

Low Cost, Bio-Renewable Carbon Fibers from Lignin/PLA Blends and Graft Copolymers

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Introduction



High strength-to-weight ratio



400-500
pounds



Advantages over glass fibers

- Specific strength
- Specific modulus
- Fatigue resistance
- Ultimate tensile and
- Compressive stress

Mainstream Application



Average Diameter	5-7 µm
Density	1.5-1.8 g/cc
Carbon content	>95%
Tensile Strength	2.5 – 7.0 GPa
Young's Modulus	250 – 400 GPa
Thermal Conductivity	180-190 (W/m-K)

- Replace Glass Fiber with Carbon Fiber → Decrease structural weight → Allow for increased length of blade → Increase power generation

Factors influencing the cost

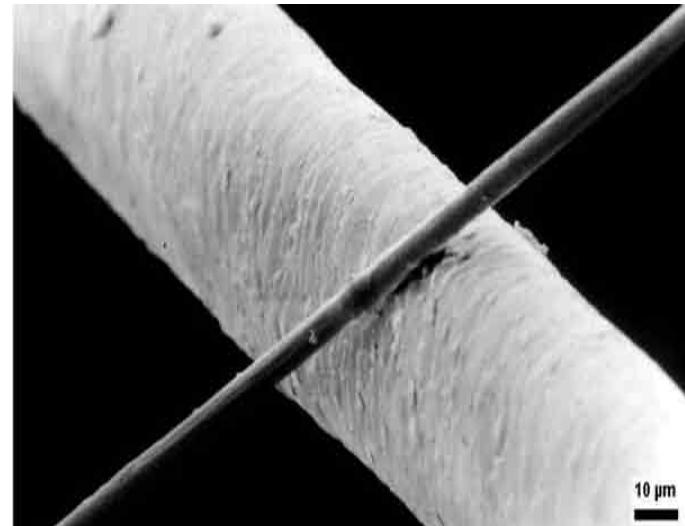
- 51 % for the precursor,
- 39 % for processing
- 10 % is for surface treatment

Cost of major parts of wind turbine

- 22% for the Tower
- 18 % for the Blades
- 22 % for gearbox and generator

Precursor materials

Precursor/ Properties	PAN	Pitch	Lignin
Tensile Strength (GPa)	2.5 – 7.0	1.5 – 3.5	0.3 -1
Modulus of Elasticity (GPa)	250 – 400	250 – 800	60
Carbon Yields (%)	68	85	60



PAN



Petroleum-based

Pitch

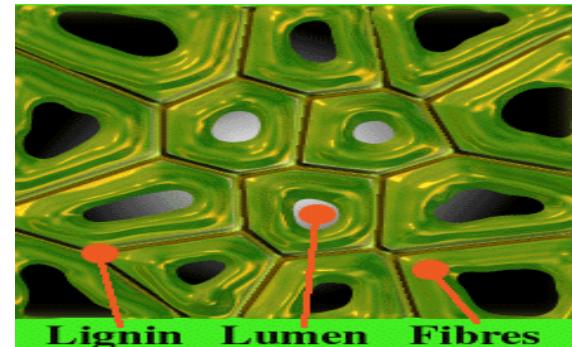


Coal or Petroleum-based

Lignin



Bio-based



Petroleum-based Feedstock
PAN, Pitch,....

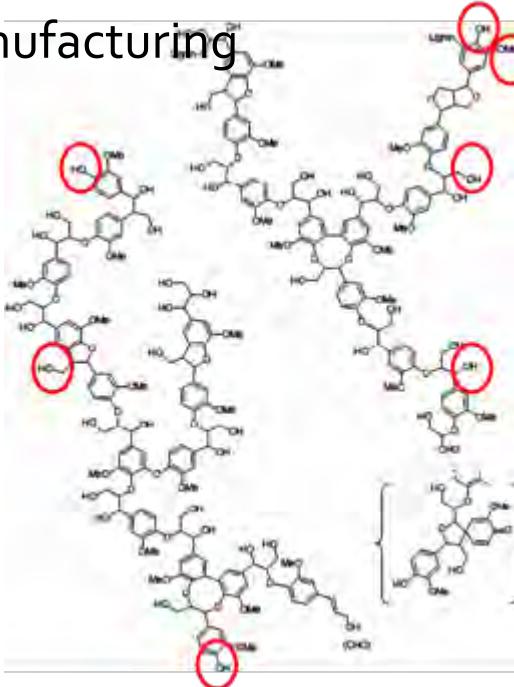


Bio renewable Feedstock
Lignin, Cellulose



Lignin

- Lignin is a highly aromatic biopolymer
- Mostly extracted from wood and yearly crops
- Byproduct of paper manufacturing
- High molecular weight



Diversity

Processing method

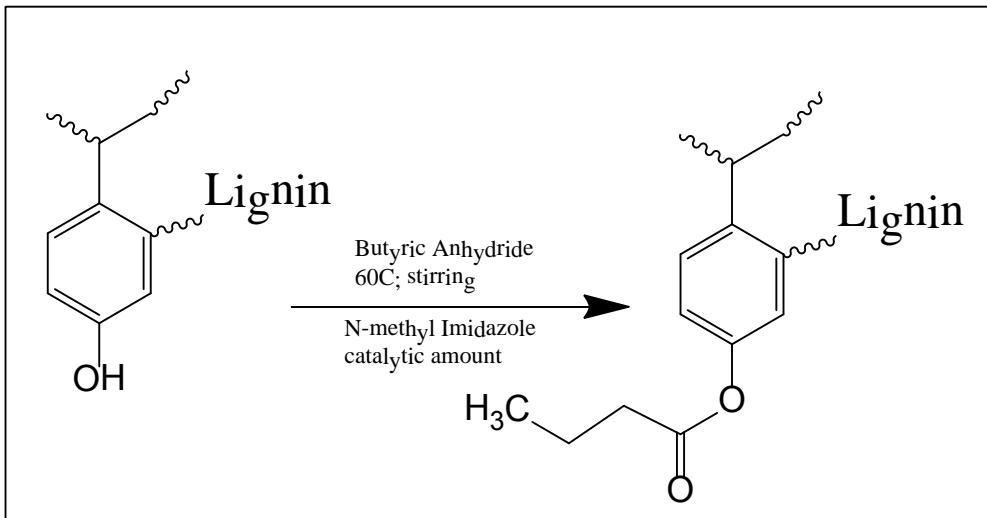
- Kraft
- Organosolv
- Soda

Precursor type

- Hard wood
- Softwood
- Agricultural



Modification of Lignin



- ✓ One-pot esterification
- ✓ Complete conversion
- ✓ High yields



Lignin

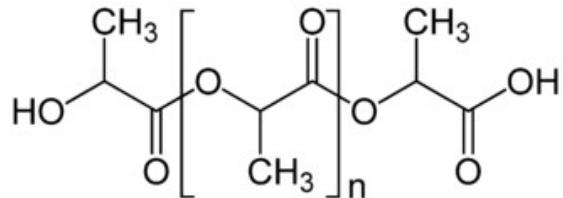


Butyrated Lignin



Polylactide (PLA)

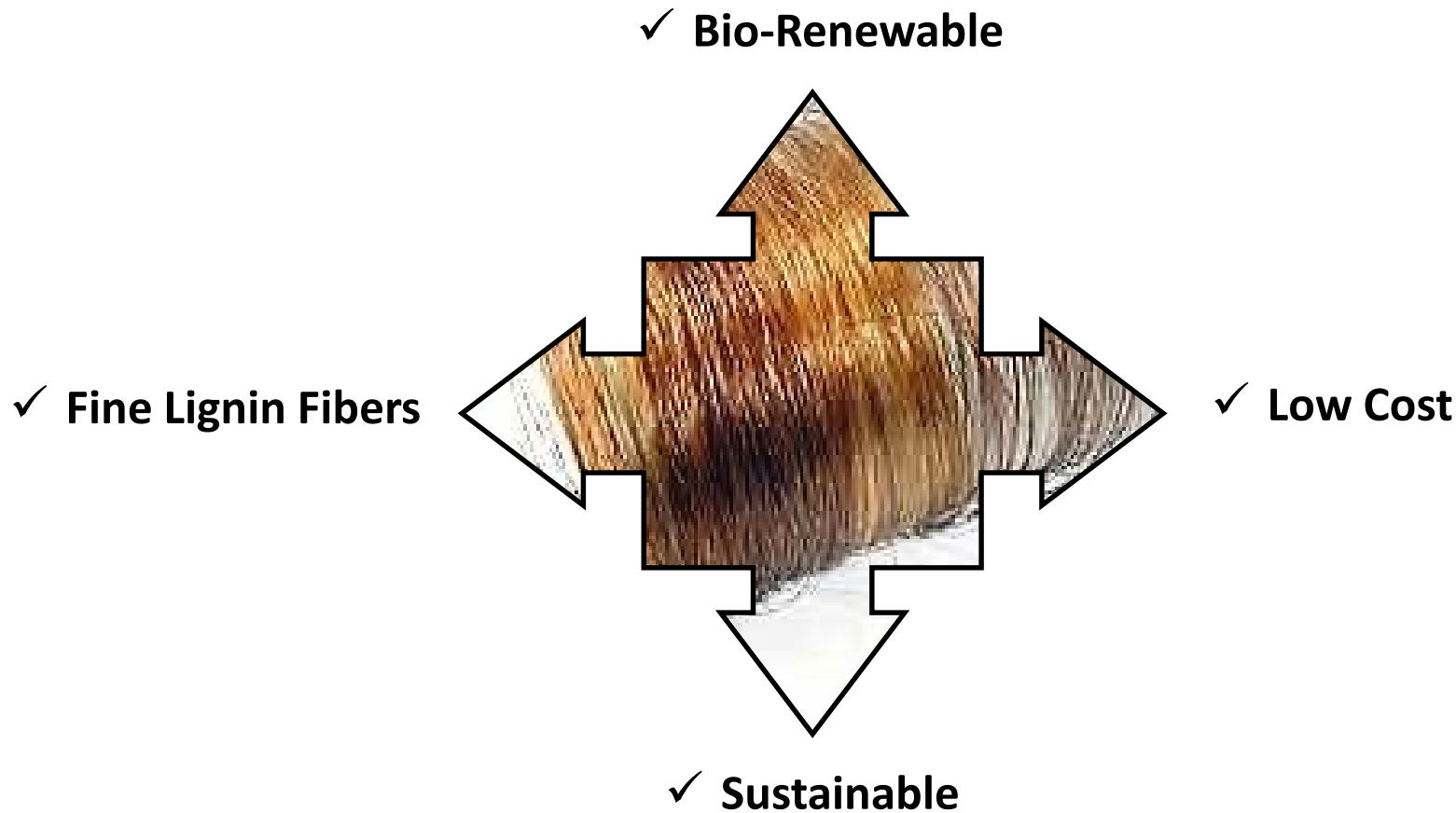
- Thermoplastic aliphatic polyester
- Derived from renewable resources, such as corn starch
- Biodegradable



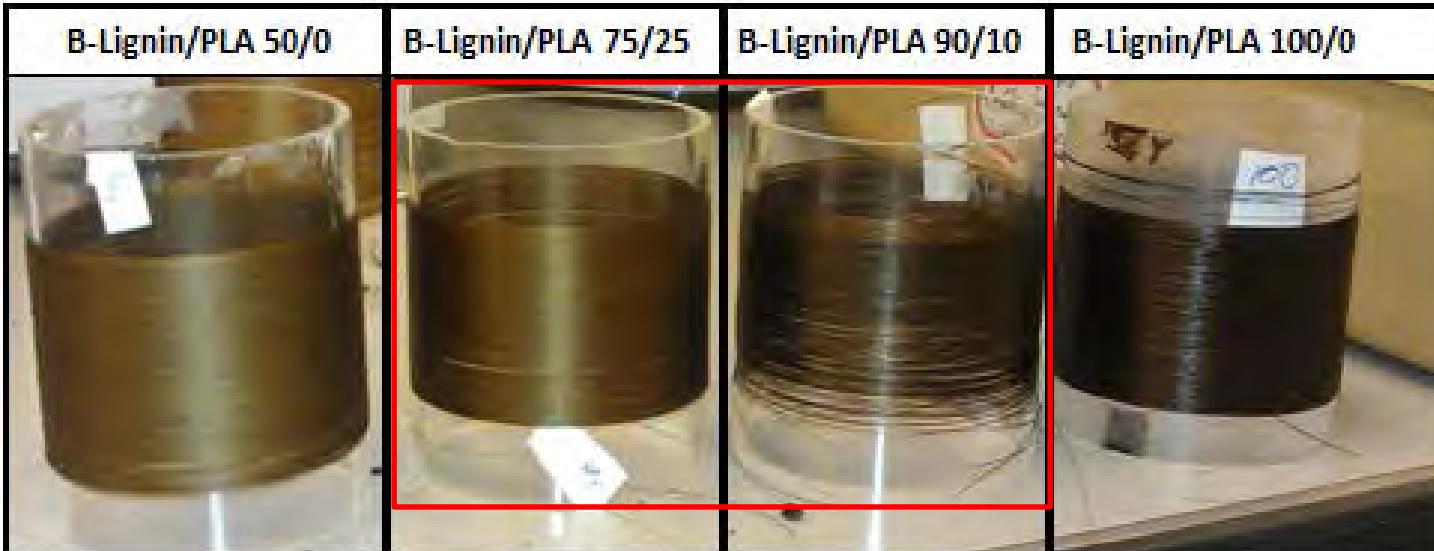
Glass transition temperature (° C)	50 - 60
Melting temperature (° C)	160 - 170

- Blending lignin with PLA also offers significant potential to make the carbon fiber production process much greener and renewable rather than utilizing petroleum based polymers

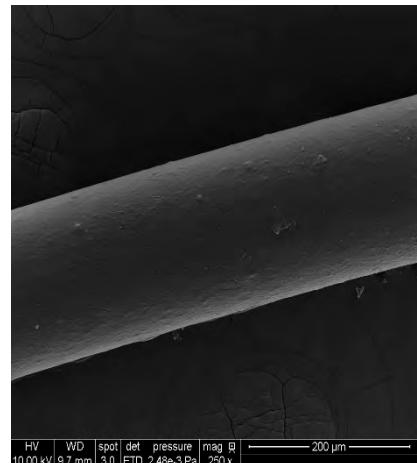
Advantages



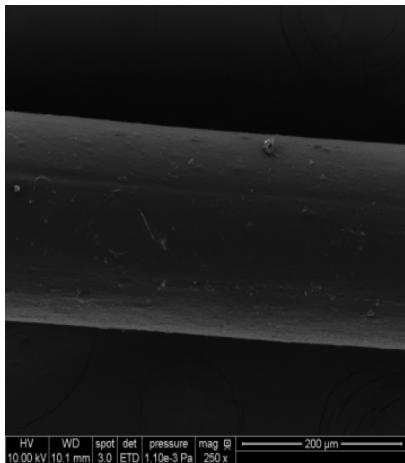
Lignin/PLA Blends



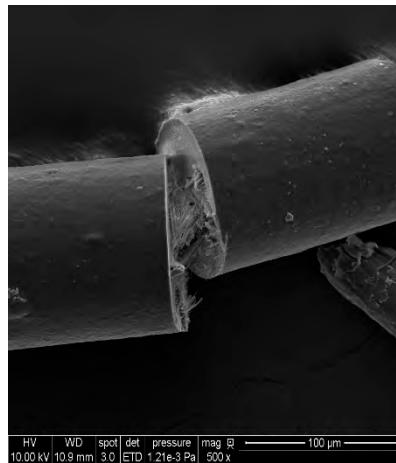
B-Lignin/PLA 50/50



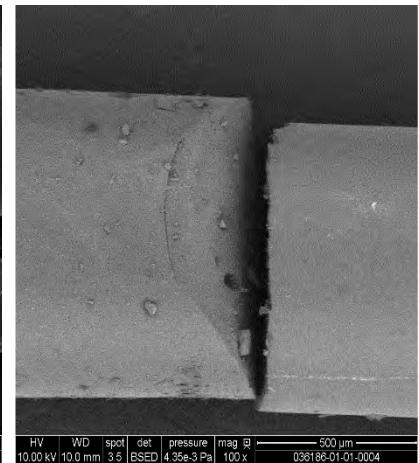
B-Lignin/PLA 75/25



B-Lignin/PLA 90/10



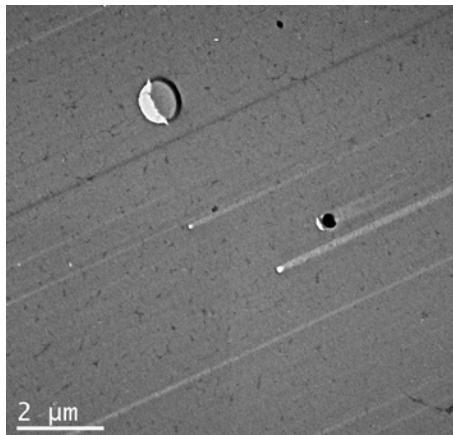
B-Lignin/PLA 100/0



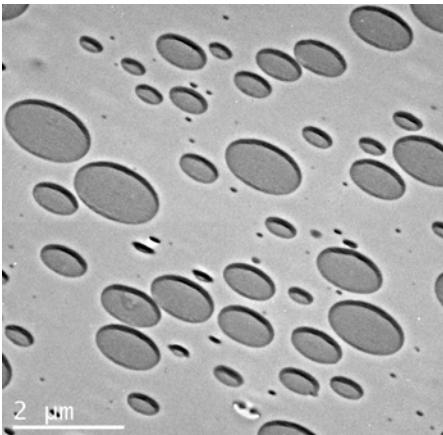
- Homogeneous fine fiber structure was observed by SEM

Morphology of Lignin/PLA Blends

B-Lignin/PLA 100/0

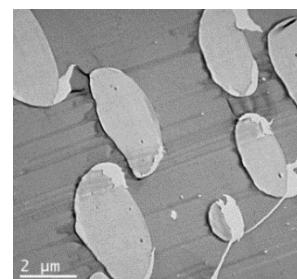


B-Lignin/PLA 50/50



TEM micrographs reveal a microphase separation in Lignin/PLA blends

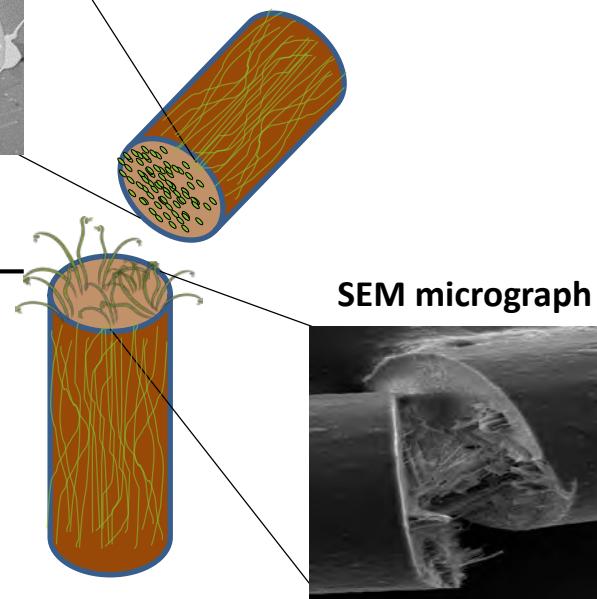
TEM morphology



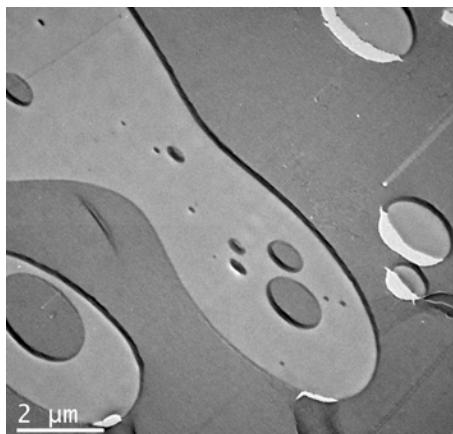
B-lignin/PLA Raw fiber

PLA fibers

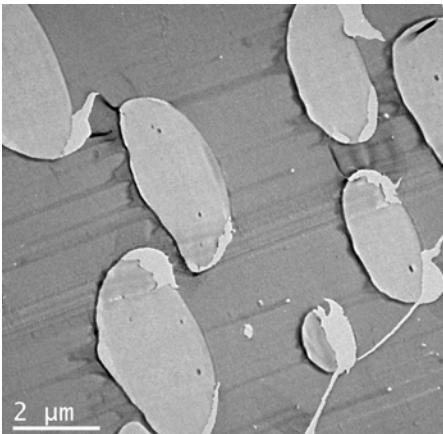
SEM micrograph



B-Lignin/PLA 75/25

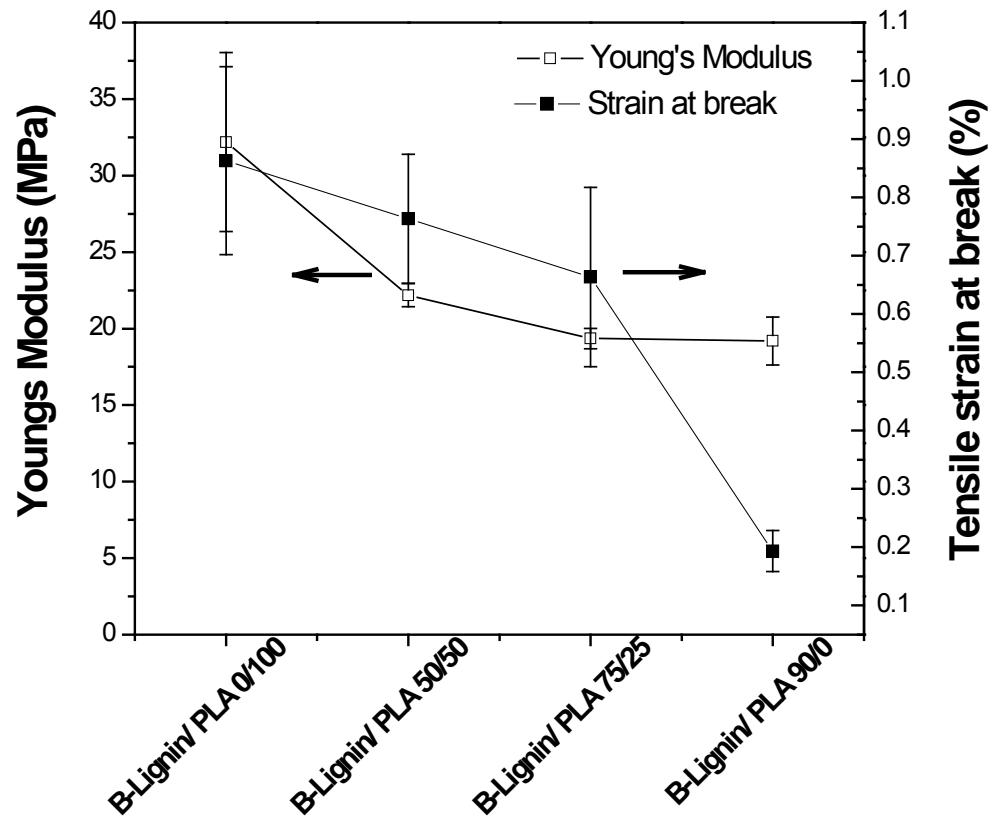
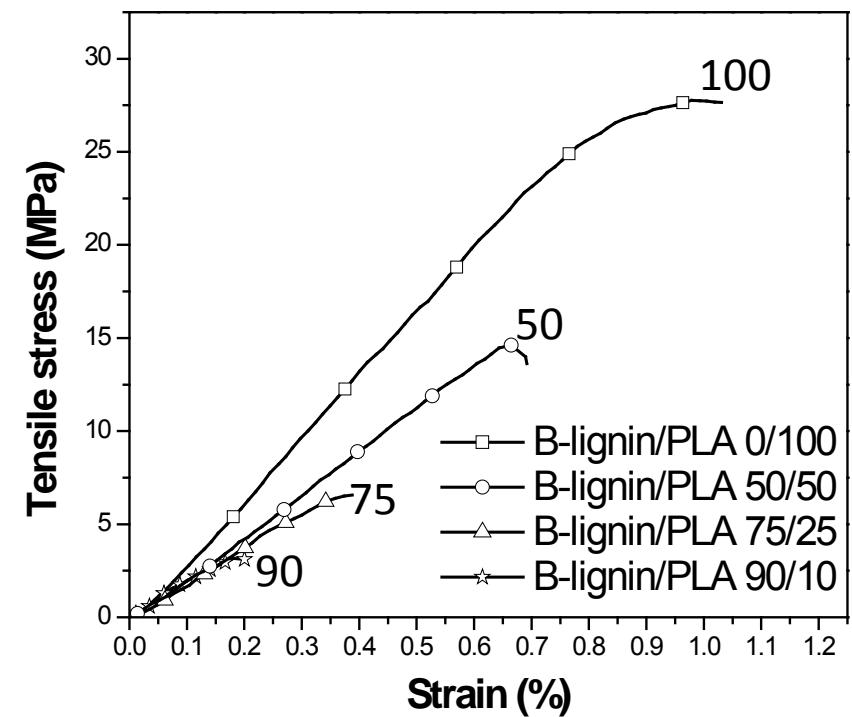


B-Lignin/PLA 90/10



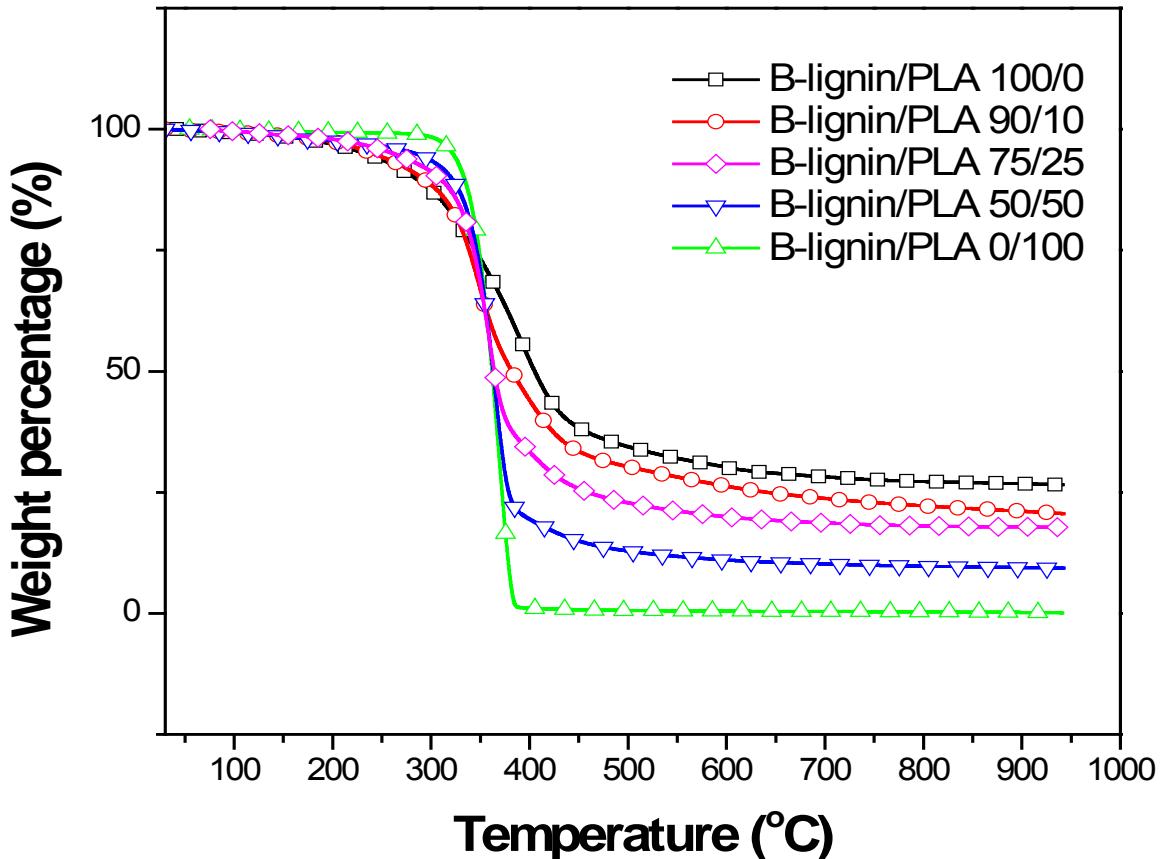
- Cross-section morphology of B-lignin/PLA blends fiber with PLA rich phase self-assembled as micro fibers inside the bulk fiber

Mechanical properties of Raw fibers



- Mechanical properties of raw fibers are dominated by the crystallinity in PLA

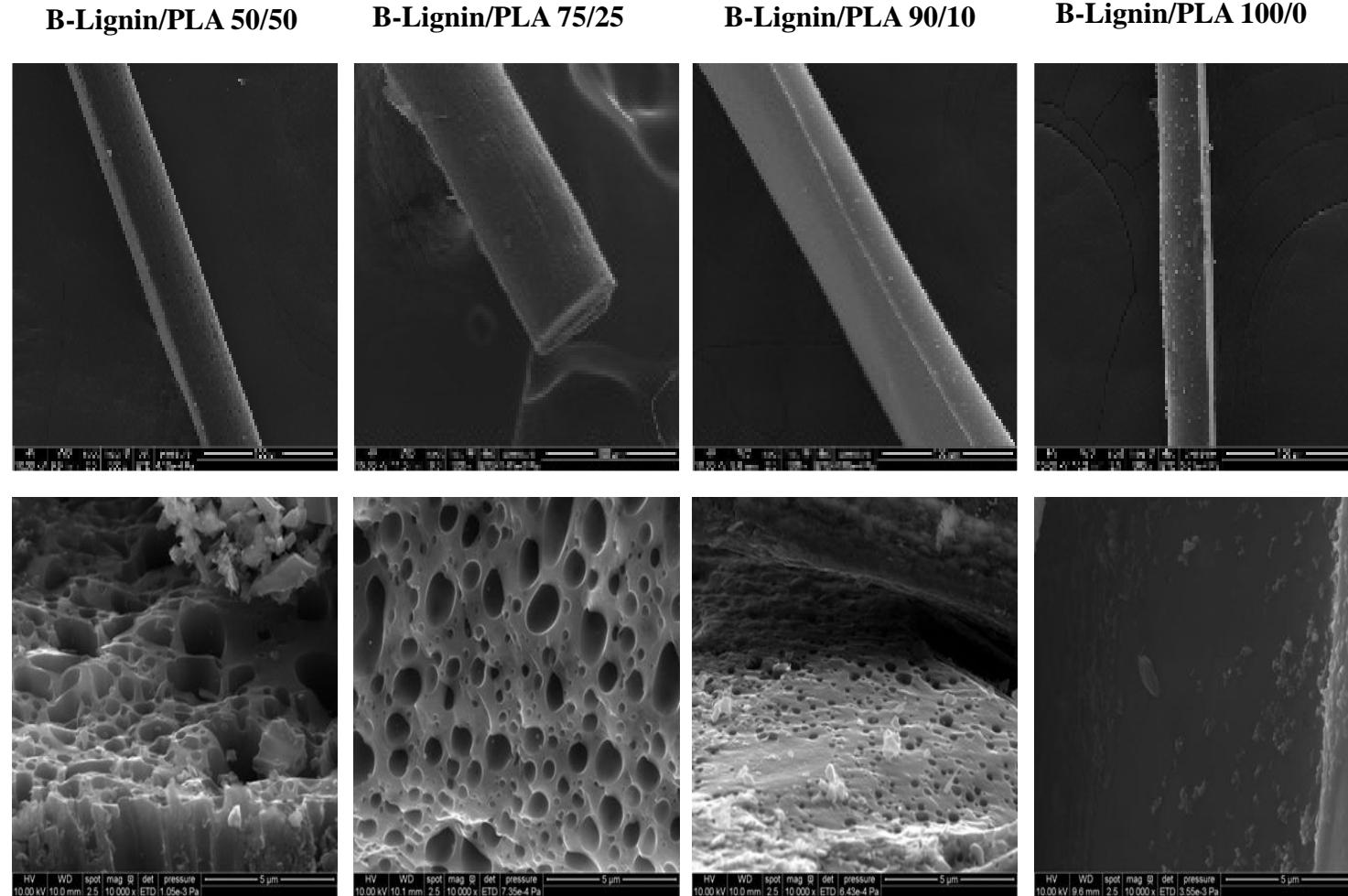
Thermal Degradation Behavior of Lignin/PLA blends



Sample	Residual carbon at 800 °C (wt. %)
B-lignin/PLA 100/0	27.3
B-lignin/PLA 90/10	22.38
B-lignin/PLA 75/25	17.99
B-lignin/PLA 50/50	9.8
B-lignin/PLA 0/100	0.36

- The carbon yield measured from the residual wt. % at 800 °C decreased from 27 to 0.36 wt. % with increase in PLA content
- Optimizing the precursor composition with high lignin concentration results in high carbon yields in the post carbonized fibers.

Influence of blending PLA on the structure of carbon fibers

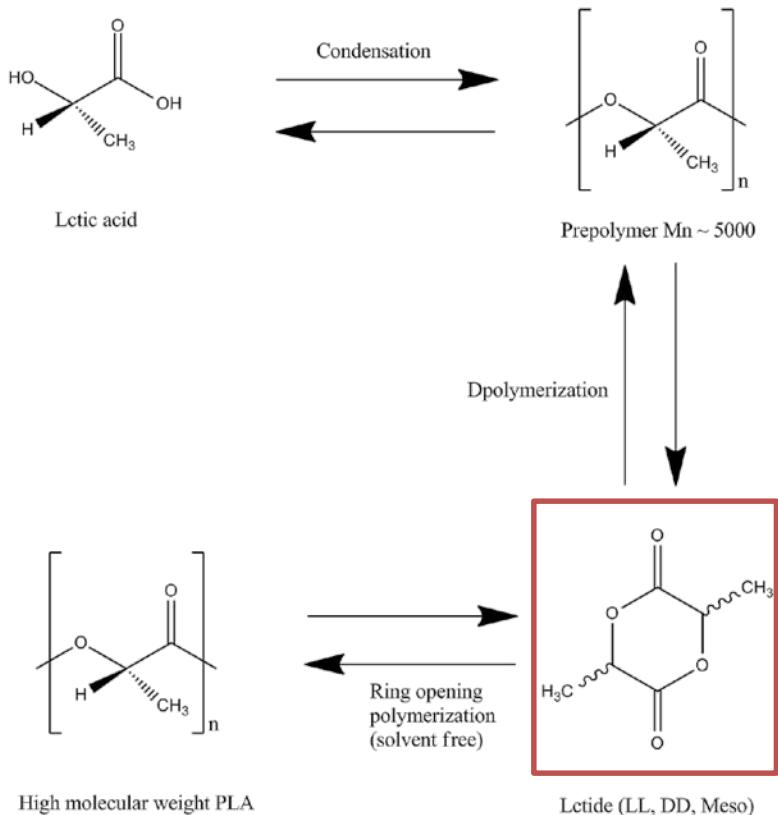


- The surface area of the pores increased from $5.13 \text{ m}^2/\text{g}$ to $535 \text{ m}^2/\text{g}$ in lignin based carbon fibers.
- The total volume of the pores increased from $0.00768 \text{ cc.g}^{-1}$ to 0.323 cc.g^{-1} .

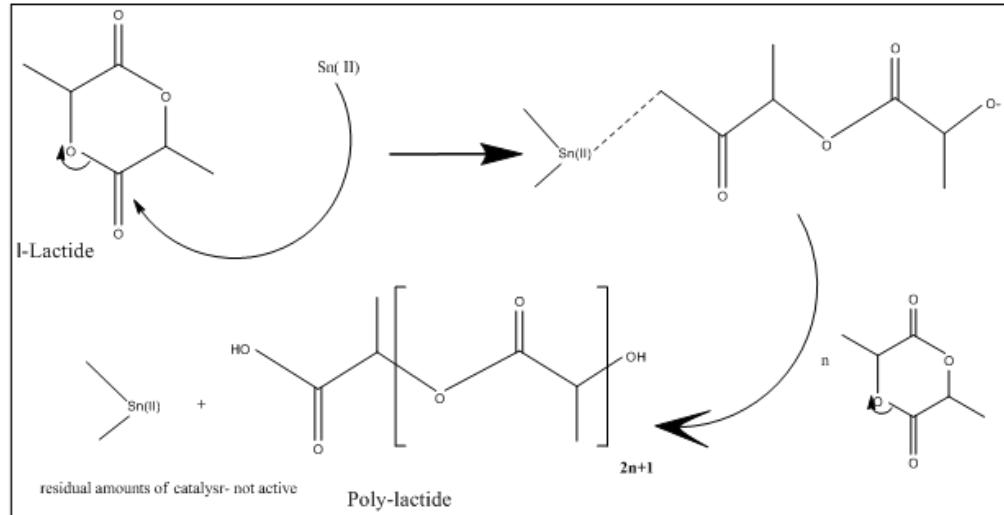
Lignin/PLA copolymers

Grafting Lignin with L-Lactide

Polymeriation of PLA from Lactic acid



Grafting Lignin with L-lactide

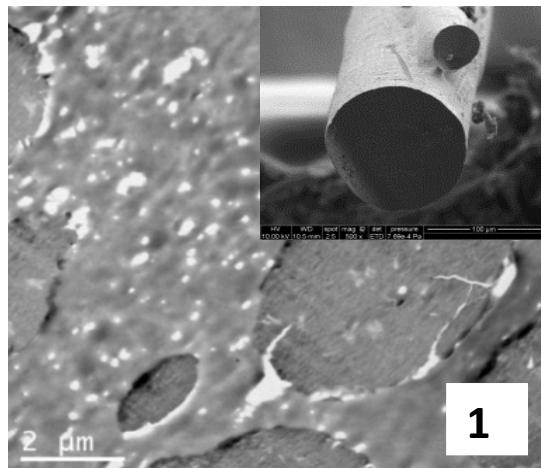
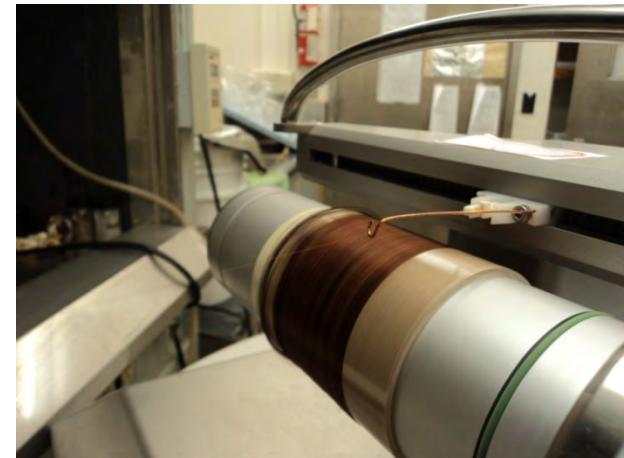


- The hydroxyl groups ($-\text{OH}$) in the lignin molecule are replaced with L-lactide grafts during the ring opening polymerization of L-Lactide to PLA.

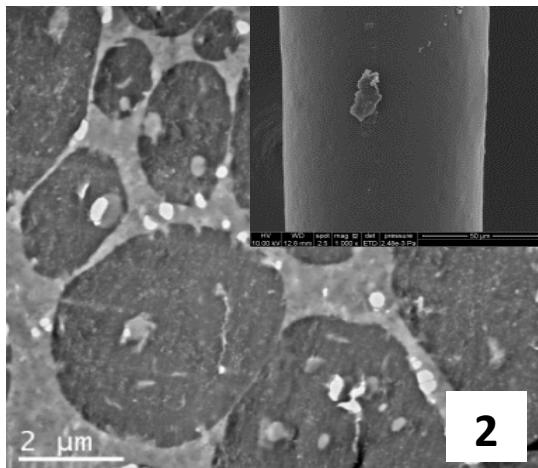
Melt Extrusion of Fibers – Spooling fine fibers from grafted lignin

B-Lignin/G-Lignin/PLA ternary blends

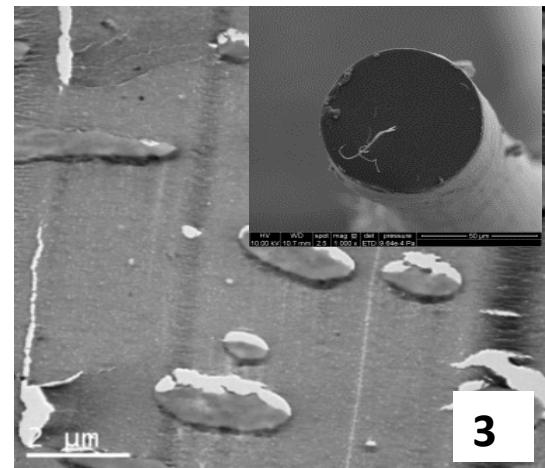
1. B-Lignin/G-lignin/PLA - 25/25/50
2. B-Lignin/G-lignin/PLA - 33.3/33.3/33.3
3. B-Lignin/G-lignin/PLA - 50/25/25



1



2

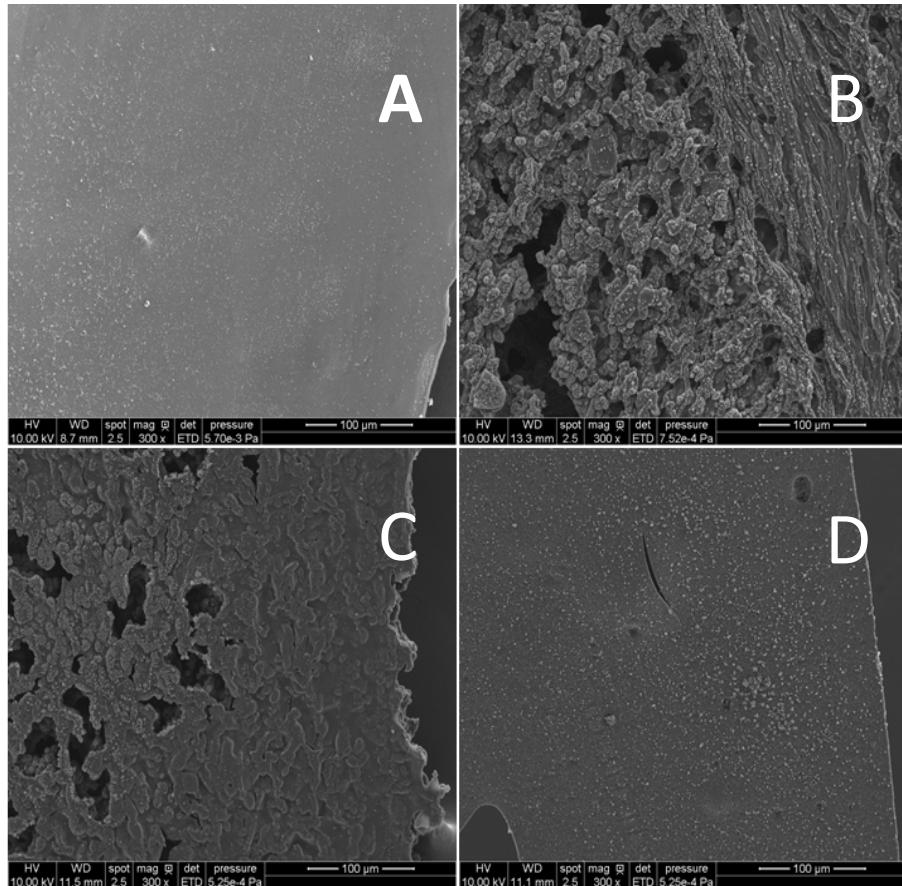


3

TEM micrographs reveal a microphase separation in Lignin/PLA blends

Fiber Characterization

Carbonized fiber structures analyzed by scanning electron microscope (SEM)



- SEM images of carbonized blended samples.
 - A. Grafted lignin
 - B. B-Lignin/G-lignin/PLA - 25/25/50
 - C. B-Lignin/G-lignin/PLA - 33.3/33.3/33.3
 - D. B-Lignin/G-lignin/PLA - 50/25/25

- Voids formed due to degradation of PLA phase

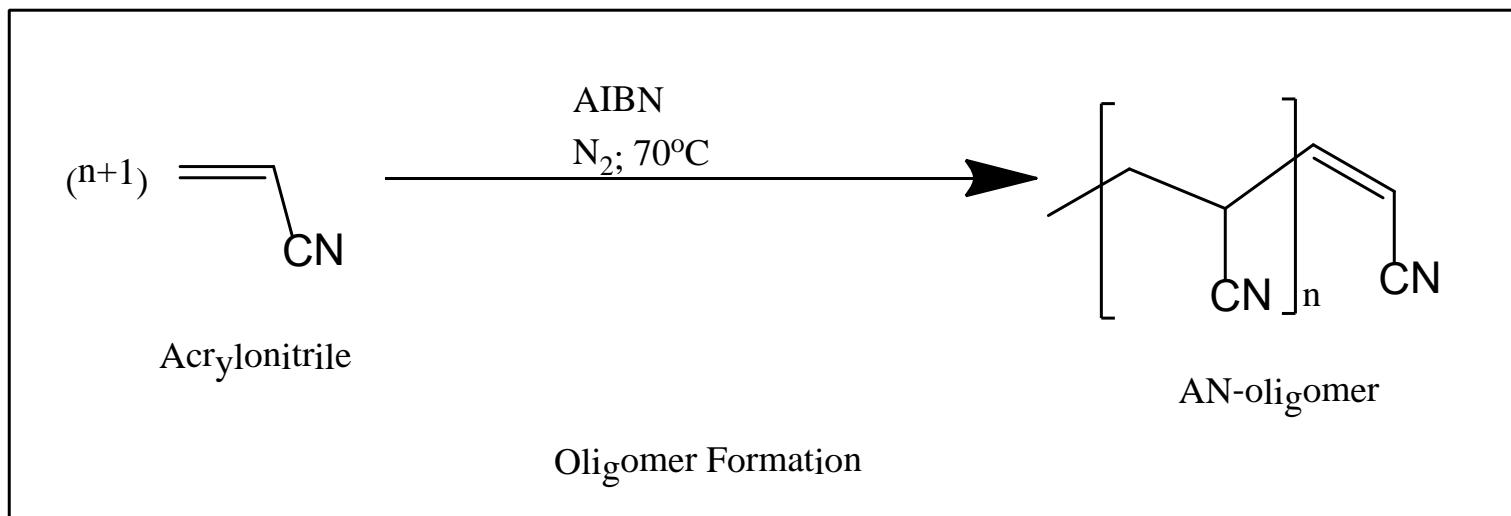
Lignin/PAN copolymers

Acrylonitrile Oligomer Synthesis

STEP 1

Synthesis of AN-Oligomer (AN-Oligomer /PAN)

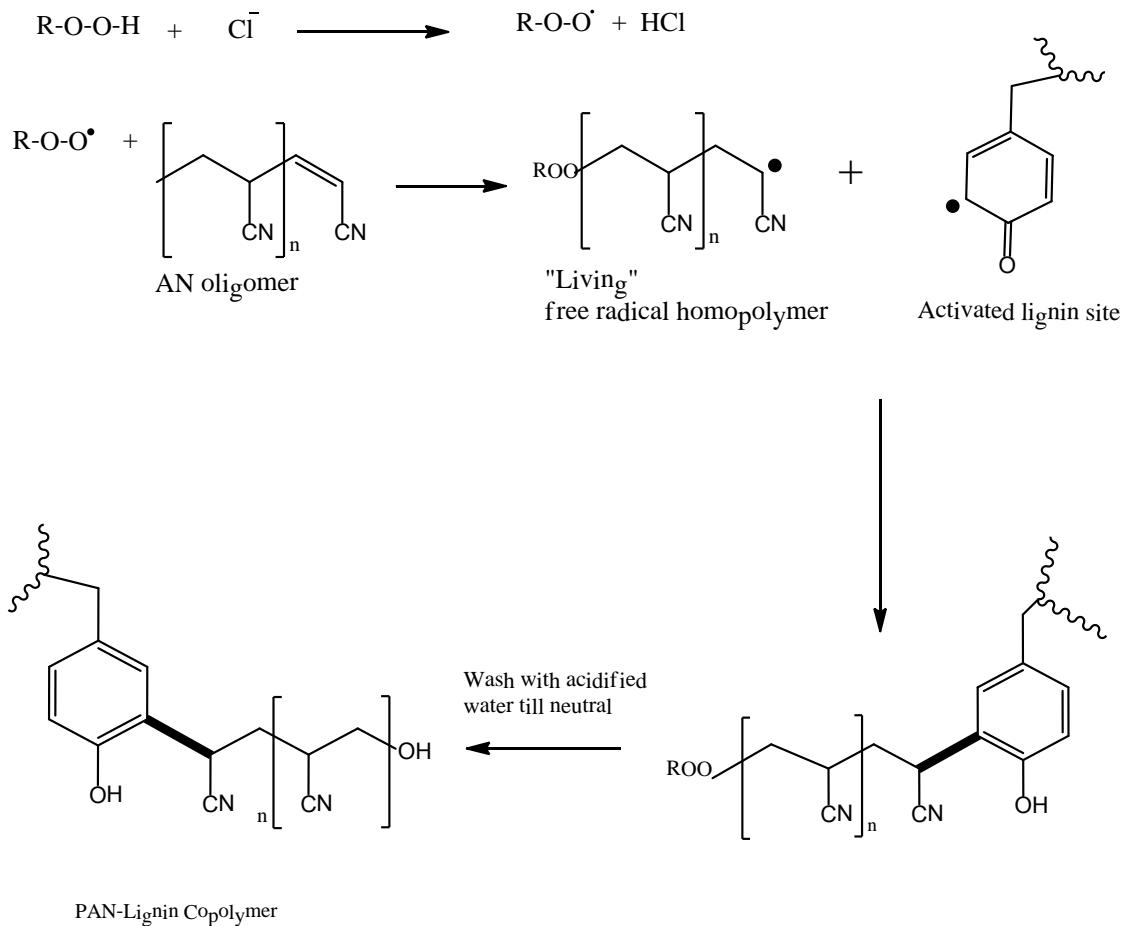
- Simple one-pot reaction at 70°C under N₂ (3 hours)
- Free radical polymerization using AIBN
- Formation of a “living” polymer with a reactive site



Copolymer formation

- $\text{H}_2\text{O}_2/\text{Cl}^-$ redox couple serves as activators for free-radical formation
- Reaction can be vigorous
- Color changes were also indicators of successful reaction
- Average yields were between 70-80%

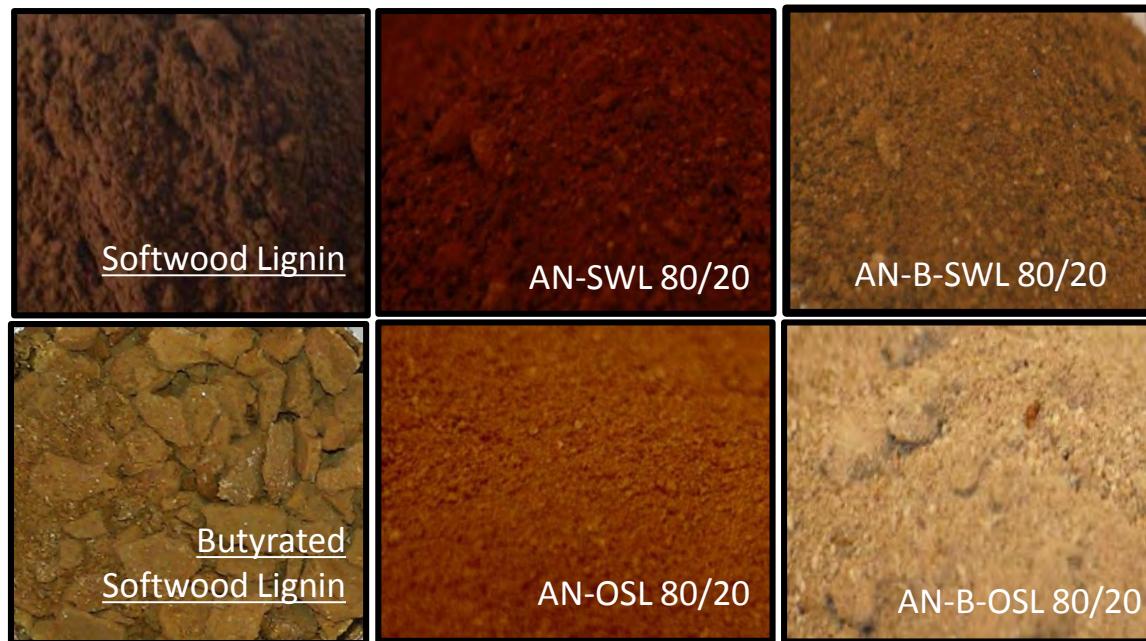
STEP 2: Activation of lignin and copolymerization



Mai, C., Milstein, O., Huttermann, A., Fungal laccase grafts acrylamide onto lignin in presence of peroxides. *Appl Microbiol Biotechnol*;51:1999

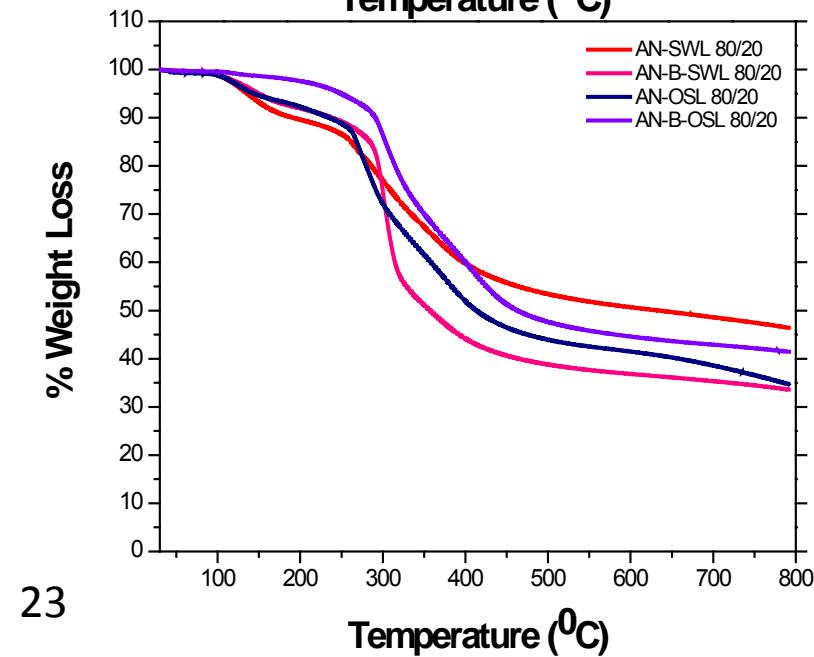
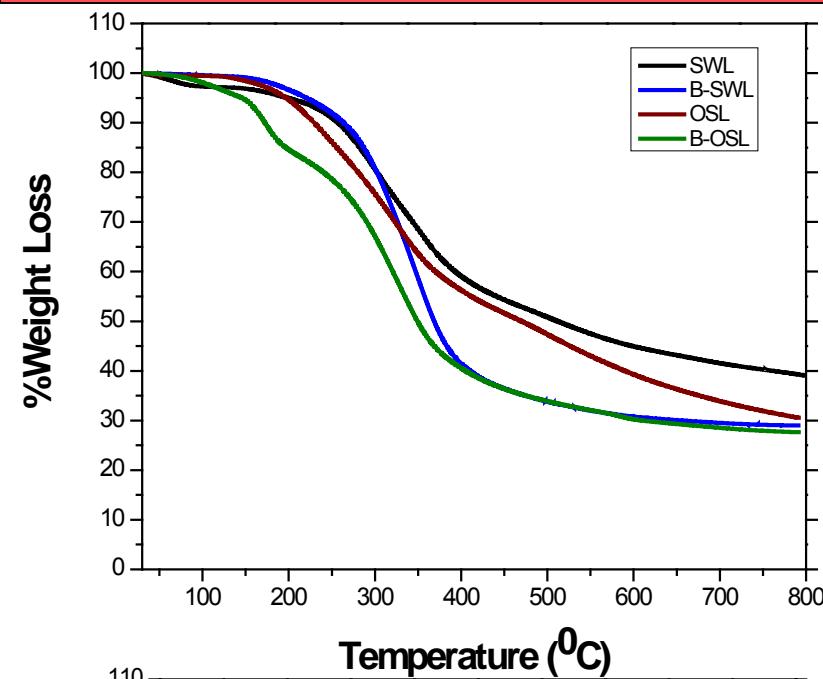
S.P. Maradur, C.H. Kim, S.Y. Kim, B.H. Kim, W.C. Kim, K.S. Yang, *Synthetic Metals*, 162 (2012)

Products and Yields



Lignin used	Ratio of PAN:Lignin	Yield
Softwood	80:20	84.12
Butyrated Softwood	80:20	80.0
Organosolv	80:20	88.9
Butyrated Organosolv	80:20	66.67

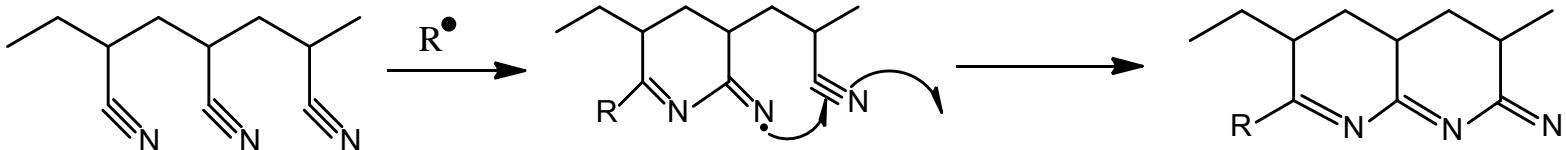
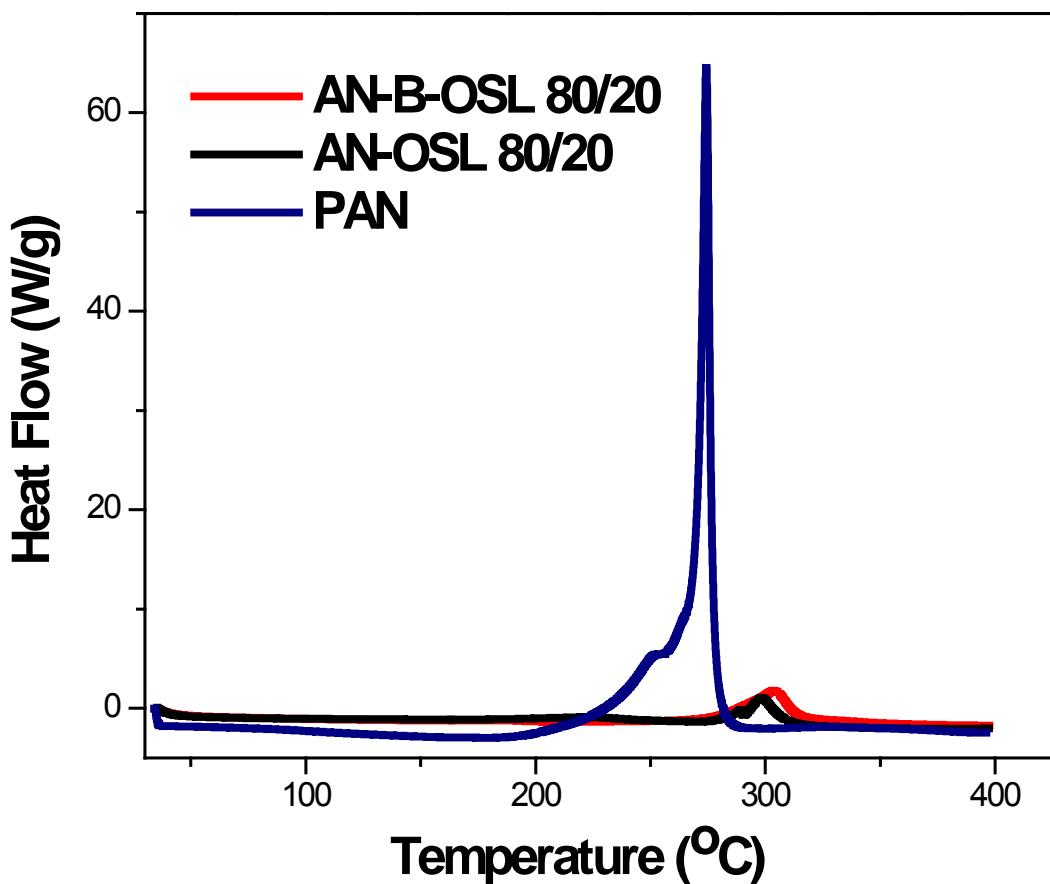
Thermal Degradation Behavior



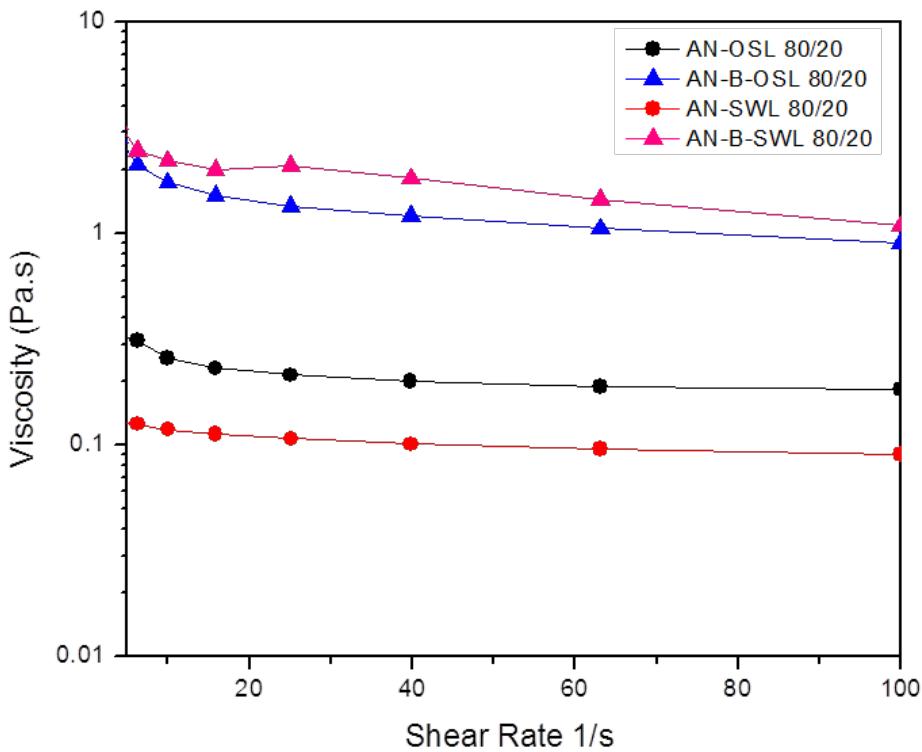
SAMPLE	Residual carbon (wt. %)
Commercial PAN (Homopolymer)	55
Softwood Lignin (SWL)	39.29
Butyrated Softwood Lignin(B-SWL)	28.69
Organosolv Lignin (OSL)	31.56
Butyrated Organosolv Lignin (B-OSL)	27.46
AN-OSL	45.56
AN-B-OSL	41.14
AN-SWL	46.42
AN-B-SWL	33.59

Thermal Oxidation

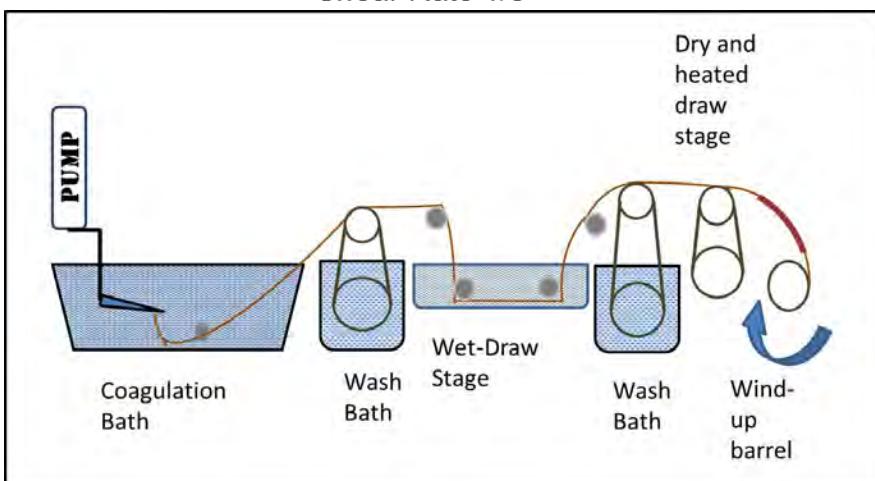
- Stabilization of PAN: Strong exothermic peak at $\sim 275^{\circ}\text{C}$
- Attributed to heat evolved during formation of a stable cyclized ladder polymer structure
- Incorporation of lignin causes lowering of the exotherm



Solution spinning

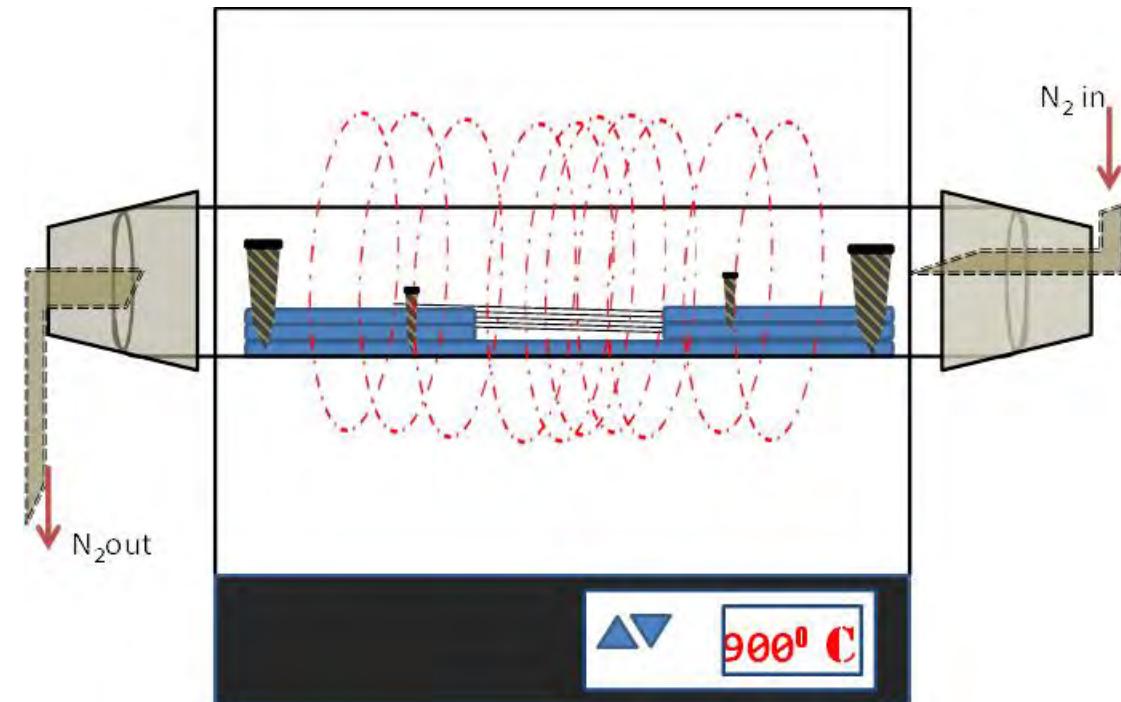


- Butyration improves the viscosity of the copolymer in 16wt% solution in DMF
- Wet spinning of copolymers gave continuous spools for pure AN homopolymer and PAN-butyrated lignin copolymers



Stabilization and Carbonization: Equipment

- Stabilization Program
- Moisture removal: 23-105 °C at 1°C/min
- Slow oxidation (105-280 °C at 3°C/min)
- Carbonization 280-900 °C at 5 °C/min
- Improvement of ordering/alignment in the fiber microstructure: Application of stress by clamping both ends of fiber tow in custom-made equipment



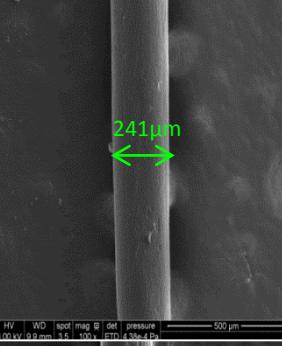
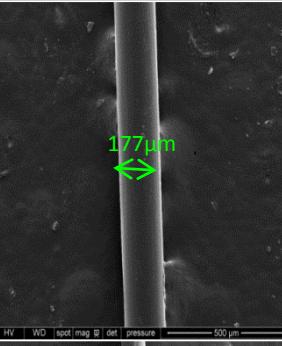
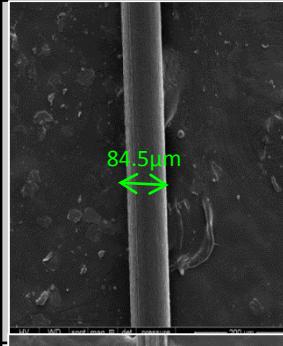
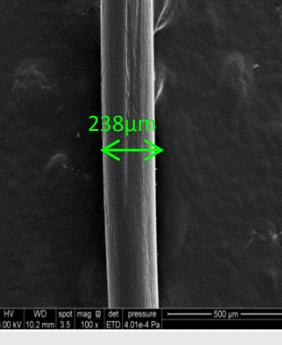
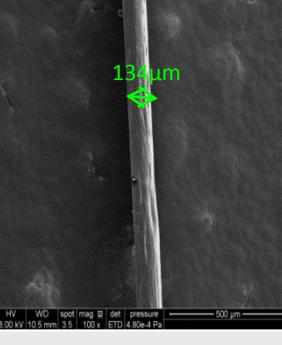
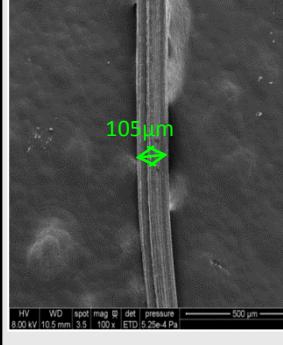
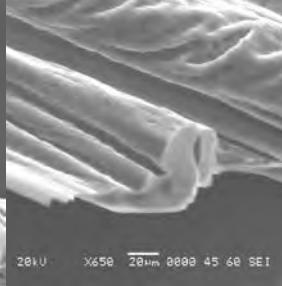
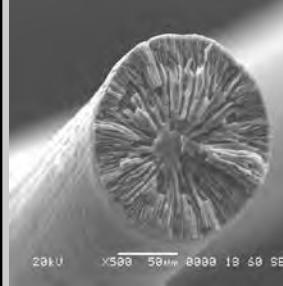
Top view



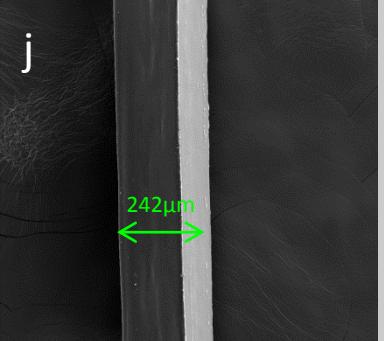
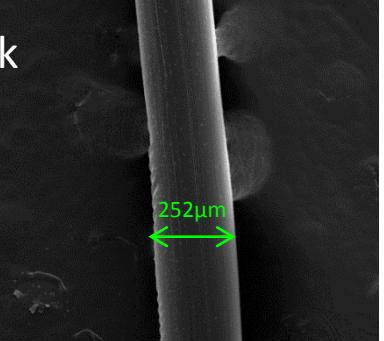
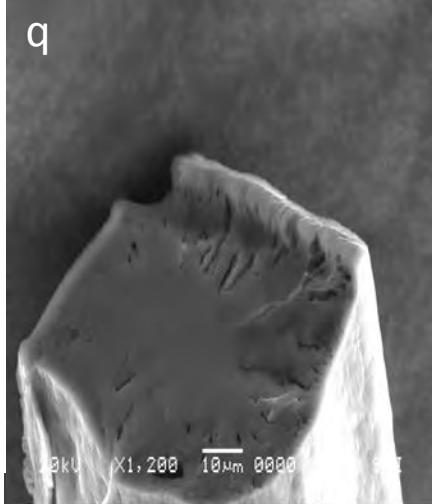
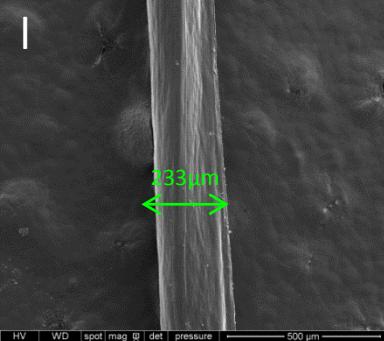
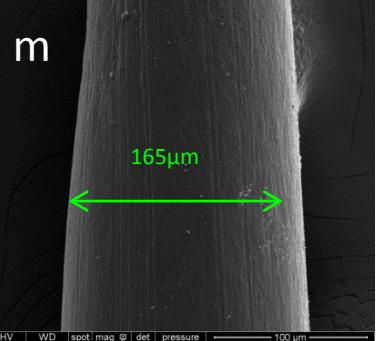
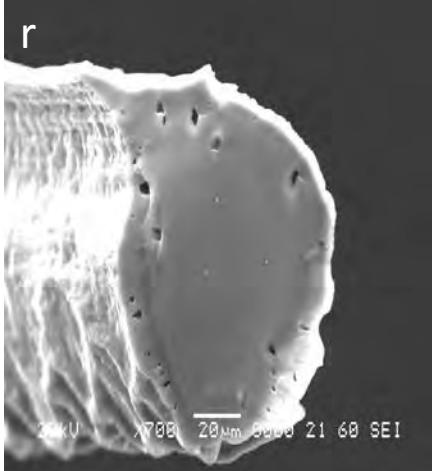
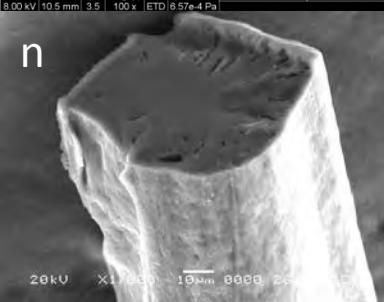
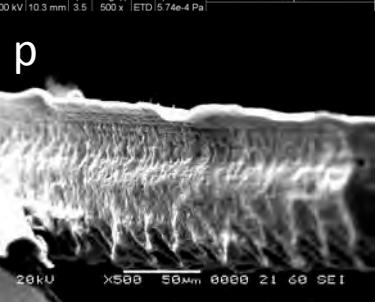
Front view



Carbonization: Morphological Analysis

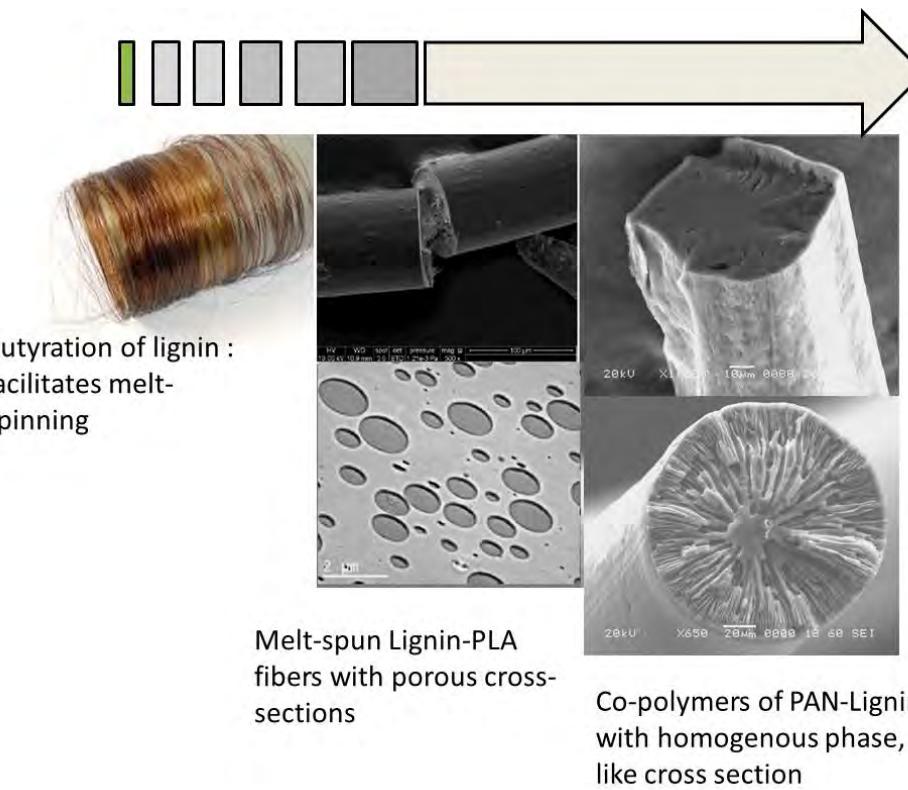
	PAN	AN-B-SWL 80/20	AN-B-OSL 80/20	
RAW				Raw PAN fiber diameter ~ 240 μm Butyrated versions of copolymer-finer fibers ~ 100-150 μm
Stabilized				Stabilization process causes slight roughening of surface, although no appreciable changes in fiber diameters were observable.
Carbonized				Carbon fibers formed with butyrated versions show cross sections akin to reported results.

Carbonization: Morphological Analysis

	AN-SWL 80/20	AN-OSL 80/20	
RAW	 j 242 μm	 k 252 μm	 q
Stabilized	 l 233 μm	 m 165 μm	 r
Carbonized	 n	 p	

Conclusion

1. Butyrate-lignin/PLA blends were prepared by melt mixing and fine fibers were successfully drawn from the blends
2. The raw fibers from all the blend and graft copolymer compositions were carbonized and the cross-section analysis on the carbon fiber shows a porous microstructure in all the fibers with PLA.
3. Copolymers of Lignin/PAN revealed layered carbon structure in the cross section



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- **Polycomp Group**



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for your kind attention!

