IACMI/R006-2020/6.13

Low Cost, High Volume, Carbon Fiber Precursor for Plasma Oxidation

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Date: January 25, 2020

Final Technical Report
PA16-0349-6.13-01

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LOW-COST, HIGH-VOLUME CARBON FIBER PRECURSOR FOR PLASMA OXIDATION

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Date Published: January 2022

Prepared by:
Institute for Advanced Composites Manufacturing Innovation
Knoxville, TN 37932
Managed by Collaborative Composite Solutions, Inc.
For the
U.S. DEPARTMENT OF ENERGY
Under contract DE- EE0006926

Project Period:
04/2018 – 12/2019

Approved for Public Release

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1. FRONT MATTER

1.1 List of Acronyms & Abbreviations

4M	4M Carbon Fiber Corporation
4XT	4XTechnologies, LLC
aMT	annual metric ton
AN	acrylonitrile
CFTF	Carbon Fiber Technology Facility
CRADA	Cooperative Research and Development Agreement
DOE	Department of Energy
DSC	differential scanning calorimetry
dtex	decitex
EERE	Office of Energy Efficiency & Renewable Energy
GPa	gigapascal
HT	high temperature (carbonization)
ksi	kilopound per square inch
LT	low temperature (carbonization)
MPa	megapascal
Msi	megapound per square inch
OPF	oxidized polyacrylonitrile fiber
ORNL	Oak Ridge National Laboratory
PAN	polyacrylonitrile
TGA	thermogravimetric analysis
T_p (°C)	temperature at peak exothermic energy release
UTK	University of Tennessee at Knoxville
VTO	Vehicle Technologies Office
VA	Vinyl acetate
MA	Methyl acrylate
XRD	X-ray Diffraction

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1.4 Acknowledgements

The information, data, or work presented herein was funded in part by the Office of Energy Efficiency and Renewable Energy (EERE), U.S. Department of Energy, under Award DE-EE0006926.

Additional support was provided by the Dralon GmbH, particularly Dr. Andreas Wego whom the authors wish to personally thank for his continued support.

The following individuals were instrumental in the completion of this work and the authors wish to thank them for their efforts.

- Drs. Kamlesh Bornani, Joshua Crabtree and Dayakar Penumadu at the University of Tennessee
- Dr. Felix Paulauskas, Bob Norris, and David McConnell of Oak Ridge National Laboratory
- Dr. Truman Bonds of 4M Carbon Fiber
- Pol Grappe, Mike Agentis, and Josh Brady of 4XTechnologies

2. EXECUTIVE SUMMARY

Light weighting with carbon fiber is critical to improving the energy efficiency of wind turbines, airplanes, and automobiles, but the high cost of carbon fiber continues to limit market growth and applications. Half of this cost is in the raw materials. For the carbon fiber market to reach the next level of adoption, the cost of both the raw materials and conversion must be reduced. This project considered the combination of low-cost, textile-grade precursors combined with the increased efficiency of plasma oxidation to greatly reduce the cost of carbon fiber.

The primary objective of this project was to make industrial-grade carbon fiber (550 ksi tensile strength, 35 Msi tensile modulus) from textile-grade PAN precursors, something that cannot be achieved with conventional oxidation and to date has not been achieved with any technology. To accomplish this, the project team iteratively optimized the process conditions in the plasma oxidation and carbonization stages to maximize the tensile properties of the resultant carbon fibers. This involved implementing experimental designs for both stages, whereby process conditions (e.g. temperature) were varied and correlated to fiber properties. Samples of oxidized PAN fibers (OPFs) were prepared using a small pilot-scale plasma oxidation oven at 4XTechnologies (4XT). The thermal, chemical, and physical properties of OPF samples were analyzed by the University of Tennessee (UTK) and Oak Ridge National Laboratory (ORNL). The OPF samples were then converted to carbon fiber by subsequent low- and high-temperature carbonization using a lab-scale furnace at ORNL. The resultant carbon fibers were tested for tensile strength also at ORNL, and the results were fed back into the experimental design.

Of the hundreds of carbon fiber samples produced over the course of the project, the best sample had an average break strength of 479 ksi and modulus of 33 Msi. While the best tensile properties achieved fell short of the final project targets of 550 ksi for break strength and 35 Msi for modulus, the team demonstrated the potential to produce industrial-grade carbon fiber using textile-grade precursors. The best performing fiber samples had tensile properties that are 87% of the goal for tensile strength and 94% of the goal for tensile modulus. With additional optimization work, it is likely that the targets could be achieved, since only a fraction of the process parameter space was explored during this project. 4XT and its affiliate (4M) have already secured funding through private equity, and there is a CRADA (Cooperative Research and Development Agreement) project currently underway with the Carbon Fiber Technology Center (CFTF) at ORNL to continue this research.

Additionally, while not an original goal of the project, the carbon fibers for most samples had diameters >8.5µm. This is considerably larger than commercially available carbon fiber products, which can impart unique properties to the composites (e.g. increased compressive strength) and decrease manufacturing costs even further. Moreover, these fibers were oxidized with plasma oxidation using residence times ranging <60mins, which would be considered fast for normal diameter fibers, but it is as much as 5x faster when factoring in the diameter of the fibers.

3. INTRODUCTION

It is well known that car manufacturers have fuel efficiency standards that they are required to meet. One of their primary means of increasing fuel efficiency is through weight reduction. Carbon fiber composites have long been used in the aerospace and wind turbine industries to reduce weight and improve energy efficiency, but their high cost has relegated them to use in only high-end automobiles.

In the fall of 2015, 4XT and the ORNL completed a joint development project for a new technology in the manufacturing process of carbon fiber that lowers the cost of carbon fiber by over 20%. This technology uses plasma to enhance and accelerate the oxidation stage of carbon fiber conversion and is aptly named plasma oxidation. Unfortunately, the cost reduction from this technology alone will likely not be sufficient to foster the adoption of carbon fiber light-weighting and energy efficiency by the larger automotive industry. However, if combined with the lower price of textile-grade carbon fiber precursor, carbon fiber prices could approach those needed to convince the automotive industry to include carbon fiber on standard vehicles.

Industrial grade carbon fiber is usually produced from a commodity-grade specialty acrylic precursor fiber. This precursor fiber is over 90% acrylonitrile (AN) and is engineered specifically for conversion to carbon fiber. This purpose-built fiber comes at a high cost that makes up 50% of the total cost of carbon fiber. The use of textile-grade PAN fibers, by contrast, could cut this cost in half. However, the reduced cost comes at a price. Compared to specialty acrylic fibers, textile-grade fibers have lower polymer molecular weights, increased cross-sectional areas and linear densities, and higher comonomer content. These properties of textile-grade fibers make it more difficult to convert into carbon fiber, usually requiring excessive amounts of time and energy during oxidation. Moreover, they tend to yield low quality (i.e. low tensile strength) carbon fibers. No commercial carbon fiber products sold today are made from textile-grade precursor fibers.

In order for textile-grade precursors to be considered a viable alternative, they must first yield quality carbon fiber. At the same time, this must be done through economical processing methods, otherwise the cost savings are erased. This is an opportunity for plasma oxidation, which addresses several of the conversion challenges associated with textile-grade precursors.

The purpose of this project is to understand the relationship between the plasma oxidation process and carbon fiber performance in order to optimize the conversion process that would enable production of industrial grade carbon fiber with commercially available textile-grade precursor without further precursor modification. The ultimate objective is to achieve minimum carbon fiber properties in the range of 33-37 Msi (230-255 GPa) for tensile modulus and 500-725 ksi (3450-5000 MPa) for tensile strength in addition to fiber tow conditions acceptable for standard downstream processing into parts for IACMI-targeted applications and broader industrial use.

As will be discussed in the background, plasma oxidation is a complex chemical process involving many process variables. Whereas conventional oxidation has three major processing variables, namely time, temperature, and tension, plasma oxidation includes plasma as a fourth

major variable. This additional variable expands the optimization challenge required to produce the best fiber product. Herein lies the great challenge and great novelty of this work.

The commercialization of plasma oxidation began in 2016 when 4M spun off from 4XT to raise private equity for the commercialization effort. Since then, 4M has funded the advancement of this technology including a modular commercial-scale oven, a reduction in oxidation residence time down to 20 min, and the design of a full pilot line.

4. BACKGROUND

Conventional oxidation
The only oxidation technology known to be used at manufacturing scale is based on conventional thermal convection ovens. The precursor is slowly heated in air over the course of 50-90 minutes in large ovens with very high gas flow rates. Over the years, this technology has been refined, with improved air flow and more efficient heating. However, these improvements have had marginal effects on reducing the overall residence time.

Advanced oxidation technologies
Several technologies have been developed as alternatives to the conventional oxidation method in an attempt to reduce oxidation time and energy as well as to allow for the use of alternative (lower cost) precursors. These technologies fall into two general categories: pretreatment and oxidation.

Pretreatment Methods:
- Heating in an inert atmosphere [1,2]
- Electron beam irradiation [3,4]
- Gamma irradiation [5]
- UV [6,7]
- Hydrogen peroxide soak [8]

Oxidation Methods:
- Plasma [9-11]
- Microwave [12,13]

Most of these methods have only been tested at a lab-scale and face severe barriers to scaling. Heating in an inert atmosphere (pretreatment) and plasma (oxidation) are the two technologies that have been proven at pilot scale. While heating in an inert atmosphere will be discussed briefly, this background focuses mainly on plasma oxidation.

Heating the fiber in an inert atmosphere as a pretreatment step was developed by researchers at Deakin University [1]. It involves heating the precursor between 250 – 400°C for less than 5 minutes in an oxygen-free atmosphere prior to conventional oxidation. During this pretreatment, a portion of the nitrile chemical groups present in the PAN fiber undergo cyclization reactions, producing a partially stabilized fiber. This allows for stabilization to be completed at an enhanced rate in a subsequent oxidation step, effectively reducing the residence time required for

oxidation to as low as20 min compared to the conventional times of 50-90 min. While effective, this pretreatment may come at a price of reduced performance of the final carbon fibers. Additionally, the effectiveness with low-cost precursor alternatives such as textile-grade fiber has not been demonstrated.

Plasma oxidation

While both the Deakin method and plasma oxidation have shown the ability to decrease the oxidation time of commercial-grade precursor from 60-90 minutes down to approximately 20 minutes [4,14], this does not decrease the cost to the DOE automotive target of $5/lb.. In order to decrease the cost of carbon fiber further to this target, lower cost precursors must be used. Plasma oxidation is the only scalable technology that has also shown the ability to economically oxidize textile-grade precursor and larger diameter precursors, both of which would drastically reduce the cost of carbon fiber. Therefore, the focus of this project is the plasma oxidation of textile-grade precursor to produce low-cost carbon fiber.

Plasma oxidation involves the indirect exposure of precursor fibers to an atmospheric plasma produced in an oven. Unlike the pretreatment method described above, plasma oxidation is a one step solution that directly replaces the conventional thermal oxidation technology currently used in carbon fiber manufacturing. Like conventional thermal oxidation, plasma oxidation has the same major process variables, including residence time, temperature profile, and fiber tension. Additionally, just as with conventional oxidation, 4M's plasma technology only uses air as a feed-gas, and it does not require supplemental oxygen.. With plasma oxidation, the heated air is energized into a plasma prior to interacting with the fiber. The plasma consists of highly reactive, oxidative gases, including some monatomic species of oxygen. These plasma species accelerate the cyclization, oxidation, and crosslinking reactions that occur during oxidation.

In addition to accelerating the stabilization reactions, plasma enhances the diffusion of reactive species into the fiber. Conventional oxidation is diffusion limited, which means the rate and extent of chemical reactions within the fiber is limited by the diffusion rate of oxygen in the air (i.e. diatomic molecular oxygen) into the fiber. The plasma gas species, being smaller and more energetic, have enhanced diffusivity compared to regular air [15]. Accordingly, the rate of plasma oxidation is faster [16]. Moreover, the penetration inwardly into the core of the fiber is considerably improved.

Oxidized PAN fibers (OPF) prepared with plasma oxidation have similar or even better properties to those prepared with conventional thermal oxidation. As shown in the Vehicle Technologies Office (VTO) development projects [17], plasma OPF has equivalent tensile properties to conventional OPF. Additionally, they possess the same types of chemical structures. However, plasma fibers tend to have a larger network/density of conjugated covalent bonds, which is the basis for the evolving pseudo graphitic structure found in carbon fibers [18]. As measured with acid digestion technique plasma fibers tend to have a different and better cross-sectional oxidative profile, with a larger ratio of skin-to-core compared to conventional OPF. Additionally, plasma fibers were shown to have a comparable weight loss under heating up to 900°C and remnant heat as measured with the thermal analysis methods TGA and DSC, respectively.

Reducing the cost of the oxidation step by increasing throughput is not alone sufficient to

decrease the cost of carbon fiber down to the target for automotive manufacturers (e.g. - $5/lb). To achieve such a drastic price reductionlower cost precursors must be used in addition to enhanced oxidation. Plasma oxidation is the only scalable technology that has also shown the ability to oxidize cheaper textile-grade precursor and larger diameter precursors, both of which would drastically reduce the cost of carbon fiber. Therefore, the focus of this project is the plasma oxidation of textile-grade precursor to produce low-cost carbon fiber.

5. RESULTS AND DISCUSSION

5.1 Materials

Two types of textile-grade precursor fibers were used for this project (Table 1). The fibers were supplied (in kind) by Dralon GmBH. The Dralon L-type fiber was a traditional textile-grade fiber based on a VA comonomer, and it came packaged as crimped, heavy tow (240k filaments). This was the first precursor used for the project, as it is an off-the-shelf product for Dralon. As is discussed further below, there were difficulties in tensioning the baled fiber with 4XT's fiber handling and oxidizing it in the plasma oxidation oven at 4XT because it was not designed to handle such a large tow size. It was also found that the crimp used in the production process for this precursor caused damage that propagated through the conversion process and led to lower carbon fiber tensile properties. Additionally, the 1.9 dtex titer produced carbon fiber diameters below 5 microns which are dangerous to handle and test because of respirable concerns. To overcome these issues, Dralon produced a smaller tow precursor packaged on bobbins using a different comonomer but a similar molecular weight to that of the L-type polymer. This Dolan X-type precursor was supplied in a variety of titers (e.g. 5.5dtex) and tow sizes (e.g. 10k)

Table 1. Properties of two types of textile-grade PAN fiber

Parameter	Dralon L	Dolan X
Comonomer(s)	VA	MA
Filament shape	Kidney	Kidney
Titer (dtex)	1.9	2.0, 3.0, 5.5, 9.0
Tow size	240k	5k, 10k, 20k, 30k
Crimp	Yes (heavy)	No
Package	Bale	Bobbin
Mfg. Scale	Production	Pilot

5.2 Technical Approach

Optimizing carbon fiber properties is a complex and time-consuming task which can take years to complete for a production carbon fiber product. The difficulty stems from the 'pseudo-independent' nature of the sequential processing stages, namely precursor spinning, oxidation,

carbonization, and finishing. Each stage has its own process variables (e.g. temperature, time, etc.), which can be controlled independently; however, the properties of the fiber from the previous stage impact the downstream stage. However, the exact properties of OPF that lead to good carbon fiber are not well defined and vary depending on the precursor and the specific oxidation method and equipment used.

Since this project is the first time that plasma oxidation and textile-grade PAN precursor have been combined, the team's first goal was to characterize the OPF material and oxidation process with this precursor. With the Dralon L-type precursor fibers, most of the effort focused on characterizing the plasma OPF, with few samples undergoing carbonization. It was the project team's goal to create a large dataset of OPF properties that could be used to establish correlations to carbon fiber properties. Such a correlation could greatly reduce the amount of time required to determine optimal carbon fiber properties. To build a robust dataset of OPF properties, a test matrix was developed covering the parameter space of the plasma oxidation process. Some 76 samples were produced as part of this test matrix. These samples underwent density measurements, tensile testing, thermal measurements, and optical microscopy at 4XT, UTK, and ORNL.

Following this exploration of the oxidation parameter space, samples were carbonized with a similar test matrix now focused on carbonization conditions. These samples were tensile tested, and the carbonization conditions were iterated which resulted in an increase in break stress and modulus. Once a plateau was reached, Dralon was asked to iterate their precursor based on the factors discussed in the Materials section above. Once this new precursor (Dolan X) was procured, the team began mapping the oxidation parameter space again but with a narrower focus based on the results of the experimental designs with the Dralon L. Again, these oxidized fibers underwent density measurements, tensile testing, thermal measurements, and optical microscopy, and after the oxidation conditions were narrowed, carbonization experimentation began with an experimental design at first and iterations afterwards based on the results.

5.3 Experimental Methods

Sample Preparation
Precursor fibers were processed as received. The plasma oxidation and carbonization processing stages were conducted in a discontinuous manner and at different locations. The majority of plasma oxidation for this project was conducted with a small pilot-scale oven (MTR2) capable of continuous processing. The MTR2 includes 4 heated modules as well as roller drives for controlling fiber tension. A smaller number of OPF samples were prepared with a commercial scale plasma oxidation oven test module, which featured a single thermal zone. Low temperature (LT) and high temperature (HT) carbonization stages were conducted sequentially using a single lab-scale furnace. Plasma OPF was first passed through the furnace for LT processing, then wound, and passed through the furnace again for HT processing. Most carbon fiber samples were collected and tested 'raw' without further surface finishing (i.e. surface treatment or sizing). Finishing was applied only to samples that were to be tested in a full-tow format (ASTM D4018), in which case a lab-scale surface treatment unit (4XT), sizing unit (Izumi Int.), and dryer (4XT) were used.

Generally, careful handling was applied to all fiber samples (i.e. – no twisting, excessive bending, etc.) to prevent unnecessary damage to the fibers. Short fiber samples (<10 inches) were stored separately in plastic bags. Each end of a sample was taped to prevent scattering. Long fiber samples (>10 inches) were spooled on paper cores, and the samples were stored and transported separately in plastic bags in order to prevent damage.

It should be noted that in a commercial scale carbon fiber production line, the different stages of the conversion occur continuously without winding in between stages. Without a full line of conversion equipment available for this project, intermediate winding and unspooling was required after plasma oxidation and low temperature carbonization stages, respectively. However, there is no limitation that would prevent plasma oxidation from operating continuously in a full line of conversion equipment. That being said, intermediate winding introduces some unknowns, including damage to the fiber. Winding and unwinding can cause defects to the fiber surface, especially for unsized fibers, which can result in decreased mechanical performance of the final carbon fibers. Therefore, it is reasonable to conclude that the results obtained in this project could be improved by operation in a full continuous line.

Density

The skeletal mass density of all fiber types was measured with helium pycnometry. Prior to measuring, fiber samples were dried in a convection oven to remove residual moisture, followed by purging with helium gas. Helium pycnometer instruments included a Quantachrome 4500 (4XT/ORNL) and a Micrometrics 3212 (UTK).

Tensile testing

The tensile properties of single fiber filaments were measured using a Textechno Favimat outfitted with a 210cN load cell and a "Robot 2" automated sample loader. The gauge length was set to 25.4mm. A pretension to 0.7cN/tex was used for most tests. At least 15 filaments were tested per sample. Strand samples (ASTM D4018) were measured with a Shimadzu universal testing machine (UTM) equipped with a 10kN load cell. A gauge length of 6inches was used, and at least 12 specimens were tested per sample.

Thermal Measurements

Thermally induced transitions and associated weight loss were measured using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. 3 milligrams of fiber sample were used for the measurements.

Microscopy

Fiber cross-sections were imaged using optical microscopy, which was performed with either a Keyence 1234 at 100x magnification or a Keyence 1234 at 500-1000x magnification. To reveal radial morphology, thin films of embedded fiber cross-sections were prepared by vertically mounting fibers in epoxy followed by extensive surface polishing and finally slicing into 1- or 100-micron thick films using an Ultramicrotome.

5.4 Results and Discussion

5.4.1 Dralon L-Type Precursor

Handling and Processability Assessment

Figure 1 shows a 240k Dralon L-type precursor tow as well as its progression through the plasma oxidation. The heavy crimp is highly visible with the precursor, but during the early stages of plasma oxidation, it disappears. Overall, the L-type precursor processed well with plasma oxidation, despite its large size and its relatively low polymer molecular weight and high polydispersity. The fiber was resilient to exothermic runaway (i.e. few burns and line breaks) over a wide range of process conditions. Moreover, this textile-grade PAN precursor required relatively short residence times (from 45 to 60mins) to hit a target density of 1.36 g/cc, compared to conventional oxidation of a standard carbon fiber PAN precursor[1].

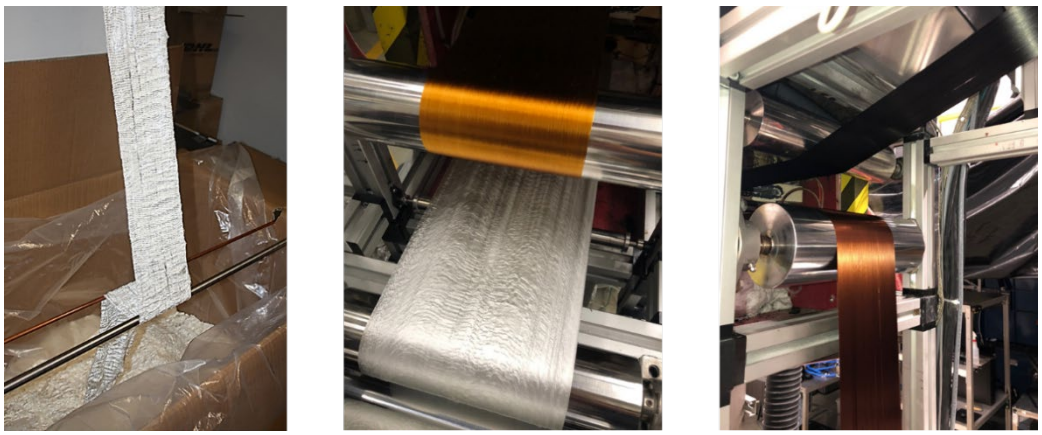

Figure 1. In-process photos of Dralon L-type fiber undergoing plasma oxidation

Radial Morphology

During the oxidation stage, the precursor fiber undergoes chemical and structural changes. As the new microstructure sets up, the diffusion of oxygen into the fiber becomes increasingly limited. As a result, the final oxidized fiber usually features a conversion gradient in the radial dimension, a phenomenon commonly referred to as the skin-core structure. In this case, the outer skin region of a filament is more reacted than the interior core regions. This shows up as transparency differences among the regions when using optical microscopy to image thin cross-sections of fiber (Figure 2).

[1] Note, textile-grade PAN typically takes much longer to oxidize compared to standard precursors for CF manufacturing.

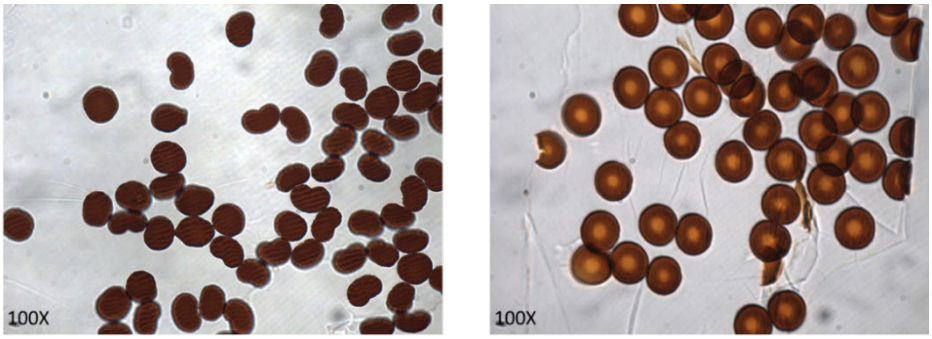

Figure 2. Optical microscopy images of OPF cross-sections showing radial morphology. (LEFT) plasma oxidized Dralon L-type precursor, (RIGHT) commercial OPF. Credit UTK.

In the case of the commercial OPF sample used as a baseline reference, the skin-core structure is highly pronounced, with several layers being discernible. In contrast, the plasma oxidized Dralon L-type material has no visible signs of an apparent skin-core structure. In theory, this is a special effect of the plasma oxidation process. Whereas conventional oxidation relies on bulky molecular oxygen in air to react and diffuse into the fiber, plasma oxidation has smaller oxygen radicals and ionic species that can more readily diffuse into the fiber. The result is a more homogeneous conversion in the radial dimension of the fiber.

Plasma oxidation is not the only factor affecting the skin-core structure. The commercial OPF sample was prepared from a commercial PAN precursor, while the plasma OPF sample was prepared from the textile-grade Dralon L-type precursor. These two fibers have vastly different polymers and average molecular weights; the commercial PAN precursor has an average molecular weight 2-4 times higher than the Dralon precursor. Accordingly, it is not entirely accurate to assume that plasma oxidation, if applied to the commercial PAN precursor, would be free of an apparent skin-core structure. A follow-up study should consider applying plasma oxidation to the commercial PAN precursor or apply conventional oxidation to the Dralon L-type precursor.

Parametric Oxidation Study with the L-Type Precursor

In the first part of the project, the team conducted a parametric study of plasma oxidation process conditions using the Dralon L-type precursor. The goal of this study was to derive correlations between plasma OPF properties (e.g. density) and the plasma oxidation process conditions (e.g. temperature), which could allow for the development of predictive models and later optimization. Likewise, the OPF properties could also be used to correlate to the resultant carbon fiber properties. To accomplish this, the team developed and executed a design of experiments. The property feedback for OPF samples included density (helium pycnometry), remnant heat (DSC), thermally induced weight-loss (TGA), and crystal structure composition (XRD). This data is found in Table 2, and details regarding the interpretation of these results are provided in the Appendix.

Table 2. L-type OPF property data

ID	Density (g/cc)	XRD		TGA[2]			DSC	
		$A_{17°}/A_{25°}$	Stabilization Index[1] (%)	300°C	450°C	900°C	T_p (°C)	ΔH (J/g)

RM30	1.3726	0.112	87.2	93.6	83.6	46.4	394.2	-119.8
RM31	1.3348	0.481	45.5	93.9	79.4	50.7	386.1	-247.4
RM32	1.3442	0.511	42.2	92.6	78.5	55.3	384.3	-243.5
RM33	1.3524	0.337	61.9	91.1	75.9	56.2	383.5	-178.7
RM34	1.3615	0.236	73.2	92.9	80.1	47.0	387.4	-144.5
RM35	1.3364	0.138	84.3	91.2	79.1	53.3	387.3	-132.7
RM36	1.3364	0.380	56.9	93.6	79.9	56.9	380.8	-180.3
RM37	1.3468	0.172	80.5	91.7	77.0	49.6	381.7	-158.7
RM38	1.3658	0.114	87.4	91.5	77.1	53.3	382.8	-161.1
RM39	1.3936	0.101	88.5	90.9	77.5	52.5	382.0	-124.8
RM40	1.3871	0.083	90.6	91.2	79.0	55.7	387.1	-100.9
RM41	1.3726	0.189	78.5	92.1	78.6	57.0	388.2	-114.4
RM42	1.3606	0.149	83.0	92.2	80.8	44.4	387.2	-103.5
RM43	1.3641	0.373	57.7	94.2	80.4	51.0	386.9	-142.7
RM44	1.3472	0.400	54.7	93.8	79.8	55.9	387.5	-147.5
RM45	1.3877	0.092	89.6	91.6	78.7	56.4	385.4	-96.7

[1] Stabilization index based on XRD peak ratios. See the appendix for more information.
[2] % mass remaining at a given temperature.

Dralon L-type Carbon Fibers

Table 3 includes a summary of the best carbon fiber samples prepared from plasma oxidized Dralon L-type fibers. Despite the large number of OPF samples prepared as part of the parametric plasma oxidation study, only 4 samples underwent carbonization, mostly due to the low quality of the initial results. Of these carbon fibers, the best carbon fiber sample had average tensile properties of 416 ksi break strength, 25 Msi modulus, and 1.66% break strain. The range of average properties for all of the carbon fiber samples was 349-416 ksi for break strength, 20-25 Msi for modulus, and break strains of 1.38-1.76%. The majority of samples had break strengths of <400 ksi.

While these carbon fiber results fulfilled Milestones 2 & 3, the Dralon L-type precursor had many disadvantages that ultimately led the project team to discontinue trialing with it. Although the heavy crimp in the L-type precursor fiber appeared to disappear during plasma oxidation, it was found to persist at a microscopic level, ending up in the resultant carbon fibers. During tensile testing, the carbon fibers would often fail at the site of the heavy crimp, which means the crimp is a defect limiting the performance of the carbon fiber. Second, the best performing carbon fibers had small equivalent diameters (~ 5um), which is undesirable for a variety of reasons. Finally, the 240k tow format was not ideal for the lab-scale plasma oxidation oven.

Fortunately, while the team was trialing the L-type material, Dralon was working on another fiber (X-type), which was more appropriate for carbon fiber conversion and lab-scale testing. As soon as the X-type precursor fiber became available (Dec. 2018), the team switched over and

began working exclusively with this precursor.

Table 3. Single filament tensile properties of carbon fibers samples prepared from plasma oxidized Dralon L-type precursor fibers

OPF Sample ID	CF Sample ID	Break Stress (ksi)		Diameter (μm)		Modulus (Msi)		Break Strain (%)	
		Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
A	473	349.3	65.6	6.65	0.54	20.60	2.11	1.64	0.24
A	474	370.0	42.1	6.59	0.55	20.73	2.34	1.74	0.18
B	577	372.0	50.9	6.28	0.83	23.15	0.60	1.57	0.19
B	580	407.0	48.2	6.67	0.46	22.48	0.62	1.68	0.19
MTR20359.1.W	707	359.1	47.8	5.62	0.24	22.46	0.65	1.55	0.18
MTR20359.1.W	735	402.9	50.9	5.79	0.40	22.06	0.50	1.76	0.20
MTR20387.1.W	843	378.4	67.0	5.56	0.33	22.94	0.71	1.60	0.27
MTR20389.1.E	891	356.5	84.1	5.17	0.54	25.03	1.87	1.38	0.27
MTR20389.1.E	903	416.0	71.1	5.08	0.58	24.21	2.30	1.66	0.28

5.4.2 Dolan X Precursor

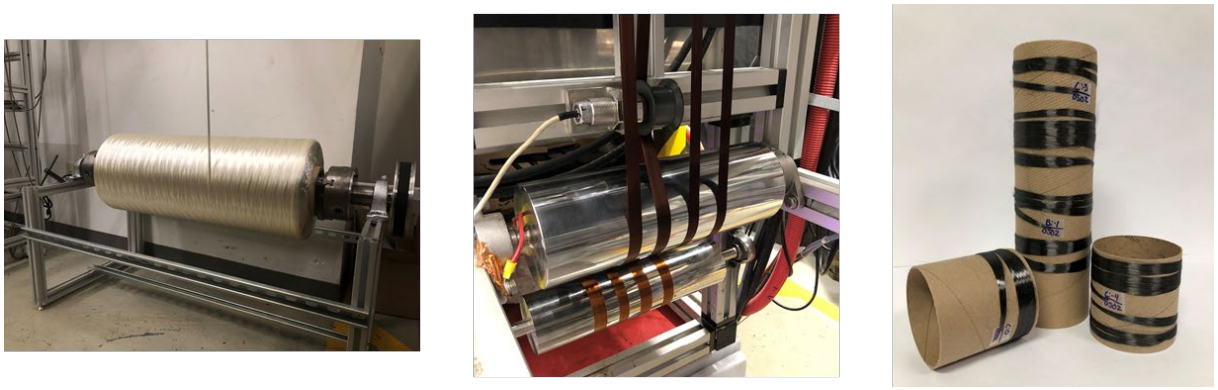

Figure 3. Photos of Dolan X-type fiber. Left-to-right: Precursor bobbin, plasma oxidation processing (4x tows), samples of resultant carbon fibers

Handling and Processability Assessment

The Dolan fibers were packaged as uncrimped tows wound on bobbins, and the tow sizes ranged from 10-30k (Table 1). From a processing and handling standpoint, the Dolan fibers had many advantages over the L-type precursor. In general, the package and tow format were much more appropriate for the processing with the team's lab-scale equipment (See Figure 3). Most notably, the tow did not require splitting prior to carbonization.

As with the L-type, the Dolan fibers ran smoothly through the plasma oxidation process, with very few burns or breaks occurring over a wide range of process conditions. Additionally, residence times for oxidation were reasonable, averaging 50-60mins to achieve a 1.36 g/cc. That said, the oxidation residence time was highly dependent on the starting titer of the precursor, with larger titers requiring longer residence times.

Radial Morphology of Plasma OPF

Figure 4 presents the cross-sections of various plasma OPF samples observed using optical microscopy. Of the plasma OPF samples analyzed with optical microscopy[2] all showed the presence of a skin-core structure, defined by transparency differences in the radial direction. Among the samples, some variations in the skin-core structure could be observed, most notably the relative ratio of skin to core area. The differences could be correlated to plasma oxidation processing conditions. Despite improved gas diffusion associated with plasma oxidation [19], plasma OPF produced from the Dolan X precursor fibers still showed defined skin-core structures.

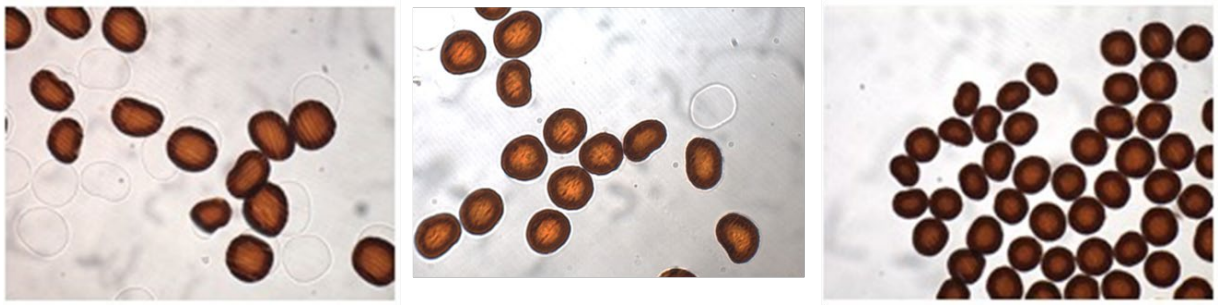

Figure 4. Optical microscopy images of plasma OPF cross-sections showing radial morphology. From left-to-right: Dolan 5.5dtex (1.3623 g/cc), Dolan 5.5dtex (1.3610 g/cc), Dolan 3.0dtex (1.3737 g/cc)

Dolan X-type Carbon Fiber

Nearly 200 carbon fiber samples were prepared from 22 different plasma OPF samples made with Dolan precursor fibers. The single-filament tensile properties of the best performing carbon fiber samples are listed in Table 4.

Most of the samples were prepared from the 5.5dtex Dolan fibers. Only a handful were made with the 3.0 and 9.0 dtex precursors, respectively. The project team decided to focus on the 5.5dtex because it produced carbon fibers with equivalent diameters in the range of 8-9.5 um. These diameters are larger than commercial carbon fibers, adding an additional novelty that became the focus of commercial partners. The best all-around sample had an average break strength of 469.3 ksi, tensile modulus of 33.62 Msi, break strain of 1.36%, and a diameter of 8.68 um.

[2] Only a limited number of the total OPF samples produced during this project were analyzed for radial morphology. Preparing these specimens is a labor-intensive process, and the project team did not have the resources to analyze every sample.

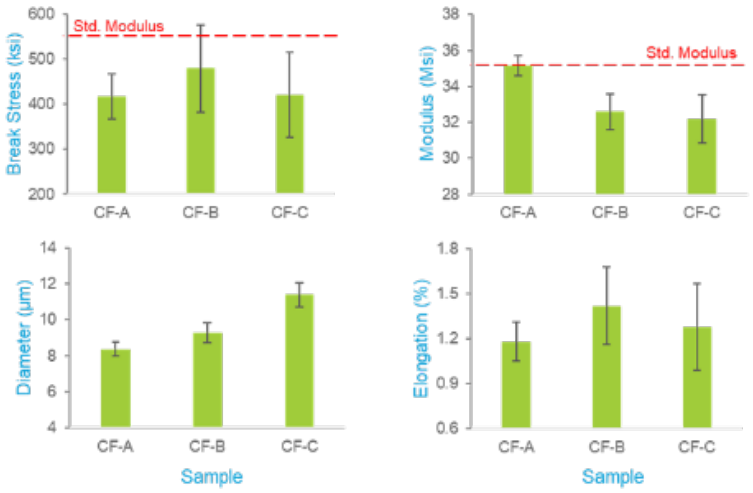

Figure 5. Single filament tensile properties of the best carbon fiber samples produced during this project. Standard modulus carbon fiber baselines are red dashed lines.

Table 4. Single filament tensile properties of carbon fibers produced from plasma oxidized Dolan precursor fibers

CF ID	Precursor dtex	Break Stress (ksi)		Diameter (µm)		Modulus (Msi)		Break Strain (%)	
		Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
1011	3.0	481.2	26.7	6.86	0.17	29.38	1.50	1.59	0.13
1013	3.0	463.1	20.6	6.65	0.53	29.43	0.37	1.53	0.07
1014	3.0	476.4	59.9	7.19	0.69	31.50	1.60	1.47	0.14
1276	5.5	460.7	36.3	8.26	0.40	33.64	0.51	1.34	0.10
1283	5.5	443.9	71.7	8.04	0.58	34.36	0.84	1.27	0.20
1286	5.5	417.3	49.6	8.36	0.39	35.13	0.55	1.18	0.13
1308	5.5	447.1	53.5	8.28	0.48	34.00	0.91	1.28	0.14
1399	5.5	469.3	87.4	8.68	0.80	33.62	1.61	1.36	0.23
1407	5.5	460.3	81.4	8.68	0.63	31.94	0.95	1.40	0.23
1745	5.5	463.8	57.7	8.76	0.71	33.14	1.08	1.36	0.17
1783	5.5	469.3	69.7	9.08	0.57	32.68	1.38	1.39	0.18
1823	5.5	462.4	86.2	9.33	0.62	32.87	1.91	1.37	0.23
1881	5.5	479.4	97.4	9.28	0.55	32.60	0.99	1.42	0.26
1788	9.0	420.8	93.8	11.39	0.68	32.19	1.36	1.28	0.29

Process Consistency

After achieving the tensile properties of sample 1399, the next step was to verify these results by replicating the sample. In addition, the full-tow tensile properties (ASTM D4018) would also be tested. Compared to single filament testing, full-tow tensile testing can reveal much higher tensile properties, particularly break strength. In some cases, the break strength of the full tow can be 10-50% greater than the values from single filament testing. In the case of sample 1399,

the full tow break strength could easily have been 550ksi or greater, which would achieve the ultimate milestone for the project.

Unfortunately, after reproducing a fiber sample using the same plasma oxidation and carbonization conditions used for sample 1399, the replicate carbon fiber sample (451) had lower tensile properties than 1399 (Table 5 and 6). Upon analysis of the process data (e.g. temperature profile), differences in the plasma oxidation process between the original and replicate sample runs were identified. It was determined that the variance in the conditions was attributable to issues with the prototype plasma oxidation equipment. The next several months were spent correcting for these issues with significant upgrades to the equipment. This included replacing broken or missing insulation pieces, adding additional process monitoring (e.g. thermocouples), and adding controls for the exhaust system.

The equipment retrofits were completed just a few months before the end of the project. An attempt to replicate sample 1399 was successful (Table 7). Unfortunately, the project ended before more parametric optimization work could be completed.

Table 5. Full-tow tensile properties (ASTM D4018) of carbon fibers produced from plasma oxidized Dolan precursor fibers

	Break Stress (ksi)				Modulus (Msi)				Failure Strain (%)			
ID	Avg	Std	Max	Min	Avg	Std	Max	Min	Avg	Std	Max	Min
451.A	366	21	390	330	33	0.4	33	32	1.09	0.06	1.16	0.99
451.B	386	23	424	350	32	0.6	33	32	1.17	0.06	1.24	1.04

Table 6. Single filament tensile properties of replicate samples of plasma OPF and carbon fibers

ID	Material Density (g/cc)	Break Stress (ksi)		Diameter (µm)		Modulus (Msi)		Break Strain (%)	
		Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
1351	1.3636	39.9	2.9	15.88	0.89	1.16	0.02	14.81	2.90
1347	1.3681	41.7	2.8	14.28	1.07	1.19	0.02	13.96	2.58
1399	1.7453	469.3	87.4	8.68	0.80	33.62	1.61	1.36	0.23
451	-	382.9	64.8	8.08	0.44	33.51	0.71	1.13	0.18

Table 7. Carbon fiber Single filament tensile properties of a replicate sample produced after maintenance and upgrades to the plasma oxidation oven.

ID	Date	Break Stress (ksi)		Diameter (µm)		Modulus (Msi)		Break Strain (%)	
		Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
1399	Pre-retrofit	469.3	87.4	8.68	0.80	33.62	1.61	1.36	0.23
1745	Post-retrofit	463.8	57.7	8.76	0.71	33.1	1.1	1.36	0.17

Update on 12/3/21: Since the end of this project, most of the sources of inconsistencies have

been resolved through hardware modification or process optimization. 4XT is actively working on an improved electrode design and fabrication method that will resolve the final issue, which was a robustness issue with their performance. This has been verified through the production of 1000 meter runs of oxidized material that was subsequently carbonized at the CFTF achieving standard modulus properties. Since the conclusion of this project, 4M has produced carbon fiber at CFTF from textile-grade acrylic fiber with an average break strength of 527 ksi, tensile modulus of35 Msi and 9.2 um diameter, which is an improvement on the properties achieved in this IACMI sponsored project. Further optimization work continues. .

6. BENEFITS ASSESSMENT

There were several benefits of this project, which while not meeting the full targets in the planned scope are but still tremendously beneficial to this research:

1. **Textile-grade precursor:** Although the target tensile properties were not achieved, the researchers achieved better carbon fiber properties than anyone else has, and there is substantial evidence suggesting that these properties can and will be achieved with this precursor using plasma oxidation. The addition of surface treatment and sizing will increase the average tensile properties, and testing the full tow, as is done in industry, has also been shown to yield higher properties than the single filament testing performed in this project.

2. **Large-diameter carbon fiber:** Using plasma oxidation, large-diameter carbon fiber was produced using oxidation times similar to conventional oxidation times used to produce conventional diameter carbon fibers. The effects this larger-diameter carbon fiber will have on composite properties are yet unknown because they have never been produced at a scale useful for producing or testing composites. However, it has been theorized that large-diameter carbon fibers will greatly increase the compressive strength of composites. There is currently a study underway at ORNL to test this theory.

3. **Heavy crimping:** It was discovered that conventional heavy crimping often used in textile fiber production damages the fibers beyond superficial appearances. Although the crimp is no longer visible after the first of four modules in the plasma oxidation oven, the effects appear to propagate through the entire conversion process and produce an inferior carbon fiber. This is an important discovery for future work with textile precursors.

4. **Plasma oxidation process:** The in-depth analysis of OPF produced using the plasma oxidation oven at 4XT showed several inconsistencies in processing that were previously unknown. This led to plasma oxidation hardware changes including increased temperature measurement locations, improved insulation, and fixtures to ensure consistent, repeatable air flow in the oven. These upgrades improved process repeatability from run to run and consistency during long processing runs. They also enhanced the understanding of the plasma oxidation process and future oven design. This undoubtedly advanced commercialization efforts well beyond what would have been possible without the testing capabilities of ORNL and UTK.

7. COMMERCIALIZATION

4M Carbon Fiber Corp., an affiliate of 4XTechnologies, is currently in the planning stages of its pilot-scale carbonization line demonstrating plasma oxidation to the industry at scale. The size of this line has not been determined, but it will be > 250aMT of carbon fiber. Several major carbon fiber manufacturers have engaged with 4M and are waiting on demonstration at the pilot scale, and therefore the pilot plant represents a barrier of entry for 4M into the carbon fiber market. 4M is currently in the fundraising stage for the plant and expects to begin construction later this year (2020). 4M will license plasma oxidation technology to new and existing carbon fiber manufacturers and support these manufacturers in the application of its technology.

As evidenced in the Benefits Assessment, this project has greatly improved the commercialization prospects of plasma oxidation and textile-grade precursor.

1. **Textile-grade precursor:** Prior to this work, no one had ever gotten close enough to industrial-grade carbon fiber properties using low-cost precursors, such as textile-grade, for it to be considered a viable option for commercialization. This work proved that industrial-grade carbon fiber can be made using textile-grade precursor. This has already led to several new potential partner engagements, as well as new commercial prospects for Dralon as a carbon fiber precursor supplier. The notion of a low-cost precursor that can lead to standard modulus carbon fiber properties is very synergistic with the cost saving aspects of plasma oxidation, and this has increased the value proposition for carbon fiber manufacturers looking to adopt it.

2. **Large-diameter carbon fiber:** As mentioned above, large-diameter carbon fiber may be very beneficial for carbon fiber applications that require high compressive strength. However, the greatest commercial benefit is the higher mass throughput that could be achieved at higher diameters in precursor production and conversion to carbon fiber. This would greatly decrease the cost of the precursor spinning process, oxidation, and carbonization, therefore greatly decreasing the cost of the resultant carbon fiber. This has also garnered attention from investors and commercialization partners.

3. **Plasma oxidation process:** The importance of the increased repeatability and consistency achieved in the plasma oxidation process during this project cannot be overstated. The lessons learned are and will be critical to the next (and future) plasma oxidation oven designs. Without this work, the commercialization of plasma oxidation may have been set back years.

The results of this project have engaged new potential partners, progressed discussions with existing ones, and improved the technical understanding of the plasma oxidation process. 4M is now better positioned than ever to commercialize this technology.

8. ACCOMPLISHMENTS

Although the final target tensile strength was not reached for this project, 4M considers it a commercial success. The research team was able to successively improve the carbon fiber properties for this precursor and believes that the target tensile strength (550 ksi) and modulus (35 Msi) will be achieved with this precursor using plasma oxidation. There are no publications or patents yet from this work, but there may be several in the future. Additionally, there were at least three major technical achievements. They are as follows:

- Carbon fiber with tensile properties of 469 ksi and 33.6 Msi were produced from textile-grade PAN precursor. To the authors' knowledge, these are the best properties ever achieved with textile-grade precursor.

- Carbon fibers were produced with diameters up to 11 μm. These are the largest diameter carbon fibers ever produced in a continuous process.

- Oxidation residence time below 60 mins for 8.5 μm carbon fiber. While the conventional oxidation residence time is unknown for this diameter of carbon fiber, researchers at ORNL estimate well over 4 hrs.

9. CONCLUSIONS

This project was a resounding success despite not achieving the final target tensile properties (550 ksi strength and 35 Msi modulus) during the period of performance. The limitations of different textile-grade precursors were discovered. The achieved properties of 469 ksi tensile strength and 33.6 tensile modulus are the best properties ever achieved with continuous processing of textile-grade precursor, and it is likely that the target properties will be achieved in the near future. Additionally, significant technical achievements were made in the field of large diameter carbon fiber, and the commercial readiness of the plasma oxidation process was greatly enhanced.

Through the course of the project, two varieties of textile-grade precursor were tested (Table 1). The large, crimped bales of precursor fiber (Dralon L) did not produce satisfactory carbon fiber mechanical properties, however this was determined to be due to the consistent tensile failure at the site of the heavy crimp. This led to the testing of another variety of textile fiber (Dolan X), supplied as an uncrimped tow spooled on a bobbin that was used to produce satisfactory carbon fiber throughout the remainder of the project. We, therefore, conclude that textile-grade precursor must contain a light or no crimp to be effective as a carbon fiber precursor.

Based on our extensive experimental matrix, we can also conclude that the maximum tensile strength for this precursor polymer is likely around the target of 550 ksi with a tensile modulus around 36 Msi. Prior research suggests that these will be achieved with the addition of surface treatment, sizing, and full-tow testing. It is well known that surface treatment and sizing of carbon fiber both increase tensile properties. Additionally, full tow testing is the standard in the industry, and tensile properties can be expected to increase by at least another 10% as compared

to the single filament testing used in this research. It is expected that with surface treatment and full tow testing these properties will be achieved.

Although not part of the scope of this project, we can also conclude that plasma oxidation can oxidize larger diameter precursor at a reasonable rate for carbon fiber production. Indeed, a 5 dtex precursor was oxidized in about 60 min which puts it on the lower end of oxidation times for conventional precursor with 1.2 dtex precursor (a standard size). The conventional oxidation residence time of the 5 dtex precursor is unknown, but theory suggests this time will be well over 4 hours for oxidation alone.

Finally, we can conclude that this project's benefits to the commercialization of plasma oxidation were tremendous. Without the in-depth analysis performed by the researchers at UTK and ORNL, 4XT would not have known about the repeatability and inconsistency issues that were uncovered in this project. Because of the continued support from UTK and ORNL and the iterative nature of the testing and improvements, the team was able to improve the repeatability and consistency of not only the lab-scale oxidation oven but also improve the designs of the pilot and production scale ovens. Overall, this was an invaluable project.

10. RECOMMENDATIONS

The research team recommends continued work with this precursor including surface treatment and full-tow testing. Research has shown that surface treatment removes surface defects that can propagate through a filament decreasing its tensile properties. Once removed, the tensile properties are increased. Sizing is used to prevent damage to the fiber while winding and handling. This damage can also decrease tensile properties. Full-tow testing is the industry standard for tensile testing of carbon fiber properties, and it is known to increase average tensile properties significantly. The addition of these to the combination of textile-grade precursor and plasma oxidation are likely to push the properties closer to their optimum, and the research team believes these properties will exceed the targets of 550 ksi for tensile strength and 35 Msi for tensile modulus. In fact, a CRADA is already underway between 4M and the Carbon Fiber Technology Facility at ORNL to perform that work. 4XT continues to plasma oxidize this precursor for that effort.

Once the carbon fiber has been optimized during the CRADA, it is recommended that 4M generate a cost model for this product at industrial-production scale. With this information, they should then reach out to automotive parts manufacturers to determine what quantities of carbon fiber would be sufficient for initial parts testing. Then 4XT and the CFTF can produce these fibers and submit them for testing by the parts manufacturers. The authors believe this to be the quickest way to achieve buy-in from the automotive industry.

11. REFERENCES

Cited References

[1] S. Atkiss and M. Maghe, “PRECURSOR STABILISATION PROCESS,” WO2019/071286.
[2] X. Qin, Y. Lu, H. Xiao, and Y. Song, “Improving stabilization degree of stabilized fibers by pretreating polyacrylonitrile precursor fibers in nitrogen,” Materials Letters, vol. 76, pp. 162–164, Jun. 2012, doi: 10.1016/j.matlet.2012.02.103.
[3] S. Park, H.-S. Kil, D. Choi, S.-K. Song, and S. Lee, “Rapid stabilization of polyacrylonitrile fibers achieved by plasma-assisted thermal treatment on electron-beam irradiated fibers,” Journal of Industrial and Engineering Chemistry, vol. 69, pp. 449–454, Jan. 2019, doi: 10.1016/j.jiec.2018.10.008.
[4] S. H. Yoo et al., “Facile method to fabricate carbon fibers from textile-grade polyacrylonitrile fibers based on electron-beam irradiation and its effect on the subsequent thermal stabilization process,” Carbon, vol. 118, pp. 106–113, Jul. 2017, doi: 10.1016/j.carbon.2017.03.039.
[5] W. Zhao et al., “Effects on the oriented structure and mechanical properties of carbon fibers by pre-irradiating polyacrylonitrile fibers with γ ray,” Journal of Materials Science, vol. 51, no. 15, pp. 7073–7084, Aug. 2016, doi: 10.1007/s10853-016-9875-x.
[6] M. S. Morales and A. A. Ogale, “Carbon fibers derived from UV-assisted stabilization of wet-spun polyacrylonitrile fibers,” Journal of Applied Polymer Science, vol. 131, no. 16, p. n/a-n/a, Aug. 2014, doi: 10.1002/app.40623.
[7] A. Y. Jo, S. H. Yoo, Y.-S. Chung, and S. Lee, “Effects of ultraviolet irradiation on stabilization of textile-grade polyacrylonitrile fibers without photo-initiator for preparing carbon fibers,” Carbon, vol. 144, pp. 440–448, Apr. 2019, doi: 10.1016/j.carbon.2018.12.012.
[8] C. Zhang et al., “Hydrogen peroxide modified polyacrylonitrile-based fibers and oxidative stabilization under microwave and conventional heating – The 1st comparative study,” Ceramics International, vol. 45, no. 10, pp. 13385–13392, Jul. 2019, doi: 10.1016/j.ceramint.2019.04.035.
[9] F. L. Paulauskas, T. White, and D. M. Sherman, “APPARATUS AND METHOD FOR OXIDATION AND STABILIZATION OF POLYMERIC MATERALS,” US 2009/0263295 A1, 22-Oct-2009.
[10] F. L. Paulauskas and D. M. Sherman, “APPARATUS AND METHOD FOR STABILIZATION OR OXDATION OF POLYMERIC MATERALS,” US7649078B1, 2010-2019.
[11] S.-W. Lee et al., “Efficient preparation of carbon fibers using plasma assisted stabilization,” Carbon, vol. 55, pp. 361–365, Apr. 2013, doi: 10.1016/j.carbon.2012.10.062.
[12] J. Liu, S. Xiao, Z. Shen, L. Xu, L. Zhang, and J. Peng, “Study on the oxidative stabilization of polyacrylonitrile fibers by microwave heating,” Polymer Degradation and Stability, vol. 150, pp. 86–91, Apr. 2018, doi: 10.1016/j.polymdegradstab.2018.02.017.
[13] J. Liu, “Microwave treatment of pre-oxidized fibers for improving their structure and mechanical properties,” Ceramics International, p. 6, 2019.
[14] J. Sloan, “4M reveals progress with plasma oxidation for carbon fiber production,” CompositesWorld, Mar. 05, 2020.
[15] L. Kong, H. Liu, W. Cao, and L. Xu, “PAN fiber diameter effect on the structure of PAN-based carbon fibers,” Fibers Polym, vol. 15, no. 12, pp. 2480–2488, Dec. 2014, doi: 10.1007/s12221-014-2480-1.
[16] F. L. Paulauskas and T. Bonds, “Atmospheric pressure plasma processing of polymeric

materials utilizing close proximity indirect exposure," US 9,447,205 B2, Sep. 20, 2016.
[17] F. Paulauskas, "Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers," presented at the 2015 U.S. Department of Energy Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington D.C., Jun. 11, 2015.
[18] F. Paulauskas, "Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers," presented at the 2014 U.S. Department of Energy Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington D.C., Jun. 17, 2014.
[19] X. Guo et al., "New insights into orientation distribution of high strength polyacrylonitrile-based carbon fibers with skin-core structure," Carbon, vol. 109, pp. 444–452, Nov. 2016, doi: 10.1016/j.carbon.2016.08.022.

Additional References

[20] X. Huang, "Fabrication and Properties of Carbon Fibers," Materials, vol. 2, no. 4, pp. 2369–2403, Dec. 2009, doi: 10.3390/ma2042369.
[21] Y. Gong, R. Du, G. Mo, X. Xing, C.-X. Lü, and Z. Wu, "Nanostructural hereditability in polyacrylonitrile based fibers studied by small angle X-ray scattering," Polymer, vol. 153, pp. 485–497, Sep. 2018, doi: 10.1016/j.polymer.2018.08.034.
[22] X. Guo, K. Zhang, J. Cheng, H. He, L. He, and J. Xu, "TEM study on the inhomogeneity of oxygen diffusion distances in single polyacrylonitrile-based carbon fibers," Applied Surface Science, vol. 475, pp. 571–576, May 2019, doi: 10.1016/j.apsusc.2018.12.268.
[23] L. Sun, L. Shang, L. Xiao, M. Zhang, Y. Ao, and M. Li, "The influence of stabilization efficiency on skin–core structure and properties of polyacrylonitrile fibers," J Mater Sci, vol. 55, no. 8, pp. 3408–3418, Mar. 2020, doi: 10.1007/s10853-019-04257-2.
[24] H. A. D. Ashtiani and R. E. Farsani, "High performance fibers production process using Taguchi experimental design," Fibers and Polymers, vol. 12, no. 8, pp. 1054–1061, Dec. 2011, doi: 10.1007/s12221-011-1054-8.
[25] S. Nunna, M. Maghe, S. Fakhrhoseini, B. Polisetti, and M. Naebe, "A Pathway to Reduce Energy Consumption in the Thermal Stabilization Process of Carbon Fiber Production," Energies, vol. 11, no. 5, p. 1145, May 2018, doi: 10.3390/en11051145.

12. APPENDIX

DSC and TGA Data Interpretation

Carbon fiber conversion is based on the thermally induced changes on PAN precursor fibers. Thermal analysis methods, including DSC and TGA provide key insights about the nature and extent of these changes at the various stages of the conversion process.

The primary thermally induced reaction in PAN precursor is the cyclization reaction of the pendant nitrile groups, which forms the characteristic infusible ladder polymer structure of oxidized/stabilized PAN fiber (OPF). The reaction is highly exothermic, and its heat flow is readily measured with DSC (Figure 6). For L-PAN precursor used in this project, the cyclization reactions begin at around 303°C and occur up to 400°C (Figure 6). The peak of the exothermic reactions occurs at around 348°C, as indicated by the maximum heat flow measured. The area under the exotherm curve is the enthalpy of cyclization (ΔH). Once the L-PAN polymer is stabilized with plasma oxidation, the thermogram curve changes, and the peak heat flow is greatly reduced compared to the virgin precursor. The remaining ΔH is a useful measurement for comparing the extent of oxidation among OPF samples.

After the precursor PAN is stabilized, the resultant OPF then undergoes low temperature carbonization, which occurs in an inert atmosphere at temperatures up to 900°C. During this stage, the OPF loses about half of its mass, as non-carbon impurities are evolved, and the fiber assumes a pseudo graphitic structure. The mass loss of the OPF in this stage is one indicator of the OPF quality, and it is commonly measured with TGA analysis (Figure 6).

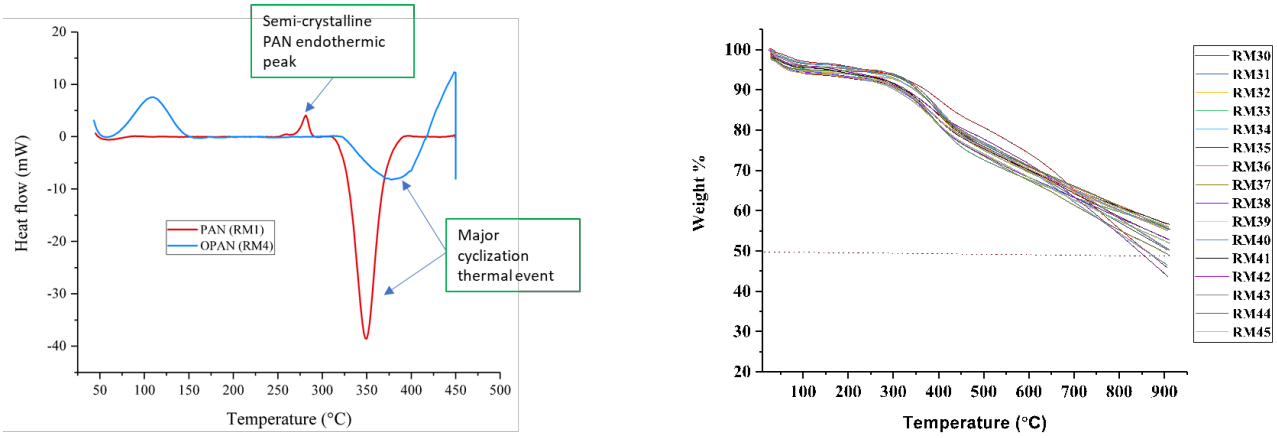

Figure 6. Thermal analysis. (LEFT) DSC thermograms and (RIGHT) TGA weight loss curves for various plasma OPF Dralon-L samples. Credit UTK.

XRD Data Interpretation

Wide angle X-ray diffraction (XRD) provides information about the evolution and changes to the microstructure of fibers that occur during the carbon fiber conversion process. It can reveal the presence and relative amounts of different amorphous and crystalline phases and subgroups therein, which are differentiated according to the amount of X-rays diffracted at different angles (Figure 7).

In the case of PAN precursor and OPF, the primary diffraction angles include $2\Theta = 17°$, $2\Theta = 25.5°$, and $2\Theta = 29°$ corresponding to the crystal planes 100, 002 and 110, respectively. The (100) plane is related to the micro-domain spacing of interlocking PAN polymer chains, the (002) plane corresponds to the hexagonal graphite type domain, and the 110 peak is related to the parallel domains of PAN polymer.

The most prominent peak for virgin PAN precursor occurs at 2Θ = 17°. After oxidation, the 2Θ = 17°peak becomes nearly nonexistent, because the PAN polymer is transformed into a networked ladder polymer that is mostly amorphous. However, the OPF does possess an early version of the graphitic domain, as evidenced by the rise of the peak at 2Θ = 25.5°.
The microstructural changes revealed by XRD can be used to quantify the extent of reaction that occurs from the precursor to the OPF. A so-called stabilization index (SI) can be calculated by ratioing diffraction peaks from the precursor and the OPF as follows:

$$SI = (A_{16°}/A_{25°})_{precursor} - (A_{16°}/A_{25°})_{OPF} / (A_{16°}/A_{25°})_{precursor} * 100$$

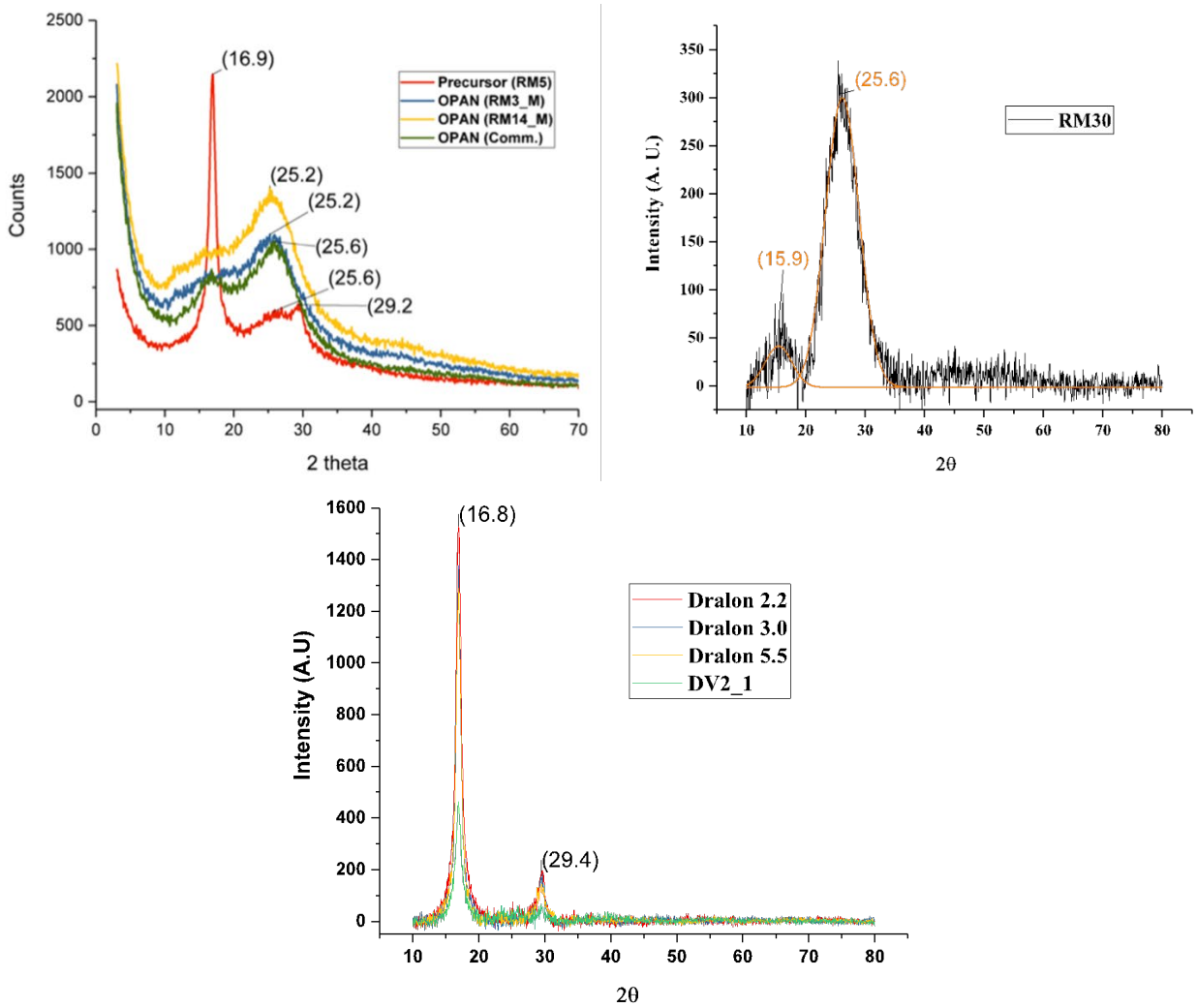

Figure 7. (TOP LEFT) XRD Spectra of various L-Type plasma OPF samples and a commercial OPF sample (TOP RIGHT) Curve fitting applied to the main feature of an WXRD spectrum of a plasma L-Type OPF sample (BOTTOM) XRD patterns of the different Dolan precursors as compared to the L-Type precursor. Credit UTK.

RAMAN Data Interpretation

Similar to XRD, RAMAN spectroscopy can provide information about the microstructure domains

present in carbon rich materials. The RAMAN spectrum of oxidized fiber includes a characteristic double hump feature occurring between 1000 and 1800 cm^{-1}. This is known as the D and G band. The hump at around 1350 cm^{-1} is the D band, and it corresponds to disordered domains of turbostratic structures, while the hump at 1580 cm^{-1} is attributable to ordered graphitic structures. The D/G band can be further decomposed into 4 sub-bands including a D" band near 1480cm^{-1}, which is attributable to a macro disorder domain.

In the case of OPF, the D/G band intensity ratio provides a means of comparing the state of the microstructure among samples.

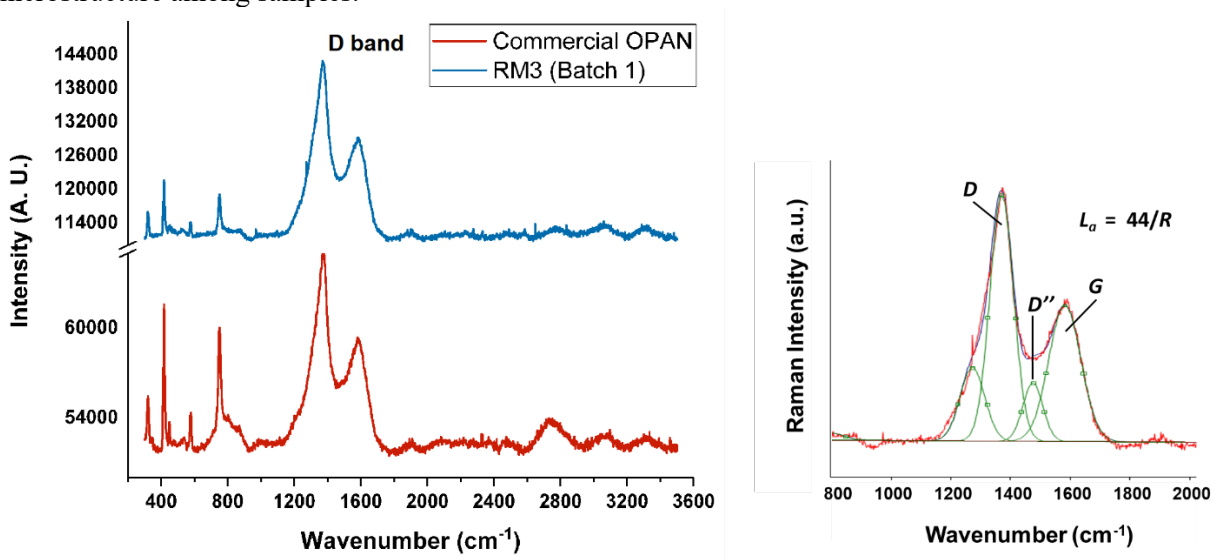

Figure 8. (LEFT) Raman spectra of a commercial OPF sample (bottom) and a plasma OPF sample (top, ID 'RM3'). (RIGHT) Raman spectrum showing cure fitting of D/G band feature. Credit UTK.

Table 8. Raman data. Credit UTK.

Sample ID	Wavenumber (cm^{-1})			$R=I_D/I_G$		La (nm)	
	D band	D" band	G band	Area	Height	Area	Height
RM3	1368	1472	1578	1.34	1.81	3.28	2.43
Comm. OPAN	1368	1472	1578	1.27	1.81	3.45	2.44

Single Filament Tensile Testing

Measuring tensile properties relies on the simultaneous measurement of elongation and axial pull force. During the test, a filament is pulled until failure. Depending on the stage of conversion, the material responds differently to axial stress (Figure 9). The precursor undergoes a characteristic plastic type deformation, while the carbonized fiber has a linear, brittle type response. Each material, precursor, OPF, and CF features a rapid failure, corresponding to a full separation of the continuous filament.

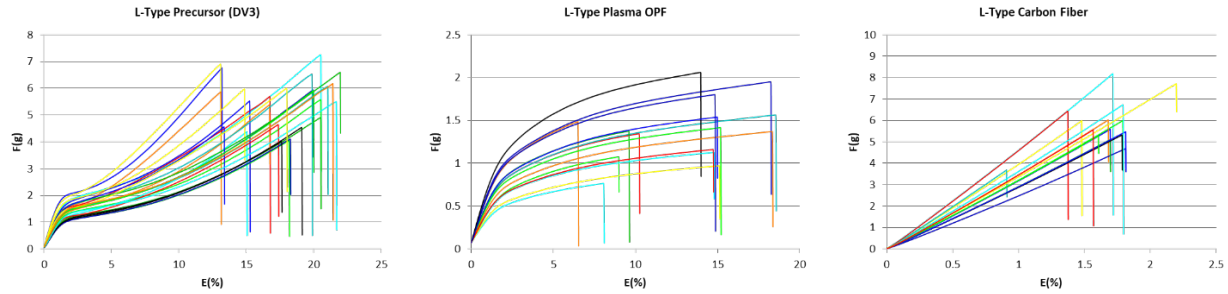

Figure 9. Favimat® generated force elongation curves. From left to right: Dralon L-type precursor, L-type plasma OPF, and L-type carbon fiber. Credit ORNL.