Developing a New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber

T. C. Mike Chung
Pennsylvania State University
302 Steidle Building
University Park, PA 16802
Phone: 814-863-1394
Email: tcc3@psu.edu

DOE Manager: Bahman Habibzadeh
Phone: 202-287-1657
Email: Bahman.Habibzadeh@ee.doe.gov

Contract No: DE-EE0008096

Project Start Date: September 1, 2017
Project End Date: August 31, 2020

Overall Objectives

- Reduce the cost of composite overwrapped pressure vessels (COPVs) by the combination of low-cost precursor, melt-spinning fiber process, low carbonization temperature, high mass yield, and high tensile strength.
- Develop a new polyolefin precursor that is melt-processible in forming fibers with good mechanical strength and high carbonization yield during the subsequent thermal conversion process to produce carbon fiber (CF).
- Prepare B-doped CF by co-carbonization with B-containing precursor, which can offer low carbonization temperature, high C yield, and high-tensile-strength CF products.

Fiscal Year (FY) 2019 Objectives

- Identify the most suitable precursors (from the precursor list with high C yields, developed in FY 2018) that are suitable for fiber-spinning operation (preferred melt fiber-spinning).
- Conduct a rheology study to find the best melt-processing condition (heating temperature and time) to spin the precursor fibers.
- Perform carbonization of the resulting precursor fibers to form carbon fibers and understand the thermal C transformation mechanism.
- Evaluate the resulting carbon fibers with X-ray diffraction (XRD), Raman, and other techniques.
- Collaborate with the Oak Ridge National Laboratory (ORNL) CF team through the LightMat consortium in fiber spinning and the carbonization/evaluation study.

Technical Barriers

- High cost of composite overwrapped pressure 700 bar vessels (COPVs).
- High cost for high-strength carbon fiber (62% of the COPV cost).
- Lack of technology in low-cost and melt-processible CF precursor that can form high-strength carbon fiber, required in the fabrication of COPVs.

Technical Targets

- DOE 2020 cost target of $10/kWh (~$1,900/system).
- 5.6 kg of usable stored hydrogen in the 700 bar COPV.

FY 2019 Accomplishments

- We discovered the polyethylene (PE)-Pitch polymer precursors, containing 20–60 wt % PE-g-Pitch polymer and 40–80 wt % free Pitch (serving as plasticizer), are suitable for melt fiber-spinning to prepare precursor fibers. This operation was carried out at both ORNL and Penn State facilities.
- The new resulting PE-Pitch precursor fibers were carbonized to form carbon fibers with C content >96% and C yield ~65% in one-step thermal heating to 1,500°C under N_2 without any mechanical tension. On the other hand, current commercial polyacrylonitrile (PAN) precursor fibers require two-step transformation reactions (stabilization in air and then carbonization under N_2) as well as constant mechanical stretching and long conversion time (a very expensive process).

- The resulting PE-Pitch-based carbon fibers show a nano-polycrystalline morphology by XRD and Raman, like those shown in commercial high-tensile-strength PAN-based carbon fibers.

INTRODUCTION

The current compressed hydrogen 700-bar on-board storage vessels for fuel cell electric vehicles are based on the CF reinforced polymer (epoxy resin) composites. The cost of this system is estimated at above $15/kWh, which is significantly higher than the DOE cost target. About 62% of the system cost comes from the cost of CF alone. The high cost of CF is associated with the deficiency in current PAN fiber precursor that requires a fiber solution-spinning process and low carbon conversion yield (<50%). Although some interesting experimental results and economic benefits of using sulfonated polyethylene precursors have been reported, there is still a considerable technological gap in considering them for the practical CF production. The required solid state sulfonation reaction of highly crystalline polyethylene (PE) fiber is problematic. This is because it results in an inhomogeneous functional group distribution that significantly impairs the effectiveness of stabilization and the subsequent carbonization reaction.

Thus, we suggest this research project focusing on the development of new polyolefin-based CF precursors that can be effectively prepared and converted to high-quality CF with high tensile strength and low cost. The cost savings can be realized through the combination of lower-cost precursor, melt-spinning fiber process, lower carbonization temperature, higher mass yield, and higher tensile strength in the resulting CF products. Our goal is to achieve the DOE cost target of $10/kWh (about $1,900 per vehicle with 5.6 kg of usable hydrogen) while also enhancing the CF mechanical properties to higher than those of Toray T700S fiber (4,900 MPa tensile strength and 230 GPa tensile modulus).

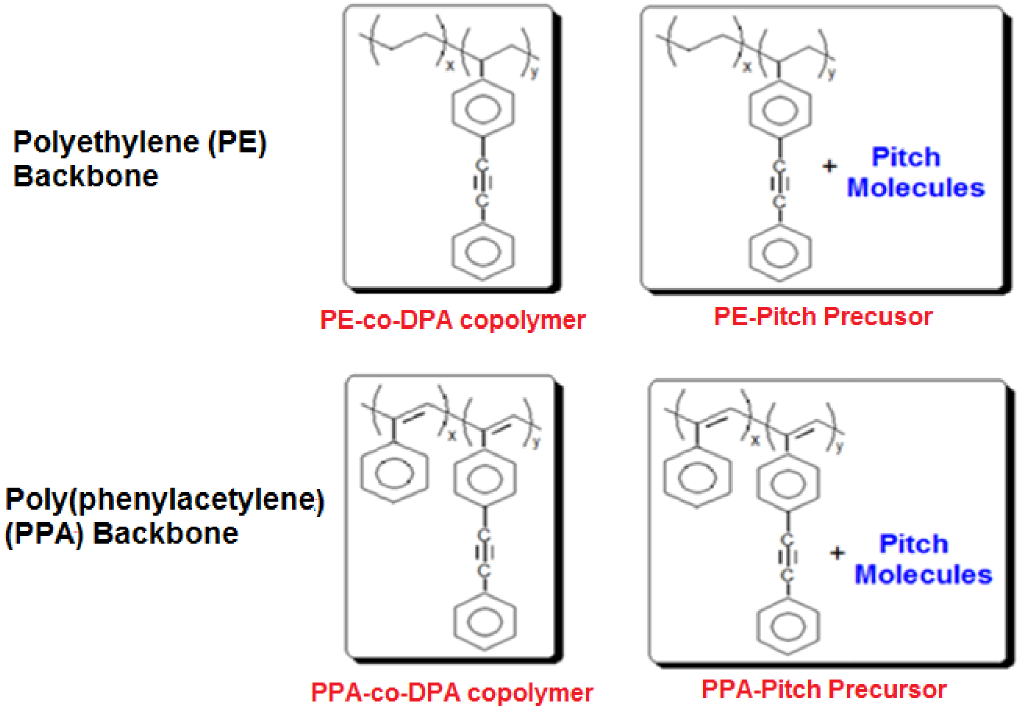
APPROACH

The research approach is based on several newly designed hydrocarbon polymers containing some reactive side groups that can effectively engage in cyclo-addition and hyper-crosslinking reactions under mild stabilization condition. The polymers are also melt-processible for spinning into fibers. With strong bonding energy along the polymer chain and a network structure, the resulting polymer fiber under tension (similar to PAN fiber) can be heated (pyrolyzed) to drive off H atoms and induce ring fusion (carbonization) to produce strong carbon fiber with high mass yield, high crystallinity, graphitic layer planes oriented along the fiber direction, and low defects.

In addition, another aspect of this research is to further increase the tensile strength of CF. The research approach is based on our previous findings in several B-containing precursors that produce BC_x materials with high yield, large crystallite size, and small d-spacing between C interlayers. Clearly, the in situ boron is catalyzing carbonization and graphitization of the BC_x material, and the substitutional B elements induce the dipole-dipole interaction between interlayers and reduce the d-spacing. The combination of large crystallite size, small d-spacing, and strong interlayer interaction shall increase mechanical strength, especially for CF with graphene sheets aligned along the fiber direction.

RESULTS

In FY 2019, we have systematically investigated the suitable processing method and conditions to carry out fiber-spinning operation on new high C-yield CF precursors (FY 2018). Specifically, we focused on two precursor systems (Scheme 1) based on polyethylene (PE) and poly(phenylacetylene) (PAA) with □-electrons conjugation along the polymer chain. Both polymers contain some (up to 10 mol %) reactive diphenylacetylene (DPA) side groups randomly distributed along the polymer chain. After a systematic study with various reactive groups, these DPA side groups were found to be the most suitable moiety for reacting with Pitch polyaromatic molecules. In fact, each DPA group reacts with two Pitch molecules in the temperature range 300°–310°C to form a very bulky side group (with the molecular weight of each side group about 1,000 g/mol). This thermally induced coupling reaction transforms PE-co-DPA copolymer to PE-Pitch CF precursors, as well as transforming PPA-co-DPA copolymer to PPA-Pitch CF precursors.



Scheme 1. Precursor structures were used in the fiber-spinning study, including PE-co-DPA copolymer, PPA-co-DPA copolymer, PE-Pitch, and PPA-Pitch CF precursors

In this report, the PE-Pitch precursor system will be used to exemplify the precursor preparation, fiber-spinning to prepare precursor fibers, carbonization to obtain the corresponding carbon fibers, and their evaluations. A starting PE-co-DPA copolymer containing 3 mol % DPA reactive comonomer units was mixed with Pitch 250M (weight ratio of PE-co-DPA/Pitch 250M = 1/10) in a melt-mixer under agitation at 310° C for 1 h. The resulting mixture was subjected to Soxhlet extraction using toluene solvent to remove free Pitch molecules with various washing cycles as shown in Table 1. After about 20 washing cycles, the washed toluene solution became completely colorless, indicating no extractable (free) Pitch molecule in the product. Further washing cycles also don't show a change of the product weight. After drying the purified product, pure PE-g-Pitch polymer (Sample 6 in Table 1) was obtained, which is a graft copolymer with a PE polymer backbone and many Pitch molecules in the side groups. The weight of the resulting PE-g-Pitch polymer is about 21 wt % of the starting PE-co-DPA/Pitch mixture. In other words, the coupling reaction more than doubles the polymer molecular weight. With knowing the weight of pure PE-g-Pitch polymer, we can estimate the free Pitch content in each precursor sample (Table 1) after various washing cycles.

Table 1. Summary of Several PE-Pitch CF Precursors Containing Various Percentages of Free Pitch Molecules after Various Soxhlet Solvent Extraction Cycles

Sample	Solvent Extraction Cycles	Remaining Weight (%)	PE-Pitch Precursor Composition	
			PE-graft-Pitch (wt %)	Free Pitch (wt %)
1	0	100	21	79
2	3	56	37	63
3	5	50	42	58
4	10	36	60	40
5	13	29	73	27
6	>20	21	100	Undetectable

Oscillation rheology measurement offers a reliable method to identify the suitable melt-processing window. The potential melt-processing window shall offer a steady melt viscosity <5,000 Pa.s and the temperature below the G'(ω) and G"(ω) crossover point. Sample 1 (containing ~80 wt % of free Pitch without washing) shows a very low melt viscosity. This precursor is difficult in forming the continuous fibers that exhibit low tensile strength. On the other hand, pure PE-g-Pitch polymer (Sample 6) shows a very high melt viscosity >10^5 Pa.s, over the acceptable range in common fiber-spinning processes. Figure 1 shows the profiles of complex viscosity (η*) and viscoelastic properties G'(ω) and G"(ω) for Samples 2–5 (Table 1) containing various percentages of free Pitch molecules that serve as plasticizer.

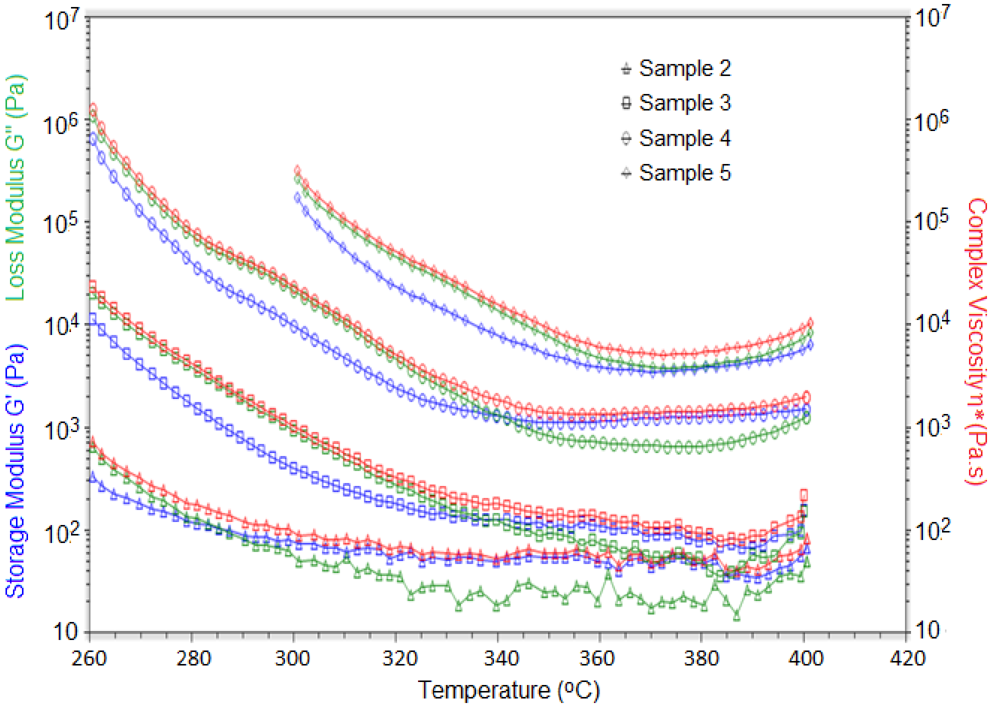


Figure 1. Rheology curves, including G' and G" values and complex viscosity η*, for four PE-Pitch precursors (Samples 2–5 in Table 1)

Although pure PE-g-Pitch copolymer (Sample 6), with very high melt viscosity, is not suitable for melt-spinning processes, this polymer is very soluble in common organic solvents (such as toluene) and can be easily processed by solution fiber-spinning techniques, including electro-spinning processes that produce the desirable microfibers by electric force. However, most of the low-cost commercial fibers are produced by melt fiber-spinning technique. In this study, we examined melt-processability for Samples 2–5 using a polymer melt fiber-spinning apparatus at ORNL. Figure 2 shows the fiber-spinning operation on Sample 4 to form PE-Pitch precursor fibers.

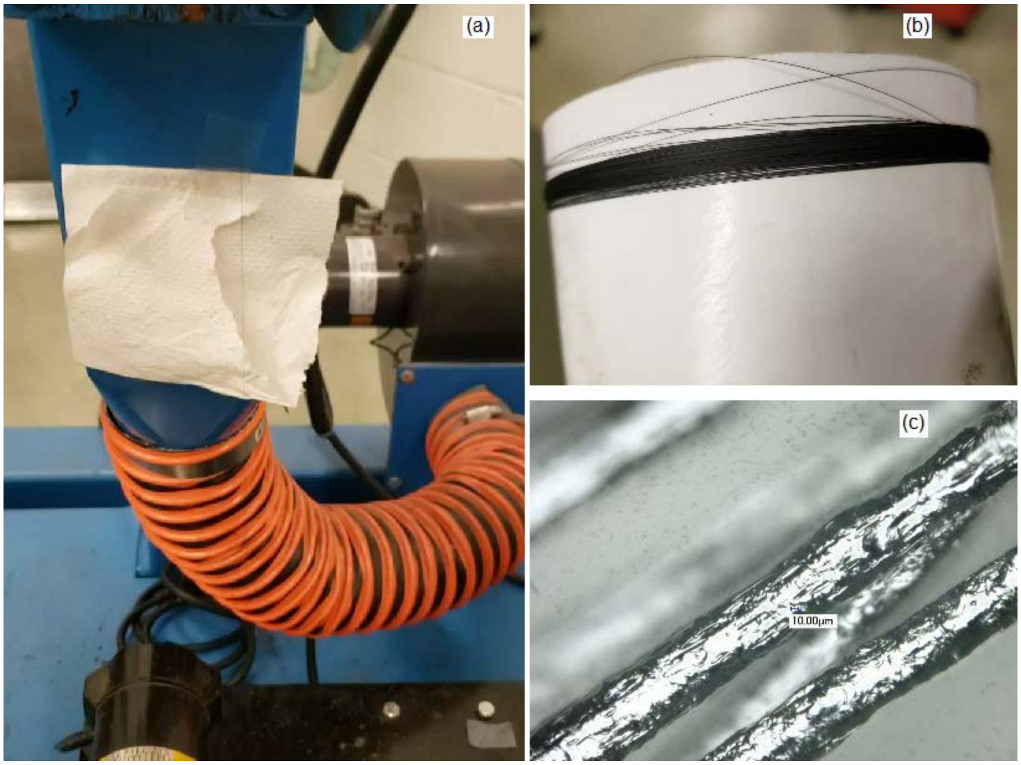


Figure 2. (a) The fiber-spinning apparatus at ORNL used to fabricate PE-Pitch precursors, (b) a resulting PE-Pitch precursor fiber from Sample 4 precursor, and (c) the magnified optical picture of this PE-Pitch precursor fiber with a fiber diameter about 30 μm

As shown in Figure 2a, we used a laboratory-scale single-filament melt-spinning apparatus at ORNL. This apparatus is composed of three units arranged in the vertical direction, which include an extrusion unit (on top), a spinneret (connected to the extrusion unit) with a die diameter of 0.1 mm (100 μm), and a take-up unit (at bottom). The extruded molten filament (in front of the paper for easy view) was directly solidified in air and collected on a take-up wheel with variable speed. The distance between spinneret and take-up unit is more than 1 m. As expected, an increase in the take-up speed leads to a reduction of fiber diameter and increase of polymer chain orientation (possibly also the mechanical properties). In the early operation, we didn't have the method to remove free Pitch molecules from the resulting PE-Pitch precursor. So, Sample 1 precursor (with only 21 wt % polymer and 79 wt % of free Pitch molecules) was heated to 320°–340°C range in the extrusion unit before extruding through the 0.1 mm (100 μm) spinneret by a piston providing a controllable pressure. Due to low melt viscosity, it was difficult to maintain the continuous fiber-spinning operation. Some resulting fibers have the fiber diameter about 80–90 μm due to low take-up speed and weak mechanical strength. Recently, the ORNL team used the same apparatus on Sample 4 precursor (with 60 wt % polymer and 40 wt % free Pitch molecules) to fabricate the corresponding PE-Pitch precursor fiber, shown in Figure 2b, with much higher mechanical strength. The melt fiber-spinning with high take-up speed (high melt viscosity) was continuous and smooth to obtain the precursor fiber with a fiber diameter about 30 μm (a good size for CF precursor fiber), shown in Figure 2c.

At Penn State, we also applied a Filabot desktop filament extruder (die diameter 1 mm) that is connected to a spooler with the rotating puller wheels to uptake the extruded filaments. The puller wheels draw the filament from the extruder (some stretching at the die), and its speed controls the extruded filament diameter. The PE-Pitch precursors (Samples 2–6) were heated to 310°–330°C in the extrude for about 10 minutes before extruding out. The extruded filament was then connected to a spooler with a constant rotating speed for reaching to the tight tolerance. The continuous PE-Pitch fibers (from Samples 3, 4, and 5) were uniform with good strength, but the diameter was high, in the range of 500–800 μm.

The resulting PE-Pitch precursor fibers (from Penn State extruder) were carbonized to transform them into the corresponding carbon fibers by heating the fiber samples to 1,500°C under N_2 atmosphere without mechanical tension. The elemental analysis shows the resulting carbon fibers with high C content >96% (like commercial PAN-based carbon fibers) and fiber diameter in the range of 300–500 µm (about 50 times of PAN-based carbon fibers and no preferred orientation and defect removal). Figure 3 compares their thermogravimetric analysis curves (Samples 2–6 in Table 1) with a heating rate of 10°C/min under N_2. It was somewhat unexpected to observe similar C yield (in the range of 63 to 67 wt %) for all samples, despite that they contain a wide range of free Pitch molecules from 0 wt % (i.e., PE-g-Pitch polymer) to 63 wt % (with only 37 wt % PE-g-Pitch polymer). The starting PE-co-DPA copolymer doesn't offer any measurable C yield and the corresponding Pitch 250M only produces 50% C yield. It is remarkable to observe 63 wt % C yield for pure PE-g-Pitch polymer precursor (Sample 6), which is significantly higher than commercial PAN polymer precursor with <50 wt % C yield. In addition, the mixtures between PE-g-Pitch and free Pitch molecules (Samples 2–5) all exhibit even higher C yields, with a trend of higher Pitch content having higher C yield. Evidently, the PE-g-Pitch polymer plays a key role in the carbonization process. The bulky side groups (with two Pitch molecules and the original DPA side group) may be actively engaging in the stabilization reaction, with the ring-fusion reactions between polymer side group and free Pitch polyaromatic molecules and the crosslinking reaction between two polymer side groups.

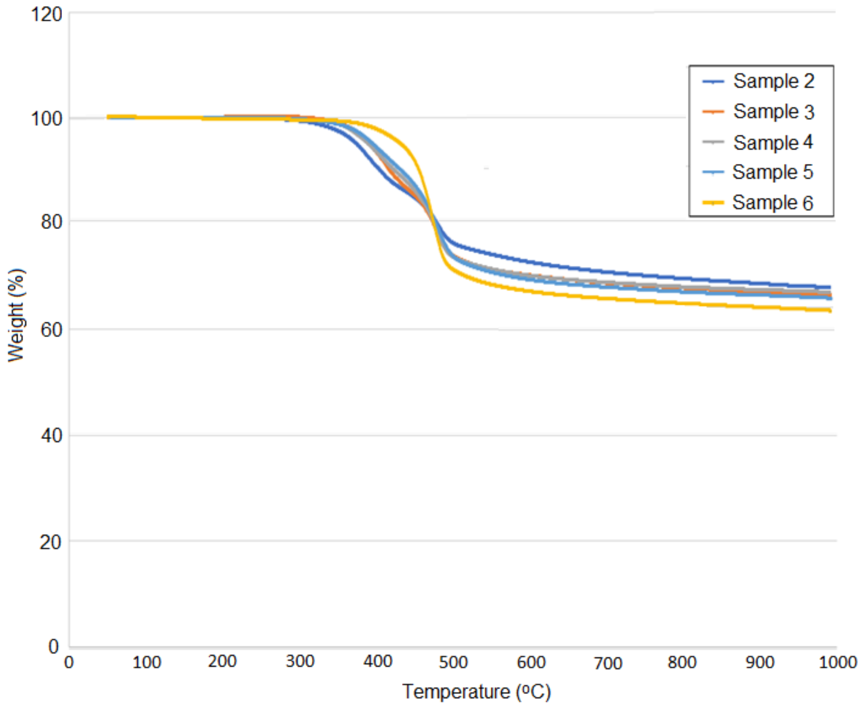


Figure 3. Thermogravimetric analysis curves of PE-Pitch precursors with various content of free Pitch from 0 to 63 wt % (Samples 2–6 in Table 1) under N_2 at 10°C/min

The resulting carbon fibers were characterized by a combination of Raman spectroscopy and XRD pattern to determine the graphitic (sp^2 carbon) structure. Raman spectroscopy is the most common and easy method to probe to inelastic scattering of light from a sample surface under ambient condition. Figure 4a shows a Raman spectrum of PE-Pitch precursor (Sample 4). There are two characteristic peaks indicating two different chemical structures; the D band near 1,334 cm^{-1} indicates a disordered structure, and the G band near 1,600 cm^{-1} indicates a graphitic structure. Their peak intensity ratio $R = I_D/I_G$ (I_D and I_G represent integral intensities of the D and G peaks, respectively) is used to calculate the relative content of sp^2 hybrid carbon atoms in the order graphitic structure of carbon fiber, which is the degree of graphitization. Both order G band and disorder D band are clearly observed in all CF samples and independent of the excitation wavelength. It was somewhat surprising to see similar Raman spectra for all samples (2–6) from pure PE-g-Pitch polymer to the PE-Pitch precursor containing 63 wt % of free Pitch molecules. The integrated intensity ratio (R) for the D and G bands, which reached 1.3 after heating at 1,500°C for 1 hour under N_2 atmosphere, is inversely proportional to the carbonization temperature. This R value is close to the values shown in many PAN-based carbon fibers [1]. In addition, we also observed the trend of R value in our poly-pitch precursors inversely proportional to the carbonization temperature. We expected the R value of PE-Pitch based carbon fibers to further decrease with the increase of heating temperature >1,500°C or increasing the heating time. Currently, we are examining other effects, including tension and fiber diameter [2], that were reported to be sensitive in forming C crystallite structure.

The observation of crystalline C domains was further confirmed and quantified by XRD measurements. Because the wide-angle diffraction patterns have coherence zones with minimum length between 1 and 2 nm, the XRD pattern reflects only the sizes and layer distances of the best ordered domains. Figure 4b shows the same carbon fiber prepared at 1,500°C for 1 h under N_2 atmosphere. Two distinctive X-ray peaks at 2θ ~24 (002) and ~43 (100) are the signature of C crystallites. The peak parameters can be used to calculate the crystallite size in the carbon fiber, with La = 3.8273 nm, Lc = 1.4322 nm, and d_{002} = 0.3674 nm. These crystal lattice parameters are similar to the reported numbers for PAN-based carbon fibers prepared at 1,500°C [3]. They are particularly close to those (La = 3.9 nm, Lc = 1.3 nm, d_{002}= 0.364 nm) of high-strength PAN-based carbon fiber reported by Naskar et al. [4].

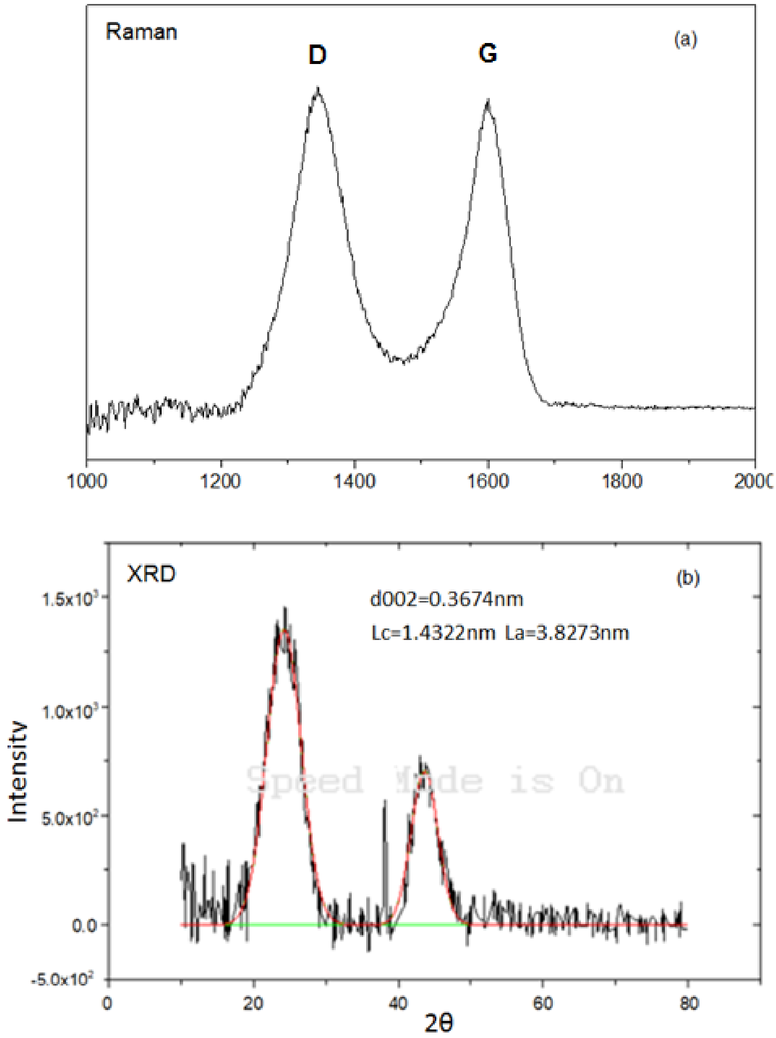


Figure 4. Raman spectrum and XRD pattern for the carbon fiber prepared by PE-Pitch precursor containing 40 wt % of free Pitch molecule (Sample 4) after heating at 1,500°C for 1 h under N_2

CONCLUSIONS AND UPCOMING ACTIVITIES

The primary goal of this exploratory research is to develop a new carbon fiber precursor system that can be fabricated and transformed to carbon fibers with a significant overall reduction of the production cost. Our research idea is based on a new polyolefin-based (pure hydrocarbon) precursor system that can exhibit a combination of advantages, including low material cost, melt fiber-spinning (low process cost), one-step thermal C conversion, and high C yield (vs. current PAN system with <50% C yield and requiring expensive solution fiber-spinning and a complicated two-step C transformation process). During FY 2018, we reported several new precursor systems that can achieve very high 80%–90% C yields after the thermal C conversion. In FY 2019, we focused on the fiber fabrication and subsequent thermal C conversion to prepare carbon fibers. Our experiments first identified the most suitable precursor system for a melt fiber-spinning process under some specific operation conditions. The resulting precursor fibers were thermally converted to the corresponding carbon fibers in one step under N_2, without the requirement of oxygen (air) and mechanical stretching. In this report, we show the carbon fibers prepared from the PE-Pitch precursor system show similar nano-polycrystalline morphology like those shown in commercial high-strength PAN-based carbon fibers. The one-step thermal conversion results without any mechanical tension during the entire carbonization process are scientifically interesting. It is well documented that PAN polymer precursor is a non-graphitizable material without constant mechanical stretching [5–8]. To prepare high-strength carbon fibers, PAN precursor fiber requires constant tension during the entire thermal C conversion process. Overall, our experimental results have answered a fundamental question, "Can our newly developed poly-Pitch polymer precursors be converted to carbon fibers with the desirable nano-polycrystalline morphology?" The answer is definitely positive.

So far, we have not addressed the mechanical properties of carbon fibers (a remaining major issue). In the coming year, we will direct our activities to the preparation of high-strength carbon fibers. They directly relate to several morphological factors, including the extent of preferred orientation of the basal planes, healing defects in the carbonaceous structure, and small filament diameter (ideal size <8 mm). They are all associated with the mechanical tension (stretching) during the thermal conversion process. In addition, we will also investigate B-containing carbon fibers with some substitutional B elements in the BC_x graphene structure, which reduce d_{002} interlay distance and induce the dipole-dipole interaction between interlayers [9–11]. The combination shall increase mechanical strength.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. T.C. Mike Chung, "Developing A New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber," presented at the DOE Hydrogen and Fuel Cells Program 2019 Annual Merit Review and Peer Evaluation Meeting, Washington, DC, April 29–May 1, 2019.
2. T.C. Mike Chung, Joseph Sengeh, Houxiang Li, and Wei Zhu, "Synthesis and Evaluation of Conjugated Poly(phenylacetylene) Derivatives as New Carbon Fiber Precursors," Carbon Conference, Lexington, KY, July 15–19, 2019.
3. T.C. Mike Chung, Gang Zhang, and Joseph Sengeh, "Developing a New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber," presented at the Tech Team Meeting, Detroit, MI, August 8, 2019.
4. T.C. Mike Chung, four quarterly DOE-EERE research performance progress reports for this project.
5. T.C. Mike Chung and Houxiang Li, "A New Class of Carbon Fiber Precursors and Production Process," submitted to U.S. Patent Office for U.S. Patent Application.
6. Joseph Sengeh, Houxiang Li, Wei Zhu, Matthew Agboola, and T.C. Mike Chung, "Synthesis and Evaluation of Soluble Conjugated Poly(phenylacetylene) Derivatives as New Carbon Fiber Precursors," Submitted to *Carbon* for publication.

REFERENCES

1. Fujie Liu, Haojing Wang, Linbing Xue, Lidong Fan, and Zhenping Zhu, "Effect of Microstructure on the Mechanical Properties of PAN-Based Carbon Fibers during High-Temperature Graphitization," *J. Mater. Sci.* 43 (2008): 4316–4322.

2. Lingqiang Kong, Hui Liu, Weiyu Cao, and Lianghua Xu, "PAN Fiber Diameter Effect on the Structure of PAN-Based Carbon Fibers," *Fibers and Polymers* 15, no. 12 (2014): 2480–2488.
3. Erich Fitzer and Wilhelm Frohs, "Modern Carbon Fibres from Polyacrylonitrile (PAN) Polyheteroaromatics with Preferred Orientation," *Chem. Eng. Technol.* 13 (1990): 41–49.
4. Ashley Morris, Matthew C. Weisenberger, Mohamed G. Abdallah, Frederic Vautard, Hippolyte Grappe, Soydan Ozcan, Felix L. Paulauskas, Cliff Eberle, Dave Jackson, Sue J. Mecham, and Amit K. Naskar, "High Performance Carbon Fibers from Very High Molecular Weight Polyacrylonitrile Precursors," *Carbon* 101 (2016): 245–252.
5. P.J.F. Harris, "Structure of Non-Graphitising Carbons," *International Materials Reviews* 42 (1997): 206–218.
6. S. Chawla, J. Cai, and M. Naraghi, "Mechanical Tests on Individual Carbon Nanofibers Reveals the Strong Effect of Graphitic Alignment Achieved via Precursor Hot-Drawing," *Carbon* 117 (2017): 208–219.
7. Z. Zhou, "Development of Carbon Nanofibers from Aligned Electrospun Polyacrylonitrile Nanofiber Bundles and Characterization of Their Microstructural, Electrical, and Mechanical Properties," *Polymer* 50 (2009): 2999–3006.
8. Maziar Ghazinejad, Sunshine Holmberg, Oscar Pilloni, Laura Oropeza-Ramos, and Marc Madou, "Graphitizing Non-Graphitizable Carbons by Stress-Induced Routes," *Scientific Reports* 7 (2017): 16551, http://doi.org/10.1038/S41598-017-16424-Z.
9. R. Hu and T.C. Mike Chung, "Synthesis and Structure Characterization of B/C Materials Prepared by 9-Chloroborafluorene Precursor," *Carbon* 34 (1996): 1181–1190.
10. Youmi Jeong, Alfred Kleinhammes, Yue Wu, and T.C. Mike Chung, "Synthesis of Boron-Substituted Carbon (B/C) Materials Using Polymeric Precursors and Evaluation for Hydrogen Physisorption," *J. Am. Chem. Soc.* 130 (2008): 6668–6669.
11. Youmi Jeong and T.C. Mike Chung, "The Synthesis and Characterization of a Super-Activated Carbon Containing Substitutional Boron (BC_x) and Its Applications in Hydrogen Storage," *Carbon* 48 (2010): 2526–2537.