

E. Interphase Analysis and Control in Fiber-Reinforced Thermoplastic Composites

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Objectives

- Develop the science underlying the formation and effects of transcrystalline regions in carbon-fiber-reinforced thermoplastic-matrix composite systems.
- Exploit the understanding developed from the research described above to allow controlled tailoring of the interphase transcrystallinity for specific applications.
- Analyze processing parameters in new thermoplastic-matrix composite technologies, specifically the DRIFT (**D**irect **R**einforcement **F**abrication **T**echnology, Southern Research Institute/University of Alabama-Birmingham) and the P4 (**P**rogrammable **P**owered **P**reform **P**rocess, Department of Energy (DOE)/Oak Ridge National Laboratory (ORNL)) processes.
- Generate composites with tailored interphases for specific applications of laminates produced by the DRIFT and P4 processes in the FreedomCAR and other DOE initiatives in lighter weight vehicles.

Approach

- Choose matrix materials relevant to the FreedomCAR and DOE automotive lightweighting materials initiatives.
- Characterize the chosen matrix materials with respect to mechanical properties and crystallinity.
- Determine the thermodynamic and practical adhesion between the chosen matrix materials and carbon fibers. The carbon fibers will be both sized and unsized.
- Identify and control the presence and size of transcrystalline regions in the matrix material adjacent to the carbon fibers.
- Manufacture laminates using the DRIFT and P4 processes having controlled transcrystalline regions.
- Perform mechanical testing, including tensile testing, impact testing and indentation testing of the laminates having controlled interphases.

Accomplishments

- Calibrated carbon-fiber resistive-heating unit for PAN- and pitch-based fibers.
- Measured the maximum shear stress, debond load and friction coefficient for pitch-based carbon fibers having different transcrystalline layer thicknesses. Thicker transcrystalline layers increased all three quantities by 25-50%.

- Measured the transcrystalline layer thicknesses at 2, 7, 15 and 50°C/minute cooling rates and determined the variability (~20%) of the transcrystalline layer thickness.
- Developed an analytical model for determining carbon-fiber temperature during resistive heating.
- Measured the tensile properties, including Young's modulus, Poisson's ratio and yield strength, of neat polypropylene.
- Developed a sample preparation procedure for examining the transcrystalline interphase regions of thermoplastic polymer beads melted onto carbon fibers.
- Completed building of a tabletop Mini-DRIFT system.
- Principal investigator Dr. Kellar and co-PI Dr. Kjerengtroen visited ORNL to discuss this project.

Future Direction

- Thermodynamic and practical adhesion measurements of thermoplastic polymer matrices with carbon fibers having various (including no) sizings will continue.
- Mechanical property determination of matrices and fibers will continue. Much of this work will be performed at SDSM&T, but some single-fiber testing work may be performed at ORNL.
- Measurement of the extent of transcrystalline regions in test pieces will be continued using an upgraded atomic-force microscope accessory.
- Laminates will be manufactured using the miniature-DRIFT apparatus developed in this research.
- Static and dynamic mechanical testing of DRIFT laminates made under controlled conditions leading to specific transcrystalline region thicknesses will be performed.
- Develop a mathematical model to predict the behavior of transcrystalline regions of carbon fibers/thermoplastic-matrix composites during a continuous manufacturing process.

Introduction

Over the past decade considerable effort has been expended to develop a new generation of vehicles that are lighter and more fuel-efficient than today's vehicles. In addition, these vehicles should retain crashworthiness and be of relatively low cost. Targets include reduction in overall weight of approximately 40%, primarily achieved through lighter body and chassis materials. Polymer-matrix composites (PMCs) have reached this target with a potential weight savings of 70%. At the current time, PMC technology has, in general, been deemed too costly, as carbon-fiber-based PMCs can cost ten times as much as steel parts. Some of this increased cost is due to the high price of carbon fibers and some due to limitations in the manufacturing process. Many of the problems in the manufacturing process are caused or exacerbated by lack of fundamental scientific knowledge of the interactions between the fibers and matrix materials.

This research is of significance to the DOE ALM in that it will help develop the necessary science base to allow more complete exploitation of PMCs having thermoplastic matrices. Traditionally, these materials have trailed the use of PMCs having thermosetting matrices, because of processability issues stemming from the low viscosity and wetting of the thermoplastic-matrix material. In addition, thermoplastic matrices are generally less strong and less stiff than thermoset matrices. This liability is further compounded by the fact that most fiber reinforcements associated with thermoplastic-matrix PMCs are of fairly short length, mainly because of the processing limitations mentioned earlier. This latter aspect is relevant because short-fiber reinforcements do not carry load as well as long- or continuous-fiber reinforcements. From the automotive perspective, short-fiber-reinforced PMCs are, therefore, most utilized in non-structural components. Further comparisons between thermoplastic- and thermoset-matrix PMCs are warranted here to highlight the focus of this

research project, namely, the role of the interface/interphase region between the fiber and the matrix.

The development of the interphase in thermoplastic PMCs is quite different from that of thermosetting matrices, which tend to be amorphous in nature. Rather, in thermoplastic PMCs, the interphase development is generally due to nucleation and growth of crystallites from the fiber surface rather than actual chemical reactions within the interphase. The interphases formed in these systems are termed transcrystalline regions, reflecting their dependence upon the thermoplastic crystallinity. There has been much speculation in the literature as to the cause for the formation of the transcrystalline region and its role in bulk composite properties. Several conclusions can be reached. First, the transcrystalline region can grow in size to tens of microns, depending upon such parameters as fiber type, morphology and fiber surface treatments such as sizings. Second, the transcrystalline region can significantly affect properties such as the strength and impact resistance. Also, in some cases, different types of transcrystalline interphases may be formed. For instance, both α and β transcrystalline regions were produced around natural fibers in polypropylene-matrix composites. These regions could be altered by inclusion of maleic anhydride in the polypropylene or on the fiber.

With respect to these novel processing routes, two examples are of particular interest to this research. The first is a low-cost process to produce continuous reinforcing fibers with thermoplastic matrices, called the **Direct Reinforcement Fabrication Technology (DRIFT)** developed by the Southern Research Institute (SRI) and now located at the University of Alabama-Birmingham (UAB). PMCs produced by this continuous-fiber technology could serve as metal replacements in structural applications, specifically for the automotive industry. Keys to optimal utilization of the DRIFT process are fiber wetting and, ultimately, adhesion of the thermoplastic matrix. Traditionally, sizings are applied to the fibers to help prevent abrasive damage, and assist with lubrication. A major component of the sizing is a coupling agent that aids in wetting, adhesion and hydrothermal stability of

the composite. Research conducted in this program utilizes thermoplastic-matrix PMCs produced by UAB or in-house using the DRIFT process.

The second novel processing route of interest is the **Programmable Powered Preform Process (P4)**. While the P4 technology does allow control over fiber length, its main potential benefit is its ability to circumvent previous PMC process limitations through robotic control. To our knowledge, no fundamental analysis of PMC interphases formed by the P4 technology has been undertaken.

This research program builds upon a multi-disciplinary effort with a strong background in interphase analysis and control in thermosetting PMC systems, and applies this experience to new thermoplastic-matrix PMC systems. The research investigates model systems deemed of interest by members of the Automotive Composites Consortium (ACC) as well as samples at the forefront of PMC process development (DRIFT and P4 technologies). Finally, the research investigates, based upon the fundamental understanding of the interphases created during the fabrication of thermoplastic PMCs, the role the interphase play in key bulk properties of interest to the automotive industry.

Project Deliverables

This research will provide a better understanding of the science, particularly with respect to adhesion, of thermoplastic matrices with fiber reinforcements. The adhesion data will be used to identify processing parameters for thermoplastic-matrix composites to tailor transcrystalline interphase formation. Transcrystalline interphases are often quite large (>10 microns) and can be stronger and stiffer than the matrix material or tougher and with greater work of fracture than the matrix. In addition, this work will produce composite samples using new processing technologies and the scientific knowledge gained with respect to adhesion and interphase formation. These test protocols are important to possible end uses for the tailored PMCs in automotive applications.

Accomplishments

Research accomplishments during the past year occurred in two primary areas: interphase formation

conditions and effect of transcrystallinity on composite performance. Progress in each of the two areas is described below.

Interphase Formation Conditions

Interphase formation conditions have been investigated in three primary areas: adhesion, mechanical property determination and extent of crystallinity as a function of formation conditions.

Adhesion: Thermodynamic-adhesion research has been mainly focused on extending the recently-developed fiber resistive-heating apparatus to the use of pitch-based fibers, while practical adhesion has been studied through microindentation testing of model composite systems.

Thermodynamic Adhesion: Thermodynamic adhesion, in this work, is primarily concerned with the measurement of the contact angle of polymer beads on fibers of interest. The melting of beads on carbon and subsequent control of cooling rate is necessary for understanding of the effect of transcrystallinity on the thermodynamic adhesion. To manufacture the beads in a manner similar to the DRIFT process, a technique to resistively heat the carbon fibers has been developed. Currently, this system has been calibrated and a variety of fibers tested to determine the reproducibility of fiber heating and of the resistivity (at 20°C) and temperature coefficient. Figure 1 shows a graph of the data obtained for several PAN-derived, carbon fibers and several pitch-based, carbon fibers. Literature values for carbon are also shown^{1,2}. As shown in Figure 1, the data for the various fiber types exhibit relatively small levels of variation, as the coefficients of variation for both the resistivity (at 20°C) and the temperature coefficients are less than 11.5% for both fiber types. Compared to the literature values, both fiber types exhibit smaller magnitude temperature coefficients (16-19 $\mu\text{ohm}^*\text{m}$ for PAN fibers and 13-15 $\mu\text{ohm}^*\text{m}$ for pitch-based fibers) and larger resistivity at 20 °C (-2.5 to -3 $\times 10^{-4} \text{ K}^{-1}$ for PAN fibers and -1 to -2 $\times 10^{-4} \text{ K}^{-1}$ for pitch-based fibers). The resistivity of carbon given in the literature varies from about 3-60 $\mu\text{ohm}^*\text{m}$ depending upon the crystal structure and the presence of impurities^{1,2}. Only one literature value for the temperature coefficient was found. The

importance of these data for this work is that pitch-based carbon fibers have the smallest temperature coefficient, which will increase the imprecision of determining the fiber temperature during resistive heating from about 2°C for PAN-based carbon fibers to about 7°C for pitch-based, carbon fibers.

Interphase regions are known to significantly affect the mechanical properties, such as strength and impact resistance, in thermoplastic composites. Generally, both the temperature and the rate of change in the temperature, affect the formation of transcrystalline regions during manufacturing processes. Thus, analyzing thermal behaviors of the transcrystalline regions during heating and cooling processes is important in understanding the mechanisms of formation/growth of the transcrystalline regions. To better understand these thermal behaviors, a model was developed.

A nonlinear differential equation was obtained by applying an energy balance principle on a finite element of the carbon-fiber model. The model was then discretized and the corresponding difference equation was coded by Matlab. A negligible temperature gradient along the fiber was observed, except at the very end regions, close to the electric poles. Therefore, conduction along the wire could be neglected. Because the time to reach the steady-state temperature is less than 200 msec, transient temperature effects can also be neglected. In addition, the natural convective heat-transfer term can be neglected, because its value is far less than that of the radiation heat-transfer term. Thus, the applied electric energy is balanced only by the radiation heat-transfer term and can be approximated further into an algebraic steady-state-temperature equation in terms of the input supply voltage as shown by Equation 1. In Equation 1, V_s is the applied voltage, r is the fiber radius and L is the length of the carbon fiber, while σ and ϵ are

$$\frac{2\sigma\epsilon(T^4 - T_\infty^4)}{r} + \frac{V_s^2}{L^2 \rho_e [1 + \alpha(T - T_\infty)]} = 0 \quad (1)$$

the Stefan-Boltzmann constant and the emissivity, respectively. Finally, T is the temperature of the fiber and T_∞ is the air temperature.

Equation 1 was solved by a root-finding algorithm. This equation shows how the temperature of a carbon fiber (T) can be controlled by adjusting the input electric voltage. However, predicting the temperature is significantly affected by the uncertainty of input parameters such as electric resistivity (ρ_e) and the temperature coefficient of resistivity (α) of the carbon fiber. The values for these parameters measured in this work are shown in Figure 1. Currently, no technique has been found to directly measure the surface temperature of the heated carbon fiber; thus, the temperature is approximated by melting thermoplastic polymers with a known melting temperature.

Practical Adhesion: To measure the practical adhesion, model unidirectional composite samples were manufactured by compression molding a thin, polypropylene/pitch-based carbon-fiber laminate at

205°C at 0.3 tons pressure for 30 minutes to erase the thermal history of the PP. After the melting hold time, the samples were cooled at 2°C/minute using the press-cooling ability and at ~50°C/minute using dry ice applied to the top and bottom mold surface. As will be shown in the *Extent of Crystallinity as a Function of Formation Conditions* section, these cooling rates produced different thicknesses of transcrystalline regions around the fibers, about 100 μm thick for 2°C/minute and 20 μm thick for 50°C/minute.

These samples were prepared for practical adhesion (microindentation) testing so that the total thickness was about 76 μm . A thin sample such as this was necessary for push-through microindentation testing. Individual fibers were located and indented using a force ramped from 0 to 60 mN over 30 seconds and held at the

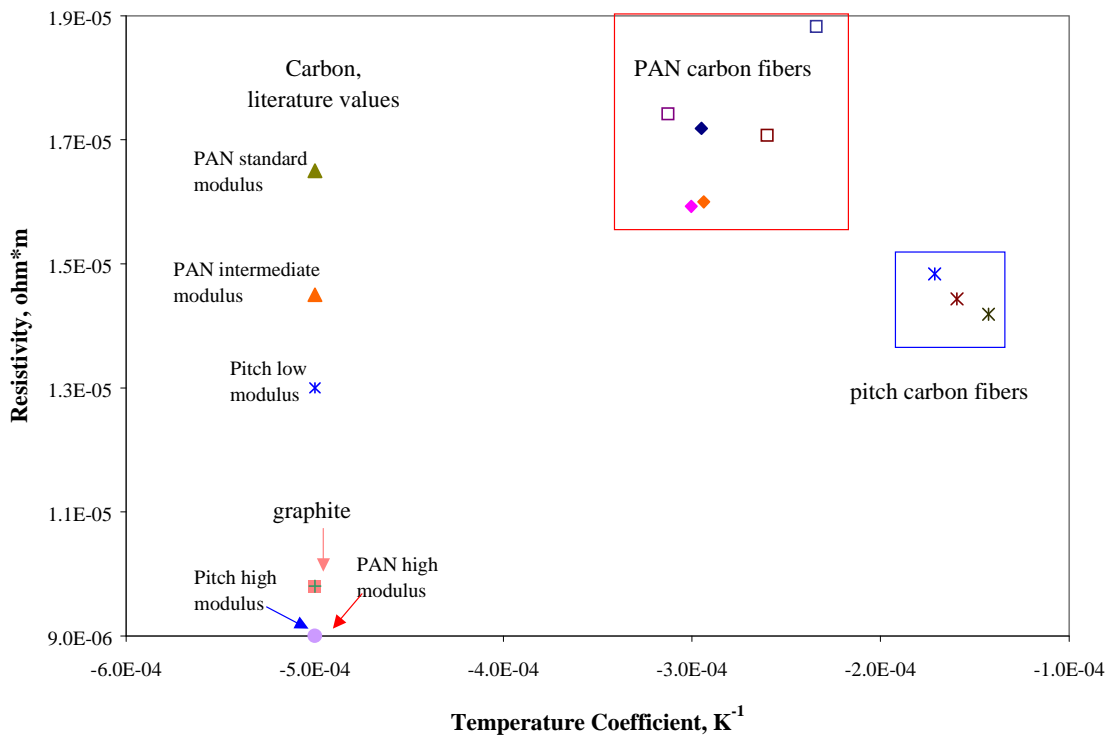


Figure 1. Temperature coefficient and resistivity at 20°C determined for the fibers used in this work compared to literature values^{1,2} for various types of carbon.

maximum value for 10 seconds. Unloading occurred over the same time range as did loading. For the cooling rates examined, at least 15 fibers were debonded.

There are typically four different regions of the load-displacement curve. Stage I is the initial loading of the fiber. In this stage, the indenter goes from no contact to full contact with the fiber surface, making this region non-linear since the contacted area of the tip is increasing with the load. Stage II is the linear sample-loading segment. The fiber and matrix are deflecting under load with no relative motion between the two. Stage III is the crack-initiation and debonding region of the curve. The initial part is where the mode II crack initiates at the fiber/matrix interface. The crack grows to an unstable state until the entire fiber is completely debonded from the matrix. Stage IV is the region where the fiber is sliding along the interface. The debond load was calculated for each test performed. Also, the maximum shear stress (MSS) was calculated from shear-lag theory and the slope of Stage II. Finally, the post-debonding behavior was modeled using a sliding-friction model.

Table 1 contains a comparison of the microindentation data for the two cooling rates. The more rapidly cooled sample, having a larger transcrystalline layer thickness (100 μm vs. 20 μm), exhibits a greater MSS (37% greater) and debond load (46.5% greater). These differences are statistically significant at the 90% level. Further, discussion of this can be found in reference 3.

Mechanical Property Determination: The tensile properties of pure polypropylene have been studied during the research period just finished. The polypropylene samples were manufactured using a Wabash press with stops to ensure a sample thickness of 2.9 mm. The specimens were heated at 5°C/minute to 200°C, held at this temperature for

10 minutes, then cooled at 10 °C/minute. Following cutting the samples to ASTM D638, Type I sample size specifications, strain gauges were affixed to determine the Poisson’s ratio and tensile tests were performed according to ASTM D638 with a rate of 5 mm/minute leading to specimen failure in approximately 1 minute. Figure 2 shows a typical stress-strain curve for these samples. At the strain rate utilized, the Young’s modulus shows in Figure 2 is 1950 MPa, while the average Young’s modulus found was 2130 ± 350 MPa. The yield strength was also found from the stress-strain curve and the mean yield strength found was 7.0 ± 2.3 MPa. Finally, the mean Poisson’s ratio was determined to be 0.326 ± 0.018.

Also, on certain samples, strain gauges were placed on both the top and bottom of the specimen. Little difference was observed between the two sides of the sample indicating that the top and bottom of the tensile samples were in the same state of tension.

Extent of Crystallinity as a Function of Formation Conditions

To investigate the extent of crystallinity as a function of formation conditions in greater detail, research efforts were directed towards two areas: 1. transcrystalline layer formation and 2. sectioning polypropylene beads on carbon fibers perpendicular to the long fiber axis.

Transcrystalline Layer Formation: Experiments were conducted to examine transcrystalline layer formation during cooling. These experiments used a hot stage mounted on a polarized microscope stage. Two thin layers of polypropylene with a small number of fibers sandwiched between the layers were placed in the hot stage and heated to approximately 200°C for 10 minutes. After this hold, the stage was slowly cooled at various rates and the crystallization recorded with a video

Table 1. Microindentation test data.

	Maximum Shear Stress, MPa	Debond Load, mN	Friction Coefficient
2°C/minute	0.37±0.13	38.7±12.5	<0.2
50°C/minute	0.27±0.05	26.4 ± 5.8	<0.1

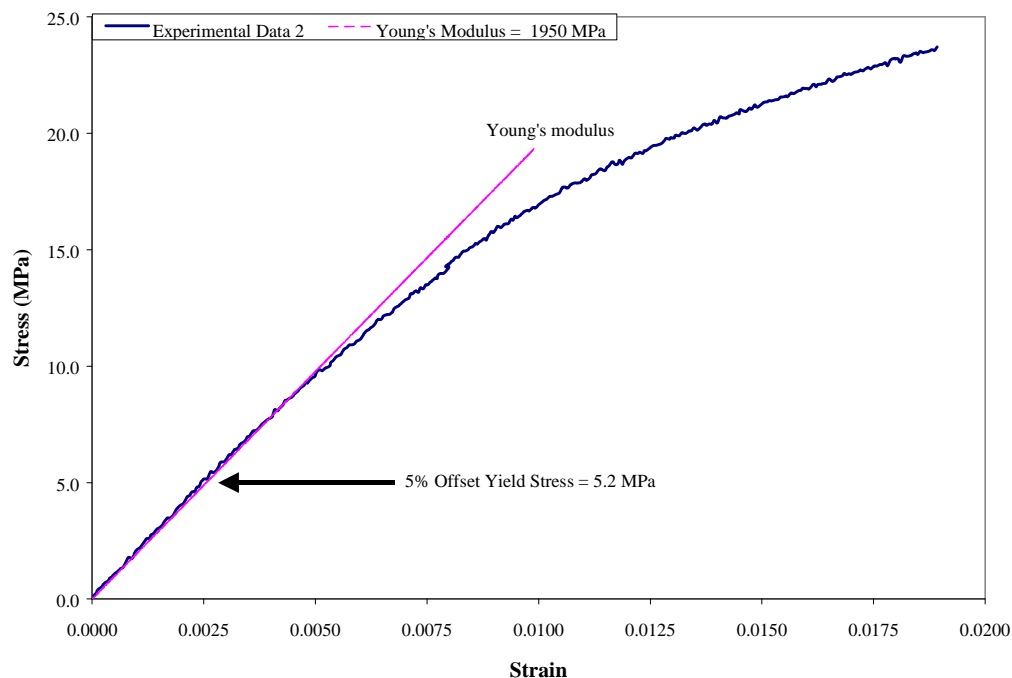


Figure 2. Typical stress-strain curve of polypropylene tested at 5 mm/minute.

camera mounted to the polarized microscope. Following examination of the transcrystalline layer by video, the samples were microtomed and etched using a potassium permanganate/sulfuric acid/orthophosphoric acid etchant. Figure 3 shows scanning electron microscope micrographs of the etched samples. As seen in Figure 3, the transcrystalline layers were quite variable in thickness. This had been observed previously, and was quantified from the video micrographs taken in this research for a PP/pitch-based carbon-fiber system. The mean transcrystalline layer thickness was 3.3 times the fiber diameter ($\sim 10 \mu\text{m}$) or about $30\text{-}35 \mu\text{m}$. The standard deviation of measurements is 0.7 times the fiber diameter, giving a coefficient of variation of about 20%. From Figure 3 and similar figures not shown in this report, the thicknesses of the transcrystalline layer were estimated. The slow-cooled ($2^\circ\text{C}/\text{minute}$) samples exhibited a significantly larger transcrystalline layer thickness ($\sim 100 \mu\text{m}$) than the other three cooling rates all of which exhibited approximately $20\text{-}\mu\text{m}$ -thick transcrystalline layers.

Sectioning polypropylene bead: To obtain samples suitable for atomic-force-microscopic examination of polypropylene beads, sectioning of the bead

perpendicular to the fiber long axis was necessary. Bead sectioning was accomplished by embedding the bead and fiber in an epoxy matrix then polishing the resultant cylinder until the bead was reached. Once the bead was found, polishing with $5 \mu\text{m}$ Al_2O_3 for 2 minutes, then $1 \mu\text{m}$ Al_2O_3 for 1 minute and $0.3 \mu\text{m}$ Al_2O_3 for 1-5 minutes was used to yield a surface suitable for atomic force microscopy (AFM).

Initial AFM interrogation of the region surrounding the carbon fiber is shown in Figure 4. In Figure 4, a $10.5 \mu\text{m} \times 10.5 \mu\text{m}$ region is shown in both height (left image) and phase (right image). The fiber is clearly observed, but no obvious transcrystalline layer was observed in this case as the transcrystalline layer is expected to be larger than the area studied. The efficacy of the sample-preparation procedure is shown in the less than 500-nm-height difference over the whole of the sample.

Effect of Transcrystallinity on Composite Performance

Research on the effect of transcrystallinity on composite performance has centered on developing a miniature DRIFT machine. The goal of this

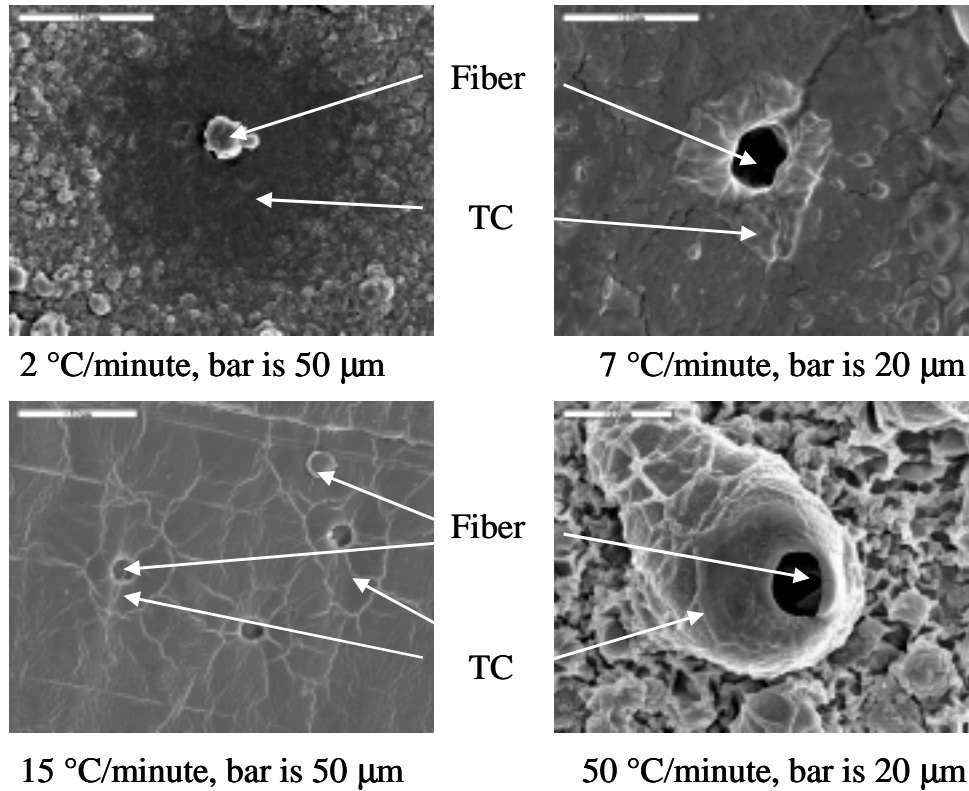


Figure 3. Transcrystalline regions developed around pitch-based, carbon fibers at various cooling rates. TC indicates transcrystalline region. In some cases, the fiber regions indicated on the graph are places where fibers had been pulled out of the surface during sample preparation.

Mini-DRIFT research was to develop a system for producing lab-scale, thermoplastic-composite prepreg samples using the DRIFT process. The DRIFT process is a procedure for making continuous-fiber prepreg materials. It specifies that a continuous-fiber reinforcement material be drawn through a molten resin after being heated beyond the temperature of the resin. While in the resin, a shear is applied to the reinforcement material leaving substantially no voids in the prepreg material (Patent Number: 5,911,932). One of the goals of this aspect of this research is to control and monitor operating parameters and their effects on fiber wetting and material properties. The parameters to be controlled include: fiber draw speed, fiber tension, fiber preheat temperature, resin temperature, and prepreg cooling. The Mini-DRIFT machine consists of four main components: a fiber

feed/tensioning system, a furnace, an impregnation tool, and a cooling unit. Flexibility to allow for processing different materials was a major design goal. The system allows different roving sizes and temperature ranges. Due to limited laboratory space, components were selected and/or designed to be compact. The fiber feed/tensioning system, the furnace, and the cooling system are attached to two industrial carts to permit portability and storage. The system produces a continuous tape of prepreg material that can then be processed, likely by compression molding, into the desired sample type for testing. Compared to the UAB system, the Mini-DRIFT system is much better controlled, allowing samples with better-understood history to be manufactured. This understanding will lead to less ambiguity in the determination of the effects of processing parameters on the final product.

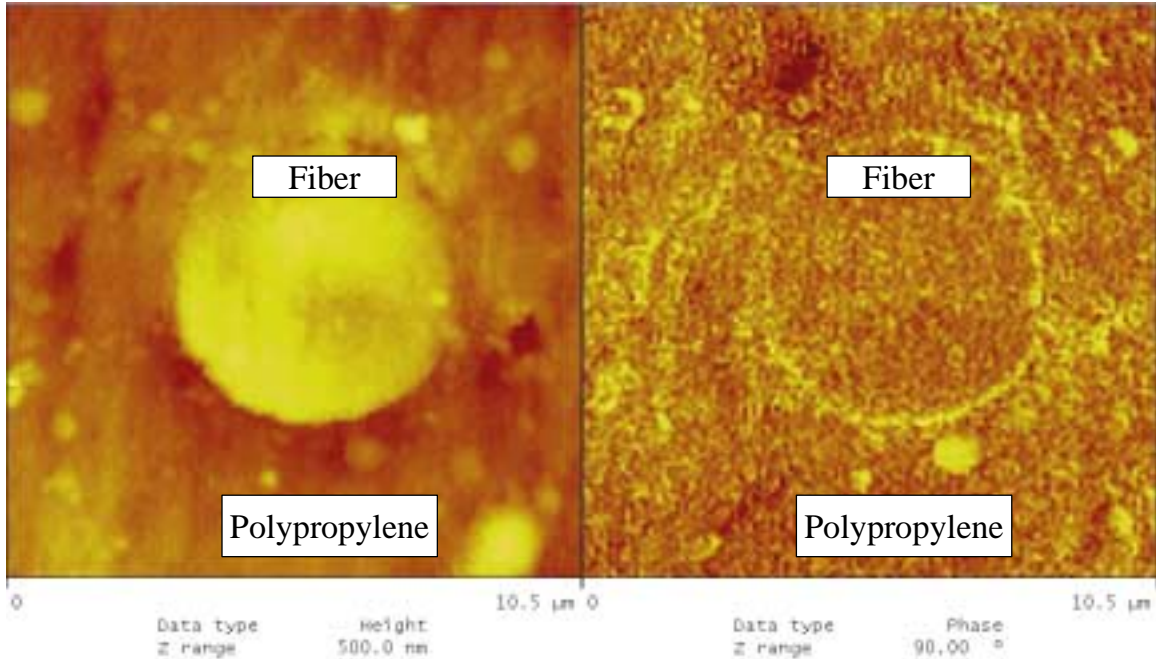


Figure 4. Atomic force micrograph of a polypropylene bead containing a carbon fiber encased in epoxy. The left image is a height image (500 nm maximum height), while the right image is a phase image (90° maximum phase change).

Summary

Highlights of our 2006 research include:

1. Calibrated carbon-fiber resistive-heating unit for PAN- and pitch-based fibers.
2. Measured the maximum shear stress, debond load and friction coefficient for pitch-based carbon fibers having different transcrystalline layer thicknesses. Thicker transcrystalline layers increased all three quantities by 25-50%.
3. Measured the transcrystalline layer thicknesses at 2, 7, 15 and 50 °C/minute cooling rates and determined the variability (~20%) of the transcrystalline layer thickness.
4. Developed analytical model for determining carbon-fiber temperature during resistive heating.
5. Measured the tensile properties, including Young's modulus, Poisson's ratio and yield strength of neat polypropylene.
6. Developed a sample preparation procedure for examining the transcrystalline interphase.
7. Regions of thermoplastic polymer beads melted onto carbon fibers.
8. Completed building of a tabletop Mini-DRIFT system.

Presentations/Publications/Patents

1. "Characterization of Transcrystalline Zones by Atomic Force Microscopy" L. Nielsen, W. Cross, L. Kjerengtroen and J. Kellar, 2006 South Dakota EPSCoR Conference, Rapid City, SD September 2006.
2. "Transcrystallinity Effects in Polypropylene Matrix Composites" S. Nielsen, W. Cross, R. McGlothlin, J. Kellar and L. Kjerengtroen, 2006 South Dakota EPSCoR Conference, Rapid City, SD September 2006.
3. Bickett, S.J., "Investigation Of Transcrystallinity In Fiber Reinforced Thermoplastic Composites," Masters of Science

Thesis, South Dakota School of Mines and Technology, 2006.

References

1. “Resistivity of Carbon, Graphite”,
<http://hypertextbook.com/facts/2004/AfricaBelgrave.shtml>, *The Physics Factbook*,
edited by Glenn Elert, 2004, accessed
December 11, 2006.
2. “Resistivity and Temperature Coefficient at
20 C,” <http://hyperphysics.phy-astr.gsu.edu/HBASE/Tables/rstiv.html>,
HyperPhysics, Carl R. Nave, 2005, accessed
December 11, 2006.
3. Bickett, S.J., “Investigation Of
Transcrystallinity In Fiber Reinforced
Thermoplastic Composites,” Masters of Science
Thesis, South Dakota School of Mines and
Technology, 2006.