C2CF: Coal to Carbon Fiber: Continuous Processing for High Value Composites

Koppers is developing a spinnable mesophase pitch from coal tar recovered from metallurgical coke production at integrated steel mills.

UK is developing stable multifilament melt spinning and continuous thermal conversion.

Prototype composite parts will be demonstrated with the carbon fiber.

Cost and technology gap analyses for the carbon fiber will be evaluated, for new markets and industries for US coal.
Overview

• Project rationale and goals

• Task Updates: Successes & Challenges
  1. Coal Tar to Mesophase Pitch
  2. Melt Spinning & Tensile Properties

• Future Direction & Challenges
• Concluding Remarks
Rationale: Source Compounds in Coal

I. Mochida et al. / Carbon 38 (2000) 305 –328

mesophase


https://www.worldcoal.org/coal/what-coal
Initial Economics: Coal Products Conclusions

- 1570 kt coal - from single site
- 80 kt coal tar (450 kt/yr US production of coal tar)
  - 16 kt of chemical oil, including valuable naphthalene
  - 24 kt of distillates creosote (for railroad tie production) and carbon black precursor (essential for tire production).
- 40 kt isotropic coal tar pitch ($800/t)
  - $32M, for binder pitch for electrodes
- 20 kt mesophase pitch
- 16 kt carbon fiber (180 kt/yr CF market)
  - $1.76B, for even-higher value composites ($50/lb CF)
- Value add relative to the isotropic CTP
  - 55x ($50/lb)
  - 5.5x ($5/lb)

Approximate Coal Tar Composition:

- Water 5%
- Light Oils 2%
- Naphthalene 10%
- Creosote 33%
- TS 41%
- Beta Resin 2%
- QI 7%
- Pitch 50%
Project Goals: ... To maximize the coal value chain

• Develop and scale efficient processing technology for ultra-low quinoline insolubles (QI) coal tar pitch and subsequent mesophase pitch

• Clarify and simplify tedious continuous multifilament spinning and thermal conversion
  • Efficient production of high performance carbon fiber products (woven carbon fiber preforms, continuous, and chopped tow)

• Demonstrate and characterize representative composite parts

• Economic & Technological Gap Analyses
Tasks Updates
Task 2: Coal Tar to Mesophase

Low QI coal tar pitch production

Small-scale mesophase production

Coal tar derived mesophase pitch

1s of kg scale currently

Mesophase = 62%
Tsp = 310 ºC
Making Mesophase

Example

START: Coal Iso Pitch:

Tsp ~ 100 °C

C/H = 18.62 wt.%

QI = 0.36 wt.%

TI = 19.83 wt.%

THFI = 11.61 wt.%

FINAL: Mesophase

~ 51 wt.% yield

~ 60 vol% mesophase

Tsp ~ 300 °C

C/H = 26.42 wt.%

QI = ~ 45 wt.%

Vacuum distillation

< 1 Torr

340 °C 5 min

~ 3 wt.% volatiles

Post processing:


Solvent-extraction [Diefendorf and Riggs (1980)]

Catalytic polymerization [Mochida et al. (1988, 1990, 1992)]
Development of Mesophase

~ 30% Mesophase

Isotropic Mesophase

~ 60% Mesophase

ASTM D4616-95.
Updates

• Isotropic binder inclusions promote spinnability
  • 100% mesophase is difficult to spin (will not flow) and Tsp too high (> 350 °C)
  • Up to ~ 40% binder inclusions spins well
    • Should be homogeneously dispersed and small (~ 10 micron)
    • Tsp ~ 305 °C
Capillary Rheology

\[ \eta = \eta_0 e^{\frac{E_a}{RT}} \]

Shear rate constant at 4362 1/s

<table>
<thead>
<tr>
<th>Sample</th>
<th>QI (%)</th>
<th>% Mesophase</th>
<th>Tsp (C)</th>
<th>Ea (kJ/mol)</th>
<th>Pitch T (C)</th>
<th>Spool speed</th>
<th>Duration (min)</th>
<th>Comments</th>
<th>Estimated viscosity at pressure spinning T (Pa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2CF-20-0425</td>
<td>58.84</td>
<td>72.83</td>
<td>317</td>
<td>154.1</td>
<td>360-386</td>
<td>0.4</td>
<td>3.17</td>
<td>can only be taken up very slowly</td>
<td>20 to 60</td>
</tr>
<tr>
<td>C2CF-20-0425 HM</td>
<td>TBD</td>
<td>55.5</td>
<td>330</td>
<td>153.5</td>
<td>398</td>
<td>2.6</td>
<td>1</td>
<td></td>
<td>~27</td>
</tr>
<tr>
<td>KCTP-038-HT7</td>
<td>55.86</td>
<td>90.05</td>
<td>308</td>
<td>235</td>
<td>~355</td>
<td>1.5-3.5</td>
<td>6.5 cont.</td>
<td>spins/spools well</td>
<td>~70</td>
</tr>
<tr>
<td>KCTP-051-HT7</td>
<td>52.97</td>
<td>57.72</td>
<td>286</td>
<td>232.4</td>
<td>~360</td>
<td>2-3.2</td>
<td>30 s</td>
<td>jet spins well but difficulty maintaining continuous tow</td>
<td>~2</td>
</tr>
<tr>
<td>KCTP-052-HT6</td>
<td>60.87</td>
<td>59.42</td>
<td>292</td>
<td>194.1</td>
<td>340-344</td>
<td>0.5-1.0</td>
<td>8 cont.</td>
<td>spins very well</td>
<td>~20</td>
</tr>
<tr>
<td>KCTP-053-HT21</td>
<td>66.8</td>
<td>77.5</td>
<td>315</td>
<td>208.5</td>
<td>365-370</td>
<td>0.4-0.7</td>
<td>6 cont.</td>
<td>spins very well</td>
<td>~64</td>
</tr>
<tr>
<td>KCTP-058-HT21</td>
<td>47.47</td>
<td>60.3</td>
<td>292</td>
<td>197.6</td>
<td>362-367</td>
<td>2.5-3.5</td>
<td>9 cont.</td>
<td>spins very well</td>
<td>~5</td>
</tr>
<tr>
<td>KCTP-059-HT23</td>
<td>55.45</td>
<td>62.59</td>
<td>306</td>
<td>203.1</td>
<td>365-371</td>
<td>1.2-2.0</td>
<td>10+ cont.</td>
<td>spins very well</td>
<td>~26</td>
</tr>
</tbody>
</table>

Pressure spinning info
Time stability of pitches (Oscillatory rheology)

Viscosity increases with time at temp

370 °C
10 rad/s
1 % strain

C2CF-20-0425
KCTP-059-HT23
C2CF-20-0425 Hotmixed

caer.uky.edu
What is a “spinnable” coal tar mesophase?

Initial target of 10 min of uninterrupted melt spinning

- **Mesophase content**
  - ~ 60 to 80 vol%
  - Well-dispersed, small (~10 micron) isotropic binder inclusions

- **Softening point temperature**
  - ~ 305 °C, < 350 °C

- **Capillary rheology**
  - Activation energy of flow of ~ 190 – 230 kJ/mol

- **Viscosity stable with time at temperature**
  - 10s of min

- **Issues for further investigation**
  - Spinnability association with chemistry of mesophase
    - aromaticity, Mw distribution, etc.
Subtask 3.1 - Melt Spinning
Pressure Spinning

- Pitch
- Tc
- N2
- ~200 psi
- Fritted SS filter
- Take-up Spool
- Temperature = 370°C

Single hole spinneret
100 micron
L/D = 5
120° entrance
20 micron frit
Multifilament Spinning

- Spooled
- Continuous, hooped green fiber tow on porous carbon screen trays

- Key Challenges:
  - Green fiber fragility
  - Start Up
  - High $T \sim 370 \, ^\circ C$
AJ Extruder System

Set up on-site Oct 2020

1” Extruder
Metering pump
Spin pack: 100 hole spinneret
Carbon Fibers - effect of % mesophase

Batch oxidation, carbonization & graphitization
Single filament tensile testing.

59.4 % Mesophase

<table>
<thead>
<tr>
<th>Mesophase sample</th>
<th>Tsp (°C)</th>
<th>QI (%)</th>
<th>% Mesophase</th>
</tr>
</thead>
<tbody>
<tr>
<td>052</td>
<td>292</td>
<td>60.9</td>
<td>59.4</td>
</tr>
<tr>
<td>053</td>
<td>315</td>
<td>66.8</td>
<td>77.5</td>
</tr>
</tbody>
</table>

77.5 % Mesophase
Radial texture of graphitized fibers
## Tensile properties

<table>
<thead>
<tr>
<th>% Mesophase</th>
<th>Fiber</th>
<th>Diameter (um)</th>
<th>Stdev (um)</th>
<th>Stress At Break (MPa)</th>
<th>Stdev (MPa)</th>
<th>Modulus (GPa)</th>
<th>Stdev (GPa)</th>
<th>Strain at Break (%)</th>
<th>Stdev (%)</th>
<th>Strain Energy Density (MJ/m³)</th>
<th>Stdev (MJ/m³)</th>
<th>N</th>
<th>CY %</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.4 %</td>
<td>PS252a-052-GF671</td>
<td>17.70</td>
<td>0.75</td>
<td>1061.0</td>
<td>296.7</td>
<td>623.6</td>
<td>42.4</td>
<td>0.17%</td>
<td>0.05%</td>
<td>0.97</td>
<td>0.51</td>
<td>40</td>
<td>79.23%</td>
</tr>
<tr>
<td></td>
<td>PS252b-052-GF671</td>
<td>17.62</td>
<td>0.95</td>
<td>1022.4</td>
<td>378.6</td>
<td>592.2</td>
<td>66.6</td>
<td>0.17%</td>
<td>0.06%</td>
<td>0.84</td>
<td>0.69</td>
<td>40</td>
<td>79.20%</td>
</tr>
<tr>
<td>77.5 %</td>
<td>PS253a-053-GF671</td>
<td>15.18</td>
<td>2.21</td>
<td>881.8</td>
<td>201.3</td>
<td>609.2</td>
<td>40.1</td>
<td>0.14%</td>
<td>0.03%</td>
<td>0.59</td>
<td>0.32</td>
<td>40</td>
<td>71.93%</td>
</tr>
<tr>
<td></td>
<td>PS253b-053-GF671</td>
<td>15.18</td>
<td>2.21</td>
<td>901.8</td>
<td>279.5</td>
<td>613.4</td>
<td>60.8</td>
<td>0.15%</td>
<td>0.05%</td>
<td>0.57</td>
<td>0.38</td>
<td>40</td>
<td>80.20%</td>
</tr>
</tbody>
</table>

- % Mesophase did not govern CF properties or yield
- Both had moduli ~ 600 GPa (87 MSI)
- Lower % mesophase showed ~ 17% increase in strength
Review of Progress

• Coal tar derived mesophase production at 1s kg scale
  • Progress defining a ‘spinnable’ mesophase
    • Mesophase and binder content
    • Softening point temperature
    • Rheology and stability

• Single filament tensile properties measured
  • Moduli up to 600 GPa (87 MSI)
  • Strength still low at ~ 1 GPa (145 ksi) – strain to failure low at 0.15%
  • Results not very sensitive to mesophase content between 59 and 78%
Future

• Multifilament melt spinning
  • Challenges:
    • Start up
    • Stability

• Quantitative and qualitative defining of SPINNABLE coal tar mesophase - measurable properties
  • Physical: Tsp, % mesophase, QI
  • Rheology: viscosity, activation energy of flow, stability with time, extensional
  • Chemistry: aromaticity index, Mw distribution

• 1s to 10s of kg of coal tar mesophase processing
  • Challenges
    • Reproducible processing of SPINNABLE mesophase

• Tasks 3.2 – 3.4 requiring continuous multifilament tow
Subtask 3.2 - Continuous Oxidation
Subtask 3.3 - Weaving
Subtask 3.4 - Continuous Carbonization
Task 4.0 - Composite Fabrication

- The green fiber is extremely fragile
- No tension required!
- 11 - 1 ft temperature zones
- Down to 0.5 inch/min
- Air or N₂
- Spooled after oxidation for subsequent weaving processing into fabric
# Gantt Chart

We are here: Oct 2020

<table>
<thead>
<tr>
<th>Task and Subtask</th>
<th>BP1</th>
<th>BP2</th>
<th>BP3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>1 Project Management and Planning</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 Coal to Monophase</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Production of Low-QI Isotropic Coal Tar Pitch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2 Production of Monophase Pitch</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 Continuous Spinning and Thermal Conversions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 Melt Spinning</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2 Continuous Oxidation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.3 Weaving and Chopping of Oxidized Fiber</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.4 Continuous Carbonization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 Composite Fabrication</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1 Representative Composite Fabrication (Woven and Injection Molded)</td>
<td></td>
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<td></td>
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<tr>
<td>5 Analysis</td>
<td></td>
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<tr>
<td>5.1 Materials Characterization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2 Economic Analysis/Technological Gap Analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task/Subtask</td>
<td>Milestone Title/Description</td>
<td>Planned Completion Date</td>
<td>Actual Completion Date</td>
</tr>
<tr>
<td>--------------</td>
<td>---------------------------------------------------------------------------------------------</td>
<td>-------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>2.2</td>
<td>Production of ≥ 1 kg pitch containing ≥ 90%-mesophase and a softening point ≥ 300 °C</td>
<td>03/31/2020</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Continuous melt spinning of ≥ 90%-mesophase pitch, with ≥ 100 filaments, for ≥ 10 minutes</td>
<td>09/30/2020</td>
<td></td>
</tr>
<tr>
<td>3.2</td>
<td>Production of non-fused oxidized mesophase pitch fiber with high strain-to-failure</td>
<td>03/31/2021</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Production of a plain weave sample from oxidized mesophase pitch fiber with ≥ 100 warp ends and produce ≥ 100 g of chopped oxidized mesophase pitch fiber</td>
<td>09/30/2021</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Production of continuous fiber composite using mesophase pitch derived carbon fiber through resin infusion and curing, as well as a ≥ 10 wt.% thermoplastic and injection molded sample, and report thermal and mechanical properties for both</td>
<td>03/31/2022</td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>Final Report for project</td>
<td>09/30/2022</td>
<td></td>
</tr>
</tbody>
</table>
Concluding Remarks

• Immediate future: Multifilament spinning
  • High modulus carbon fiber has been demonstrated
  • Stable & robust multifilament tow processing demonstration is key

• Scale up spinnable coal tar mesophase production
  • 10s of kg up to tonnes scale processing

• Sharpen the value prospect for future scale up
  • Cost of coal tar mesophase & carbon fiber processing
  • Market for fiber (continuous, chopped)
    • Final value add relative to coal tar binder pitch

• The CF market is approximately 180 kt/yr (with ~10% CAGR)
  • Opportunity for pitch to take some PAN market share (pitch currently at ~ 5%)
  • Only 3 major producers of pitch-based structural carbon fiber
    • Mitsubishi Chemical “Dialead” - JAPAN
    • Nippon Graphite Fiber “Granoc” - JAPAN
    • Solvay Composite Materials “Thornel” - USA
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