Lower Cost Carbon Fiber Precursors

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Project ID #
LM004

Overview

Timeline

- Project start : 04/2009
- Project end: 09/2012
- 70% demonstration of performance criteria

Budget

- Total project funding
  - DOE share: $1,800,000
- Funding received in FY11
  - $600,000
- Funding for FY12
  - $300,000 (6 months)

Barriers

- Barriers addressed
  - Cost (significantly low-cost precursors)
  - Performance (Strength 250 ksi and modulus 25 Msi)
  - Manufacturability

Partners

- Hills, Inc. (Fiber spinning)
- University of NC at Chapel Hill (Microscopy)
- Courtesy fibers from FiberVision

Objectives

- Weight reduction of automotive composites by use of low-cost carbon fiber.
- Projected ~$5/lb (manufacturing cost) carbon fibers with polyolefins.
- Specific Objectives:
  - ***Develop and produce modified polyolefin fiber that can be rendered infusible by an accelerated method.***
  - ***Obtain carbonized fiber from the stabilized precursors by applying optimal conversion parameters***.
    - Demonstrate 200 ksi tensile strength and 20 Msi modulus in carbonized fibers (October 2010 – September 2011)
    - Demonstrate 250 ksi tensile strength and 25 Msi modulus in carbonized fibers (October 2011 – September 2012) Will be delayed due to budget reduction.

Milestones

- Go/No-Go Milestone FY'11:
  – Optimize parameters for intermediate target properties 200 KSI & 20 MSI and demonstrate that (September 2011).
    - Obtained 201.4 ksi strength and 21.6 Msi modulus (average properties)
- Go/No-Go Milestone FY'12:
  – Carbonize & spool polyolefin-based carbon fiber (250 KSI & 25 MSI). Will be delayed due to budget reduction.

Approach/Strategy

Polyolefin-based carbon fibers offer:

- Significant cost benefit through
  - High carbon yield (70% vs. 50% in PAN) and low raw material cost
  - Ease of precursor fiber handling and melt-processibility
- High performance/cost ratio

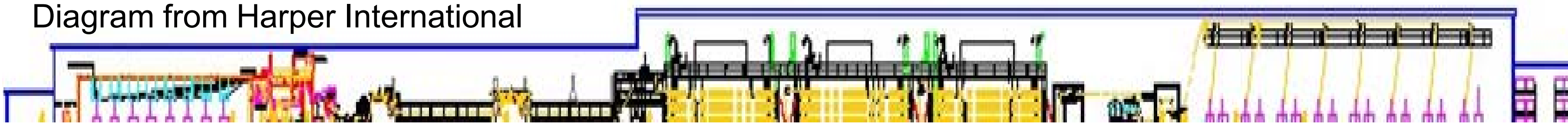
Lignin-based carbon precursor requires more work on making tension-tolerant fiber

PAN-based textile appears to be successful candidate but raw material cost is very high ($3/lb in fiber form) compared to PE ($1-2/lb).

CF derived from polyolefin can provide higher value in terms of performance to cost ratio than any other precursor currently under consideration.

Executive Overview

Diagram from Harper International



Spooling & Packaging	Surface Treatment	Carbonization/ Graphitization	Stabilization & Oxidation		Precursors
$0.61	$0.37	$2.32	$1.54	Baseline **PAN** Today - $9.88	$5.04
$0.41	$0.33	$1.48	$0.99	High Volume - $7.85	$4.64

Precursor type	Carbon (%)		$/lb (as-spun)	Melt-spinnable	Best achieved properties		Problem
	Theoret-ical	Practical yield			Strength (KSI)	Modulus (MSI)	
Conventional PAN	68	45-50	>4	No	500-900	30-65	High cost
Textile PAN*	~ 68	45-50	2-3	No	400+	30	High variation in properties
Polyolefin**	86	65-80	1-2	Yes	380	30	Slow stabilization step

↑ High Yield (Theoretical, Practical yield) — ↑ Inexpensive ($/lb) — ↑ Properties Proven At Small Scale (Strength, Modulus) — ↑ Obstacle Being Addressed (Problem)

* Ongoing work
** Hexcel work (2004)

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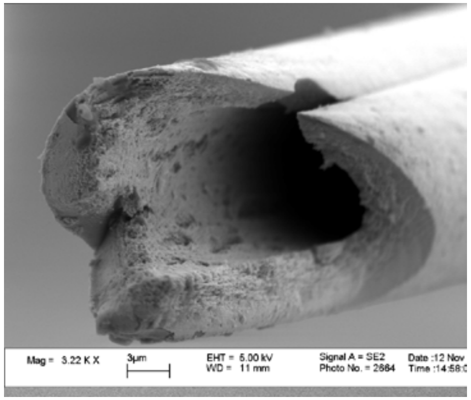
Approach/Strategy (2)

Off-the-shelf polyolefin resin or commercially available polyethylene plastic produces 20 μm diameter filaments by conventional spinning.

- These fibers when thermo-chemically stabilized and carbonized gave 150 ksi tensile strength and 15 Msi tensile modulus.
- Large diameter filaments caused inefficient sulfonation at the core of fibers.

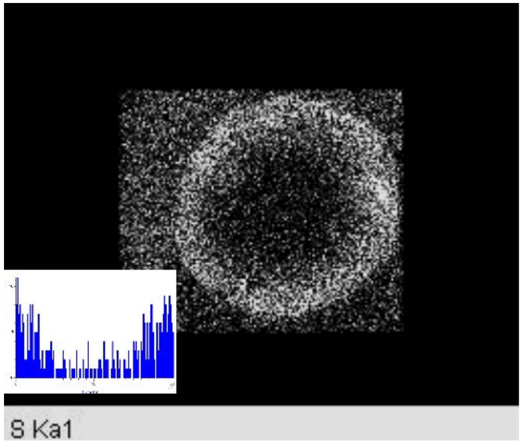


Making small diameter filament was essential to validate the concept of making carbon fiber of desired strength from commercial polyolefin resins.

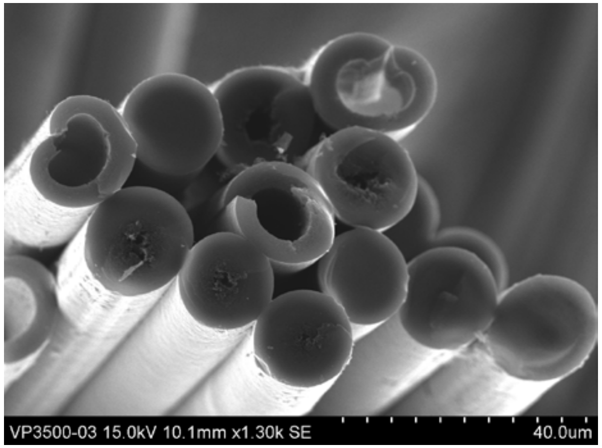
- Small diameter precursor filaments allowed more or less uniform crosslinking across the diameter of the filaments. Those fibers (10 μm) gave 200 ksi strength and 21 msi modulus.

Technical Accomplishments

Identified challenges with proper thermochemical stabilization of precursor



(a)



(b)

Figure (a) Mapping of elemental S on the fiber cross-sections during EDS study in a scanning electron microscope (SEM) and quantitative linescan of elemental S across the filament diameter (inset) and (b) carbonized filaments from such stabilized fibers with no core or weak amorphous core.

- Hollow cores in many of the fibers cause weak mechanical properties.
- Optimal temperature range for accelerated functionalization of LLDPE fibers is identified.
- Degree of functionalization is critical for CF properties.
- Smaller diameter filaments are being studied now.

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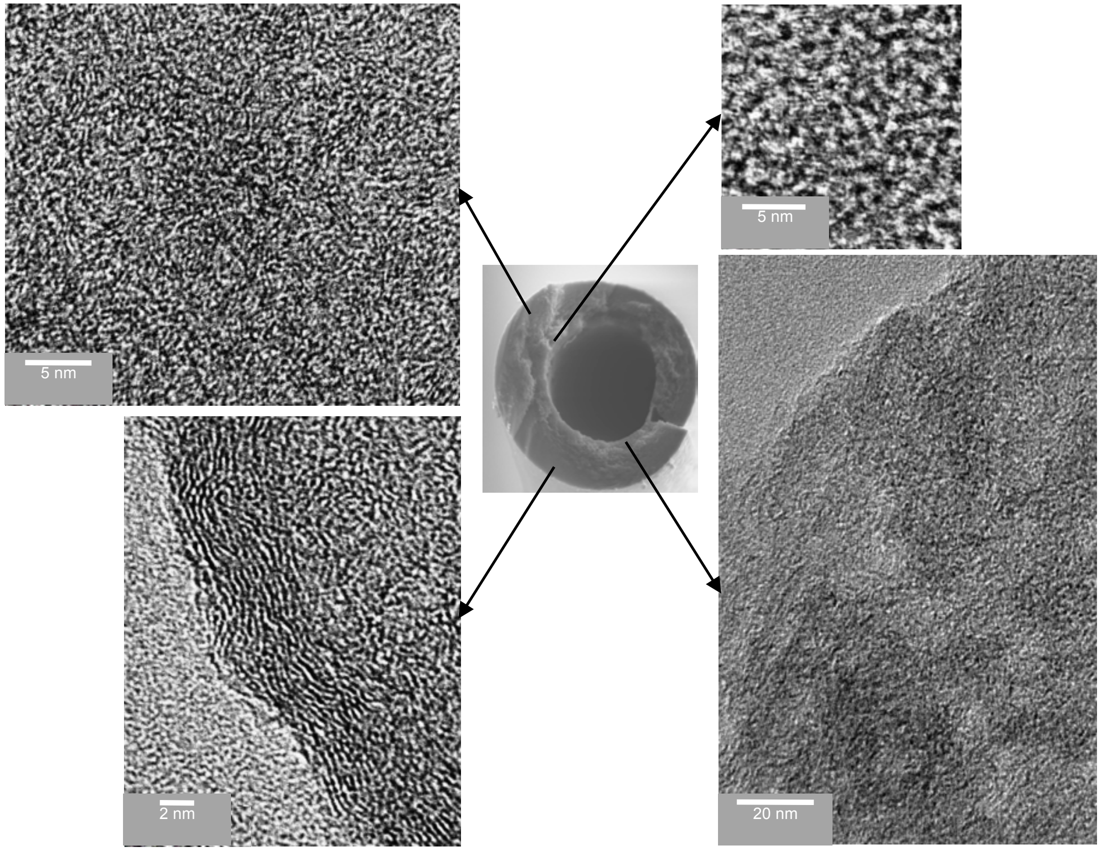
Technical Accomplishments (2)



Kinetic data for the degree of sulfonation correlates with the structure of carbon fiber derived from sulfonated polyethylene (PE). Transmission electron micrographs obtained on the regions near the outer surface of a hollow fiber (left) and inner surface (right) show differences in graphitic and porous structures. Outer surfaces show relatively ordered microstructure.

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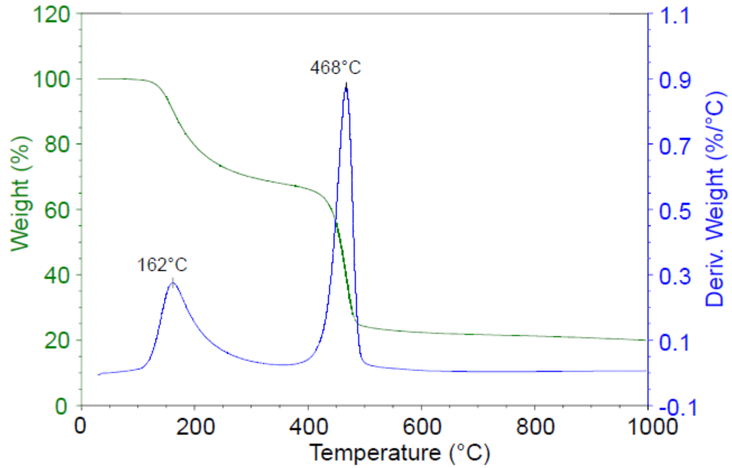
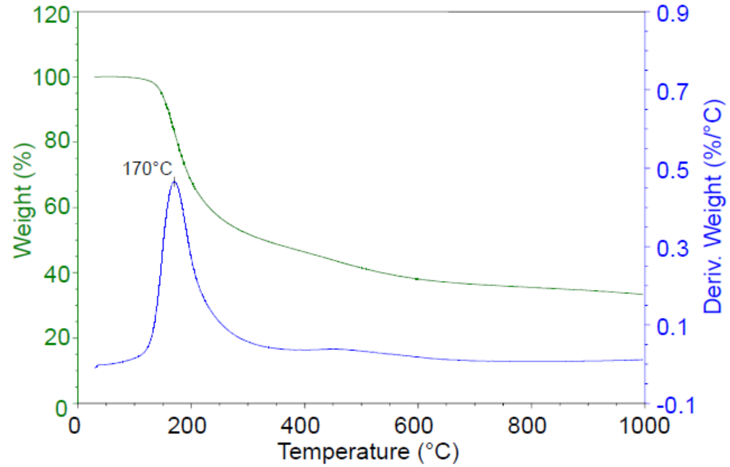
Technical Accomplishments (3)

Brute-force reduction of filament diameter using bi-component spinning technique was adopted and precursor fibers of 10 μm diameters were made. This method allowed us to get good starting material for the proof of concept.



TGA of partially functionalized PE fiber



TGA of fully functionalized PE fiber

Fully functionalized PE fibers gave >65% carbon yield (with respect to neat PE). The conversion conditions are important to achieve good mechanical properties from the same fully functionalized precursor.

Technical Accomplishments (4)

Fully functionalized PE fibers are brittle in nature. Handling of tow was improved in the modified sulfonation reactor.

The issue of interfilament bonding during thermal treatment was identified as one of two major obstacles in FY 2010. After undertaking numerous studies, optimized fiber treatments were identified and interfilament bonding even with small diameter fibers has been eliminated.

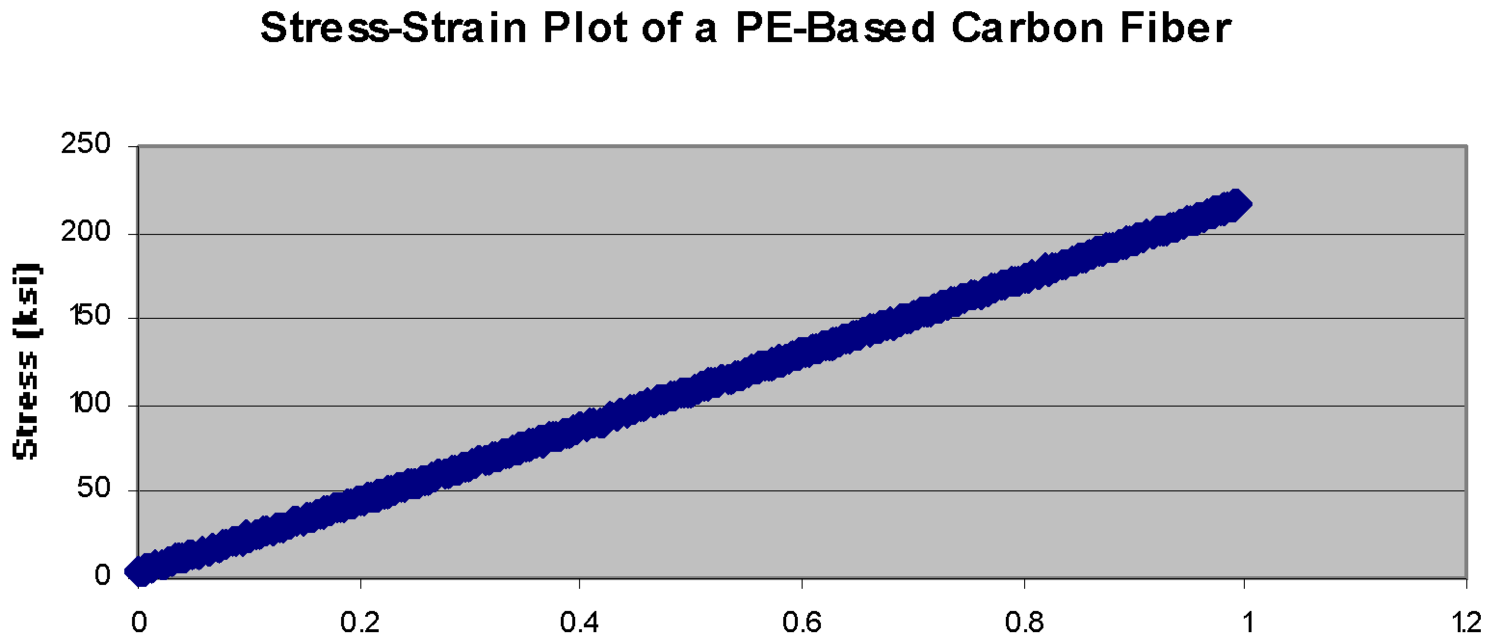
Technical Accomplishments (5)

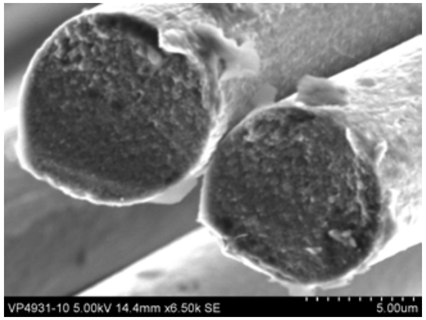
Mechanical properties of precursor and carbon fiber samples at room temperature.

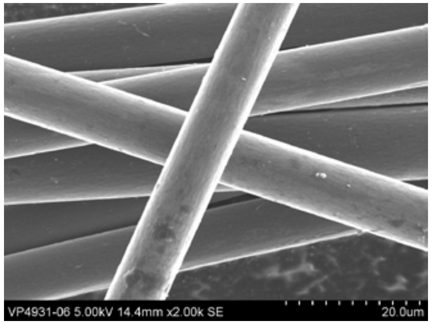
Sample	Source	Diameter (μm)	Maximum Filament Stress (ksi)	Maximum Filament Modulus (Msi)	Ultimate Elongation (%)
Precursor A	-	9.4	2.0	0.013	>200
Precursor B	-	9.1	1.5	0.013	>200
Precursor C	-	18	22	0.15	100
Carbon Fiber 1	Precursor A	12.6	91.3	4.4	2.0
Carbon Fiber 2	Precursor A	10.6	86.7	6.1	1.4
Carbon Fiber 3	Precursor B	10.7	121	5.3	2.4
Carbon Fiber 4	Precursor B	9.3	237	11.5	2.1
Carbon Fiber 5	Precursor C	15.8	129	17.2	0.76
Carbon Fiber 6	**Precursor B**	**10.0**	**201.4**	**21.6**	**0.91**

The milestone for the FY11 (200 ksi strength and 20 Msi tensile modulus) is met.

Technical Accomplishments (6)







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Collaboration and Coordination with Other Institutions

- Collaboration with Hills, Inc. (Fiber spinning equipment manufacturer)
  - Technology of making small diameter filaments from off-the-shelf plastic resins is being investigated
- FiberVision (JV of Hercules' Fiber division)
  - Donated PE & PP resin and fibers (Courtesy: Dr. C. Wust)
- Collaboration with electron microscopy research staff member at University of North Carolina at Chapel Hill.
  - Fiber microtoming
  - TEM analysis

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Proposed Future Work

- Meet the target of 250 ksi and 25 Msi mechanical properties of carbonized filaments (FY13) Delayed from FY12 due to budget reduction.
  - Sulfonation time still needs to be shortened (~ 1h) and proper sulfur management system needs to be developed (FY13-14).

- Submit phase II follow-up proposal (FY12-13) that would address following issues
  - Scaling-up of the stabilization (sulfonation) technology and associated challenges(FY13-14):
    - Sulfonation involves processing of fibers through corrosive chemical bath (continuous vs. batch processing?)
    - Thermal treatment of sulfonated fibers requires specially designed furnace (how to handle recycling of desulfonated products for cost-effectiveness?)
    - Recycled precursor and stabilization

Summary

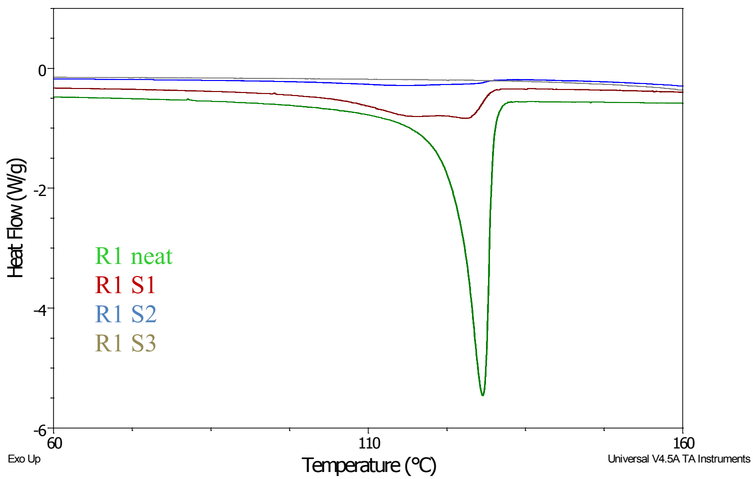
- Polyolefin-based carbon fibers were produced with tensile strength of 200 ksi and a modulus of 21 Msi (FY11).
  - **Some filaments with 230 + Ksi strengths were tested in FY12.**
- The effects of tension, temperature, time, processing method, reagent concentration to control functionalization kinetics and tensile properties of final carbon fibers are partly understood.
- The success of achieving good mechanical properties at >60% yield in PE-based carbon fiber justifies the project's relevance to both weight reduction objectives of vehicles and cost-reduction goal of automotive grade carbon fibers.
- If this novel technology becomes scalable (which we plan to demonstrate in future FY13-14), it will make the carbon fiber production technology more economically attractive.

Technical Back-Up Slides

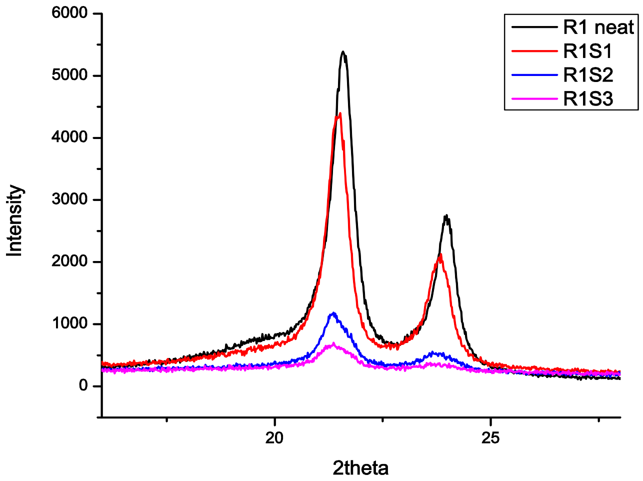
Characterization

DSC shows elimination of crystallinity in some polyolefin precursors with increased degree of functionalization.

The wide-angle x-ray diffraction (XRD) patterns of the corresponding filaments are shown in Figure 3b. Presence of an orientated amorphous phase in the functionalized fibers.



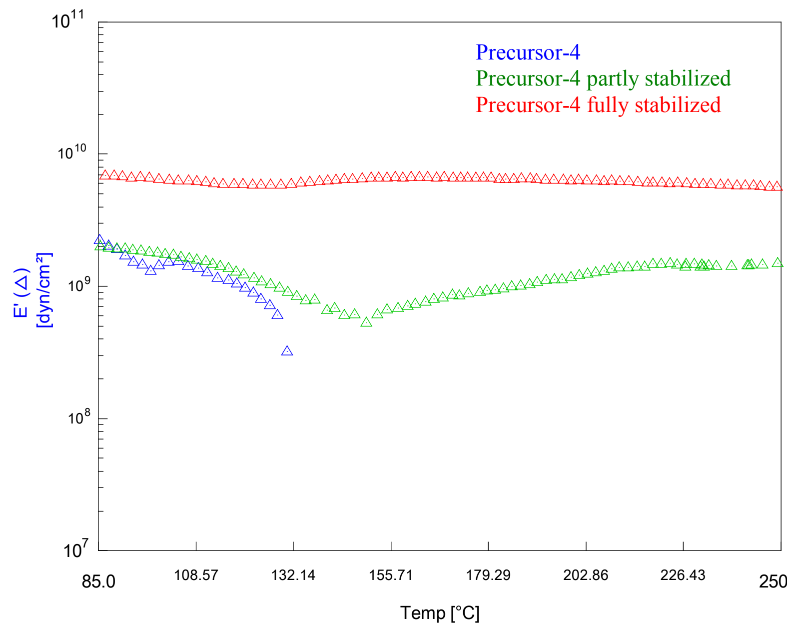
(a)



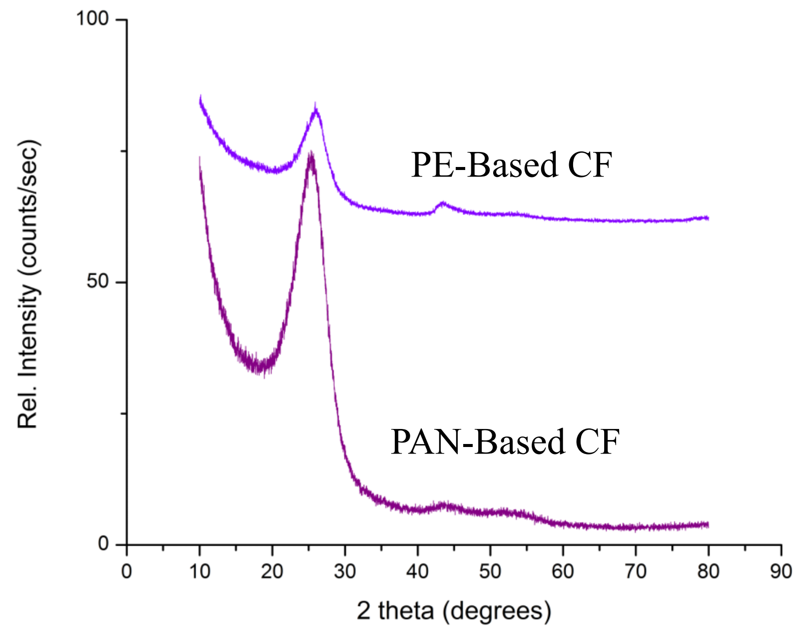
(b)

Figure (a) DSC thermograms of precursor fibers at different degree of functionalization and (b) their wide-angle XRD patterns.

Characterization (2)



DMA data of precursor fibers showing different degree of fuctionalization



WAXRD data of representative carbonized filaments

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Approach/Strategy (2)

Polyolefin resin selection was made based on commercially available plastics.

Alternative resin was physical modification of commercial material.