
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

Project Start Date: September 1, 2017
Project End Date: August 30, 2020

Overall Objectives

- Reducing 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 while maintaining high tensile strength.
- Developing 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).
- Preparing boron (B)-doped CF by co-carbonization with B-containing precursor, which can offer low carbonization temperature, high carbon (C) yield, and CF products with high tensile strength.

Fiscal Year (FY) 2018 Objectives

- Investigate the chemical routes to prepare several newly designed polymer precursors.
- Confirm the resulting monomer and polymer structures by gel permeation chromatography curves and nuclear magnetic resonance spectra.
- Evaluate the thermal conversion of new polymer precursors to C materials and identify the suitable precursors that are melt-processible and can achieve high carbonization mass yield

>80%, compared with 50% yield in current polyacrylonitrile (PAN) precursor.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- High cost of 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 fabricating COPVs.

Technical Targets

This project is conducting fundamental studies of developing new CF precursors and a production process to reduce the cost of COPVs that meet the following DOE hydrogen storage targets:

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

FY 2018 Accomplishments

- Conducted a systematic study (design, synthesis, and evaluation) of various hydrocarbon polymers to understand the most suitable polymer structure that can generate high carbonization mass yield (>80%).
- Discovered four new polymer precursors with high C yield >80% (more than 60% higher than that of the current PAN precursor, which exhibits C yield ~50%).
- Synthesized B-containing Pitch precursor that enhances the carbonization process.
- Studied melt viscosity and viscoelastic properties of polyethylene-Pitch precursor and

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

identified the suitable melt fiber-spinning condition to form fibers.

- Collaborated with Oak Ridge National Laboratory through the LightMAT consortium in thermal conversion study.

INTRODUCTION

The current 700-bar compressed hydrogen onboard storage vessels for fuel cell electric vehicles are based on 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 the current PAN fiber precursor that requires a fiber solution-spinning process and has a low carbon-conversion yield (<50%). Some interesting experimental results and economic benefits of using sulfonated polyethylene precursors have been reported, but there is still a considerable technological gap in considering them for 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 distribution of functional groups that significantly impairs the effectiveness of stabilization and the subsequent carbonization reaction.

Thus, we suggested this research project to focus on developing new polyolefin-based CF precursors that can be prepared effectively and converted to high-quality CF with high tensile strength and low cost. The cost savings can be achieved 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 property to higher than those of Toray T700S fiber (4,900 MPa tensile strength and 230 GPa tensile modulus).

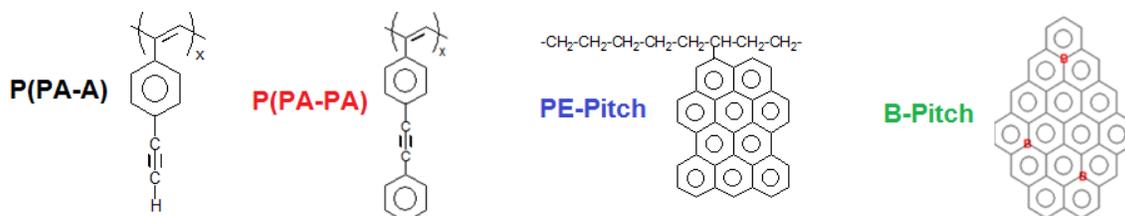
APPROACH

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 a 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 hydrogen atoms and induce ring fusion (carbonization) to produce a strong CF 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 carbon fiber. 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 will increase mechanical strength, especially for carbon fiber with graphene sheets aligned along the fiber direction.

RESULTS

In FY 2018, we have systematically investigated (i.e., design, synthesis, and evaluation) a series of hydrocarbon precursors. Our experimental results show four new precursors (illustrated below in Scheme 1) that achieve our first year (Phase 1) goal, with the C yield >80% (more than 60% higher than that of the current PAN precursor that exhibits a C yield ~50%). The detailed preparation procedures and evaluation for each precursor were reported in our DOE quarterly reports.



Scheme 1. Four new C precursor structures, including poly(acetylphenylacetylene) P(PA-A), poly(phenylacetylphenylacetylene) P(PA-PA), poly(ethylene-co-pitch) (PE-Pitch), and boron-containing pitch (B-Pitch)

Figure 1 shows the thermogravimetric analysis (TGA) curves of these new precursors, which were conducted in both Oak Ridge National Laboratory and Pennsylvania State laboratories with consistent results. All four samples show more than 80% C yields after heating to 1,500°C; three of them are near or above 90% yields. They are almost reaching the theoretical values for the precursor that only engages in the cyclo-addition and ring-fusion reactions with the removal of hydrogen atoms. It is interesting to note a slight dip (weight loss) at >1,250°C for the B-Pitch precursor, which may be associated with the limited B content (~2%) in the large graphene planal sheet during the carbonization at high temperatures. This phenomenon was well-documented in our previous papers (*Carbon* 34, 1181–1190, 1996; *Carbon* 48, 2526–2537, 2010). Overall, they are all potentially good precursors for our second year (Phase 2) research that will focus on preparing and evaluating CFs.

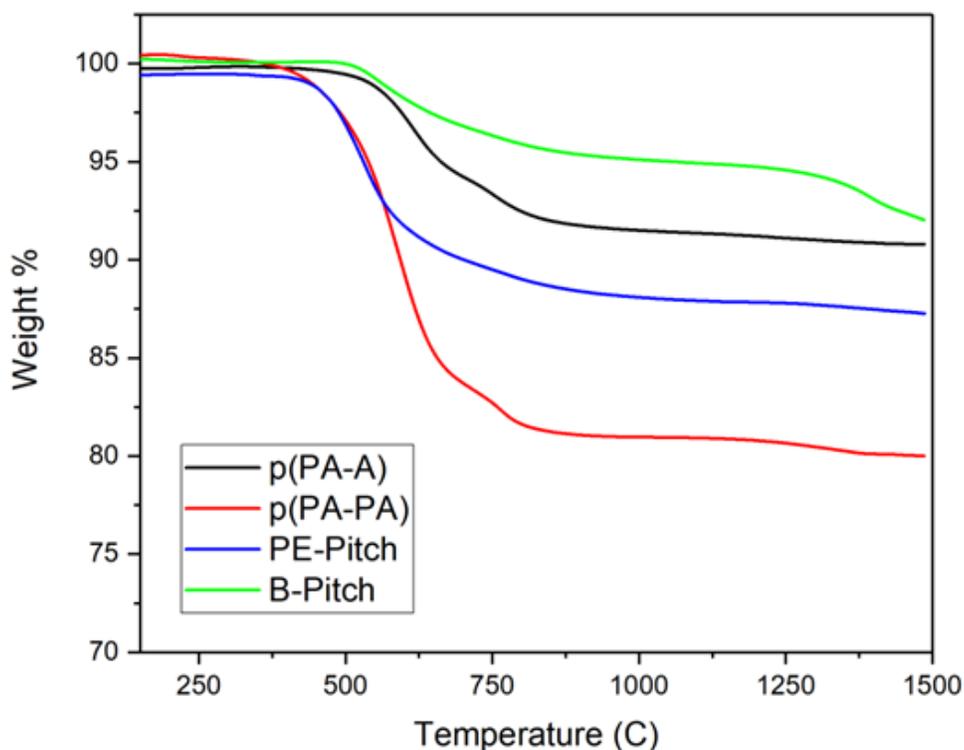
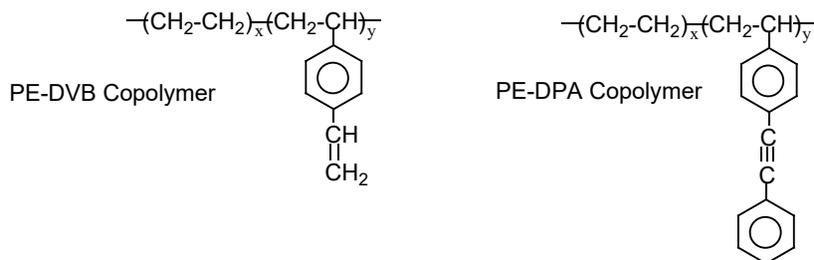


Figure 1. TGA curves of four new C precursors, including poly(PA-A), poly(PA-PA), PE-Pitch, and B-Pitch, measured at the heating rate of 10°C/min under N₂ atmosphere

Four new high-C-yield precursors represent four different processing conditions in forming fibers. We decided to focus on the PE-Pitch precursor, which is most unique in the field and has good potential to achieve our Phase 2 goal: showing a new CF production method with a combination of low-cost (scalable) precursor, efficient fiber melt-spinning process to form strong fibers, high C conversion, and high-quality CF end products. The preparation of PE-Pitch precursors involves two types of PE copolymers (illustrated below in

Scheme 2) with reactive side groups that can engage cyclo-addition and ring fusion with Pitch (polyaromatic) molecules.



Scheme 2. Two reactive PE copolymers, including poly(ethylene-co-divinylbenzene) (PE-DVB) and poly(ethylene-co-vinylidiphenylacetylene) (PE-DPA)

Two reactive PE copolymers—including PE-DVB copolymer containing styrene ($-\phi-C=C$) side groups and PE-DPA copolymer containing diphenylacetylene ($-\phi-C\equiv C-\phi$) side groups—were synthesized by metallocene-mediated copolymerization reactions using various metallocene catalysts. The detailed experimental results were discussed in our previous DOE quarterly report. The chemistry affords random copolymers with high molecular weight and narrow molecular weight and composition distributions. Table 1 summarizes several resulting PE copolymers with a broad range of copolymer compositions. The availability of a broad range of reactive PE copolymers helped us to identify the suitable thermal/reaction conditions (with scope and limitations) for carrying out the coupling reaction between reactive PE copolymers and Pitch molecules to form PE-Pitch precursors. Ideally, the resulting PE-Pitch precursors in a molten state can subsequently be melt-processed (melt fiber-spinning) into PE-Pitch fibers.

Table 1. Summary of Reaction Condition and Result of PE-DVB and PE-DPA Copolymers

PE copolymer ^a	Polymerization Condition					Polymerization Results	
	Metallocene Catalyst ^b	[Cat] (umol/L)	Ethylene pressure (psi)	[Co-Monomer] (M)	Temp/Time (°C/min)	Cat. efficiency (kg/mol*hr)	Functional group (mol%)
PE-DPA-1	$[(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2$	100	50	0.33	40/60	268	8.4
PE-DPA-2	$[(C_5Me_4)SiMe_2N(t-Bu)]TiCl_2$	100	50	0.16	40/60	310	4.5
PE-DVB-1	$rac-Et(Ind)_2ZrCl_2$	25	20	0.95	50/60	2000	3.8
PE-DVB-2	$rac-Et(Ind)_2ZrCl_2$	25	20	0.32	50/60	1888	1.8
PE-DVB-3	$rac-Et(Ind)_2ZrCl_2$	25	20	0.16	50/60	2363	1.1

^a Autoclave reactor (500 ml) with toluene solvent (230 ml) in all reactions.

^b MAO/Cat. Ratio= 1500.

Several experimental results (reported in our quarterly reports) had shown the successful coupling reactions between the resulting PE-DVB or PE-DPA copolymers and Pitch molecules to form PE-Pitch precursors. Both reactive side groups exhibit a facile cyclo-addition reaction with Pitch molecules under a specific thermal condition (relatively low temperature) during the stabilization step. It is essential to identify the processing window that also allows the in situ melt fiber-spinning into PE-Pitch precursor fibers.

Rheology of the polymer melt, such as complex viscosity (η) and viscoelastic properties (i.e., storage modulus $G'(\omega)$, loss modulus $G''(\omega)$, and $\tan(\delta)$), provides a great deal of information about polymer melt that is associated with polymer structure (solid-like or liquid-like) and its melt-processability at a specific thermal condition. An ARES-G2 oscillatory rheometer with 8-mm parallel plates was used in this investigation. The 8-mm sample disc was prepared by molding the mixture of PE copolymer and Pitch material under a specific temperature, in which a homogeneous mixture was achieved without any significant reaction between two materials. Figure 2 compares the profiles of melt viscosity and viscoelastic properties between a mixture of PE-DPA copolymer (9 mol% DPA units) with Pitch 118M (1/10 wt. ratio) and a pure Pitch 118M sample (reference) during the heating process.

The solid material (polymer) will decrease its melt viscosity with the increase of temperature if the material is completely stable throughout the whole thermal process. However, in our cases, possible thermal-induced coupling reactions occur that increase the material mass and break the decreasing trend of melt viscosity. The specific breaking point will provide very important information on the structure change. As shown in Figure 2, the raw Pitch reference sample shows that all the G' , G'' viscosity values systematically decreased with heating temperature until reaching 325°C. In further increasing the temperature (>325°C), all three values turn sharply higher. Evidently, the chemical reaction among raw Pitch molecules in Pitch is initiated at a heating temperature beyond 325°C, and Pitch molecular weight increases with heating temperature. As discussed in our quarterly report, the same Pitch 118M material exhibits a liquid-crystalline mesophase at ~400°C with large polyaromatic sheet structures. On the other hand, the mixture of PE-DPA/Pitch 118M (1/10 wt. ratio) shows the breaking point at a much lower temperature (~200°C). With only 10% PE-DPA copolymer, the mixture exhibits about one order higher melt viscosity and G' and G'' values before the turning point (200°C). After reaching >200°C, all three η , G' , and G'' values increase to two orders of magnitude higher than those of the reference Pitch 118M sample at the same heating temperatures. The results clearly indicate that the coupling reaction between PE-DPA copolymer and Pitch 118 molecules is initiated at ~200°C; the coupling reaction continues in the mixture beyond this temperature (>200°C) to rapidly increase the material melt viscosity and viscoelastic properties.

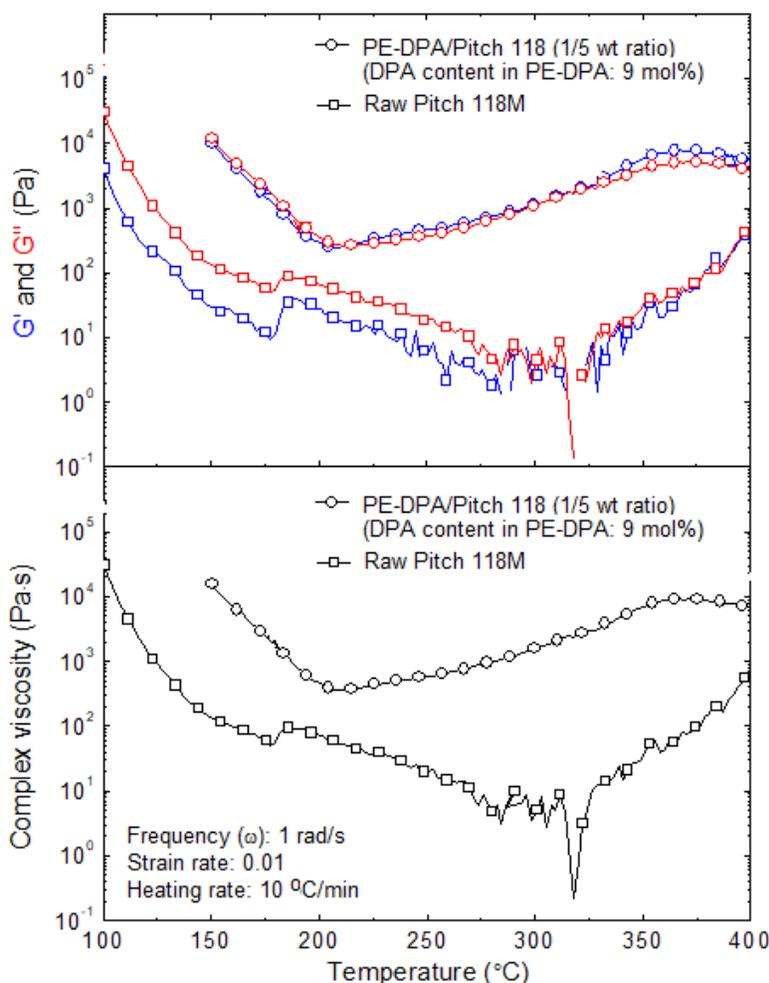


Figure 2. Comparison of (top) G' and G'' values and (bottom) complex viscosity during the thermal heating process between reference Pitch 118M and a mixture of PE-DPA copolymer (9 mol% DPA content) and Pitch 118M molecules with 1/10 wt ratio

The profiles of melt viscosity (η) and viscoelastic properties (i.e., storage modulus $G'(\omega)$, loss modulus $G''(\omega)$, and $\tan(\delta)$) for each specific mixture offer us very important information in the subsequent melt fiber-spinning process. Because of the continuous evolution of chemical structure during the thermal heating (stabilization step), the consideration of suitable spinning temperature will be based not only on the processability of fiber-spinning but also on the quality of the resulting PE-Pitch precursor fibers. In other words, based on the rheological properties at processing temperatures in Figure 2, we will also know the extent of the coupling reaction between the reactive PE copolymer and Pitch molecules at the specific temperature. As discussed, the extent of the coupling reaction determines the quality of the PE-Pitch precursor. It is highly desirable to have a melt-processible PE-Pitch precursor that also contains more than 50% volume fraction of PE-Pitch structure because the resulting PE-Pitch fiber will exhibit good mechanical properties that allow in situ stretching during the subsequent carbonization process. It also offers high carbonization yield. The ideal processing temperature is essential in realizing our goal, with a new low-cost and high-quality CF production method, through the lower-cost precursor, melt-spinning fiber process, higher mass yield, and higher tensile strength in the resulting CF products.

A Filabot desktop filament extruder equipped with a spooler, shown in Figure 3 (top), was applied in the melt fiber-spinning process. Based on the preliminary experimental results, this simple equipment is capable of melt-processing PE-Pitch precursors. Typically, the reactive PE copolymer (either PE-DVB or PE-DPA) was melt-mixed with Pitch 118M (with a specific weight ratio) in a reactor equipped with a mechanical stirrer at a specific temperature for a specific time. After achieving a homogeneous PE copolymer/Pitch mixture (containing some PE-Pitch and many free Pitch molecules), this homogeneous mixture was fed into the extruder with a controlled temperature and screw rotation speed. The PE-Pitch melt was extruded from the nozzle, and the extruded filament was then connected to a spooler with a constant rotating speed to reach the tight tolerance. The puller wheels draw the filament from the extruder, and its speed controls the extruded filament diameter. Figure 3 (bottom) shows several resulting PE-Pitch filaments that are relatively uniform in diameter and show good mechanical strength.



Figure 3. (top) Melt fiber-spinning of a PE-Pitch precursor using a Filabot desktop filament extruder and a spooler with the rotating puller wheels; (bottom) several PE-Pitch fibers prepared by the melt fiber-spinning process

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2018 (Phase 1), we developed four new C precursors—including P(PA-A), P(PA-PA), PE-Pitch, and B-Pitch—that exhibit very high C yields (higher than the Phase 1 project objective of 80%) after heating to high carbonization temperatures. The experimental results were confirmed by Oak Ridge National Laboratory. In addition, we also investigated the fabrication of PE-Pitch precursor fibers. In a systematic study to understand the preparation of PE-Pitch precursor and its melt-processing condition, we expanded the chemistry to synthesize two reactive copolymers (PE-DVB and PE-DPA) that can engage in coupling reactions with Pitch molecules to form PE-Pitch precursors under elevated temperatures. This thermal-induced coupling reaction was monitored by melt rheology measurement. The same rheological results on PE-Pitch precursors also helped us identify the suitable melt-processing temperature for fiber spinning. Following this useful rheology

information, we successfully prepared several PE-Pitch fibers with various filament diameters. The preliminary results are very encouraging in this PE-Pitch approach. However, it is still a long way to achieve high-quality PE-Pitch precursor fibers. The immediate research activities in the coming year are to understand the effects of structure and composition in both reactive PE copolymer and Pitch material, the extent of the coupling (cyclo-addition) reaction, and the suitable fiber melt-spinning condition to obtain high-quality PE-Pitch fibers. The resulting PE-Pitch fibers will be carbonized to form the final CF products. We will certainly study the resulting CF quality, mechanical strength, and carbonization yield.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. 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, June 2018.
2. Mike Chung, “Developing a New Polyolefin Precursor for Low-Cost, High-Strength Carbon Fiber,” presented at the 2018 DOE Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 2018.

REFERENCES

1. R. Hu and T.C. Chung. *Carbon* 34 (1996): 595.
2. R. Hu and T.C. Chung. *Carbon* 34 (1996): 1181.
3. R. Hu and T.C. Chung. *Carbon* 35 (1997): 1101.
4. Youmi Jeong, Alfred Kleinhammes, Yue Wu, and T.C. Mike Chung. *J. Am. Chem. Soc.* 130 (2008): 6668.
5. Youmi Jeong and T.C. Mike Chung. *Carbon* 49 (2011): 140.