NATIONAL INSTITUTE OF AEROSPACE

Advanced Aerospace Materials: A “Beyond The Next” Workshop

Carbon Fibers and Carbon Nanotube based Materials

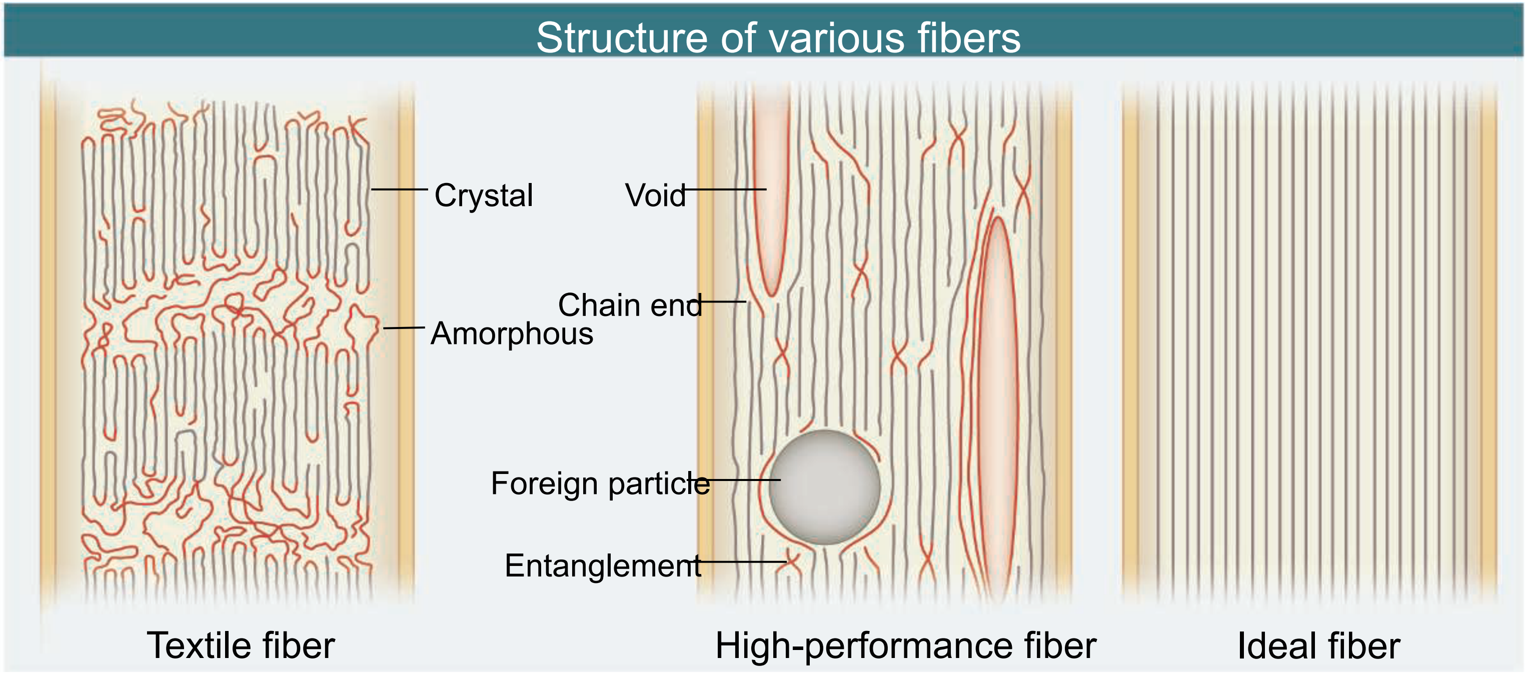
Satish Kumar
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0295
satish.kumar@gatech.edu

June 21 -22, 2016
National Institute of Aerospace, Hampton VA 23666

Outline

- Carbon fibers
- Functional materials
- Load transfer and tailoring the Interfacial shear properties

Fiber Structure and Tensile Strength

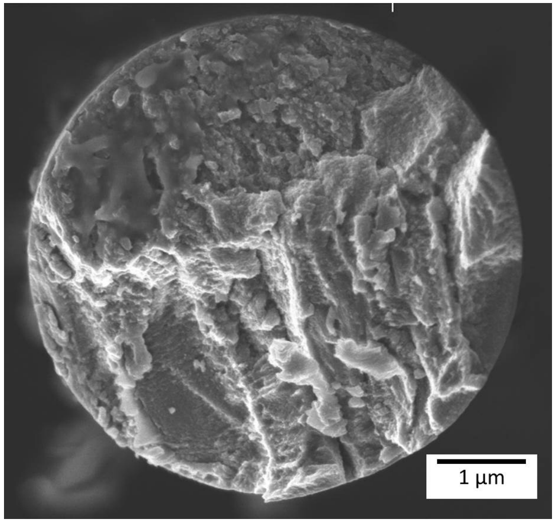


0.5 GPa   3 - 6 GPa   30 to >100 GPa

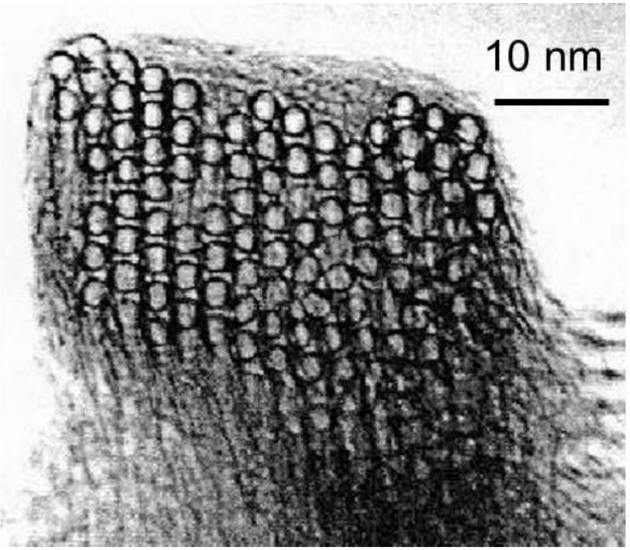
HG Chae and S Kumar, *Science*, **319**, 908 (2008)

Carbon Fibers

PAN based carbon fiber
Top down approach



Carbon Nanotubes
Bottom up approach



Science, **273**, 483 (1996)

Diameter: 5 µm
Tensile strength: 3.1 N/tex (5.6 GPa)
Tensile modulus: 155 N/tex (280 GPa)

Strength demonstrated at short gage length: 6.7 N/tex (or GPa/ g/cm^3) (12 GPa)

Diameter: 1 nm
Tensile strength: 20 – 67 N/tex (45 – 150 GPa)
Tensile modulus: 467 N/tex (1060 GPa)

Carbon fiber timeline

	~1965	1980	1990	2016	Theoretical
Diameter		7	5	1 – 5	
Strength (GPa)	~1.0	3.5	5.5	7 – 12	>100 GPa
Modulus (GPa)	100	230	275	>350	1060 GPa
		Commercial		TRL 1-2	

Carbon Fibers

Satish Kumar, School of Materials Science and Engineering, Georgia Institute of Technology
Email: satish.kumar@gatech.edu

- **Strength**: After 50 years of development, the strength of the state-of-the-art carbon fibers (5.6 GPa for IM7) is only <10% of the theoretical strength (>60 GPa) of the carbon carbon-carbon bond. **Modulus:** High strength carbon fibers have relatively low modulus (276 GPa for IM7 fiber vs 1060 GPa for graphite). *Under DARPA funding, gel spinning route has shown significant increase in modulus and potential of increased strength.*

- **Electrical and Thermal Conductivity:** State-of-the-art-high strength carbon fibers have relatively low electrical conductivity (~60,000 S/m vs ~1,000,000 S/m for graphite) and low thermal conductivity (<15 W/m/K vs 1000 W//m/K for graphite). Under DARPA/AFOSR sponsorship, *PAN/CNT based carbon fibers have been shown to have enhanced conductivity values, as compared to PAN based carbon fibers.*

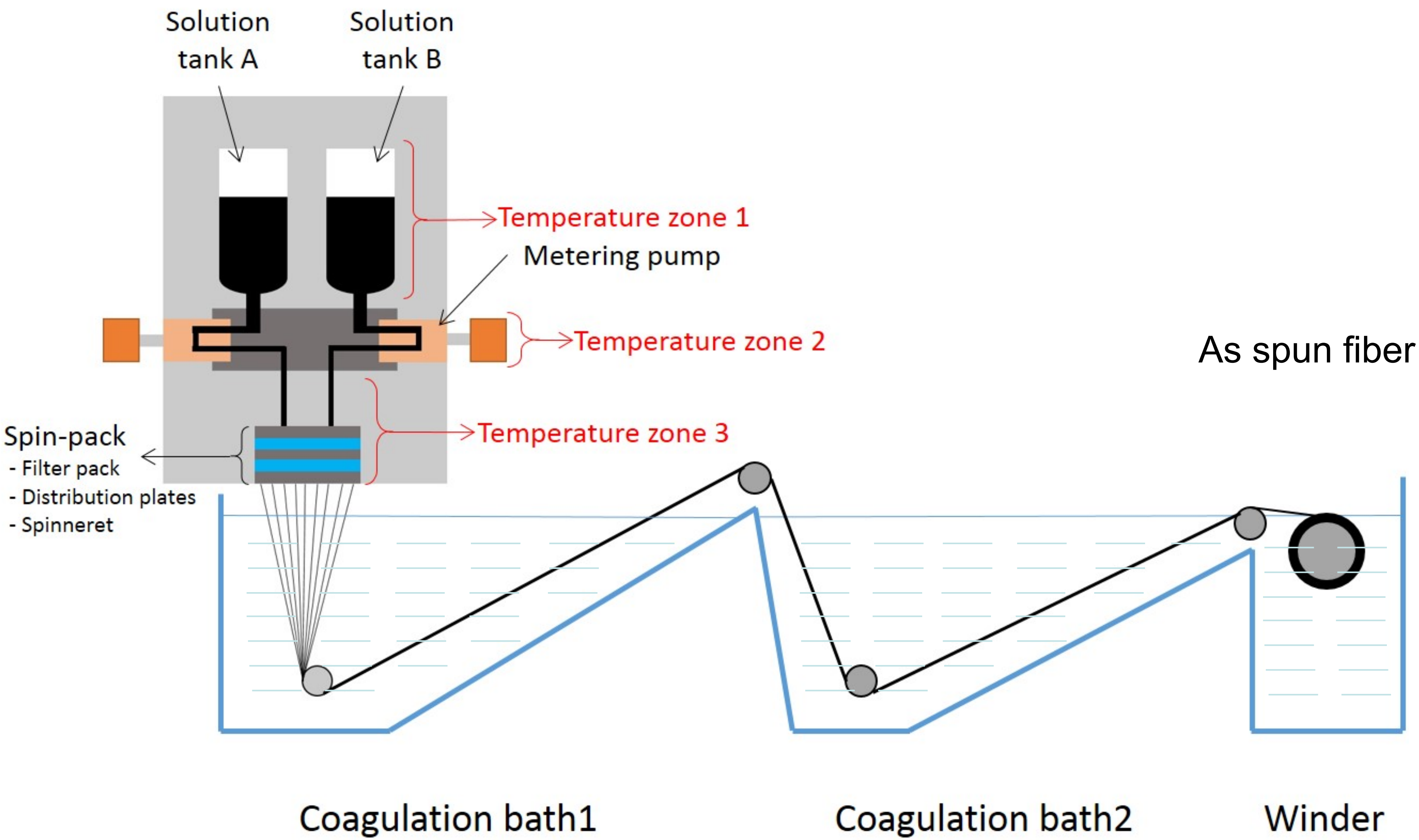
- **Density**: Density of the high strength carbon fibers is ~1.76 g/cm^3. It will be desirable to further reduce this density significantly. *With funding from Boeing, hollow carbon fibers with density of 1.2 g/cm^3 have been processed.*

- **Functionality**: High strength carbon fibers are currently passive materials. It will be desirable to introduce additional functionality in these high strength fibers. *Super paramagnetic properties is an example of functionality beyond electrical and thermal conductivity, that has been demonstrated under AFOSR sponsorship.*

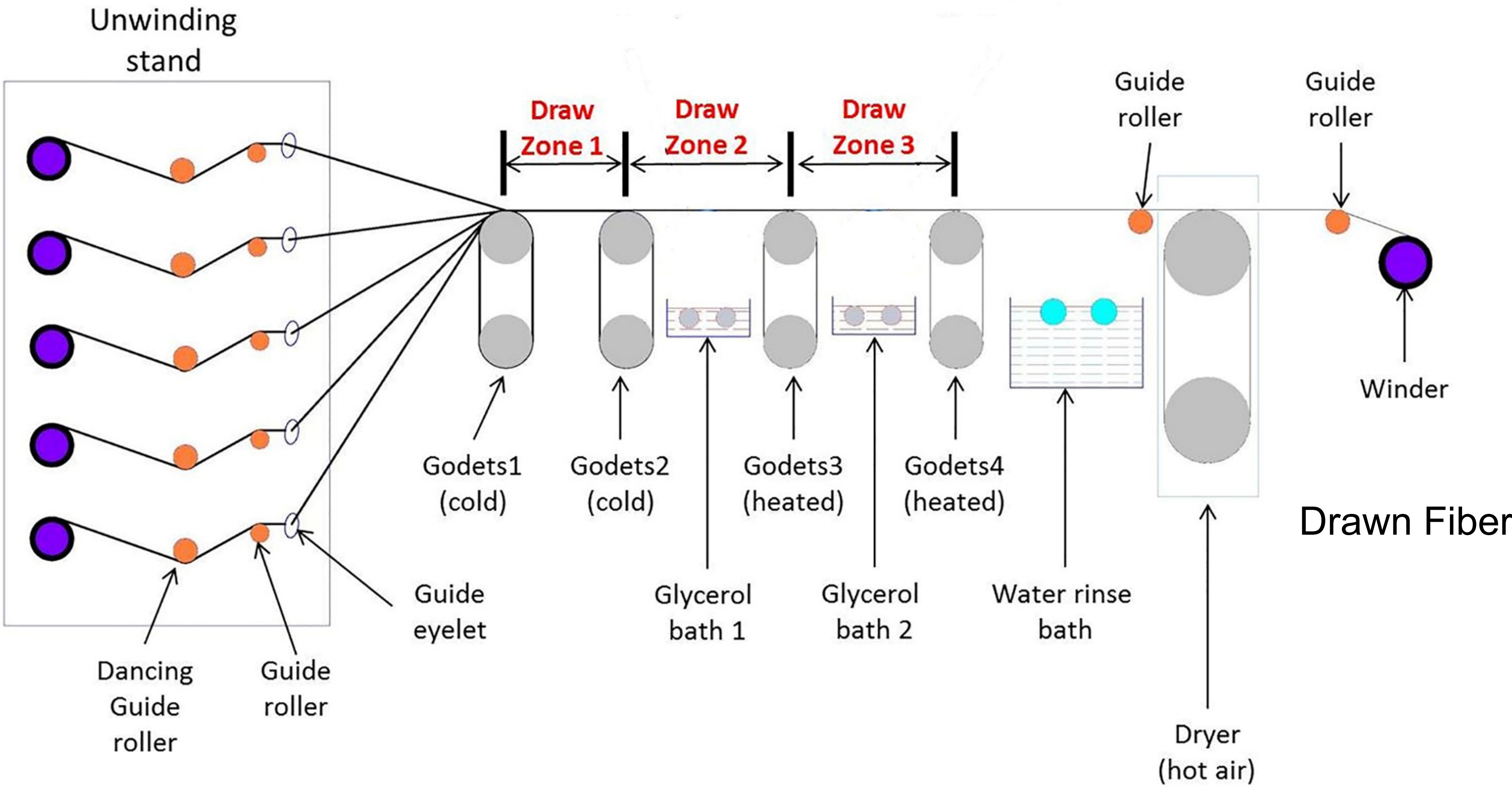
- **Energy**: Approximately 40% cost of the high strength carbon fibers is due to energy used during stabilization and carbonization. It is desirable to reduce this energy significantly. *Under AFOSR and DOE funding, progress is made in this area using Joule heating of PAN/CNT fibers.*

- **Bio – renewable content**: Carbon fibers are produced from polyacrylonitrile (PAN). PAN is the product of petroleum industry. Currently there is an effort underway to incorporate bio-renewable materials such as lignin and cellulose nano crystals (CNC) in these fibers. *Under RBI sponsorship PAN/lignin blend fibers as well as PAN/CNC fibers have been processed using gel spinning, with promising results for enhanced sustainability.*

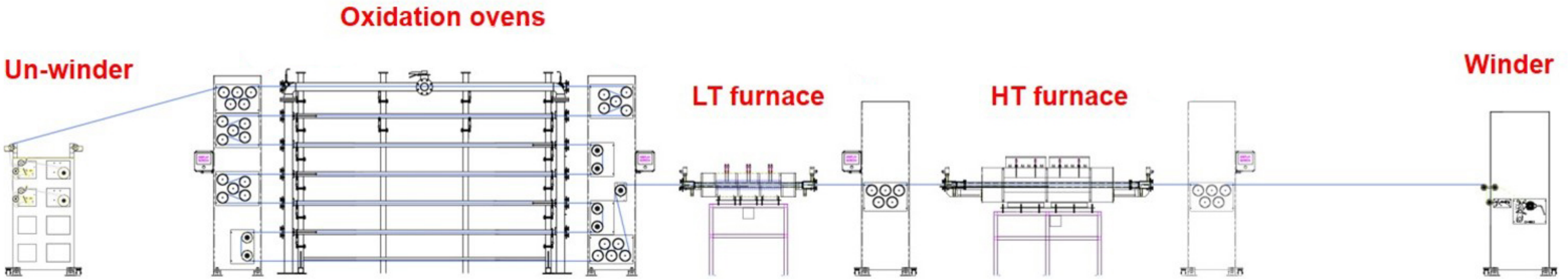
Schematic description of fiber spinning system



Schematic description of fiber drawing system

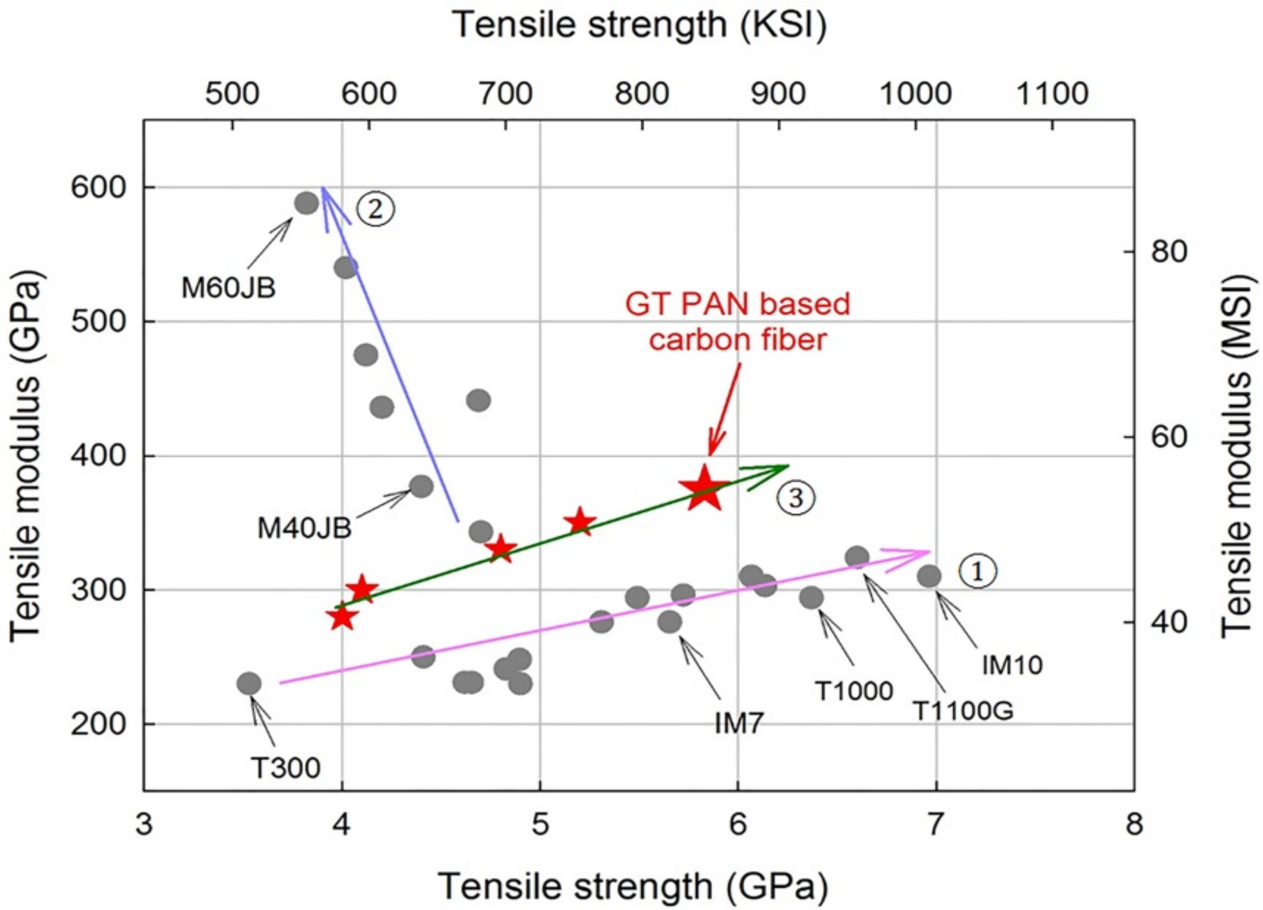


Equipment – continuous carbonization



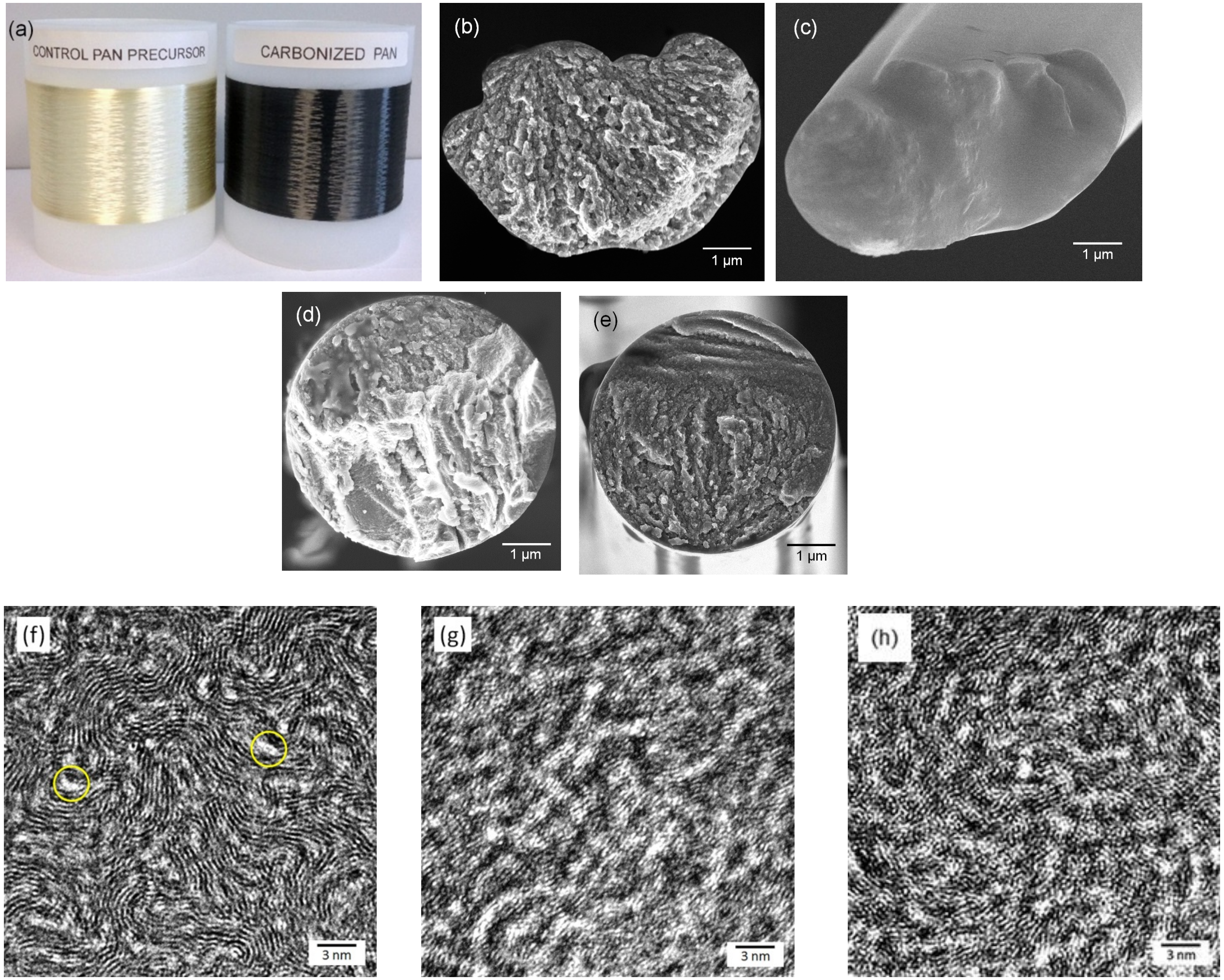
- Line has been tested for continuous carbonization of 100 to 6000 filament tows.
- Stabilization zones: 180 – 300 ^{o}C
- LT furnace: up to 1000 ^{o}C
- HT furnace: up to 1600 ^{o}C

Progress towards High Strength High Modulus Carbon Fiber



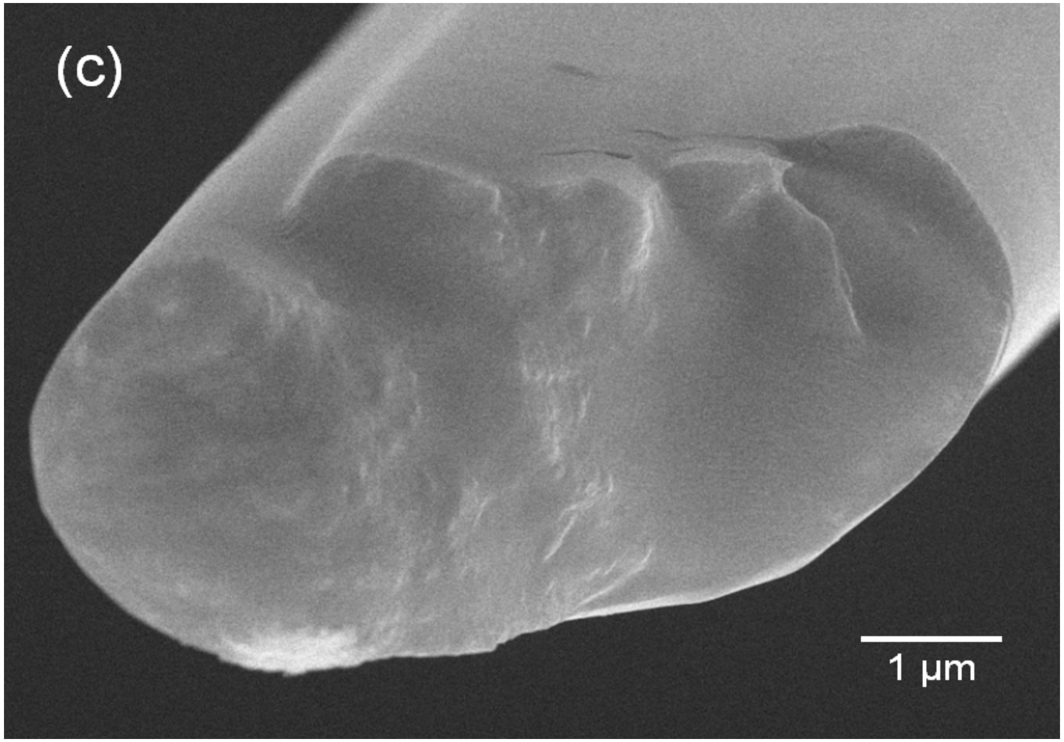
30% increase in modulus without reduction in strength.

Carbon, 2015


(a)
CONTROL PAN PRECURSOR
CARBONIZED PAN
(b)
1 μm
(c)
1 μm
(d)
1 μm
(e)
1 μm
(f)
3 nm
(g)
3 nm
(h)
3 nm

Carbon, 2015

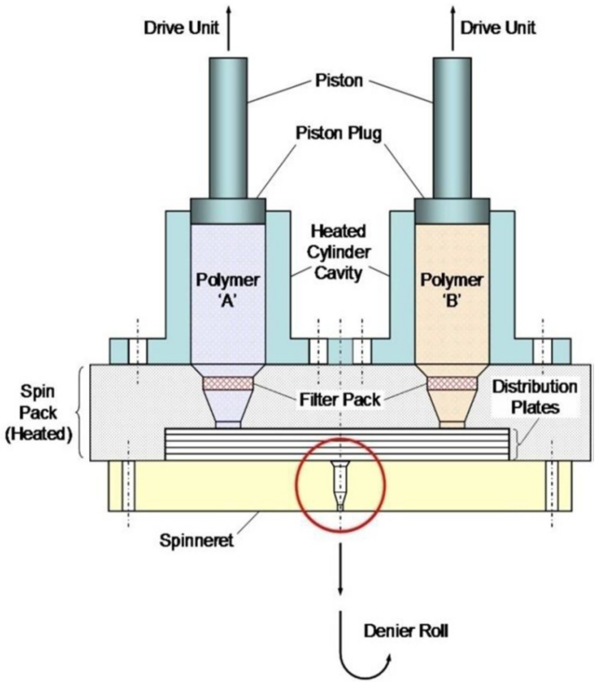
Gel spun PAN based carbon fiber

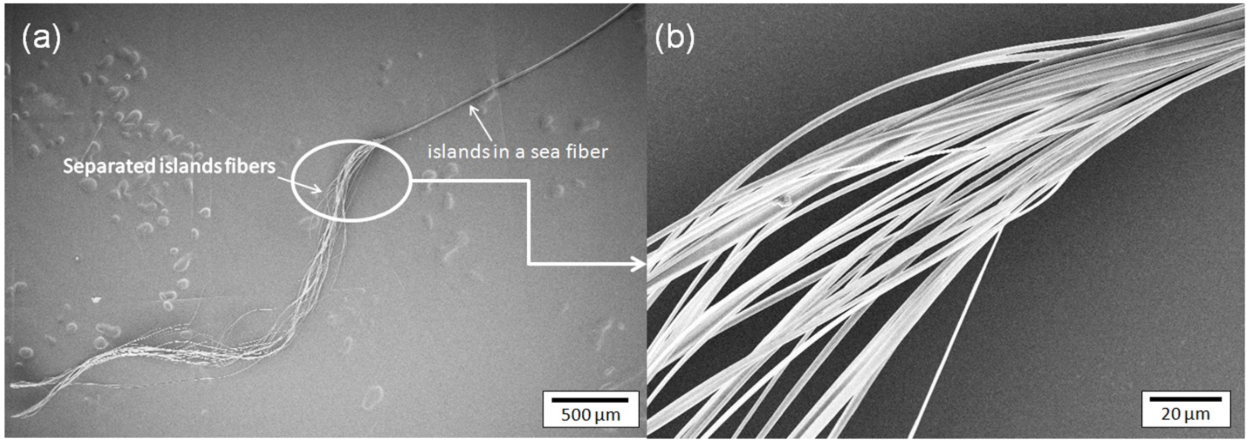


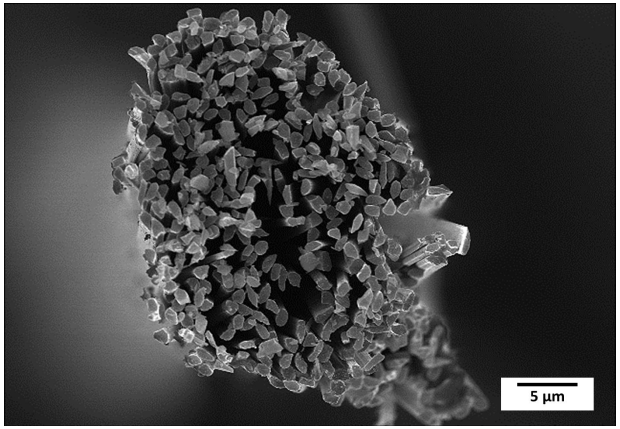
Tensile strength 12 GPa

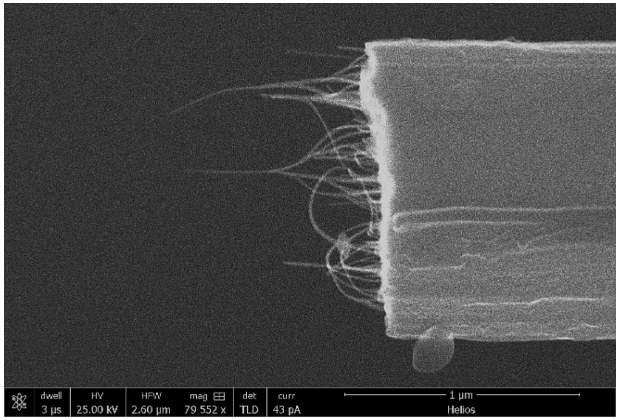
Carbon, 2015

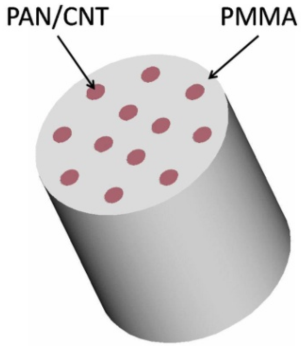
Patent Literature

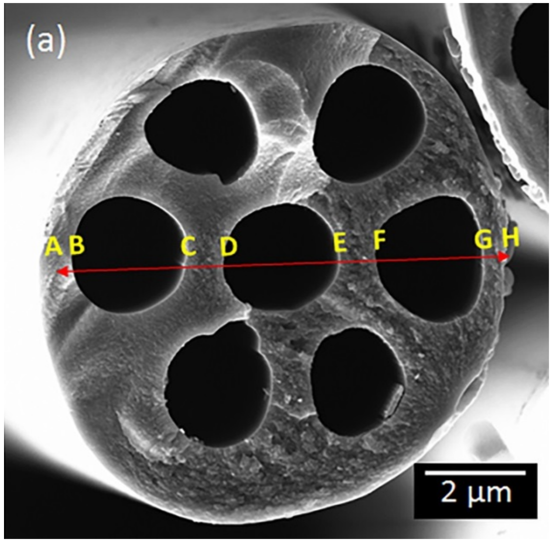




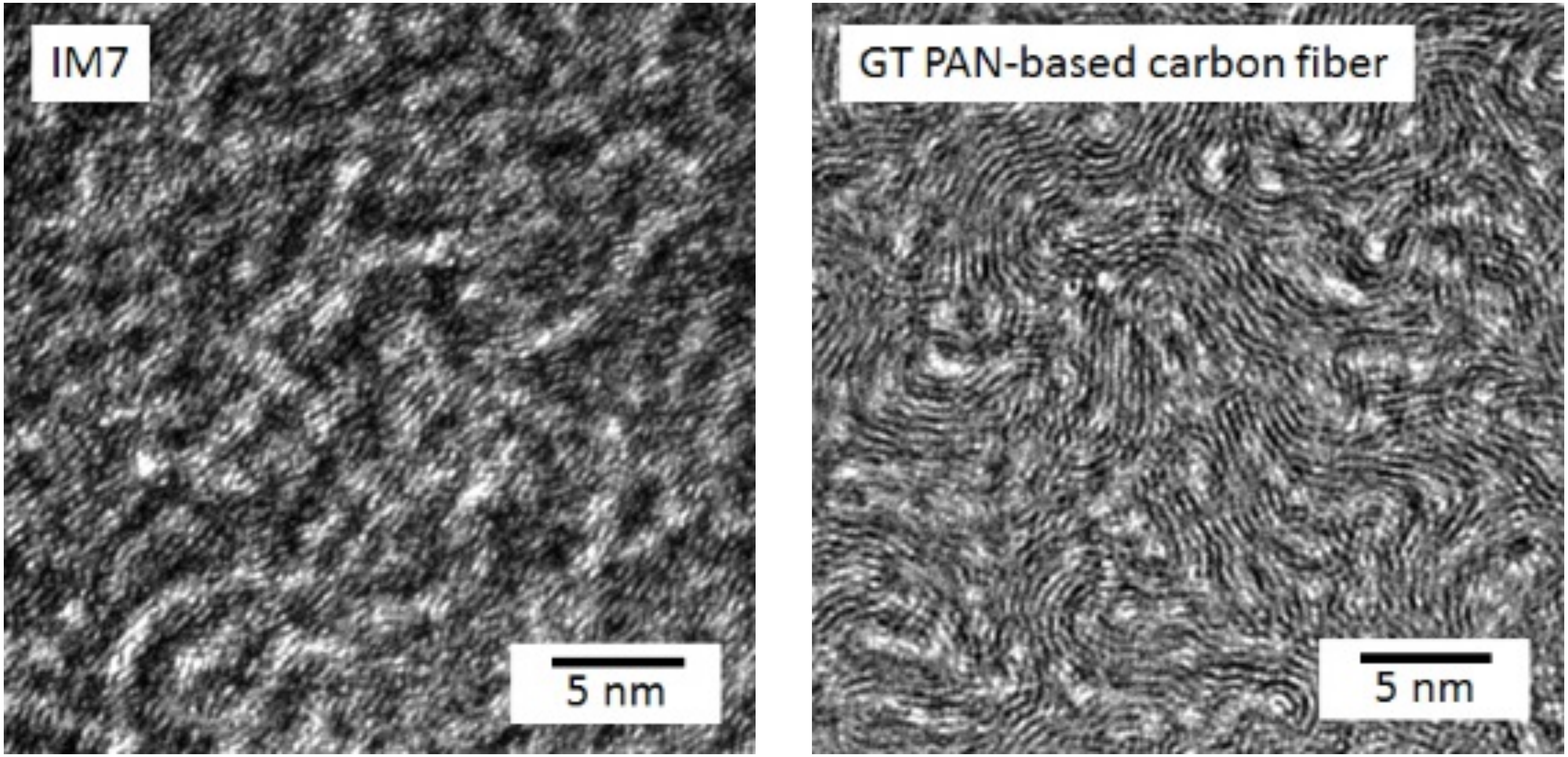






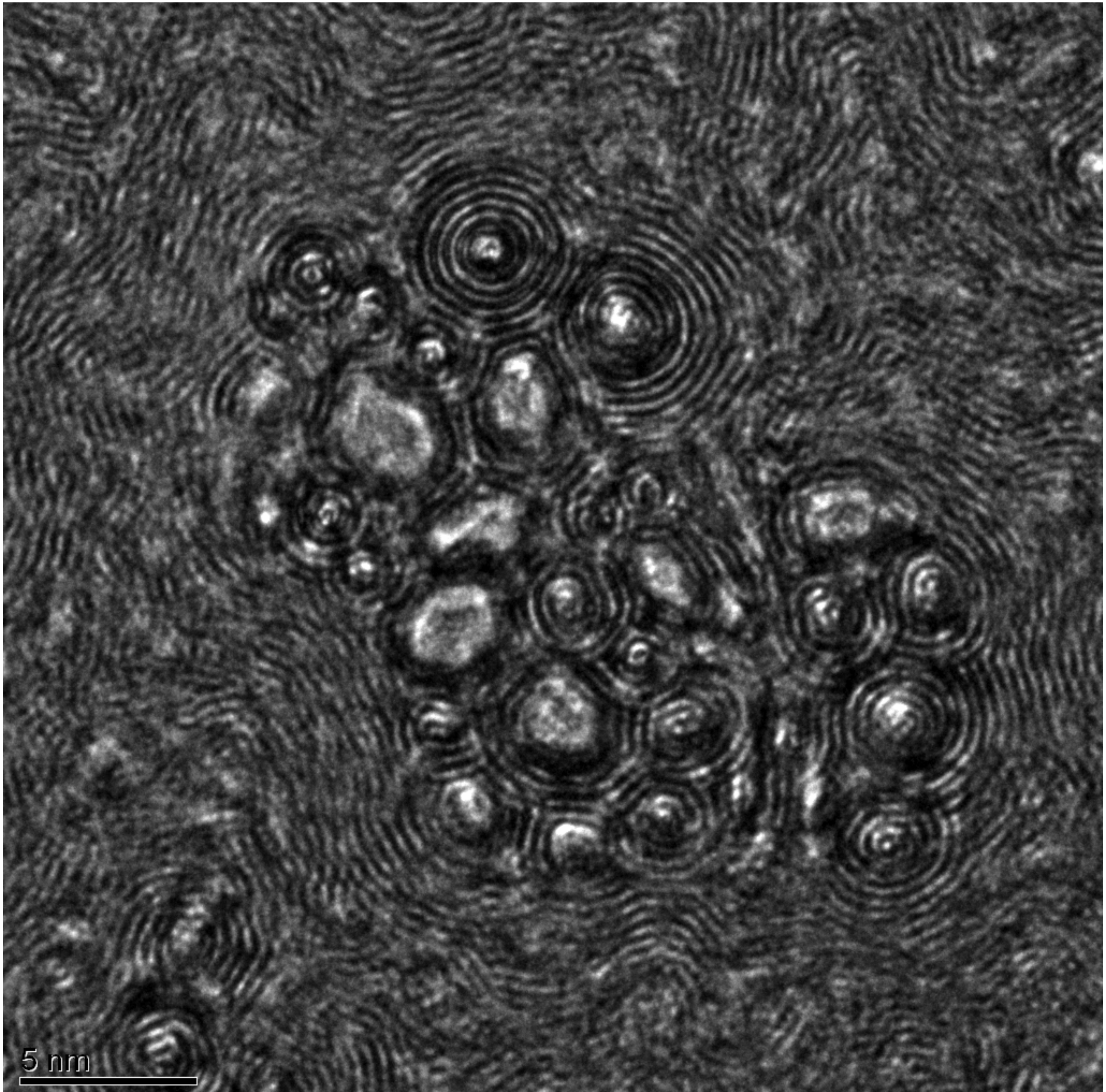


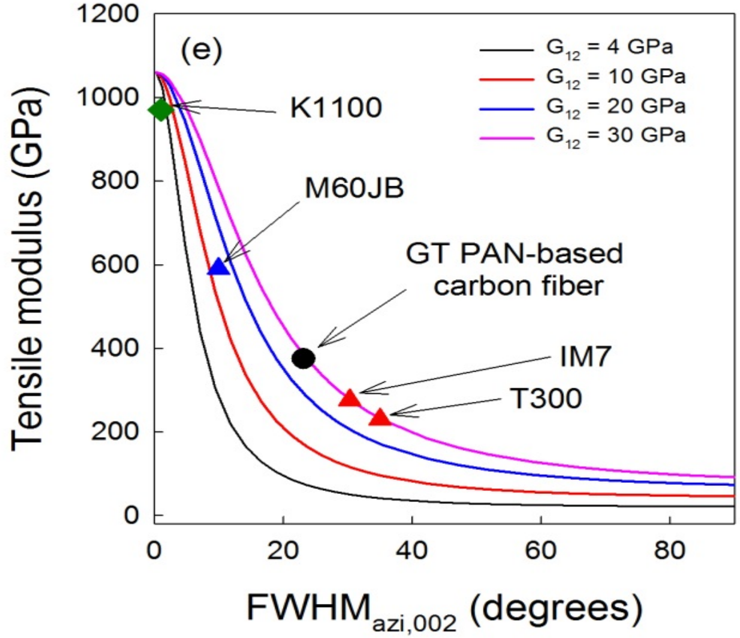
Carbon Structure thickness ~ 1 µm Carbon, 2014, 2015



Carbon, 2015

Carbon,
2015



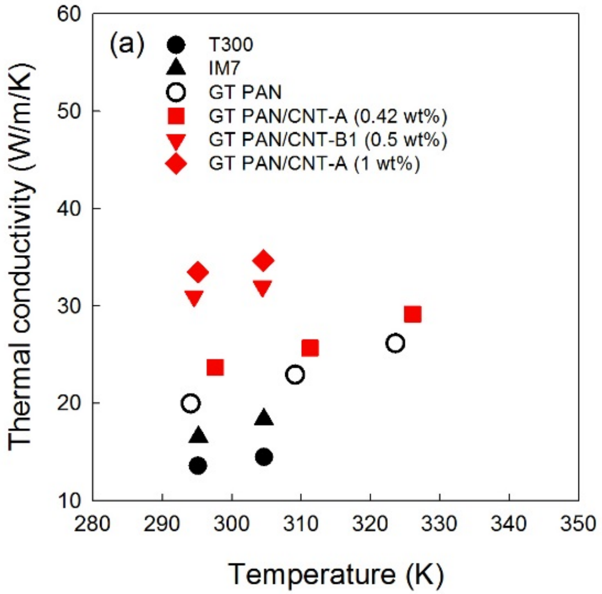


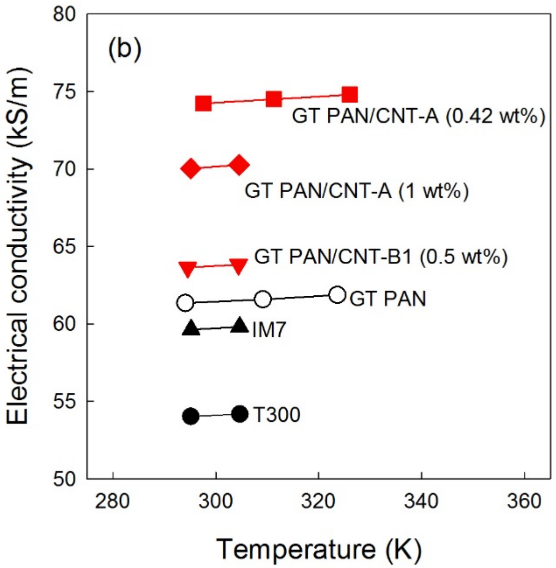
- Inter-planar shear modulus in graphite is 4 GPa.
- In turbostratic graphite high strength carbon fibers, inter-planar shear modulus value is 30 GPa.

Carbon, 2015

Enhanced thermal and electrical conductivity carbon fiber

>50% increase in carbon fiber thermal conductivity with 1wt% CNT
>25% increase in carbon fiber electrical conductivity with 0.5 to 1wt% CNT



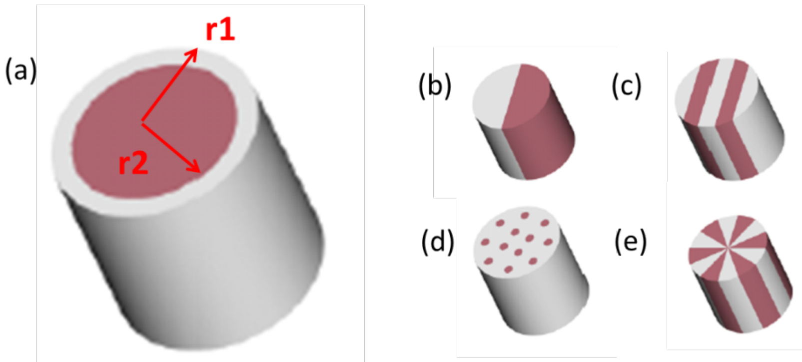


We can also process carbon fibers with super paramagnetic properties

Carbon fibers containing BNNTs are also being processed.

Carbon, 2015

Functionality in the fibers including in the carbon fibers can be introduced at the desired location



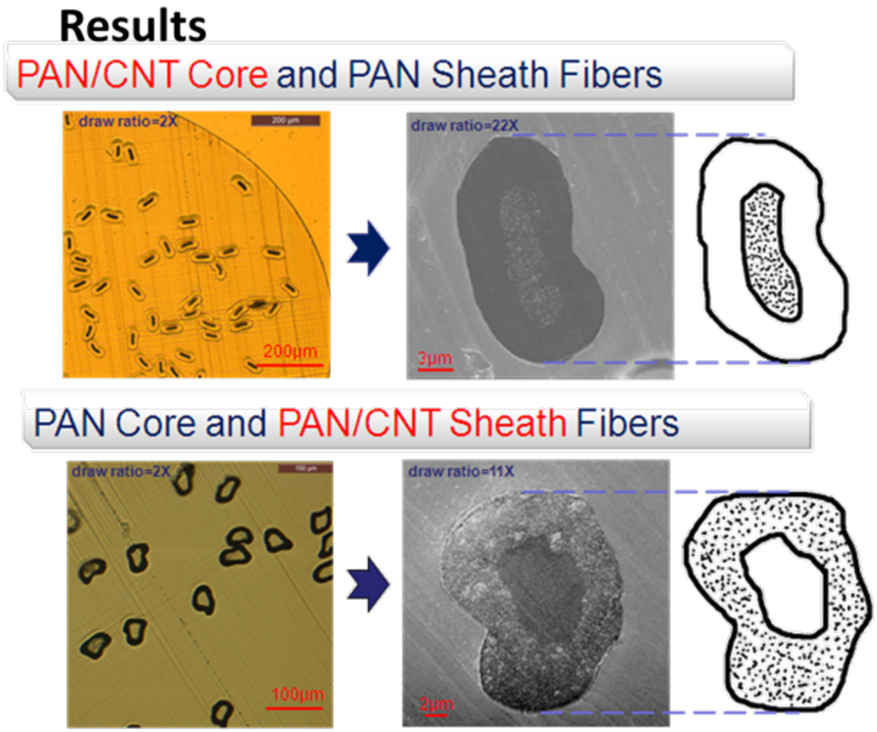


Figure 3 The optical and SEM images and their schematics of bi-component fibers

Using this approach functional fibers can also be made using other nano materials – introducing corresponding functionality in the sheath or in the core. A different nano material and hence a different functionality can be introduced in each component.

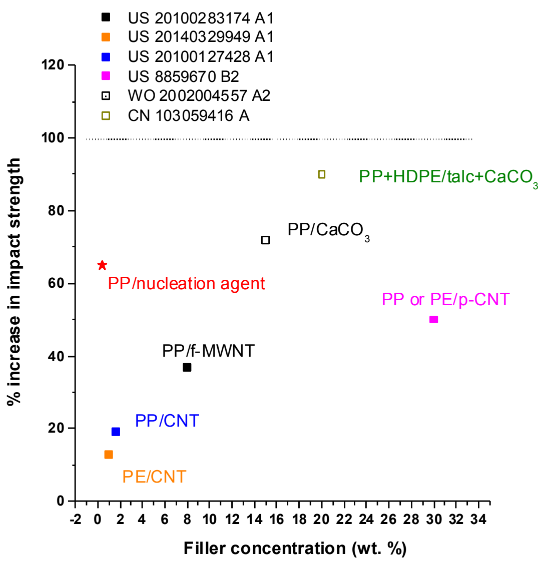
Hypothesis

Tailored **CNT/polymer interphase** is needed for achieving high performance CNT based materials. This can be done by modifying the CNT surface chemistry by **covalent and/or non-covalent** means.

Tailored interphase – impact strength of polypropylene

Interphase I – no improvement

Interphase II – 70% increase

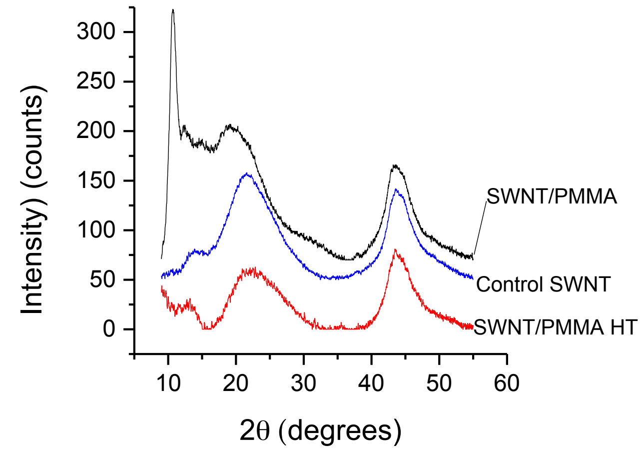


Interphase III – 150% increase

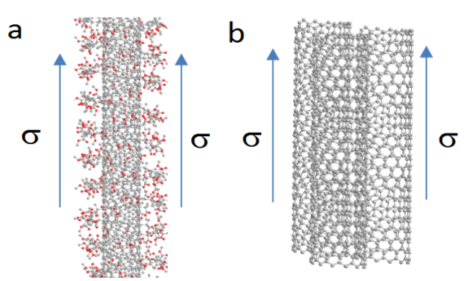
Load Transfer

Interfacial shear stress

Evidence of ordered PMMA wrapping



A factor of six increase in bucky paper modulus has been achieved using this approach.



35 wt% PMMA wrapped on SWNT

This behavior is expected to provide the breakthrough for narrowing the gap between CNT's experimentally achieved mechanical properties and their theoretical potential

"Beyond the next" materials

- What new materials with high performance structural properties are on the horizon?

  - Carbon fibers with a tensile strength of 12 GPa and tensile modulus in the range of 400 to 600 GPa.

  - Structural carbon fibers with factor of two increase in electrical and thermal conductivity over current state of the art carbon fibers.
  - Structural carbon fibers with superparamagnetic properties.
  - Structural carbon fibers with high thermal conductivity, but low electrical conductivity.

  - Structural hollow carbon fibers with density below 1 g/cm^3.

  - Carbon nanotube based macroscopic materials that significantly bridge the gap between their current experimental mechanical property values and their theoretical potential. Tailoring the interphase will be the key.

Acknowledgements

Research Scientists

Dr. Prabhakar Gulgunje
Dr. Kishor Gupta

Post-doctoral fellow

Dr. Sourangsu Sarkar

Ph.D. students

Amir Davijani
Clive Liu
Po-Hsiang Wang
Huibin Chang
Jeffery Luo
Shruti Venkatram

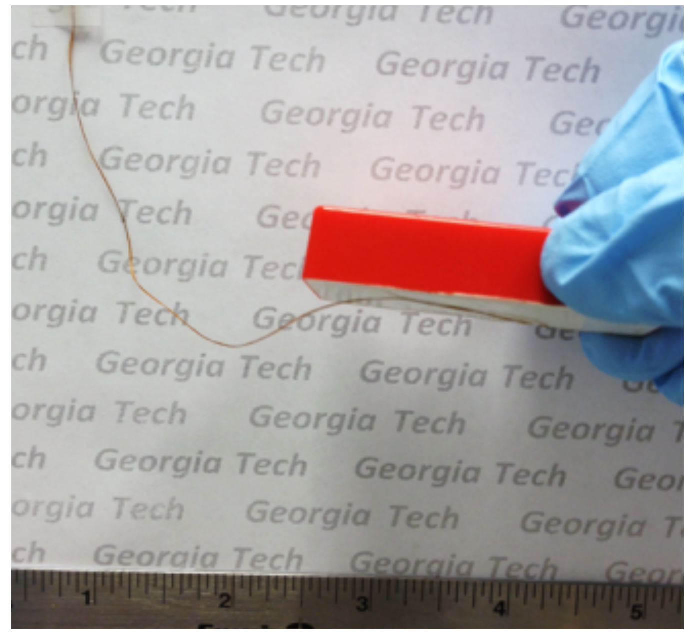
AFOSR
DARPA
ONR
NIST
CNI
SABIC
Boeing Company
Universal Technology Corporation
Georgia Research Alliance

Many collaborators

Past group members

Progress towards functional carbon fiber

High strength super-paramagnetic PAN precursor fibers containing iron oxide nano particles have been made. This concept can be extended to make super paramagnetic carbon fibers. By using multi-component fiber spinning approach, electrical conductivity, thermal conductivity, para magnetic behavior, as well as other desired functionality can be inserted in selected location in the carbon fiber cross-section.



Carbon fibers with microwave absorption capability can be made

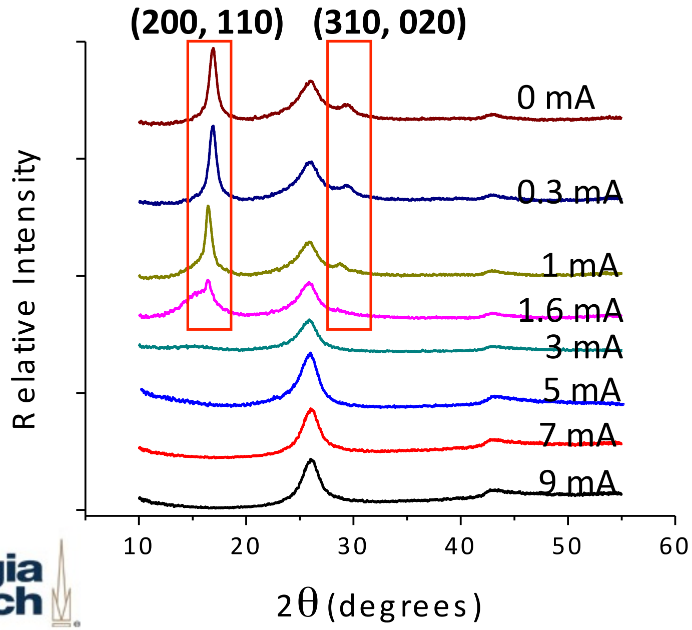
A. T. Chien et al, *Polymer*, 2014

Progress towards low energy carbon fiber

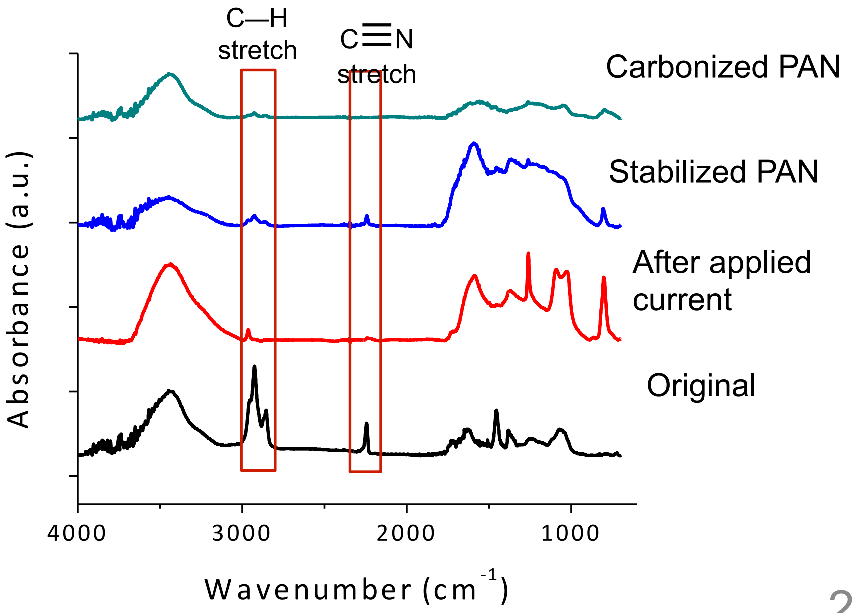
A.T. Chien et al., Polymer, 2014

By using CNTs in PAN, fibers have been stabilized and possibly carbonized by applying electric current, rather than via external heating in furnaces

- **WAXD**

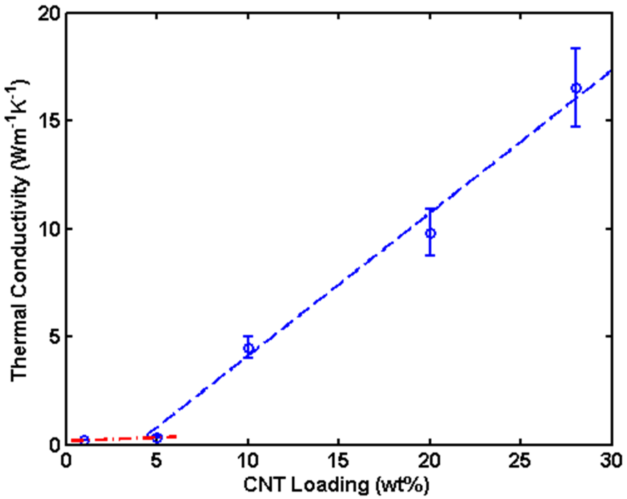


- **FT-IR**

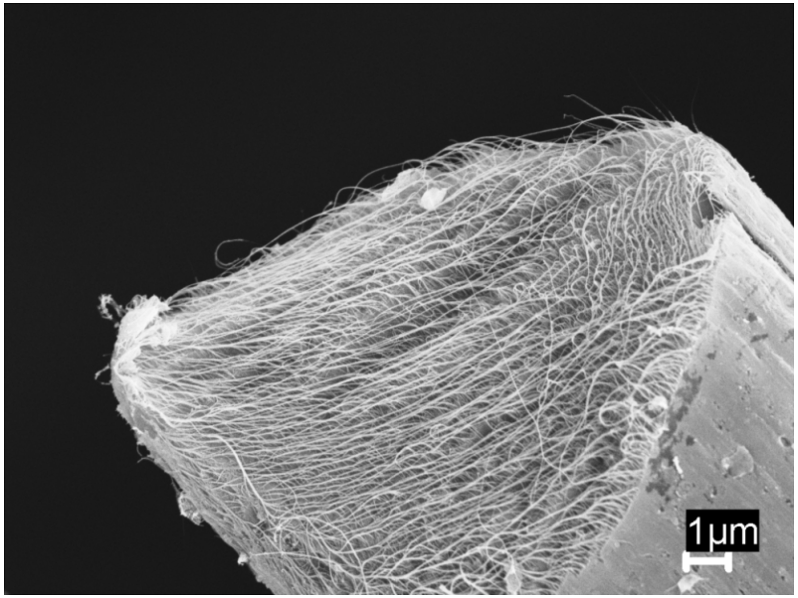


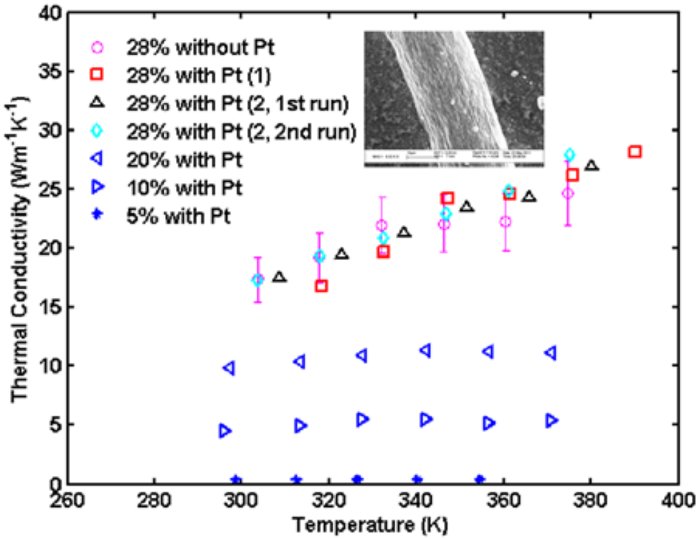
Thermally and electrically conducting polymeric fibers

PEK/CNT Fibers



- Axial electrical conductivity 240 S/m
- Thermal conductivity as high as 17 W/m/K
- Density ~1.3 g/cm^3

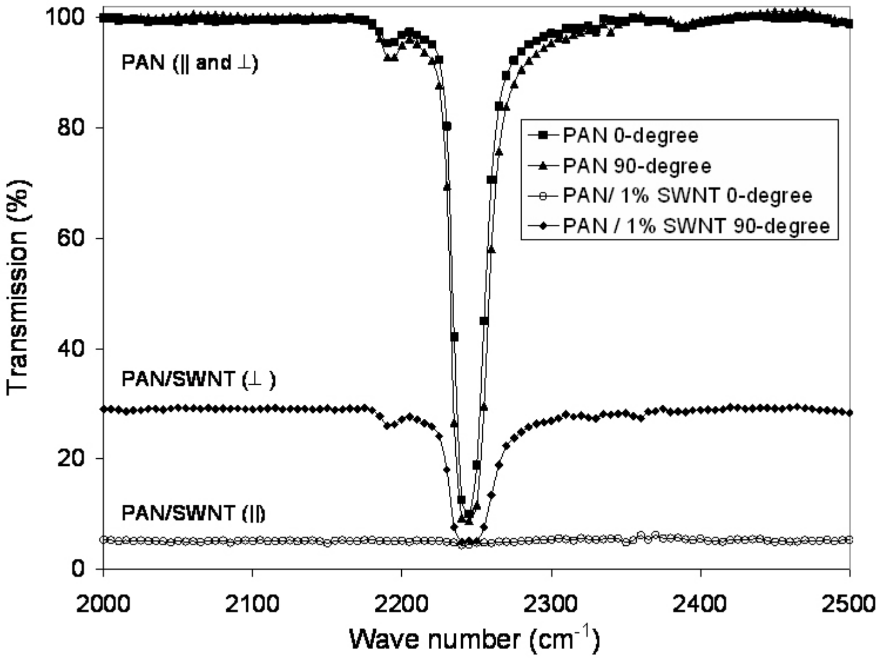




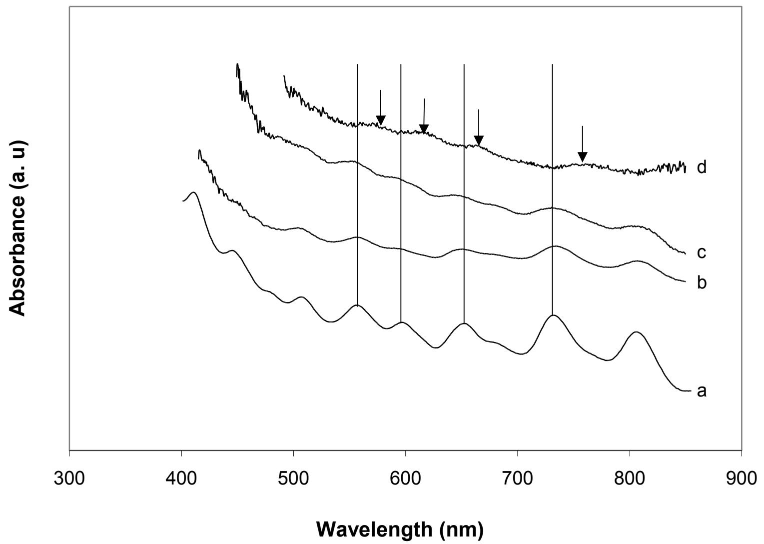
R Jain, YH Choi, Y Liu, ML Minus, HG Chae, JB Baek, S Kumar *Polymer,* **51,** 3940-3947 (2010)
J Moon, K Weaver, B Feng, HG Chae, S Kumar, JB Baek, GP Peterson, *Review of Scientific Instruments*, **83**, 016103 (2012)

Optical Properties of Polymer/CNT Films and Fibers

Anisotropic Infra-red absorption in PAN/SWNT fiber



van Hove transitions in SWNT dispersion and PVA/SWNT films

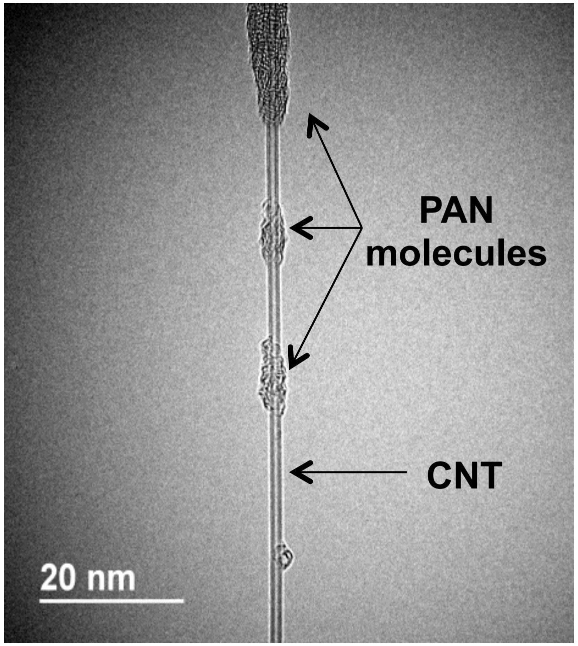


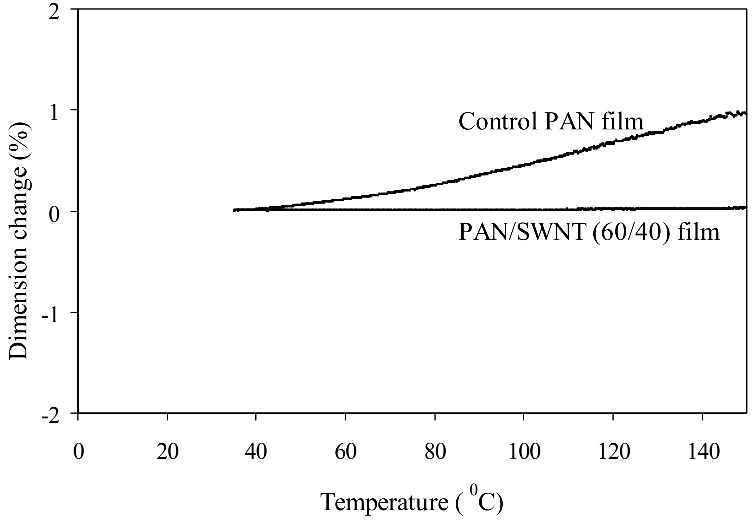
(a)PVP/SDS/SWNT aqueous dispersion
(b)PVA/PVP/SDS/SWNT film (1 wt% SWNT)
(c)PVA/PVP/SDS/SWNT film (5 wt%)
(d)PVA/SWNT film (1 wt%)

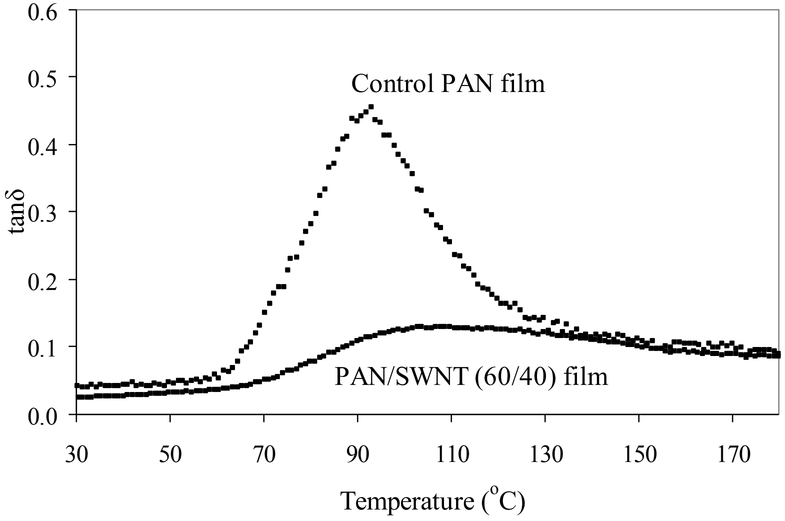
- TV Sreekumar, T Liu, BG Min, H Guo, S Kumar, RH Hauge, RE Smalley, Advanced Materials, 16(1), 58 (2004).
- XF Zhang, T Liu, TV Sreekumar, S Kumar, VC Moore, RH Hauge, RE Smalley, *Nano Lett*, **3**(9), 1285 (2003).

PAN/SWNT (60/40) Film

- Electrical conductivity (~10^4 S/m) – comparable to electrically conducting polymers such as polythiophene, polypyrrole, and polyaniline.
- Tensile strength (100 MPa) and modulus (11 GPa) higher than that of SWNT bucky paper or the polymer, and comparable to those of the engineering thermoplastics
- Films exhibit high degree of dimensional stability (CTE <2 ppm/^{o}C)
- Polymer molecular motion above glass transition temperature is dramatically suppressed.
- Low density (~1 g/cm^3)
- Thermally stable and exhibits Chemical resistance



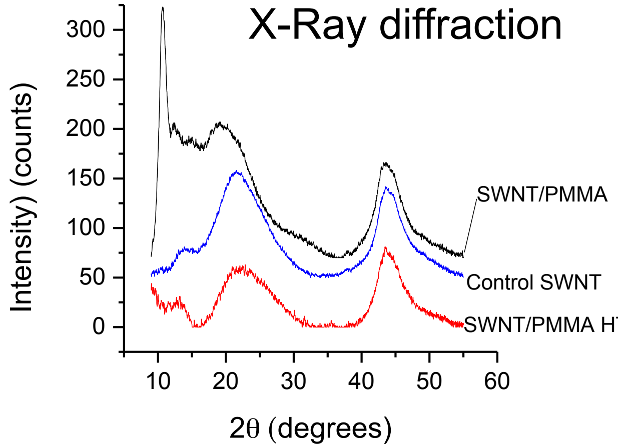


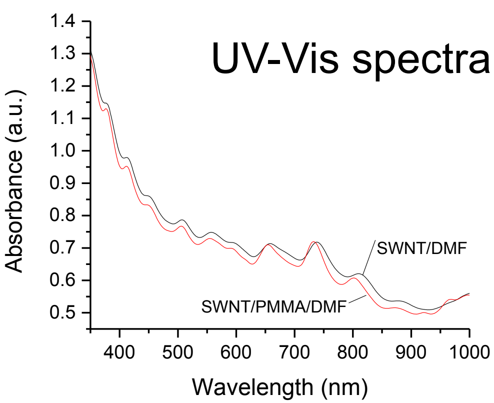


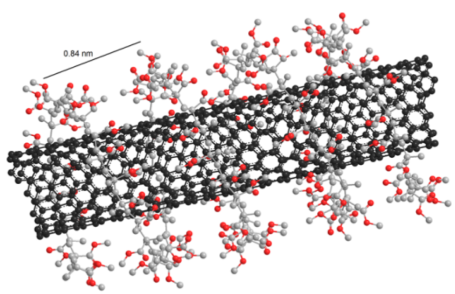
H Guo, TV Sreekumar, T Liu, M Minus, S Kumar, *Polymer*, **46**, (2005) 3001-3005

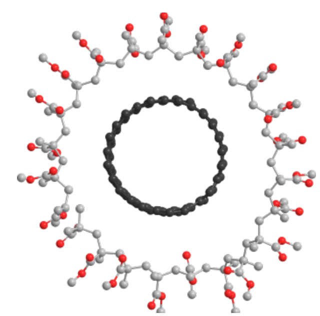
SWNT/Polymer interaction

- Selective wrapping of PMMA on SWNTs. This wrapping was not observed on FWNTs and MWNTs.
- Wrapping monitored by X-ray diffraction: PMMA /SWNT showed a new strong intensity peak at ~0.84 nm, while this peak was not observed in PMMA/FWNT and PMMA/MWNT.
- The 0.84 nm peak has been attributed to helically ordered PMMA on SWNT.
- Helical wrapping of polymers on CNTs has been discussed in the literature for nearly two decades, this is the first time such a behavior has been confirmed by X-ray diffraction and first time observed for PMMA.
- The observation of PMMA /SWNT interaction (and lack of this interaction in PMMA/FWNT and PMMA/MWNT) may **be important for developing low density, high strength, functional polymer/ CNT system.**

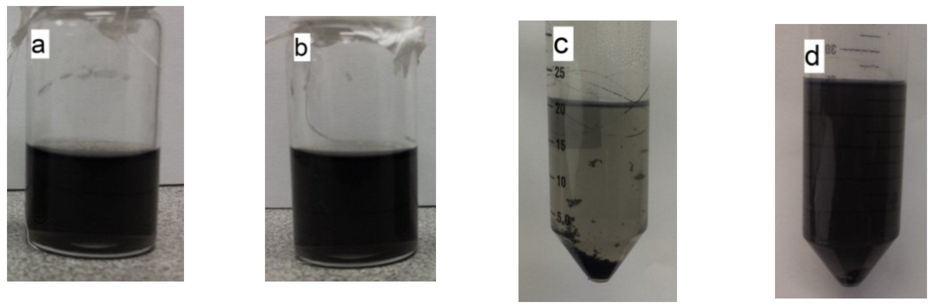








Polymer, 2015



As sonicated (a) SWNT/DMF, and (b) SWNT/PMMA/DMF suspensions. (c) SWNT/DMF suspension after 2 hour centrifugation, d) SWNT/PMMA/DMF suspension after 72 hour centrifugation.