NIST Annual Fire Conference 2007

Polyacrylonitrile (PAN) / Multi-Walled Carbon Nanotube (MWNT) and Cellulose / MWNT Composite Fibers for Fire Barrier Applications

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Challenges

1) Furniture and mattress fires still cause ~1000 deaths/yr and cost $ 500 M/yr

   1) **Objective**: to evaluate the effectiveness of nanoadditive based flame retardants in reducing the flammability of flexible foams

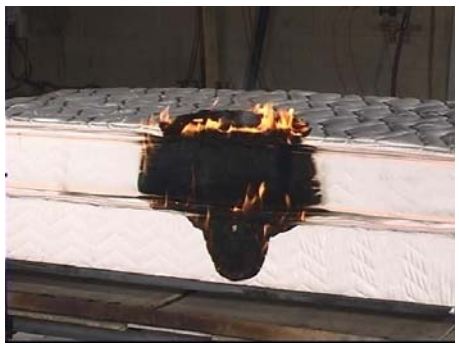
   2) **Objective** : to improve the ability of barrier fabrics to prevent flame spread in mattresses and furniture using nanoadditives

2) Environmental degradation (UV, oxidation) in fire fighter turnout gear severely affects the performance

   1) **Objective :** to evaluate the ability of carbon nanotubes to stop these degradation mechanisms in turnout gear

Barrier Materials

- Fabric combustion creates high heat flux exposure
- Polymers shrink when burned so barriers crack and fail
- Fabric costs focus industry on low performing commodity polymers
- Water insoluble environmentally additives required
- No suitable bench-scale test currently exists for barriers



Fire barrier fibers candidates*

- Cotton
- Aramid
- Melamine/aramid
- Novoloid
- Melamine/modacrylic/polyester

Achieve (by using CNTs in PAN and Cellulose)

- Fire barrier
- Higher strength
- Higher char yield
- Reduced thermal shrinkage

*US Consumer Safety Commission Report, 2004

Group Experience with PAN

Past studies

Focusing on

Fibers/Films

Supercapacitor electrodes

Next generation carbon fiber

Showed

- Good CNT (SWNT/MWNT/CNF) dispersion in PAN
- Better mechanical properties
- Good orientation of CNTs
- Reduced thermal shrinkage

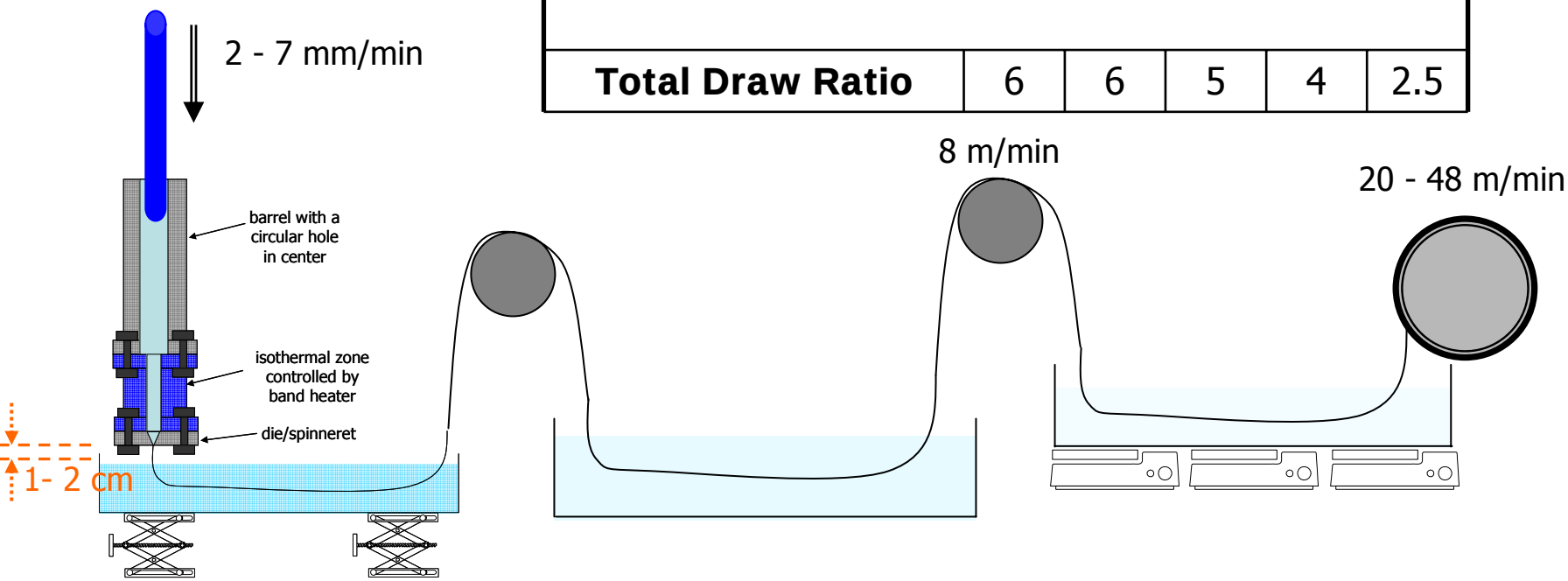
Group's Past Papers on PAN/CNTs

1. "**Oriented and Exfoliated single wall carbon nanotubes in polyacrylonitrile**", *Polymer*, **47**, (2006)
2. "**Single wall carbon nanotube dispersion and exfoliation in polymers**", *J. Appl. Polym. Sci.*, **98** (3), 985-989 (2005).
3. "**Oxidative stabilization of PAN/SWNT composite fiber**", *Carbon*, **43** (3), 599-604 (2005).
4. "**A comparison of reinforcement efficiency of various types of carbon nanotubes in polyacrylonitrile fiber**", *Polymer*, **46**, 10925-10935 (2005).
5. "**Structure and properties of polyacrylonitrile/single wall carbon Nanotube composite films**", *Polymer*, **46**, 3001-3005 (2005).
6. "**The processing, properties, and structure of carbon fibers**", JOM, Publication of the Minerals, Metals, and Materials Society, **57**, 52-58 (2005).
7. "**Properties and structure of nitric acid oxidized single wall carbon nanotube films**", *J. Phys. Chem B*, **108**, 16435-16440 (2004).
8. "**Morphology and properties of polyacrylonitrile/single wall carbon nanotube composite films**", *Fibers and Polymers*, **45** (3), 198-203 (2004).
9. "**Out-of-plane preferred orientation of SWNT films**" *Applied Phys Lett*. **84** (12) 2172 (2004).
10. "**SWNT/PAN Composite Fibers**",*Advanced Materials*, **16**, 58-61 (2004).
11. "**Single Wall Carbon Nanotube Films**", *Chemistry of Materials,* **15**, 175 (2003).
12. "**Quantitative Characterization of SWNT Orientation by Polarized Raman Spectroscopy**", *Chemical Physics Letters*, **378** (3-4), 257-262 (2003).
13. "**SWNT/PAN Composite Film-based Supercapacitor**," *Carbon*, **41**, 2440-2442 (2003).

Experimental

Fiber Spinning:

MWNT (%)	0	5	10	15	20
Total Draw Ratio	6	6	5	4	2.5



CB1: DMF/Water = 70/30 CB2: DMF/Water = 20/80 DB: Boiling Water

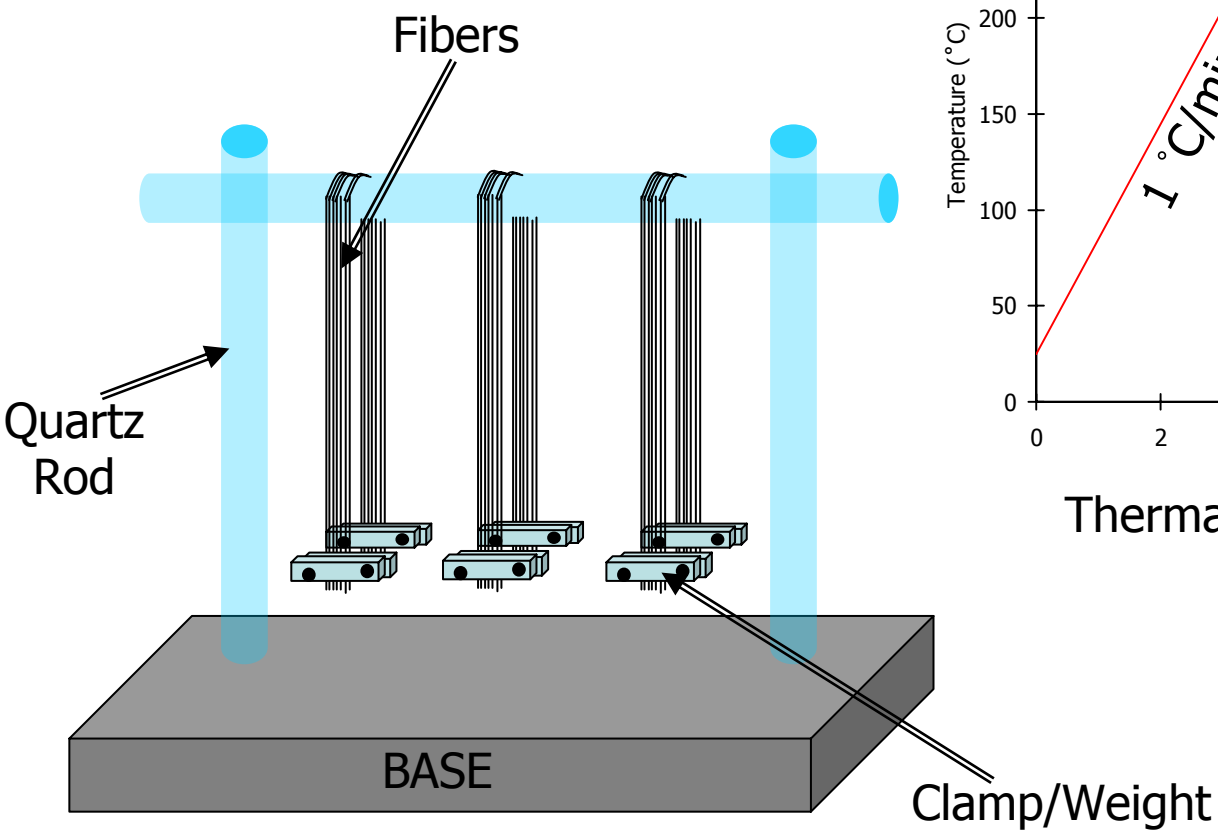
CB1: first coagulation bath; **CB2**: second coagulation bath; **DB**: drawing bath

Barrel diameter = 16 mm
Spinneret hole diameter = 250 μm

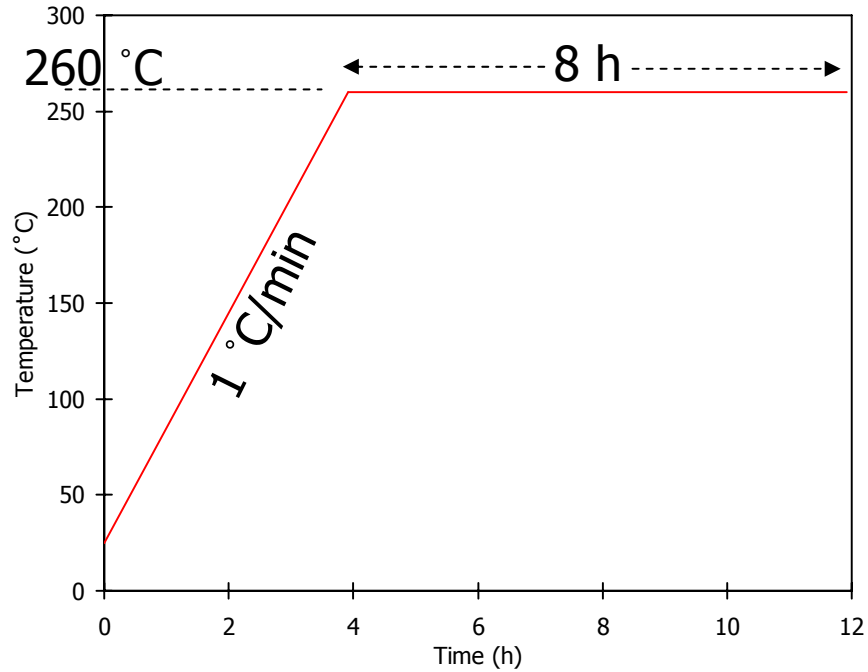
Fiber spools were left to dry in a vacuum oven at 50 °C for at-least 7 days

Experimental

Fiber Stabilization:

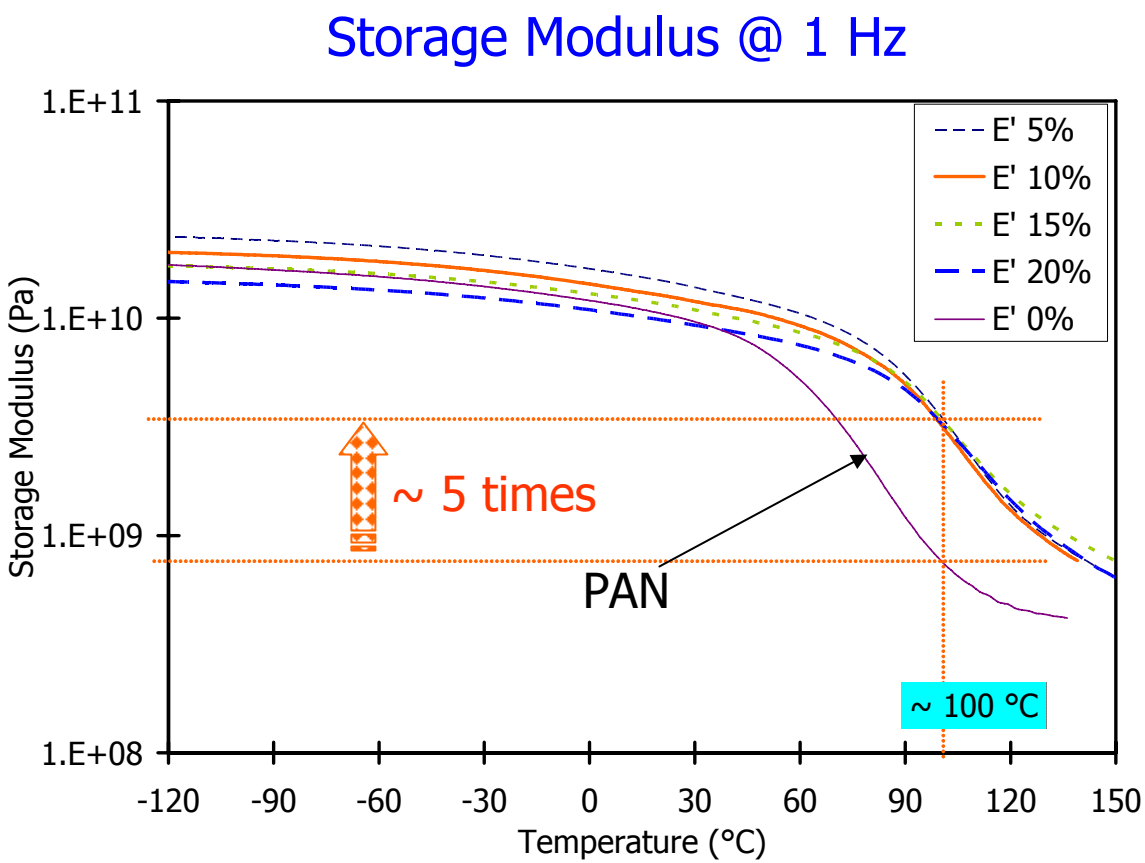


Set-up for Fiber Stabilization



Thermal Cycle for Stabilization

Dynamic Mechanical Analysis

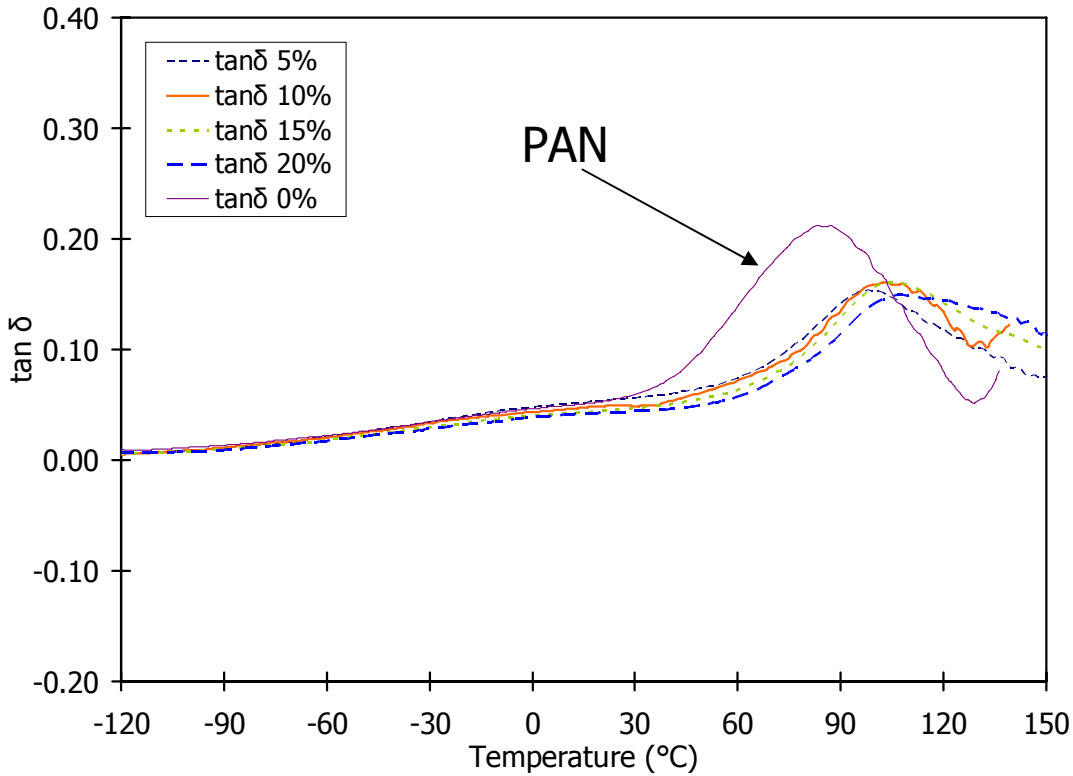


- Composite fibers showed significantly higher storage modulus than control PAN above 40 °C
- Modulus of 5% composite fiber at 100 °C is nearly 5 times than that of control PAN fiber

Dynamic Mechanical Analysis

$$\tan\delta = \frac{E''}{E'}$$

@ 1 Hz



Activation Energy

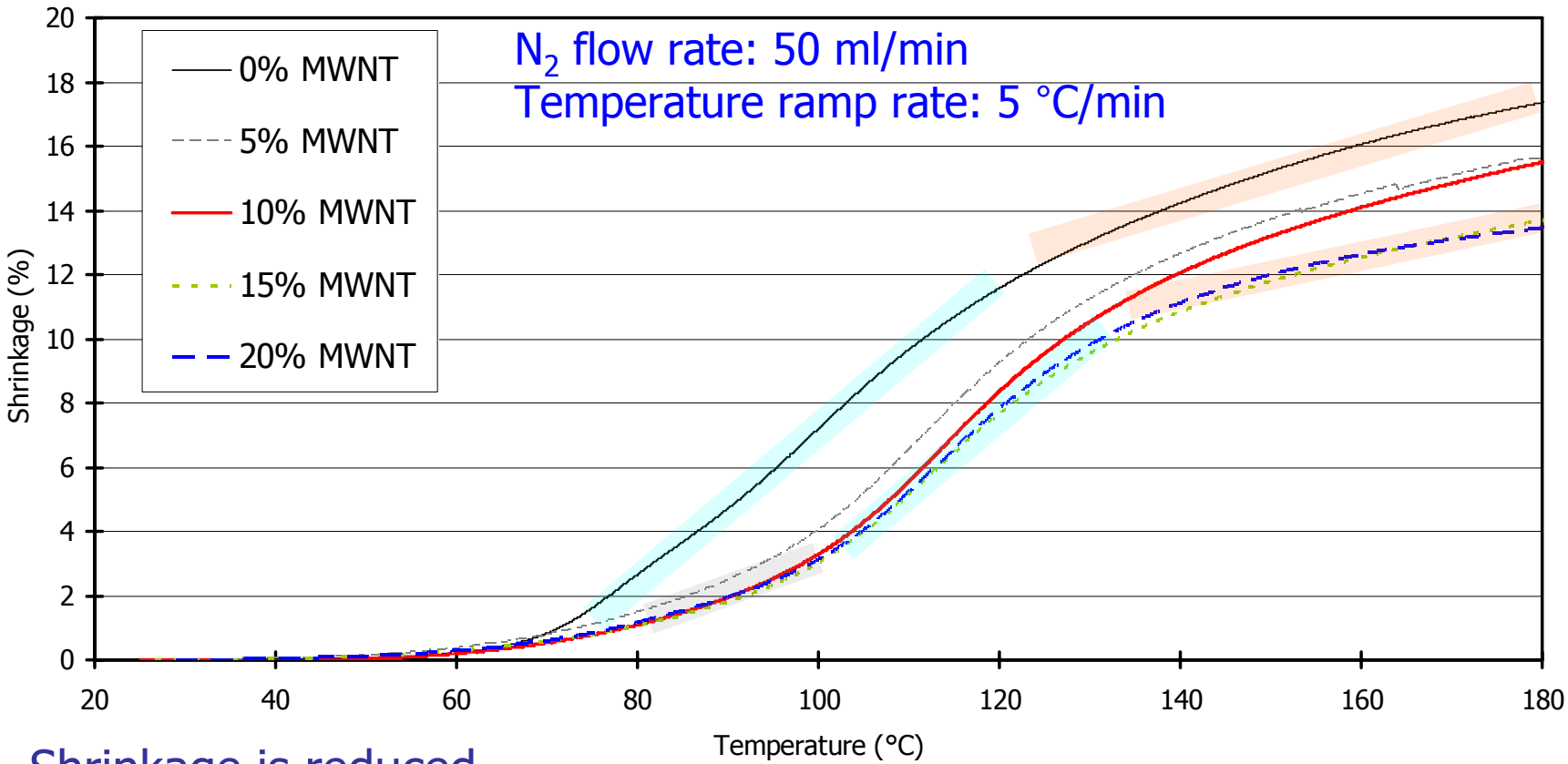
$$\log(\omega) = \frac{-E_a}{RT}$$

MWNT %	0	5	10	15	20
T_g (°C) (@ 1 Hz)	85	99	103	106	110
E_a (kcal/mol)	45.7	42.4	46.0	46.8	47.8

MWNTs constrained the motion of PAN chains

- Glass transition temperature (T_g) shifted to higher temperatures with increase in MWNT content

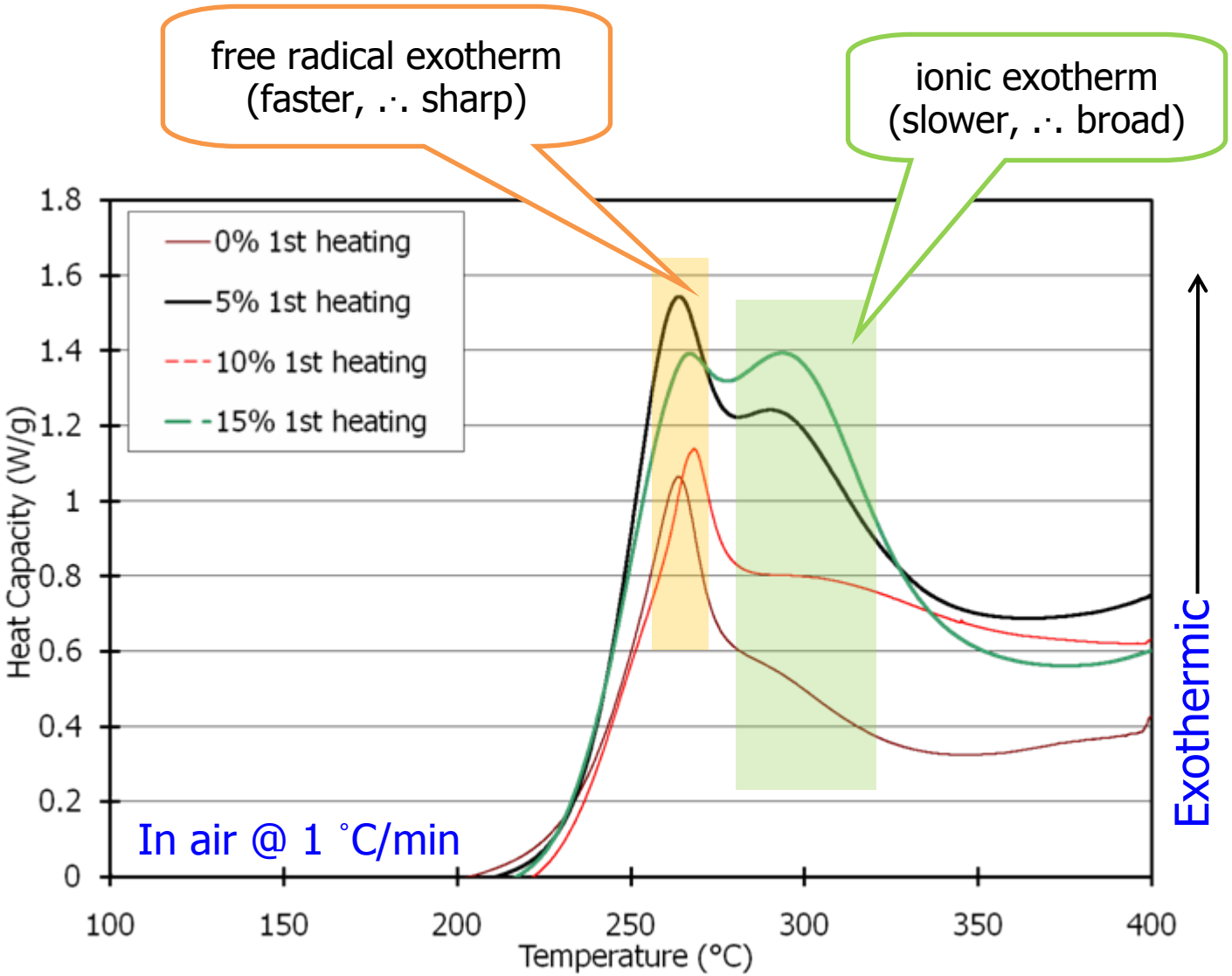
Fiber Shrinkage from TMA



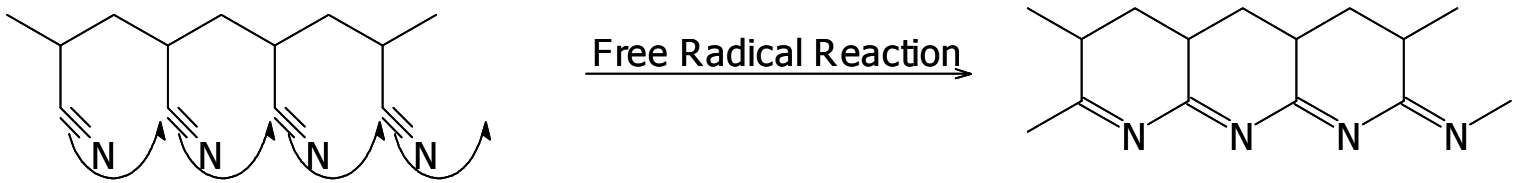
- Shrinkage is reduced after the addition of MWNTs

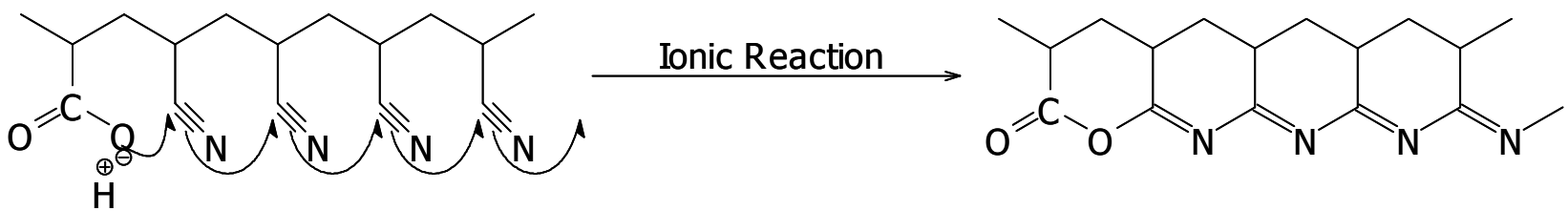
MWNT %	0	5	10	15	20
Shrinkage @ 180 °C (%)	17.4	15.6	15.5	13.7	13.5

Differential Scanning Calorimetry

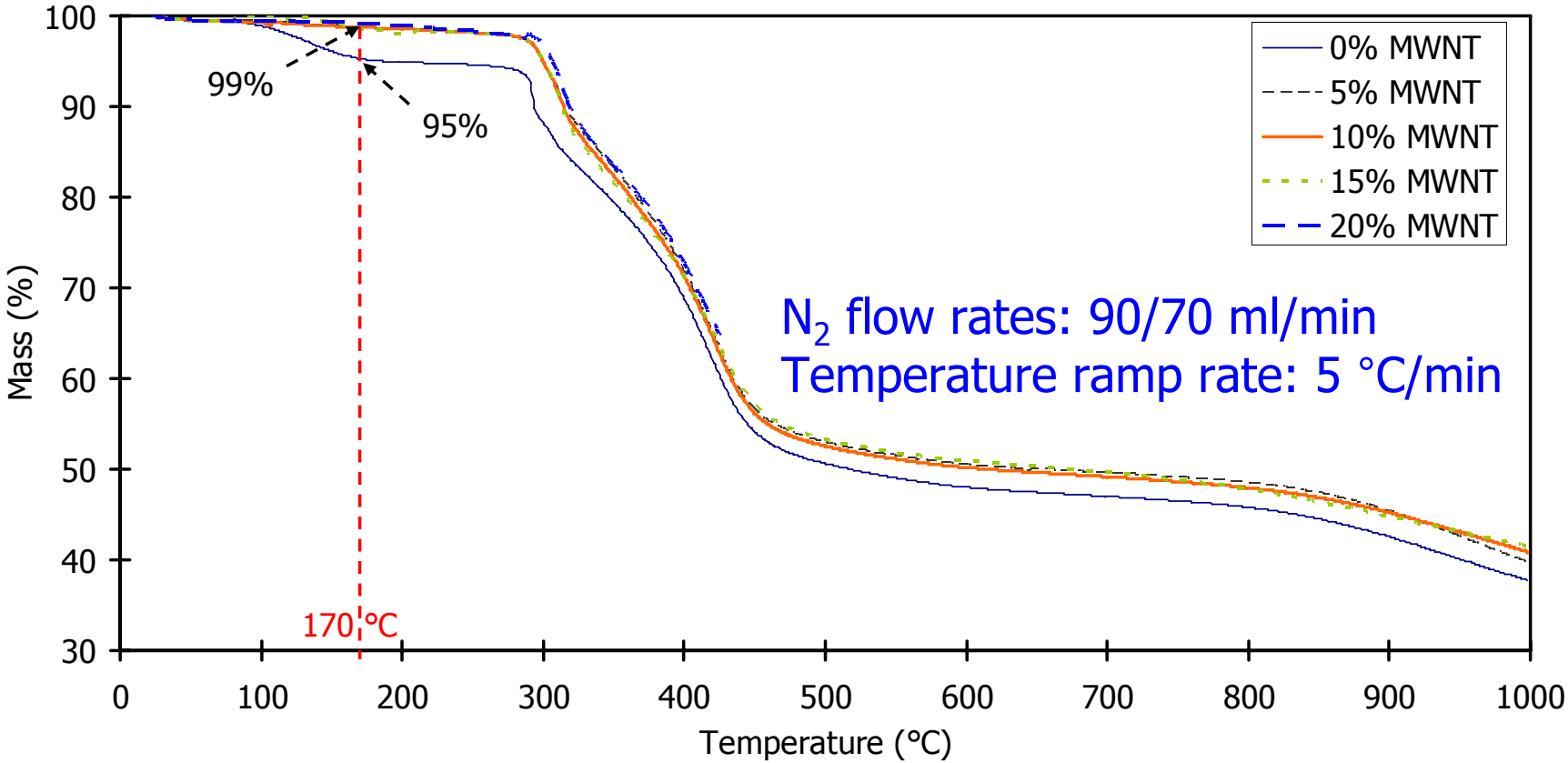


PAN Cyclization Reactions





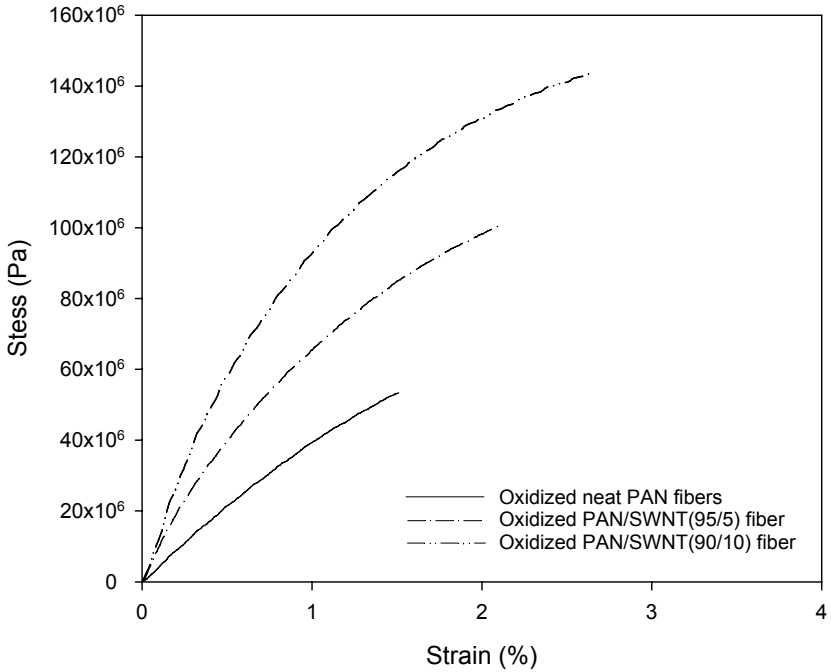
Thermogravimetric Analysis of Various Fibers



- Weight loss before 170 °C in control PAN can be attributed to DMF loss*
- Char yield slightly improved after the addition of MWNTs

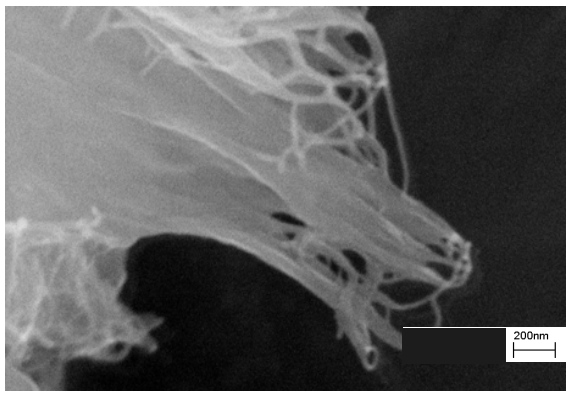
*b.p. of DMF ~160 °C

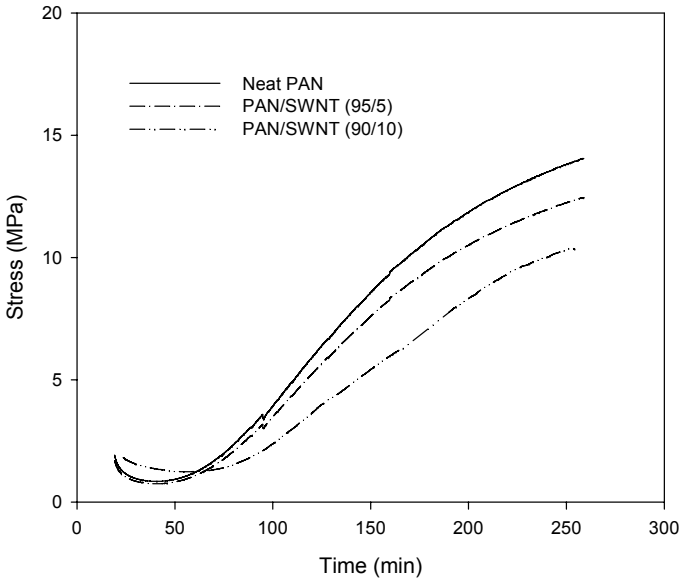
PAN/SWNT Fiber Stabilization



After Stabilization (for 10% SWNT fiber)

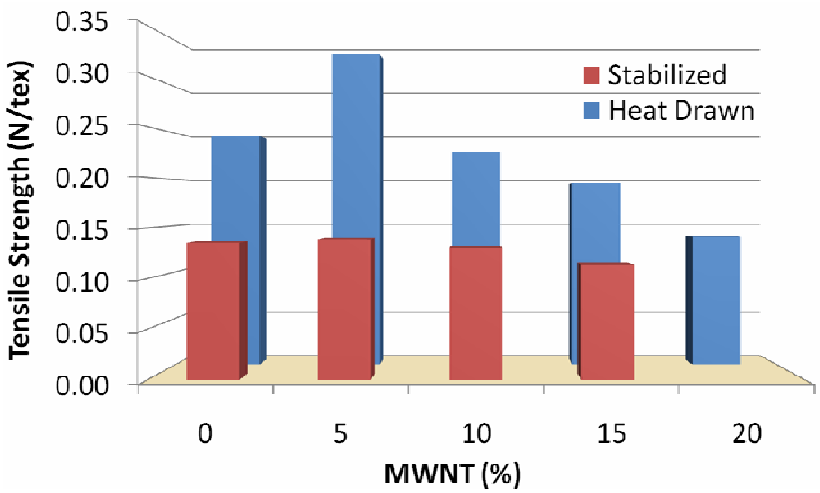
- Strength improved by 100%
- Modulus improved by 160%
- Strain improved by 115%

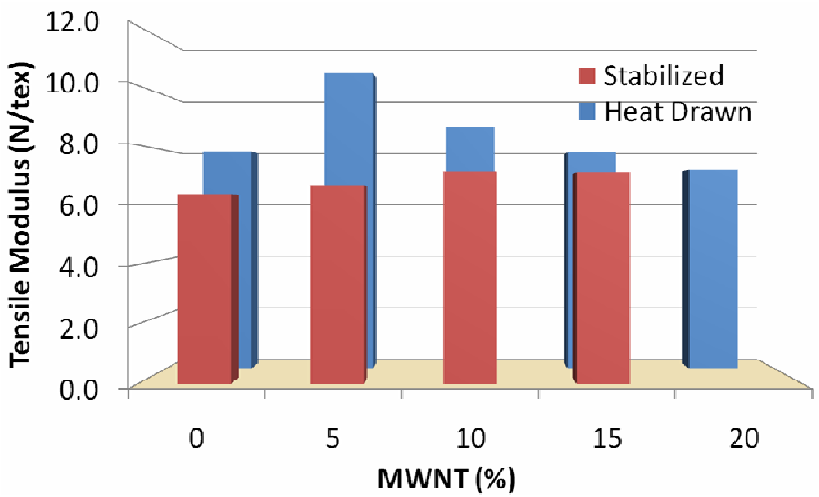


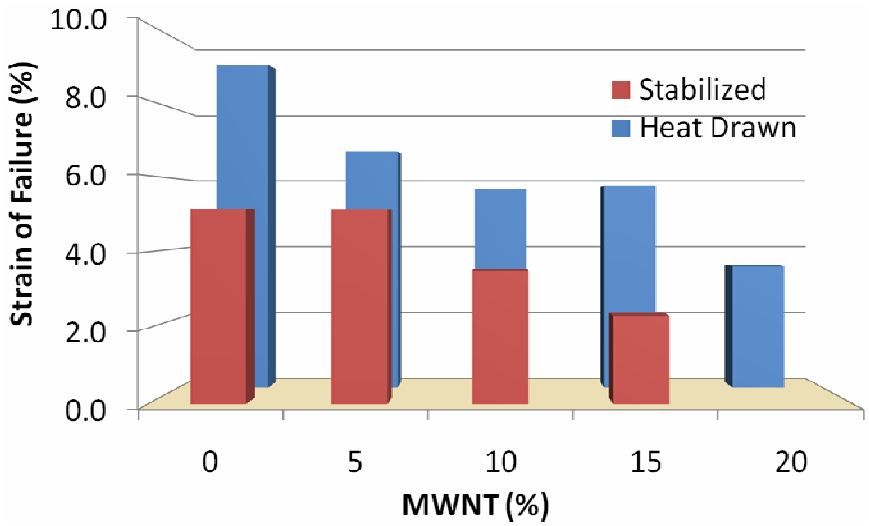


Min, Sreekumar, Uchida, Kumar. Carbon, 43 (2005) 599-604

Tensile Properties (Before and After Stabilization)







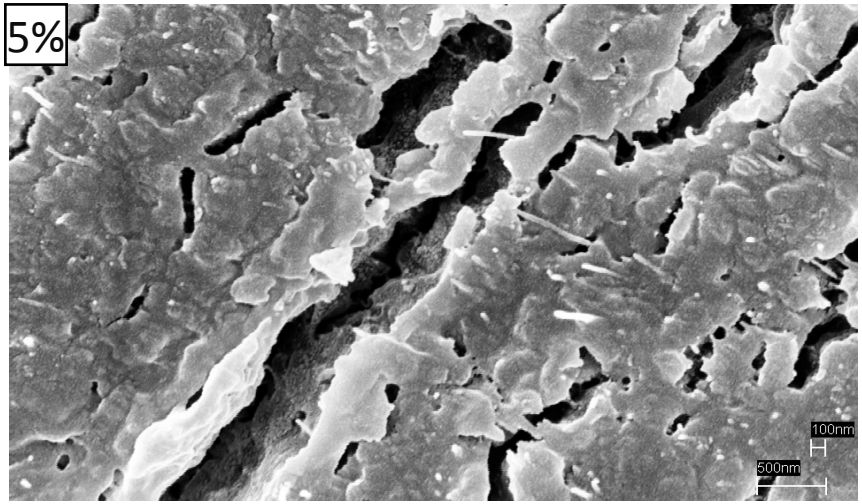
Before Stabilization

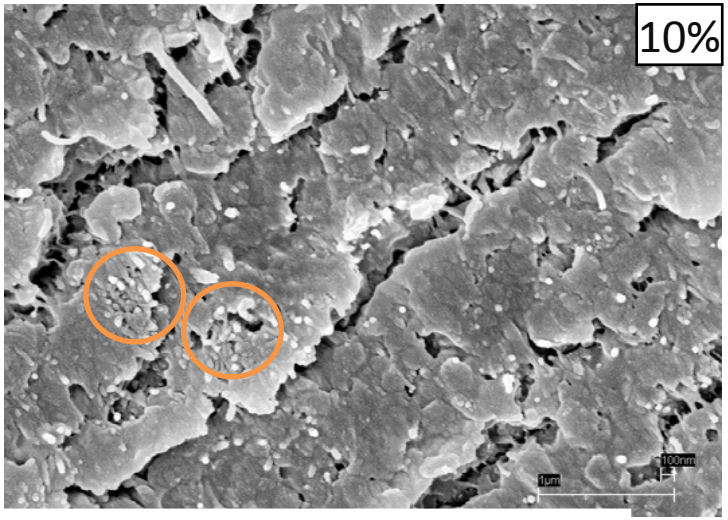
- 5% composite fiber showed highest strength and modulus
- Properties decreased with increasing % of MWNTs

After Stabilization

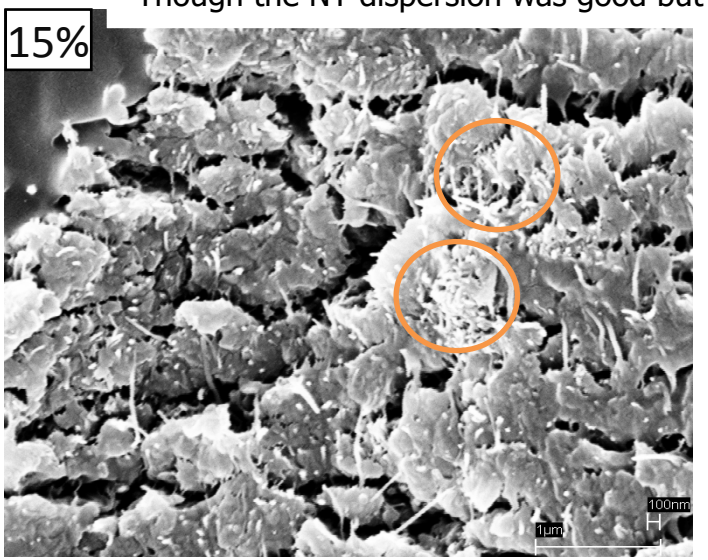
- Properties reduced after stabilization
- 0 and 5% MWNT fibers showed comparable strength and strain
- Modulus increased with increasing % of MWNTs

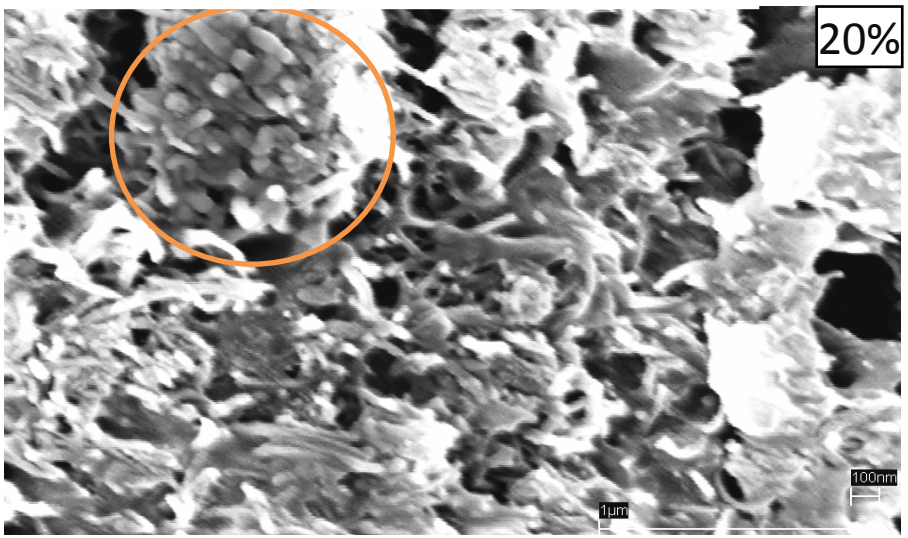
MWNTs Dispersion in PAN matrix



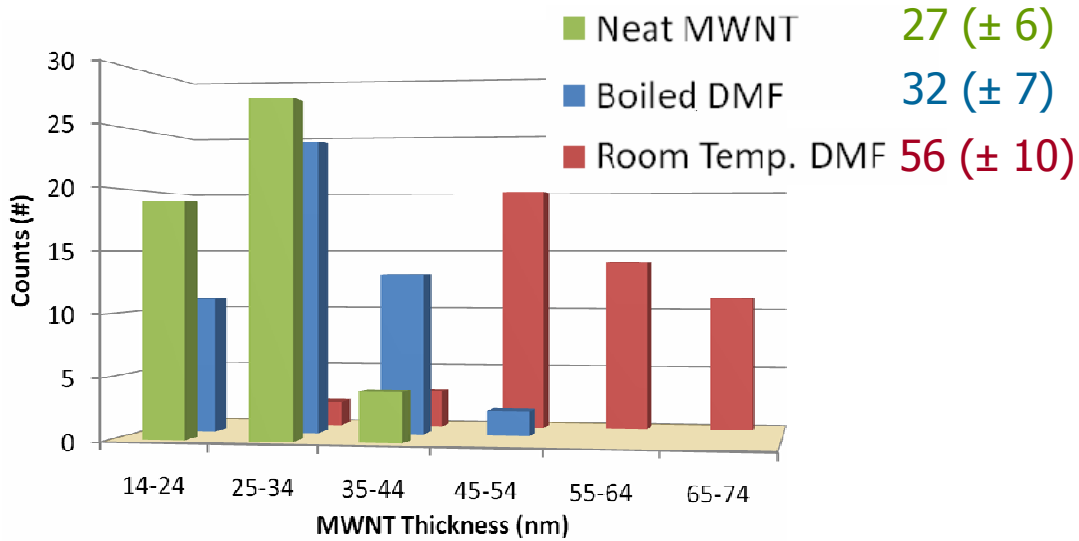


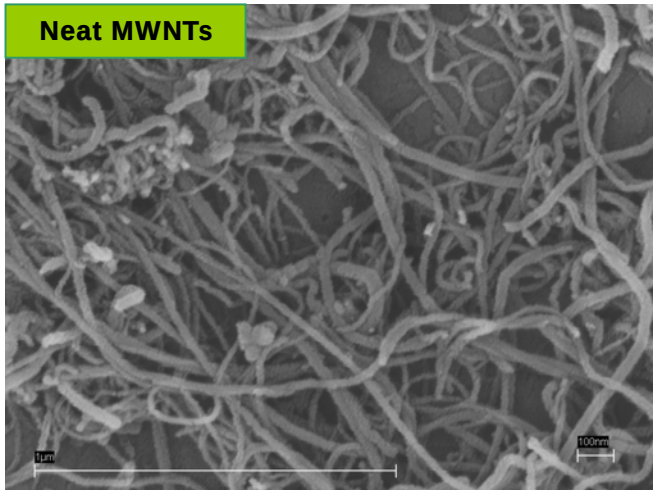
In certain regions MWNTs are entangled with each other but very well wetted with the polymer.
Though the NT dispersion was good but distribution was not efficient in higher MWNT content systems.



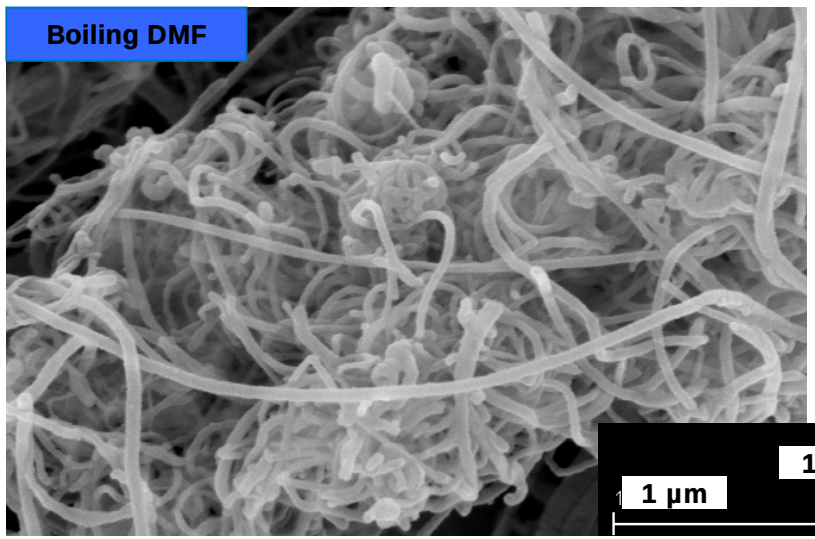


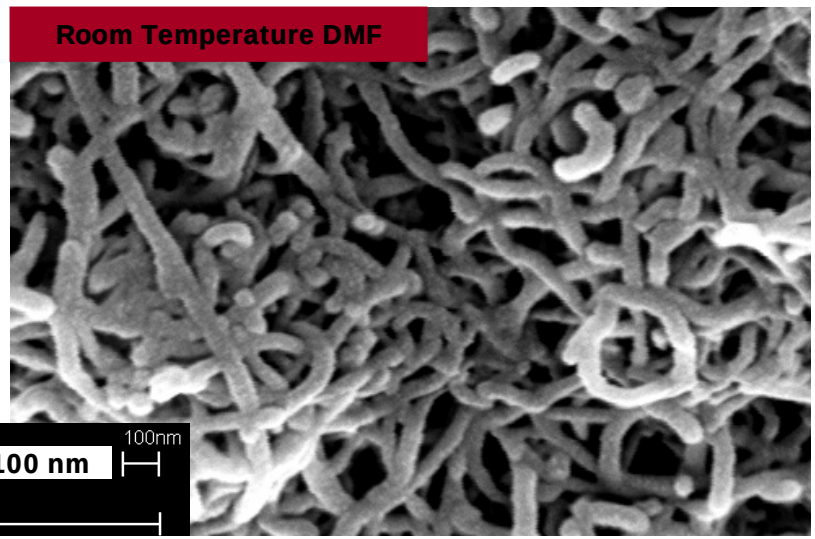
PAN Coating on MWNTs



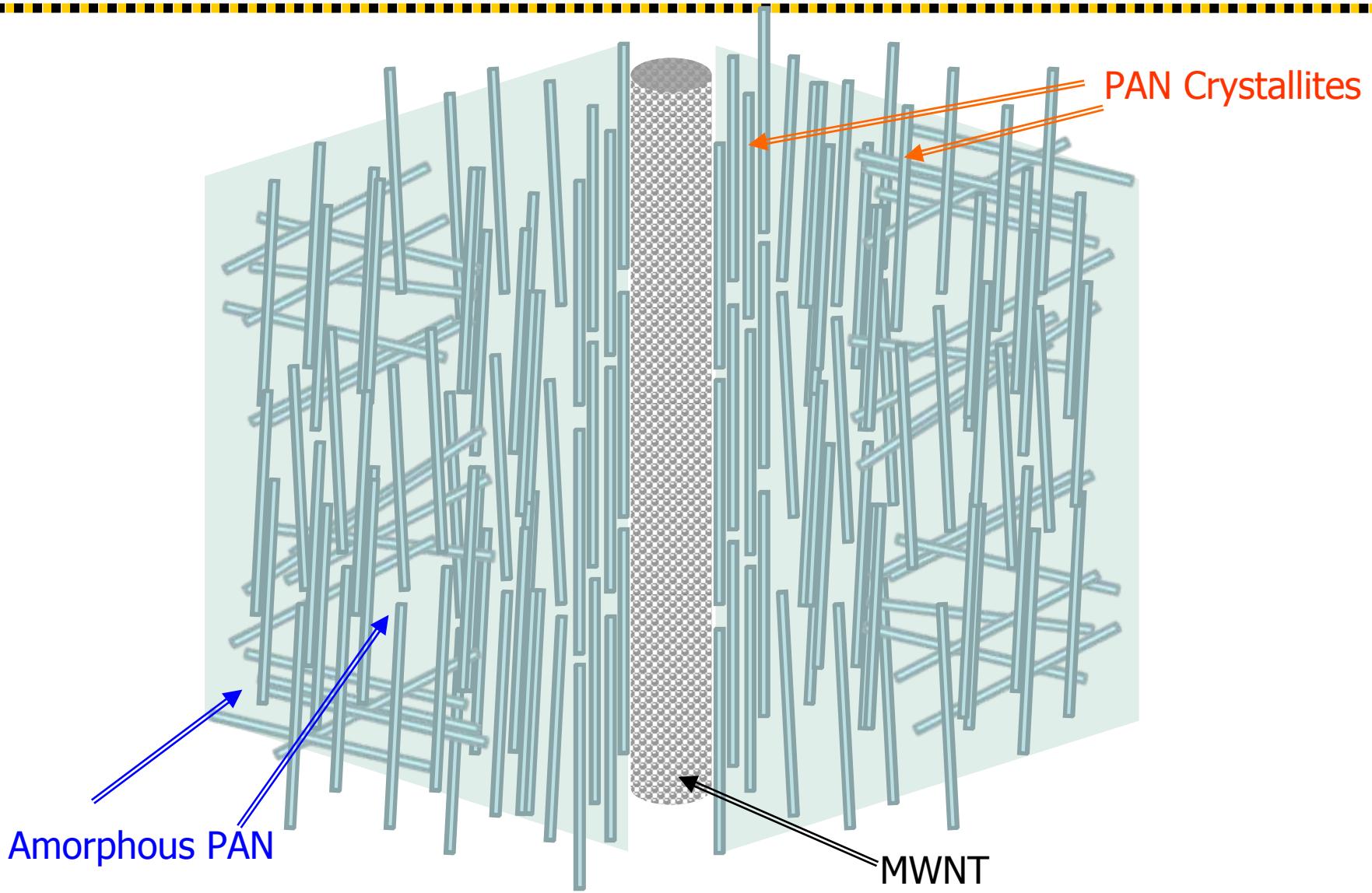


MWNTs recovered on a PTFE filter by dissolving the 15% MWNT/PAN fiber with DMF





Schematic: PAN Coating on MWNTs



Summary

- MWNTs were found to be coated/wetted with PAN
- MWNTs improved the thermo-mechanical properties of PAN fiber
- MWNTs reduced the shrinkage of PAN fiber

Future Work

- Modify processing …so that MWNTs' properties can be translated into composite fibers at higher concentrations
- Study the NT concentration effect with SWNT/PAN and VGCNF/PAN systems

"Thank You"

Cellulose / MWNT Composite Fibers for Fire Barrier Applications

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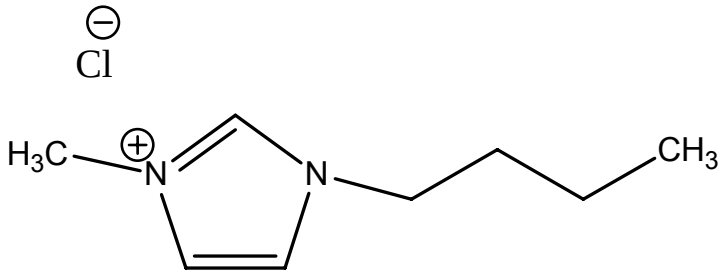
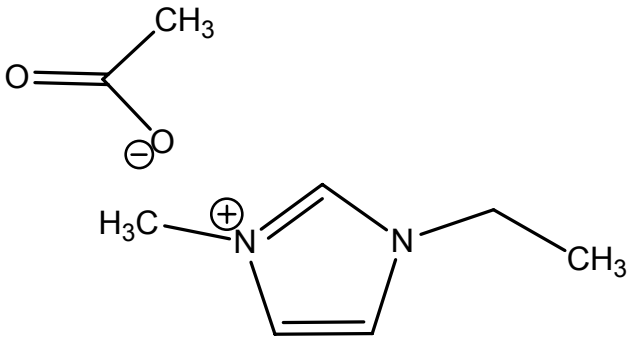
Why Ionic Liquid

- Low volatility
- Favorable solvating properties for diverse compounds
- Considered as environmental friendly or "green" solvents
- Many classes of chemical reactions can be performed in ionic liquids
- Known to assist CNT dispersion
- Recent studies show solubility of cellulose in ionic liquids*



1-butyl-3-methylimidazolium chloride (**BMI Chloride**)



1-ethyl-3-methylimidazolium acetate (**EMI acetate**)

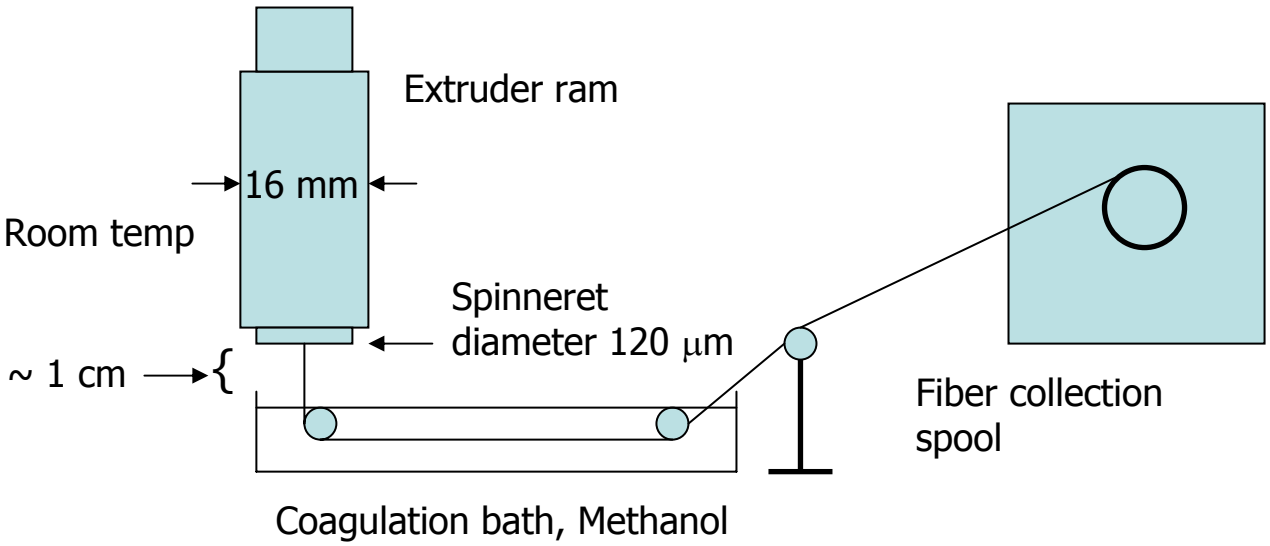
*Swatloski et al, J. Am. Chem. Soc. 2002, 124, 4974-4975

*Gupta et al, Langmuir 2007, 23(3) 1325-1319

Spinning: Cellulose & Cellulose + 1% MWNT Composite Fiber

- Disperse MWNTs in EMI acetate by shearing
- Cellulose (DP ~800) and cellulose + 1% MWNT in EMI acetate (10 wt % sol)
- Spin draw ratio ~ 1
- As spun fiber is kept in methanol bath to extract ionic liquid
- Dried in vacuum oven at 50 °C for 2-3 days

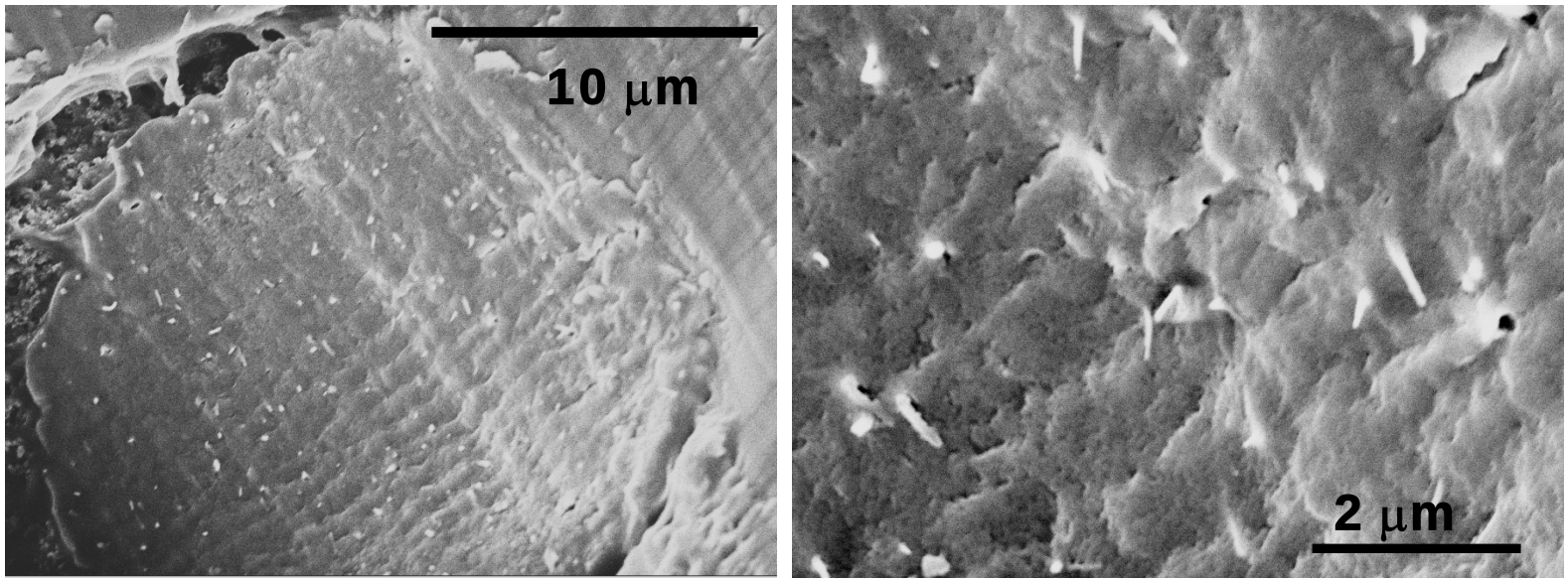
Dry-jet-wet spinning



Cellulose Fiber

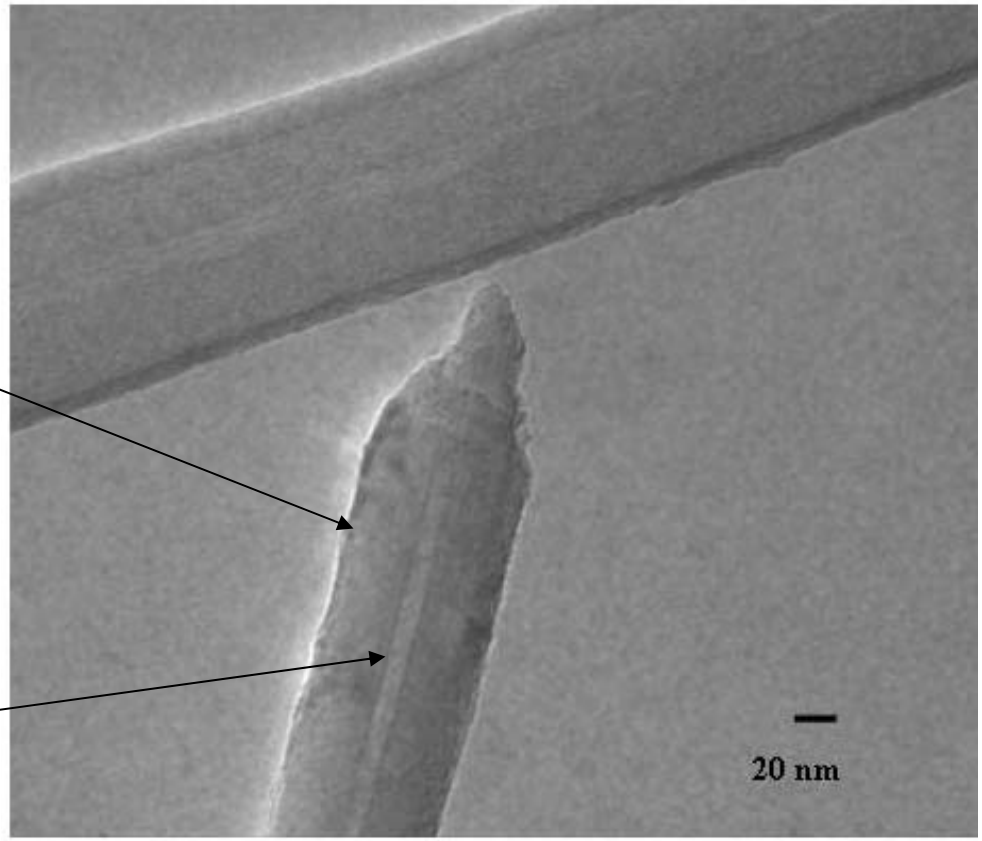
Cellulose + 1 wt% MWNT Fiber

SEM of Cellulose + 1% MWNT Fiber Cross Section



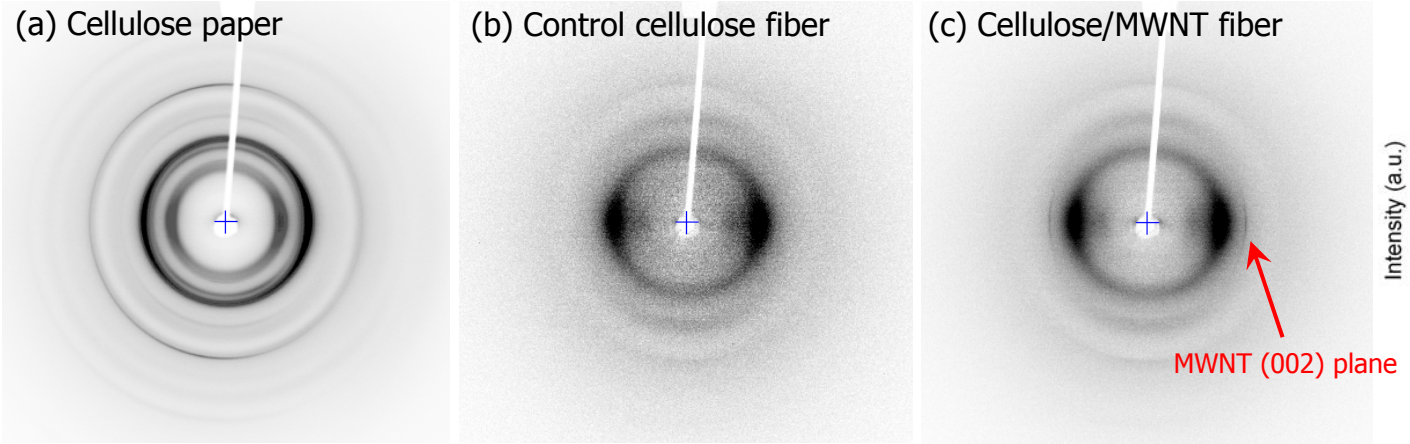
Uniform dispersion of MWNT in the polymer matrix

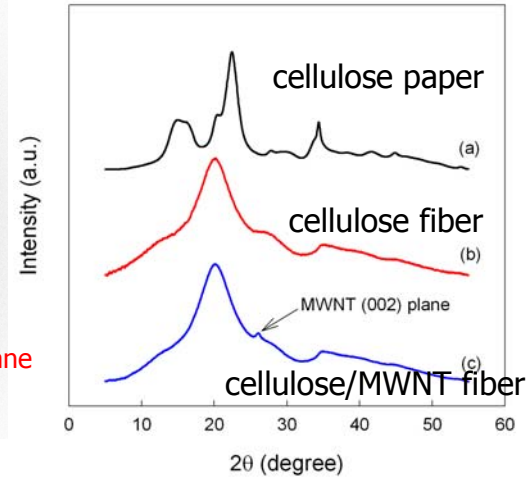
TEM of Cellulose + 1% MWNT Composite Fiber



Coating of cellulose on carbon nanotubes observed

WAXD Analysis on Cellulose Fibers





- Cellulose paper – Cellulose type (I) crystal
- Cellulose & cellulose/MWNT fiber from ionic liquid – Cellulose type (II) crystal

	Crystallinity (%)	Crystal size $_{2\theta\sim20^{o}}$ (nm)	$f_{2\theta\sim20^{o}}$	$FWHM_{2\theta\sim20^{o}}$ (degree)	$f_{MWNT,2\theta\sim26^{o}}$
Control cellulose fiber	42	1	0.107	33	NA
Cellulose/MWNT fiber	45	1	0.106	36	0.738

f represents Herman's orientation function

- Both control cellulose and cellulose/MWNT fibers have comparable crystal structure
- MWNT orientation in composite fiber appears to be high considering no drawing process

WAXD Analysis on Cellulose Fibers

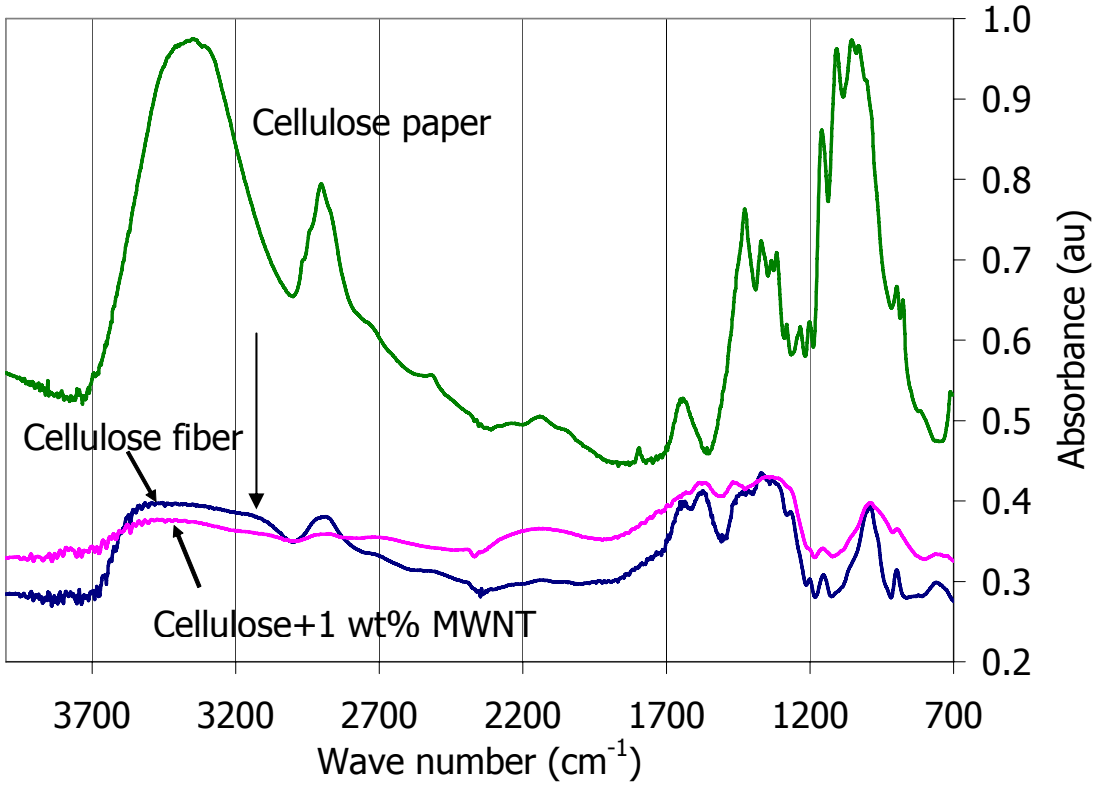
	Crystallinity (%)	Crystal size $_{2\theta\sim20^{o}}$ (nm)	$f_{2\theta\sim20^{o}}$	$FWHM_{2\theta\sim20^{o}}$ (degree)	$f_{MWNT,2\theta\sim26^{o}}$
Control cellulose fiber	42	1	0.107	33	NA
Cellulose/MWNT fiber	45	1	0.106	36	0.738

f represents Herman's orientation function

	Crystallinity (%)	Crystal size (nm)	Orientation (XRay)
Cotton	~ 70	5-10	0.62 - 0.70
Wood pulp	60		
Regenerated Cellulose (alkali)	35		
Rayon (viscose)	38 - 40	2 - 3	0.31 - 0.91
Rayon (staple fiber)	30 - 40	5 - 7	
Cellophane film	30 - 40		

From Polymer Handbook, Fourth Edition

FTIR Spectroscopy



- Appearance of a new contribution at ~ 3115 cm^{-1} due to intermolecular H-bonding [OH(2)-O2]
- Indicates transformation of Crystal Structure I for cellulose pulp to crystal structure II for cellulose fiber

Tensile Properties

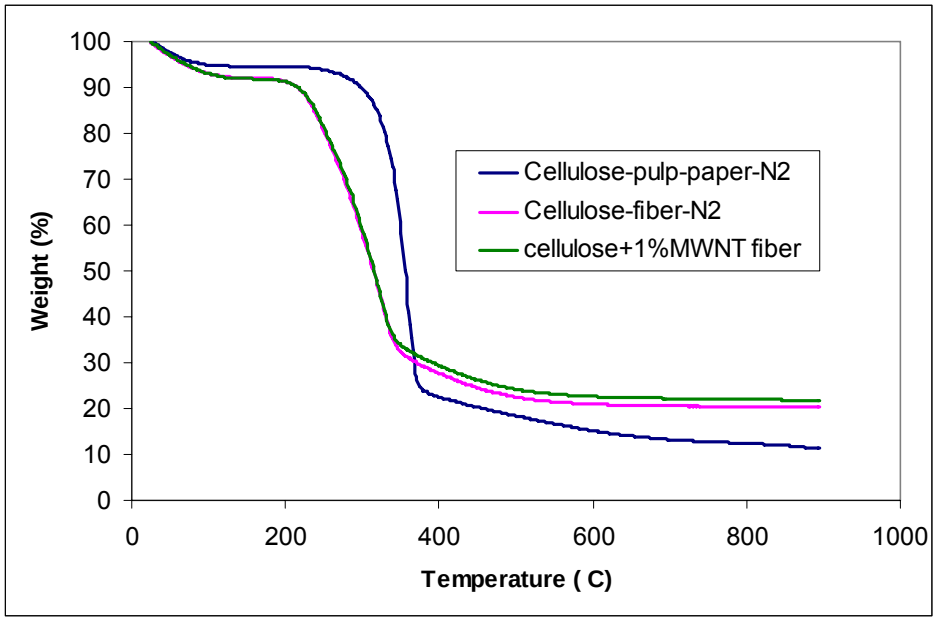
	Fiber Diameter (μm)	Strength (MPa)	Modulus (GPa)	Strain to Failure (%)
Cellulose	29.2 ± 4.1	113 ± 26	8.4 ± 1.7	5.2 ± 0.9
Cellulose + 1% MWNT	26.2 ± 1.2	137 ± 7.5	10.8 ± 0.5	7.4 ± 1.7

	Tensile Strength (MPa)	Tensile Modulus (GPa)	Strain to Failure (%)	Reference
Rayon fiber	500	2.2		Canche-Escamilla et al, J. Mater. Sci (2006) 41, 7296-7301
Cotton fiber (Grade G.12)	640		8.0	P.Bhama Iyer, S. Srenivasan et al, J. App. Polym Sci (1991) 42, 2915-2922
Cotton fiber (treated with 5N KOH)	550			S.H. Zeroniam, K.W. Alger, J. App Polym Sci (1976) 20, 1689-1693
Cotton (1% formaldehyde crosslinked)	740	1.8	4.7	D.S. Verma et al (1974) 18, 3745-3759
Cellulose fiber (DP ~ 650, from RTIL)	204			Hao Zhang et al, Adv Mater. (2007) 19, 689-704

Thermogravimetric Analysis (TGA)

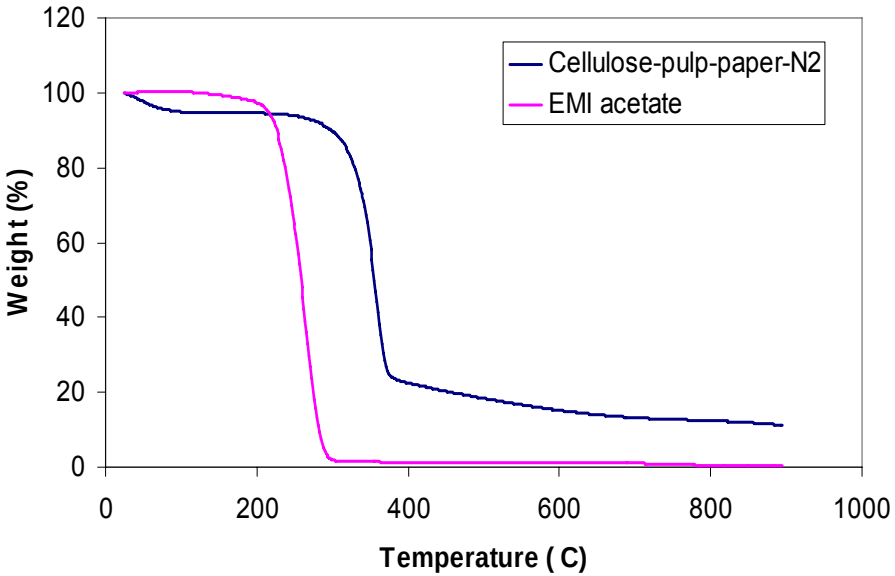
Char Yield at 800 °C in Nitrogen @ 10 °C/min

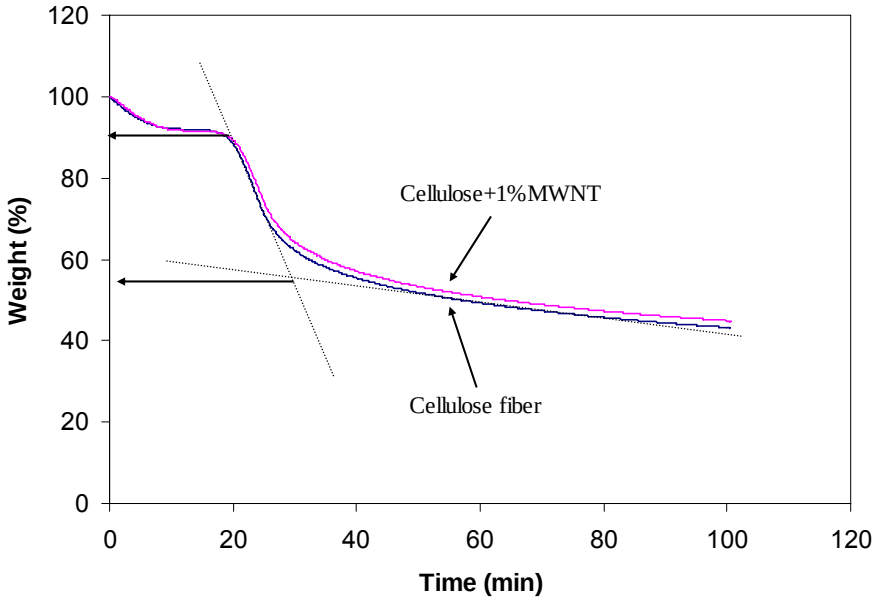
Cellulose pulp paper	12%
Cellulose fiber	20%
Cellulose + 1% MWNT fiber	22%



	Yield (%)	Reference
Cotton (@ 800 °C in N_2)	12	Dae-Young Kim et al, Cellulose (2001) 8, 29-33
Cotton (impregnated with 5.6% H_2SO_4)	38	Dae-Young Kim et al, Cellulose (2001) 8, 29-33
Cotton (530 °C in air, using hydroxymethyl dicyanamide flame retardant)	34.5	C. M. Tian et al, J of Therm Anal & Cal. (1999) 55, 93-98

TGA: Quantification of EMI Acetate in Fiber





TGA Isothermal of Cellulose and Cellulose + 1% MWNT fiber at 270 °C for ~ 80 min in N_2

~ 35% EMI acetate still remains in cellulose and cellulose + 1% MWNT composite fiber

Conclusions

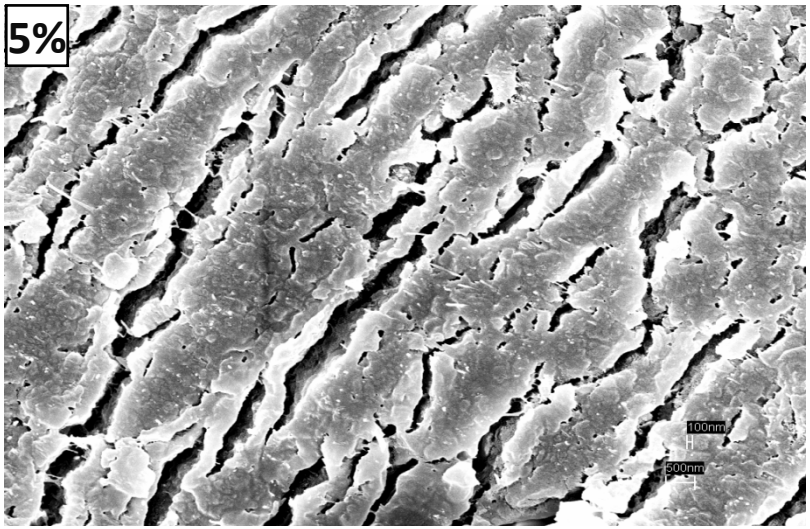
- Uniform dispersion of MWNT in cellulose
- Reinforcement of cellulose by addition of 1% MWNT
- Transformation of cellulose-I for starting pulp to cellulose-II for cellulose fiber
- High orientation of MWNT even at low draw ratio
- Enhanced char yield for cellulose and composite fiber relative to cellulose pulp
- High retention of ionic liquid in cellulose fiber

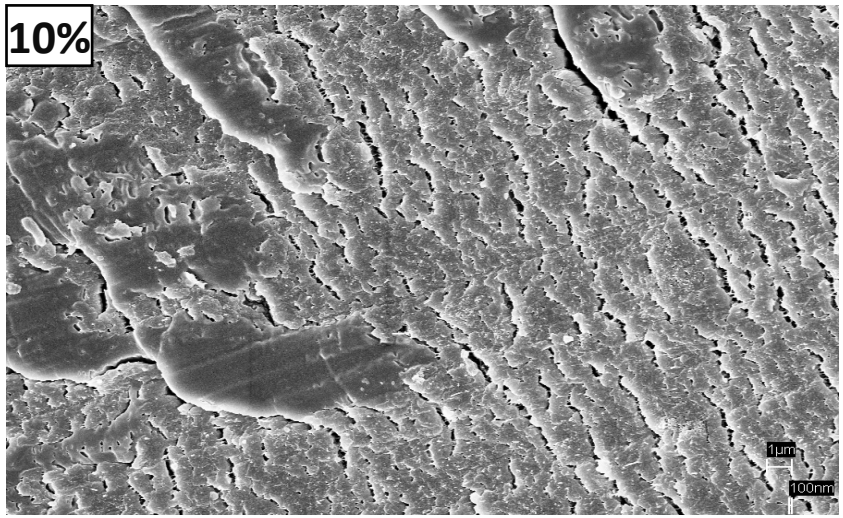
Future Work

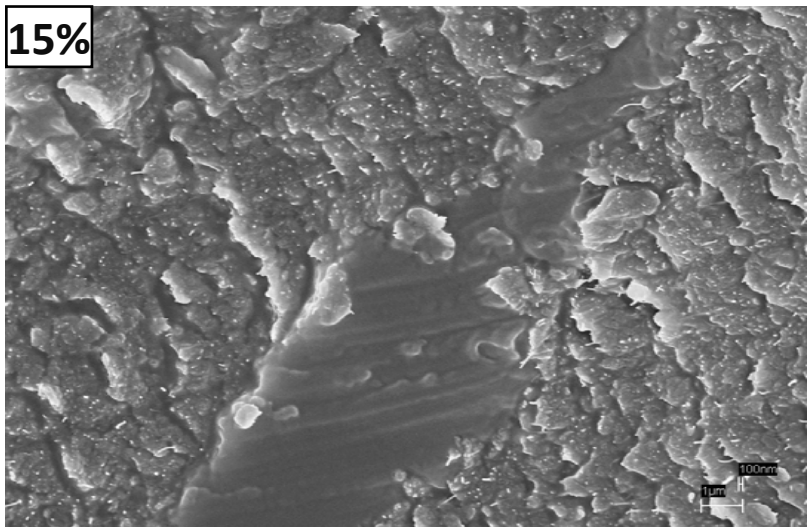
- Optimize coagulation conditions for ionic liquid removal during/after spinning
- Composite fiber at higher carbon nanotubes loading
- Spinning cellulose and composite fiber using higher molecular weight cellulose (DP 1300)
- Study the fire barrier properties of cellulose and composite fibers

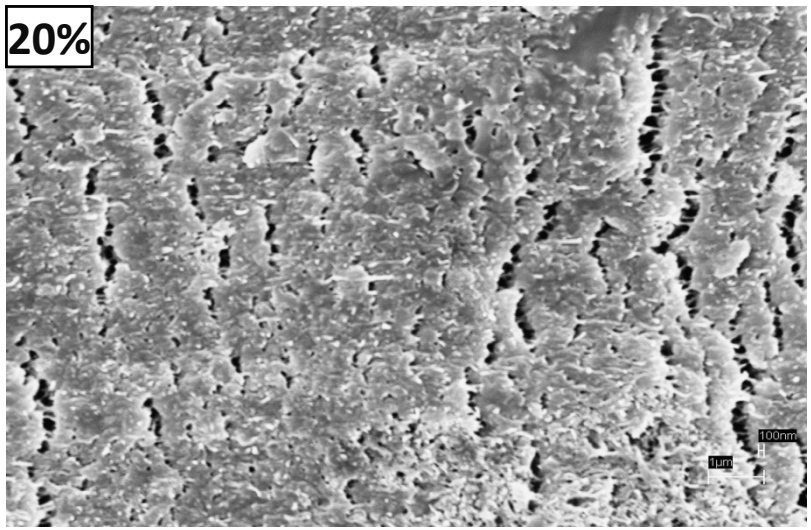
Questions ?

Uniform MWNTs Dispersion in PAN matrix

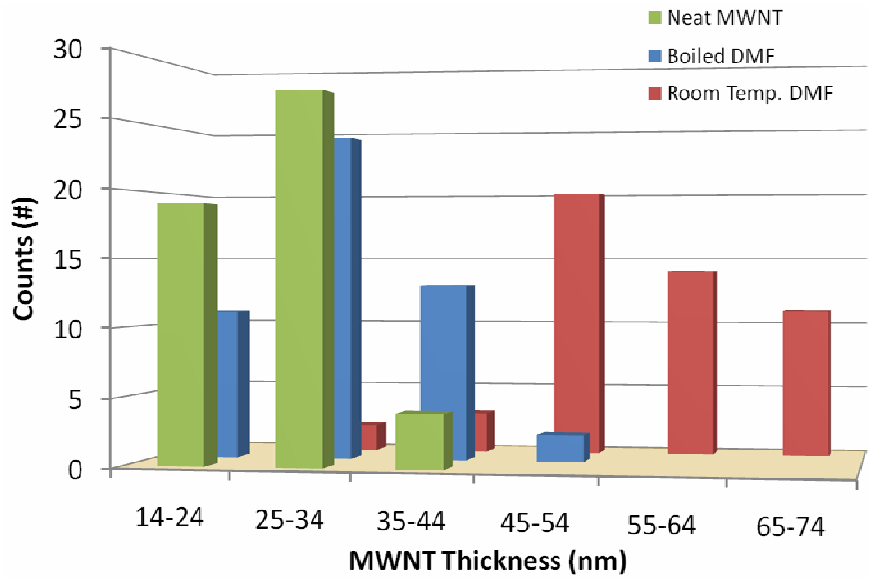


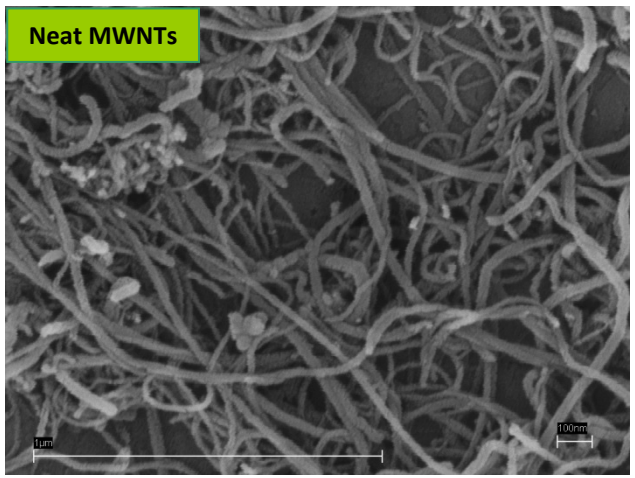


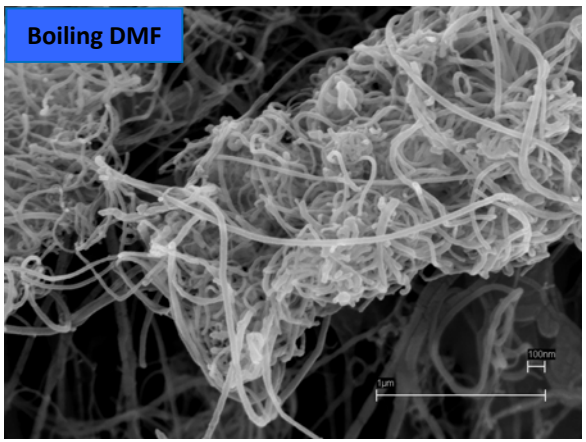


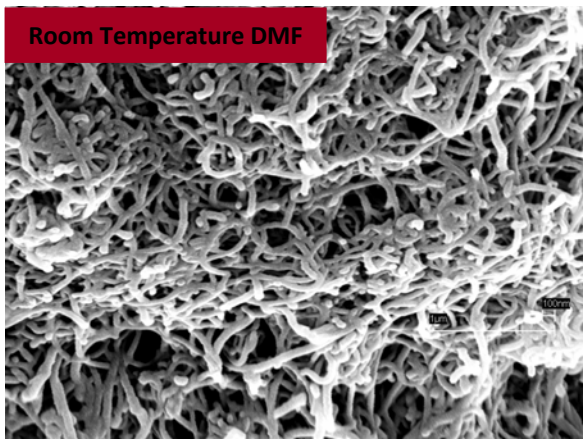


PAN Coating on MWNTs









SEM image of MWNTs recovered on a PTFE filter by dissolving the 15% MWNT/PAN composite fiber with DMF