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Carbon fibers derived from sustainable precursors

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Carbon fibers derived from sustainable precursors

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Outline

- Literature Review: carbon fiber precursors
  PAN, mesophase pitch, rayon, and lignin
- Motivation and Objectives
- Experimental
  - Melt spinning with ECN organosolv lignin
  - Solution spinning with acetylated Indulin AT
- Results and Discussion
- Conclusions
- Future Work

Carbon Fiber Characteristics

- ✓ Excellent Strength and Stiffness = high performance
- ✓ Light-weight = fuel-efficient
- ✓ Outstanding Electrical and thermal conductivity
- ✓ Fire-retardant

- ☐ Not Cost-Competitive
- ☐ Current precursors are not bio-based and fibers are not produced by environmentally-friendly processes

Production of Carbon Fibers: Background

precursors

wet or melt spinning →

precursor fibers

Oxidative stabilization →
200-300°C
1-24 h

stabilized fibers

↓ Carbonization
800-1700°C
inert atmosphere

Carbon fibers

Carbon does not melt !

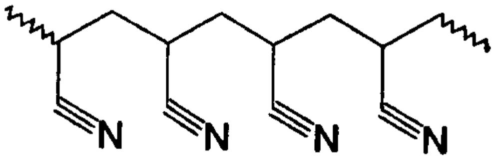
Therefore, carbon fibers must be produced from a solution or melt processible precursor, and the precursor fibers must be carbonized

Carbon Fiber Precursors

- Polyacrylonitrile (PAN)
- Mesophase pitch
- Rayon
- Lignin (current research)

PAN Precursors

The precursor for PAN-based carbon fibers is actually a copolymer.

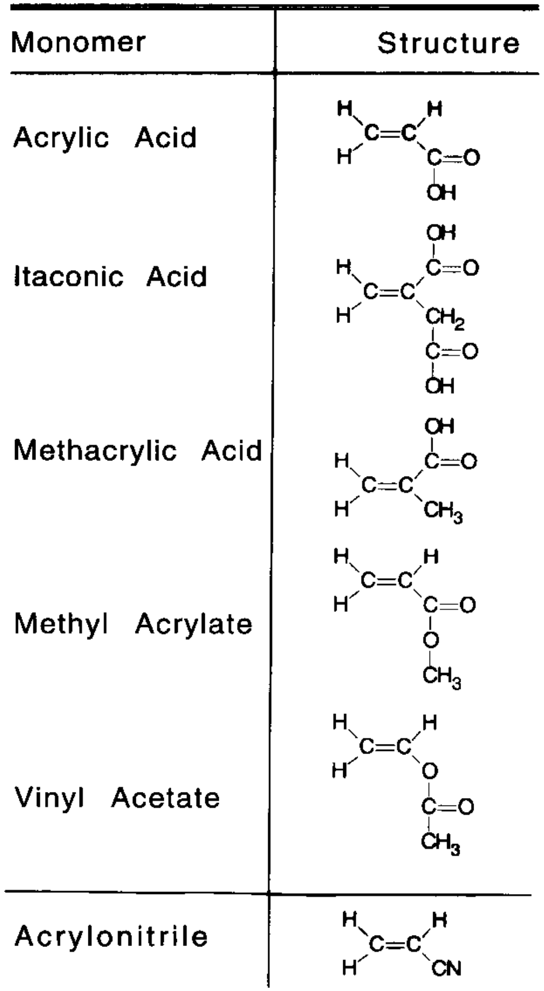


Polyacrylonitrile

I

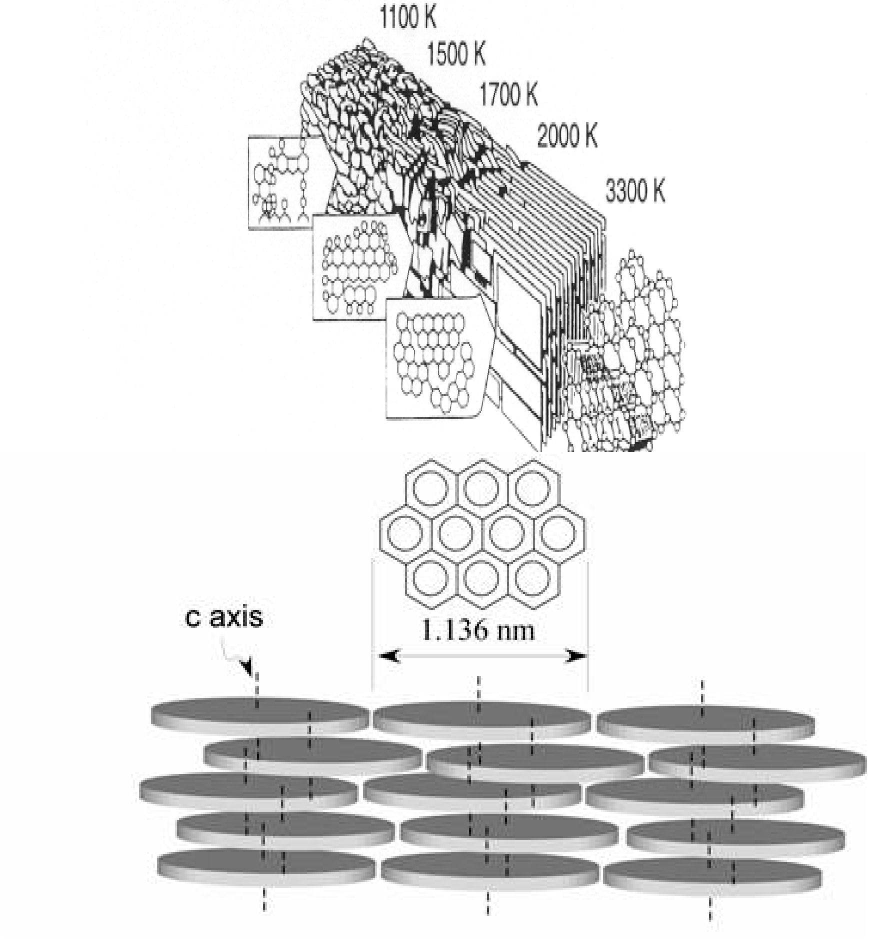
Evolution of HCN and other toxic gases during stabilization and carbonization

Buckley & Edie, 1986
Fitzer & Manocha, 1998

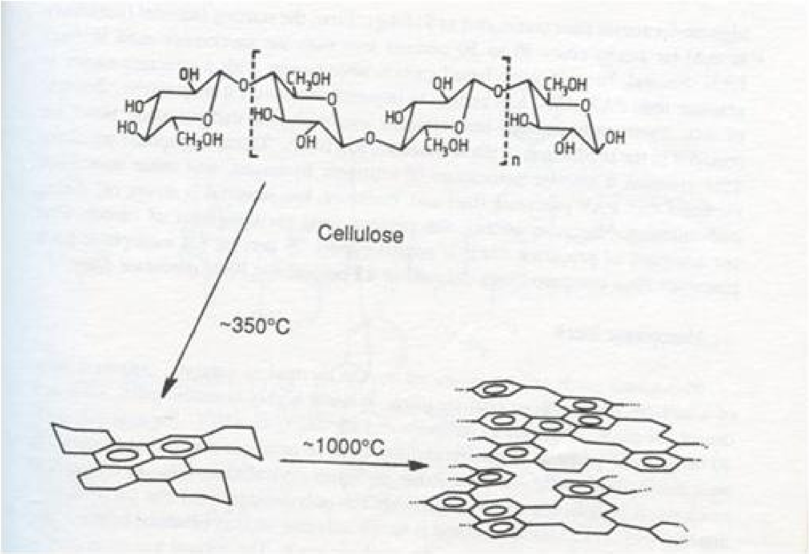


Monomer	Structure
Acrylic Acid	
Itaconic Acid	
Methacrylic Acid	
Methyl Acrylate	
Vinyl Acetate	
Acrylonitrile	

Precursors: Mesophase Pitch and Rayon



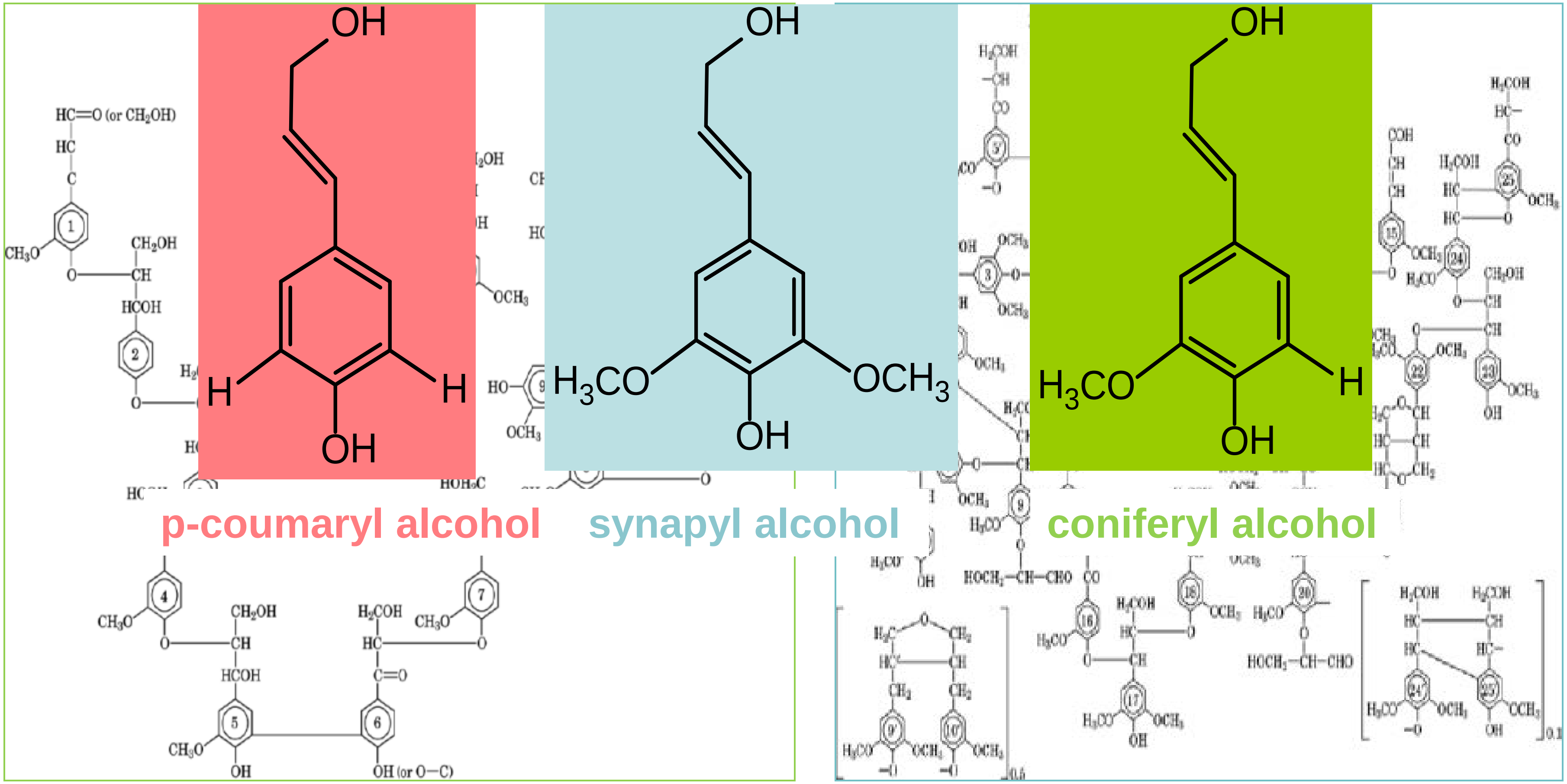
Kundu, ..Ogale, CARBON 2008



Buckley & Edie, 1986

Not for structural applications

Chemical Structure of Lignin



p-coumaryl alcohol

synapyl alcohol

coniferyl alcohol

Softwood Lignin

Hardwood Lignin

E. Alder, Wood Science & Technology, 11, 169 (1977)
H. H. Nimz, Angew. Chem. Int. Ed., 13, 313 (1974)

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Lignin

Source:
wood, grass, wheat straw, etc

Separation process:
kraft, soda, organosolv pulping, etc

Literature Review

- Different lignin precursor, NaOH solution for dry-spinning / melt spinning. 1969, Otani
- Steam exploded hardwood lignin followed by hydrogenation and several extraction steps, melt-spinning. 1991, K. Sudo *et al*
- Organosolv (acetic acid) hardwood lignin based carbon fiber, melt-spinning 1993, Y. Uraki *et al*; 1995, S. Kubo *et al*
- Organosolv (acetic acid) softwood lignin, melt-spinning, 1998, S. Kubo *et al*
- Hardwood kraft lignin, melt spinning. 2002, J. F. Kadla *et al*
- Acetylated softwood kraft lignin, melt-spinning. 2008, R. C. Eckert
- Softwood kraft lignin using hardwood kraft lignin as plasticizer, melt-spinning. Baker, F. S. EERE, U.S. Dept of Energy Project ID # lm_03_baker

Mechanical properties of lignin based CF

Precusor Type	Diameter (µm)	Elongation (%)	Modulus (GPa)	Tensile strength (MPa)	Reference
Steam Exploded hardwood	7.6 ± 2.7	1.63 ± 0.19	40.7 ± 6.3	660± 230	K. Sudo *et al*, 1992
Organosolv Hardwood	14-35	0.64-1.12	2.17-39.1	13.3-355	Y. Uraki *et al*, 1995
Organosolv Softwood	84 ± 15	0.74 ± 0.14	3.59 ± 0.43	26.4 ± 3.1	S. Kubo *et al*, 1998
Kraft Hardwood	46 ± 8	1.12 ± 0.22	40 ± 11	422 ± 80	J. F. Kadla *et al*, 2002
Kraft Softwood, acetylated	5-100	N/A	N/A	N/A	Robert C., 2008
Hardwook		2.03	82.7	1070	D. A. Baker, 2013
Rayon based carbon fiber	5-25		100	100-1000	Buckley & Edie; Fitzer& Manocha
PAN based carbon fiber	5-15	2	100-500	3000-7000	Buckley & Edie; Fitzer& Manocha
Mesophase pitch based carbon fiber	5-15	0.6	200-800	1000-3000	Buckley & Edie; Fitzer& Manocha

Goal:

Lignin-based carbon fibers with higher performance properties

Specific objectives:

Chemical modification of separated lignin

Preparation of lignin based carbon fiber
- **Spinning**
- **Thermostabilization**
- **Carbonization**

Microstructure and Properties
- **Tensile**
- **Nanotexture and Graphitic Crystallinity**

Experimental

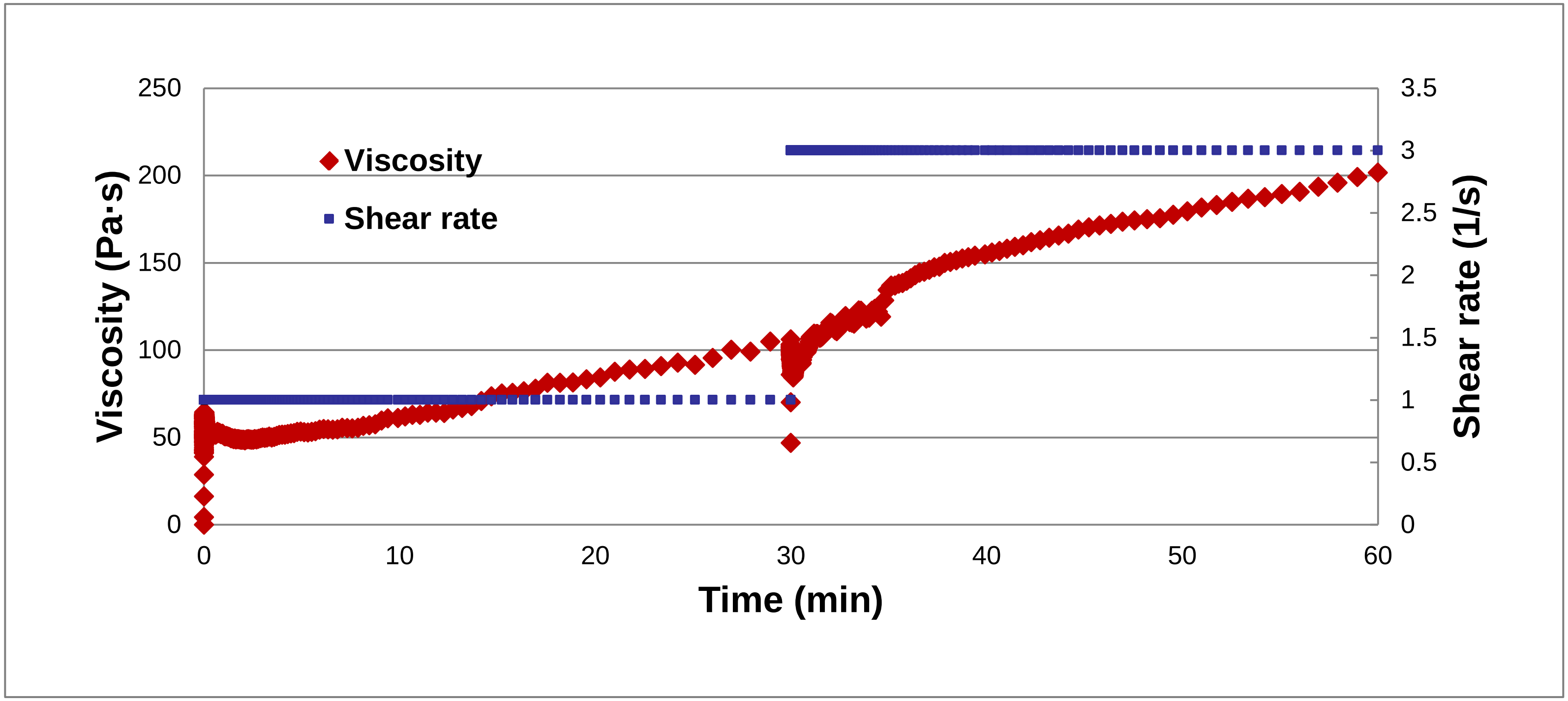
Materials

- **ECN lignin (Organosolv lignin, Energy Research Centre of the Netherlands)**
- **SKL Softwood Kraft lignin (Indulin AT, MeadWestvaco, Charleston, SC)**

Melt spinning of ECN organosolv lignin

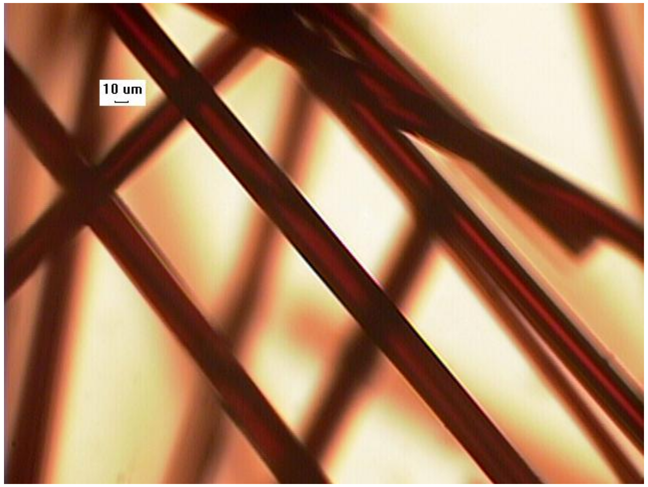
- **Source: Poplar wood lignin from ethanol/H_2O pulping**
- **Softening point: 155ºC**
- **Decomposition temperature: ~280ºC from TGA result in N_2 purge**

Transient shear viscosity of ECN lignin (@ 160ºC)

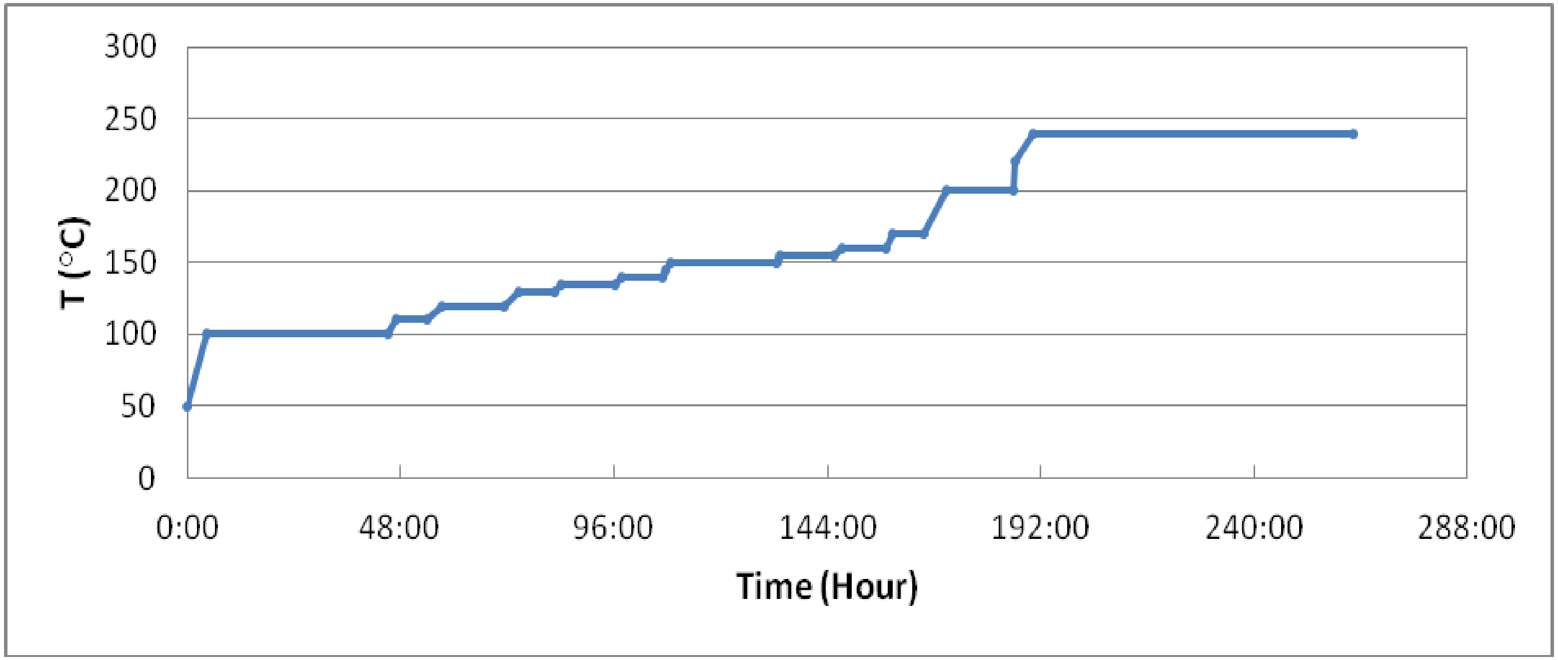


Melt spinning of ECN lignin

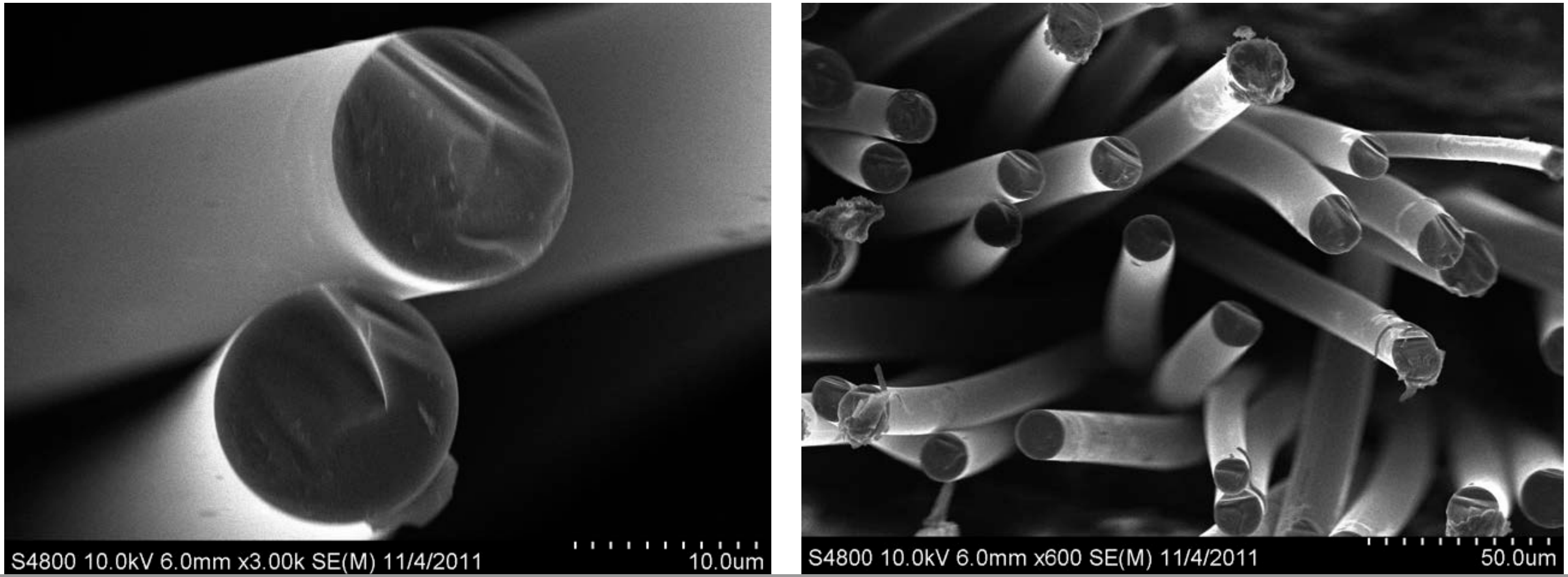
- Instron Capillary Rheometer
- Temperature: 160°C
- Winding rate: 190 m/min
- Capillary diameter: 254 µm
- Fiber diameter: 29 ± 1 µm



Thermostabilization of ECN fibers



It takes more than 10 days to stabilize to prevent fibers from being tacky



ECN carbon fibers had a smooth surface and circular cross section

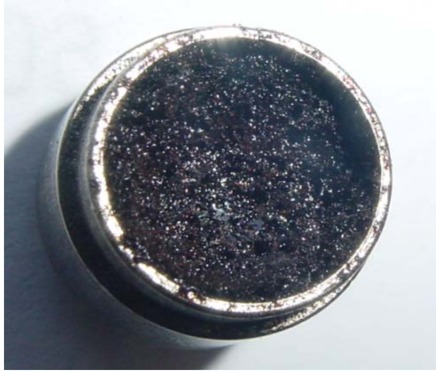
Mechanical properties of ECN carbon fibers

Diameter (μm)	Elongation (%)	Modulus(GPa)	Tensile strength (MPa)
14±1	1.4±0.4	34±4	450±130

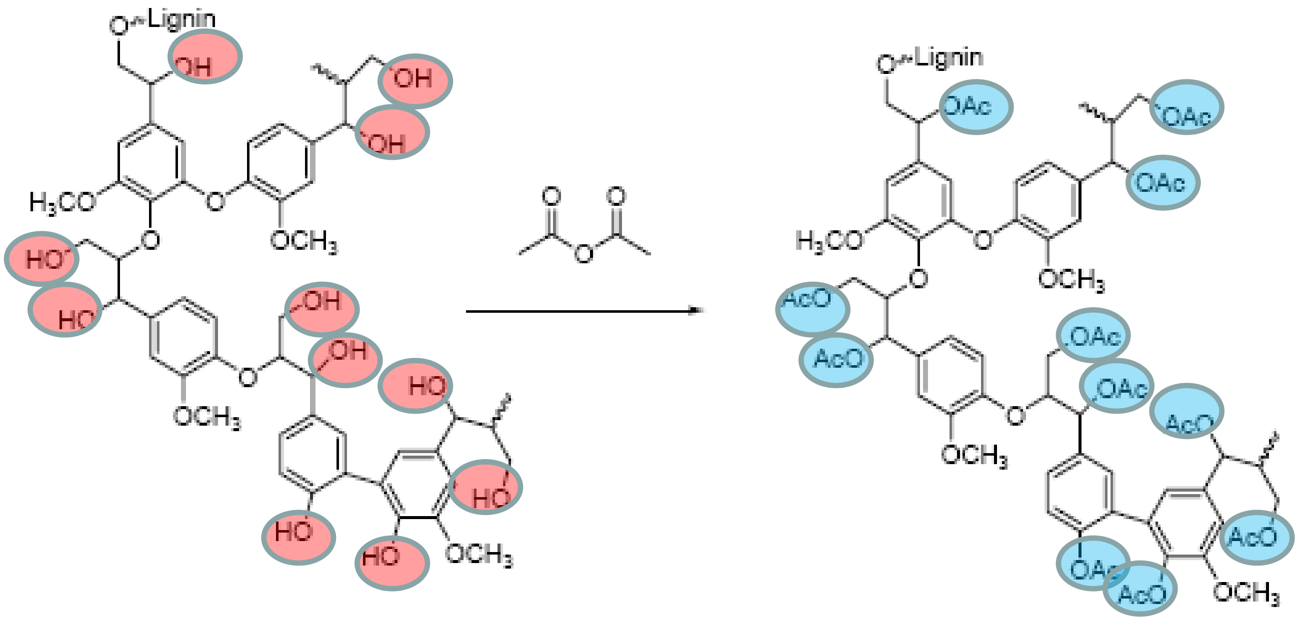
Indulin AT Lignin

- **Indulin AT (Softwood Kraft lignin, MeadWestvaco, Charleston, SC)**

- **No Softening Point, charring occurred due to high molecular weight fraction and dehydration reaction**



Previous modification of Indulin AT-Acetylation with high extent of substitution on -OH group and fractionation

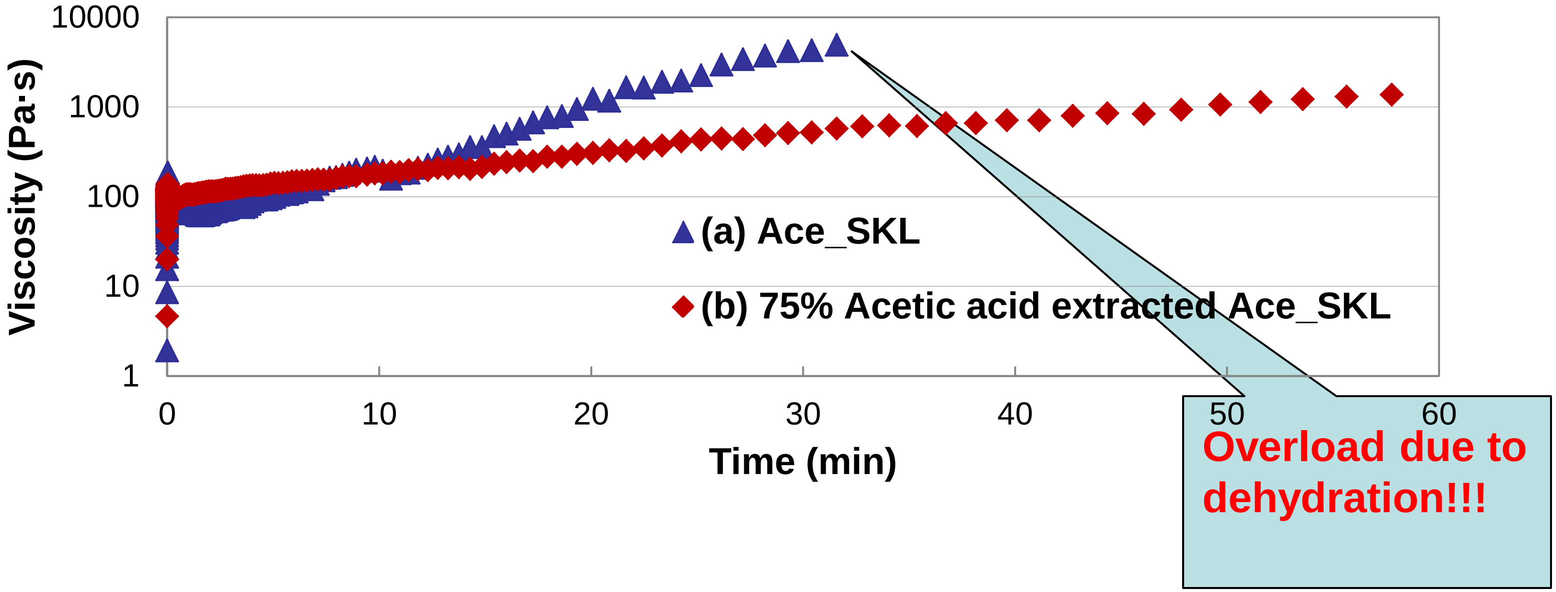


- 1 g lignin + 15 ml acetic anhydride, 85°C, 2 hour
- Acetylated Indulin AT (Ace-SKL) had a softening point between 156 and 167°C

- **Ace-SKL had a softening point, but unstable melt viscosity.**

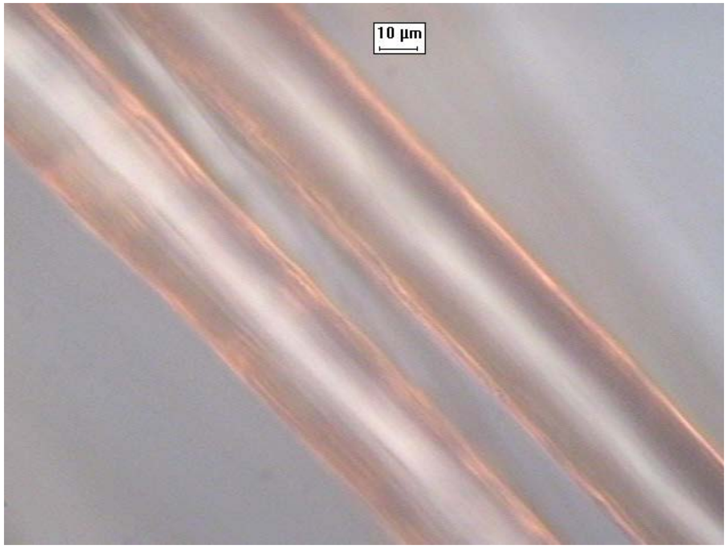
- **Ace-SKL was extracted with 75% acetic acid aqueous solution. Resulted material (75%AA-Ace-SKL) had a softening point of 136-145°C.**

- **75% acetic acid extracted Ace-SKL had relatively stable melt viscosity.**



Overload due to dehydration!!!

- **75%AA-Ace-SKL was melt spun into fibers**
- **75%AA-Ace-SKL fibers became tacky during oxidative stabilization**



Thermostabilization

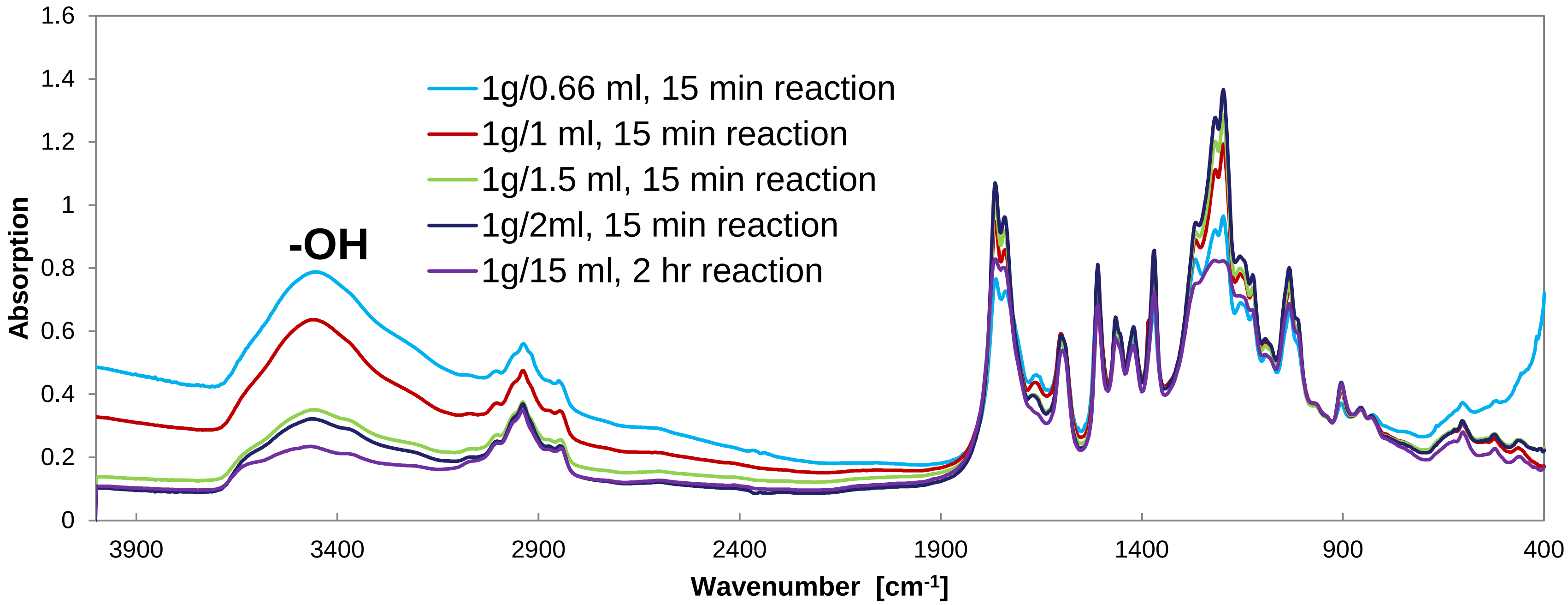
As-spun Ace-SKL fibers

Tacky Ace-SKL fibers

Ace-SKL fibers obtained from high extent of acetylation (15 ml AA/g SKL) could not be stabilized due to the presence of a significant extent of substitution of hydroxyl groups by thermally stable acetyl groups

Alternative way:

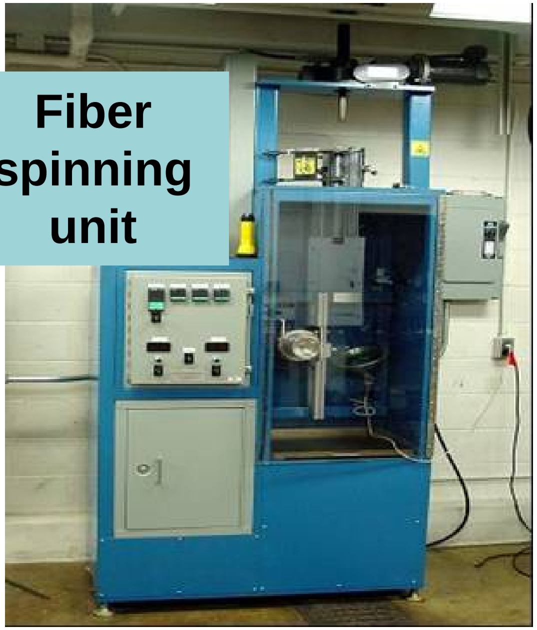
- **Ace-SKL lower extent of -OH group substitution, which is favorable for thermostabilization**
- **Solution spinning instead of melt spinning**



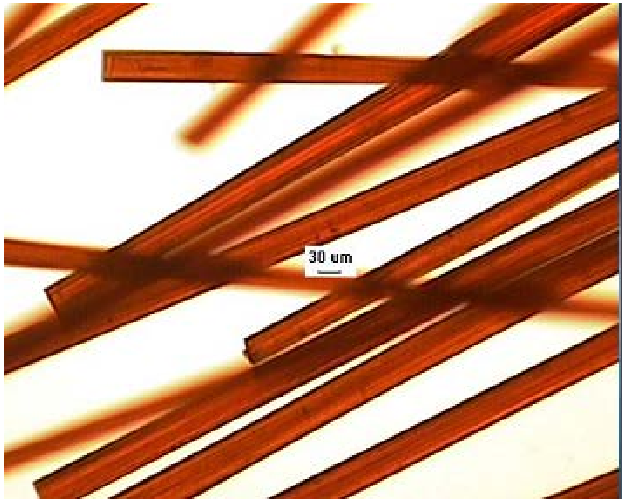
- **Spectra normalized with peaks at 856 cm^{-1} (C-H bending on benzene rings).**
- **The hydroxyl peak decreased as the amount of acetic anhydride per gram of SKL increased.**
- **Higher content of hydroxyl group is favorable for thermostabilization.**

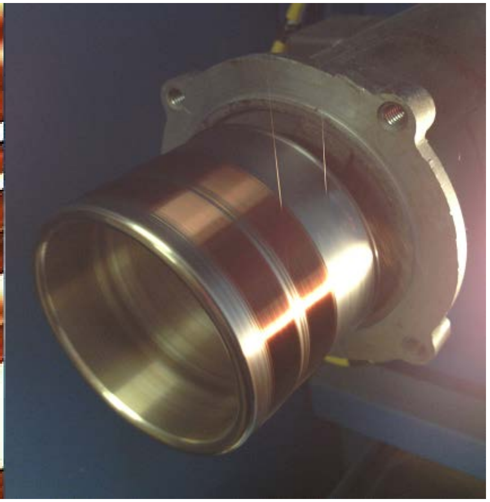
Solution spinning with Ace-SKL

- Ace-SKL acetone solution concentrated
- Take up speed: 50 m/min
- Spinneret diameter: 75-150 μm
- Fiber diameter: 27±3 μm



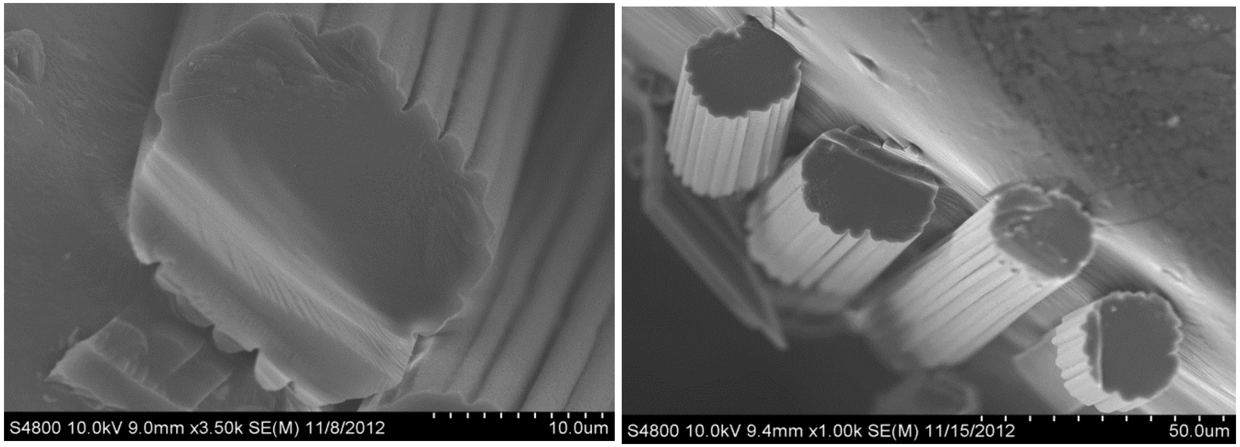
Fiber spinning unit



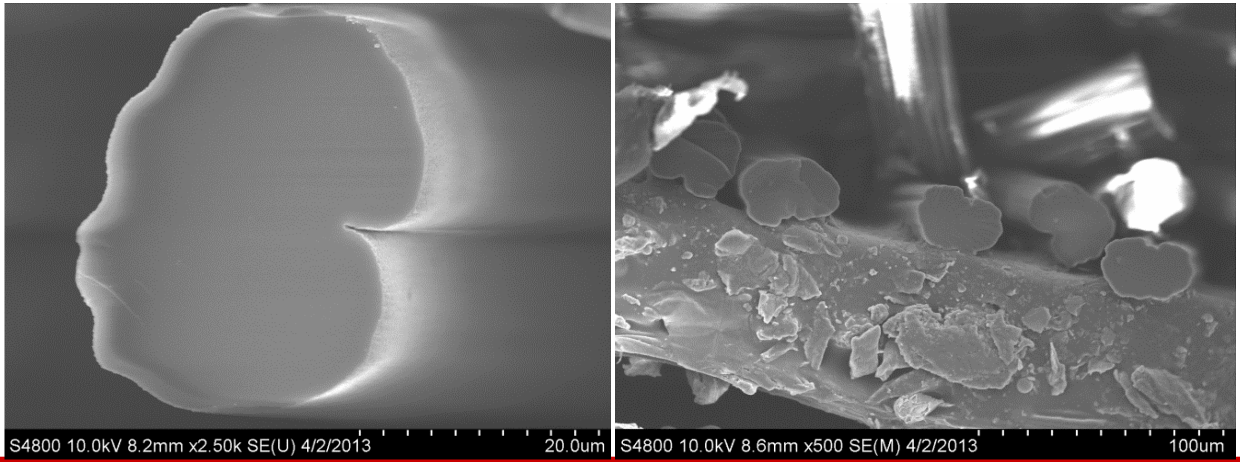


Solution spinning with Ace-SKL

2.1 g Ace-SKL / ml acetone, 45-45°C spinning



2.1 g/ml acetone room temperature spinning

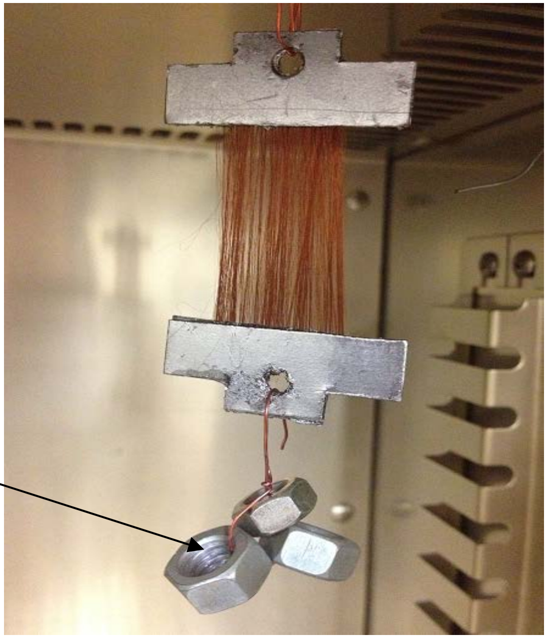


Thermostabilization of Ace-SKL fibers under tension

Stabilization with constant load

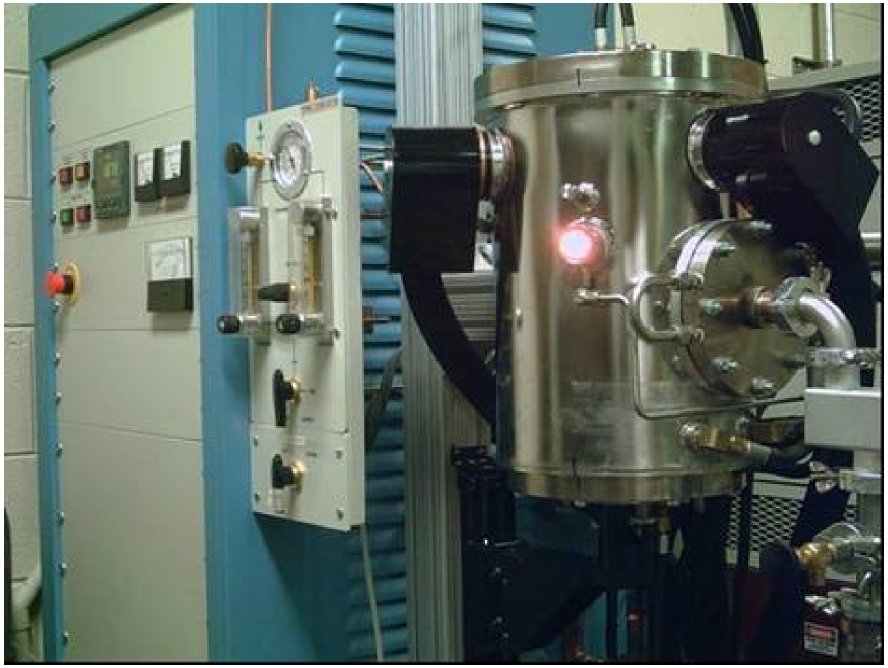
As-spun fiber was glued on both ends with hook and hanging in the oxidation oven with weight loaded.

Fibers can be stabilized and extended up to 800% of original length during stabilization.



Weight

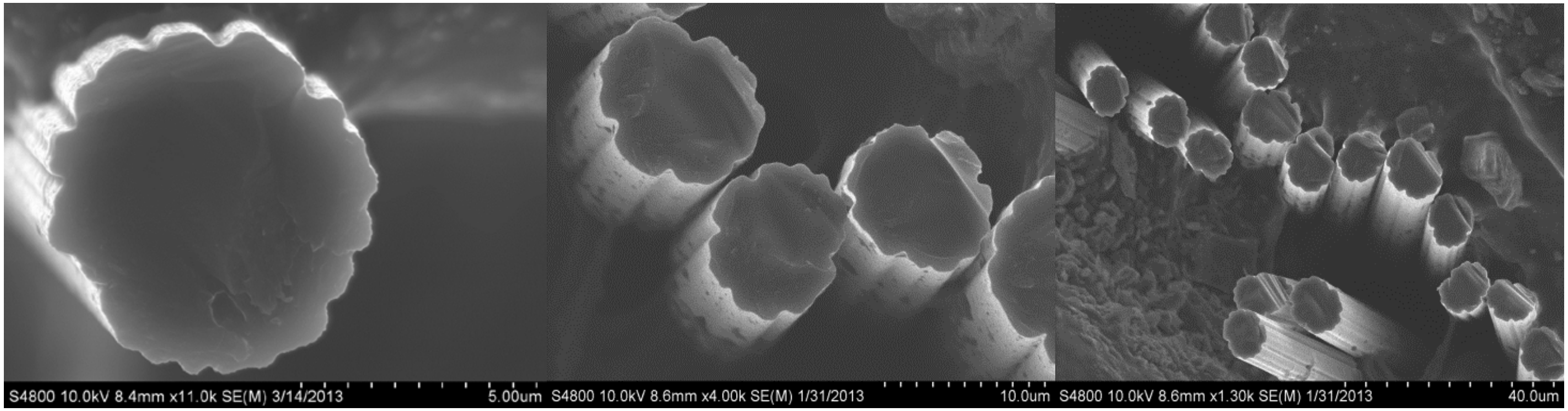
Carbonization of stabilized Ace-SKL fibers



Carbonization and Graphitization furnaces: 1000-2700°C

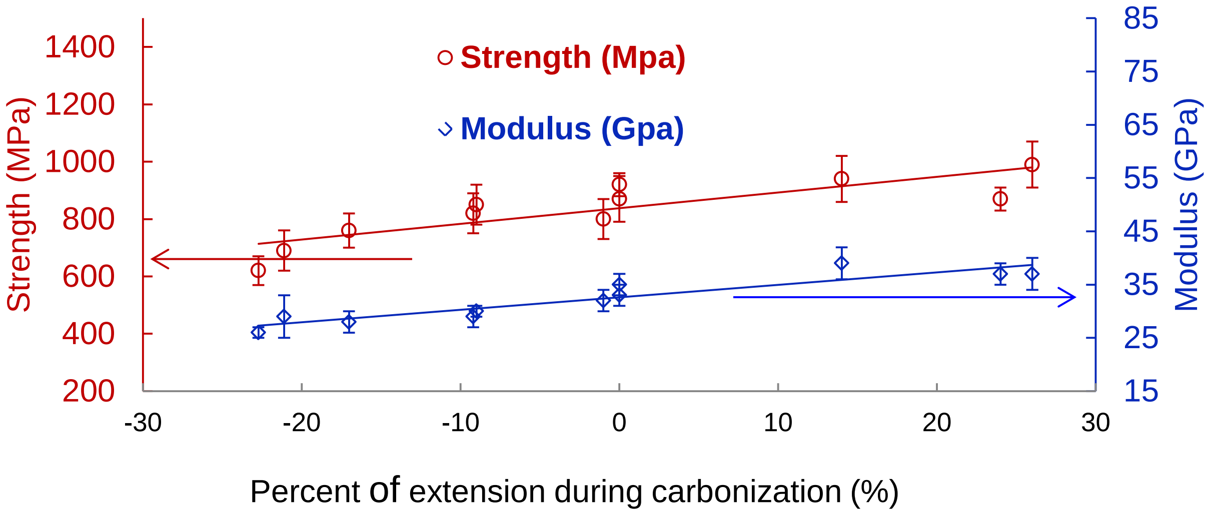
Carbonization under tension

1000ºC carbonized



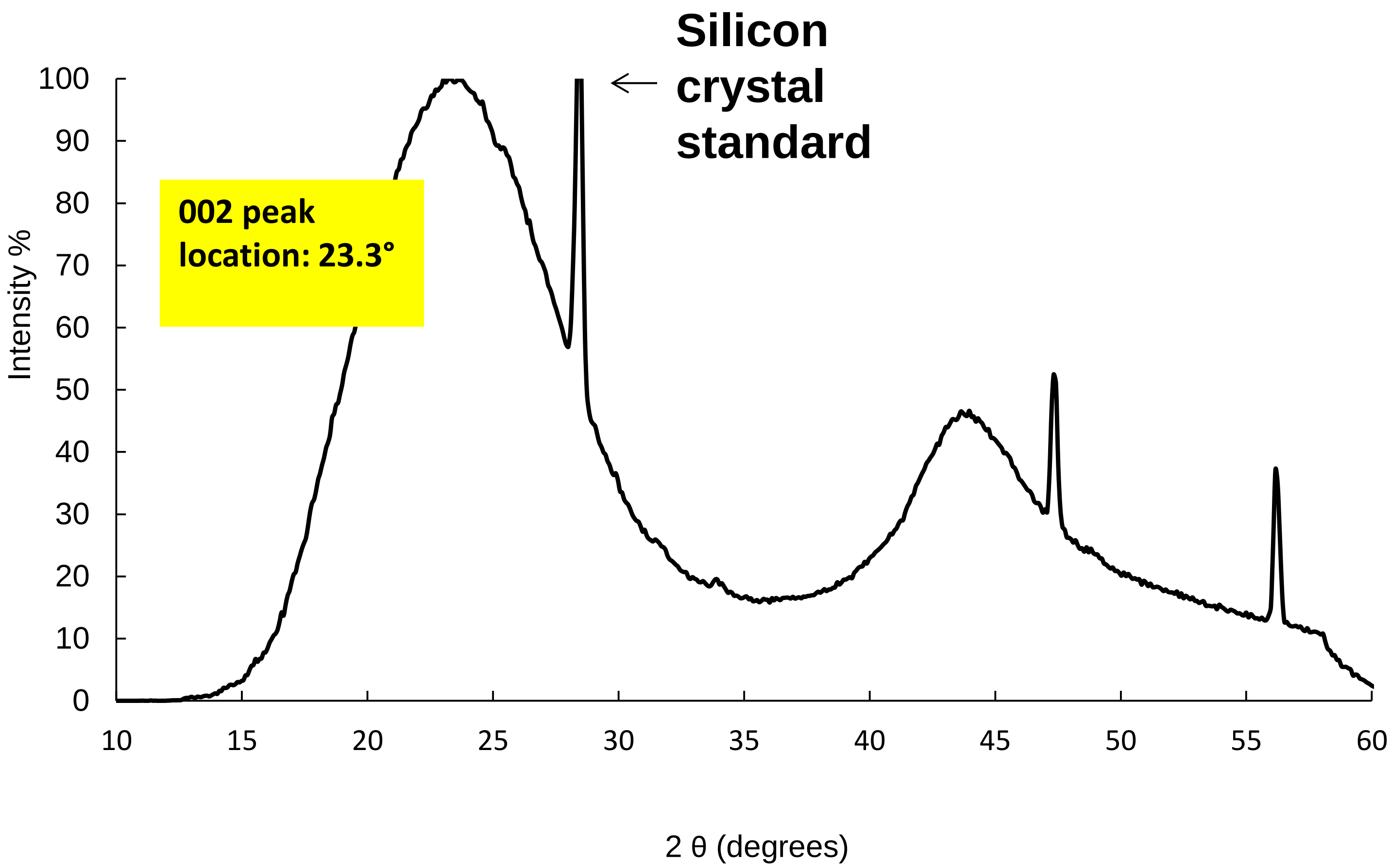
- **Crenulated CF have 35% larger surface area as compared with equivalent circular fibers**
- **This could lead to higher fiber-matrix interfacial bond strength, and ultimately better realizability of carbon fiber properties in the composites**

Mechanical properties of Ace-SKL carbon fibers



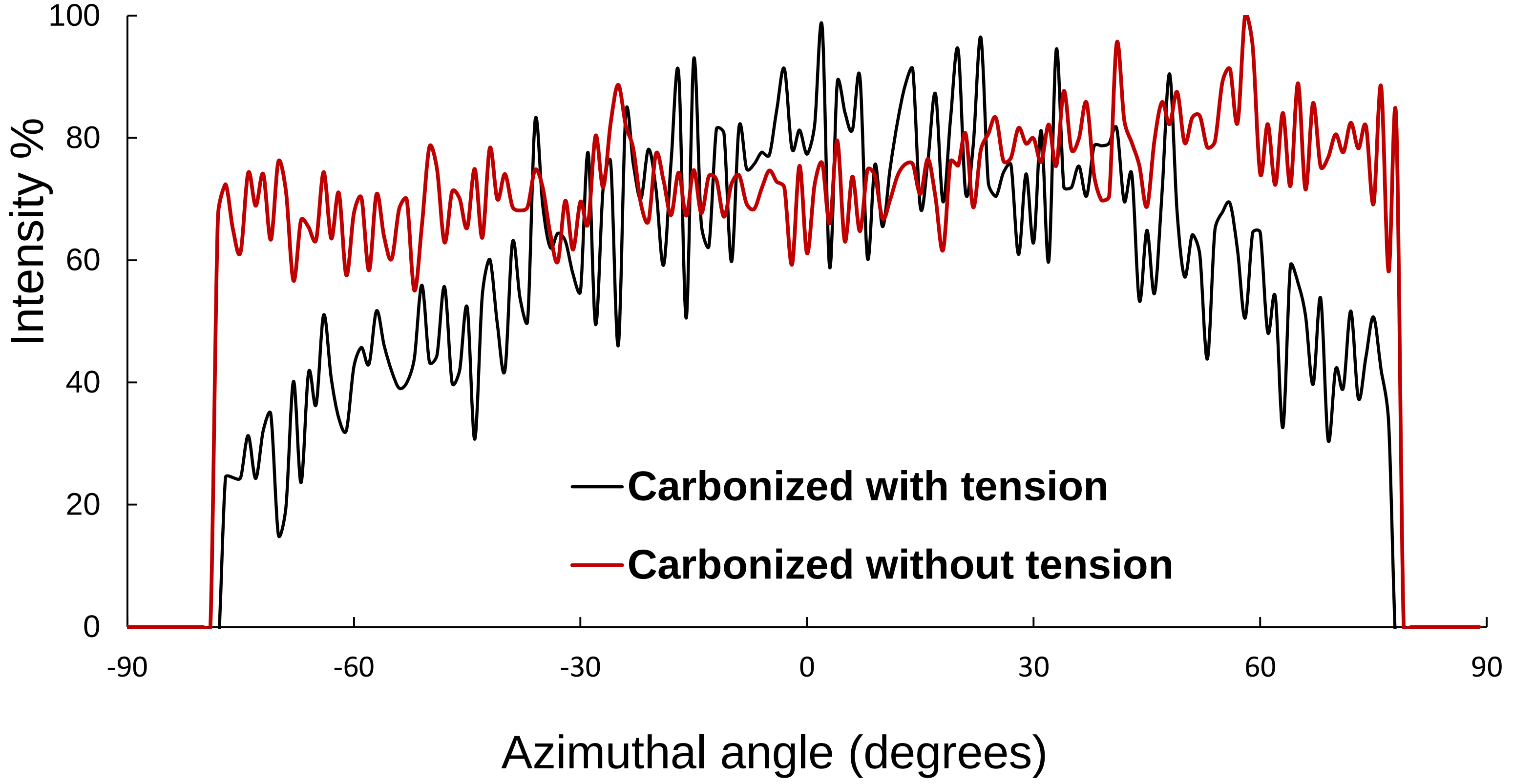
	Diameter (µm)	Strength (MPa)	Apparent Modulus (GPa)	Apparent strain to failure (%)
Ace-SKL CF (processed without tension)	**22.5 ± 0.4**	**510 ± 50**	**30 ± 2**	**1.7 ± 0.1**
Ace-SKL CF (processed with tension)	**5.9 ± 0.2**	**1050 ± 70**	**35 ± 3**	**3.0 ± 0.2**

Ace-SKL CF X-ray Diffraction Spectrum



Silicon crystal standard

002 peak location: 23.3°


Intensity %
100
80
60
40
20
0
-90
-60
-30
0
30
60
90
Azimuthal angle (degrees)
Carbonized with tension
Carbonized without tension

Conclusions

- A softwood kraft lignin was modified by controlled acetylation and the precursor (Ace-SKL) was solution-spun into fibers, which is capable of thermal-oxidation.
- Mechanical properties of Ace-SKL carbon fibers (CF) can be enhanced by tension. The tensile properties reported here is among the best for lignin-based CF.
- Crenulation on Ace-SKL CF surface lead to larger surface area and potential higher fiber-matrix interfacial strength.

Next steps…

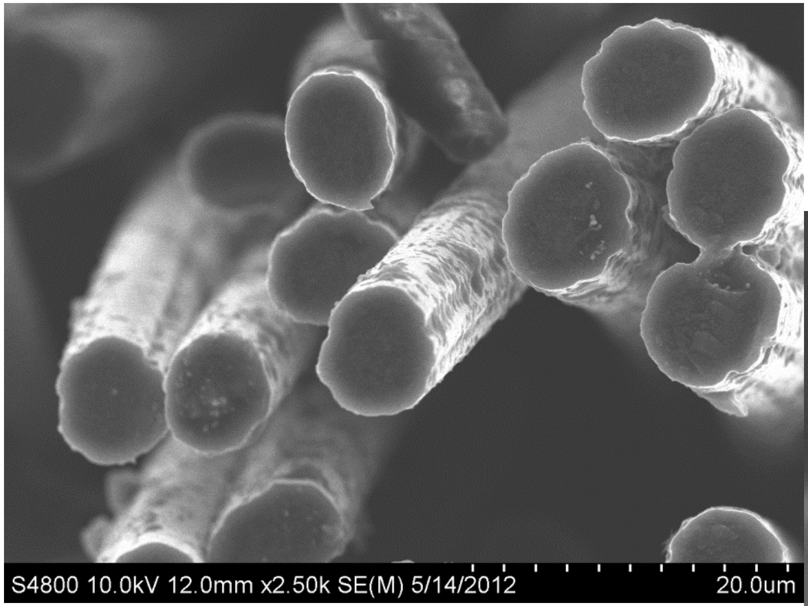
- Rheology of spinning solution is being studied
- Relationship between fiber cross-section shape and mechanical properties will be studied
- UV/thermostabilization to increase stabilization speed

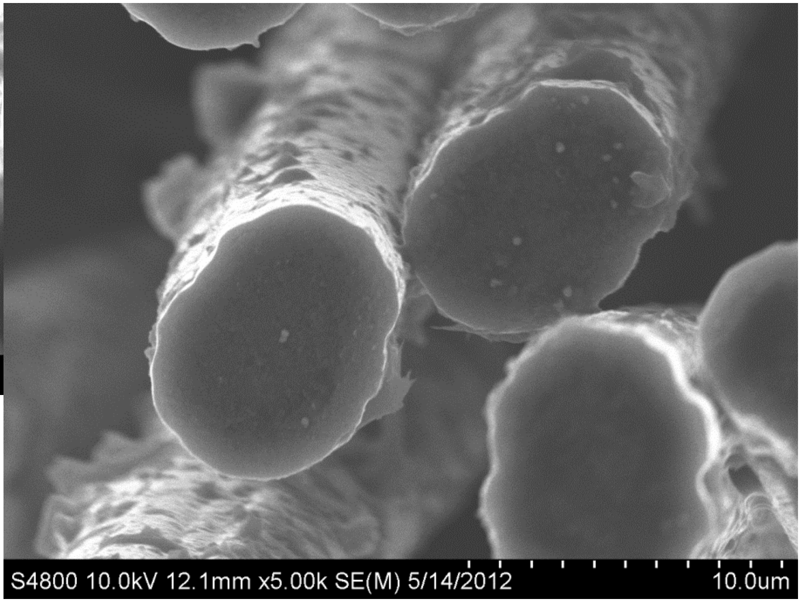
Acknowledgment

ARL-SERDP Grant WPSON-10-03 / W911NF-10-2-0024

ARL/UD/Drexel/Clemson team members including Dr. Marlon Morales and Dr. Young-pyo Jeon

ECN, Netherlands for providing lignin





2400ºC carbonized

Crenulated surface are desirable for enhancing fiber-matrix interfacial area