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

Principal Investigator: Jon J. Kellar
Department of Materials and Metallurgical Engineering
South Dakota School of Mines and Technology
501 E. St. Joseph Street
Rapid City, SD 57701-3901
605-394-2343, 605-394-3369, jon.kellar@sdsmt.edu

Technology Area Development Manager: Joseph A. Carpenter
(202) 586-1022; fax: (202) 586-1600; e-mail: joseph.carpenter@ee.doe.gov

---

Contractor: South Dakota School of Mines and Technology
Contract No.: DE-FG02-04ER46117

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) 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 lightweight 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

- Demonstrated transcrystalline layer formation for Kevlar and pitch-based carbon fibers and polypropylene matrix.
- Measured matrix crystallinity by differential scanning calorimetry
- Designed an apparatus to allow for controlled, resistive, carbon-fiber heating for thermodynamic adhesion and transcrystallinity experiments.

  - 2 students traveled to University of Alabama-Birmingham to meet with Dr. George Husman and view the DRIFT system in place at that university and to obtain DRIFT samples.
  - Presented a poster at the National DOE/NSF EPSCoR Conference.
- Presented a poster at the Joint North Dakota/South Dakota EPSCoR Conference.

Future Direction

- Thermodynamic and practical adhesion measurements of polypropylene and polyphenylene sulfide with carbon fibers having various (including no) sizings.
- Indentation testing of initial DRIFT laminates with a new nanoindentation machine recently purchased by the South Dakota School of Mines and Technology (SDSM&T).
- 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 begun using a new atomic force microscope accessory, to be purchased with funds from this grant to complement the optical microscopy performed thus far.
- Static and dynamic mechanical testing of DRIFT and P4 laminates will be continued.
- Manufacture of a mini-DRIFT system to allow better control of material temperatures and heating and cooling rates and therefore allow controlled sample manufacture has begun.
- Travel by two of the Principal Investigators to ORNL to procure samples, perform testing and better understand the processing techniques used to fabricate samples will occur.

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 Automotive Lightweighting Materials 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 **D**irect **Rei**nforcement **F**abrication **T**echnology (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 hygrothermal stability of the composite. Research conducted in this program will utilize thermoplastic-matrix PMCs produced by UAB 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 critical to the future success of Automotive Lightweighting Materials. 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 generally 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 three primary areas: adhesion, mechanical property determination, and extent of crystallinity as a function of formation conditions. Progress in each of the three areas is described below.

Adhesion

In the past year, thermodynamic and practical adhesion research has been mainly focused on designing, manufacturing and calibrating several new testing systems and instrumentation. A new microbond test system has been calibrated for both thermodynamic and practical adhesion. The new microbond test system utilizes the high-precision force measurements afforded by our dynamic mechanical analyzer (DMA) and precise determination of all the geometric factors associated with microbond testing to achieve the maximum consistency in the microbond test results. This consistency is shown in Table 1 (ci represents confidence interval) in which the new test system decreased the coefficient of variation (COV) by 54% over the best results our research group had previously achieved (ci represents confidence interval). With respect to microbond testing by other groups a similar decrease is observed as typical COV are in the 10-20% range.

In addition, a Nano-XP nanoindenter was purchased during the past year and our group has been working to develop procedures after discussions with Dr. Edgar Lara-Curzio of the Oak Ridge National Laboratory (ORNL) for performing microindentation practical adhesion tests. Initial work of this type has focused on using glass-fiber polypropylene and carbon-fiber polypropylene composites manufactured by the DRIFT process and obtained from Dr. George Husman of the UAB. This initial work has concentrated on identifying the primary issues associated with testing. Of particular importance are obtaining flat surfaces without debonding the fibers from the matrix prior to testing and splitting of the fibers during indentation.

To simulate DRIFT manufacturing of samples for microbond practical adhesion testing and thermodynamic adhesion measurements, a furnace capable of resistively heating carbon fibers was manufactured. Figure 1 shows both an overview and a close-up of the fiber heating assembly of this apparatus. Figure 2 shows the resistance versus temperature of three of the six carbon fibers. The important issue from Figure 2 is that the slope of the resistance-temperature curve is essentially the same for all three fibers. The difference in the data is due to slight differences in the diameter of the carbon fibers. Also, the linearity of the resistance-temperature curve is very high (>0.995) in all cases.

Finally, contact angles of polypropylene on carbon fibers have been measured for slow cooling conditions. In the cases studied thus far, polypropylene has exhibited a close to zero contact angle, indicating that molten polypropylene wets carbon fibers if given sufficient time.

Mechanical Property Determination

To manufacture samples for mechanical testing, a Wabash heatable-coolable press was used to manufacture blanks from which tensile and DMA samples could be cut. As control of the heating and cooling rates is critical for the success of this work, the first area studied was the profile of the heating and cooling rate at different points on the surface of the press. The heating rate was

Table 1. Comparison of microbond test data

Test Data	Average COV/ Average ci (%)	Improvement in Data Scatter COV/ci ratios
2001 data	45.7/18.6	5.0/4.8
2002 data	41.4/19.8	4.5/5.1
2003 data	19.7/8.5	2.2/2.2
Current setup data	9.1/3.9	NA

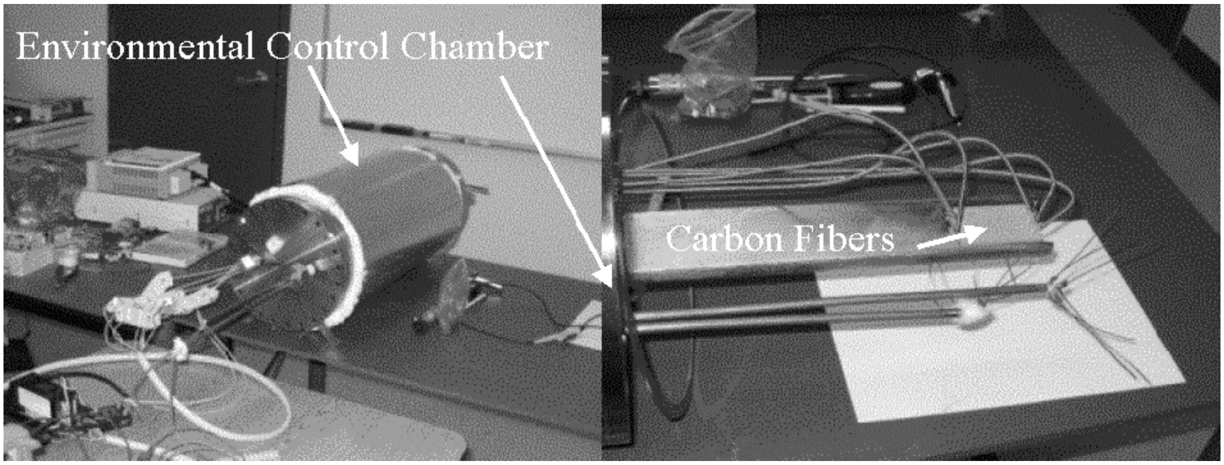

Figure 1. Apparatus for resistively heating carbon fibers. The left photo shows the full apparatus, while the right photo shows a close-up of the fiber-heating portion of the apparatus.

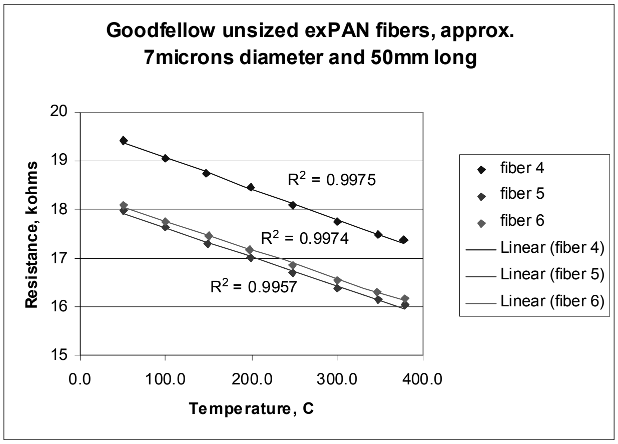

Figure 2. Measured carbon-fiber resistance as a function of applied temperature.

expected to be reasonably consistent across the platens; but, due to the way platen cooling is conducted, the cooling rate (which is more important in this work than the heating rate) was expected to be quite variable. As Figure 3 (right) shows, the heating rate was constant across the platen to about 0.2 ºC for a 6 ºC/minute heating rate. For the cooling rate, the left graph in Figure 3 indicates that the cooling rate varies by about ±2 ºC for an 18 ºC/minute cooling rate. Therefore, the cooling rate varies by about a factor of 3 compared to the heating rate. Examination of Figure 3 indicates that the central region of about 6” by 6” has a relatively stable cooling rate. Hence, mechanical testing samples were cut from this region.

Both tensile testing and DMA samples have been manufactured. The tensile testing has measured the Young’s modulus and yield strength of samples made from carbon-fiber polypropylene prepreg (Baycomp) laminates. Thus far, little difference has been observed for different cooling rates. The reasons for this are being studied, but are likely due to the development of the transcrystalline layer in this system.

For DMA testing of bulk polypropylene samples, Figures 4 and 5 show the storage and loss moduli (Figure 4) and creep compliance (Figure 5). The storage and loss moduli are relatively constant as a function of cooling rate between about 5 and 20 ºC/minute. As the crystallinity of the matrix is greater at slower cooling rates compared to faster cooling rates, this indicates that the matrix crystallinity has little effect when a sinusoidal load is applied at 1 Hz with an amplitude of 15 micrometers. Conversely, the creep compliance is a function of the cooling rate, and hence, the matrix crystallinity. The creep compliance was approximately twice as great when the cooling rate was ~7.5 ºC/minute as compared to when the cooling rate was ~21 ºC/minute.

Extent of Crystallinity as a Function of Formation Conditions

Crystallinity formation was studied by two types of experimentation. In one type of experiment, bulk polypropylene samples were placed in a

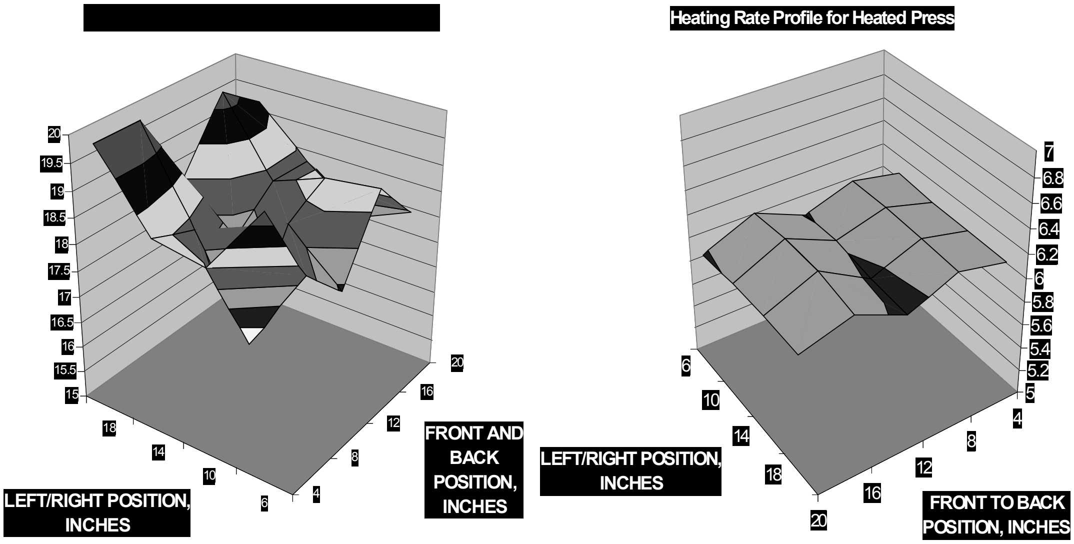

Figure 3. Cooling (left) and heating (right) rate profiles for the Wabash press (the numbers on either side represent the distance from the center of the press).

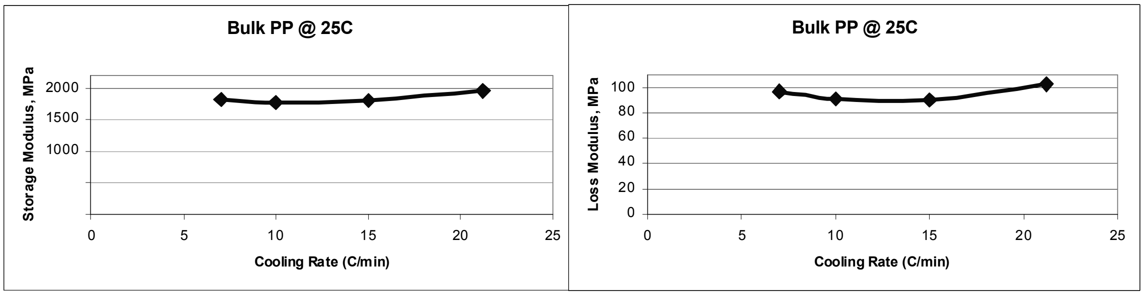

Figure 4. Storage modulus (left) and loss modulus (right) of bulk polypropylene as a function of cooling rate.

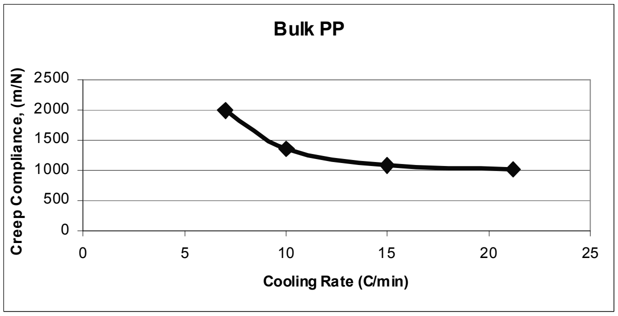

Figure 5. Creep compliance of bulk polypropylene as a function of cooling rate.

differential scanning calorimeter (DSC) and the crystallization endotherm was used to determine the amount of crystallization. Figure 6 shows the results from these two types of experimentation. Isothermal crystallization, Figure 6 (left), shows little difference in the crystallization as a function of hold time at the isothermal crystallization temperature (115 ºC). This is because essentially all the crystallization occurs in the first two minutes. For nonisothermal crystallization, Figure 6 (right), the cooling rate is varied then the amount of crystallization is determined from the endothermic crystallite melting during the next heating cycle. The amount of bulk crystallization is quite dependent upon the cooling rate, for cooling rates less than 10 ºC/minute. Nonisothermal crystallization typically is a better representation of the cooling during DRIFT and P4 processing.

In addition to bulk testing, experiments were conducted to examine transcrystalline layer formation during cooling. These experiments used a hot stage mounted on a polarized microscope

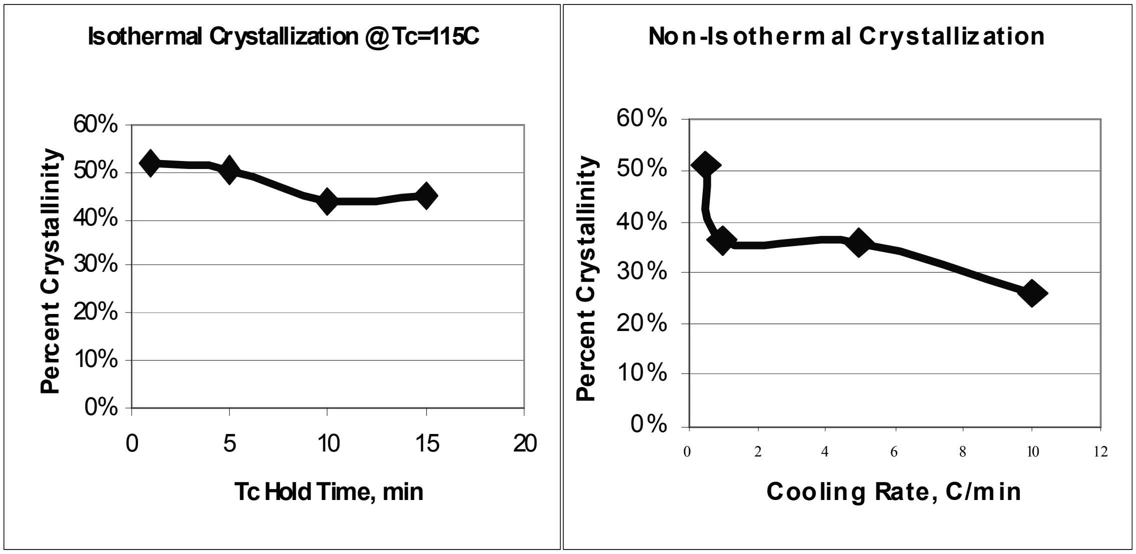

Figure 6. Isothermal (left) and non-isothermal (right) determination of bulk polypropylene crystallization.

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 ºC for 10 minutes. After this hold, the stage was slowly cooled (~4 ºC/minute) and the crystallization recorded with a video camera mounted to the polarized microscope. Figures 7 and 8 show transcrystalline layer formation for pitch-based, carbon fibers (Figure 7) and Kevlar® fibers (Figure 8). Glass fibers and ex-PAN (polyacrylonitrile) carbon fibers were also tested. The glass fibers used did not show any transcrystallinity, while the ex-PAN fibers intermittently showed transcrystallinity. The ex-PAN transcrystallinity generally took the form of hemispherical regions growing from the fiber surface rather than the more lamellar regions seen in Figures 7 and 8. This is most likely due to the number of nucleation sites on the ex-PAN fibers

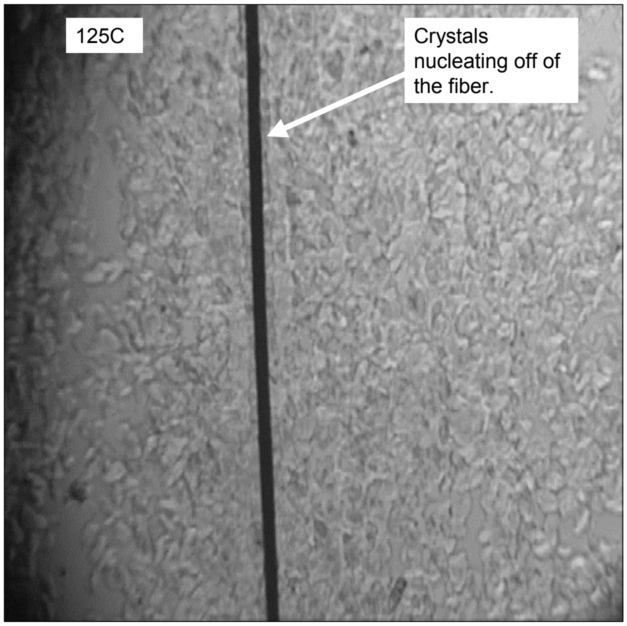

Figure 7. Transcrystalline layer on pitch-based carbon fibers.

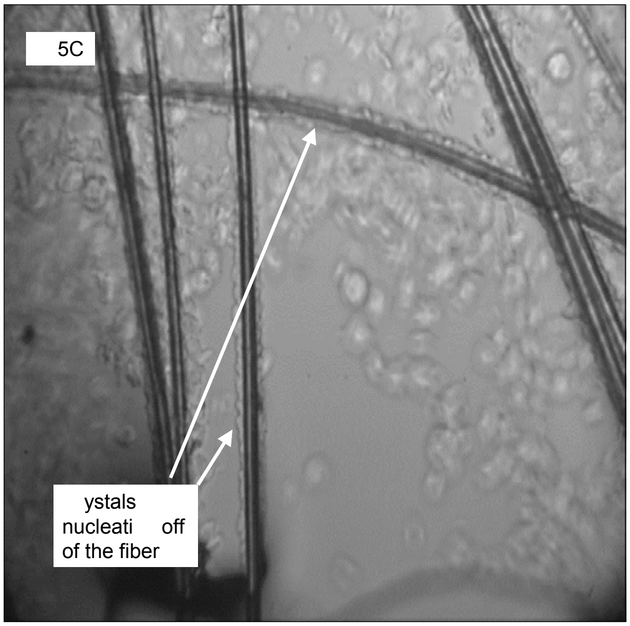

Figure 8. Transcrystalline layer on Kevlar fibers.

being much les than the number of nucleation sites on pitch or Kevlar® fibers. Links to videos of these results can be found at:
http://hpcnet.org/thermoplastic.

Summary

Highlights of our FY2005 research include:

1. Demonstrated transcrystalline layer formation for Kevlar and pitch-based carbon fibers and polypropylene matrix.
2. Measured matrix crystallinity by differential scanning calorimetry
3. Designed an apparatus to allow for controlled, resistive, carbon-fiber heating for thermodynamic adhesion and transcrystallinity experiments.
4. 2 students traveled to University of Alabama-Birmingham to meet with Dr. George Husman, to allow better design of a tabletop mini-DRIFT system.