supplementary Notes.	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Available From: National Technical Information Service/NTIS, 5285 Port Royal Road, Springfield, Virginia 22161. Phone 703.605.6000, Fax 703.605.6900, Email [orders@ntis.fedworld.gov]	12b. DISTRIBUTION CODE

ABSTRACT (Maximum 200 words)

The main goals of this research program at UTSI were: 1) to produce low cost carbon fibers and 2) to develop specific carbon-based material technologies to meet current and future high performance fiber-reinforced composite needs of FTA and other organizations. UTSI has been carrying out the relevant research programs since it received the carbon fiber spinning technologies and accessories as a donation from ConocoPhillips. Under this DoT sponsored program, significant progress has been made in continued development and refinement of the low-cost carbon fiber production and composite application technologies. The task at hand is a major multidisciplinary effort and will need to be continued to reach successful completion and for continuous improvements. The webpage of the UTSI carbon fiber program is on line. The content of this site is regularly updated, with the latest major progresses and accomplishments at (http://www.utsi.edu/research/carbonfiber/index.htm).

14. SUBJECT TERMS Carbon Fiber, Carbon Fiber Production, Thermal Processing, Carbon Composites, Carbon Fiber Reinforced Polymeric, CFRP	15. NUMBER OF PAGES 60
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

Low Cost Carbon Fiber Technology Development
for
Carbon Fiber Composite Applications

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FTA Report Number: FTA-TN-26-7028-2007.1

January 2008

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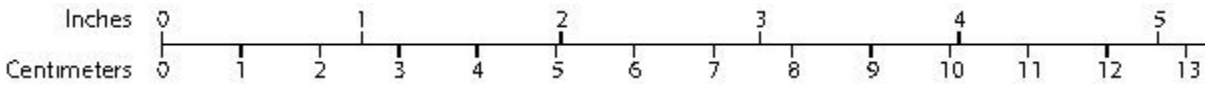

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Acronyms

CF	Carbon Fiber
CFRP	Carbon Fiber Reinforced Polymer
C	Celsius
CO	Carbon Monoxide
CO_2	Carbon Dioxide
DoT	Department of Transportation
DSC	Differential Scanning Calorimetry
FTA	Federal Transit Administration
g/cm^3	Grams per cubic centimeter
Gpa	Giga Pascal (10E9 Pa)
H_2	Hydrogen
H_2O	Water
Hg	Mercury
ILSS	Interlaminate Shear Strength
lpm	Liter Per Minute
kN	Kilo Newton
mm	Millimeter
Mpa	Mega Pascal (10E6 Pa)
PAN	Polyacrylonitryle
psi	Pound per Square Inch
R&D	Research and Development
SEM	Scanning Electron Microscopy
SFFT	Single Fiber Fragmentation Test
TGA	Thermal Gravimetric Analysis
UTSI	University of Tennessee Space Institute
VI	Virtual Instrument
Wt%	Weight Percent

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Executive Summary

A spin lab was setup from equipment donated to UTSI by ConocoPhillips and purchased or custom made. Pitch based carbon fiber has been successfully produced, thermally treated, and mechanically characterized. Various composites have also been made and evaluated. The main goals of this research program at UTSI were to produce low cost carbon fibers and to develop specific carbon-based material technologies to meet current and future high performance fiber-reinforced composite needs of transit industry and other organizations. UTSI has been carrying out the relevant research programs since it received the carbon fiber spinning technologies and accessories as a donation from ConocoPhillips. Under this DoT sponsored program, significant progress has been made in continued development and refinement of the low-cost carbon fiber production and composite application technologies. The following accomplishments have been made based on our efforts to date.

The pitch-based low-cost carbon fiber production technologies have principally been reproduced in our laboratory, with fiber spinning throughput around 1 pound/hour achieved. Pitch fibers with diameters below 10 microns have been spun and demonstrated, indicating potential for further improvements in carbon fiber properties. Preliminary experiments have indicated that partial alignment of fibers can be achieved at laydown stage during bowing spin. The composite samples made from the partially-aligned carbon fibers have confirmed the anisotropy of fiber reinforcement. The pitch fibers have been successfully processed into carbon fibers with very good mechanical strength and modulus. However, thermal processing was relatively slow, because of the batch processing method, slow drying and stabilization processes, and low density of green fiber materials. Better processing methods and equipments need to be developed to accommodate the current green fiber production rate.

The final heat treatment temperature currently at 1500 °C has produced carbon fibers with good mechanical properties. In order to produce carbon fibers with higher modulus and excellent thermal and electrical conductivity for multifunctional materials, higher temperature (> 2200 °C) treatment or graphitization systems are required, and recommended to be investigated further in the next phase. Varied forms of carbon fiber-reinforced polymer (CFRP) composites have been successfully produced in the lab, using several fabrication techniques, indicating great potential of the CFRP composites for low-cost applications in automobiles, public transit vehicles, concrete reinforcements and many other areas. The carbon fibers produced in our lab have consistently and significantly increased the strength and modulus of the CFRP composites we have made. However, much higher mechanical properties could be attained, if the carbon fiber volume fraction is increased, and fiber alignment and fiber-matrix bonding are further improved.

Fiber alignment, surface bonding properties related to fiber surface conditioning treatment and volume fraction are three major challenging issues that have impacted the final properties of the composites that are produced from our low-cost carbon fibers. The properties of the fibers produced and evaluated compare well with the pitch based commercially available fiber. Further R&D is needed to establish the commercial feasibility of this process and its long term applications development potential. A dedicated webpage of the UTSI carbon fiber program is on line. The content of this site is periodically updated, with the latest major progresses and accomplishments at (http://www.utsi.edu/research/carbonfiber/index.html).

1. Introduction

In December of 2004 The University of Tennessee Space Institute received state of the art lab equipment and technologies pertinent to low cost pitch based carbon fiber technology program from ConocoPhillips. The University developed a plan to continue the development of the low cost carbon fiber production and application technologies at the institute. Prior to the University receiving this technology, the pitch based carbon fiber development efforts has been under research and developments for more than 25 years by a number of different companies, including Union Carbide, Exxon, DuPont and ConocoPhillips.

The objective of this program was set to develop production technologies for low cost carbon fiber for a variety of commercial applications. A number of technologies that are currently using synthetic fibers can use high strength lightweight and low cost carbon fibers to reduce weight, improve performance, and generate new applications that are in demand. Low cost carbon fiber could provide enormous advantages to technologies for future every day life including advanced technology applications that are not commercially feasible at higher carbon fiber prices. Low cost carbon fiber (from pitch) is a national goal established to accomplish a number of technological breakthroughs. Huge savings in energy consumption would be possible with the use of lightweight high strength structures and body panels in the Automobile industry, and will lead to improvements in a number of other technology areas.

Implementation of the low cost carbon fiber technology program was established and made possible at UTSI with partial funding from the FTA under this research program "Low Cost Carbon Fiber Technology for Carbon Fiber Composite Applications." The major goals of the research program at UTSI are to produce low cost carbon fibers and to develop carbon based material technologies to meet existing and future FTA and other funding organizations needs for high performance carbon fibers. This report is the final technical report of this phase of our study to appraise the funding agency the contract managers and others of progress accomplished during the period of performance of this program, to date.

The main goals of this research program at UTSI were: 1) to produce low cost carbon fibers and 2) to develop specific carbon-based material technologies to meet current and future high performance fiber-reinforced composite needs of FTA and other organizations. UTSI has been carrying out the relevant research programs since it received the carbon fiber spinning technologies and accessories as a donation from ConocoPhillips. Under this DoT sponsored program, significant progress has been made in continued development and refinement of the low-cost carbon fiber production and composite application technologies. The task at hand is a major multidisciplinary effort and will need to be continued to reach successful completion and for continuous improvements. A dedicated webpage of the UTSI carbon fiber program is on line. The content of this site is regularly and continuously updated, with the latest major progresses and accomplishments at (http://www.utsi.edu/research/carbonfiber/index.html).

2. Production and Characterization of Carbon Fibers

2.1 Research Labs and Equipments for Carbon Fibers

Large efforts have been made to establish research labs at UTSI for carbon fibers production, processing, composites fabrication and characterization. The process of bringing the UTSI spin lab online was systematic but time-consuming as certain components in the lab involved precision instrumentation. Initial efforts comprised of installing and testing spin lab equipments, and the procurement of a number of special furnaces for heat treatment of green pitch fibers, including drying, stabilization and carbonization.

UTSI initiated and completed assembling different spin lab subcomponents, equipments and equipping the lab with basic supporting utilities. Since the equipment received had little installation documentations, the assembly included identification and verification of utilities needs, controls, connection of electrical system and determination of safe control and operations procedure of individual subsystems, components and the working of all of the subsystems cumulatively, including documenting their installation and developing operational manuals. The spin lab system is composed of a number of highly specialized and sophisticated components and has a number of built-in interlocking devices that need to be tested individually, tracked and functionally verified. Furthermore, the operation of the various components for ideal spinning of pitch based carbon fiber needed to be well understood. Necessary steps were taken, verified and checked out as for the identification and safe operation of the system and its components are concerned.

Towards accomplishing the assembly and installation steps, UTSI had limited but helpful support from one current and one retired ConocoPhillips employees who had been contracted to help our lab engineers and technicians with the specific information for assembly of the spin lab and with the setup of the carbon fiber characterization lab. A few photographs showing the overall lab condition, including different components and systems of the UTSI carbon fiber spin lab, are provided in Figures 1 to 4.

Figure 1 Carbon fiber spinning apparatus mounted on the mobile fiber collection platform with the secondary gas heater, showing most of the components, unassembled

Figure 2 UTSI Spin Lab, a close view of the spin tower, control panel and the fiber collection platform with the secondary gas heater (white duct) in the foreground

Figure 3 UTSI Spin Lab, side view, showing the extruder system and the control panels for various pumps

Another important part of the carbon fiber process is the heat treatment aspect of the fiber processing. Heat treatment is a key step of the carbon fiber production. Various specialty furnaces have been examined from different sources, including the inventory of UTSI research equipments. Two furnaces shown in Figure 4 have been obtained and set up for drying, oxidative stabilization and pre-carbonization. A retort chamber that was delivered as a part of the original equipment has been reconfigured for more uniform heating under the oxidation atmosphere.

Figure 4 Drying and stabilization (left) and pre-carbonization (right) furnaces

The pre-carbonization furnace can be operated at temperatures up to 1200 ºC. During pre-carbonization, fibers are heated in inert atmosphere and volatiles along with decomposition gases, for example, H_2O, CO_2, CO and H_2 are removed from the reactor chamber. The heating

profiles are designed to balance several conflicting factors, e.g. slow enough to maintain the rate of mass transfer to avoid surface irregularities while finishing the overall processing at the shortest possible time. A Labview based controller has been implemented to automate the process. This also allows the operator to set the heat treatment steps remotely, i.e. the operator does not need to be present physically near the furnace during the heat treatment. The user interface of the LabView Virtual Instrument (VI) is shown in Figure 5. This controller has been designed as generic as possible to allow wide applications to other furnaces in this project.

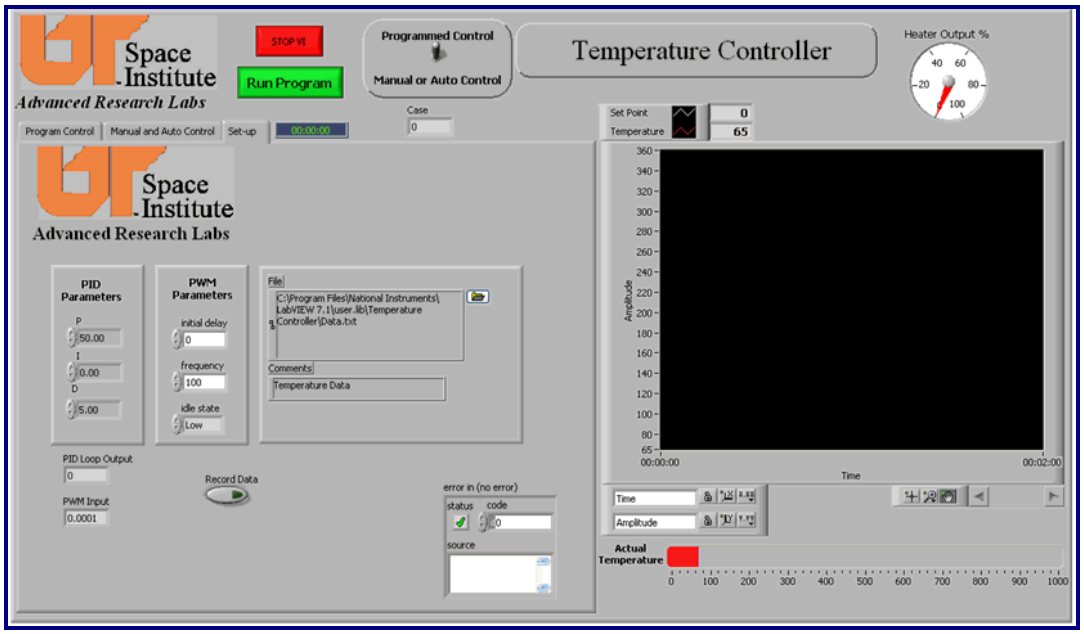

Figure 5 LabView-based temperature control interface panel

A high temperature furnace that can be operated up to about 2400 ºC for carbonization and graphitization has also been obtained, shown in Figure 6. Unlike PAN fibers, pitch-based carbon fibers tend to attain higher tensile strengths and higher thermal and electrical conductivity at higher temperature. Such carbon fibers are highly desirable to be used as multi-functional materials.

Figure 6 A high temperature furnace for carbonization and graphitization

The furnaces have been used to process UTSI fibers in batches and produce carbon fiber materials for composite preparation and evaluation purposes. While work is going on to bring the required specialty furnaces operational, we plan to start working on improving the heat treatment process itself by employing innovative methods such as infra-red, inductive and microwave heating techniques.

2.2 Carbon Fiber Production Processes

Pitch-based carbon fibers are produced from a series of processing steps, principally consisting of precursor preparation, fiber spinning, stabilization, carbonization and sometimes graphitization. One of the special features of the pitch-based carbon fiber technology at UTSI is that the precursor pitch contains about 10 to 20 wt% of spin solvent which enables the melt blow spinning at high production rate. The use of spin solvent also requires an additional drying step once the fiber spinning is completed.

2.2.1 Fiber Precursor Pitch

Experimental efforts were initiated to look into the pitch chemistry to improve the processing efficiency, particularly to reduce the drying and stabilization time while maintaining or improving the quality of final carbon fibers. The fiber precursor currently employed at UTSI is the solvated mesophase pitch produced from a discontinued commercial plant by ConocoPhillips. It contains thermally processed pitch oils as a spin solvent and has fundamental influences on the mesophase pitch property, fiber spinning operation, and the processing of green fibers.

In order to have a more efficient and simple process, the logic approach is to replace the current spin solvent with certain substances that have additional functionalities, including some oxygen-containing functional groups in the precursor mesophase pitch. The first step, however, is to remove the existing spin solvent. Various common organic solvents have been used to extract the spin solvent by stirring the slurry (pitch particle size, < 150μ) at varied temperatures and using Soxhlet extractor. The extent of spin solvent removal was determined by thermal gravimetric analysis (TGA).

Figure 7 shows the TGA curves for the determination of the spin solvent content in the solvated mesophase pitches. The thick red line is the temperature profile with the heating time (the x axis), and weight loss curves (the y axis) show the spin solvent released. For two different particle sizes (smaller than 150μ and 300μ, thin red and blue lines, respectively), the original mesophase pitch had a spin solvent content around 14 wt%. The samples extracted in Soxhlet (green and purple curves) showed much reduced residual solvent contents. The small particles (< 150 microns, No.100 mesh) had about 3% residual spin solvent using toluene as extraction solvent, roughly half of that for the larger particles (< 300 microns, No. 50 mesh). This indicated that the control step for the solvent removal was mainly diffusion related.

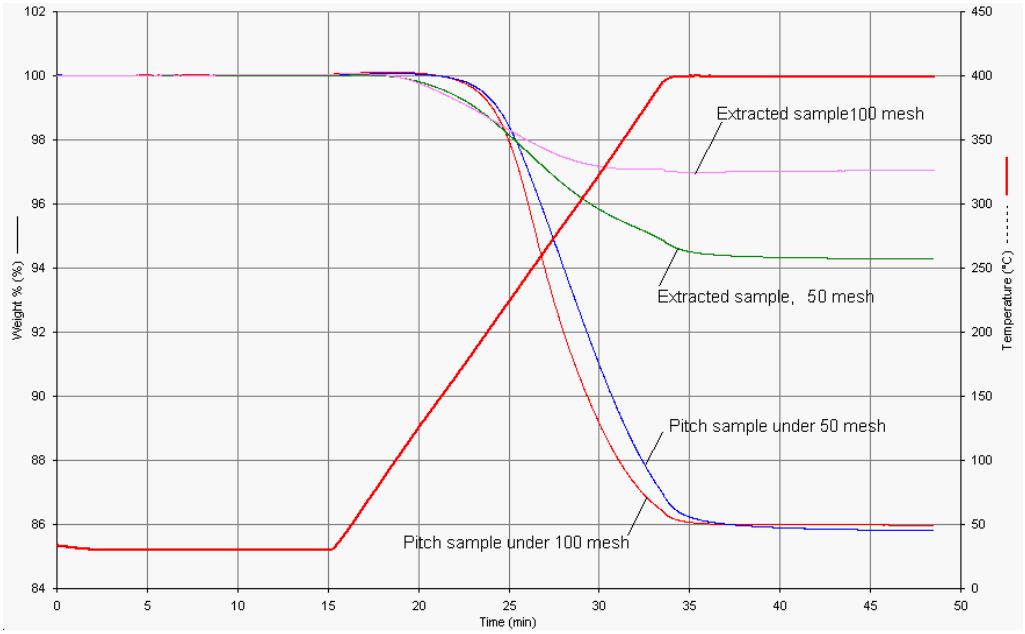

Figure 7 Residual concentrations of spin solvent in original and extracted pitch samples

In addition to the particle size, other variables such as, extraction temperature and extraction time were also investigated for the toluene-pitch system, shown in Figures 8 and 9. For a relatively short extraction time of 30 min, the increase in extraction temperature from ambient to 50 °C was quite effective, as shown in Figure 8.

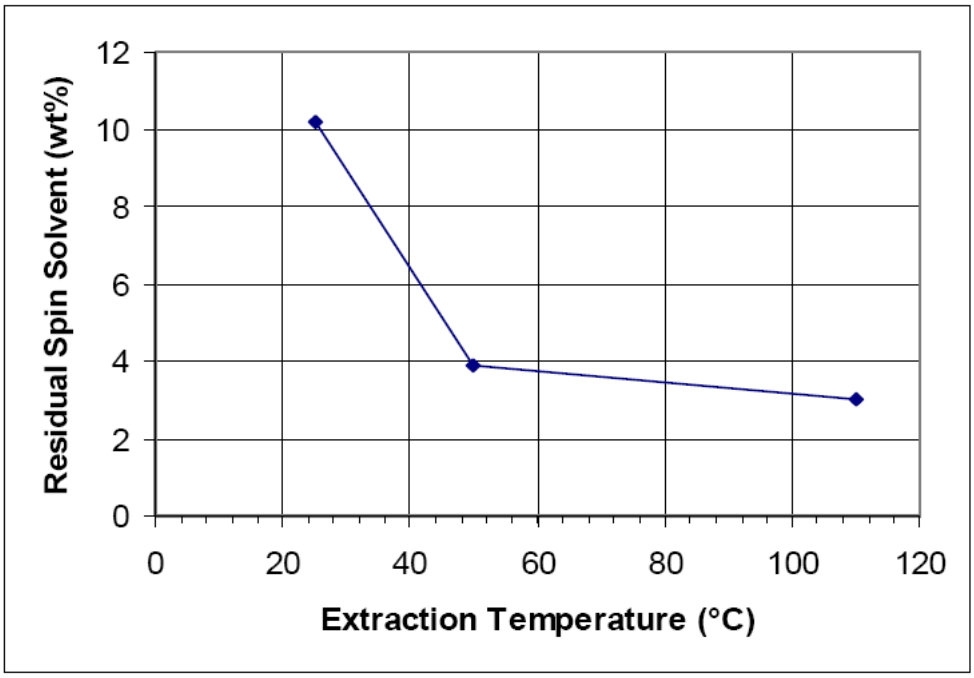

Figure 8 Effect of extraction temperature on spin solvent removal

The extraction at ambient temperature for 30 min only removed small amount of spin solvent as shown in Figure 9. The data points have been connected by line just to indicate the general trend. A few hours seemed to be required to reach an equilibrium state and a longer time (48 hours) did not seem to help remove more pitch oils.

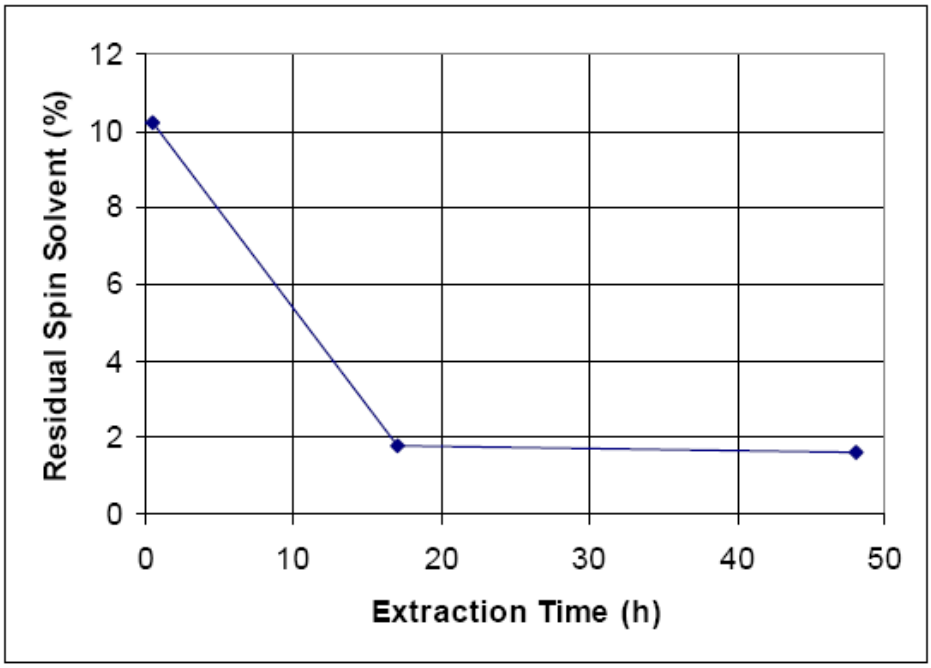

Figure 9 Effect of extraction time on spin solvent removal

2.2.2 Fiber Spinning

During the first six month after the initiation of the program, we have successfully produced carbon fibers in the UTSI spin lab during the first spinning trial effort. The initial spinning was performed on an original solvated mesophase pitch almost continuously for more than two hours on February 2, 2006. Figure 10 shows a picture of UTSI officials and researchers examining the new green fibers produced shortly after the first run.

Figure 10 Newly spun fibers from lab scale spinning equipment at UTSI

The fibers spun initially had relatively large diameters around 28 microns. The fiber diameter has been found to be strongly influenced by the attenuation of the molten pitch near the die tip. The primary gas flow rate has been varied systematically to investigate its effect on the fiber diameters. Figure 11 shows the fiber diameter values of two different fiber batches with the primary gas flow at 40 and 80 liter per minute (lpm). The average diameter of the fiber was about 10 microns for the higher flow rate, reaching the target range for carbon fibers commercially made from PAN and pitch. A histogram chart shown in Figure 12 indicated that there was about 2 micron variation within the fiber batch produced at 80 lpm primary gas.

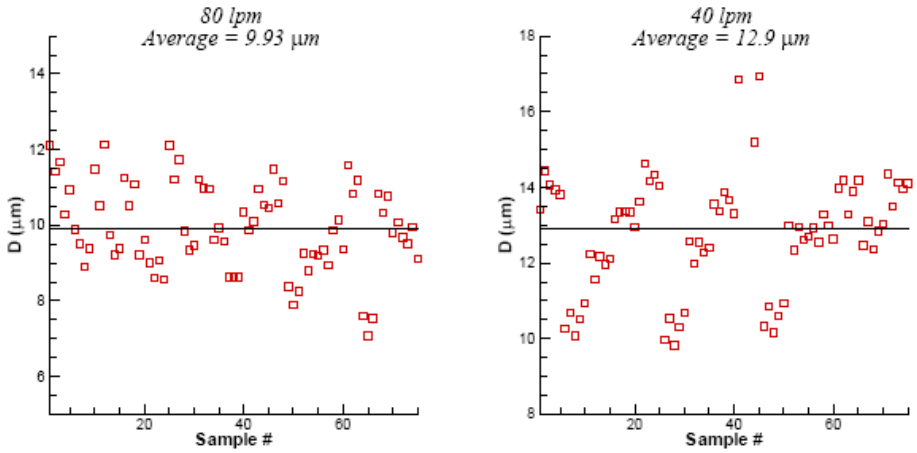

Figure 11 Diameter of fibers produced at two primary gas flow rates (80 and 40 lpm)

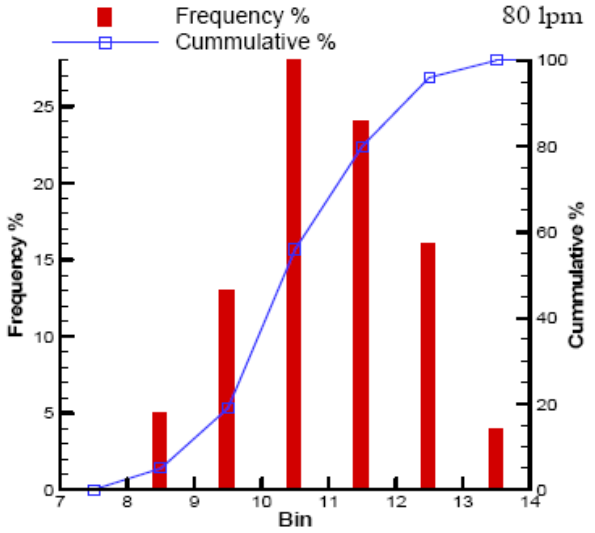

Figure 12 Distribution of fiber diameter for primary gas flow at 80 lpm

2.2.3 Drying and Stabilization

The green pitch fibers were then thermally processed into carbon fibers through a few thermal processing steps, namely drying, oxidative stabilization and carbonization. In order to produce sufficient amount of carbon fibers for the fabrication of different composites, many runs of drying and stabilization were carried out at temperatures slightly above 300 °C in a specially modified furnace chamber with a reaction volume about 3 cubic foot. Carbonization was followed with the process temperature ramped up to 1050 °C for most experiments and some high temperature carbonization was conducted up to 1550 °C. The heating profiles were modified to optimize the properties of the final carbon fibers produced. Oxidative stabilization is an important step to avoid softening and melting of carbon fibers at higher processing temperatures. The step could take a long time, some in the order of several hours, and is a time

consuming step in the continuous processing of fibers. For example, the fibers may be spun continuously at about 80 to 100 mph, and an impractical length of equipment would be required if the thermal processing is operated in a continuous fashion. In other word, fast processing time is essential for industrial processing. Key parameters involved in the oxidation process includes: 1) final oxidation temperature, 2) rate of heating and the total time required for oxidation, 3) softening point of mesophase pitch and the green fiber, and 4) concentration of oxidant. Our primary objective is to minimize the time and temperatures required for oxidation. If possible, completely eliminating this step would enable the continuous processing of fibers. Before the ideal process is developed, fibers are produced and processed continuously in the mat form and by batch processing.

2.2.4 Carbonization

After drying and stabilization, pitch fibers were carbonized up to 1050 °C in inert gas atmosphere, to generate sufficient amount of carbon fiber samples for various evaluations and different composite fabrications. As such, the green fibers produced have very low density and are very weak and fragile, demanding large reactor volume and large quantity flow of process gases. Improved precursor pitch, and modified fiber spinning, drying and stabilization steps can all have great impact in developing a compact and low-cost carbon fiber production process.

More than 50 batches of carbonization runs have been carried out so far. The structure and properties of these carbon fibers have been characterized by various methods, as described in the following sections. To obtain higher strength and more balanced modulus, high temperature carbonization is required. A furnace with graphite heating elements has been obtained and modified to accomplish this objective. Initial test had confirmed its heating capacity. Further modifications are planned to maintain highly clean and gas tight environment for the production of the advanced carbon fibers.

2.3 Characterization of Fiber Products

The structure of carbon fibers are very important from microscopic to nano-scales in understanding the properties of fiber products and processing related issues to improve the fiber quality and the performance of their composites. Comparing the conventional PAN and other pitch-based carbon fibers, substantial differences in their properties at the macroscopic, microscopic and nanometer levels are expected. Differences are mainly due to the different precursors, special fiber spinning and fiber processing methods employed.

2.3.1 Optical Microscopy

The fiber samples including green fibers, stabilized fibers, and carbonized fibers, are mounted in epoxy resin and polished carefully. The transverse and longitudinal sections of each fiber were investigated using an optical microscope with a reflected light. As the graphene layer planes of crystallites in mesophase pitch and graphite are optically anisotropic, the orientation of these aggregates within the fibers can be determined using polarized light. The optical micrographs of green fiber, stabilized green fiber, 1050 °C carbonized fiber, 1500 °C carbonized fiber, and pitch-based commercial carbon fiber P25, are shown in Figures 13 through 19.

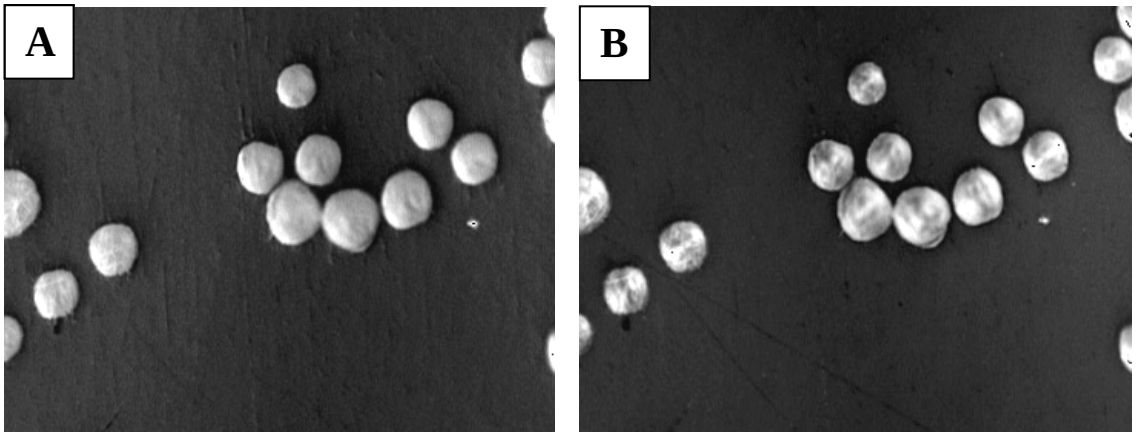

Figure 13 Cross-sectional view of green fibers under (A) normal light and (B) polarized light

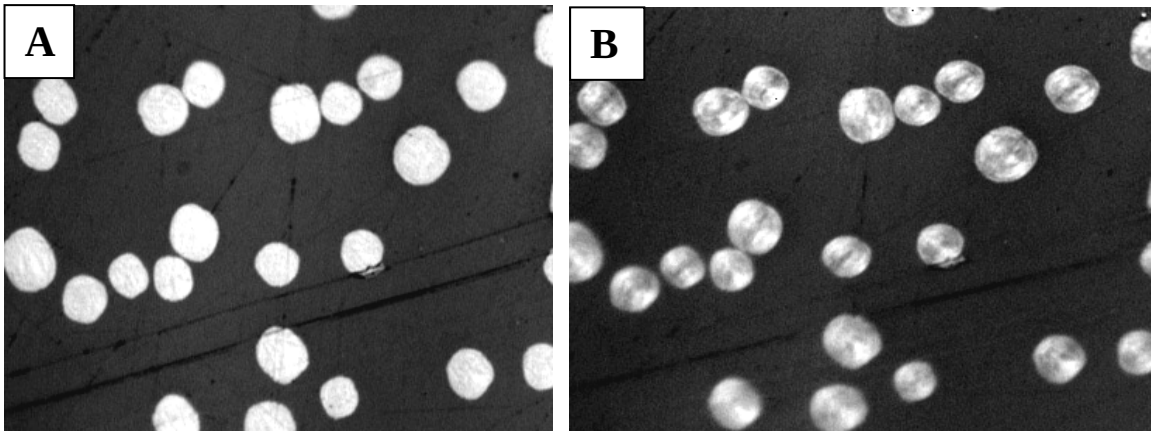

Figure 14 Cross-sectional view of stabilized green fibers under (A) normal light and (B) polarized light

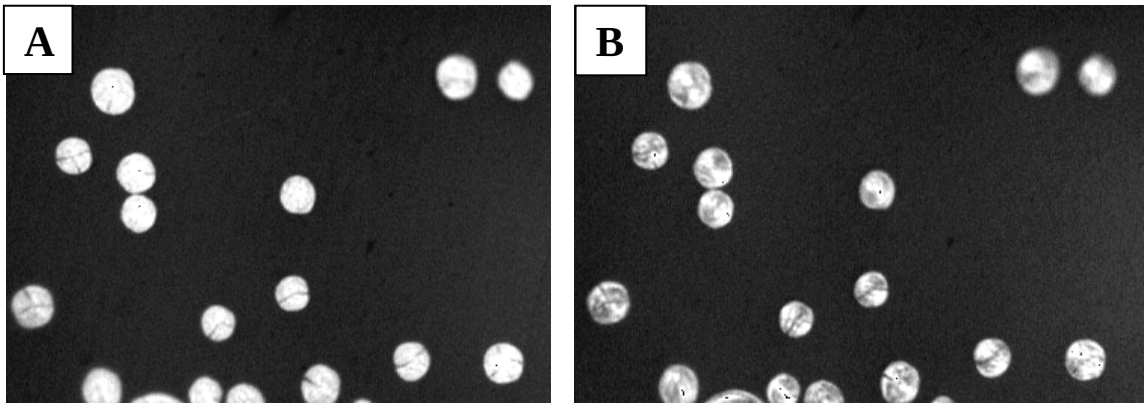

Figure 15 Cross-sectional view of carbon fibers (1050 °C) under (A) normal light and (B) polarized light

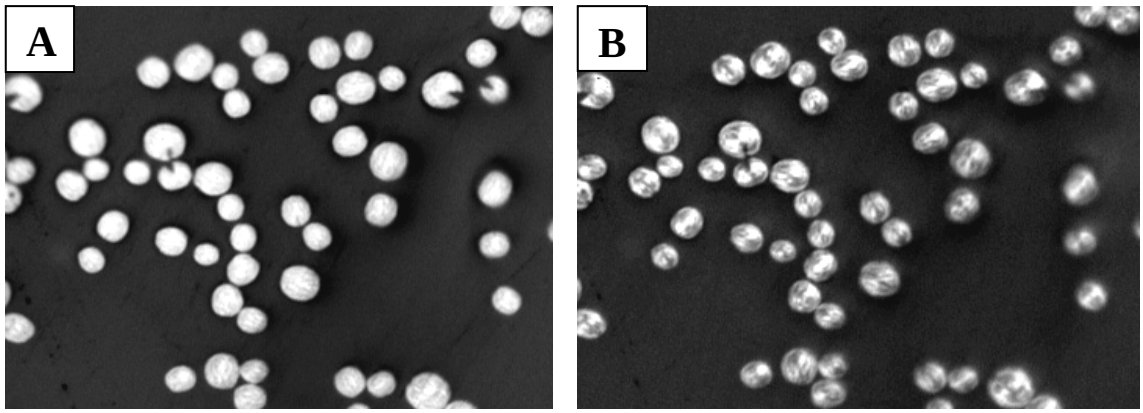

Figure 16 Cross-sectional view of carbon fibers (1500 °C) under (A) normal light and (B) polarized light

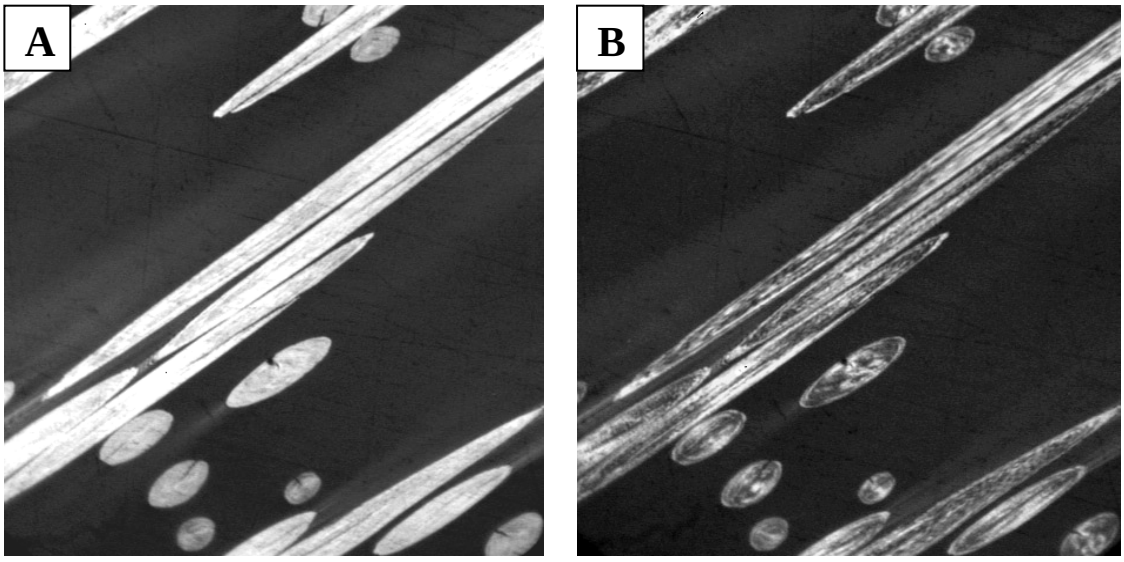

Figure 17 Longitudinal sections of carbon fibers (1050 °C) under (A) normal light and (B) polarized light

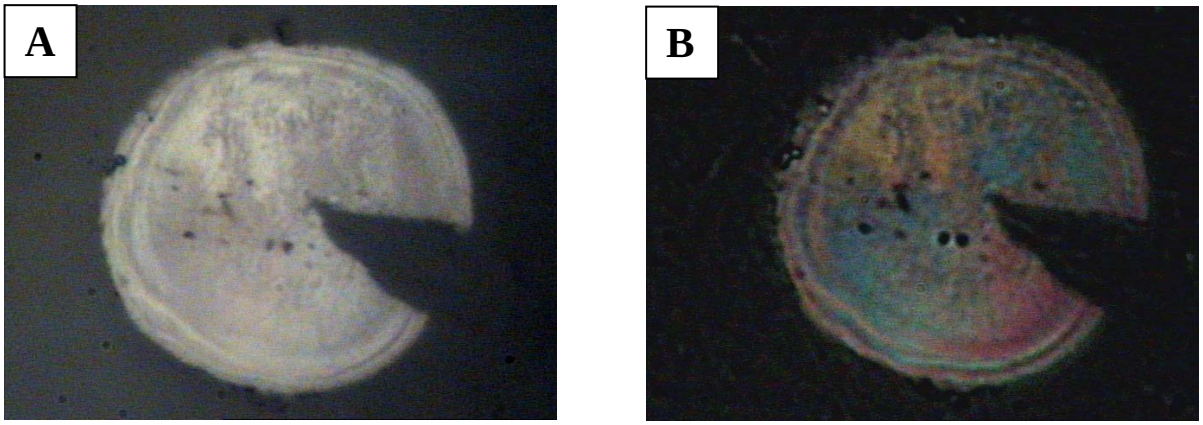

Figure 18 Cross-sectional structure of a carbon fiber with a crack under (A) normal light and (B) polarized light

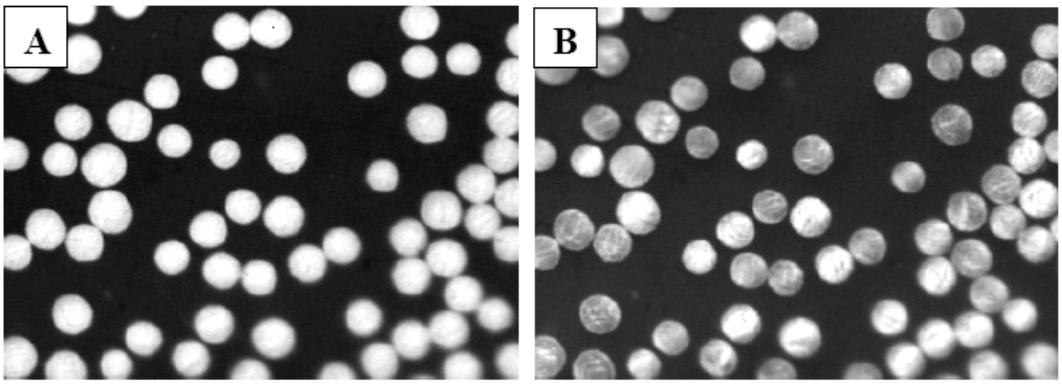

Figure 19 Cross-sectional view of commercial pitch based carbon fiber P25 under (A) normal light and (B) polarized light

The following observations have been made:

- As compared with a commercially available pitch-based carbon fiber P25, the carbon fiber prepared at UTSI spin lab has a small diameter but poor uniformity of fiber diameter.
- A number of carbon fibers have a crack structure (Fig. 15-A, Fig. 16-A, Fig. 17-A, and Fig. 18). The size of the crack increased as the carbonization temperature increased from 1050 °C to 1500 °C.
- The polarized light optical micrographs indicate the orientation of crystallite in the fibers from green pitch fibers to carbonized fibers. A schematic representation of these structures is shown in Figure 20.

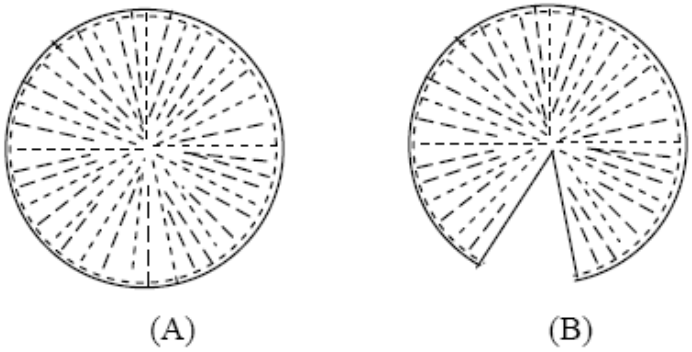

Figure 20 Schematic representation of cross-sectional structure (A) circumferential orientation in the skin and radial orientation in the center, (B) fiber with a crack (Pacman-like)

Overall the UTSI carbon fibers have a larger crystallite dimension and higher degree of orientation than the commercial P25 fibers.

2.2 Scanning Electron Microscopy (SEM)

The structure of various fibers was also investigated using SEM. As observed by optical microscopy, some fibers have a radial crack propagating along the fiber axis. Additionally, ridge-like features can be observed in the outer surfaces. A typical image of a fiber carbonized at 1050°C is shown in Figure 21 at different magnifications. In the literature, the presence of such cracks has been attributed to the radial orientation of the crystal structures of the mesophase pitch. To eliminate such crack there are suggestions to introduce some form of randomness into the pitch prior to spinning. This can be accomplished possibly by introducing turbulence upstream of the capillary exit. The ridges along the fiber length are somewhat more complex probably due to release of spin solvents in the precursor pitch.

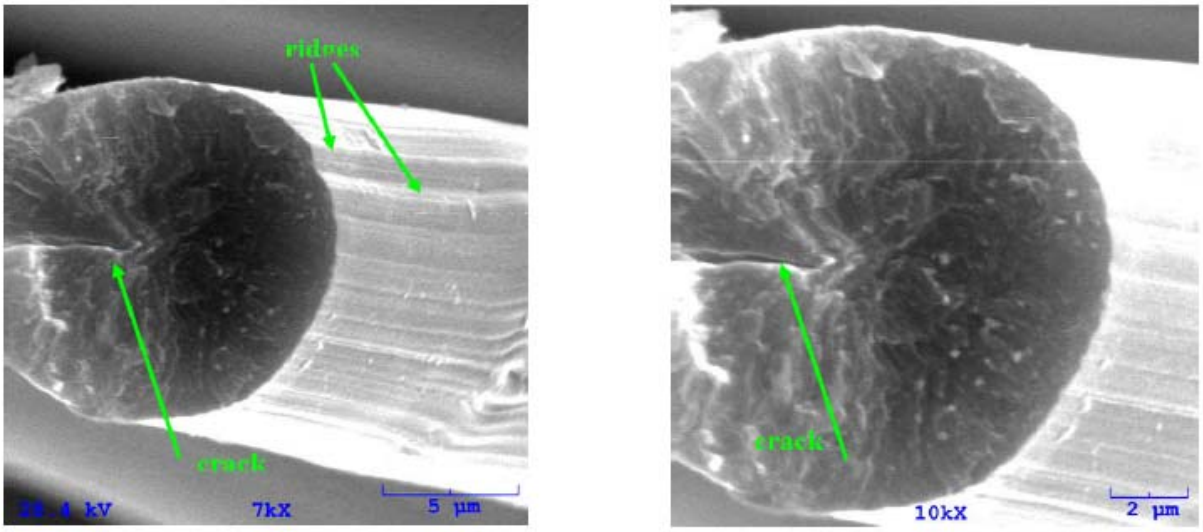

Figure 21 SEM images showing ridges on the fiber surface and a crack propagating from the fiber axis

Figure 22 shows two representative micrographs of fibers carbonized at 1050 °C, revealing the general structural features of the carbon fibers produced at UTSI. These fibers have a round cross section, and there are tracks or ridges (e.g. pointed by A and D) running on the outer surfaces along the fiber length, typical of mesophase pitch precursors. However, a radial crack (marked by B and E in the photos) propagating along the fiber axis was more often observed. Since the heat treatment temperature of 1050 °C is considered relatively low for graphitic structure formation, the detailed features across the section were difficult to recognize (e.g. areas C and F in the photos). Due to the release of spin solvents at spinning, some voids may also be observed on the fiber surface, at the location G in the right photo.

Our fiber spinning method produces round fibers under normal conditions. Occasionally, slightly different cross sections may be observed, as show in Figures 22 and 23. The outline of the fibers was close to a rounded “square”, rather than circular. At much higher magnification, graphitic stacking could hardly be observed even at the zoomed central areas, in the right photo.

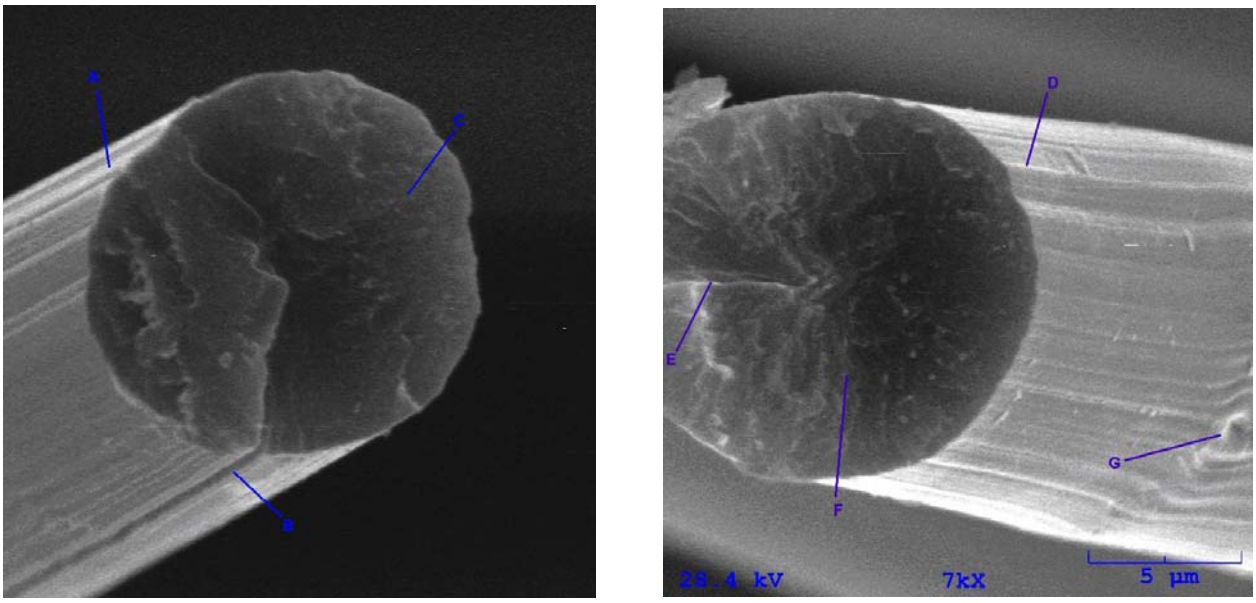

Figure 22 SEM micrographs showing internal structure of fibers carbonized to 1050 °C

Investigations were also made to examine the structural features of fibers carbonized up to 1550°C. A cross sectional overview of some strands of carbonized fibers is shown in Figure 24. These fiber samples produced more recently had quite uniform and small diameters, about 10 microns, with straight outline in axial directions. Some fibers contained a longitudinal crack.

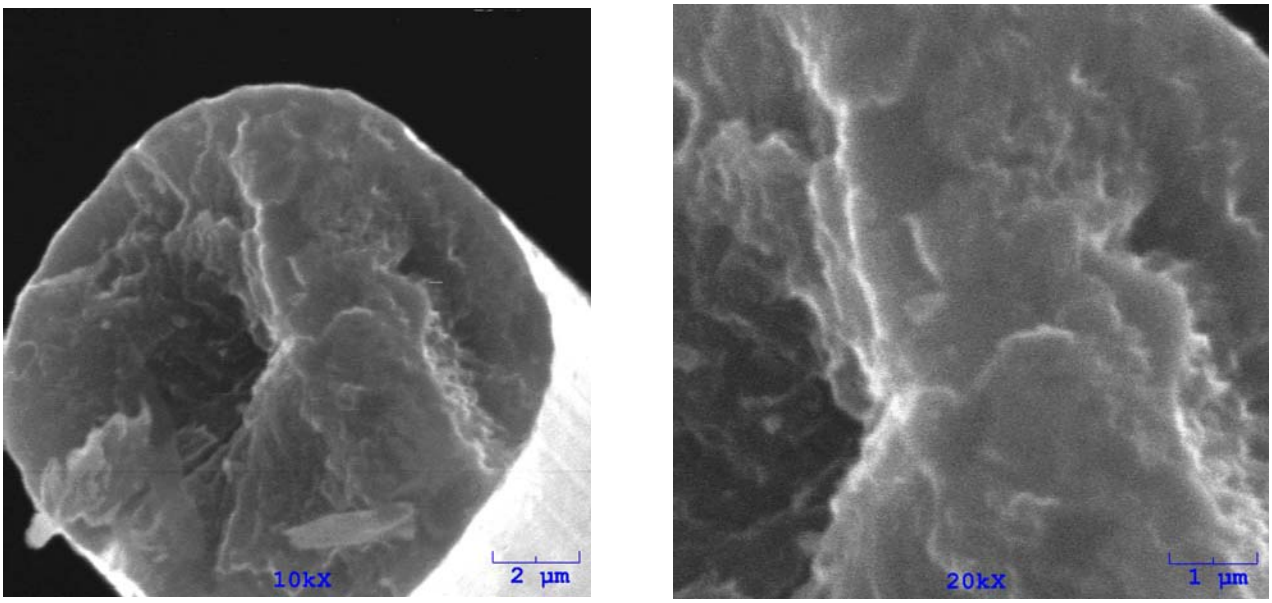

Figure 23 SEM micrographs showing rounded shape and zoomed central area of a carbonized fiber, heat treated at 1050 °C

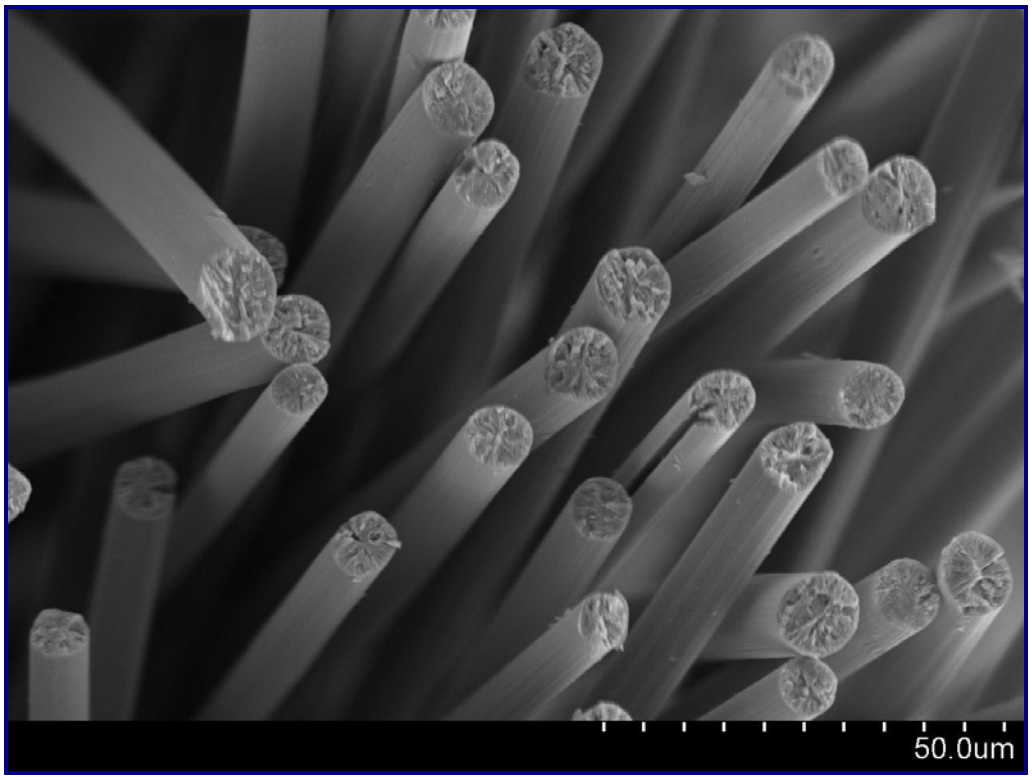

Figure 24 SEM image of pitch-based carbon fibers processed at 1550 °C

Figure 25 shows the SEM micrograph of carbon fibers containing detailed structure in terms of principal arrangements of graphene staking across the fiber surfaces. Although the carbonization temperature of 1550 °C was insufficient to develop perfect graphite structure, texture characteristic of mesophase-derived carbons can be recognized. In this case, the graphene layers were folded to some extent, but oriented generally in radial directions. These so called folded radial structures are considered very desirable for mechanical strength and modulus. Such a structure is quite consistent with the observation by optical microscopy described earlier. More detailed studies on the microstructure will be carried out in the future.

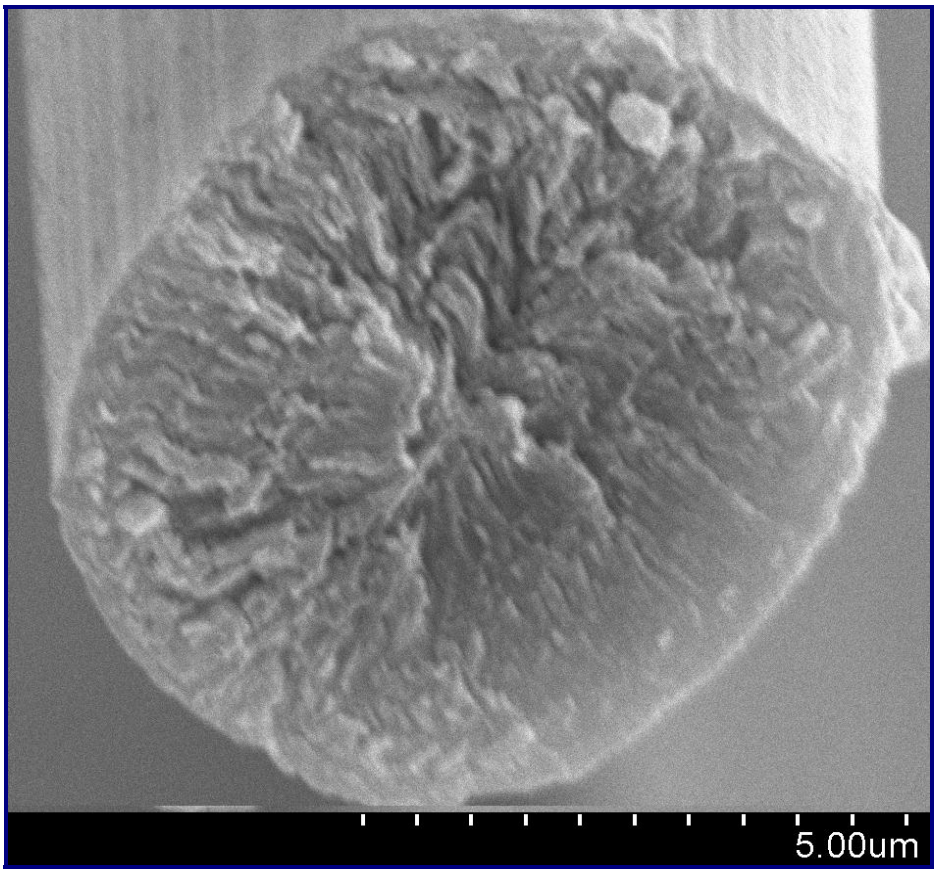

Figure 25 SEM micrograph of carbon fiber processed at 1550 °C

2.3 Carbon Fiber Strength and Stiffness by Single Filament Testing

Mechanical properties of the carbonized fibers, e.g. tensile strength and modulus, are continuously evaluated by single filament tests. Individual fiber filaments are carefully mounted on special sample support mounts, before their diameters are measured by a laser micrometer. Fiber length used for these tests is 10 mm. The fiber analyzer instrument, FDAS765, by Diastron Limited, is a high resolution dimensional measurement system, with force resolution of 0.005 gram and positional repeatability of 0.1 microns.

The FDAS765, automatically performs diameter measurements at several longitudinal points, records the elongations and calculates various parameters related to tensile fracture. Data gathered are transferred to a PC for recording and further analysis.

Figure 26 shows a typical curve from tensile test performed on a single filament carbon fiber produced at UTSI. This sample was processed at a relatively medium temperature heat treatment at 1550 °C. Typically, nearly linear load-extension relationship is observed, after the initially relaxed fiber sample is fully stretched.

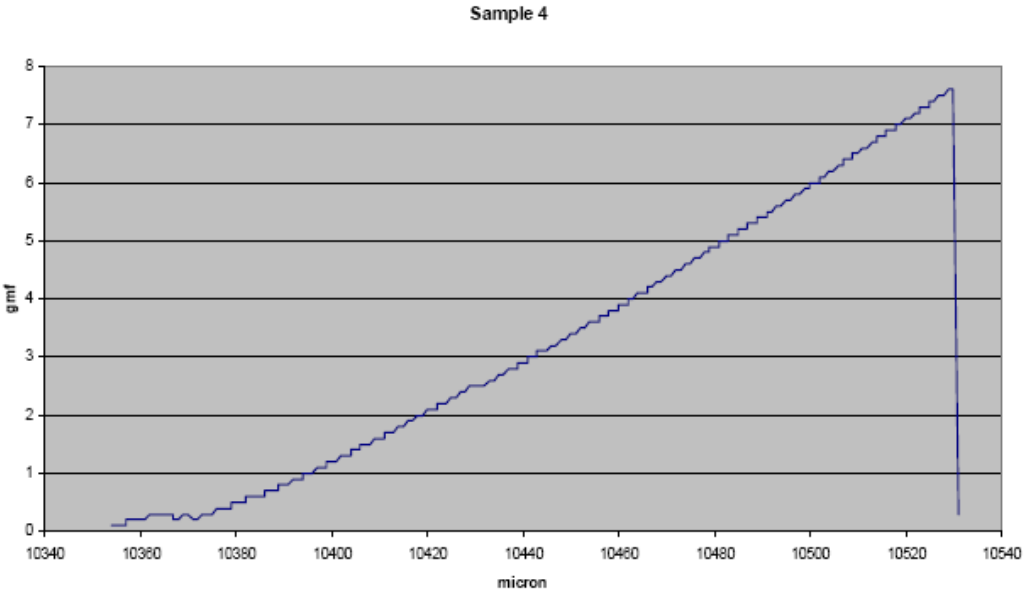

Figure 26 Elongation of a single filament carbon fiber versus applied tension

Considerable efforts have been made to master the skills of handling hardly-visible small fiber samples which are around 10 micron or less in diameter and to define measurement protocol and to validate results. Useful data for carbon fiber mechanical properties are obtained from sufficiently large numbers of single filament tests for statistical analysis. A typical plot of a large number of samples measured is shown in Figure 27. Variations between different fibers are clearly shown in this figure.

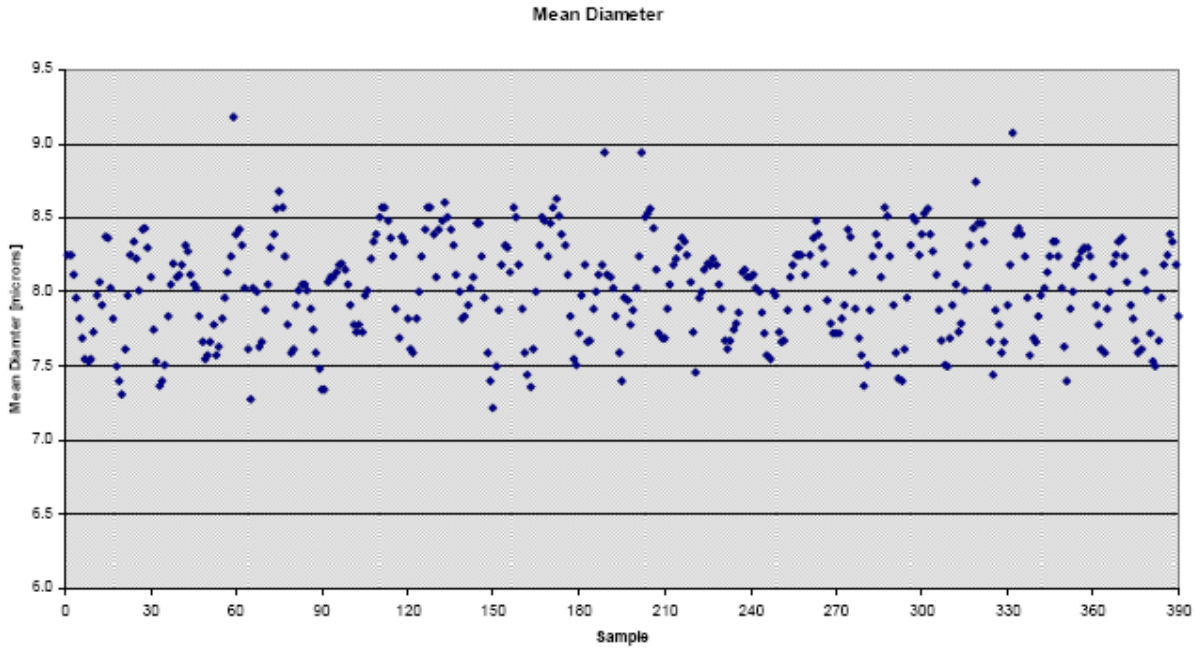

Figure 27 Diameter measurements from a large number of heat treated fibers

2.4 Fiber Surface Modification and Interfacial Shear Strength

Carbon fiber with good mechanical properties can be produced in the UTSI lab. But the efficient translation of these good mechanical properties into composites has not been achieved. Besides the negative effects from trapped air bubbles or voids, low fiber volumes, and uneven fiber loading, the composites obtained from this form of fiber and epoxy have poor interlaminar shear strength (ILSS). This has been attributed to weak adhesion or poor bonding between the carbon fiber surface and the resin matrix; and fiber surface modification by introducing functional groups and increasing surface area can effectively improve the ILSS of carbon fiber composites.

2.4.1 Surface Treatment of carbon fibers

Oxidative treatment in air was employed in our experiments. A bundle of carbon fibers (Spin speed at 40 lpm, carbonization temperature at 1050 °C) was treated in a muffle oven preheated at 400 °C in air for 1 hour. The single fiber fragmentation tests were used to characterize the ILSS of the composites fabricated from the carbon fibers before and after oxidation treatment.

2.4.2 Interfacial Shear Strength

A filament more than 15 inch long was pulled out from a bundle of carbon fibers. A section of 5 inches was used for specimen. Another part of the fiber was used for measurements of fiber diameter and tensile strength. For the fragmentation tests, at ends of the fiber, two clamps were used to keep the fiber straight and centered in the silicon rubber form (mold) prepared in our lab, as shown in Figure 28. The specimen form was filled with epoxy resin (epoxy/hardener = 5/1) which was cured with a similar procedure as used for the carbon fiber composite fabrication. The specimen was then polished carefully until it is transparent and the fiber can be clearly seen against the light. A simple test apparatus (in Figure 29) was designed to pull both ends of the specimen slowly apart. This apparatus was placed on the top of an x-y-table and a holder was mounted on the back to connect the apparatus to the optical microscope in Figure 30 with a polarized light. Pictures and movies can be taken using a digital camera.

Figure 28 Silicon rubber forms (molds) for specimen fabrication

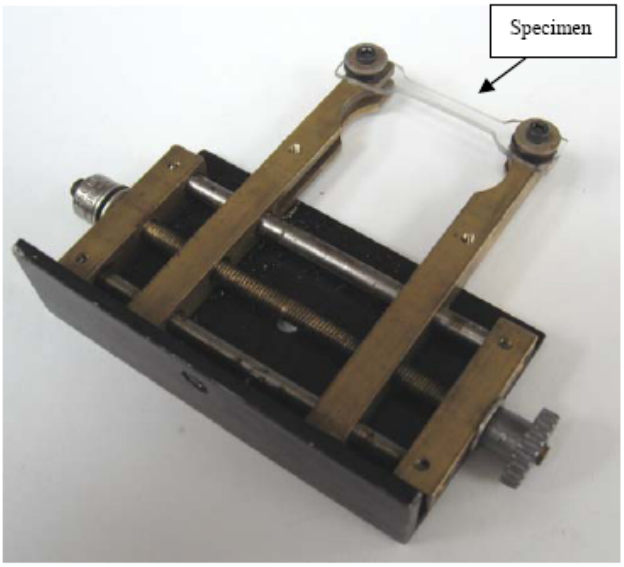

Figure 29 Test apparatus with specimen holders

Figure 30 Microscope with test apparatus and cross-polarized light

The strain of specimen was calculated by directly measuring the change in distance between the two points pre-marked on the specimen under the microscope. The fragmentation took place with increasing strain and stopped as a strain reached about 2%. The average fragment length $\bar{l}$ can easily be measured using an optical microscope with polarized light, Figure 31. Based on the references, the critical fiber length l_c is given as follows

$$l_c = \frac{4}{3}\bar{l} \qquad (1)$$

The interfacial shear strength, τ, can be calculated with the following relationship:

$$\tau = \frac{\sigma_f \times d}{2 \times l_c} \qquad (2)$$

Where σ_f is the fiber strength as evaluated from single fiber tensile tests, d is the fiber diameter and l_c is the critical fragment length of the fiber.

The interfacial shear strength, τ, can be calculated from the fiber tensile strength, σ_f, the fiber diameter, d, and the critical fragment length, l_c.

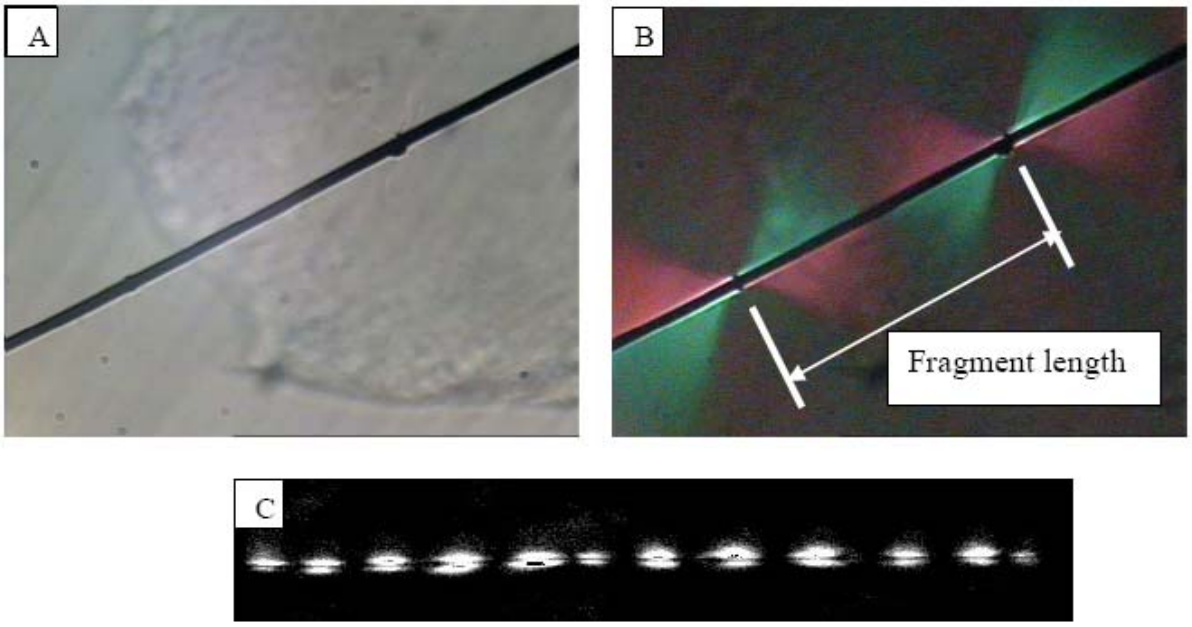

Figure 31 Typical interface patterns for carbon fiber /epoxy system. (A) normal light; (B) cross-polarized light; and (C) cross-polarized light at a small magnification

Some unusual interface patterns can be seen under the microscope as shown in Figure 32. Cracks with matrix deformation (Figure 32-A) indicate a good bonding between fiber surface and matrix; and fiber slip (Figure 32-B) in the matrix indicating a weak bonding. Figure 33 shows a change in interface patterns with strain applied. The debonding zone at a fiber break increased with an increasing strain. It was found that the oxidative treatment of carbon fiber can reduce the debonding length.

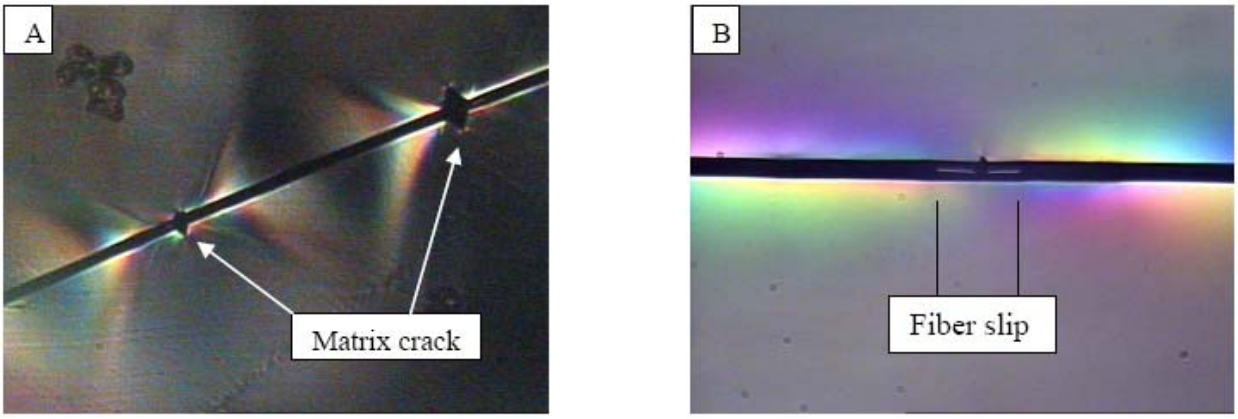

Figure 32 Interface patterns for carbon fiber /epoxy system. (A) crack with a deformation into matrix; (B) carbon fiber slip in the matrix

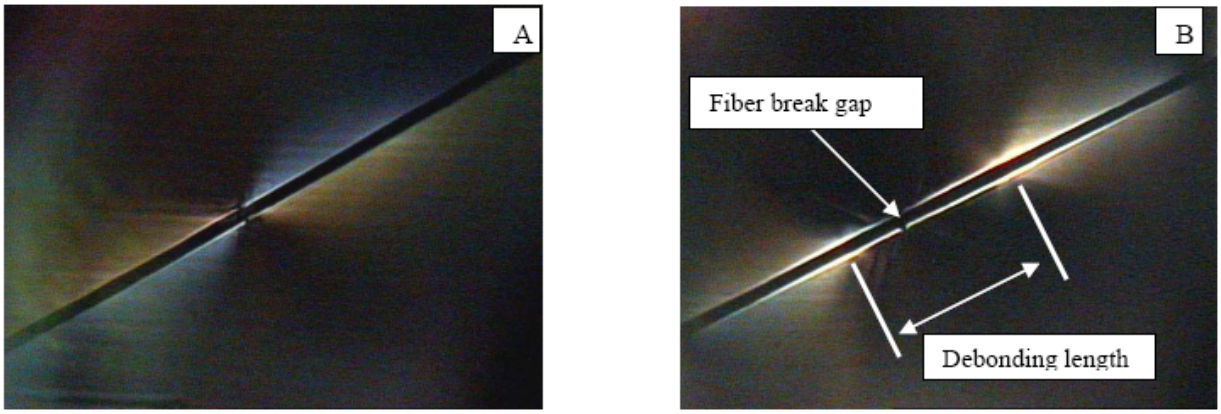

Figure 33 Interface patterns for carbon fiber /epoxy system. (A) low strain applied; (B) high strain applied

Table 1 lists interfacial shear strength calculated with the equations 1 and 2. The oxidative treatment of carbon fiber in air at 400 °C can improve the interfacial shear strength between the fiber and the epoxy.

Table 1 Interfacial Shear Strength Comparing Untreated Carbon Fiber with Oxidized Carbon Fiber

System	Sample No.	Fiber average diameter μm (St. Dev.)	Fiber tensile strength MPa (St. Dev.)	Critical length μm	Interfacial shear strength MPa
UTSI Carbon Fiber (1050C) / Epoxy	1	12.46 (0.57)	464.95 (304.88)	654.5	4.4
	2	13.09 (0.35)	620.32 (402.63)	550.4	7.4
	3	12.62 (0.54)	728.91 (670.46)	692.5	6.6
	Mean				**6.1**
400C Oxidized UTSI Carbon Fiber/Epoxy	1	11.9 (0.78)	640.01 (635.99)	553.9	6.9
	2	13.05 (1.00)	1063.6 (162.12)	589.2	11.8
	3	12.93 (0.75)	242.1 (70.68)	640.7	2.4
	Mean				**7.0**

2.5 Other Surface Properties of Carbon Fibers

The mechanical properties of carbon fiber composites can be influenced by the wetting characteristics and collective interaction of the fibers. Parameters that determine collective interactions of the fibers are the fiber volume fraction, fiber aspect ratio and orientation. The requirements for interface interaction related to wetting characteristics may vary from strong bonds for structural applications to weak bonds for energy absorption applications. In order to have a good understanding of the characteristics of the interface, different evaluation methods have been investigated.

For wetting properties, two candidate measurement methods have been identified and evaluated. Dynamic method based on the rate of wicking of a bundle of carbon fiber has been described by Chwastiak. A schematic of the experimental setup is shown in Figure 34. The thermal gravimetric analyzer (TGA) is used to measure weight changes, with water and glycerin used as wetting agent.

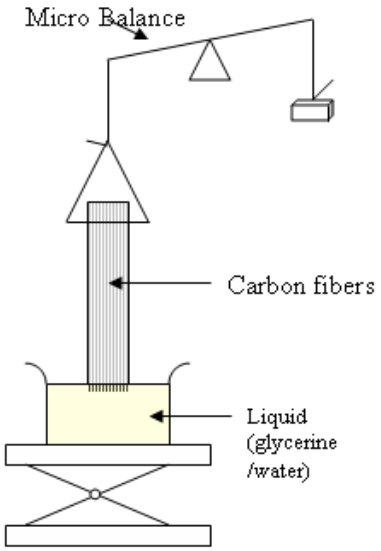

Figure 34 Wicking rate tests - Experimental setup

The free energy of wetting can be evaluated from the circumference of all the filaments in the yarn bundle and a determination of the magnitude of the viscous forces, gravitational forces and inertial forces resisting liquid flow in the yarn bundle.

The force terms could be evaluated as functions of fiber/bundle properties and the wicking rate. Experiments have been conducted on glass fibers, PAN fibers and pitch-based carbon fibers. Figure 35 shows some results of weight gain and weight gain rate for different fibers and fluids. For glass fiber and carbon fiber, there is a maximum weight gain peak observed. The fiber loading seems to affect the wicking rate with time, probably due to misalignment of some fiber samples. The technique is considered a valuable tool to evaluate the surface properties of fiber products with uniform diameter and alignment.

Another method that has been evaluated for the wetting measurement of single fiber is based on the inflection angle of the drop profile as described by Rebouillat. Optical microscopes at UTSI have been tested for image acquisition of the fiber-drop system at acceptable resolution. An experimental setup is shown in Figure 36. The original digital image has been enhanced to allow for an accurate extraction of the edge profiles. A typical droplet image and its processing are shown in Figure 37. The inflection angle is obtained at the point of maximum slope. A typical slope curve for Glycerin on our carbon fiber is shown in Figure 38. The contact angle is then obtained from the relation between the fiber diameter and the max drop radius.

This method is considered as a better approach as it eliminates the requirement to measure the drop length. The measurements of drop length can be quite subjective to the operator because there is a steep variation in the meniscus angle near the point where the fluid first touches the fiber surfaces.

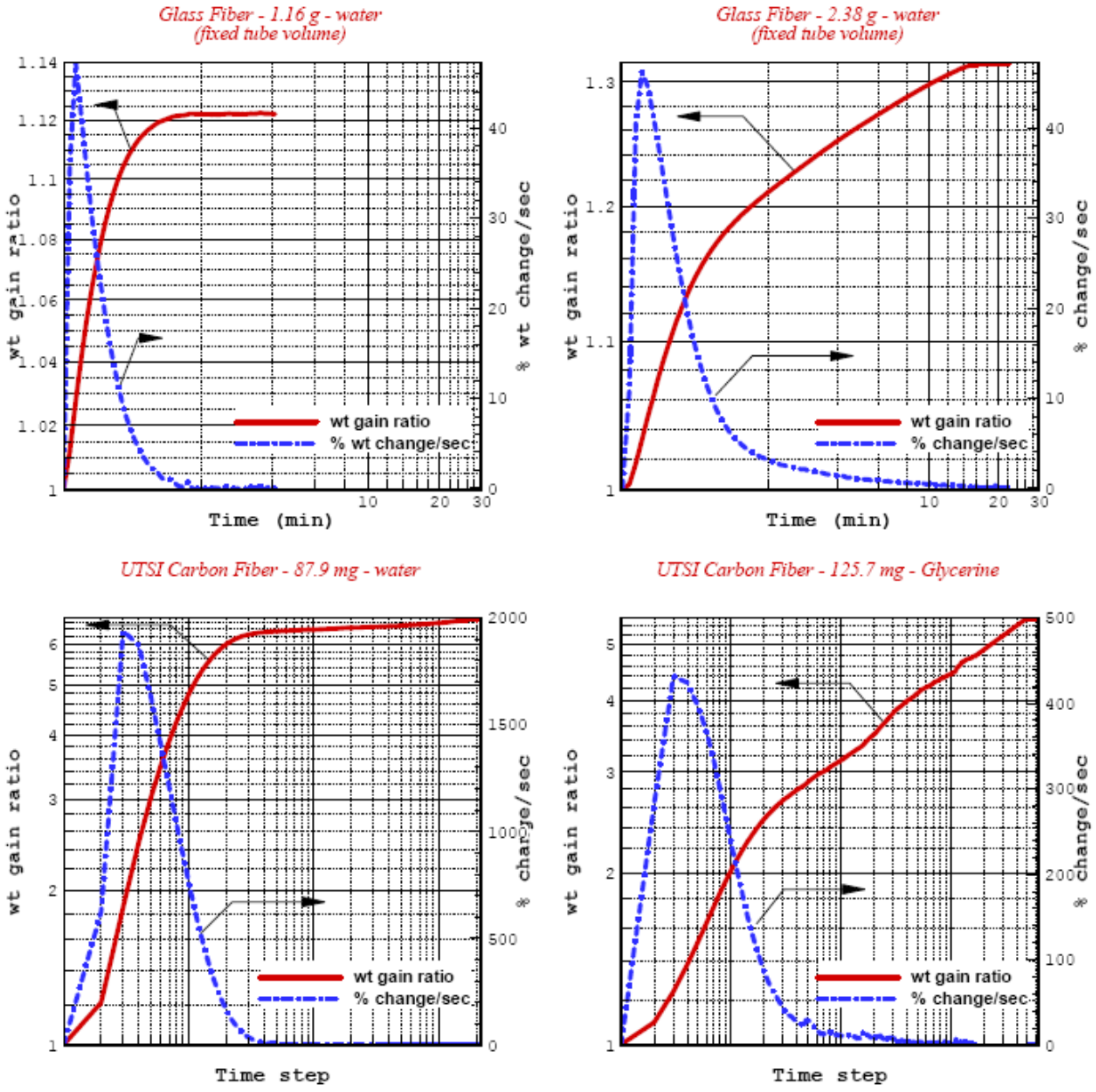

Figure 35 Weight gain and its rate of different fluids on glass and carbon fibers

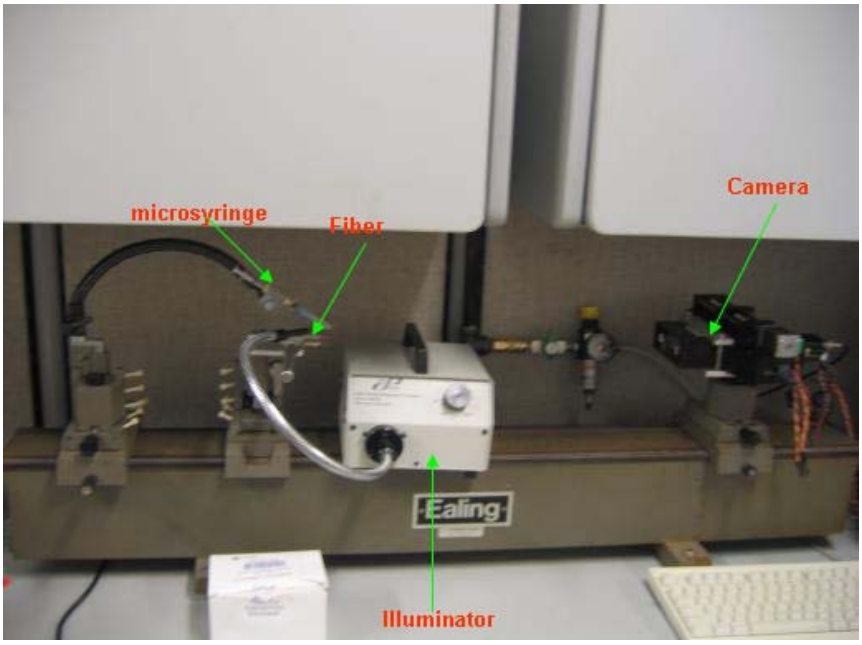

Figure 36 Experimental setup for the contact angle measurement

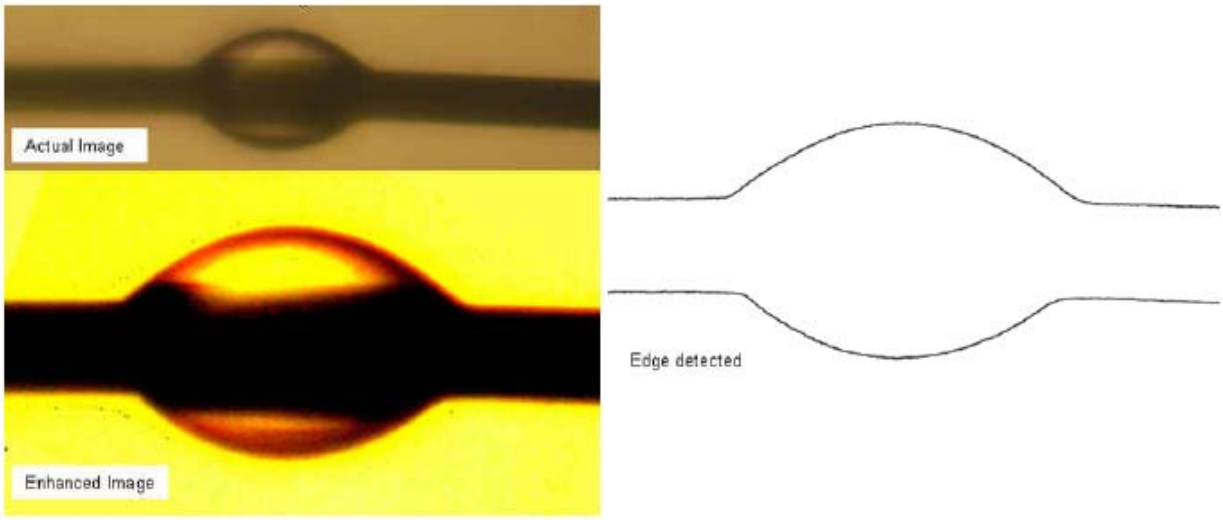

Figure 37 Droplet edge detection for contact angle measurement using inflection angle

Both the wicking rate method and the contact angle method have their advantages and disadvantages. Estimating precise contact angle measurement in very small diameters is a challenge. We hope that by using the two methods, we will be able to make useful measurement, which should help us quantitatively evaluate the fiber surfaces and to determine sizing methods for various applications. Further studies and calibrations for these methods are needed in the future.

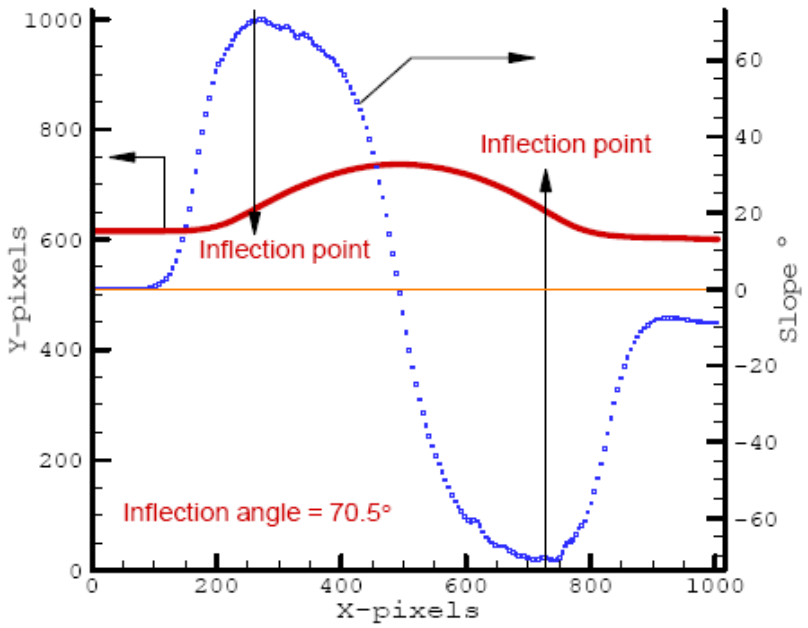

Figure 38 Inflection angle estimation from droplet profile

3. Fabrication and Characterization of Carbon Fiber-reinforced Composites

The primary purpose of this effort is to assess the potential for a wide range of composite applications of our low-cost carbon fibers spinning and processing techniques. The composite samples are fabricated using long (continuous) or chopped (small segments of various length) carbon fibers. The properties of the composites that will be evaluated are strength (tensile, compressive and/or bending), endurance (fatigue) and thermal conductivity and electrical conductivity. The following sections describe the progress made in the experimental fabrications of carbon fibers-reinforced composites.

3.1 Matrix Materials

Our first activity was to identify the right type of resins that may be used with our carbon fibers. Typical resins could be epoxy, vinyl ester or polyester resins. Based on our literature survey, epoxy resins were chosen. Some of the characteristics of epoxy resins compared to others are:

- Epoxy resins are known for its incredible toughness and bonding strength;
- Quality epoxy resins can support reinforcements up to 2000 psi compared to 500 psi for vinyl ester resins and even less for polyester resins;
- Epoxy resins offer greater capability in flexing and straining with fibers without micro-fracturing;
- Cured epoxy tends to be very resistant to moisture absorption;
- Epoxy resins can bond dissimilar or cured materials making repairs that could be stronger and reliable;

- Epoxy resins are compatible with all sorts of fibers, prevent delamination and offer excellent results in reparability whereas vinyl esters are great for glass fiber but do not work well with Kevlar and carbon fibers.

3.2 Forms of Carbon Fibers

Different forms of carbon fibers were prepared in the UTSI lab. They have been/will be used as reinforcing fibers for the fabrication of CF/epoxy composites.

1. Continuous fibers. A bundle of carbon fiber produced in the UTSI lab is shown in Figure 39. It can be aligned with a relatively high degree of fiber orientation for use of composite fabrications.

Figure 39 A bundle of carbon fibers (continuous fibers)

2. Chopped fibers. A bundle of carbon fiber was cut to 0.5-0.1 inch fiber length. The chopped fibers are shown in Figure 40.

Figure 40 Chopped carbon fibers

3. Fiber rope or tow. A bundle of carbon fiber was wound to form a rope (Figure 41).

Figure 41 Carbon fiber rope

4. Carbon fiber mat. A bundle of UTSI carbon fiber can easily be fabricated to a carbon fiber mats by using polymers as binders. Several carbon fiber mats have been prepared from continuous or chopped carbon fibers and the sample are shown in Figures 42-45.

Figure 42 Carbon fiber mat made from a bundle of carbon fiber and PVA binder

Figure 43 Carbon fiber mat made from strands of carbon fiber and phenolic resin binder

Figure 44 Carbon fiber mat made from chopped carbon fiber (2-10 mm) and phenolic resin binder

Figure 45 Carbon fiber mat made from a bundle of carbon fiber and epoxy resin binder

3.3 Fabrication of Carbon Fiber-reinforced Resin Composites

3.3.1 Hot Compression Molding Technique

Carbon fiber composites were first made in the UTSI lab using a hot compression molding technique. The first geometry is a flat plate. The model for the plate and the hot press equipment used are shown in Figure 46. The dimensions of the plate mold is about 2” x 6” x 1/8”.

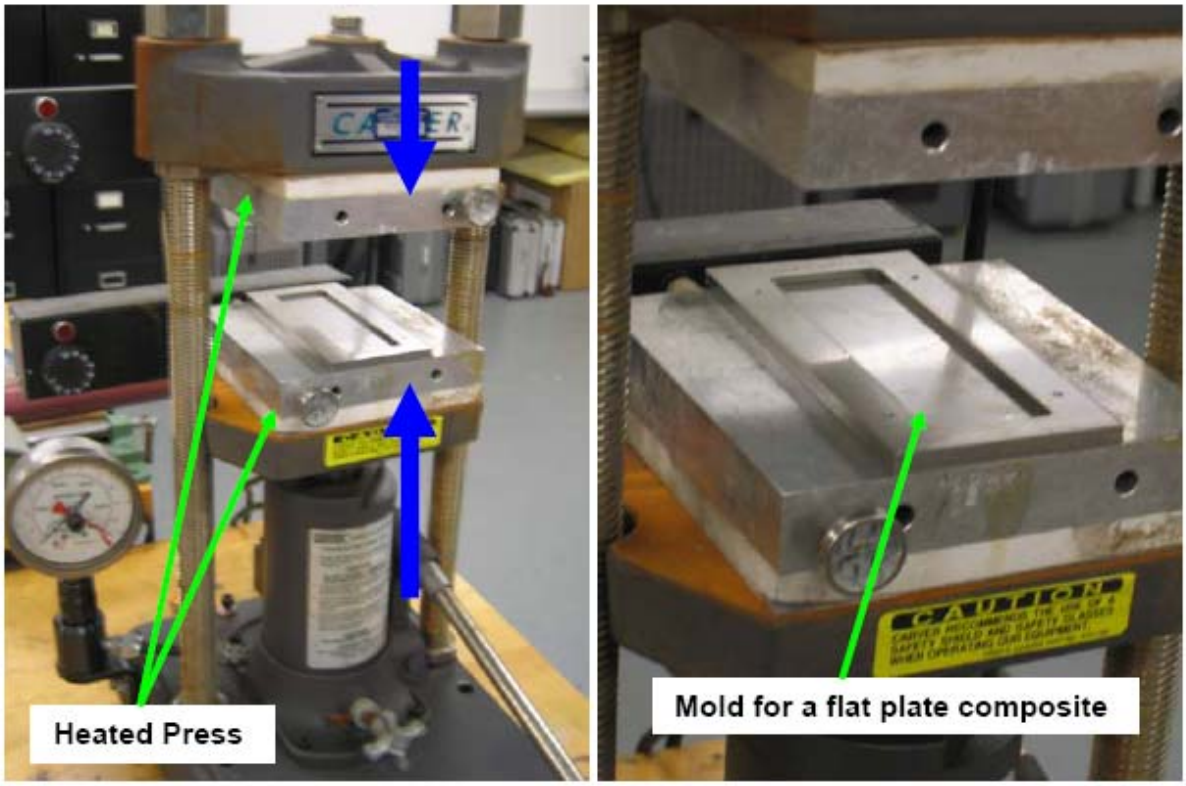

Figure 46 Hot compression molding equipment and the mold for a flat plate test composite

Composites were made using three different forms of carbon fibers made in the UTSI spin lab. They are 1) continuous fibers, 2) fiber rope or tow form and 3) chopped fibers with 0.5 inches long. Figure 47 shows three typical rectangular bars made from these different forms of carbon fibers. Our initial analysis shows some voids present in the composites as shown in Figure 48. Figure 49 shows cross sections of the composite obtained from a scanning electron microscope (SEM). There are trapped bubbles and voids that dominate the image including fibers. During the application of the resin to the fibers of different forms very small air bubbles are formed in the mixture and due to the application technique, we have not made any effort to remove the bubbles. There is also the probability of incomplete wetting of all the fibers surfaces in this process. Bubbles negatively influence the integral properties of the composites.

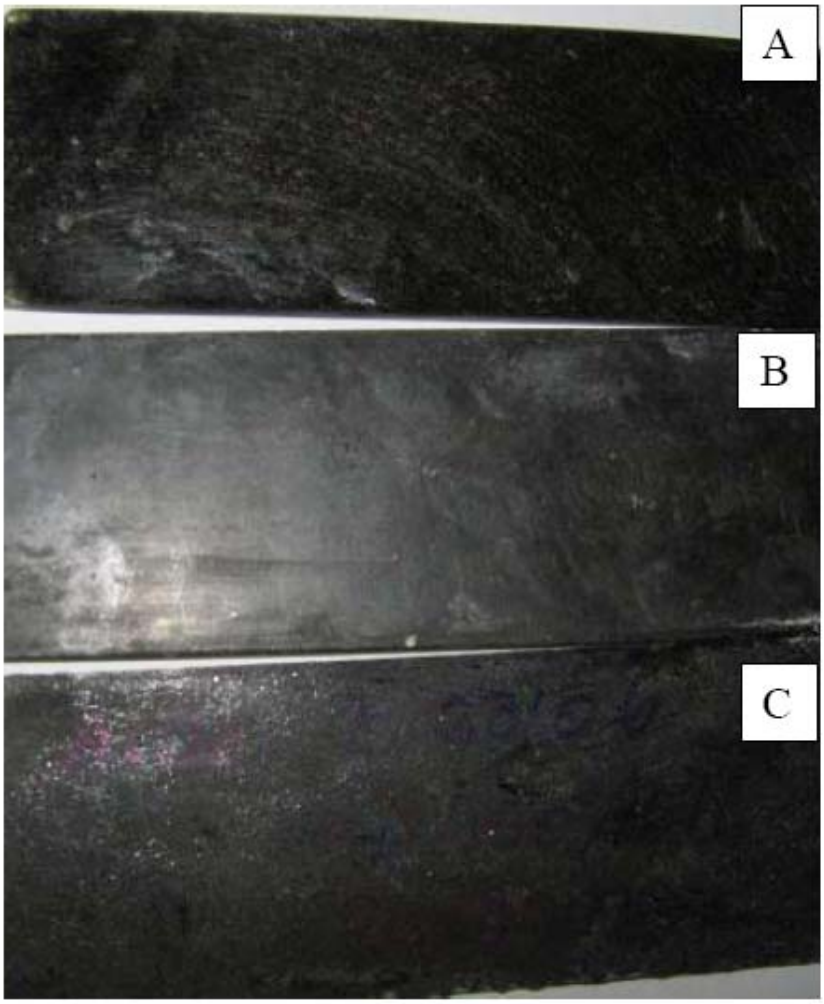

Figure 47 Typical composites made using UTSI's carbon fibers of different forms (A) fiber rope; (B) chopped fiber; and (C) continuous fiber (random)

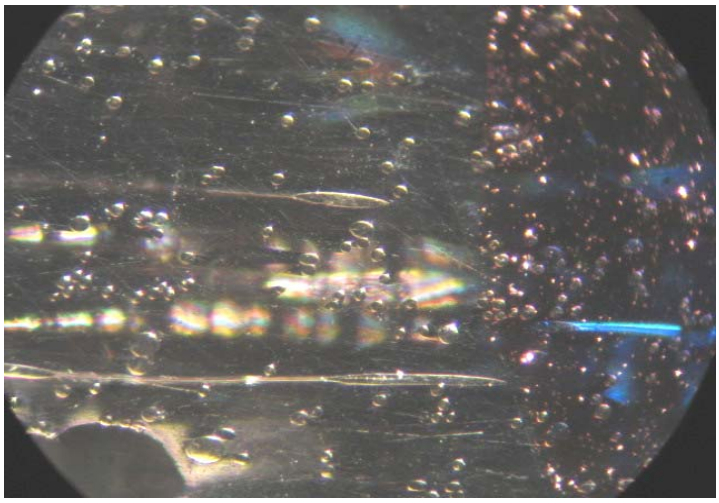

Figure 48 Cross section of a carbon fiber composite, showing trapped air bubbles

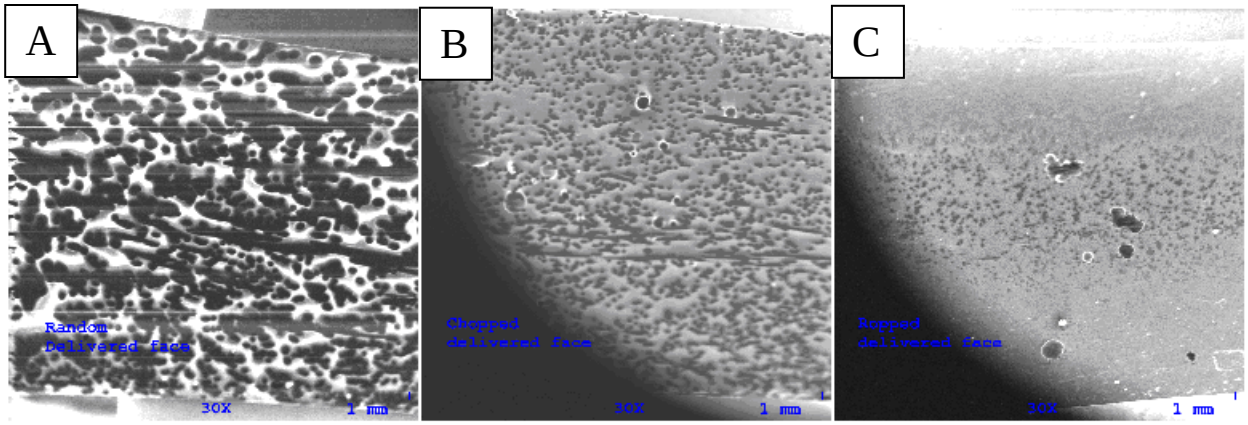

Figure 49 Cross sections of different composites showing fiber distribution within the composite and some voids present in the composites. (A) continuous fiber (random); (B) chopped fiber; and (C) fiber rope

3.3.2 Vacuum Bagging Technique

To remove air bubbles and reduce excessive matrix resin, vacuum bagging technique was then employed to make CF/epoxy composites. The composite was fabricated in two steps as shown in Figure 50. The first step was done in a vacuum bag to remove air bubbles and reduce excessive matrix resin. The carbon fiber (chopped fiber, continuous fiber, or aligned carbon fiber) soaked with epoxy resin was placed on a steel plate (mold). On the top, a release fabric was draped over any portion in contact with the resin, the bleeder/breather material was then added to absorb excessive resin and make the vacuum distributed evenly within the bag. The carbon fiber/epoxy system was cured at room temperature in the bag under a vacuum of 27" Hg for 3-4 hours. During the first step, it can be seen that most of the air bubbles and excessive epoxy were removed from carbon fiber/epoxy system. After that, the vacuum pump was stopped; the air bag, the bleeder/breather material, and the release fabric were removed. The carbon fiber/epoxy was still soft because epoxy was not fully cured. The second step was done using the hot press equipment (see Figure 46). Another steel plate (mold) was placed on the top of carbon fiber/epoxy. The carbon fiber/epoxy was further cured under pressure for 2-3 hours to make a carbon fiber/epoxy plate with smooth surfaces and a uniform thickness. The plate was then transferred to an oven preheated at 70^{o}C and fully cured for 24 hours.

With this technique, we made chopped carbon fiber composites and continuous carbon fiber composites. The following describes the preparation of these composites and their physical and mechanical properties.

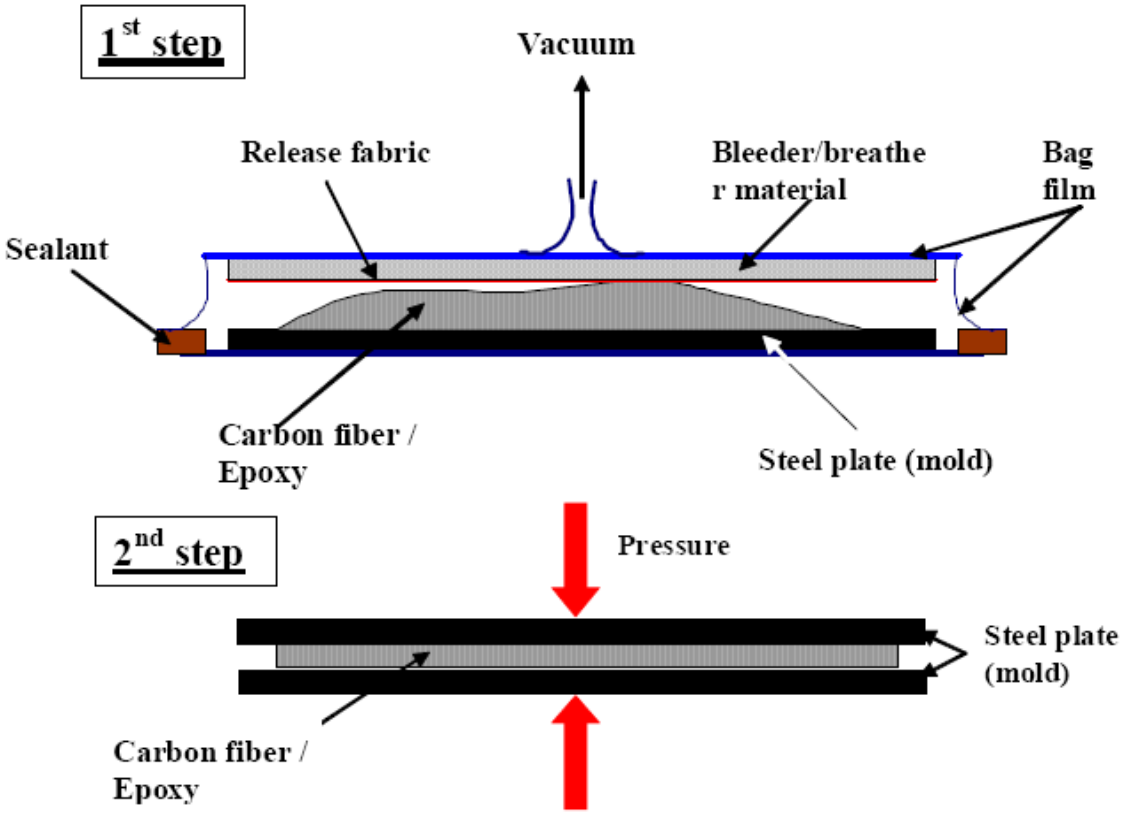

Figure 50 Vacuum bagging and press technique for making carbon fiber/epoxy composites

3.3.2.1 Chopped carbon fiber composite

A. Preparation of composites

Chopped carbon fiber composite was first prepared with the vacuum bagging technique. One part of chopped carbon fiber (spin speed = 40 Lpm, carbonization temperature = 1050 °C, and 0.5 – 0.1 inch long) and ten parts of epoxy resin (epoxy / hardener = 5/1) were hand-mixed in a container. The carbon fiber/epoxy system was fabricated to a composite plate using the method described above. The composite plate contains ~ 14 wt % of carbon fiber. Our pre-examinations indicated that small amount of air bubbles and uneven fiber loading were present in the resin matrix.

As a comparison, a cured epoxy resin plate without any fibers inside was also prepared. The measurements of apparent density and electric resistivity, and tensile tests were conducted on the carbon fiber composite plates and a cured epoxy resin plate. The individual, cured plate was cut to a nominal dimension of ~ 130 mm by 12.5 mm. Each of test samples was weighed with a balance first. Its dimensions and electrical resistance were then measured with a calibrator and an electrical bridge, respectively. Apparent density and electrical resistivity were measured and calculated before the tensile tests.

Tabs were bonded to the tensile samples to help protect them from damage from the grips during testing, as shown in Figure 51. The tensile samples were tested in a MTS machine with a 550 kN load cell and a head speed of 0.1 inch per minute. An extensometer was used to measure strain. The ASTM D3039 standard was used as a guide to the testing and calculations reported.

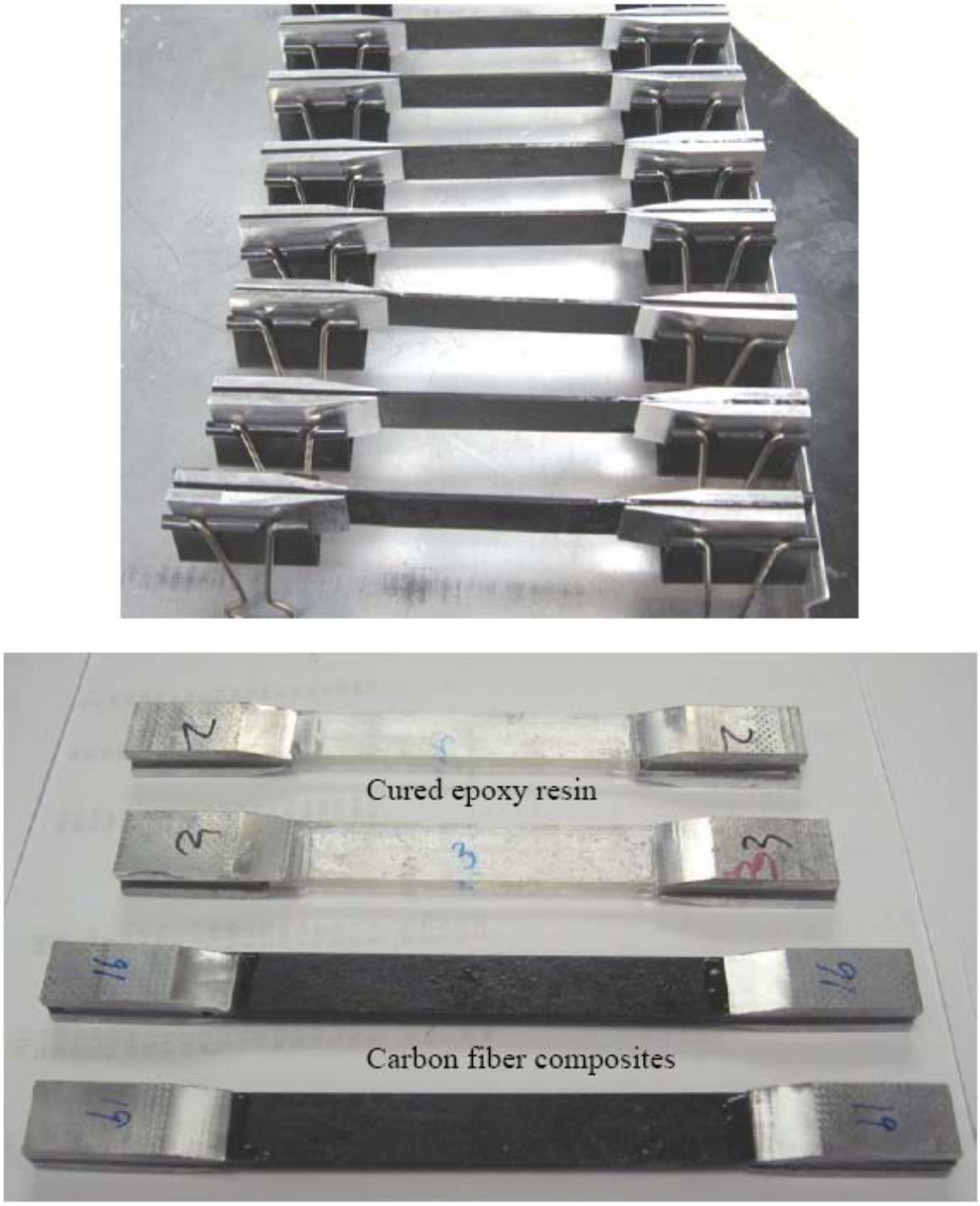

Figure 51 Specimens for tensile tests

B. Physical and mechanical properties

Physical and mechanical properties of cured epoxy resin and chopped carbon fiber/epoxy resin composite are listed in Tables 2 and 3. The typical stress-strain curves for each material are shown in Figures 52. The composite displays a 2.2 time increase in Young's modulus and almost the same tensile strength as compared with a cured epoxy resin.

The variations in electrical resistivity and tensile strength of chopped carbon fiber composite samples listed in Table 2 suggest an uneven fiber loading present in the composite material.

Table 2 Physical and Mechanical Properties of Chopped Carbon Fiber Composites
(~ 14 wt % of carbon fiber)

Specimen #	Physical properties		Mechanical properties		
	Apparent density (g/cm^3)	Electrical resistivity ($\Omega*cm$)	Tensile strength (Mpa)	Ultimate strain (%)	Young's modulus (Gpa)
A*	1.17	3.805	13.17	0.28	4.7
B*	1.16	4.943	16.54	0.36	4.6
Average	**1.17**	**4.374**	**14.86**	**0.32**	**4.7**
*Cut from the edge of the composite plate where it may contain more epoxy resin					
1	1.18	0.368	34.49	0.59	5.8
2	1.18	0.278	21.77	0.47	5.7
3	1.09	0.309	34.11	0.68	5.7
4	1.18	0.711	26.92	0.59	5.8
5	1.18	0.237	25.89	0.41	6.3
Average	**1.16**	**0.380**	**28.64**	**0.55**	**5.9**
Std. deviation	0.04	0.17	4.94	0.10	0.22

Table 3 Physical and Mechanical Properties of Cured Epoxy Resin
(0 wt % of fiber)

Specimen #	Physical properties		Mechanical properties		
	Apparent density (g/cm^3)	Electrical resistivity ($\Omega*cm$)	Tensile strength (Mpa)	Ultimate strain (%)	Young's modulus (Gpa)
1	1.39	$> 10^6$	30.37	1.37	2.6
2	1.03	$> 10^6$	22.89	0.97	2.6
3	1.21	$> 10^6$	18.66	0.72	2.7
4	1.20	$> 10^6$	35.65	1.51	3.0
s	1.19	$> 10^6$	28.47	1.17	2.7
Average	**1.20**	**$> 10^6$**	**27.21**	**1.15**	**2.7**
Std. deviation	0.11	-	5.91	0.28	0.15

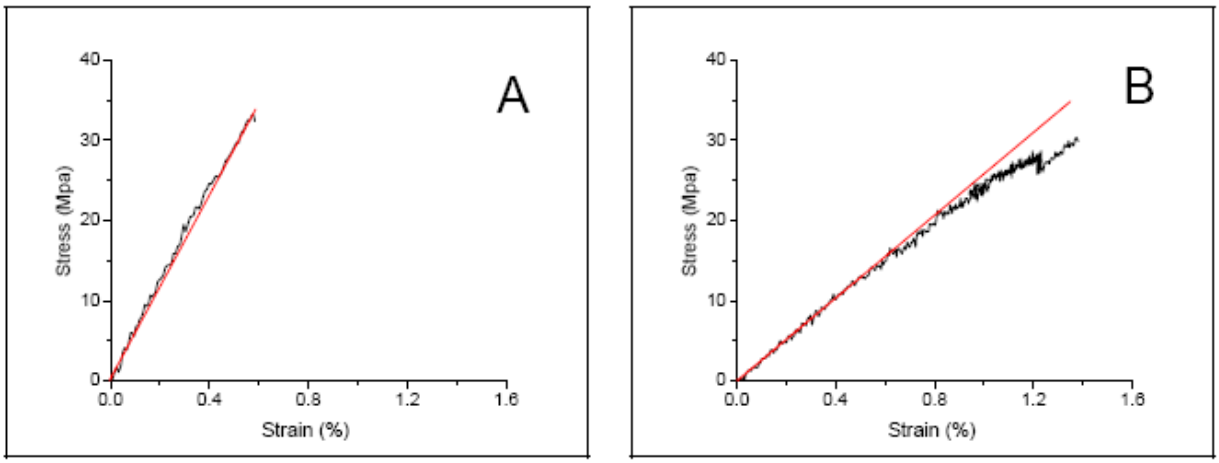

Figure 52 Typical stress-strain curves of carbon fiber composite (A) and cured epoxy resin (B)

3.3.2.2 Continuous carbon fiber composite

A. Preparation of composites

To increase the tensile strength and improve the uniformity of fiber loading of carbon fiber composites, a bundle of continuous carbon fiber was aligned first and then was fabricated into a composite using a vacuum bagging technique described above. A bundle of carbon fiber (spin speed = 40 Lpm and carbonization temperature = 1050 °C) was warped around a glass bottle (its circumference is equal to the length of composite plate) with a stretch force to make a fiber roller with a uniform thickness. The fiber roller round the glass bottle was then rolled over the epoxy resin (epoxy/hardener = 5/1) on a flat surface to make carbon fiber layer wetted with epoxy resin. A layer of impregnated carbon fiber with unidirectional fiber alignment was formed when the fiber roller was cut from the glass bottle. Several such layers were used to make final composite. An aligned carbon fiber/epoxy composite made with the above method is shown in Figure 53.

For the measurements of apparent density and electric resistivity, and tensile tests, a composite plate was cut to a nominal dimension of ~ 150 mm by 12.5 mm for a sample with 0° of fiber alignment and another composite plate was cut into ~ 150 mm by 25 mm for a sample with 90° of fiber alignment.

Figure 53 Aligned carbon fiber composites

B. Physical and Mechanical Properties

Physical and mechanical properties of the carbon fiber composite at 0° or 90° are listed in Tables 4 and 5. The typical stress-strain curves for each material are shown in Figure 54.

Table 4 Physical and Mechanical Properties of Carbon Fiber Composites with a 0° of Fiber Alignment (13-18 wt % of fiber)

Specimen #	Physical properties		Mechanical properties		
	Apparent density (g/cm^3)	Electrical resistivity ($\Omega*cm$)	Tensile strength (Mpa)	Ultimate strain (%)	Young's modulus (Gpa)
1	1.12	0.045	93.69	0.94	9.6
2	1.18	0.045	72.00	0.65	11.1
3	1.11	0.039	81.61	0.83	9.8
4	1.09	0.035	75.48	0.79	9.6
5	1.09	0.040	78.36	0.84	9.2
6	1.14	0.088	71.87	0.74	8.7
7	1.08	0.092	72.43	0.67	10.8
8	1.21	0.077	62.12	0.63	9.9
Average	**1.13**	**0.057**	**75.95**	**0.76**	**9.8**
Std. deviation	0.043	0.022	8.58	0.10	0.72

Table 5 Physical and Mechanical Properties of Carbon Fiber Composites with a 90° of Fiber Alignment (13-18 wt % of fiber)

Specimen #	Physical properties		Mechanical properties		
	Apparent density (g/cm^3)	Electrical resistivity ($\Omega*cm$)	Tensile strength (Mpa)	Ultimate strain (%)	Young's modulus (Gpa)
1	0.882	0.196	23.61	0.78	3.00
2	0.930	0.250	27.70	0.80	3.30
3	0.942	0.182	28.11	0.90	3.10
4	0.898	0.135	26.07	0.95	3.09
5	0.930	0.203	24.54	0.75	3.16
Average	**0.916**	**0.193**	**26.01**	**0.84**	**3.13**
Std. deviation	0.023	0.037	1.74	0.08	0.099

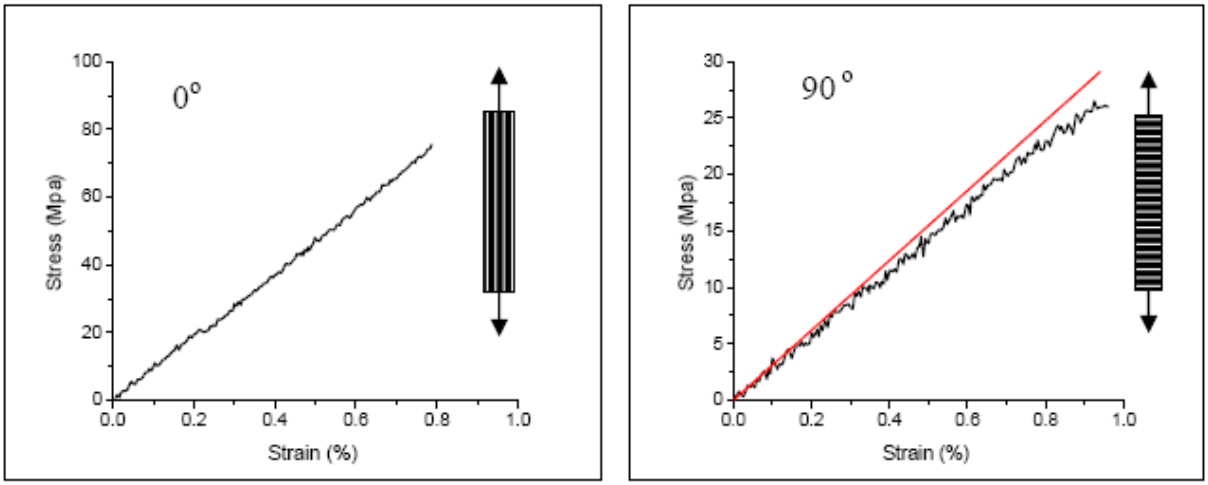

Figure 54 Typical stress-strain curves of carbon fiber composites at 0° and 90°

The following results are obtained:

- Aligned carbon fiber (1050 °C) reinforced epoxy resin composite measured with a 0° of fiber alignment displays a 2.8 times increase in tensile strength and a 3.6 times increase in Young's modulus as compared with a cured epoxy resin.
- Aligned carbon fiber reinforced epoxy resin composite has a high electrical conductivity or low electrical resistivity as compared with its matrix and chopped carbon fiber composite. The electrical resistivity of the carbon fiber composite is anisotropic. It changes from 0.057 to 0.193 $\Omega*cm$ when the sample was measured from 0° to 90° of fiber alignment.
- The mechanical properties of the composite are also anisotropic. The tensile strength and Young's modulus measured at 0° of fiber alignment are much higher than those measured at 90° of fiber alignment.

- Electrical conductivity and mechanical properties of the carbon fiber composite are consistent in action. They depend considerably on the nature of fiber, fiber alignment, fiber concentration, and molding conditions. It suggested that the electrical conductivity might be used to predict the mechanical properties of carbon fiber composite.
- The apparent density of carbon fiber composite is lower than that of the cured epoxy resin. This indicates that a lot of pores exist inside the composite. It is believed that the mechanical properties will be improved greatly if the density of composite is increased (porosity decreased) by choosing best molding conditions, and increasing the fiber content (current is 13-18 wt%).

C. SEM analysis of carbon fiber composite

The aligned carbon fiber composite and its fracture surface were analyzed with a SEM. The typical micrographs are shown in Figures 55-57. It was found that carbon fibers are embedded in the epoxy resin; and the volume fraction of carbon fiber and epoxy is less than the normal one reported in references. The fracture surface shows a considerable amount of air bubbles and voids that are present in the composite. In Figures 56 and 57, some fibers were pulled out from matrix and left a hole on the fracture surface; some fibers show a debonding area between the fiber surface and the matrix, which suggest that the interlaminar shear strength between fiber and the epoxy is poor and need to be improved.

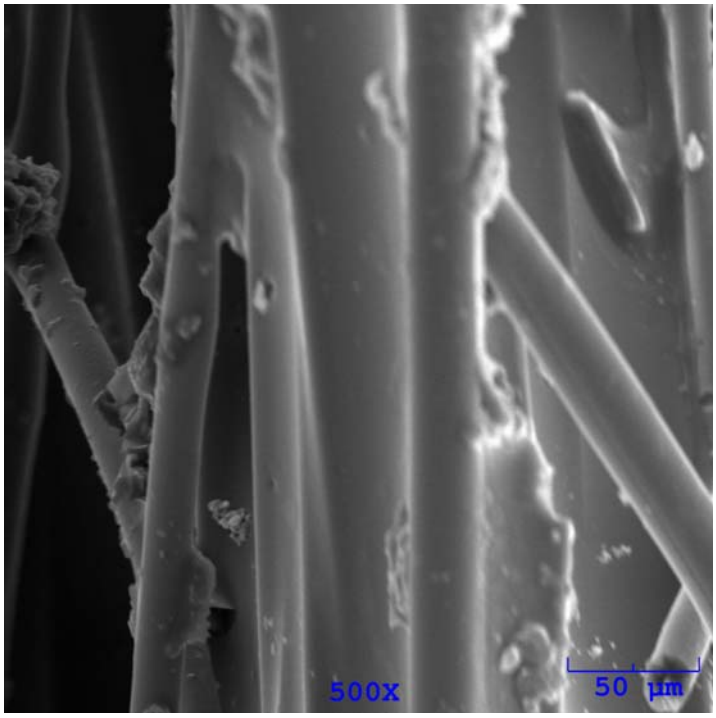

Figure 55 SEM micrograph of carbon fiber composite

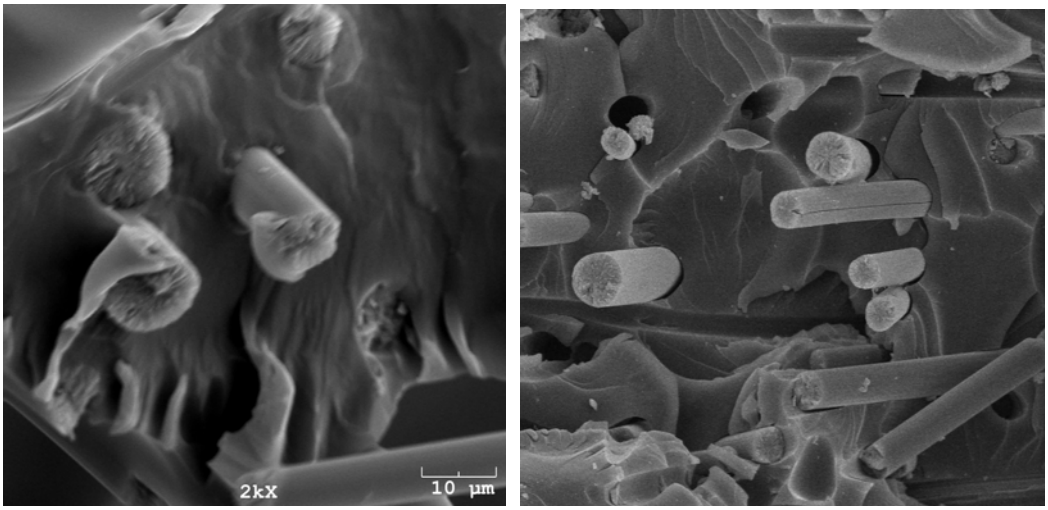

Figure 56 SEM micrograph of fracture surface of carbon fiber composite showing good and bad bondings

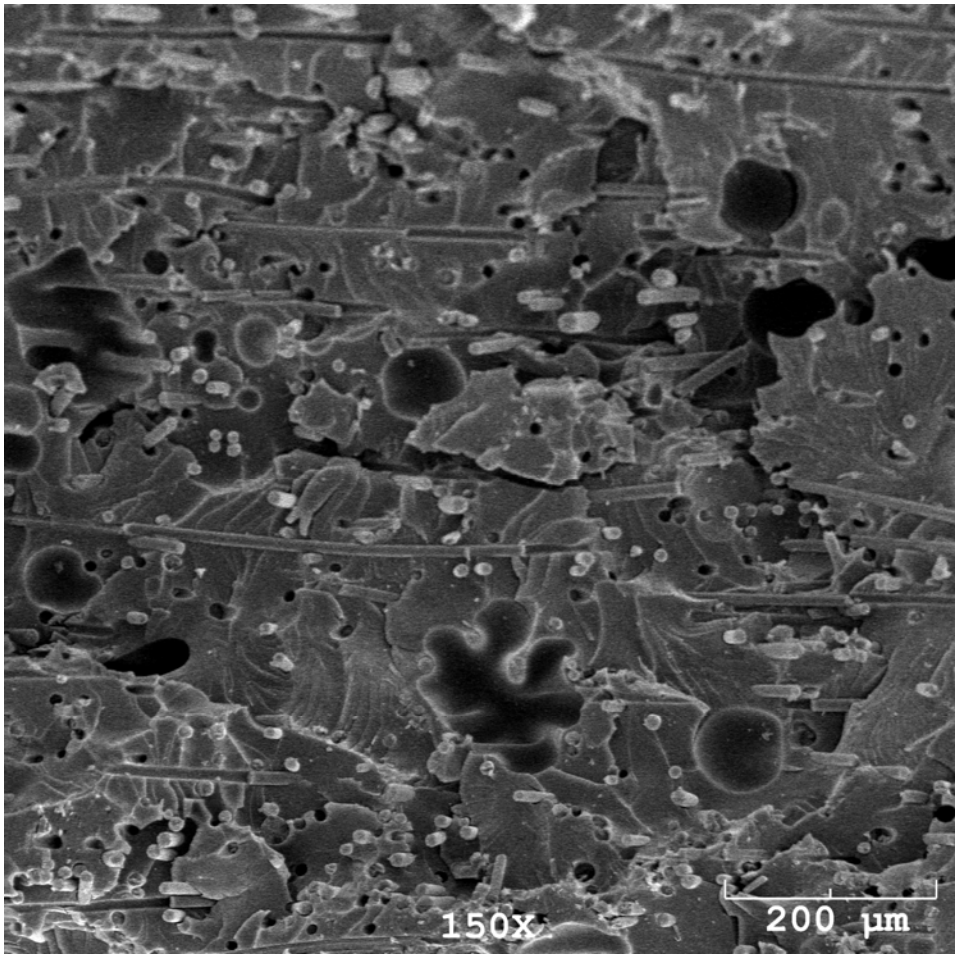

Figure 57 SEM micrograph of fracture surface of carbon fiber composite showing air bubbles and aligned fibers inside composite

3.3.3 Vacuum Bagging - Diffusion Technique

To increase the density and decrease the air bubbles inside the carbon fiber composites, a vacuum bagging –diffusion technique shown in Figure 58 was employed to make carbon fiber composites. Several bundles of carbon fiber (spin speed = 40 Lpm and carbonization temperature = 1350 °C) were partially aligned and put inside the space between two steel plates. The carbon fibers were vacuumed/pressured under a vacuum level at 28' Hg for 30 minutes. Then the epoxy resin (epoxy/hardener= 5/1) was allowed to enter the system from one end while keeping the vacuum pump running on the another end as shown in Figure 58.

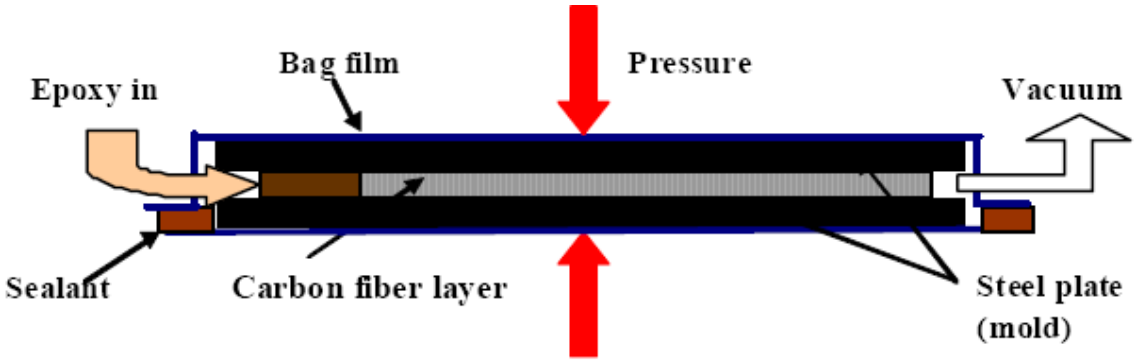

Figure 58 Vacuum bagging-diffusion technique for making carbon fiber/epoxy composites

Physical and mechanical properties of the carbon fiber composite at ~ 0° or ~ 90° are listed in Tables 6 and 7. The typical stress-strain curves for each material are shown in Figure 59. With a vacuum bagging – diffusion technique, we found we can prepare a carbon fiber composite of higher apparent density and tensile strength, more smooth surface and even fiber loading as compared with using a vacuum bagging- stress technique. However, more effort is needed to improve the fiber volume and fiber alignment.

Table 6 Physical and Mechanical Properties of Carbon Fiber Composites with a ~ 0° of Fiber Alignment (10-13 wt % of fiber)

Specimen #	Physical properties		Mechanical properties		
	Apparent density (g/cm^3)	Electrical resistivity (Ω*cm)	Tensile strength (Mpa)	Ultimate strain (%)	Young's modulus (Gpa)
1	1.20	0.124	99.00	1.14	8.7
2	1.20	0.090	80.00	0.77	10.4
3	1.21	0.106	101.00	0.99	10.2
4	1.18	0.085	67.70	0.79	8.6
5	1.22	0.114	84.70	0.89	7.7
6	1.21	0.103	73.80	0.94	7.9
Average	**1.20**	**0.103**	**84.37**	**0.92**	**8.9**
Std. deviation	0.01	0.01	12.24	0.13	1.04

Table 7 Physical and Mechanical Properties of Carbon Fiber Composites with a ~ 90° of Fiber Alignment (10-13 wt % of fiber)

Specimen #	Physical properties		Mechanical properties		
	Apparent density (g/cm^3)	Electrical resistivity ($\Omega*cm$)	Tensile strength (Mpa)	Ultimate strain (%)	Young's modulus (Gpa)
1	1.16	0.79	54.06	1.33	4.1
2	1.17	0.64	45.90	1.24	3.7
Average	**1.17**	**0.72**	**49.98**	**1.29**	**3.9**

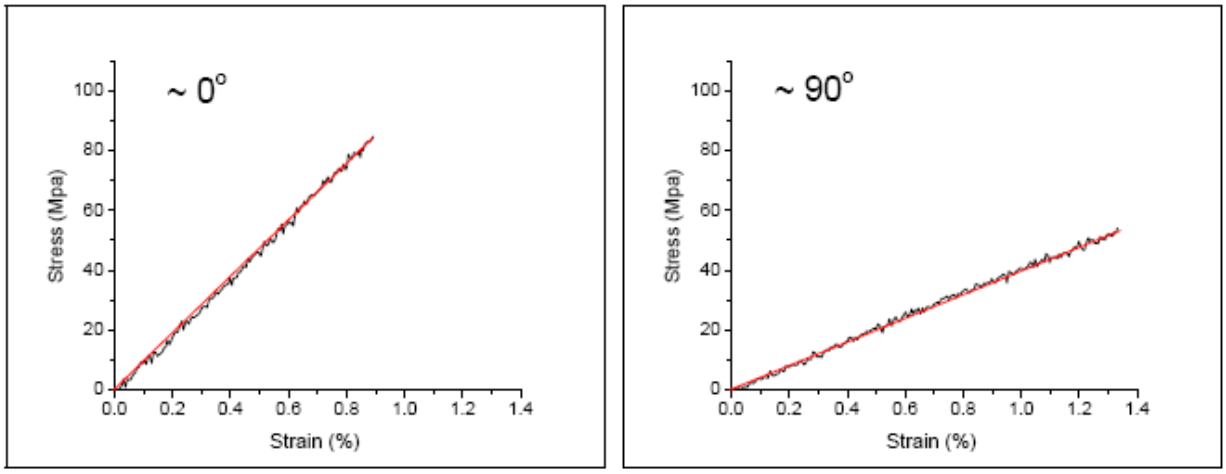

Figure 59 Typical stress-strain curves of carbon fiber composites at ~0° and ~90°

4. Conclusions and Recommendations

A spin lab was setup from components donated to UTSI by ConocoPhillips. Pitch based carbon fiber has been successfully produced, thermally treated, and mechanically characterized. Various composites have also been made and evaluated. The main goals of this research program at UTSI were to produce low cost carbon fibers and to develop specific carbon-based material technologies to meet current and future high performance fiber-reinforced composite needs of transit industry and other organizations. UTSI has been carrying out the relevant research programs since it received the carbon fiber spinning technologies and accessories as a donation from ConocoPhillips. Under this DoT sponsored program, significant progress has been made in continued development and refinement of the low-cost carbon fiber production and composite application technologies. Specifically, the following conclusions and recommendations can be made based on our efforts to date.

1. The pitch-based low-cost carbon fiber production technologies have principally been reproduced in our laboratory, with fiber spinning throughput around 1 pond/hour achieved.

2. Pitch fibers with diameters below 10 microns have been spun and demonstrated, indicating potential for further improvements in carbon fiber properties.

3. Preliminary experiments have indicated that partial alignment of fibers can be achieved at laydown stage during bowing spin. The composite samples made from the partially-aligned carbon fibers have confirmed the anisotropy of fiber reinforcement.

4. The pitch fibers have been successfully processed into carbon fibers with very good mechanical strength and modulus. However, thermal processing was relatively slow, because of the batch processing method, slow drying and stabilization processes, and low density of green fiber materials. Better processing methods and equipments need to be developed to accommodate the current green fiber production rate.

5. The final heat treatment temperature currently at 1500 °C has produced carbon fibers with good mechanical properties. In order to produce carbon fibers with higher modulus and excellent thermal and electrical conductivity for multifunctional materials, higher temperature (> 2200 °C) treatment or graphitization systems are required, and recommended to be investigated further in the next phase.

6. Varied forms of carbon fiber-reinforced polymer (CFRP) composites have been successfully produced in the lab, using several fabrication techniques, indicating great potential of the CFRP composites for low-cost applications in automobiles, public transit vehicles, concrete reinforcements and many other areas.

7. The carbon fibers produced in our lab have consistently and significantly increased the strength and modulus of the CFRP composites we have made. However, much higher mechanical properties could be attained, if the carbon fiber volume fraction is increased, and fiber alignment and fiber-matrix bonding are further improved.

8. Fiber alignment, surface bonding properties related to fiber surface conditioning treatment and volume fraction are three major challenging issues that have impacted the final properties of the composites that are produced from our low-cost carbon fibers. It is recommended that these areas be further investigated in the next phase.

The task at hand is a major multidisciplinary effort and will need to be continued to reach successful completion and for continuous improvements. The properties of the fibers produced and evaluated compare well with the pitch based commercially available fiber. Further R&D is needed to evaluate the commercial feasibility of this process and its long term applications development potential. A dedicated webpage of the UTSI carbon fiber program is on line. The content of this site is periodically updated, with the latest major progresses and accomplishments at (http://www.utsi.edu/research/carbonfiber/index.html).

5. References

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3. Balaguru, Perumalsamy N. and Shah, Surendra P., *Fiber Reinforced Cement Composites*, New York: McGraw-Hill, Inc, p 17, 1992.
4. Chwastiak, S., "A wicking method for measuring wetting properties of carbon yarns," Journal of Colloid and Interface Science, Vol. 42, No.2, 1973.
5. Rebouillat, S., "Wettability of single fibers-beyond the contact angle approach," International Journal of Adhesion and Adhesives, Vol. 19, 303-314, 1999.

Appendix A

1. Literature Review

Survey of the current state-of-the-art in publicly available literature begun early in the project and was continued throughout the program in the following areas:

1. Solvents for mesophase pitch preparation,
2. Heat treatment processes (stabilization, carbonization/graphitization),
3. Single fiber and fiber bundle characterization methodologies,
4. Composite preparation – matrices and making methods,
5. Composite testing methods,
6. Applications suited for low cost carbon fiber reinforcement.
7. Applications suited for low cost carbon fiber reinforcement.
8. Solvents for mesophase pitch preparation,
9. Heat treatment processes (stabilization, carbonization/graphitization),
10. Single/bundle fiber characterization,
11. Characterization of surface adhesion properties,
12. Interaction between fibers and matrix,
13. Composite preparation – matrices and methods,
14. Fiber mixing/distribution methods and evaluating methods,
15. Composite testing methods,
16. Applications suited for low cost carbon fiber reinforcement.

An extensive list of publicly available literature and patented information available have been reviewed and has greatly enhanced our understanding of the manufacturing and spinning process and has helped in identifying test methods that are used to characterize fibers and composites. A number of literature surveys were taken to investigate which methods would be best to determine the properties of carbon fibers that are produced at UTSI. Some of the observations from the literature survey related to fibers and composite characterization are presented below. Specifically single fiber testing including fragmentation testing, also known as the tensile test, and three-point bending test for composites were studied in detail.

1.1 Carbon Fiber Evaluation Methodologies

Single fiber characterization techniques, Single Fiber Fragmentation Test (SFFT): One of the most popular testing methods of evaluating interface properties of fiber matrix composites in the industry today is the single fiber fragmentation test (SFFT). In this test, tensile testing machine is used to pull opposite ends of the specimen apart, which results in uniform tensile stress distribution in the gauge section. To estimate the force and strain properties in the specimen, strain gauges are used. A full stain gauge bridge (Wheatstone bridge) configuration is used to measure the electrical output, which correlates with the strain values [(1)]. This technique determines the bonding characteristics between fiber and matrix on the microscopic level [(1)]. During this elongation technique, the experiment is usually performed under a lighted microscope, so the fiber fragmentation process can be observed “The fiber inside the resin breaks

into increasingly smaller fragments at locations where the fiber's axial stress reaches its tensile strength" [(1)]. The single fiber fragmentation testing procedure was very useful in determining the characteristics and strength of single carbon fibers used in studying of composites made at UTSI. While the results of this test seem to be accurate, it is still reasonable to perform characterization tests using single fibers and bundles of fibers for better and complete evaluations. A large number of single fibers might be needed to adequately determine the elongation region or deformations statistically, with a number of segments testing.

1.1.1 Single fiber testing

Various other instruments, such as a FDAS765 High Resolution Dimensional Measurement System fiber testing instrument (detail specs can be found in Appendix A) was used to determine diameter and tensile properties of single fibers. A Scanning Electron Microscopy (SEM – Hitachi model S-570), Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) can be used to observe the change in fiber characteristics at a microscopic level[(2)].

1.2 Composite testing

1.2.1 Three-Point Bending Test

Another useful testing method to determine the bending stresses and properties of the carbon composite material is called three-point bending test. This test can be performed with a MTS machine at room temperature to determine the bending stresses of a particular composite. With a constant crosshead speed, the ultimate flexural strength and flexural modulus can be calculated.

1.2.2 Interaction Between Fibers and Matrix

One of the basic fundamental properties that affect any composite material is the interaction between fibers and matrix. Understanding this concept helps us estimate the fiber contribution within the materials and predicting the composite's behavior. A list of parameters affecting this interaction is given below (3):

- Condition of the matrix: uncracked or cracked
- Matrix composition
- Geometry of the fiber
- Type of fiber: for example, steel, polymeric, mineral, or naturally occurring fibers
- Surface characteristics of fibers
- Stiffness of the fiber in comparison with matrix stiffness
- Orientation of the fibers: aligned versus random distribution
- Volume fraction of fibers to matrix
- Rate of loading
- Durability of the fiber in the composite and the long-term effects

While these are just the basic fundamental concepts of interactions and failures between the fibers and matrix within any composite materials, more research within this area is needed in the future. Especially once the properties and characteristics of our particular carbon fibers are better known or have been completely determined.

Another major research area is directional lay-down of the spun (green) fibers. This requirement is in part due to the need to stay compatible with the PAN and other fibers existing weaving technologies. To evaluate this requirement we are looking into process technologies that would lead to mainly aligned fibers which can then be made into woven products which are important to produce composites of complex shapes having high strength and other desired directional properties. Specific patent searches were conducted to determine existing methods for organizing fibers at lay-down and sorting the fibers to be parallel in the final mat. In the coming months, a roving mechanism which had been previously conceptually developed will be designed to work with the existing fiber lay-down device. Further research into improved directional lay-down will be conducted until a satisfactory solution has been developed.

Heat treatment is a major part of carbon fiber manufacturing process and does influence the final properties of carbon fibers. Uniform heating to proper temperature in controlled environments is important in producing fibers with consistently uniform and good characteristics. To ensure uniform heating, more work needs to be performed once the final production process has been established. Since we have been contemplating to develop continuous carbon fibers in tow form, then we are looking into computational models for heating bundled (tows) carbon fibers. A review of modeling techniques available for heat transfer through porous media in the literature has been conducted. Based on this review, a simplified single-phase convective heat transfer model could be utilized. This model could then be advanced to incorporate two-phase analysis incorporating mass diffusion in addition to heat transfer. Mass diffusion is a significant part of the heating process during the initial drying phase.

Appendix B Single Filament Test

Data Sheet – FDAS765

FDAS765 High Resolution Dimensional Measurement System

Measurement system for rapid analysis of cross sectional data from hair and other small fibres.
Quick and easy scanning procedure.
Automated calculation of key parameters such as major/minor axes and cross sectional area.
Accurate measurement with resolution of better than 1µ.
Compatibility with Dia-Stron Miniature Tensile Testing Systems

System Description

General Information

The FDAS765 fibre dimensional system is supplied as a fully operational unit, comprising the UV1000 control unit, dimensional test module including Mitutoyo laser micrometer and UvWin applications software. Alternatively the FDAS765 may be incorporated with the MTT675 automated tensile tester or with the ALS1500 sample loading module.

Control Unit

The common universal control unit (UV1000) supports the dimensional module and other measurement modules including the MTT variants, Cyclic Tester, Bending Module and the automated sample loading modules (ALS). The commonality of the control unit permits compatibility across the product range, allowing the user to integrate testing capability in line with changing needs. The control unit has no user interface and all methods are entered through the PC software.

FDAS765 Dimensional Analysis Module

The test module incorporates the Mitutoyo scanning laser micrometer (LSM500) for measurement of fibre diameter. The fibres are permanently mounted on small tabs and held in place by the instrument during measurement. The FDAS765 model has a fibre straightening facility to ensure that the fibre is orthogonal to the laser beam. Fibres are not cylindrical in cross section and to obtain an accurate measure they are rotated in the laser and multiple measurements made. Rotation is achieved via a DC motor fitted with a shaft encoder to monitor the angle and multiple measurements are taken so that major and minor axes together with cross sectional area can be determined. The fibre may be measured at a single point, or scanned along up to a 24mm length in discrete ‘slices’. In addition, the fibre can be rotated to user selected angles so that the dimensional aspects can be determined. This facility is important when measuring such properties as bending moment of single fibres.

UvWin PC Applications Software

The FDAS765 is operated through UvWin PC application, a 32Bit software programme written for Windows™ NT, 2000 & XP. The instrument protocols are selected from user interactive dialogues and the software includes method options for specific applications, data display and storage. In addition there are a range of analysis tools designed for particular applications. Data

export to other PC applications is through formatted text files suitable for import into Excel and other similar software. Data report gives full details of all scans along the fibre.
UvWin supports the complete range of Dia-Stron fibre testing instruments, including the automated sample loading modules, and gives a familiar Windows platform over the range of applications.

Specifications

Sample size: 3.2, 5, 10, 20, 30mm
Linear slices per sample: 1 – 200
Laser type: Mitutoyo LSM 500
Controller: Mitutoyo LSM 6000
Measuring range: 5 – 2000 microns
Resolution: 0.1 microns*
Repeatability: 0.06 microns
Scan Rate: up to 1600 scans/sec*
Laser beam width at focus: 200 microns
Software: Windows NT, 2000 & XP
Communications: RS232, USB serial adapter
Power: Universal supply 85-265vac, 47-63Hz, 100W
* - Software selectable
System Components:
FDAS765 Laser Scan Micrometer
Mitutoyo LSM 6000 Controller
UV1000 Control Unit.
PU1100 Pneumatic Unit.
UvWin PC Applications Software including manuals.
Mains cord and serial cable.

Dia-Stron Limited, 9 Focus Way, Andover, SP10 5NY, UK
Telephone +44(1264) 334700. Fax+44(1264) 334686. Info@diastron.com

The carbonized fibers were tested using the single fiber tensile tester shown in Figure B1. The initial results show that UTSI fibers possess expected strength for the heat treatment temperatures of about 1000º C. PAN-based carbon fibers of known strength were also measured for comparison and gaining confidence in the results. Better fiber clamping devices are being made and a data acquisition system based on LabView is also in progress to automate the testing process.

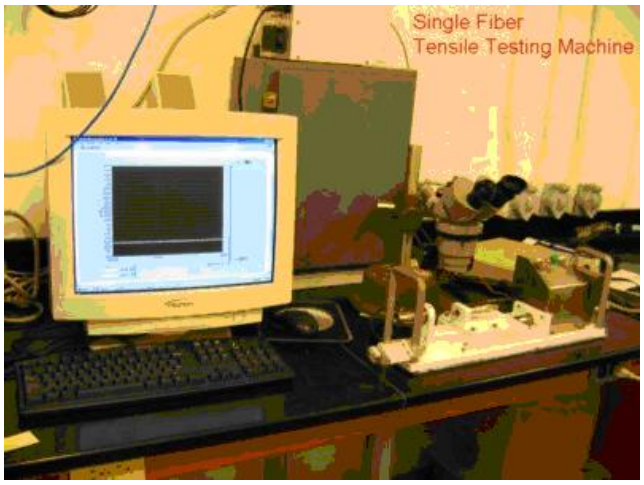

Figure B 1 Fiber tensile strength testing instrument

Fiber characterization: Initially we had to recondition our manually loaded and operated single fiber tensile tester in order to bring it a usable condition. Later on we reconditioned a second single fiber tensile tester which can also measure the fiber diameter and installed it in the carbon fiber characterization lab. This equipment (Dia-Stron, shown in Figure B3) is fully automated and computer controlled. Short fiber samples are prepared manually on special mounts. Up to a dozen fibers (segments) are carefully glued onto dumbbell shaped Plexiglas cartridges at both ends and are loaded onto specially made mounting tracks. The machine is programmed to select and move each fiber automatically for diameter measurement and breakage tensile stress evaluation. The fiber diameter is measured at different azimuthal and longitudinal locations and the measurement results are reported as averaged per station. Multiple fiber samples can be evaluated in sequence and averaged for obtaining more accurate property values. We have tested multiple samples of UTSI fibers and found the fiber diameter and failure stress results to be in good agreement with the measurements made by scanning electron microscope (SEM) and the single fiber tensile tester, respectively.

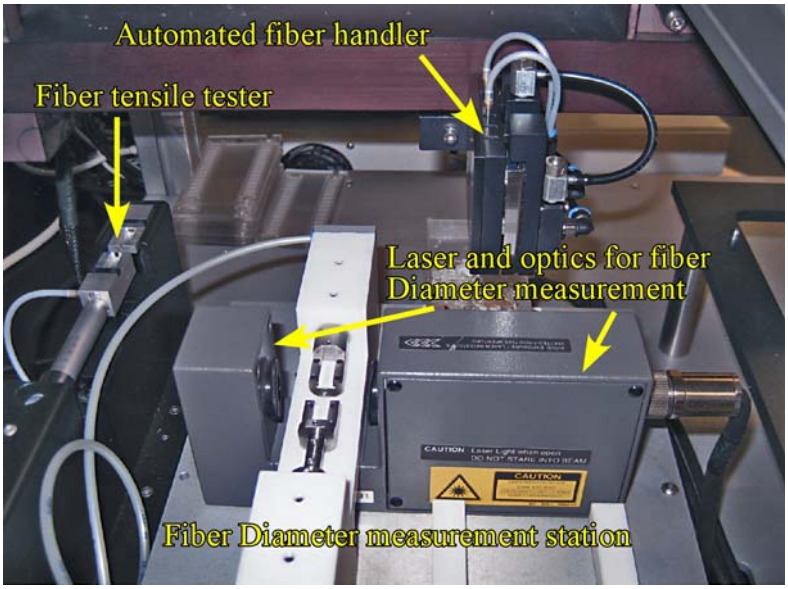

Figure B 2 Automated multi-sample, single fiber diameter and tensile measurement system, DiaStron.