

Nano Tailored Carbon Fiber



STTR Phase II funded by AFOSR (FA9550-10-C-0030)

Program manager: Dr. Joycelyn Harrison

Review meeting, Dayton OH

June 4th, 2012

Han Gi Chae

Nano Engineered Materials Corp.

E-mail: hangi.chae@gmail.com

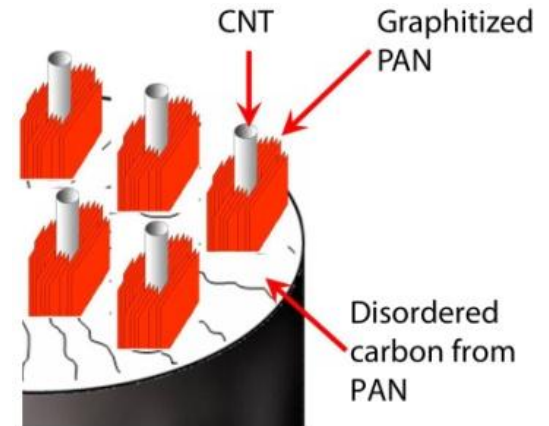
OUTLINE

- **BACKGROUND**
- **TECHNICAL PROGRESS**
 - **PRECURSOR FIBER SPINNING**
 - **BATCH STABILIZATION AND CARBONIZATION**
- **ACKNOWLEDGEMENT**

BACKGROUND

Gel spinning

- Highly oriented precursor fiber processing
- Tensile properties of gel spun fiber is superior to those of the solution spun fiber
(Tensile strength > 1 GPa, tensile modulus > 25 GPa)
- Typical solution spun PAN precursor properties
(Tensile strength < 0.8 GPa, tensile modulus < 15 GPa)



Small diameter fiber

Precursor diameter	Carbon fiber diameter
10 μm	5 μm
6 μm	3 μm

Carbon nanotube

incorporation in PAN matrix

- Carbon nanotube (CNT) not only reinforce PAN fiber, but also template crystallization behavior of PAN in the vicinity of CNT
- The CNT templated PAN crystalline phase is graphitized at a relatively low temperature, resulting in additional reinforcement effect in carbon fiber

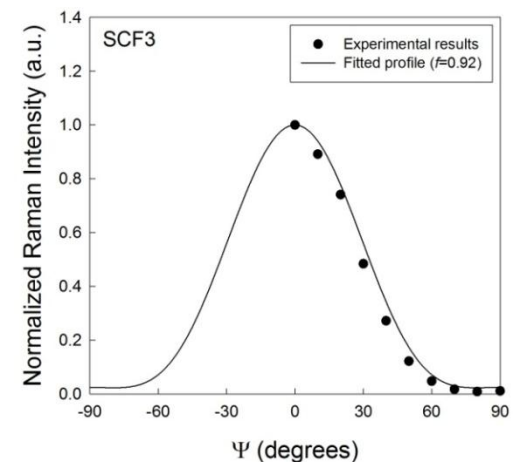
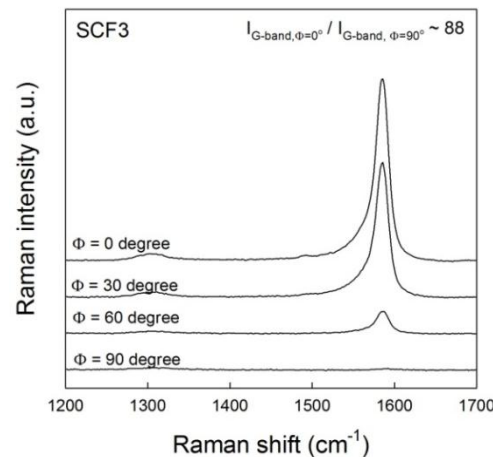
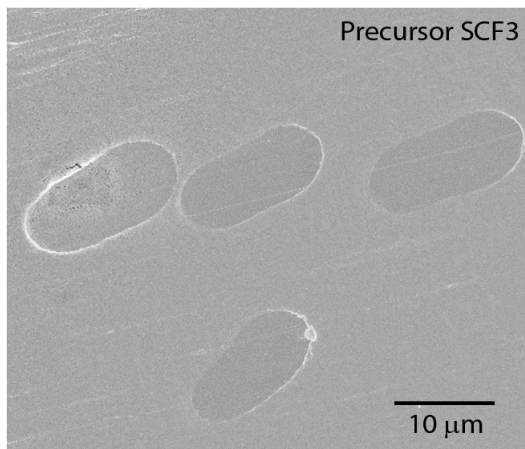
PRECURSOR FIBER SPINNING

- **Single component fiber spinning**
 - Effect of spin draw ratio on the precursor fiber properties
 - Effect of gelation bath composition on the fiber circularity
- **Bi-component fiber (sheath-core) fiber spinning**
 - Effect of solution concentration on the precursor fiber properties
 - Effect of gelation bath temperature on the fiber circularity
 - Processing optimization for small diameter precursor fiber
 - Effect of solution preparation method and high molecular weight polymer on the precursor fiber properties

Single component fiber spinning – Effect of spin draw ratio

- The higher spin draw ratio produced improved tensile properties for fully drawn fiber

	SCF1	SCF2	SCF3
Polymer/solvent/concentration	PAN-co-MAA (240,000 g/mol) / DMAc / 14.5g/dL		
CNT (concentration)	XO122UA (1 wt%)		
Gelation bath temperature	-50 °C methanol		
Spin draw ratio	3	5	10
Hot draw ratio*	11	8.2	6.4
Total draw ratio	33	41	64
Effective fiber diameter (μm)	14.5	13.5	10.1
Tensile strength (GPa)**	0.72 ± 0.08	0.76 ± 0.08	0.86 ± 0.07
Tensile modulus (GPa)**	17.3 ± 1.8	18.5 ± 1.2	21.6 ± 1.5
Strain to failure (%)**	8.6 ± 0.8	8.5 ± 0.7	7.6 ± 0.6



Circularity of precursor fiber

- In order to have optimum stabilization and carbonization through the fiber cross-section, obtaining circular cross-sectional shape is important.
- In composites, circular fiber will lead to the closest carbon fiber packing.
- Cause of irregular shape and unevenness
 - irregular shape of spinneret hole
 - inhomogeneity of spinning dope
 - fast coagulation rate
- Possible solutions
 - Study coagulation bath conditions - such as bath composition and temperature
 - Study the effect of spinning dope concentration

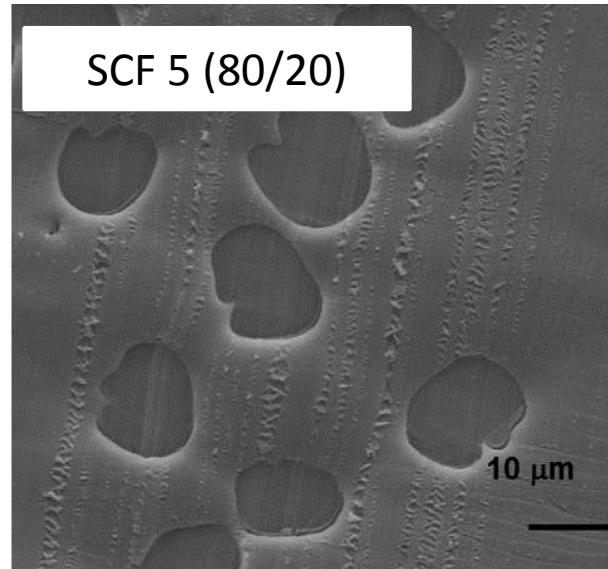
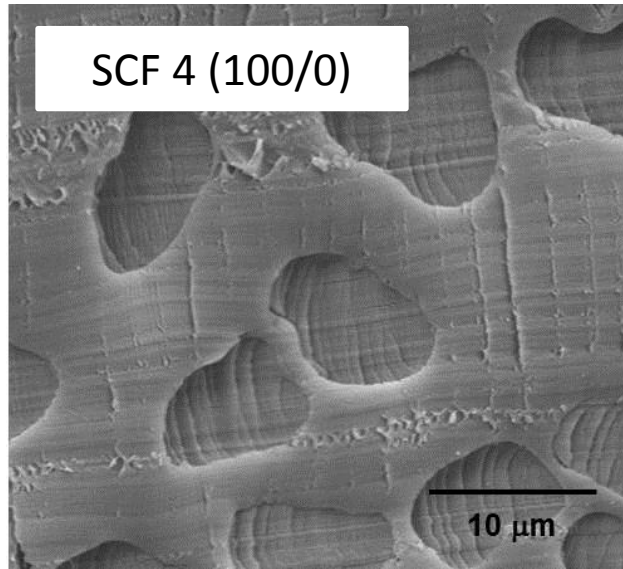
Single component fiber spinning – Effect of gelation bath composition (1)



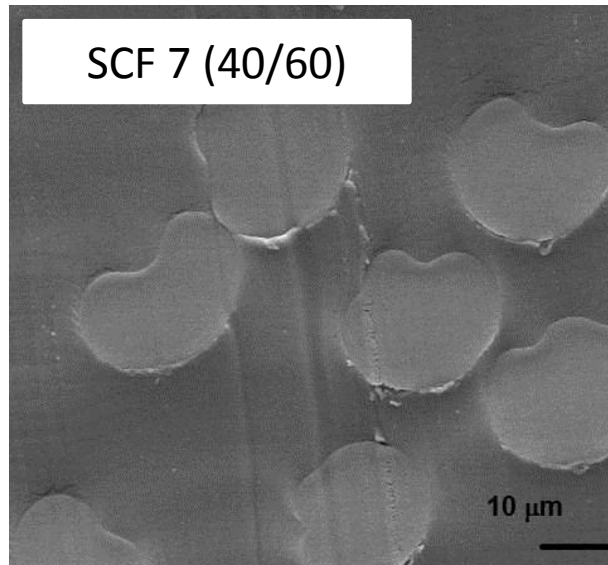
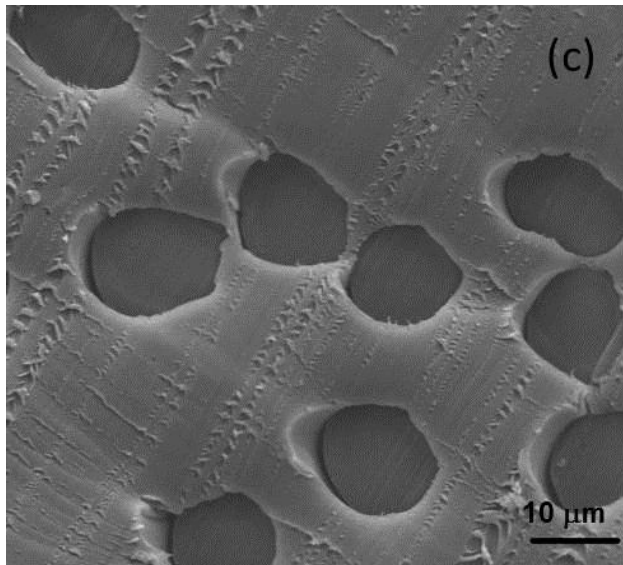
	Gelation bath composition (methanol/DMAc)			
	SCF4 (100/0)	SCF5 (80/20)	SCF6 (60/40)	SCF7 (40/60)
Polymer/solvent/concentration	PAN homo-polymer (700,000 g/mol) / DMAc / 7.5g/dL			
CNT (concentration)	CNTs were not used in these trials			
Gelation bath temperature	-50 °C			
Spin draw ratio	1	1	1	1
Cold draw ratio*	1.55	1.55	1.55	1.23
Hot draw ratio*	8.6	7.6	8.1	5.2
Total draw ratio	13.3	11.8	12.6	6.4
Effective fiber diameter (μm)	10.4	12.8	11.3	16.6
Tensile strength (GPa)**	1.4 ± 0.1	0.8 ± 0.1	0.9 ± 0.1	0.6 ± 0.1
Tensile modulus (GPa)**	24.1 ± 2.1	19.9 ± 2.3	21.9 ± 1.8	17.9 ± 1.5
Strain to failure (%)**	8.0 ± 0.6	6.2 ± 0.6	7.1 ± 1.1	7.6 ± 0.5
Crystallinity (%)***	61	50	54	48
Crystal size (nm)***	13.7	11.0	13.4	12.2
f _{PAN} ***	0.91	0.90	0.90	0.87

- The best tensile properties were obtained with 100% methanol bath at -50 °C.
- Circular fiber is desired for even oxidation throughout fiber cross-section
- Fiber circularity – depends on solvent/non-solvent exchange rate
(coagulation medium and temperature)

Single component fiber spinning – Effect of gelation bath composition (2)



- 60/40 (methanol/DMAc) bath produced near circular cross-section



Single component fiber spinning – Processing optimization

	SCF8	SCF9	SCF10
Polymer/solvent/ concentration	PAN-co-MAA (240,000 g/mol) / DMAc / 14 g/dL		
CNT (concentration)	XO122UA (0.5 wt%)		
Gelation bath temperature	-50 °C methanol		
Spin draw ratio	3	3	6
Cold draw ratio	2.3	1.8	1.4
Hot draw ratio*	5.5	7.3	4.5
Total draw ratio	38	39	38
Effective fiber diameter (μm)	10.5	10.5	10.1
Tensile strength (GPa)**	1.1 ± 0.1	1.2 ± 0.1	1.0 ± 0.1
Tensile modulus (GPa)**	28.5 ± 0.9	27.3 ± 1.5	25.7 ± 1.9
Strain to failure (%)**	7.0 ± 0.6	7.1 ± 0.5	7.0 ± 0.5

* Cold and hot drawing conducted at room temperature and at 170 °C using glycerol bath, respectively.

** Fiber effective diameter was determined from SEM cross-sectional images. Tensile testing conducted using gauge length of 25.4 mm and cross-head speed of 1%/s.

- From single component composite fiber, the targeted tensile properties of precursor fiber were obtained (tensile strength > 1 GPa and tensile modulus > 25 GPa).

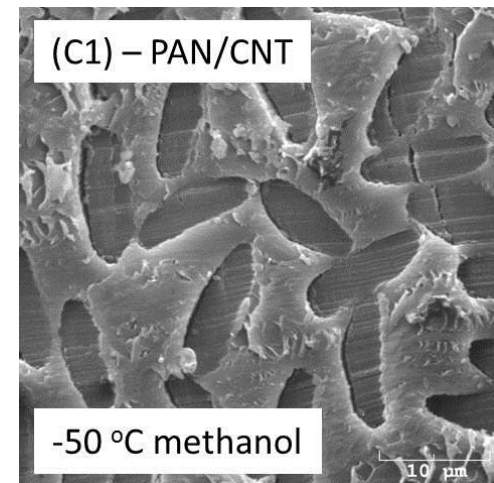
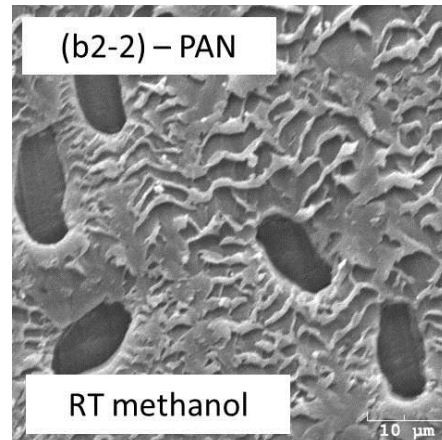
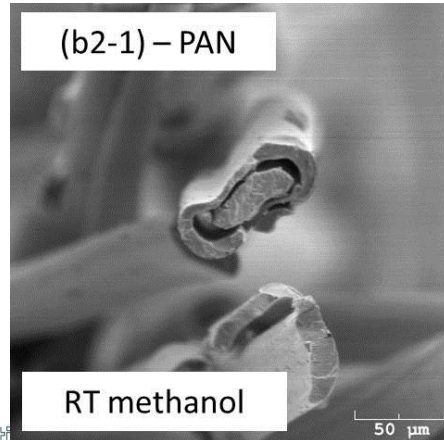
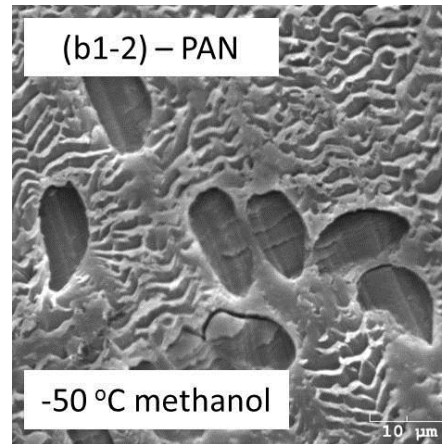
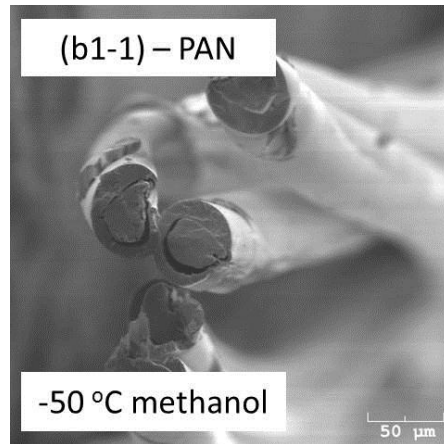
Bi-component fiber (sheath-core) spinning



	BCFc1	BCFc2	BCFc3	BCFc4	BCFc5	BCFc6	BCFc7
Polymer/solvent	PAN-co-IA (520,000 g/mol) / DMAc						
Concentration (g/dL)	10	11	11.5	11.5	12	12	11
CNT (concentration)	CNTs were not used in these trials						SP0300 (1 wt%)
Gelation bath composition	100% methanol						
Gelation bath temperature (°C)	-50	-50	20	-50	20	-50	-50
Spin draw ratio	3	3	2.5	2.5	2.5	2.5	3
Cold draw ratio*	1.3	1.3	1.3	1.3	1.3	1.3	1.25
Hot draw ratio*	4.7	5.7	5.4	5.1	6.7	5.7	5.6
Total draw ratio	18.3	22.2	17.6	16.6	21.8	18.5	21.0
Effective fiber diameter (μm)	8.1	10.4	9.7	9.8	8.2	8.9	6.9
Tensile strength (GPa)**	0.7 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	0.7 ± 0.1	1.0 ± 0.1	0.9 ± 0.1	1.0 ± 0.2
Tensile modulus (GPa)**	21.5±1.0	19.1±1.0	27.3±3.8	23.3±4.0	26.4±1.3	25.3±1.6	23.8±2.8
Strain to failure (%)**	5.5 ± 0.2	5.5 ± 0.2	5.4 ± 0.4	5.3 ± 0.4	6.3 ± 0.3	5.8 ± 0.5	6.9 ± 0.7
Crystallinity (%)	53	52	57	54	56	55	52
Crystal size (nm)	13.3	10.9	13.2	12.6	12.9	12.8	12.5
f _{PAN} ***	0.87	0.84	0.92	0.89	0.91	0.91	0.88

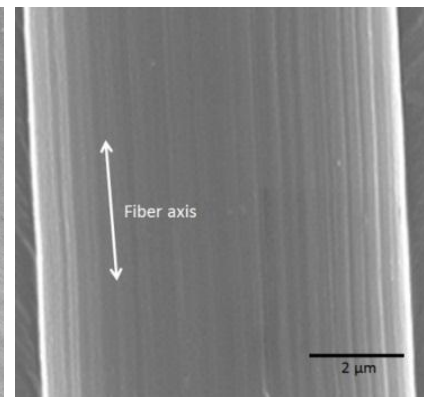
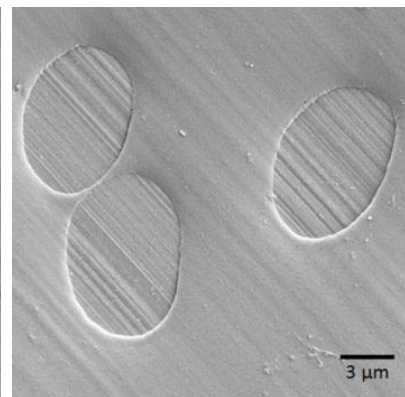
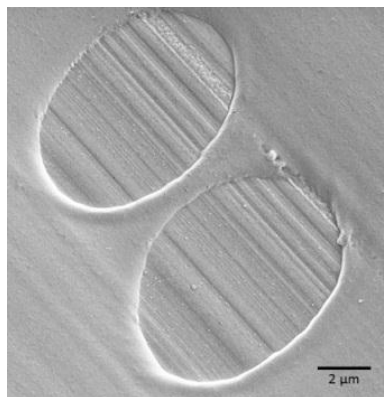
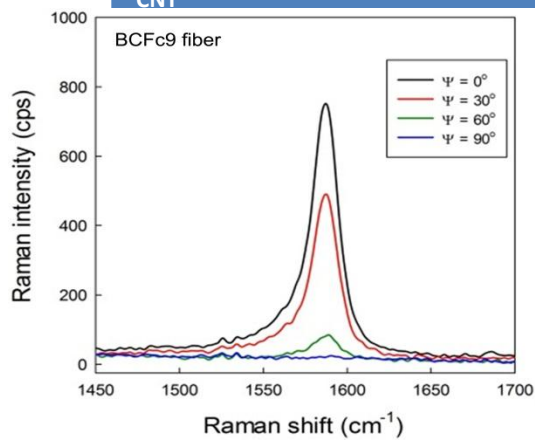
- Effect of solution concentration (BCFc1, 2, 4, and 6)
 - For a given polymer, the higher tensile properties were obtained at higher solution concentration.

- Effect of gelation bath temperature (BCFc3 and 5 vs. BCFc4 and 6) and CNT (BCFc7) on the fiber circularity and fiber properties
 - As compared to single component fiber spinning using room temperature gelation bath, bi-component fiber showed collapsed cross-sectional structure, suggesting solvent/non-solvent exchange rate is different due to the sheath component.
 - PAN/CNT composite fiber has more collapsed cross-section than control fiber, indicating that CNT incorporation affects the coagulation behavior.



Bi-component fiber (sheath-core) spinning – Processing optimization

	BCFc8	BCFc9
Polymer/solvent/concentration	PAN homo-polymer (250,000 g/mol) / DMF / 14.5g/dL	
CNT (concentration)	XO122UA (0.75 wt%)	
Gelation bath temperature	-50 °C methanol	
Flow rate (sheath/core) (cc/min)	0.7 / 0.3	
Spin draw ratio	3	3
Cold draw ratio	1.36	1.19
Hot draw ratio	5.0	7.06
Total draw ratio	20.4	25.2
Effective fiber diameter (μm)	7.9	6.9
Tensile strength (GPa)	0.89 ± 0.09	1.11 ± 0.09
Tensile modulus (GPa)	21.5 ± 2.0	21.9 ± 1.5
Strain to failure (%)	7.6 ± 1.0	9.7 ± 1.0
Crystallinity (%)	64	66
Crystal size (nm)	10.0	10.3
f_{PAN}	0.90	0.91
f_{CNT}	0.91	0.93



SUMMARY

PRECURSOR FIBER SPINNING

- Various spinning trials including single- and bi-component fiber spinning conducted to obtain precursor fiber for carbonization.
- The obtained precursor fiber properties are as follows:
 - Tensile strength: **0.6 – 1.4 GPa**
 - Tensile modulus: **16 – 28 GPa**
- Various spinning parameters including gelation bath composition, gelation bath temperature, spin draw ratio, and solution concentration were changed to obtain circular cross-section fiber with good tensile properties.
- Upon processing optimization, we obtained relatively circular small diameter precursor fiber from sheath-core bi-component spinning.

BATCH STABILIZATION AND CARBONIZATION

- Carbonization trials for single component fibers
- Carbonization trials for bi-component fibers (sheath-core)

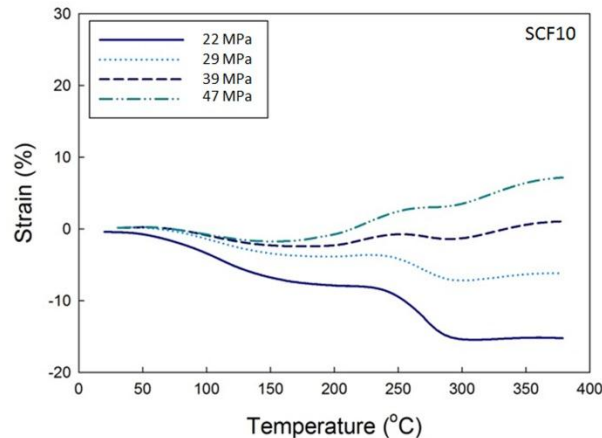
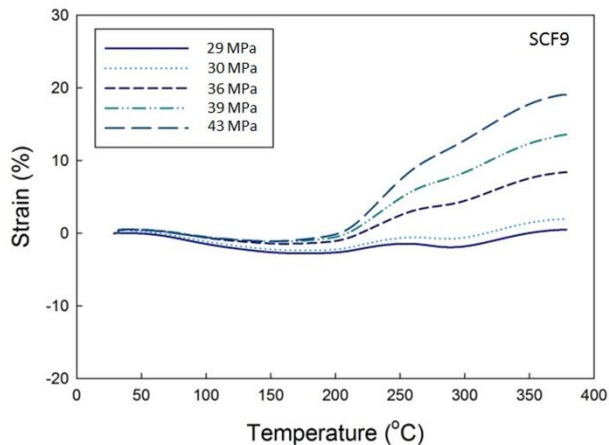
Background for stabilization and carbonization

- **PAN-based carbon fiber typically takes two steps of heat treatment.**
 - **Stabilization (or Oxidation) and Carbonization**
- **During Stabilization under oxygen environment, various chemical reactions occur to obtain thermally stable structure.**
 - Cyclization, dehydrogenation, oxidation, and cross-linking
 - During stabilization, three important processing parameters such as residence time, temperature, and tension are considered to be key factors
 - Under- or over-stabilized precursor fiber will result in lower property carbon fibers
- **During carbonization, oxygenated structure will be cross-linked, and nitrogen and oxygen will be removed. Depending on carbonization temperature, turbo-stratic graphitic or graphitic structure will be formed.**
 - The key processing parameters for carbonization will be tension and temperature

Carbonization – single component fibers (processing optimization)

Precursor PAN-co-MAA/CNT composite fiber

	SCF9	SCF10
Polymer/solvent/ concentration	PAN-co-MAA (240,000 g/mol) / DMAc / 14 g/dL	
CNT (concentration)	XO122UA (0.5 wt%)	
Gelation bath temperature	-50 °C methanol	
Spin draw ratio	3	6
Cold draw ratio	1.8	1.4
Hot draw ratio*	7.3	4.5
Total draw ratio	39	38
Effective fiber diameter (μm)	10.5	10.1
Tensile strength (GPa)**	1.2 ± 0.1	1.0 ± 0.1
Tensile modulus (GPa)**	27.3 ± 1.5	25.7 ± 1.9
Strain to failure (%)**	7.1 ± 0.5	7.0 ± 0.5



- SCF9 showed more stretching than SCF10 under similar tension during heat treatment
- Maximum tension
 - SCF9: 43 MPa
 - SCF10: 47 MPa

Carbonization – single component fibers (processing optimization)

Preliminary carbonization trials

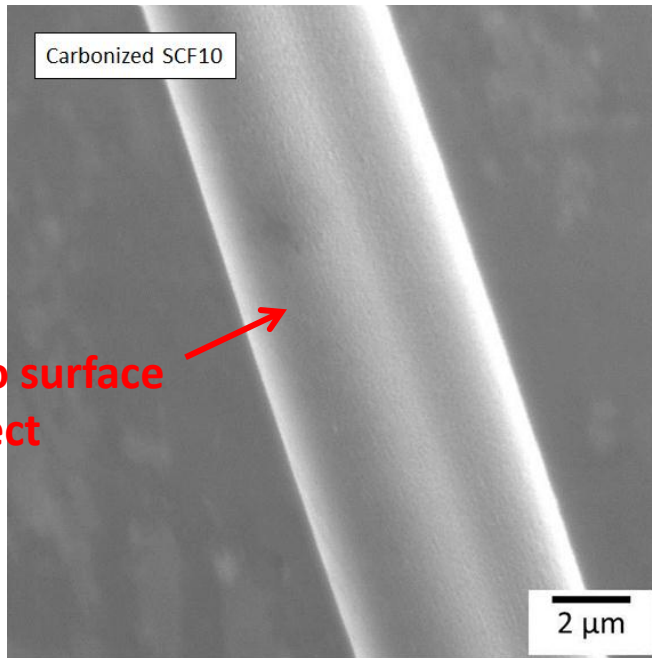
- Tension for SCF10: 46 MPa and for SCF9: 43 MPa
- Carbonization temperature: 1300 °C under argon environment

Sample ID	Trial	Residence time (min)		Effective diameter (μm)	Tensile strength (GPa)**	Tensile modulus (GPa)**	Strain to failure (%)**
		at 265 °C*	at 300 °C*				
SCF10	1 st	100 min	30 min	5.7	2.4 ± 0.3	273 ± 24	1.0 ± 0.1
	2 nd	90 min	30 min		2.1 ± 0.4	293 ± 18	1.1 ± 0.3
	3 rd		20 min		3.1 ± 0.4	290 ± 22	1.1 ± 0.1
	4 th		10 min		2.9 ± 0.3	303 ± 24	1.1 ± 0.1
SCF9	1 st	110 min	30 min	5.4	4.4 ± 0.6	316 ± 26	1.4 ± 0.1

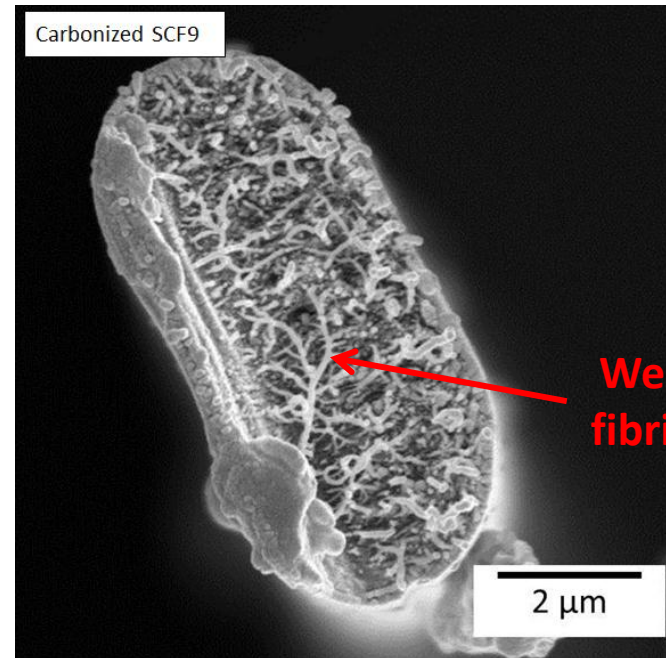
* Heating rate for stabilization and carbonization was 5 °C/min

** Tensile testing was done using 6 mm gauge length and cross-head speed of 0.1%/s

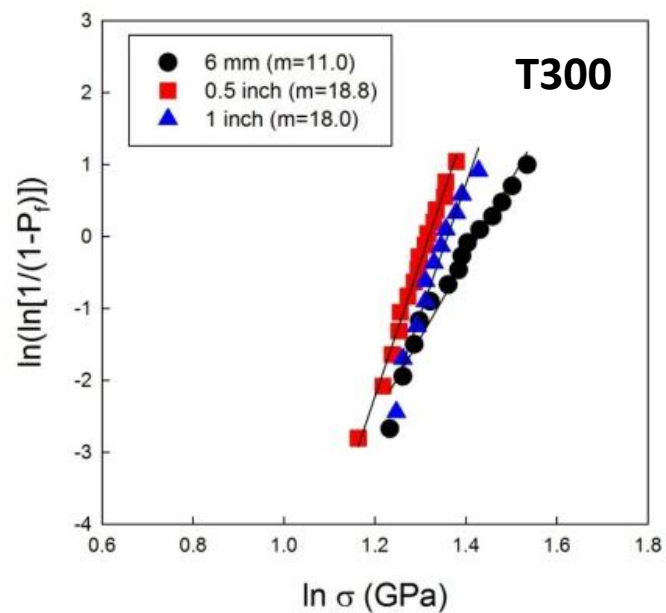
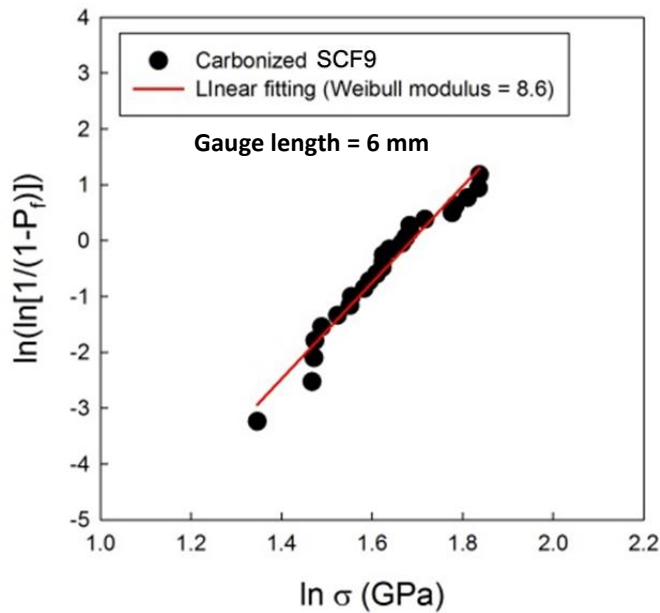
- Under similar tension condition, the carbonized SCF9 exhibited better tensile properties.
- Based on TMA results, SCF9 showed more stretching than SCF10. This suggests that the molecules in SCF9 can be aligned better than in SCF10 under similar stabilization condition.



Little or no surface defect



Well developed fibrillar structure



Processing optimization for SCF9 fiber

- Tension: 43 MPa (based on precursor fiber diameter)
- Carbonization temperature: 1300 °C under Argon environment

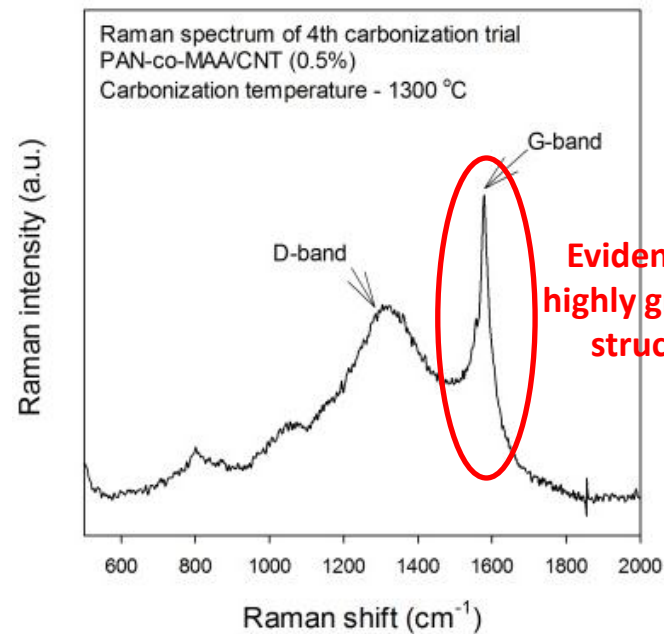
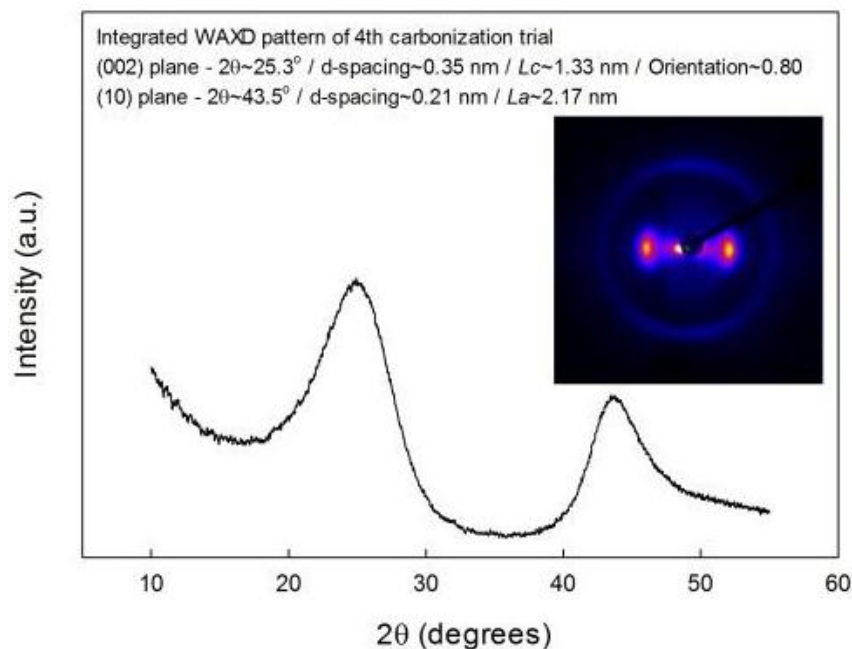
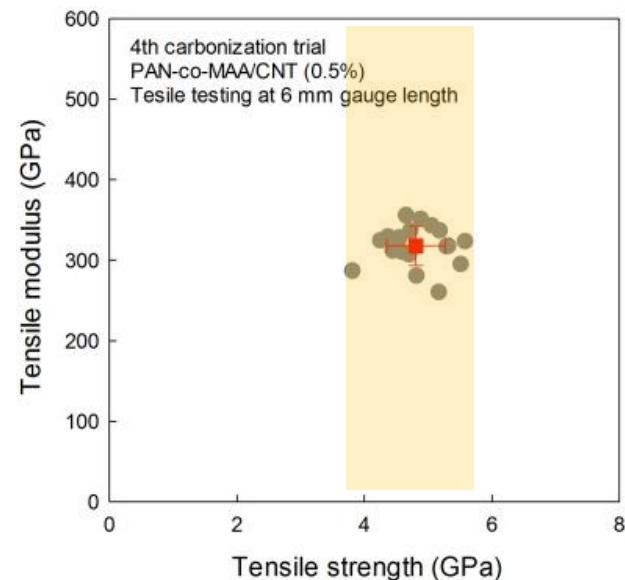
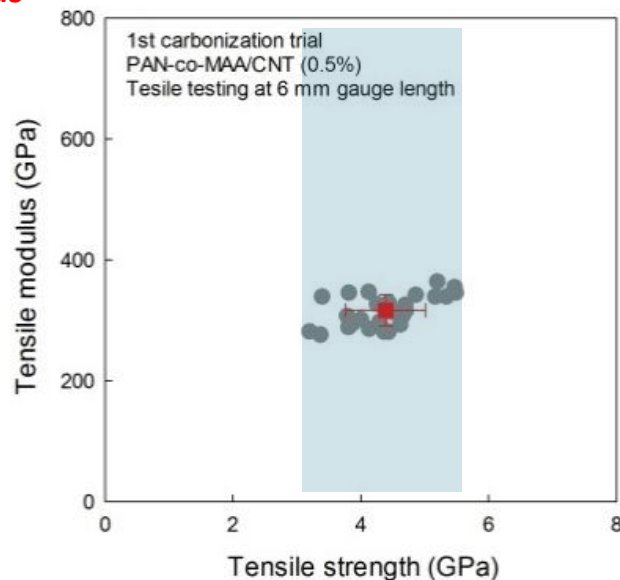
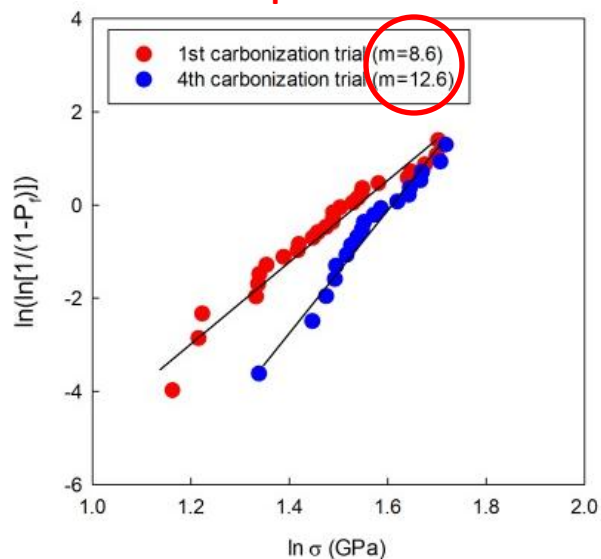
Trial	Stabilization temp (°C) / residence time (min)		Effective diameter (μm)*	Gauge length (mm)	Tensile strength (GPa)***	Tensile modulus (GPa)***	Strain to failure (%)***
	1 st	2 nd					
1 st	265 / 110	300 / 30	5.35	6	4.4±0.6	316±26	1.4±0.1
2 nd	265 / 120	300 / 30		6	4.2±0.9	277±41	1.5±0.2
3 rd	265 / 120	300 / 25		6	4.5±0.6	287±25	1.5±0.2
4 th	265 / 130	300 / 30		6	4.8±0.5	318±24	1.5±0.2
5 th ***	265 / 140	300 / 30		6	3.9±0.5	258±29	1.5±0.1
6 th -1	265 / 140	300 / 30		6	4.1±0.8	296±37	1.4±0.2
6 th -2				12.7	3.5±0.6	310±24	1.1±0.1
6 th -3				25.4	3.1±0.4	316±22	1.0±0.1
7 th	265 / 130	320 / 10		6	4.0±0.6	320±31	1.2±0.2
8 th	265 / 130	320 / 20		6	4.4±1.0	326±40	1.3±0.3
9 th	265 / 130	320 / 30		6	3.5±0.7	337±32	1.0±0.2

* Carbon fiber diameter in the current report is based on SEM calibration.

** For 5th trial, tungsten clamp slipped out of the fiber after carbonization while the furnace was being cooled down to room temperature (at about 500 °C).

*** All the carbon fiber tensile testing was done at strain rate of 0.1%/s at different gauge lengths using RSA III .
Typically 20 – 30 specimens were tested for each gauge length.

Improved Weibull modulus

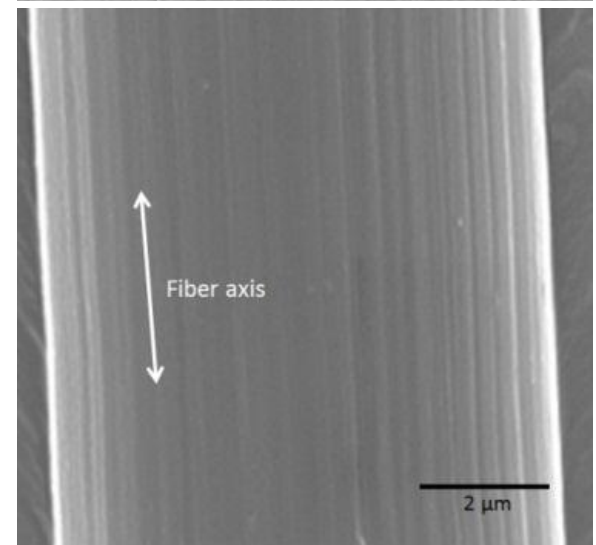
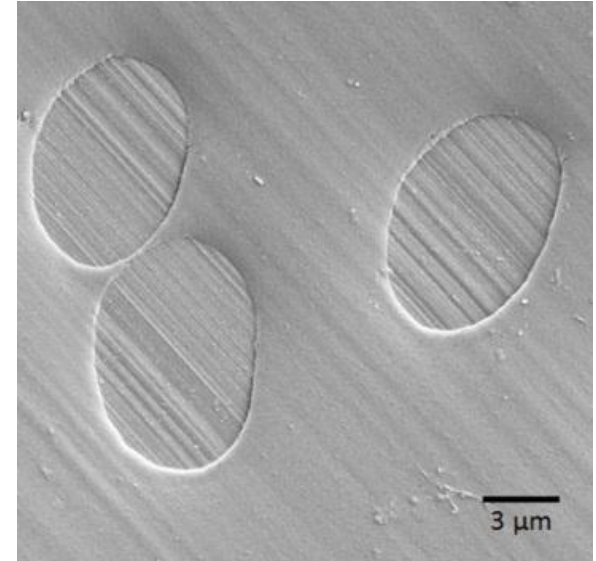


Evidence for highly graphitic structure

Carbonization – bi-component fibers (core fiber, processing optimization)

Precursor PAN-co-MAA/CNT composite fiber

	BCFc9
Polymer/solvent/concentration	PAN homo-polymer (250,000 g/mol) / DMF / 14.5g/dL
CNT (concentration)	XO122UA (0.75 wt%)
Gelation bath temperature	-50 °C methanol
Flow rate (sheath/core) (cc/min)	0.7 / 0.3
Spin draw ratio	3
Cold draw ratio	1.19
Hot draw ratio	7.06
Total draw ratio	25.2
Effective fiber diameter (μm)	6.9
Tensile strength (GPa)	1.11 ± 0.09
Tensile modulus (GPa)	21.9 ± 1.5
Strain to failure (%)	9.7 ± 1.0
Crystallinity (%)	66
Crystal size (nm)	10.3
f_{PAN}	0.91
f_{CNT}	0.93



* Sheath component was removed during drawing procedure

Carbonization – bi-component fiber (processing optimization)

Preliminary carbonization trials

- Higher pre-tension resulted in higher tensile strength and modulus under similar residence time during stabilization

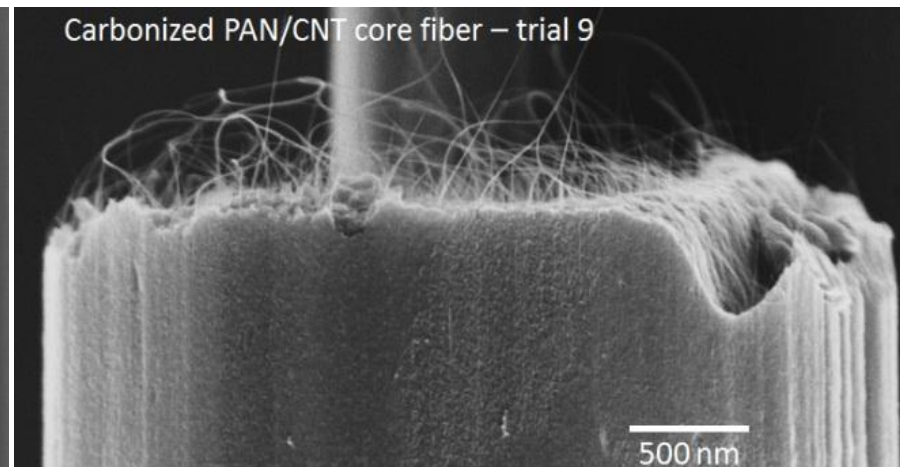
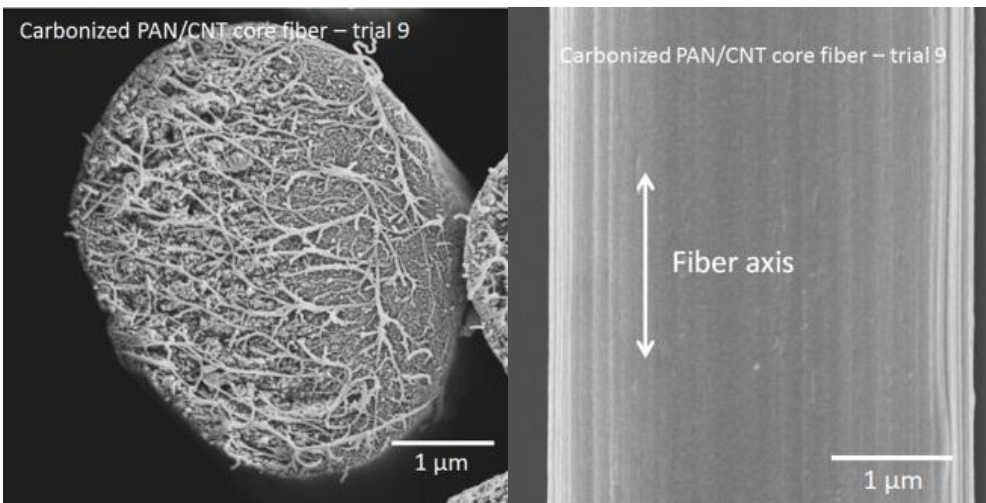
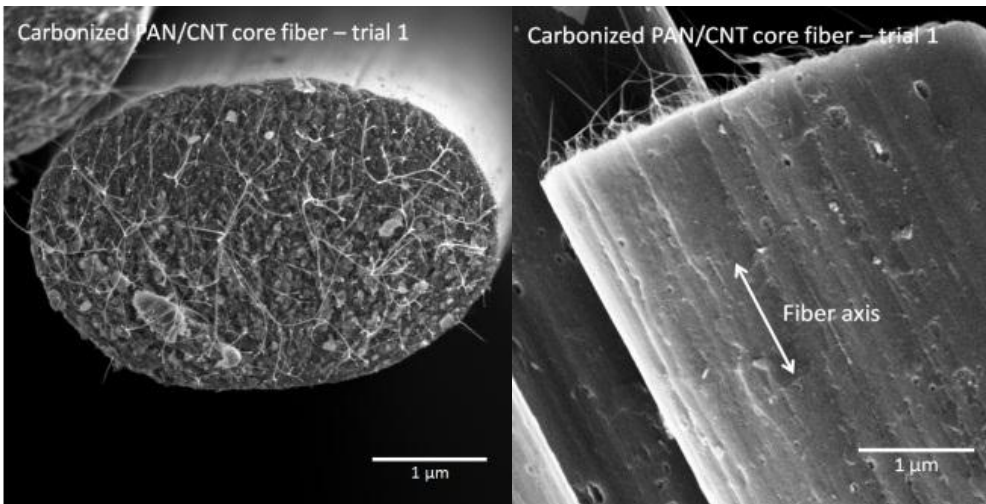
Trial	Pre-tension (MPa)	Stabilization time		Effective diameter (μm) ‡	Tensile strength (GPa) *	Tensile modulus (GPa) *	Strain to failure (%)*	Weibull modulus
		at 260 °C (min)	at 305 °C (min)					
1 st #	25.5	50	30	3.76	3.83±0.37	271±31	1.41±0.19	5.9
6 th #	25.5	90	10	3.76	3.83±0.61	295±24	1.30±0.22	6.3
7 th #	27.3			3.54	4.22±0.57	315±35	1.33±0.17	7.4
8 th #	29.4			3.52	4.90±0.69	339±24	1.43±0.16	7.0
9 th #	34.7			3.50	5.48±0.58	362±15	1.52±0.15	9.0

‡ Effective diameter was calculated from the SEM cross-sectional images of various fibers. At least 20 different cross-sections were observed and used to calculate cross-sectional area (by ImageJ image analysis software).

* Tensile testing was done at 6 mm gauge length at a constant strain rate of 0.1%/s.

In all the trials, carbonization was done at 1300 °C in an inert environment (argon). The ramping rate was at 5 °C/min and temperature was held at 1300 °C for 5 min.

- Carbon fiber (trial 1) under poor stabilization condition exhibited defect structure (void) on fiber surface
- On the other hand, carbon fiber under good stabilization shows little or no surface defect. In addition, well developed fibrillar structure (20 – 30 nm in diameter) was also observed in trial 9 fiber
- Tensile strength of trial 1 – 3.8 GPa
- Tensile strength of trial 9 – 5.5 GPa

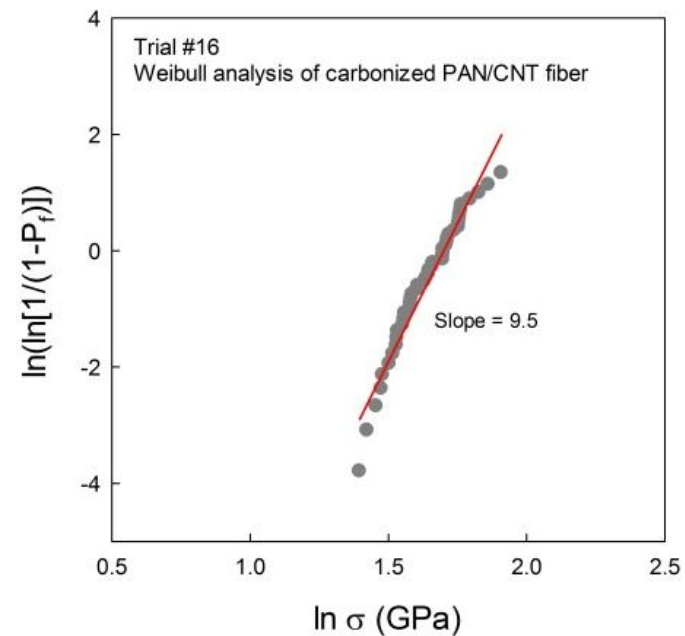
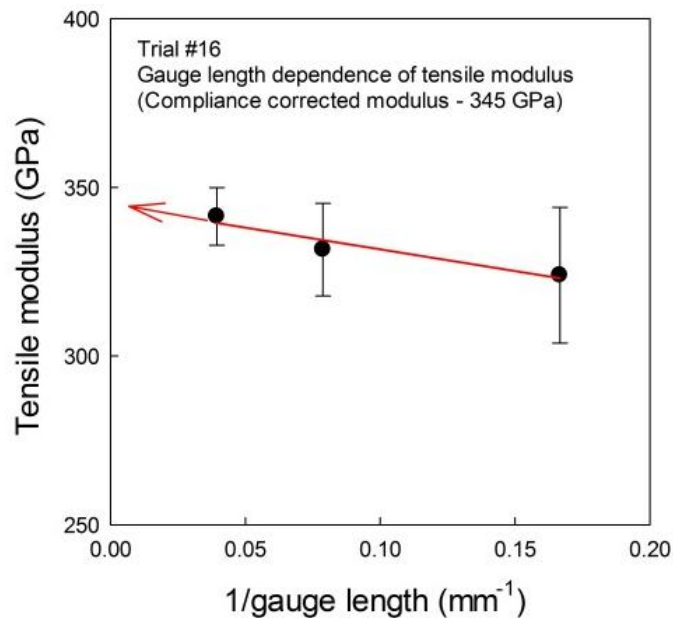
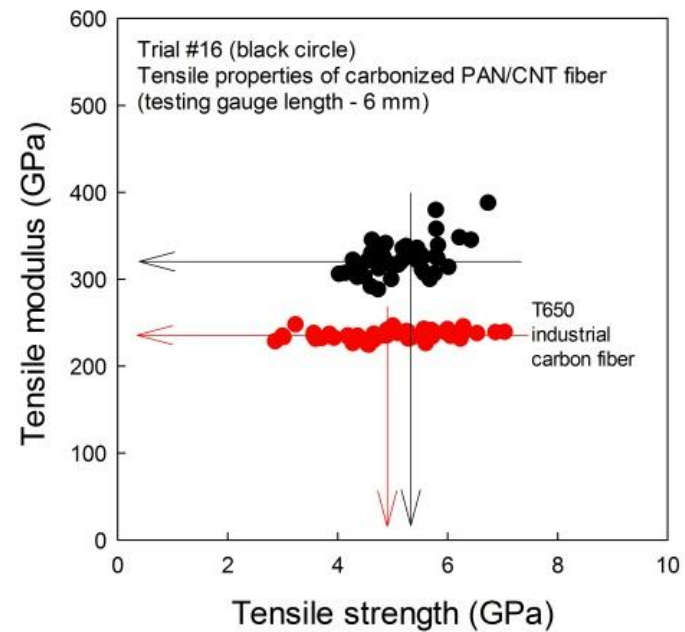
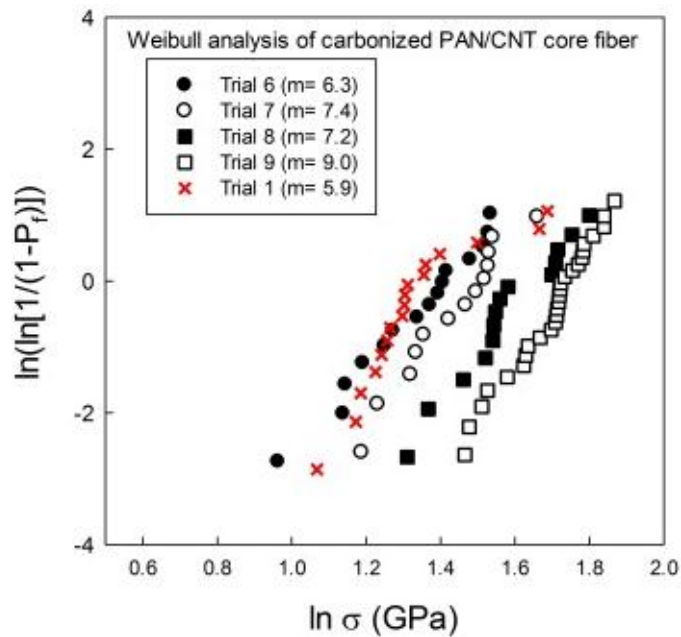


Trial	Pre-tension (MPa)	Stabilization time		Effective diameter‡ (μm)	Gauge length (mm)	Tensile strength* (GPa)	Tensile modulus* (GPa)	Strain to failure* (%)	Weibull modulus
		at 260 °C (min)	at 305 °C (min)						
9-1	36.4	100	10	Fiber breakage during stabilization					
9-2	34.7	100	10	Fiber breakage during stabilization					
9-3	34.7	100	10	3.50	6	3.93 ± 0.85	315 ± 15	1.24 ± 0.27	-
9-4	34.7	100	10	Fiber breakage during stabilization					
9-5	25.5	100	10	3.50	6	2.20 ± 0.47	238 ± 30	0.91 ± 0.12	-
9-6	30.6	100	10	3.50	6	2.47 ± 0.52	289 ± 24	0.85 ± 0.14	-
9-7	34.7	100	10	Fiber breakage during carbonization					
9-8	34.7	100	10	3.50	6	4.01 ± 0.57	312 ± 22	1.28 ± 0.19	-
9-9	34.7	90	10	3.50	6	3.87 ± 0.67	346 ± 34	1.11 ± 0.16	-
9-10	34.7	96	3	3.50	6	4.06 ± 0.63	320 ± 15	1.26 ± 0.16	-
9-11	34.7	100	10	Fiber breakage during stabilization					
9-12	33.2	90	10	3.50	6	3.67 ± 0.56	308 ± 22	1.18 ± 0.24	-
9-13	33.2	100	10	3.50	6	4.40 ± 0.77	319 ± 17	1.37 ± 0.20	-
10	33.2	124	3	3.39	6	4.19 ± 0.43	317 ± 15	1.39 ± 0.14	9.6
11		124	17	3.36		4.03 ± 0.42	323 ± 17	1.29 ± 0.11	10.2
12		96	3	3.41		4.52 ± 0.90	340 ± 25	1.37 ± 0.20	4.9
13		96	17	3.54		4.27 ± 0.74	310 ± 20	1.40 ± 0.18	5.9
14		130	10	3.42		4.84 ± 0.64	316 ± 16	1.55 ± 0.18	8.0
15		90	10	3.40		4.68 ± 0.64	314 ± 20	1.52 ± 0.19	7.7
16		110	0**	3.51	6	5.33 ± 0.55	326 ± 21	1.62 ± 0.15	9.5
					12.7	4.67 ± 0.46	328 ± 11	1.44 ± 0.14	8.8
					25.4	4.41 ± 0.40	341 ± 9	1.28 ± 0.11	11.1
17			110	20	3.42	6	4.26 ± 0.59	325 ± 25	1.34 ± 0.12

‡ Linear density (tex) was obtained from vibroscope method and effective diameter was calculated assuming carbon fiber density of 1.8 g/cm³.

* Tensile testing was done at 6, 12.7, and 25.4 mm gauge length as indicated at a constant strain rate of 0.1%/s.

** For trial 16, the second stage of stabilization was done by heating up to 305 °C at a heating rate of 5 °C/min, and then proceed for carbonization without holding at 305 °C.



SUMMARY AND KEY-OUTCOMES

BATCH STABILIZATION AND CARBONIZATION

- Various carbonization trials were conducted using single- and bi-component (sheath-core) precursor fibers.
- Processing optimization was carried out by varying stabilization conditions such as tension, temperature and residence time.
- The highest average tensile properties from single component ($\sim 10\ \mu\text{m}$) precursor fibers are,
 - Tensile strength: 4.8 GPa (the highest tensile strength for a single test 6.5 GPa)
 - Tensile modulus: 337 GPa (the highest tensile modulus for a single test 360 GPa)
- The highest average tensile properties from bi-component ($\sim 7\ \mu\text{m}$) precursor fibers are,
 - Tensile strength: **5.5 GPa** (the highest tensile strength for a single test **6.8 GPa**)
 - Tensile modulus: **362 GPa** (the highest tensile modulus for a single test **389 GPa**)

ACKNOWLEDGEMENT



- Air Force Office of Scientific Research
- Japan Exlan, Co. (Japan)
- Carbon Nanotechnologies, Inc (CNI)/Unidym
- Georgia Institute of Technology
- Collaborators – Dr. Fred Cook, Dr. Anselm Griffin, Dr. Satish Kumar, Dr. Prabhakar Gulgunje, Dr. Manjeshwar Kamath, Kevin Lyons