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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](image)

Evolution of HCN and other toxic gases during stabilization and carbonization

Buckley & Edie, 1986
Fitzer & Manocha, 1998
Precursors: Mesophase Pitch and Rayon

Kundu, ..Ogale, CARBON 2008

Not for structural applications

Buckley & Edie, 1986
Chemical Structure of Lignin

E. Alder, Wood Science & Technology, 11, 169 (1977)
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
- Acetylated softwood kraft lignin, melt-spinning. 2008, R. C. Eckert
# Mechanical properties of lignin based CF

<table>
<thead>
<tr>
<th>Precursor Type</th>
<th>Diameter (µm)</th>
<th>Elongation (%)</th>
<th>Modulus (GPa)</th>
<th>Tensile strength (MPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam Exploded hardwood</td>
<td>7.6 ± 2.7</td>
<td>1.63 ± 0.19</td>
<td>40.7 ± 6.3</td>
<td>660 ± 230</td>
<td>K. Sudo et al, 1992</td>
</tr>
<tr>
<td>Organosolv Hardwood</td>
<td>14-35</td>
<td>0.64-1.12</td>
<td>2.17-39.1</td>
<td>13.3-355</td>
<td>Y. Uraki et al, 1995</td>
</tr>
<tr>
<td>Organosolv Softwood</td>
<td>84 ± 15</td>
<td>0.74 ± 0.14</td>
<td>3.59 ± 0.43</td>
<td>26.4 ± 3.1</td>
<td>S. Kubo et al, 1998</td>
</tr>
<tr>
<td>Kraft Hardwood</td>
<td>46 ± 8</td>
<td>1.12 ± 0.22</td>
<td>40 ± 11</td>
<td>422 ± 80</td>
<td>J. F. Kadla et al, 2002</td>
</tr>
<tr>
<td>Kraft Softwood, acetylated</td>
<td>5-100</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>Robert C., 2008</td>
</tr>
<tr>
<td>Hardwook</td>
<td></td>
<td>2.03</td>
<td>82.7</td>
<td>1070</td>
<td>D. A. Baker, 2013</td>
</tr>
<tr>
<td>Rayon based carbon fiber</td>
<td>5-25</td>
<td></td>
<td>100</td>
<td>100-1000</td>
<td>Buckley &amp; Edie; Fitzer&amp; Manocha</td>
</tr>
<tr>
<td>PAN based carbon fiber</td>
<td>5-15</td>
<td>2</td>
<td>100-500</td>
<td>3000-7000</td>
<td>Buckley &amp; Edie; Fitzer&amp; Manocha</td>
</tr>
<tr>
<td>Mesophase pitch based carbon fiber</td>
<td>5-15</td>
<td>0.6</td>
<td>200-800</td>
<td>1000-3000</td>
<td>Buckley &amp; Edie; Fitzer&amp; Manocha</td>
</tr>
</tbody>
</table>
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/H₂O pulping
- Softening point: 155ºC
- Decomposition temperature: ~280ºC from TGA result in N₂ 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

<table>
<thead>
<tr>
<th>Diameter (µm)</th>
<th>Elongation (%)</th>
<th>Modulus(GPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 ± 1</td>
<td>1.4 ± 0.4</td>
<td>34 ± 4</td>
<td>450 ± 130</td>
</tr>
</tbody>
</table>
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.
- 75% AA-Ace-SKL was melt spun into fibers
- 75% AA-Ace-SKL fibers became tacky during oxidative stabilization

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
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 and Graphitization furnaces: 1000-2700°C

Carbonization under tension
1000°C 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

<table>
<thead>
<tr>
<th></th>
<th>Diameter (µm)</th>
<th>Strength (MPa)</th>
<th>Apparent Modulus (GPa)</th>
<th>Apparent strain to failure (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ace-SKL CF (processed without tension)</td>
<td>22.5 ± 0.4</td>
<td>510 ± 50</td>
<td>30 ± 2</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Ace-SKL CF (processed with tension)</td>
<td>5.9 ± 0.2</td>
<td>1050 ± 70</td>
<td>35 ± 3</td>
<td>3.0 ± 0.2</td>
</tr>
</tbody>
</table>
Ace-SKL CF X-ray Diffraction Spectrum

Silicon crystal standard

002 peak location: 23.3°
Carbonized with tension

Carbonized without tension

Azimuthal angle (degrees)

Intensity %
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
Crenulated surface are desirable for enhancing fiber-matrix interfacial area.

2400°C carbonized