Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids

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Project ID: ST148

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Overview

Timeline

• Project Start Date: 10/01/17
• Project End Date: 9/30/20
• Percent Complete: 78%

Budget

• Total task funding
  – $900k
• $257k in FY18
• $322k in FY19
• $321k in FY20

Barriers

• Barriers Addressed
  – A: System Weight and Volume
  – B: System Cost
  – G: Materials of Construction

Partners

• Project Lead: ORNL
• Interactions/Collaborations
  ➢ 525 Solutions
Main Objective: The overarching goal of this proposal is to develop a novel plasticized melt-spinning process to replace the current solution spinning process based on nonvolatile task-specific ionic liquids (ILs). During the second year of this project (current reporting year), we have accomplished:

- Down selection of IL for plasticization
- Demonstration of melt spinning of PAN fibers based on ILs
- Technoeconomic analysis for scale-up of the IL production

Relevance to Barriers and Targets

- The ability to melt-spin the PAN into fibers has been identified as a significant cost-driver for high strength carbon fiber production.
- The fiber production has a direct correlation to the costs of a hydrogen storage system where the carbon fiber cost is 75% of the total system cost
- To replace the current solution spinning process with a novel plasticized melt-spinning process based on nonvolatile task-specific ionic liquids (ILs)
**Approach**

**Why Ionic Liquids?**

Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.

- Ionicity
- Nonvolatility
- Thermal Stability
- Nonflammability
- Tunable Hydrophobicity
- Wide Liquid-Phase Temperature (-100°C to around 300°C)
- Wide Electrochemical Window
- Tunable Lewis Acidity

Ideal as plasticizers and designer solvents

Approach: Ionic-Liquid Strategy to Nonpolymeric Liquid Precursors for Formation of Carbons under Ambient Pressure

Key Features

• Nonpolymeric but negligible vapor pressure
• Polymerization strategy toward highly charged and crosslinked polymers
• Liquid precursors for N-doped carbonaceous materials (types of N-dopants and other elements)


Approach: Project Milestones

• Milestone 1: Investigate how the molecular structures of ILs dictate plasticizing interactions with PAN (FY 17-18)
  – 1.1 Demonstrate > 30 wt% IL solubility in PAN
  – 1.2 PAN-IL synthesis with carbon yield > 50%
  – 1.3 Demonstrate > 10 °C decrease in PAN melt temperature
  – Go/No-Go Point #1: Demonstrate > 15 °C decrease in PAN melt temperature

• Study chemical interactions of ILs with PAN to control cyclization of degree (FY18-19)
  – 2.1 Down selection of IL for plasticization
  – 2.2 Demonstration of melt spinning of PAN fibers based on ILs
  – 2.3 Technoeconomic analysis for scale-up of the IL production
  – Go/No-Go Point #2: Demonstration of tensile properties of resultant fibers

• Integrate the information gained from the above two tasks to develop IL-assisted melt spinning systems (FY19-20)
  – 3.1 Preliminary analysis of scale-up
  – 3.2 Scale-up IL to >1 kg production for IL to realize anticipated decreased cost
  – 3.3 Demonstration of filament diameter of ~20 micrometer after carbonization
  – 3.4 Demonstration of melt spinning with recycled ionic liquids
Accomplishment: Down selection of IL for plasticization

- PAN-IL composites were investigated by TGA.
  - Illustrates the thermal stability
  - Quantifies carbon yield
- Adding ILs to PAN originally decreases the carbon yield.
  - Proves IL disrupts PAN chain alignment
- Recycling or Removal of ILs results in the increase of carbon yield and likely linked to the crosslinking pathway change.
- ILs containing bromide anions have higher carbon yields.
Accomplishment: Demonstration of Melt Spinning PAN Fiber Based on ILs

• Fiber spinning experiments were performed on a melt extruder
• Melt extruder is ideal for small sample sizes
  – 3-5 total grams of material
• Initial testing parameters are:
  – Rotor ≈ 150-160 °C
  – Header ≈ 150-170 °C
  – Rotational speed ≈ 90 RPM
  – Take up speed ≈ 60 ft/min
• 30 wt.% PAN in 5 different IL
  – [C₃mim]Br, [C₄mim]Br, [MPCNIIm]Br, [C₄mim]Cl, [MPCNIIm]Cl
Accomplishment: Morphology/Size of PAN Fiber Precursor (SEM)

High resolution SEM images of A) as spun PAN fiber from PAN-[C₄mim]Br composite, B, C) cross section of as spun fiber, D) PAN fiber after washing, and E, F) cross section of washed fiber
Accomplishment: Morphology/Size of PAN Fiber Precursor (XRD)

<table>
<thead>
<tr>
<th>Fiber Sample</th>
<th>Crystallinity (%)</th>
<th>Crystal size (nm)</th>
<th>Crystalline orientation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₃mim]Br</td>
<td>63.4</td>
<td>11.45</td>
<td>74</td>
</tr>
<tr>
<td>[C₄mim]Br</td>
<td>63.1</td>
<td>7.86</td>
<td>78</td>
</tr>
<tr>
<td>[C₄mim]Cl</td>
<td>49.3</td>
<td>7.11</td>
<td>70</td>
</tr>
<tr>
<td>[MPCNIm]Br</td>
<td>38.9</td>
<td>8.08</td>
<td>81</td>
</tr>
<tr>
<td>[MPCNIm]Cl</td>
<td>61.9</td>
<td>9.66</td>
<td>75</td>
</tr>
</tbody>
</table>

The XRD patterns and calculated structural data (crystallinity, crystal size and crystalline orientation) of the as-spun PAN-IL fibers containing [C₃mim]Br, [C₄mim]Br, [MPCNIm]Br, [C₄mim]Cl, and [MPCNIm]Cl have been performed and results are summarized in above table. One example with [C₄mim]Br is shown in above figure.

- The crystallinity order: [C₃mim]Br ≈ [C₄mim]Br > [MPCNIm]Cl > [C₄mim]Cl >[MPCNIm]Br
- The crystal size order: [C₃mim]Br > [MPCNIm]Cl > [MPCNIm]Br > [C₄mim]Br > [C₄mim]Cl
- Thus, the PAN-[C₄mim]Br fiber showed the almost highest crystallinity and the second smallest crystal size.
Accomplishment: Comparison of 30% PAN in [C₄mim]Br melt spun fiber properties resulting from Atlas and the single-shot apparatus with 100 µm die

A single-shot extruder based on simple plunger and barrel assembly (Alex James & Associates Fiber) appointed with a 100 µm aperture is used to melt spin PAN/[C₄mim]Br composite. The melt was pressurized through the 100 µm die by a screw-driven press. The resulting monofilament was taken up on an analogue winding unit. Winder unit take up speed was increased until the fiber became unstable and broke, then slightly reduced in speed to stability and maintained for the duration of the extrusion. The as-spun fibers were then subjected to a post-spinning draw and washing step using a set of two rollers and a draw ratio of 2x (V_r2=2V_r1) which stretched the fibers through a boiling DI water bath.

<table>
<thead>
<tr>
<th>30% PAN in C4mimBr</th>
<th>As-spun fiber</th>
<th>Washed fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atlas (1/8 inch)</td>
<td>100 micron die</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>68</td>
<td>88.3</td>
</tr>
<tr>
<td>Elastic modulus (MPa)</td>
<td>2700</td>
<td>2100</td>
</tr>
<tr>
<td>Extension (%) at break (mm/mm)</td>
<td>75</td>
<td>87.4</td>
</tr>
<tr>
<td>Diameters (µm)</td>
<td>56.8</td>
<td>36.8</td>
</tr>
</tbody>
</table>
Accomplishment: Morphology/Size of PAN Fiber Precursor (XRD)

- Structures of the as-spun PAN-[C$_4$ mim]Br and washed fibers produced with single-shot apparatus (100 µm die) were investigated by XRD.

- The removal of ILs slightly influences the crystallinity and crystal size of the PAN fibers. The as-spun fiber showed 43.9% crystallinity with 8.8 nm crystal size. Washing increased crystallinity to 69.9% and crystal size to 9.5 nm.

XRD results of as-spun PAN-[C$_4$ mim]Br and washed fibers
Accomplishment: Elemental Composition of PAN Fiber Precursor Surface by EDS

• EDS characterizes the elemental composition of the surface of the fibers.

• As spun fiber have a thin coating of ionic liquids on the surface.
  – Denoted by a bromide or chloride elemental response.

• Washed fibers show no evidence of IL on surface
  – Accounts for the smaller fiber diameters.
Accomplishment: PAN Fiber Precursors Characterization

- DSC shows the as-spun fiber exhibits a smaller, wider exotherm compared to composite.
  - DSC of washed PAN fibers elude to stabilization process

![Diagram of PAN fiber precursors]

- Carbon yield increases from the melt to over 50 wt.% for the washed PAN fibers.
  - Higher carbon yield indicates an increase in crystallinity
  - Weight loss intervals correspond to stabilization process and low temperature carbonization

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>PAN (%)</th>
<th>Melt</th>
<th>As Spun Fiber</th>
<th>Washed Fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAN</td>
<td>100</td>
<td>33.4</td>
<td>31.4</td>
<td>----</td>
</tr>
<tr>
<td>C₃Br</td>
<td>30</td>
<td>20.6</td>
<td>44.4</td>
<td>53.7</td>
</tr>
<tr>
<td>C₄Br</td>
<td>30</td>
<td>24.4</td>
<td>36.8</td>
<td>53.8</td>
</tr>
<tr>
<td>C₄Cl</td>
<td>30</td>
<td>13.1</td>
<td>29.3</td>
<td>45.0</td>
</tr>
<tr>
<td>CNBr</td>
<td>30</td>
<td>26.5</td>
<td>38.4</td>
<td>58.5</td>
</tr>
<tr>
<td>CNCl</td>
<td>30</td>
<td>21.0</td>
<td>33.1</td>
<td>52.2</td>
</tr>
</tbody>
</table>
Accomplishment: Functional Group Characterization of Fibers

- FTIR was used to analyze the functional groups of PAN through out the fiber processing.
- PAN has a dominate IR band at 2240 cm\(^{-1}\) → C≡N stretching modes.
  - Intensifies throughout the fiber spinning process.
  - C≡N neighbor distance decreases
- As-spun fibers and washed fibers have formation of 2 new IR bands.
  - 1610 cm\(^{-1}\) → C=C and C=N vibrations, N-H stretching
  - 1680 cm\(^{-1}\) → C=O bending (oxygen uptake)
- **PAN fibers are partially cyclized!**
Comparison in Mechanical Performance of As-Spun Fiber and Washed Fiber

- Tensile strength is the stress needed to break a sample.
  - Tensile strength increases with the removal of ILs from fibers.
  - Amorphous regions dominate structure in as-spun fibers

- The modulus shows the rigidity/stiffness of fibers.
  - The modulus increases with the removal of the ILs form the fibers.
  - Comparative to literature values for PAN precursors
Mechanical Performance of PAN Fiber Precursors—Elongation

- The as spun fibers are able to be stretched or elongated upwards of 100% of its original length.
  - Ionic liquids are acting as a lubricant stretching the amorphous region of the polymer chains.
- Removal of ILs result in a decrease in fiber extension.
- Fibers are in favor of stretching or drawing while in the presence of ILs.
Technology scale-up stages

Few mL to 3 L

Laboratory/ Bench Laboratory Pilot

Pilot/ Demonstration

500 L

Commercial

(adapted from AIChE, March 2015, 58)
# Preliminary Scale-up Cost Analysis

<table>
<thead>
<tr>
<th></th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
<th>Year 4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Production Runs Per Day</strong></td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td><strong>Operating Days Per Year</strong></td>
<td>280</td>
<td>280</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td><strong>Reactor Per Run, L</strong></td>
<td>20</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td><strong>Ionic Liquid Per Run, kg</strong></td>
<td>14.00</td>
<td>350.00</td>
<td>350.00</td>
<td>350.00</td>
</tr>
<tr>
<td><strong>PLA Per Run, kg</strong></td>
<td>6.00</td>
<td>150.00</td>
<td>150.00</td>
<td>150.00</td>
</tr>
<tr>
<td><strong>Ionic Liquid Loss, kg/run</strong></td>
<td>0.05</td>
<td>1.16</td>
<td>1.16</td>
<td>1.16</td>
</tr>
<tr>
<td><strong>Daily Energy Used, kWh</strong></td>
<td>100.00</td>
<td>2,500.00</td>
<td>2,500.00</td>
<td>2,500.00</td>
</tr>
<tr>
<td><strong>PLA Cost, $/kg</strong></td>
<td>$5.00</td>
<td>$3.00</td>
<td>$3.00</td>
<td>$3.00</td>
</tr>
<tr>
<td><strong>Ionic Liquid Cost, $/kg</strong></td>
<td>$10.00</td>
<td>$7.00</td>
<td>$7.00</td>
<td>$7.00</td>
</tr>
<tr>
<td><strong>Energy Cost, $/kWh</strong></td>
<td>$0.14</td>
<td>$0.14</td>
<td>$0.14</td>
<td>$0.14</td>
</tr>
<tr>
<td><strong>Ionic Liquid Replenishment Cost, $/run</strong></td>
<td>$0.46</td>
<td>$8.09</td>
<td>$8.09</td>
<td>$8.09</td>
</tr>
<tr>
<td><strong>PLA Cost, $/run</strong></td>
<td>$30.00</td>
<td>$450.00</td>
<td>$450.00</td>
<td>$450.00</td>
</tr>
<tr>
<td><strong>Daily Energy Cost, $</strong></td>
<td>$14.00</td>
<td>$350.00</td>
<td>$350.00</td>
<td>$350.00</td>
</tr>
<tr>
<td><strong>Production Per Run, kg</strong></td>
<td>5.0</td>
<td>125.0</td>
<td>125.0</td>
<td>125.0</td>
</tr>
<tr>
<td><strong>Annual PLA Cost</strong></td>
<td>$33,600.00</td>
<td>$252,000.00</td>
<td>$252,000.00</td>
<td>$252,000.00</td>
</tr>
<tr>
<td><strong>Annual Ionic Liquid Cost</strong></td>
<td>$517.44</td>
<td>$4,527.60</td>
<td>$4,527.60</td>
<td>$4,527.60</td>
</tr>
<tr>
<td><strong>Annual Energy Cost</strong></td>
<td>$15,680.00</td>
<td>$196,000.00</td>
<td>$196,000.00</td>
<td>$196,000.00</td>
</tr>
<tr>
<td><strong>Annual Production, kg</strong></td>
<td>5,600.0</td>
<td>70,000.0</td>
<td>70,000.0</td>
<td>70,000.0</td>
</tr>
<tr>
<td><strong>Annual Production Cost, $</strong></td>
<td>$38,037.44</td>
<td>$354,527.60</td>
<td>$354,527.60</td>
<td>$354,527.60</td>
</tr>
<tr>
<td><strong>Production Cost, $/kg</strong></td>
<td>$6.79</td>
<td>$5.06</td>
<td>$5.06</td>
<td>$5.06</td>
</tr>
</tbody>
</table>
Assumptions

• IL and PAN costs are @ ton scale

• The IL used for the preliminary cost analysis is \([C_{4}mim][Br]\) (the best performing IL to date)

• The operating schedule is 280 days/year

• The production cost include only the direct costs associated with PAN/IL dope preparation and IL recycle (process inputs, IL, water, PAN and energy cost)

• Optimization of all parameter at a smaller scale (20 L) is needed to get a more accurate sensitivity analysis to build a 500 L continuous fiber extrusion plant

• Operating expenses, equipment, and depreciation will be included in a final proforma
Responses to Previous Year Reviewers’ Comments

• “It is not clear how any residual IL in carbon fiber might affect its mechanical properties.”
  − The related information has been provided in slides 16 and 17.
• “Recommendations include that the project team (1) needs a comprehensive cost model, and of particular concern is the time required to wash the fiber”
  − 525 Solutions performed a comprehensive cost model in slides 18, 19, and 20. Based on 525 Solutions’ experience with fiber spinning from IL solutions, while the fiber wash step is critical to the overall process, the contact time at larger scale can be significantly decreased by increasing the washing bath temperature, or adding a counter current flow column that would allow the ILs to be washed off the fiber fast without compromising fiber’s morphology and strength.
• “The approach of the technoeconomic analysis needs to change to focus on the cost of the PAN fibers or the carbonized fiber, using traditional PAN as a baseline. Determining the cost of the IL alone does no good in determining whether using ILs results in cost savings.”
  − 525 Solutions performed a comprehensive cost model in slides 18, 19, and 20. The model include costs associated with PAN fiber production. The final proforma will include the estimated OPEX associated with the final carbon fiber production.
• “The project team should delete the TechPAN work and concentrate on melt spinning of commercial PAN.”
  − While we did not focus on TechPAN this year following the reviewer’s opinion, we still think that TechPAN work is important and would like to collaborate with Dr. Matthew Weisenberger at University of Kentucky.
Collaboration and Coordination

Project Team

Dr. Sheng Dai
Oak Ridge National Laboratory
Ionic liquids, carbon materials, and their energy-related applications

Dr. Huimin Luo
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Ionic liquids and their energy-related applications

Dr. Halie Martin
University of Tennessee-Knoxville
Postdoctoral Research Associate responsible for polymer characterization

Dr. Richard T. Mayes
Oak Ridge National Laboratory
Carbon materials and their energy-related applications

Dr. Amit Naskar
Oak Ridge National Laboratory
Carbon materials and their energy-related applications

Dr. Gabriela Gurau
525 Solutions, Inc.
Ionic liquids and their scale-up synthesis
Remaining Challenges and Barriers

• Investigation how the molecular structures of ILs dictate plasticizing interactions with PAN.
  – Ionic liquids with higher nitrile component lead to increased plasticizing interactions with PAN
    • New targeted anions including \( \text{(C(CN)}_3^- \) 

• Study how the chemical interactions of ILs with PAN can be used to control the cyclization degree in unique ladder structures
  – Demonstrate and understand the mechanical properties of as-spun fibers and fibers washed with water.

• Integrate the information gained from the above tasks to develop IL-assisted melt spinning systems.
  – Increase in the PAN concentration for melt spinning will lower the cost and increase mechanical properties
Proposed Future Work

• Remainder of FY20
  – Investigate properties of recycled ionic liquids (ORNL)
  – Investigate if IL can be used with a small amount of water or not
  – Technoeconomic analysis of IL production identifying synthetic inefficiencies and cost drivers (525 Solutions)

• Into FY21
  – Demonstrate melt spinning with recycled ionic liquids (ORNL)
  – Demonstration of filament diameter of ~20 micrometer after carbonization (ORNL)
  – Scale-up IL to >1 kg production for IL to realize anticipated decreased cost (525 Solutions and ORNL)
  – Technoeconomic analysis of scale-up (525 Solutions)

• Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.

Any proposed future work is subject to change based on funding levels
Summary: Progress and Accomplishments

• The melting temperature of PAN has been demonstrated to be suppressed by over 100 °C by the addition of ionic liquids.
  • Lower production temperatures decreases cost of carbon fiber production.

• The ability to successfully melt spin uniform and homogeneous PAN fibers.
  • Utilizing benchtop melt extruders allows us to determine the processability before scaling up.
  • Surface of fibers are smooth and without defects.

• Preliminary experiments show that the PAN fibers can be stabilized at lower temperatures with carbon yields > 50 %.

A novel plasticized melt-spinning process to replace the current solution spinning process based on nonvolatile task-specific ionic liquids

Acknowledgements