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

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Introduction

Advantages over glass fibers
- Specific strength
- Specific modulus
- Fatigue resistance
- Ultimate tensile and compressive stress

High strength-to-weight ratio

Ford Mustang with carbon fiber body panels

400-500 pounds
Replace Glass Fiber with Carbon Fiber → Decrease structural weight → Allow for increased length of blade → Increase power generation

### Mainstream Application

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Diameter</td>
<td>5-7 μm</td>
</tr>
<tr>
<td>Density</td>
<td>1.5-1.8 g/cc</td>
</tr>
<tr>
<td>Carbon content</td>
<td>&gt;95%</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>2.5 – 7.0 GPa</td>
</tr>
<tr>
<td>Young’s Modulus</td>
<td>250 – 400 GPa</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>180-190 (W/m-K)</td>
</tr>
</tbody>
</table>

### 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

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## Precursor materials

<table>
<thead>
<tr>
<th>Precursor/Properties</th>
<th>PAN</th>
<th>Pitch</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (GPa)</td>
<td>2.5 – 7.0</td>
<td>1.5 – 3.5</td>
<td>0.3 -1</td>
</tr>
<tr>
<td>Modulus of Elasticity (GPa)</td>
<td>250 – 400</td>
<td>250 – 800</td>
<td>60</td>
</tr>
<tr>
<td>Carbon Yields (%)</td>
<td>68</td>
<td>85</td>
<td>60</td>
</tr>
</tbody>
</table>

- **PAN**: Petroleum-based
- **Pitch**: Coal or Petroleum-based
- **Lignin**: Bio-based
Petroleum-based Feedstock
PAN, Pitch,....

Bio renewable Feedstock
Lignin, Cellulose
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 + Butyric Anhydride → Butyrated Lignin

(Reaction conditions: 60°C, stirring; N-methyl Imidazole catalytic amount)
Polylactide (PLA)

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

```
CH₃
HO-CH₃-O-CH₃
```

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>50 - 60</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>160 - 170</td>
</tr>
</tbody>
</table>

- 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

- Bio-Renewable
- Fine Lignin Fibers
- Sustainable
- Low Cost
Lignin/PLA Blends

- Homogeneous fine fiber structure was observed by SEM
Morphology of Lignin/PLA Blends

TEM micrographs reveal a microphase separation in Lignin/PLA blends

TEM morphology

PLA fibers

B-lignin/PLA Raw fiber

- 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 are dominated by the crystallinity in PLA
### Thermal Degradation Behavior of Lignin/PLA blends

<table>
<thead>
<tr>
<th>Sample</th>
<th>Residual carbon at 800 °C (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-lignin/PLA 100/0</td>
<td>27.3</td>
</tr>
<tr>
<td>B-lignin/PLA 90/10</td>
<td>22.38</td>
</tr>
<tr>
<td>B-lignin/PLA 75/25</td>
<td>17.99</td>
</tr>
<tr>
<td>B-lignin/PLA 50/50</td>
<td>9.8</td>
</tr>
<tr>
<td>B-lignin/PLA 0/100</td>
<td>0.36</td>
</tr>
</tbody>
</table>

- 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 m²/g to 535 m²/g in lignin based carbon fibers.
- The total volume of the pores increased from 0.00768 cc.g⁻¹ to 0.323 cc.g⁻¹.
Lignin/PLA copolymers
Grafting Lignin with L-Lactide

Polymeriation of PLA from Lactic acid

- The hydroxyl groups (-OH) in the lignin molecule are replaced with L-lactide grafts during the ring opening polymerization of L-Lactide to PLA.
Graft copolymer as compatibilizer in Lignin-poly(lactic acid) binary blends

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

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

![Chemical Reaction Diagram]

Acrylonitrile (n+1) reacts with AIBN under N₂ at 70°C to form an AN-oligomer. The diagram shows the 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

\[
\begin{align*}
\text{R-O-O-H} + \text{Cl}^- & \rightarrow \text{R-O-O}^- + \text{HCl} \\
\text{R-O-O}^- + \begin{array}{c}
\text{CN} \\
\text{CN} \\
\text{n}
\end{array} & \rightarrow \begin{array}{c}
\text{CN} \\
\text{n}
\end{array} + \begin{array}{c}
\text{CN} \\
\text{n}
\end{array} + \begin{array}{c}
\text{CN} \\
\text{n}
\end{array}
\end{align*}
\]

"Living" free radical homopolymer

Activated lignin site


## Products and Yields

<table>
<thead>
<tr>
<th>Lignin used</th>
<th>Ratio of PAN:Lignin</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>80:20</td>
<td>84.12</td>
</tr>
<tr>
<td>Butyrated Softwood</td>
<td>80:20</td>
<td>80.0</td>
</tr>
<tr>
<td>Organosolv</td>
<td>80:20</td>
<td>88.9</td>
</tr>
<tr>
<td>Butyrated Organosolv</td>
<td>80:20</td>
<td>66.67</td>
</tr>
</tbody>
</table>
**Thermal Degradation Behavior**

### Sample Comparison

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Residual carbon (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial PAN (Homopolymer)</td>
<td>55</td>
</tr>
<tr>
<td>Softwood Lignin (SWL)</td>
<td>39.29</td>
</tr>
<tr>
<td>Butyrated Softwood Lignin (B-SWL)</td>
<td>28.69</td>
</tr>
<tr>
<td>Organosolv Lignin (OSL)</td>
<td>31.56</td>
</tr>
<tr>
<td>Butyrated Organosolv Lignin (B-OSL)</td>
<td>27.46</td>
</tr>
<tr>
<td>AN-OSL</td>
<td>45.56</td>
</tr>
<tr>
<td>AN-B-OSL</td>
<td>41.14</td>
</tr>
<tr>
<td>AN-SWL</td>
<td>46.42</td>
</tr>
<tr>
<td>AN-B-SWL</td>
<td>33.59</td>
</tr>
</tbody>
</table>
Thermal Oxidation

- Stabilization of PAN: Strong exothermic peak at ~275°C
- Attributed to heat evolved during formation of a stable cyclized ladder polymer structure
- Incorporation of lignin causes lowering of the exotherm

![Graph showing heat flow vs. temperature for different materials](image)

![Chemical structures](image)
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
Carbonization: Morphological Analysis

<table>
<thead>
<tr>
<th></th>
<th>PAN</th>
<th>AN-B-SWL 80/20</th>
<th>AN-B-OSL 80/20</th>
</tr>
</thead>
<tbody>
<tr>
<td>RAW</td>
<td><img src="image1" alt="RAW PAN fiber" /></td>
<td><img src="image2" alt="RAW AN-B-SWL 80/20 fiber" /></td>
<td><img src="image3" alt="RAW AN-B-OSL 80/20 fiber" /></td>
</tr>
<tr>
<td></td>
<td>Raw PAN fiber diameter ~ 240 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Butyrated versions of copolymer-finer fibers ~ 100-150 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stabilized</td>
<td><img src="image4" alt="Stabilized PAN fiber" /></td>
<td><img src="image5" alt="Stabilized AN-B-SWL 80/20 fiber" /></td>
<td><img src="image6" alt="Stabilized AN-B-OSL 80/20 fiber" /></td>
</tr>
<tr>
<td></td>
<td>Stabilization process causes slight roughening of surface, although no appreciable changes in fiber diameters were observable.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonized</td>
<td><img src="image7" alt="Carbonized PAN fiber" /></td>
<td><img src="image8" alt="Carbonized AN-B-SWL 80/20 fiber" /></td>
<td><img src="image9" alt="Carbonized AN-B-OSL 80/20 fiber" /></td>
</tr>
<tr>
<td></td>
<td>Carbon fibers formed with butyrated versions show cross sections akin to reported results.</td>
<td></td>
<td></td>
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</table>
# Carbonization: Morphological Analysis

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<tr>
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<td></td>
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<td><img src="#" alt="Carbonized Image" /></td>
</tr>
</tbody>
</table>

- **AN-SWL 80/20**
  - 242 μm
  - 165 μm

- **AN-OSL 80/20**
  - 252 μm
  - 165 μm
1. Butyrated-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.
• Gauri Ramasubramanian, Keke Chen and Edward J. Angus
• Polycomp Group

• Support of the Iowa Alliance for Wind Innovation and Novel Development (IAWIND) and Siemens for funding this research work
Thank You! for your kind attention!