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14. ABSTRACT Report developed under STTR contract for topic AF08-T028. Polyacrylonitrile/carbon nanotube composite fibers are processed and used to produce high strength and high modulus carbon fibers. In order to produce composite fibers, several spinning technologies have been used, which are called gel spinning and bi-component spinning. Carbonization process of the composite fiber was optimized to obtain high strength and high modulus carbon fiber. The resulting carbon fibers possessed average tensile strength up to 5 gigapascal (GPa) and average tensile modulus up to 410 GPa. The highest strength and modulus to date are 7.1 GPa and 476 GPa, respectively. These nanotailored carbon fibers will have superior mechanical properties as well as better electrical and thermal conductivity as compared to the conventional carbon fibers, which should result in significant weight savings and functionality in various aerospace composite systems.						
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Nanotailored Carbon Fibers (STTR Phase I final technical report)
(Dr. Charles -Y.-C. Lee; AFOSR/NA)

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1. Project Objectives

In STTR Phase I project, the primary objectives of NEM corp were given as follows.

- To process high tensile strength polyacrylonitrile (PAN)/carbon nanotube (CNT) composite fibers using single-component gel spinning (fiber diameter $> 9 \mu\text{m}$).
- To process high tensile strength PAN/CNT composite fibers using gel spinning and core-shell bi-component geometry (fiber diameter $\sim 6 - 7 \mu\text{m}$).
- To process high tensile strength PAN/CNT composite fibers using gel spinning and islands-in-a-sea bi-component geometry (fiber diameter $\sim 2 \mu\text{m}$).
- To investigate the effect of precursor fiber on the resulting carbon fiber properties, various precursor fibers were prepared using homo-polymer or co-polymer with various molecular weight with various fiber diameter.
- To optimize stabilization conditions (residence time, temperature, and tension) to achieve the highest tensile strength and highest tensile modulus stabilized fiber.
- To optimize carbonization conditions (temperature, tension) to maximize tensile strength and tensile modulus of the resulting carbon fibers.

2. Work performed

2.1 Precursor fiber preparation

PAN/CNT precursor fibers were prepared using gel spinning technology¹. In order to have precursor fibers with various fiber diameter, single-component and bi-component (core-shell and islands-in-a-sea geometry) spinning technology has been used. Homo-PAN (molecular weight - 250,000 g/mol) and PAN-methacrylic acid (MAA) co-polymer (molecular weight - 240,000 g/mol and 520,000 g/mol) are used to investigate the effect of polymer type on the resulting carbon fiber. High purity CNT (lot no. XO122UA, Unidym, Inc., 1 wt% catalytic impurity) was used in the current study. Figure 1 shows the high resolution transmission electron microscopy (HRTEM) image and schematic of CNT, indicating that it is the mixture of double-, triple-, and few- wall carbon nanotubes.

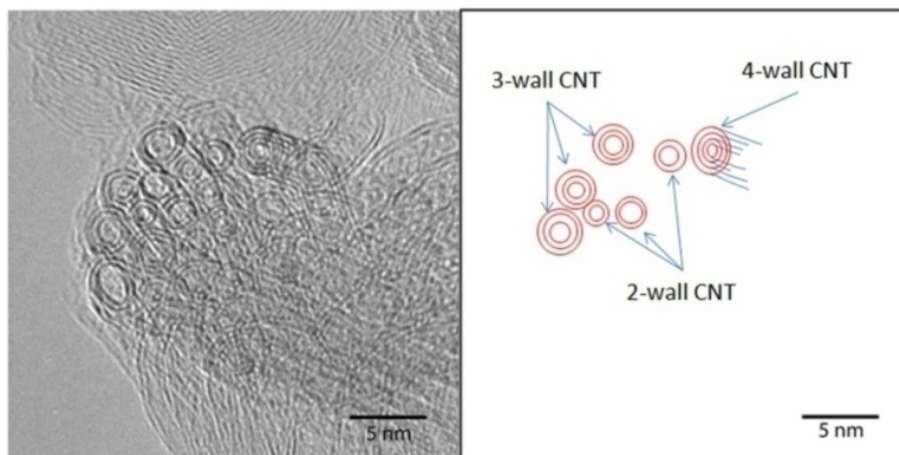


Figure 1. High resolution transmission electron micrograph of CNT (left) and schematic showing the mixture of 2-wall, 3-wall and 4-wall CNT (right).

For spinning dope preparation, polymers were dissolved in dimethylformamide (DMF) or dimethylacetamide (DMAc) at a concentration of 15 wt% (for 250,000 g/mol homo-PAN and 240,000 g/mol PAN-MAA) and 13 wt% (for 520,000 g/mol PAN-MAA). In order to minimize the impurity incorporation, solvents were purified by vacuum distillation. CNTs were dispersed in DMF or DMAc at a concentration of 40 mg/L using 24 hr bath sonication (Branson 3510R-MT, 100 W, 42 kHz) at room temperature. Optically homogeneous CNT/DMF or DMAc dispersion was added to the polymer solution. The excess amount of solvent was removed by vacuum distillation at 90 °C, while stirring, to obtain the desired solution concentration (15 wt% or 13 wt%). CNT concentration was set to be 1 wt% with respect to polymer. For bi-component spinning, poly(methyl methacrylate) (PMMA, molecular weight - 350,000 g/mol) was used for fugitive component (shell or sea component). The 30 g of PMMA was dissolved in 100 mL of DMF or DMAc. Spinning and drawing processes are described as follows.

- Single-component gel spinning

Spinning dope was spun at 31.4 m/min using 120 μm diameter single hole spinneret at 110 °C into a methanol bath maintained at -50 °C. The air gap between spinneret and the methanol bath was kept about 2 - 3 cm. The as-spun fibers were taken up at 100 m/min and kept immersed in cold methanol bath (maintained ~ -30 to -40 °C) for 2 days, to ensure gelation. The gel fiber was further drawn (hot draw ratio ~ 5) at about 165 °C in glycerol bath followed by washing in ethanol and vacuum drying at 50 °C for 3 days. Figure 2 shows the schematics of solution preparation, spinning, and drawing process.

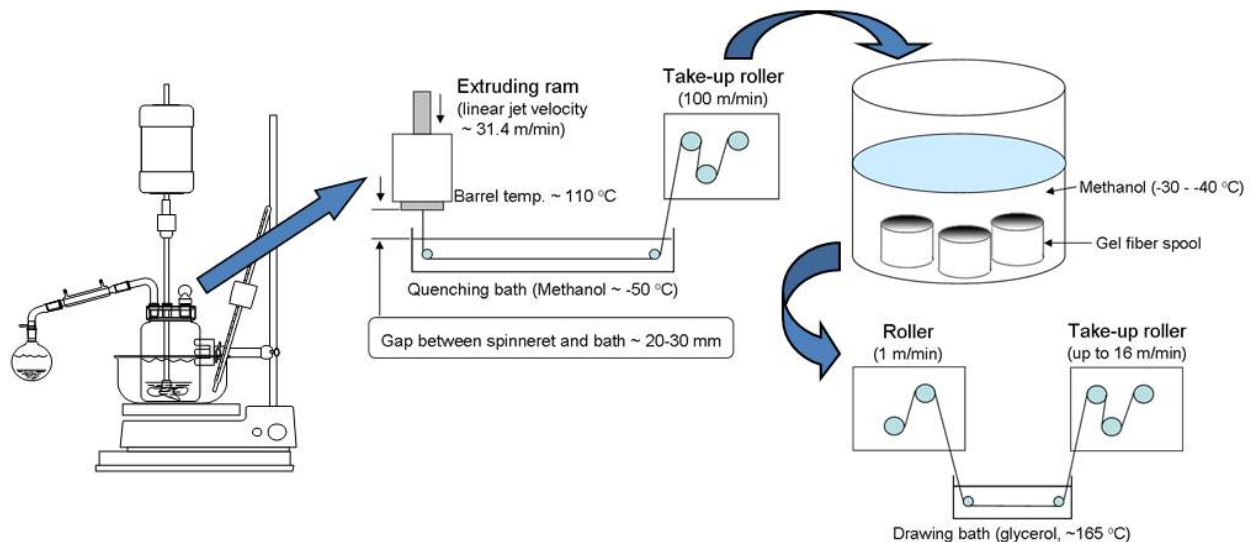


Figure 2. The schematics of spinning dope preparation, gel spinning, and hot drawing process. Drawing conditions (fiber feeding speed and take-up speed) were adjusted to obtain the highest draw ratio.

- Bi-component gel spinning (core-shell and islands-in-a-sea geometry)²

Both core-shell and islands-in-a-sea bi-component fibers were processed using spinneret of 250 μm diameter. The schematic of the bi-component spinning setup and of core-shell and islands-in-a-sea geometries are given in Figure 3. While maintaining the spinneret temperature at 100 °C, the spinning dopes (both PAN/CNT solution and PMMA solution) were extruded at a volumetric flow rate of 1.0 cm^3/min , which is equivalent to the linear

jet speed of about 40 m/min based on the spinneret diameter. The gelation bath conditions are the same as single-component gel spinning. The as-spun gel fibers were take up at 125 m/min (spin draw ratio ~ 3), and kept immersed in cold methanol bath for 1 day. For core-shell fibers, shell component (PMMA) was removed by dissolving it in nitromethane bath prior to hot drawing in 165 °C glycerol bath. The hot draw ratio of core fibers was as high as 9 times (total draw ratio ~ 30 times). Islands-in-a-sea fibers were drawn without removing sea component (PMMA) in stages at 100 and 160 °C using in-line heater. Due to the limited drawability of islands-in-a-sea fiber, the total draw ratio was less than 4 times. The drawn fibers were subsequently vacuum dried at 50 °C for 3 days.

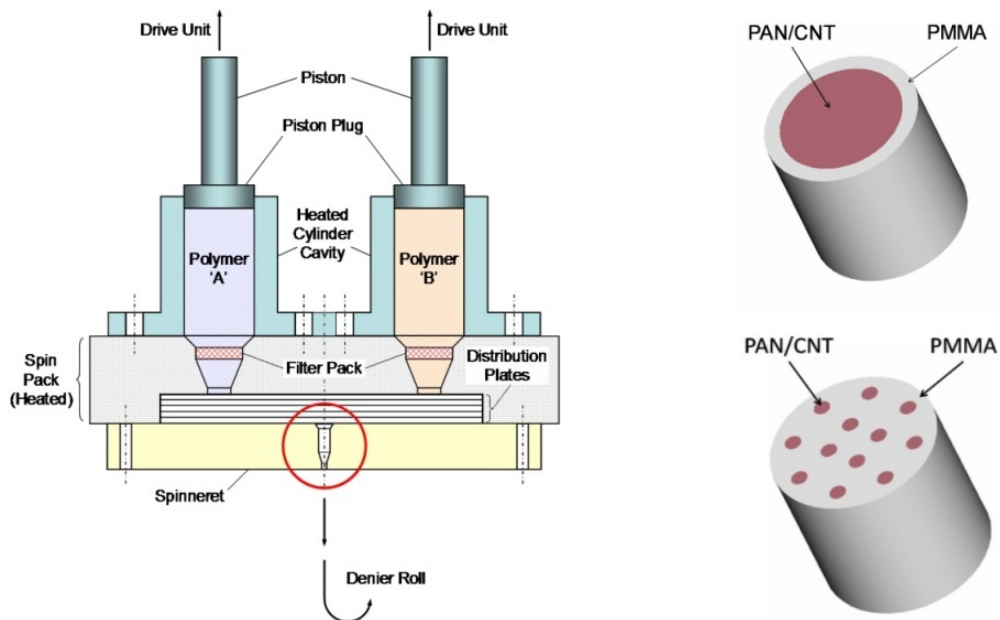


Figure 3. Schematics of bi-component spinning apparatus (left), core-shell (top right) islands-in-a-sea geometry (bottom right) bi-component fiber.²

2.2 Stabilization and carbonization²⁻⁴

Stabilization and carbonization optimization was conducted in both batch and continuous manner. More than 50 trials have been conducted to-date. Selected results from these trials are presented in this report as follows. Processing optimization was achieved by adjusting various processing conditions as follows.

- For a given precursor fiber, stabilization time and tension was varied to find the optimal conditions in batch process. Tension during stabilization and carbonization was adjusted as illustrated in Figure 4.
- For a given stabilized fiber using batch process, carbonization temperature and tension was varied to obtain the best carbon fiber.
- Continuous process was also conducted for stabilization and carbonization. For continuous process, tube type furnace was used. In most cases, the residence time was adjusted to optimized the processing at various temperatures.

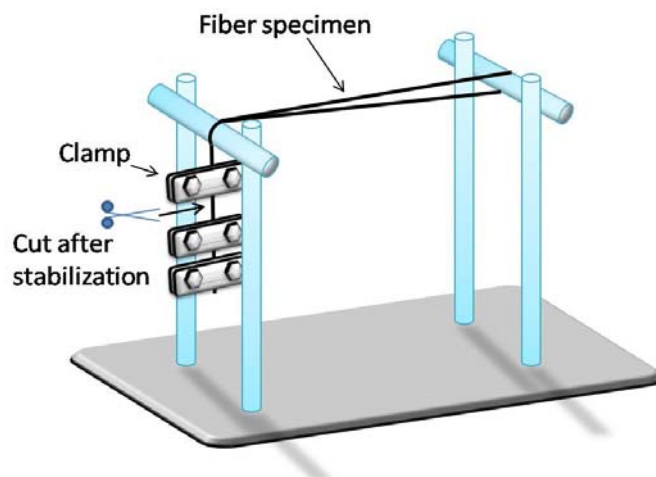


Figure 4. The schematic description of fixture to stabilize and carbonize the PAN/CNT fibers. By changing number of clamps or filaments, tension during stabilization and carbonization was varied to obtain the best fibers without fiber breakage.

3. Results

3.1 Effect of processing and materials parameters on the resulting carbon fibers

Single component PAN/CNT composite fibers were prepared using gel spinning technology, and islands-in-a-sea type (islands component – PAN/CNT and sea component – PMMA) composite fibers were also prepared. Table 1 lists the tensile properties of various fibers. The fiber diameter was largest for precursor fiber P1, while its tensile strength and modulus are the best among all the precursor fibers.

Table 1. Properties of various precursor fibers.

	P1 (Single component)	P2 (Single component)	P3 (Bi-component, islands-in-a-sea type)
CNT type/content	XO122UA/1 wt%	XO122UA/1 wt%	XO122UA/1 wt%
Polyacrylonitrile	Co-polymer*	Homo-polymer	Co-polymer*
Molecular weight (g/mol)	240,000	250,000	240,000
Fiber type	Single component	Single component	Bi-component (islands-in-a-sea geometry)
Diameter (μm)	16.7	9.0	2.1
Tensile strength (GPa)	1.1 ± 0.1	1.0 ± 0.2	0.6 ± 0.1
Tensile modulus (GPa)	31.7 ± 1.5	17.6 ± 2.9	16.2 ± 1.1
Strain to failure (%)	7.0 ± 0.6	9.0 ± 0.8	7.2 ± 0.4

*copolymer contained 4 wt% methacrylic acid

• Batch carbonization of P1 and P2

Fiber was often found to be broken during carbonization, whereas the fibers were intact after stabilization. The best tensile properties from P1 and P2 are listed in Table 2. For P1, initial stress during stabilization was 22 MPa and carbonization was conducted at 1100 °C. For P2, initial stress was set to be 20 MPa and carbonization temperature was 1100 °C. The reason to set

different initial stress was to keep the fiber unbroken during stabilization. P2 was frequently broken at more than 20 MPa stress. This may be attributed to the precursor fiber properties. P2 has lower strength and modulus than those of P1. As discussed earlier, the high tensile properties of gel spun PAN/CNT fibers originated from various factors such as molecular orientation, interaction between matrix and CNT, etc.

Table 2. Tensile properties of the carbonized P1 and P2 at 1100 °C.

	Carbonized P1(10.2 μm)				Carbonized P2 (5.4 μm)		
Gauge length (mm)	1	6	12.7	25.4	6	12.7	25.4
Tensile strength (GPa)	3.2 ± 0.6	2.4 ± 0.5	2.0 ± 0.8	1.4 ± 0.5	3.3 ± 0.5	2.4 ± 0.5	2.0 ± 0.5
Tensile modulus (GPa)	204 ± 22	258 ± 23	289 ± 28	281 ± 32	229 ± 38	236 ± 59	213 ± 57
Strain to failure (%)	1.5 ± 0.4	0.9 ± 0.2	0.7 ± 0.2	0.5 ± 0.2	1.4 ± 0.2	1.0 ± 0.2	1.0 ± 0.3

Tensile strength and modulus of the carbonized P1 as a function of gauge length is plotted in Figure 5. Tensile strength of the PAN/CNT based carbon fiber exhibits stronger gauge length dependence than that for the commercial T300. However, it should be noted that the carbonized fiber was found to be broken after carbonization, and the diameter of carbonized fiber P1 is almost 50% larger than that of T300. At small gauge length the tensile strength of the carbonized P1 exceeds that of the T300. Tensile modulus of the carbonized P1 is higher than that of T300. It is also noted that the P1 is carbonized only at 1100 °C. A higher carbonization temperature will lead to further increase in tensile strength and modulus. As compared to the carbonized P1, the properties of carbonized P2 exhibited the higher tensile strength and strain to failure, while their modulus is much lower than that of the carbonized P1 fiber. As we discussed earlier, it is clear that the modulus of precursor fiber is very important to obtain high modulus fiber. Tensile strength difference may come from the stabilization conditions, which were not optimal for both fibers.

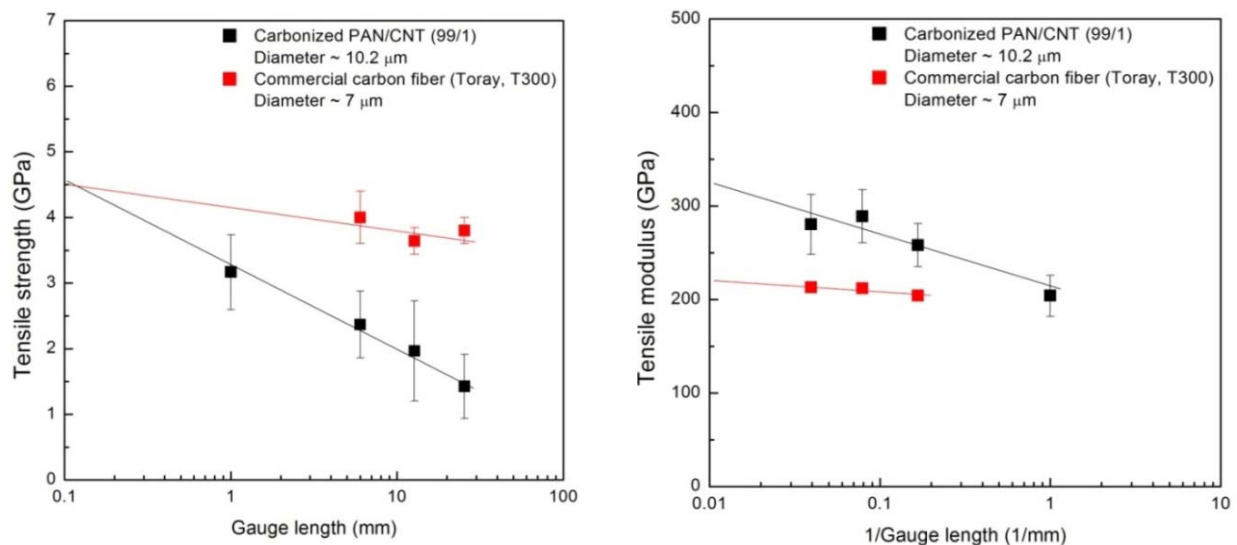


Figure 5. Tensile strength and modulus of carbonized fibers as a function of gauge length.

- **Continuous carbonization of P2**

P2 was also stabilized and carbonized using continuous process, and the carbon fiber properties are listed in Table 3. It should be noted that the carbonization temperature was 1200 °C. Tensile strength and modulus values were as high as 7.5 GPa and 450 GPa, respectively. Figure 6 exhibits the cross-sectional view of carbonized fiber and plot of tensile modulus as a function of tensile strength.

Table 3. Tensile properties of carbonized precursor P2.

Effective diameter (μm)	Gauge length (mm)	Tensile strength (GPa)	Tensile modulus (GPa)	Strain to failure (%)
5.7	6	3.8 ± 1.3	261 ± 66	1.39 ± 0.20

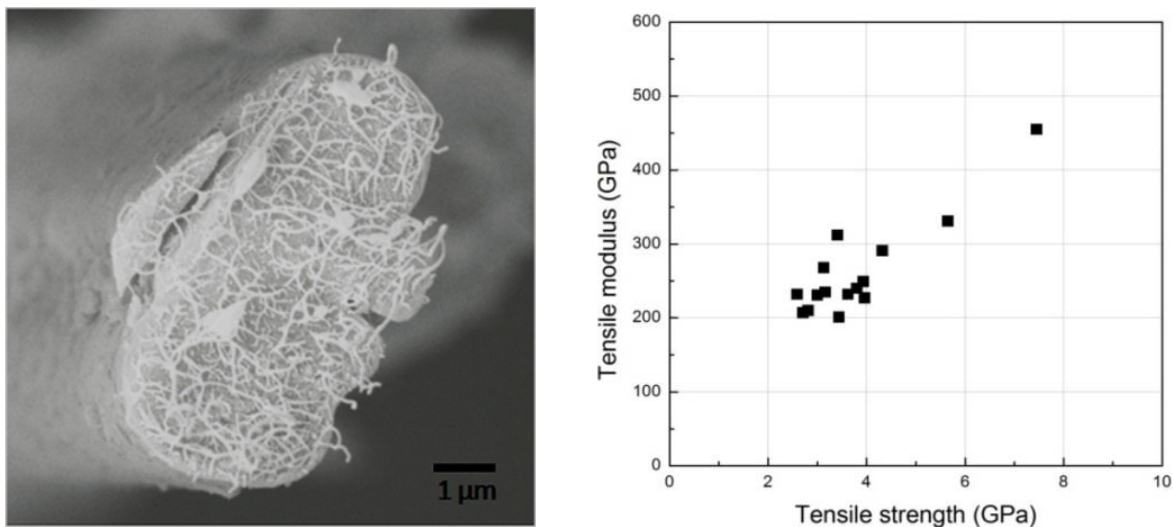


Figure 6. Tensile fractured cross-section (left) of the carbonized P2 and a tensile modulus vs tensile strength plot (right).

Figure 7 shows the SAXS 2D pattern of carbonized P2 and commercial carbon fibers (T300). The carbonized P2 fibers prepared in the current study shows relatively narrow streak along the equator, while T300 has broader intensity distribution. In addition, the integrated scan in Figure 7c also reveals that the carbonized P2 fiber has lower scattering intensity than T300. This indicates that the small angle scatterers (elongated micro-voids and foreign particles, etc) in the carbonized P2 fibers are much less than in T300. This is very important because highly aligned morphology greatly affects the carbon fiber modulus and less defect affect the carbon fiber strength. This supports why the carbonized P2 fibers have higher modulus than T300. It should be also noted that the carbonization temperature of T300 is known to be in the range of 1300 - 1400 °C. Although the temperature for the continuously carbonized P2 fibers is 1200 °C, the resulting fiber shows similar tensile strength to T300. This implies that there is still room for property enhancement.

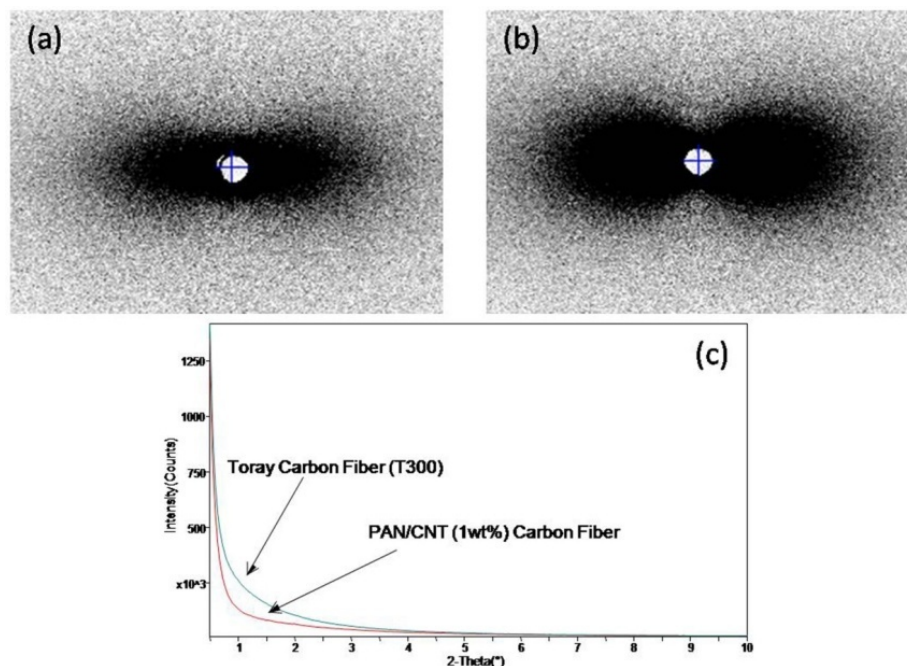


Figure 7. SAXS 2D patterns of (a) the carbonized P2 and (b) T300. (c) Integrated scan of (a) and (b).

- **Batch carbonization of P3**

Islands-in-a-sea type fibers were stabilized without removing sea component (PMMA). The initial stress was about 22 MPa, and the residence time was 1.5 hr at 285 °C and 0.5 hr at 330 °C. Fibers were not broken after stabilization, whereas they were found to be broken after carbonization. In order to obtain high strength and modulus carbon fiber, it is critical to find the proper condition to process without fiber breakage. Mechanical testing was done for multi-filament carbon fibers (1200 filaments).

Table 4. Tensile test results of the carbonized precursor P3.

Effective diameter (μm)	Gauge length (mm)	Tensile strength* (GPa)	Tensile modulus* (GPa)	Strain to failure* (%)
1.06	6	2.4 ± 0.2	168 ± 9	1.60 ± 0.09

*Tensile test was conducted on carbon fiber bundle (1200 filaments)

Tensile tested specimen showed carbonized islands fibers did not fail by compressive stress (Figure 8, top right), indicating that the compressive strength of these fibers is higher than their tensile strength. High resolution SEM images of the fiber cross-section showed 60 - 70 nm diameter fibril structure and very uniform carbon matrix. Ribbon type of fibers with about 200 nm thickness were also observed (arrow in Figure 8, bottom).

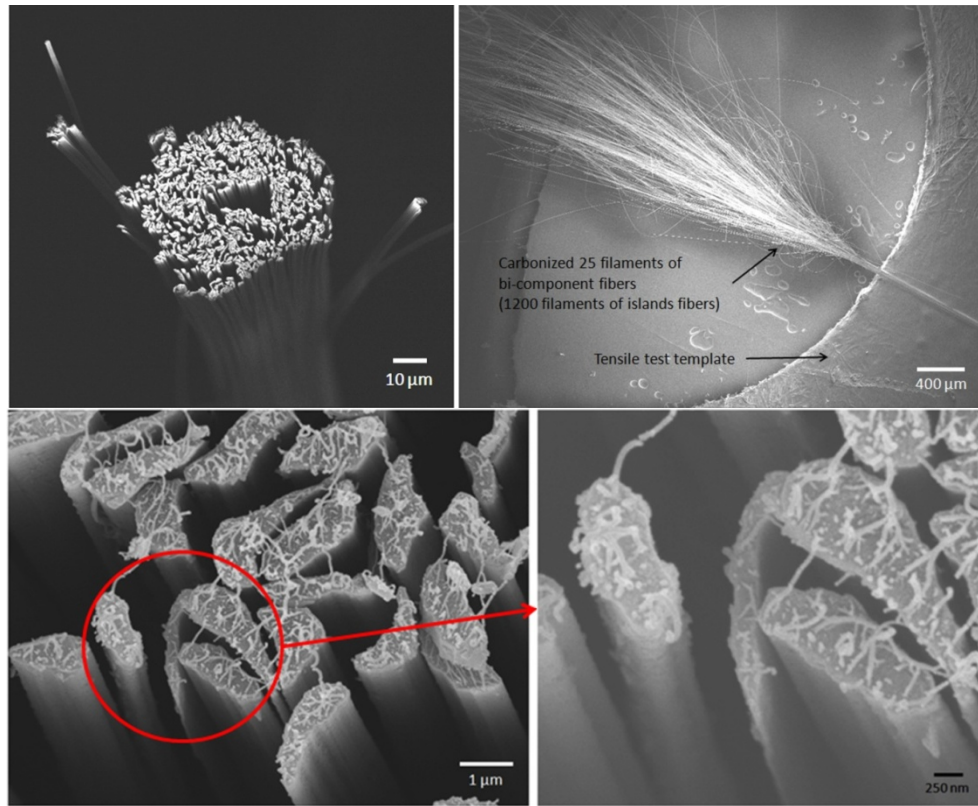


Figure 8. SEM images of cross-sectional view of carbonized islands fiber bundle (top left), tensile tested islands fiber bundle on template suggesting that the compressive strength of these fibers is higher than their tensile strength (top right), and high resolution images of cross-sectional view showing that ribbon-shape carbon fiber with less than 200 nm thickness.

The effort to test the individual filaments was done for the carbonized P3 fibers. After tensile testing, the remained fiber on template was observed using high resolution SEM. The cross-sectional view of tensile tested fiber was used to calculate the effective diameter using image analysis software (Image J software, NIH), and calibrate the tensile testing results. Table 5 and Figure 9 show the calibrated tensile results and SEM images of each specimen. Considering fiber breakage, we observed very high modulus up to 464 GPa. Further processing optimization will lead to the nano-tailored carbon fiber with improved modulus and strength.

Table 5. Calibrated tensile testing results based on corrected effective diameter by SEM.

Sample no.	Effective diameter (μm)	Tensile strength (GPa)	Tensile modulus (GPa)	Strain to failure (%)
1	2.16	0.7	91	0.77
2	1.88	1.5	155	0.92
3	2.46	1.2	173	0.68
4	1.56	2.9	464	0.57

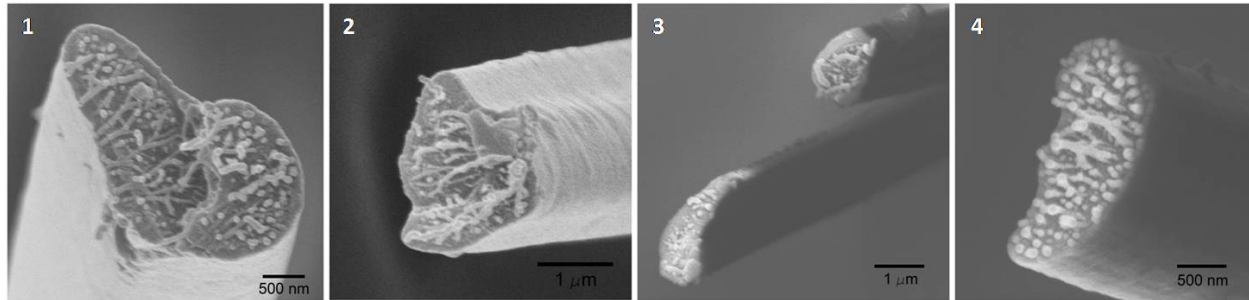


Figure 9. High resolution SEM images of the carbonized P3 fiber. Each sample was observed after tensile fracture.

3.1 Effect of precursor fiber properties on the resulting carbon fibers

Based on the previous results, it is concluded that one needs to have precursor fibers with modulus more than 25 GPa for high modulus and small diameter for high strength carbon fiber. Therefore, small diameter precursor fibers were processed using core-shell geometry, and the core fibers were able to be drawn to high draw ratio (~ 30 times) by removing shell component before drawing. Both homo-polymer and co-polymer (methacrylic acid, 4 wt%) were used to produce composite fibers with CNT (1 wt%) as shown in Table 6.

Table 6. Properties of precursor fibers processed using core-shell bi-component spinning.

	P4	P5
Polymer	Homo-PAN (250,000 g/mol)	Co-polymer (MAA* - 4 wt%) (520,000 g/mol)
CNT type/content	XO122UA (CNI Inc., 1 wt% catalytic impurity) / 1 wt%	
Effective diameter (μm)	7.4	6.3
Tensile strength (GPa)	1.1 ± 0.1	1.0 ± 0.2
Tensile modulus (GPa)	25.7 ± 2.1	24.6 ± 3.3
Strain to failure (%)	8.0 ± 0.6	7.0 ± 1.1
Crystallinity (%)	58	62
Crystal size (nm)	9.3	9.5
Crystal orientation (f_c)	0.88	0.86

* MAA - Methacrylic acid

• Batch carbonization of P4 - Effect of stabilization optimization

In previous sections, the most of fibers were broken during carbonization due to the gas purging problem and tension adjustment. Therefore, the environmental condition was corrected, and in most trials, fibers were found to be unbroken after carbonization. In this section, we demonstrated the importance of stabilization optimization to obtain better carbon fibers. Table 7 lists processing conditions and tensile properties, showing the effect of stabilization on the resulting carbon fiber properties. As shown in table, initial stress (pretension) during stabilization was set to be 27 MPa and carbonization was conducted at 1100 °C. The tensile strength of carbonized fibers increased by changing stabilization condition (showing the best value at P4-2 condition), suggesting that over-stabilized fibers would not result in high strength carbon fiber and optimizing the stabilization condition is critical. However, tensile modulus was not significantly affected by the stabilization because the tension during stabilization and

carbonization was same for all the trials. It can be also noted that increase in tensile strength led to the increase in strain to failure of carbon fiber. This also implies that the optimal stabilization condition results in structural perfection. All the tensile testing data points are plotted in Figure 10. It is very obvious that tensile modulus distribution is in narrow range, which is typical behavior of commercial carbon fiber. Gauge length dependency of tensile properties is also notably reduced as compared to the previous trials (Figure 5).

Table 7. Stabilization and carbonization conditions, and tensile properties of carbonized fibers.

	P4-1	P4-2	P4-3	P4-4
Pre-tension (MPa)	27	27	27	27
Stabilization at 285 °C	0.5 hr*	1 hr*	1.5 hr*	2.5 hr*
Stabilization at 330 °C	1 hr*	1 hr*	1 hr*	1 hr*
Carbonization	Room temp. to 1100 °C (5 °C/min)**			
Effective Diameter (μm)	4.0	4.0	4.0	4.0
Gauge length (mm)	6.0	6.0	6.0	6.0
Tensile strength (GPa)	3.9 ± 0.4	4.0 ± 0.5	3.7 ± 0.4	3.3 ± 0.3
Tensile modulus (GPa)	271 ± 28	264 ± 25	270 ± 25	274 ± 23
Strain to failure (%)	1.44 ± 0.18	1.51 ± 0.14	1.38 ± 0.09	1.20 ± 0.14

* The time represents residence time at a given temperature

** For all the cases, carbonization conditions are same

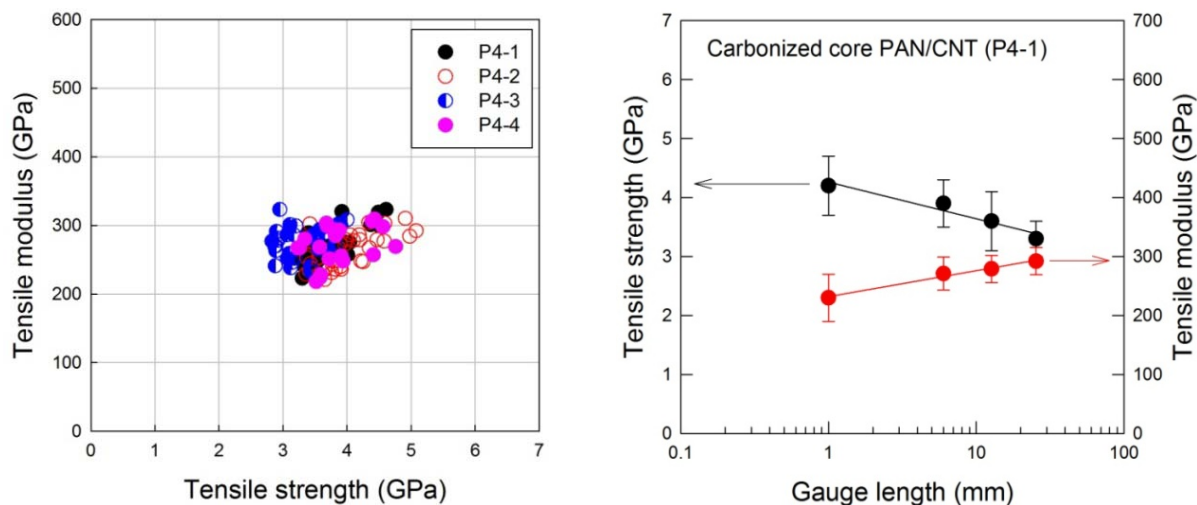


Figure 10. Tensile modulus vs. tensile strength of core PAN/CNT fibers carbonized at 1100 °C (left) and gauge length dependence of tensile properties (right). P4-1, P4-2, P4-3, and P4-4 refer to three different batches of carbonized fibers.

Figure 11 shows SEM images of carbonized core fibers. Based on the cross-sectional images, the fiber diameter ($4.0 \pm 0.2 \mu\text{m}$) was calculated using image analysis software (Image J, NIH) and used for tensile testing. Nano-fibrillar structure with 40 - 70 nm diameter was also observed. In addition, the surface of carbon fibers are very smooth, suggesting that well-controlled stabilization led to the reduced defects. Unlike other gel-spun fibers, the fibers used in this study exhibited near circular cross-sectional shape.

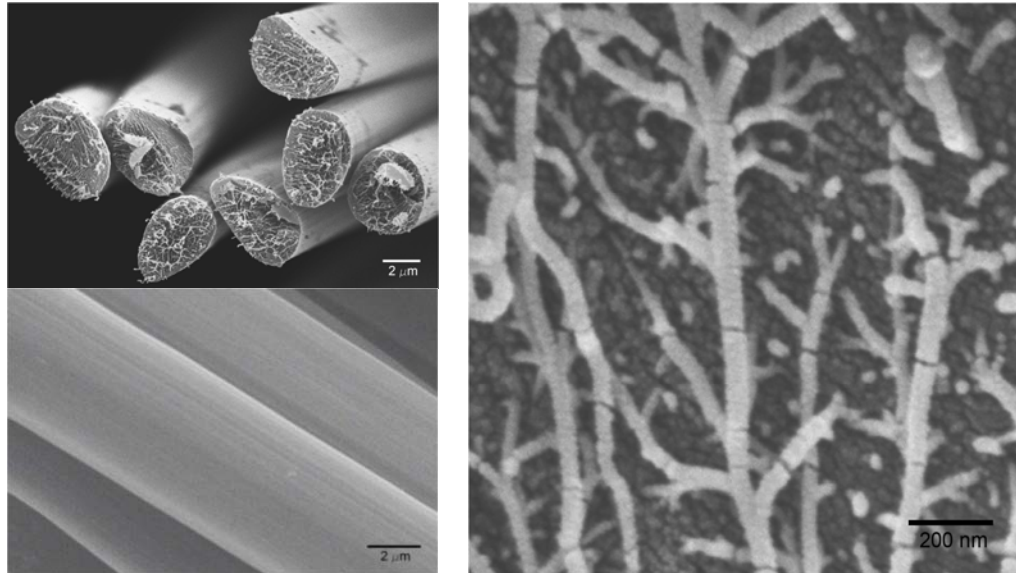


Figure 11. SEM images of carbonized core PAN/CNT fibers. Cross-sectional view (left-top), fiber surface (left-bottom), and high resolution image of cross-sectional view (right).

Wide angle X-ray diffraction (WAXD) study shows that all the fibers have similar crystal size in transverse (~ 1.2 nm) and axial direction (~ 1.8 nm). Integrated and azimuthal scans of WAXD 2D pattern (P4-1 fiber) is plotted in Figure 12. As can be seen in azimuthal scan, there are two-phase orientation in carbonized core PAN/CNT fibers. In previous researches, CNT reinforced PAN fibers have been shown that there are highly ordered crystal regions in the vicinity of CNT and these higher ordered regions are sustained even after stabilization and carbonization, resulting in nano-fibrillar structure. Azimuthal scan in this study confirms that there is indeed highly ordered phase than bulk carbon material.

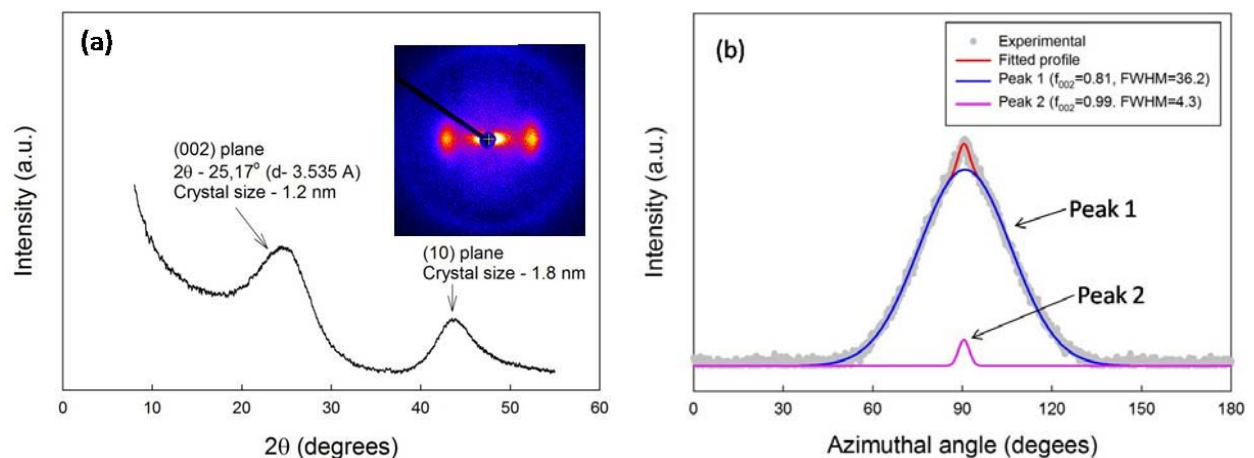


Figure 12. WAXD 2D pattern and analysis results for the carbonized fiber P4-1. Integrated scan (a) and azimuthal scan (b).

- **Batch carbonization of P4 - Effect of carbonization temperature**

In order to obtain the highest tensile strength, it is generally known that the stabilized PAN fiber needs to be carbonized in the range of 1300 - 1600 °C. Table 8 lists the various optimization trials for P4 fibers. By increasing carbonization temperature to 1300 °C with slight

adjustment of stabilization conditions, we successfully obtained tensile strength of 5.0 GPa and tensile modulus of 300 GPa. For the carbon fiber processed using the core-shell geometry, the best tensile strength and modulus to date were 7.1 GPa and 440 GPa, respectively (Figure 13).

Table 8. Tensile properties of the carbonized P4 and processing conditions.

	Diameter (μm)	Testing gauge length (mm)	Tensile strength (GPa)	Tensile modulus (GPa)	Strain to failure (%)
P4-5	3.7	6	4.5 ± 0.4	251 ± 21	1.81 ± 0.17
		12.7	4.1 ± 0.5	264 ± 15	1.54 ± 0.17
		25.4	3.9 ± 0.5	265 ± 20	1.48 ± 0.17
	- Tension for stabilization - 35 MPa, tension for carbonization - 9 MPa - Stabilization - 285 °C (45 min), 330 °C (1 hr) - Carbonization - RT to 1300 °C (5 °C/min, 5 min holding)				
P4-6	3.7	6	4.9 ± 0.7	295 ± 39	1.67 ± 0.16
	- Tension for stabilization - 41 MPa, tension for carbonization - 10 MPa - Stabilization - 285 °C (45 min), 330 °C (45 min) - Carbonization - RT to 1300 °C (5 °C/min, 5 min holding)				
P4-7	3.7	6	4.6 ± 0.4	271 ± 21	1.72 ± 0.16
	- Tension for stabilization - 41 MPa, tension for carbonization - 10 MPa - Stabilization - 285 °C (45 min), 330 °C (45 min) - Carbonization - RT to 1300 °C (5 °C/min, 5 min holding)				
P4-8	3.7	6	4.7 ± 0.5	295 ± 26	1.61 ± 0.19
	- Tension for stabilization and carbonization - 19 MPa - Stabilization - 285 °C (45 min), 330 °C (45 min) - Carbonization - RT to 1300 °C (5 °C/min, 5 min holding)				
P4-9	3.7	6	5.0 ± 0.7	300 ± 35	1.68 ± 0.20
	- Tension for stabilization and carbonization - 25 MPa - Stabilization - 285 °C (45 min), 330 °C (45 min) - Carbonization - RT to 1300 °C (5 °C/min, 5 min holding)				

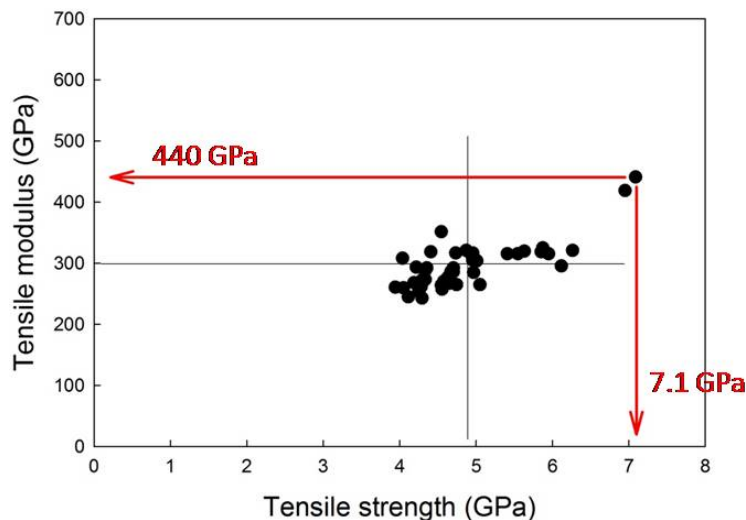


Figure 13. Tensile modulus vs tensile strength of carbonized core PAN/CNT (P4-6) fiber.

- **Batch carbonization of P5 - Effect of copolymer**

Core-shell fiber using co-polymer (PAN-MAA, methacrylic acid, 4 wt%) was processed and used for stabilization and carbonization. The carbonization temperature was limited to 1100 °C. Table 9 shows the tensile properties of the resulting carbon fiber and processing conditions. As can be seen, tensile strength and modulus are higher than the similarly carbonized P4 fibers (Table 7). Therefore, one can expect further improvements in properties upon processing optimization.

Table 9. Tensile properties of the carbonized P5 and processing conditions.

	Diameter (μm)	Testing gauge length (mm)	Tensile strength (GPa)	Tensile modulus (GPa)	Strain to failure (%)
	3.0	6	4.4 ± 0.8	410 ± 37	1.07 ± 0.16
P5-1	• Tension for stabilization - 33 MPa, tension for carbonization - 7.5 MPa • Stabilization - 285 °C (30 min), 330 °C (30 min) • Carbonization - RT to 1100 °C (5 °C/min)				

4. Key Outcomes

- Key outcomes from core PAN/CNT fiber (carbonized at 1300 °C, diameter ~ 3.7 μm)
 - Tensile strength (5.0 GPa, best to date - 7.1 GPa)
 - Tensile modulus (300 GPa, best to date - 440 GPa)
 - Strain to failure (1.68%, best to date - 2.15%)
- Key outcomes from core PAN-MAA/CNT fiber (carbonized at 1100 °C, diameter ~ 3 μm)
 - Tensile strength (4.4 GPa, best to date - 6.1 GPa)
 - Tensile modulus (410 GPa, best to date - 476 GPa)
 - Strain to failure (1.07%, best to date - 1.37%)
- Key outcomes from islands PAN-MAA/CNT fiber (carbonized at 1100 °C, diameter ~ 1 μm)
 - Tensile strength (1.5 GPa, best to date - 2.9 GPa)
 - Tensile modulus (181 GPa, best to date - 464 GPa)
 - Strain to failure (0.87%, best to date - 1.28%)

5. Technical Feasibility

PAN/CNT composite fibers are processed and used to produce high strength and high modulus carbon fibers. In order to produce composite fibers, several spinning technologies have been used, which are called gel spinning and bi-component spinning. Carbonization process of the composite fiber was optimized to obtain high strength and high modulus carbon fiber. The resulting carbon fibers possessed average tensile strength up to 5 GPa and average tensile modulus up to 410 GPa. The highest strength and modulus to date are 7.1 GPa and 476 GPa, respectively. The current research indicates that further processing optimization and continuous

processing will lead to the next generation carbon fiber whose tensile strength, tensile modulus, and strain to failure are >7.0 GPa, >450 GPa, and >1.5%, respectively. These nanotailored carbon fibers will have superior mechanical properties as well as better electrical and thermal conductivity as compared to the conventional carbon fibers, which should result in significant weight savings and functionality in various aerospace composite systems.

6. References

1. Chae, H. G.; Minus, M. L.; Kumar, S., *Polymer* **2006**, *47* (10), 3494-3504.
2. Chae, H. G.; Choi, Y. H.; Minus, M. L.; Kumar, S., *Composites Science and Technology* **2009**, *69* (3-4), 406-413.
3. Chae, H. G.; Kumar, S., *Science* **2008**, *319*, 908-909.
4. Chae, H. G.; Minus, M. L.; Rasheed, A.; Kumar, S., *Polymer* **2007**, *48* (13), 3781-3789.