

---

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

Sheng Dai (Primary Contact), Halie Martin, Huimin Luo, Richard Mayes, and Amit Naskar  
Oak Ridge National Laboratory  
1 Bethel Valley Road  
Oak Ridge, TN 37830  
Phone: (865) 576-7307  
Email: [dais@ornl.gov](mailto:dais@ornl.gov)

DOE Manager: Bahman Habibzadeh  
Phone: (202) 287-1657  
Email: [Bahman.Habibzadeh@ee.doe.gov](mailto:Bahman.Habibzadeh@ee.doe.gov)

Subcontractor:  
525 Solutions, Inc., Tuscaloosa, Alabama

Project Start Date: July 1, 2017  
Project End Date: June 30, 2020

## Overall Objectives

- Investigate how the molecular structures of ionic liquids (ILs) dictate plasticizing interactions with polyacrylonitrile (PAN) for controlling glass transition temperatures and rheological properties of PAN-IL composites.
- Study how the chemical interactions of ILs with PAN can be used to control the cyclization degree in intermediate ladder structures.
- Integrate the information gained from the above two tasks to develop IL-assisted melt-spinning systems that demonstrate considerably enhanced production efficiencies and improved structural properties of PAN fibers.

## Fiscal Year (FY) 2018 Objectives

- Identify and synthesize task-specific ionic liquids with enhanced nitrile interactions between the PAN and that of the IL.
- Characterize the miscibility of the IL in PAN polymer spectroscopically and demonstrate >30 wt% PAN solubility in IL.

- Demonstrate the preparation of PAN-IL melts with carbon yield >50%.
- Demonstrate a >15°C decrease in PAN-IL melt temperature through differential scanning calorimetry.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

- System Weight and Volume
- System Cost
- Durability/Operability.

## Contribution to Achievement of DOE Hydrogen Storage Milestones

This project has contributed to achievement of the following DOE milestone from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan:

***Milestone 2.7: Crosscutting: Reduce the high-volume cost of high-strength carbon fiber by 25% from \$13 per pound to ~\$9 per pound. (4Q, 2020)***

Synthesizing nitrile-rich ionic liquids that will interact with PAN, decreasing the melt temperature of PAN, and allowing for melt-spinning fibers as well as the recyclability of the IL will result in a decrease in production cost of carbon fiber. Increased interactions between nitriles on IL and PAN will increase carbonization, increasing the strength of the carbon fiber.

## FY 2018 Accomplishments

- Synthesized PAN-IL melts with up to 50 wt% PAN, focusing on two cation imidazolium-based targets of 1-alkyl-methylimidazolium

---

<sup>1</sup> <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

( $C_n$ mim]) and 1-(3-cyanopropyl)-3-methylimidazolium ([MPCNIm]).

- Characterized the carbon yield of PAN-IL composites based on carbon chain length on ionic liquid, counter anion, and PAN concentration. Preliminary results indicated that after removing the IL from the composite, the carbon yield increased by about 20% compared to the original melt composite.
- PAN-IL composites suppressed the melting temperature of PAN by 20°C when compared to neat PAN. Composites with 30 wt% PAN showed the greatest melting point depression of  $\geq 35^\circ\text{C}$ .

## INTRODUCTION

The production of high-strength carbon fibers is an energy-intensive process, and thus, it is costly. One significant cost yet to be mitigated involves the production of polyacrylonitrile (PAN) fibers prior to carbon fiber production. The current technology for PAN fiber production involves wet spinning [1]. In this process, the fibers are dissolved and fed through coagulation and rinse baths to remove the solvent and to produce fibers. This intensive process is inherently inefficient [2], which has a direct correlation to the costs of hydrogen storage systems, where the carbon fiber cost is nearly 75% of the total system cost [3]. Melt spinning the PAN into fibers would allow for significant reductions of production cost, estimated at a nearly 50% reduction of overall cost per pound [3]. This cost would be reduced through decreased capital investments, utilities, and labor, while exhibiting a 3-times-faster spinning speed [2]. However, melt-spinning virgin PAN and many PAN copolymers used to produce high-strength carbon fibers is impossible due to polymer degradation.

It is well known that the strong dipole-dipole interaction between nitrile groups in PAN leads to its degradation before melting, which makes cost-efficient melt processing impossible. There have been exciting developments in a new class of chemicals called ionic liquids, which consist of an anion associated with an organic cation, and these materials have enormous potential to act as nonvolatile “green chemistry” solvents for a broad range of chemical processes [4,5]. The ability to synthesize highly nitrile-rich ionic liquids—which have negligible vapor pressure, exhibit low toxicity, and are carbon generators upon carbonization—makes using ionic liquids in the melt-spinning production of high-strength carbon fibers an attractive alternative production route. If both the cation and anion of the IL can be functionalized with nitriles, then the interactions with PAN increase and will decrease the melting temperature. Thus, this allows the melt-spinning of PAN, which results in decreased production costs vital to the necessary decrease in hydrogen storage costs.

## APPROACH

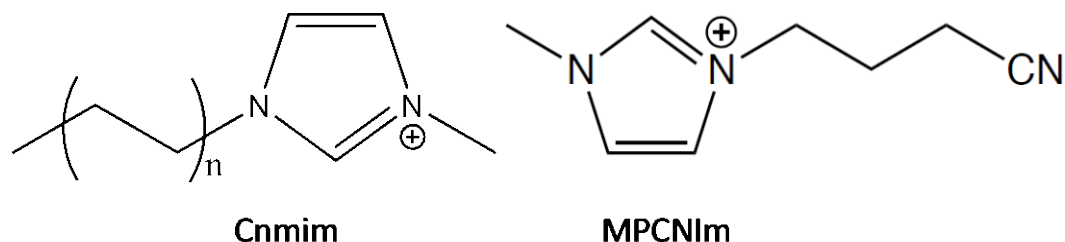
We capitalize on the vast knowledge of carbon-fiber processing at Oak Ridge National Laboratory (ORNL) including the ORNL Carbon Fiber Technology Facility (CFTF), which is equipped with both small- and large-scale fiber-spinning and carbon-fiber conversion capabilities. This will be coupled with our multi-functional IL synthesis experience and capabilities that are well-known worldwide. Our emergent plasticized melt-spinning process has the potential to dramatically cut the cost and energy associated with producing PAN-based carbon fibers. Developing the new generation of PAN-fiber melt-spinning systems represents a vital step toward the efficient precursor development for low-cost, high-strength carbon fibers used in composite overwrapped pressure vessel applications. And it will ensure that the United States will maintain a technological lead in developing and deploying advanced energy technologies.

## RESULTS

During FY 2018, we focused on synthesizing and characterizing new imidazolium-based ionic liquids for the formation of PAN melt composites:

- The two main cations for the ionic liquids under investigation were 1-alkyl-methylimidazolium ([C<sub>n</sub>mim]) and 1-(3-cyanopropyl)-3-methylimidazolium ([MPCNIm]) (Figure 1). The ability to adjust the carbon alkyl chain length and nitrile group on the cation allows for further investigation into a structure-property relationship between the polymer and the IL. Ionic liquids containing a variety of counter anions were used including bromide (Br<sup>-</sup>), chloride (Cl<sup>-</sup>), acetate (OAc<sup>-</sup>), and dicyanamide (DCA<sup>-</sup>). However, the acetate and dicyanamide anions did not form melts.
- The effect of carbon alkyl chain length and nitrile groups on cations were monitored in our PAN-IL melt investigation. Increasing the carbon alkyl chain length of the IL increased the time and energy needed to form a continuous melt with PAN.

- Melts were formed with different percentages of PAN in ILs, with PAN weight percentages ranging from 20 wt% to 50 wt%. Incorporating a lower weight percentage of IL plasticizer is an important achievement because ILs have the potential to be a cost driver while also potentially resulting in deleterious effects in the mechanical properties.



**Figure 1. Chemical structure of two ionic liquid cations**

The second achieved milestone in FY 2018 was synthesizing PAN-IL composites with carbon yields greater than 50%. The results are listed in Table 1.

**Table 1. Thermophysical Characterization of PAN-IL Composites**

| Ionic Liquid            | PAN (%) | Physical Appearance | Carbon Yield (%) |               | Melting Temperature $T_m$ (°C) |
|-------------------------|---------|---------------------|------------------|---------------|--------------------------------|
|                         |         |                     | Original         | After Washing |                                |
| ---                     | 100     | white powder        | 33.4             | ---           | 325                            |
| [C <sub>2</sub> mim]Br  | 20.3    | light yellow gel    | 23.9             |               | 292.02                         |
|                         | 30.0    | light yellow gel    | 20.6             | 61.5          | 311.47                         |
|                         | 46.8    | light yellow gel    | 36.2             |               | 306.83                         |
|                         | 50.7    | black melt          | 30.1             |               | 298.05                         |
| [C <sub>4</sub> mim]Br  | 19.9    | yellow gel          | 15.7             |               | 308.82                         |
|                         | 30.0    | dark brown gel      | 24.4             | 59.4          | 303.20                         |
|                         | 46.5    | dark brown melt     | 35.0             |               | 302.94                         |
|                         | 50.4    | black melt          | 39.2             |               | 297.29                         |
| [C <sub>8</sub> mim]Br  | 20.0    | brown gel           | 13.0             |               | 313.18                         |
|                         | 25.0    | brown gel           | 15.7             |               | 310.62                         |
|                         | 30.0    | brown gel           | 19.0             |               | 309.34                         |
| [C <sub>10</sub> mim]Br | 20.0    | yellow gel          | 10.4             |               | 307.38                         |
|                         | 30.0    | yellow gel          | 18.7             |               | 306.66                         |
| [C <sub>4</sub> mim]Cl  | 20.5    | brown gel           | 8.33             |               | 303.79                         |
|                         | 29.9    | yellow gel          | 13.1             | 56.1          | 305.60                         |
|                         | 45.6    | dark brown melts    | 26.1             |               | 298.68                         |
|                         | 50.5    | black melt          | 28.8             |               | 309.63                         |
| [MPCNIm]Br              | 20.0    | light yellow gel    | 15.3             |               | 312.13                         |
|                         | 27.4    | yellow melt         | 23.9             |               | 310.09                         |
|                         | 30.0    | yellow melt         | 26.3             | 61.4          |                                |
|                         | 33.4    | brown melts         | 26.5             |               | 308.35                         |
|                         | 49.0    | brown powder        | 41.7             |               | 295.14                         |
| [MPCNIm]Cl              | 30.0    | yellow melt         | 21.1             | 52.3          | 270.24                         |

- Using thermal gravimetric analysis (TGA), we found that the carbon yield for PAN-IL composites was higher from IL with shorter carbon alkyl chain lengths on the substituents. The carbon yield was generally higher for composites where the IL contained a nitrile substituent.

- The carbon yield was higher for ILs containing a bromide counter anion instead of a chloride when containing the same carbon alkyl chain lengths. A higher carbon yield is correlated to a high-strength carbon fiber.
- The recyclability of the ionic liquids was also monitored. The PAN carbon yield after washing the composite increases by 20% compared to the PAN-IL melt, as shown in Figure 2. The recycling of IL through sample washing of the composites increases the economical prospect of using ILs in a plasticized melt-spinning process for PAN fiber production.

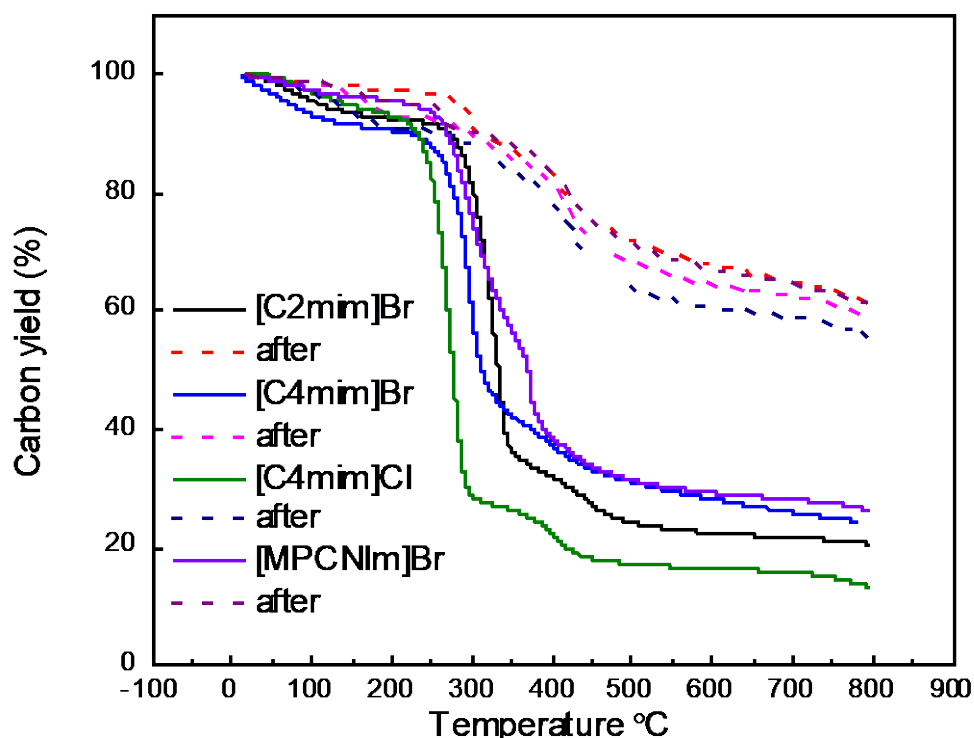


Figure 2. TGA plots of ~30 wt% PAN in IL melts before (solid lines) and after contact with water (broken lines)

Ionic liquids act as a plasticizer to suppress the melting temperature of PAN. During FY 2018, we monitored these transitions through differential scanning calorimetry (DSC), as shown in Table 1 and Figure 3.

- The melting temperature of pure PAN is at about 325°C [6]. However, this results in pure PAN being unprocessable in the melt because the polymer chains crosslink at a temperature lower than melting.
- Ionic liquids suppress the reactions between PAN nitriles at elevated temperatures. This is observed in the melting temperatures for PAN-IL composites, which are  $\geq 20^\circ\text{C}$  lower than pure PAN. The decrease in the melting temperature should allow PAN fibers to be melt-spun.
- In general, as the concentration of PAN increases in the composite, the melting temperature decreases, as shown in Figure 4 for composites containing [C<sub>4</sub>mim]Cl.
- The lower melting temperatures will lower the amount of energy necessary to process these materials into fibers.

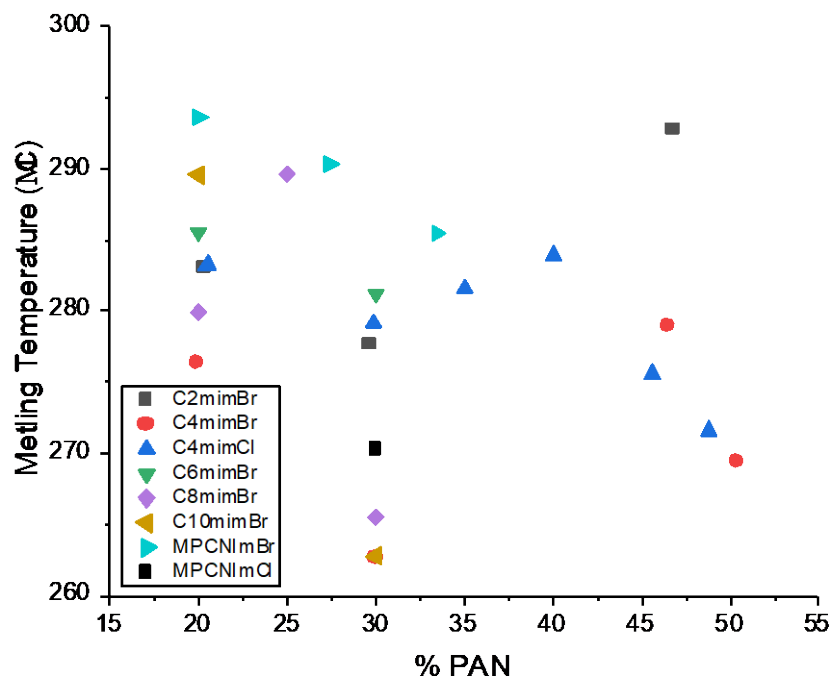


Figure 3. Melting temperature of PAN-IL composites

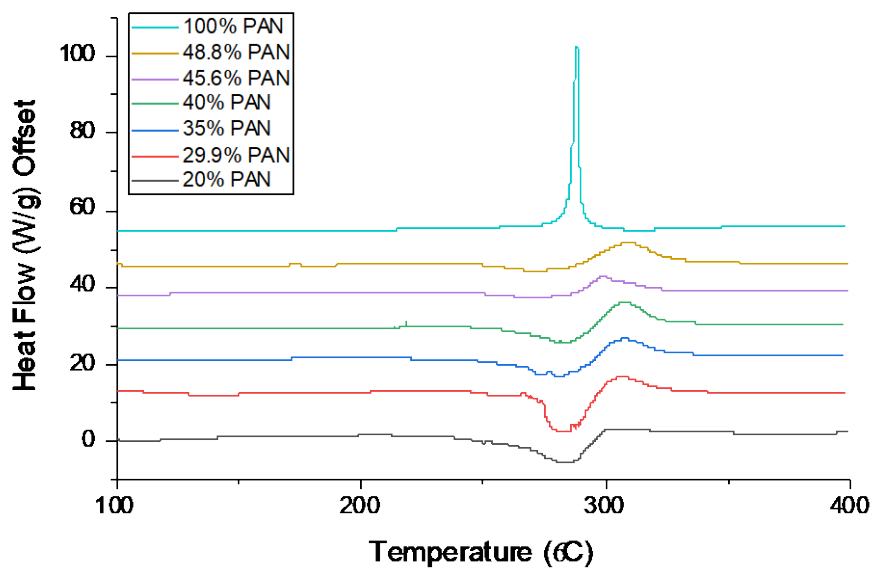


Figure 4. DSC characterization of PAN and PAN-[C4mim]Cl composites

## CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2018, this project began with the synthesis and thermophysical characterization of the targeted task-specific ionic liquids, focusing on two imidazolium cations including 1-alkyl-methylimidazolium ([C<sub>n</sub>mim]) and 1-(3-cyanopropyl)-3-methylimidazolium ([MPCNIm]). We focused on the miscibility of PAN with various ionic liquids and determined that we can produce composites with up to 50 wt% PAN and form uniform composite melts. We recorded the IL decomposition temperatures, carbon-yield productions, and melting temperatures of the PAN-IL composites. We observed that the carbon yield increased after the composite had been washed, similar to the process that the PAN fiber will go through after spinning; furthermore, the melting temperatures of the composites were lower than that of the pure PAN powder.

Studies for FY 2019 will include the following:

- Work with a subcontractor to identify the IL for scale-up and optimization synthesis based on melting temperature and rheology studies of the composite.
- Demonstrate the ability to melt-spin PAN fibers based on IL and characterize the fibers using DSC, TGA, and scanning electron microscopy.
- Perform a techno-economic analysis for scale-up of the IL production.
- Demonstrate the tensile modulus and tensile strength of melt-spun PAN fibers before and after washing.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. S. Dai, “Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids,” presented at 2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, Washington, D.C., June 14, 2018.

## REFERENCES

1. T.-Y. Wang, H.-C. Chang, Y.-T. Chiu, and J.-L. Tsai, “The Index of Dry-Jet Wet Spinning for Polyacrylonitrile Precursor Fibers,” *Journal of Applied Polymer Science* 132 (2015): 41265.
2. B.A. Newcomb, “Processing, Structure, and Properties of Carbon Fibers,” *Compos. Part A* 91 (2016): 262–282.
3. C.D. Warren and F.L. Paulauskas, “Development of Low-Cost, High-Strength Commercial Textile Precursor (PAN-MA),” In *DOE FCTO Annual Progress Report* (2014).
4. Z. Ma, J.H. Yu, and S. Dai, “Preparation of Inorganic Materials Using Ionic Liquids,” *Advanced Materials* 22 (2010): 261–285.
5. H. Wang, G. Gurau, and R.D. Rogers, “Ionic Liquid Processing of Cellulose,” *Chemical Society Reviews* 41 (2012): 1519–1537.
6. A.K. Gupta, D.K. Paliwal, and P. Bajaj, “Melting Behavior of Acrylonitrile Polymers,” *J. Appl. Polym. Sci.* 70, no. 13 (1998): 2703–2709.