

CRADA (NFE-17-06574) Final Report: Carbon Fiber Surface Treatment



Felix Paulauskas
Joshua Nowak
David Martin
Truman Bonds

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CARBON FIBER PLASMA SURFACE TREATMENT

Felix Paulauskas
Carbon and Composites Group, Oak Ridge National Laboratory

Joshua Nowak, David Martin, and Truman Bonds
RMX Technologies, Knoxville, Tennessee

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ABSTRACT

This project focused on developing and applying a new surface treatment technology to carbon fiber applications. During the course of this work, two different treatment prototypes were developed and explored. Highly reactive surface chemistries were successfully applied to carbon fiber, resulting in surface oxygen content as high as 27%. Enhanced composite properties of a 45% increase in the interfacial strength and a 10% increase in tensile and flexural strength were demonstrated for thermoplastic resins. This enhancement was performed while proving that the plasma surface treatment process does not damage the fiber. Treatment times were as low as 1 min.

FINAL REPORT

1. PROJECT GOALS/OBJECTIVES

The objective of this project is to scale a previously developed novel atmospheric plasma technology that will replace the current electrochemical surface treatment technology used in carbon fiber manufacturing. This outdated electrochemical-based technology is only suitable for expensive resin systems such as epoxy. The goal of this project is to construct a lab-scale continuous-operation plasma surface treatment (PST) device that can process sufficient material to fabricate and test coupon samples to prove the performance advantages for carbon fiber composites. The project technical goals were

1. Design and build a plasma device capable of surface treating 1 t of carbon fiber per year
2. Generate >25% surface oxygen on carbon fiber as measured by x-ray photoelectron spectroscopy (XPS)
3. Fabricate part coupons that demonstrate a 25% part strength increase compared with conventional surface treatment
4. Fabricate part coupons using a low-cost thermoplastic resin that has the same performance as epoxy resin

NOTE: The PST technology has been designated as export controlled by the US Department of Energy's Oak Ridge National Laboratory (ORNL) export control office. Therefore, no images of the actual treatment hardware nor design details can be shared in publicly available documents.

2. BACKGROUND

The electrochemical surface treatment technology currently used in carbon fiber manufacturing is outdated and only suitable for expensive resin systems such as epoxy, which is used by the aerospace industry. A significant technology gap must be overcome before surface treatment and sizing of current and next-generation low-cost carbon fibers can be used with low-cost resins and processes. Feasibility studies of this surface treatment technology were completed, and the technology is licensed to RMX Technologies (now known as 4X Technologies). Presently, additional engineering work remains to establish continuous lab-scale processing and to show scalability.

The novel atmospheric plasma technology developed by ORNL, RMX, and C.A. Litzler Co. will replace the current technology in new and existing carbon fiber and composite manufacturing plants. The team

selected for this project has experience working together in applying plasma technology to carbon fiber applications.

The effectiveness of PST in modifying the surface of carbon fiber has been established. The next step is developing a continuous process that can treat enough fiber to fabricate composite part coupons for mechanical testing. This step requires additional engineering work to resolve technical issues. A flexible device will be constructed that allows for interchangeable components to test a variety of plasma exposure equipment and to reduce overall technical risk for the project.

3. ACCOMPLISHMENTS

1. Designed, built, and tested two different PST reactor prototypes.
2. Optimized the PST process to maximize the production of oxidative surface chemistries, achieving elemental surface oxygen levels in the range of 12%–27%.
3. Iteratively improved the PST hardware design, improving reliability and scalability.
4. Achieved a 40%–45% increase in the interfacial strength of a single-filament specimen in polypropylene resin.
5. Achieved a 10% increase in the tensile and flexural strengths of nylon chopped-fiber composite coupon parts.
6. Demonstrated that the PST technology does not damage the tensile properties of fibers.
7. Showed that PST can rapidly increase the amount of reactive surface oxygen groups: treatment times were as low as 1 min.

4. PROGRESS AND STATUS

During this project execution period, the project team addressed significant issues such as FIMABOND single-fiber pullout instrument repair, calibration, and resin curing protocol optimization steps associated with measuring the single-fiber pullout strength.

4.1 EFFECTS OF EPOXY CURING CONDITIONS ON SINGLE FIBER PULLOUT STRENGTH

As part of the protocol development task, the team measured the single-fiber pullout strength of a handful of baseline samples. The single-fiber pullout test method measures the interfacial strength of a single filament of carbon fiber embedded in a droplet of resin. It ultimately measures the strength required to debond the fiber from the resin matrix. Better adhesion between the fiber and the resin matrix results in higher interfacial strength, which corresponds to the composite's macro strength properties.

The goal was to test the pullout strength in epoxy resins cured at higher temperatures ($>100^{\circ}\text{C}$). Increasing the maximum cure temperature should provide more energy to activate reactions between the surface chemistries produced by the plasma and the epoxy components. However, changing the curing conditions should also lead to changes in the physical properties of the epoxy matrix. Accordingly, it was first necessary to test the baseline, non-plasma-treated AS4 carbon fibers at the new curing conditions. Figure 1 displays the results of these baseline tests.

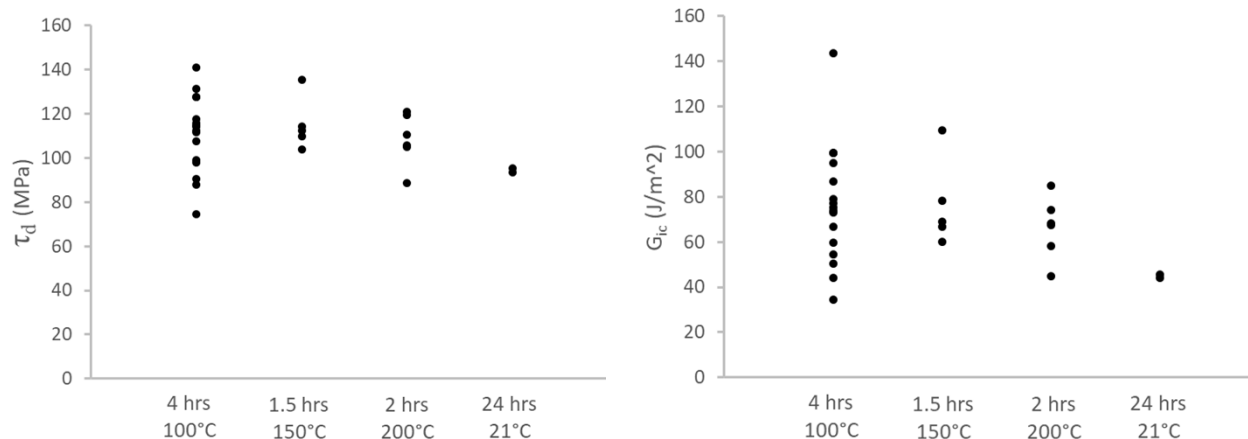


Figure 1: Single-fiber pullout test results in epoxy cured using four different cure temperatures. (*left*) Local interfacial shear strength and (*right*) interfacial energy release. Fiber was as-received Hexcel AS4.

A range of temperatures and dwell times was selected based on the manufacturer's specified ranges for an epoxy system consisting of Epon 828 epoxy and 14 phr Epikure 3223 hardener: room temperature for 24 h, 100°C for 4 h, 150°C for 1.5 h, and 200°C for 2 h. The duration at the maximum temperature of 200°C should have been for 1 h because curing occurs more rapidly at higher temperature. Among the samples, no statistical difference could be found in interfacial strength properties, as shown in Figure 1. However, the number of good specimens tested was far below the target of 12–15 needed for a good comparison (except for the baseline 100°C condition). Nevertheless, because none of the data points fell outside the extremes of the baseline 100°C condition, increasing the cure temperature is not likely to significantly affect interfacial bonding with as-received AS4 carbon fibers. The same would not necessarily be true for the plasma-treated samples, which possessed many times more oxygen moieties on the surface, especially carboxyl groups.

4.2 SUMMARY OF TECHNICAL ACCOMPLISHMENTS

The project consisted of two distinct phases based on the sequential development of two PST reactor prototypes.

4.2.1 Phase 1

In the first phase, the project team designed, built, and tested a first-generation lab-scale prototype PST reactor, known as the PST-1. The PST-1 had a 6 ft processing length, and it was capable of continuously and simultaneously processing up to $3 \times 24,000$ tows of carbon fiber. The PST-1 featured a remote atmospheric plasma injection system. With this system, plasma generated in remote chambers was injected into a primary treatment chamber. This system isolated the high-voltage plasma components from the electroconductive carbon fibers, preventing damage to the fiber and hardware.

The PST-1 was commissioned in March 2018, and it was tested throughout the following 9 months. Initially, the project team focused on enhancing the concentration of reactive oxygen functional groups on the surfaces of the carbon fibers. To determine the elemental and chemical makeup of the fibers' surfaces, the project team used XPS. For oxidative surface treatments, the atomic surface oxygen content is affected most directly, and it served as the key metric for feedback.

In the carbon fiber manufacturing process, the carbonization conversion stage occurs in an inert atmosphere that has a maximum recommended 15 ppm oxygen concentration. When the carbon fiber exits the high-temperature carbonization furnace, they are chemically inert, and the atomic oxygen

concentration on the carbon fiber surfaces is assumed to be zero. The project team contacted multiple carbon fiber producers to obtain virgin carbon fiber from the exit of the high-temperature carbonization stage, without success. The carbon fiber producers would only agree to supply carbon fiber after the surface treatment and before the sizing application. This condition describes the as-received fiber for this project, specifically AS4 carbon fiber manufactured by Hexcel.

Generally, the carbon fiber manufacturers use an electrochemical-based surface treatment process, a technology that is more than 50 years old. This surface treatment provides a maximum atomic surface oxygen content of around 10%, but the successive washing and drying stages used with this surface treatment technology reduce the concentration of atomic oxygen to 6%–8%. Multiple XPS evaluations of the as-received Hexcel AS4 fiber confirmed this level of atomic oxygen on the surface of the carbon fiber (~6%–8%). These fibers were the baseline for this project. This fiber was subsequently subjected to the PST.

After several months of parametric optimization, including more than 100 samples analyzed via XPS, the PST-1 achieved a surface atomic oxygen content of more than 20%, depending on the process conditions, as shown in Figure 2. This oxygen content is nearly triple the amount initially found on the surfaces of the as-received Hexcel AS4 carbon fiber. The PST-1 could have increased the surface oxygen content even further; however, prior investigations indicated that too much surface oxygen can disrupt the surface lattice structure in such a way that decreases the overall strength of the fiber. The upper limit was not explored in this work.

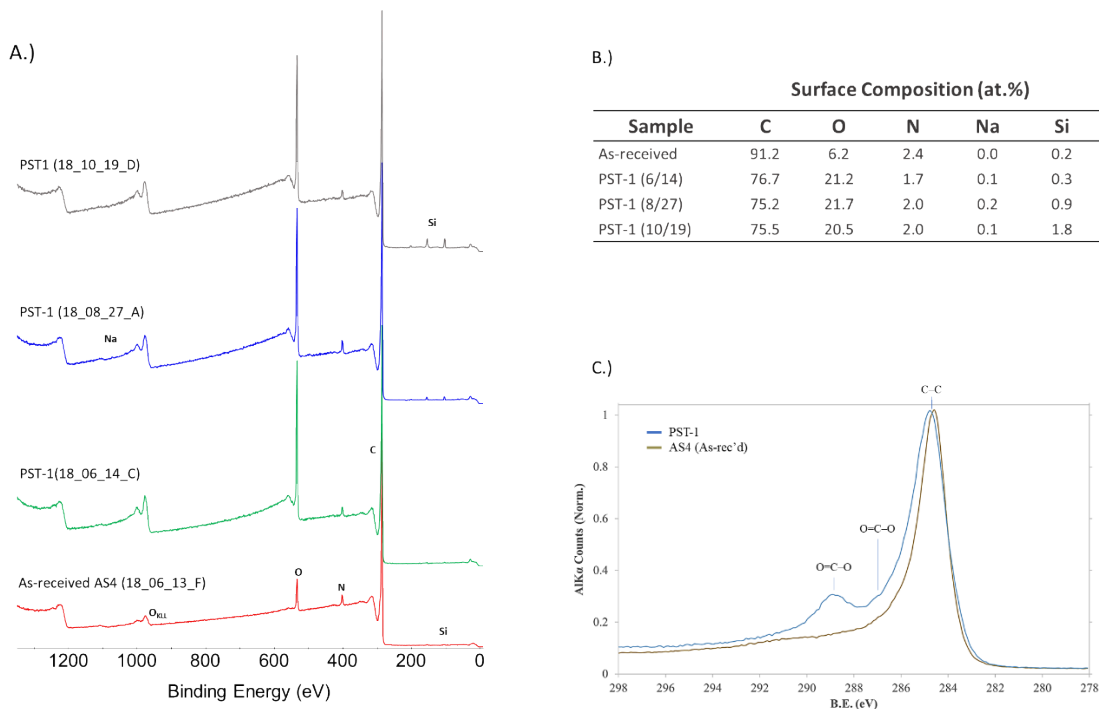


Figure 2: Comparison of XPS analysis of Hexcel AS4 commercial carbon fibers with PST-1 plasma surface treated AS4 carbon fibers. (A) Survey spectra of as-received AS4 and various PST-1 plasma-treated samples. (B) Surface composition of the samples. (C) XPS high-resolution C1s spectra of plasma-treated and as-received carbon fiber samples. The plasma-treated samples had 3–4× the amount of surface oxygen moieties, which consisted of carboxyl, carbonyl, and alcohol groups. Samples were collected from June to October 2018.

Additionally, without a virgin carbon fiber for comparison, coupling between the surface chemicals from the electrochemical surface treatment and subsequent PST could not be easily distinguished. The plasma

could react with carbon sites in the surface lattice, couple with existing oxidative groups, or both. XPS confirmed that carbon sites were altered by the PST, according to the C–C band shift in the C1s spectrum shown in Figure 2c. Moreover, the plasma-treated virgin carbon fibers would not be significantly different because the initial oxidation favors lower energy carbon sites in the surface lattice. Ideally, a PST unit could be incorporated into a full carbon fiber conversion line for testing, and it should be the focus of a future project.

In addition to chemical evaluation using XPS, an industry partner provided composite testing. The industry partner and the project team decided to focus on thermoplastic resins because of growing market demand for thermoplastic-based carbon-fiber reinforced polymer composites. Additionally, thermoplastics such as polypropylene are generally inert and typically have deficiencies in interfacial bonding in carbon-fiber reinforced polymer composites. PST can increase bonding with thermoplastics.

Initial evaluation involved measurements of interfacial strength of plasma treated carbon fibers in a polypropylene resin using the single-fiber pullout test method. After several iterations, a 40%–45% increase in the local interfacial shear strength was achieved with plasma-treated AS4 fibers compared with the as-received fibers, as shown in Figure 3. Generally, the interfacial strength increased with increasing atomic surface oxygen content. The best results were achieved at around 21% surface oxygen, which was also the maximum tested.

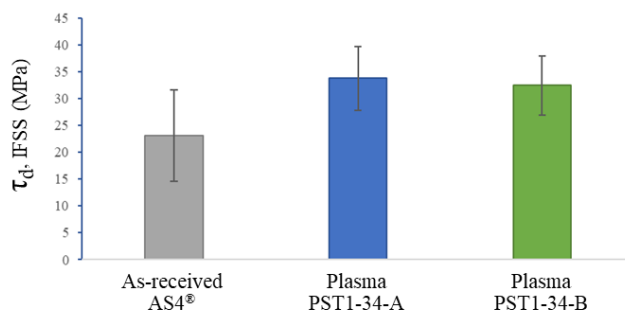


Figure 3: Local interfacial shear strength (IFSS) measured by single-fiber pullout of two plasma-treated carbon fiber samples and the as-received baseline Hexcel AS4 in a polypropylene matrix. The plasma-treated fibers had atomic surface oxygen contents of around 21% each.

After achieving the promising results from the single-fiber pullout testing, the project team (with the help of the industry partner) progressed to assessing performance in ASTM Standard part coupons prepared by fiber chopping, compounding, and injection molding. However, plasma surface treating enough continuous material was a challenge for the limited scale of the PST-1. Each batch of parts required more than 18 h of continuous operation, which posed additional challenges for hardware reliability. Ultimately, several hardware changes were necessary to achieve reliable performance for the duration of these long runs. These changes included an upgrade to the exhaust end caps mounted at either end of the reactor. This upgrade made the system less susceptible to air ingress from the surrounding room. Additionally, a system of rollers and bars was added to control the tow band spread. A consistent tow spread was essential to ensuring that the fibers were evenly exposed to the plasma. Lastly, several thermocouples were added to help determine when the reactor was at steady state.

Table 1 lists the strength test results. In a nylon (PA-66) resin, PST improved the tensile and flexural strengths by 10%. In the case of polypropylene, coupons made with plasma-treated fibers had lower flexural strength properties than the as-received AS4. However, the tensile strength of these parts improved by 12%

Table 1: Strength test results of chopped fiber injection-molded part coupons prepared with plasma- and non-plasma-treated AS4 carbon fibers in polyamide 6,6 (PA) and polypropylene (PP) matrices

Sample	Surface treatment method	Resin	Tensile modulus (Gpa)	Tensile strength (Mpa)	Flex modulus (Gpa)	Flex strength (Mpa)
Baseline	EC*	PA66	21.4	201.0	17.2	297.0
PA-PST	Plasma	PA66	20.0	212.3	17.4	324.0
Baseline	EC	PP	16.1	70.5	10.1	116.0
PP-PST	Plasma	PP	14.3	79.6	9.9	108.0

*Electrochemical

4.2.2 Phase 2

Applicator/PST Technology Improvement

The PST-1 prototype was an effective proof of concept, but its ability to be scaled up was limited by several design deficiencies. The supplemental heating system was inefficient and difficult to control. Very little of the heat put into the system was delivered to the fiber, and components were poorly insulated from one another. Likewise, the plasma system was also inefficient. A large portion of the reactive species produced by the plasma failed to reach the carbon fiber. Furthermore, the plasma hardware had many complicated pieces, which, at commercial scale, would be too expensive and large.

To improve the controllability, robustness, scalability, and operational friendliness, the project team elected to design and build a new PST prototype. The new prototype, named the PST-2, incorporated two major design improvements. First, the plasma source(s) were relocated to be closer to the carbon fiber tow ban. This configuration allowed the fiber to be exposed to a higher concentration of reactive plasma species. Second, a more direct method for concentrating heat at the fiber was utilized. This method was more efficient, and it provided more straightforward control.

Before building the PST-2, the new plasma design and the new proprietary heater system were both tested by using standalone prototypes. The data collected from these efforts were input to the design of the PST-2. After a long delay caused by the COVID-19 pandemic, the PST-2 was finally constructed and commissioned during the summer of 2020. Like the PST-1, the PST-2 was capable of continuously surface treating multiple tows of carbon fiber.

Initial experiments with the PST-2 focused on optimizing the oxidative chemistries generated on the fiber surfaces. Using parametric optimization experiments, the surface chemistry was evaluated for different combinations of process conditions. As shown in Figure 4, a maximum surface oxygen content of nearly 22% was achieved on Hexcel AS4 using a 5 min residence time. This result is identical to the results achieved using PST-1, as shown in Figure 5. Moreover, the PST-2 did not decrease the surface treatment level (surface energy) compared with the PST-1.

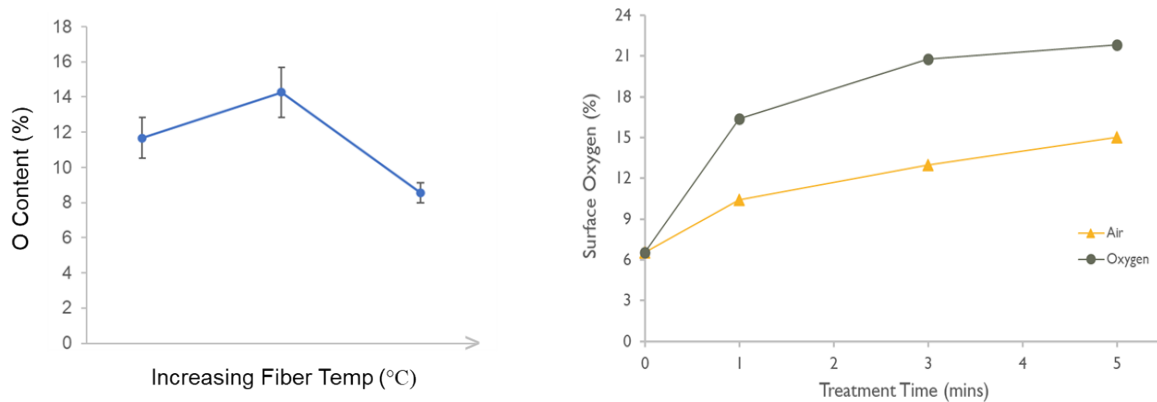


Figure 4: Optimization of carbon fiber surface oxygen content in the PST-2. Oxygen content as a function of (*left*) the carbon fiber temperature and (*right*) the treatment time and feed gas used.

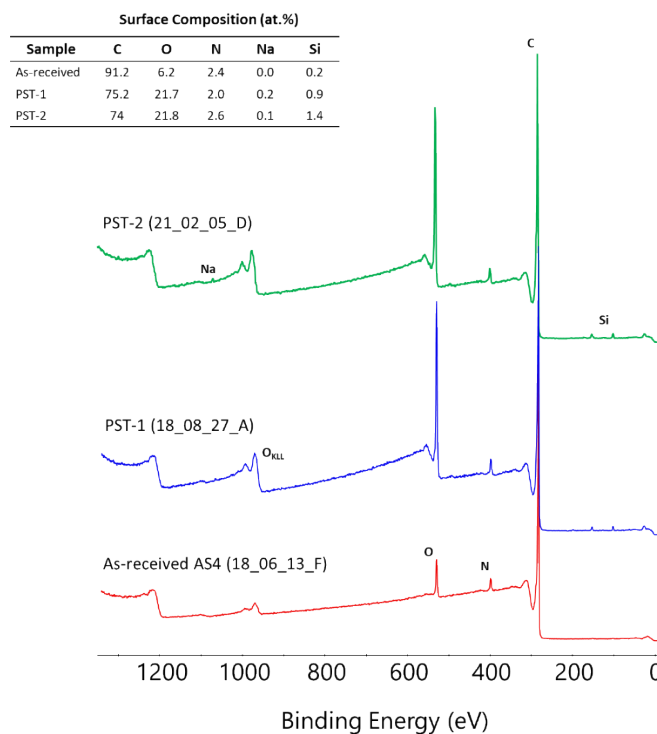


Figure 5: XPS survey spectra. (*bottom*) The as-received AS4 commercial carbon fibers, (*middle*) fibers plasma treated with the PST-1, and (*top*) fibers plasma treated with the PST-2. The surface chemical makeup was very similar for the PST-1 and PST-2.

Next, samples from the PST-2 were tested for interfacial strength using the FIMABOND test system at ORNL. The project team selected two resins for testing: nylon (PA-66) and epoxy. These were selected based on information provided by a market research study that investigated current opportunities for enhanced surface treatments in the carbon fiber market. The research study was conducted near the beginning of Phase 2 by a third-party market research firm. The study revealed an industry emphasis on nylon thermoplastics over polypropylene as well as a majority emphasis on epoxy-based carbon-fiber reinforced polymer composites. Improved interfacial bonding and better wet out (epoxy) were among the top performance factors cited.

Table 2 lists adhesion strength test results. Although plasma surface treated samples had significantly more surface oxygen moieties than the as-received AS4, this characteristic did not translate to better interfacial strength properties in nylon resin. However, before the pullout tests, the fiber samples were coated with a nylon-compatible commercial sizing agent. Applying sizing is standard practice for finishing carbon fibers, but the process has many variables, including coat weight, drying conditions, and the chemical compatibility with the surface-treated carbon fibers. The effects of the sizing applied to the fibers after surface treatment could not be separated, and a future study should consider testing fibers without the sizing applied.

Table 2: FIMATEST adhesion strength test results for AS4 carbon fibers in a PA66 resin system

Sample	N	n	l_e (μm)	τ_{app} (MPa)	G_{ic} (J/m ²)	τ_d (MPa)	τ_f (MPa)
Baseline (not plasma treated)	14	9	117.2 (21.2)	56.24 (6.41)	41.18 (11.81)	87.41 (11.76)	16.16 (1.53)
Plasma A	21	15	109.2 (23.3)	56.25 (10.83)	32.49 (16.28)	72.39 (19.13)	12.29 (4.62)
Plasma B	22	13	96.67 (10.41)	67.50 (15.53)	39.12 (19.60)	87.12 (20.80)	13.71 (2.40)

N: total number of specimens; n: number of “good” specimens. Toss criteria: embed depth (l_e) < 10× fiber diameter (d_f) || frictional stress (τ_f) = 0 || Irregular resin matrix elongation. Standard deviation included in parentheses. τ_d : local interfacial shear strength; G_{ic} : interfacial energy release, τ_{app} : apparent interfacial shear strength.

In addition to nylon resin, fibers were also tested in an epoxy resin. For this testing, surface-treated fiber samples were left unsized so that only the interface between the fiber and the epoxy resin was tested. Thus, direct interactions between the fiber surface and the epoxy could be tested via single-fiber pullout testing. Figure 6 shows the results of the single-fiber pullout tests in epoxy resin. As with the nylon resin, the plasma treatment did not improve the interfacial properties in epoxy. However, the results indicated that the curing conditions used for preparing the epoxy may not have been appropriate for maximizing bonding with the plasma-treated samples. A maximum cure temperature of 100°C was used for curing the specimen. This temperature is on the low end for activating esterification reactions between the carboxyl groups on the plasma-treated fibers and the epoxy groups¹. The project team intended to test this theory, but FIMABOND equipment issues at the end of the project prevented further testing.

¹ K. Horie, M. Hiromichi, and I. Mita, “Bonding of epoxy resin to graphite fibres,” *Fibre Science and Technology* 9 (4): 253–264 (1976), [https://doi.org/10.1016/0015-0568\(76\)90008-7](https://doi.org/10.1016/0015-0568(76)90008-7).

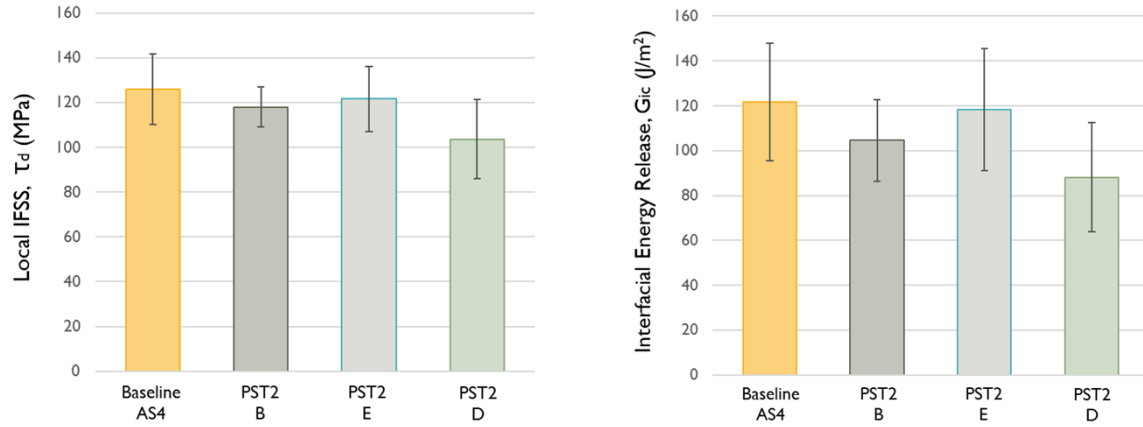


Figure 6: Single-fiber pullout test results in epoxy resin. (*left*) Local interfacial shear strength (IFSS) and (*right*) interfacial energy release. Error bars represent the standard deviation.

5. PLANS FOR FUTURE WORK

This technology currently supports several ORNL projects involving carbon fiber fabrics. Additional follow-on studies are required to examine (1) fiber–matrix adhesion using epoxy cure conditions that will maximize bonding by achieving three- to four-fold increased carboxyl groups generated on the fibers, (2) how interactions between fiber loading and plasma treatment affect fiber–matrix adhesion and part mechanical properties, and (3) fiber topology and surface chemistry, using raw carbon fibers as the feed stock and how these affect fiber–matrix adhesion and part mechanical properties.

