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

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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) 2019 Objectives

- Investigate thermophysical properties of PAN-IL composites.
- Optimize the IL concentration in the PAN polymer for minimal IL content while still suppressing the melt temperature (T_m) allowing melt spinning of the composite.

- Target IL-PAN composite synthetic optimization and small-scale melt-spinning process optimization.
- Complete preliminary techno-economic analysis of IL production identifying synthetic inefficiencies and cost drivers.

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 Plan¹:

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

Technical Targets

This project is investigating how the molecular structures of ILs dictate plasticizing interactions with PAN for controlling glass transition temperatures and rheological properties of PAN-IL composites and studying how the chemical interactions of ILs with PAN can be used to control the cyclization degree in intermediate ladder structures. Insights gained from this project can provide a more detailed and fundamental structure–property relationships for melt spinning and production of PAN fibers.

- A 25°C decrease in the glass transition temperature, T_g
- A 15°C decrease in melt temperature, T_m
- A carbon yield >45%.

FY 2019 Accomplishments

- The melt spinning of PAN fibers has been demonstrated with preliminary experiments using a benchtop laboratory mixing extruder (LME).

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

- The fibers exhibited uniform cross sections, free from micro-voids, with smooth surface morphologies.
- The structural evolution from PAN powder to PAN-IL composite melts to PAN fibers as a function of ILs was investigated.
- A preliminary techno-economic analysis of IL production identifying synthetic inefficiencies and cost drivers was completed.

INTRODUCTION

The production of high-strength carbon fibers is an energy intensive, and thus costly, process. One significant cost that has yet to be mitigated involves the production of 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 produce fibers. This intensive process is inherently inefficient [2]. This 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 production cost reductions, estimated at near 50% overall cost per pound reduction [3]. This would be reduced through decreased capital investments, utilities, and labor all 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 the cost-efficient melt processing impossible. There have been exciting developments in a new class of chemicals called ionic liquids, consisting of an anion associated with an organic cation, and these materials have enormous potential to act as nonvolatile “green solvents” for a broad range of chemical processes [4, 5]. The ability to synthesize highly nitrile-rich ionic liquids, with negligible vapor pressure, that exhibit low toxicity and are carbon generators upon carbonization makes utilizing 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, the interaction with PAN increases, which will decrease the melting temperature allowing for the melt-spinning of PAN, resulting in decreased production costs vital to the necessary decrease in hydrogen storage costs.

During Year 2 of this project, three main tasks have been conducted. The melt spinning of PAN fibers has been demonstrated with preliminary experiments using a benchtop LME. Utilizing the LME allows us to determine the processability of the composites before scaling up to an industrial melt spinner. The as-spun fibers exhibited uniform cross sections, free from micro-voids, with smooth surface morphologies. The structural evolution from PAN powder to PAN-IL composite melts to PAN fibers as a function of ILs has been investigated utilizing differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Initial cost assessment for scale-up of the IL production has been performed. Our research can provide a foundation to understand the influence of ILs on melt spinning PAN fibers and give the guidelines for the more cost/energy efficient production of PAN carbon fibers.

APPROACH

We will capitalize on the vast knowledge of carbon fiber processing at Oak Ridge National Laboratory (ORNL) including the ORNL Carbon Fiber Technology Facility, 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 the production of PAN-based carbon fibers. The development of 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 will ensure the United States maintains a technological lead in developing and deploying advanced energy technologies.

RESULTS

Thermophysical Characterization of ILs, PAN, and PAN-IL Composites

We synthesized ILs 1-ropyl-3-methylimidazolium bromide ([C₃mim]Br), 1-butyl-3-methylimidazolium bromide ([C₄mim]Br), 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl), 1-(3-cyanopropyl)-3-methylimidazolium bromide ([MPCNIm]Br), and 1-(3-cyanopropyl)-3-methylimidazolium chloride ([MPCNIm]Cl) in our laboratory. Their structures can be found in Figure 1.

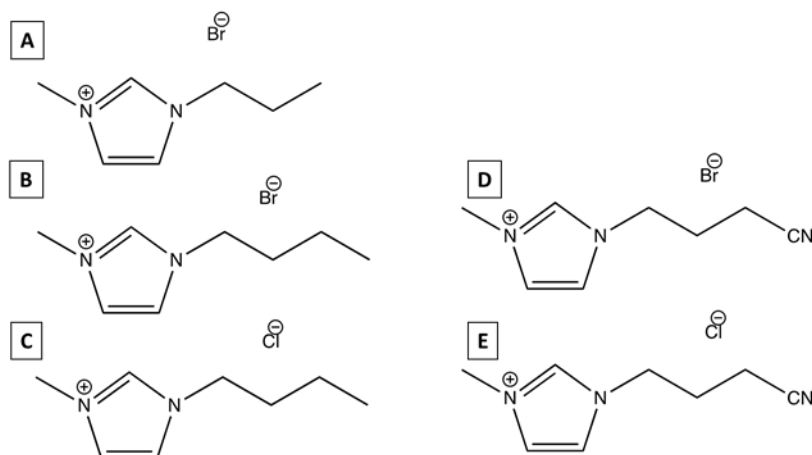


Figure 1. Structure of ionic liquids (A) [C₃mim]Br, (B) [C₄mim]Br, (C) [C₄mim]Cl, (D) [MPCNIm]Br, and (E) [MPCNIm]Cl

It is necessary to understand the plasticization effects the ILs have on PAN during the composite stage in order to determine the melt spinning processability of PAN into fibers. The glass transition temperature (T_g) and melting temperature (T_m) for 30 wt % PAN in five ILs can be obtained from DSC thermographs and are listed in Table 1. The ILs have depressed the T_m of PAN composite melts by more than 150°C and the T_g up to 35°C. As shown Table 1, as the plasticizing ionic liquid becomes bulkier or larger, by either an increase in carbon chain length or a nitrile on the end of the alkyl chain, the T_m and T_g are depressed less when compared to a smaller alkyl chain. However, when the ionic liquid cation is the same, the ionic liquid with a Cl⁻ has lower T_g and T_m compared to the same cation with a Br⁻. For example, for composites with 30 wt % PAN in [C₄mim]Cl the T_m is 108.3°C and in [C₄mim]Br the T_m is 139.0°C. This could be attributed to two general ideas: the chloride anion is smaller than the bromide anion, and the chloride anion has a larger electronegativity compared to bromide. It has been hypothesized that with the addition of ILs into a PAN matrix, the ILs will create more disorder between the polymer chains [6]⁶ In Table 1, the heat of fusion (ΔH_f) for ILs containing Cl⁻ is larger than Br⁻ with the same corresponding cation. The smaller ΔH_f , such as for 30 wt % PAN in [C₃mim]Br, corresponds to a higher disordered state as a result of the IL penetrating into the crystalline domains of PAN and disrupting chain alignment [6, 7]. These DSC results suggested that PAN precursor fiber should be easily melt-spun at low temperatures for the production of carbon fiber precursors.

Table 1. DSC Data for Five PAN Composite Melts Containing 30 wt % PAN

Ionic Liquid	T_g (°C)	T_m (°C)	$\Delta T = T_f - T_i$ (°C)	ΔH_f (J/g)
[C ₃ mim]Br	72.1	107.6	43.9	1.12
[C ₄ mim]Br	82.1	138.4	39.6	6.38
[C ₄ mim]Cl	76.6	108.3	69.9	10.2
[MPCNIm]Br	103.2	157.2	85.6	6.97
[MPCNIm]Cl	85.38	150.6	76.7	18.1

Preliminary Melt Spinning Experiments

An Atlas LME was used to perform preliminary melt spinning experiments. The LME uses rotational shearing and provides extensive mixing of the PAN-IL composites before extrusion. The LME has a maximum working temperature of 400°C, variable rotational speed of 5–260 rpm, and an orifice with a size of 1/8 in. The temperature of the rotor and orifice header are controlled separately through two PIDs. Combining the LME

with the take-up system (TUS), we can spool and slightly stretch the fiber during formation. The TUS has a maximum take-up speed of 250 ft/min. The LME is a beneficial preliminary tool because it can process fibers with a small sample starting size (~3 grams). For initial experiments, the rotor temperature was set to 150°C, the header temperature was set to 160°C, and rotational speed was set to 90 rpm. When the melted polymer composite is extruded from the orifice, also known as the extrudate, the polymer was picked up using tweezers and wrapped around the take-up spool. The take-up speed for spinning of the PAN precursor was approximately 60 ft/min. The five PAN-IL composites that were tested all contained 30 wt % of PAN. The ILs chosen for the initial composites included [C₃mim]Br, [C₄mim]Br, [C₄mim]Cl, [MPCNIm]Br, and [MPCNIm]Cl. The PAN fibers from these composites are shown in Figure 2.

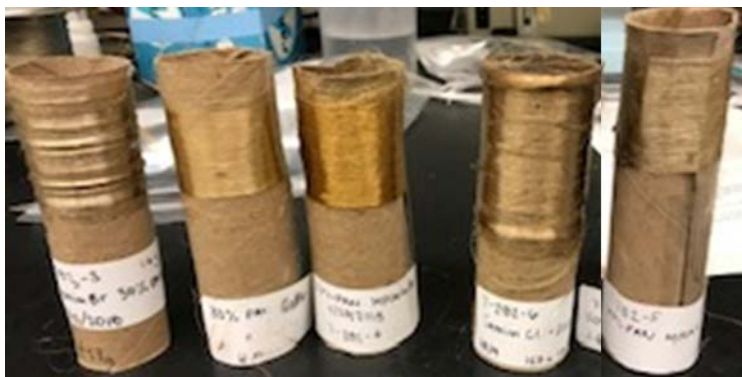


Figure 2. Melt spun PAN fiber from PAN-IL composites containing [C₃mim]Br, [C₄mim]Br, [MPCNIm]Br, [C₄mim]Cl, and [MPCNIm]Cl in order from left to right

Characterization of Melt Spun PAN Fibers

The as-spun PAN fiber precursors are shown in Figure 2 and the diameters of the fibers are listed in Table 2. Samples sizes for initial spinning experiments were approximately 3 grams, and we were able to produce 60% of the original composite melt in fiber form. After the fibers were spun, both the as-spun fibers and fibers contacted with water were characterized by using SEM, DSC, and TGA. SEM provided the characterization of the surface morphology and the cross section of the fibers. Figure 3 shows the morphology and cross section of the PAN fibers from a composite containing 30 wt % PAN in [C₄mim]Br. In Figure 3A, the as-spun PAN-[C₄mim]Br fibers exhibit an overall smooth surface morphology. Commercially available PAN fibers, typically manufactured through solution spinning, exhibit rough surface morphologies where the surfaces are often deformed with long, rough grooves or striations. Figure 3B shows the circular cross sections of the as-spun fiber. This is a major achievement as most commercially processed solution-spun PAN fibers exhibit a kidney bean shape or have a skin-core structure. A symmetric cross section increases the prospect of the fiber exhibiting a lower porosity, which would increase the tensile strength of the fibers. The surface morphology was also analyzed after removing the residual ionic liquid from the PAN fiber. In Figure 3C and 3D, the surfaces of the washed fibers are noted to exhibit more charging effects than the as-spun fibers as shown by the increase in white areas on the fiber surface in the images. This is a result of the IL having an anti-charge effect on the fibers. After washing, the fibers still exhibit a relatively smooth surface and no voids form within the core of the fibers. The washing of the fibers does not generate an increase in inhomogeneities on the surface or within the cross section, which could potentially result in enhanced mechanical properties of the final carbon fibers. The removal of the ILs does not have a large effect on the size of the PAN fibers, as seen in Table 2. Considering the very rudimentary method employed for fiber generation and lack of precise tensioning during pulling the fiber, formation of homogeneous fibers without void is a significant accomplishment. The fiber diameter variation can be minimized by deployment of a scaled-up fiber spinning process. This concludes that the removal of the ionic liquids does not have an impact on the integrity of the fibers.

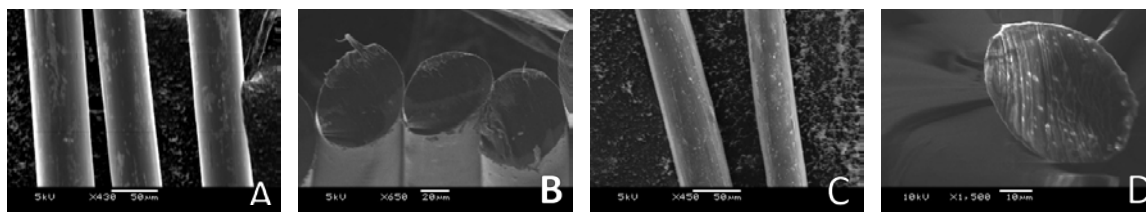


Figure 3. SEM images of (A) as-spun PAN fiber from [C₄mim]Br, (B) cross section of as-spun fiber, (C) PAN fiber after washing, and (D) cross section of washed fiber

Table 2. Diameters of Melt-Spun PAN Fibers

Fiber Sample	As-Spun Fiber Diameter (μm)	Washed Fiber Diameter (μm)
[C ₃ mim]Br	56.2 \pm 1.6	53.4 \pm 7.6
[C ₄ mim]Br	56.8 \pm 2.0	45.6 \pm 7.9
[C ₄ mim]Cl	54.7 \pm 0.8	45.3 \pm 8.7
[MPCNIm]Br	59.6 \pm 2.5	47.9 \pm 14.1
[MPCNIm]Cl	53.4 \pm 1.7	48.6 \pm 10.4

Secondary thermophysical characterization experiments were conducted to confirm and verify the successful realignment of polymer chains during the spinning extrusion and drawing phase. The top figure of Figure 4 shows that the as-spun PAN fiber has a smaller exotherm at 300°C, and lower total heat evolved over a larger temperature range, compared to the PAN-[C₄mim]Br composite melt. The decrease in exotherm size indicates that the PAN fibers are in favor of a subsequent oxidative stabilization process [7, 8]. The cyclization exotherms for the as-spun fibers appear over a larger range compared to the composite melts, for example, in the top figure of Figure 4, the as-spun fiber exotherm ranges from 289°C to 345°C (a range of 56°C) compared to the composite melt exotherm range of 296°C to 333°C (a range of 37°C). The increased range of the exotherm for the as-spun fibers is more desirable than the smaller range or intense exotherms of the composite melts because there is reduced chance for damage to the fibers during the oxidation process [8]. Before the exotherm occurs, there is a small endotherm for the as-spun fibers. This endotherm is a result of the ionic liquid present within the fibers and its decomposition. After the ILs are removed from the PAN fiber precursors (by contacting with water), the exothermic performances have an even lower onset temperature (~215°C), lower peak temperature (~262°C), and broader DSC exotherm (~215°C to 305°C) compared to the as-spun fibers. The washed fibers generally have a lower heat released (ΔH), which implies that the stabilization time required for the oxidation of the fibers can be reduced [7, 8]. This process is where the polymer chains begin to crosslink and form the offset ladder intermediate structure, a characteristic for PAN fibers, where the PAN undergoes a transition from linear polymer chains into a more rigid, stable ladder structure. Initially the amorphous region of the PAN stabilizes followed by the oriented crystalline regions.

Understanding the thermal stability at different phases of the PAN fiber precursor stabilization process can illuminate the evolution of the carbon yield. TGA was performed on the as-spun PAN fiber precursors and after the fiber precursors had been contacted with water. TGA plots for PAN-[C₄mim]Br samples are shown in the bottom figure of Figure 4. Initially, the IL, the 30 wt % PAN in [C₄mim]Br melts, and the as-spun fiber have an obvious weight loss around 100°C from the vaporization of water. The IL, PAN composite melt, and as-spun fiber experience a large weight loss at approximately 300°C from the thermal degradation of the IL. These two characteristic weight losses (100°C and 300°C) are not seen for the washed fiber as most of the water and the IL are removed. It is also noted that the carbon yield increases from the composite melt (24.3%) to the as-spun fiber (36.8%) and to the washed fiber (53.8%). The TGA data for the four other PAN-IL composites are listed in Table 3. The increase in the carbon yield is a direct result of the polymer chains having a higher content of oriented crystalline regions forming stronger ladder structures during stabilization. ILs containing a bromide anion result in a higher carbon yield for PAN at all stages compared to chloride-containing IL when the ILs have the same cation. An increase in the carbon yield will result in better

mechanical properties of the carbon fiber because there will be less non-carbon atoms to remove during the carbonization step.

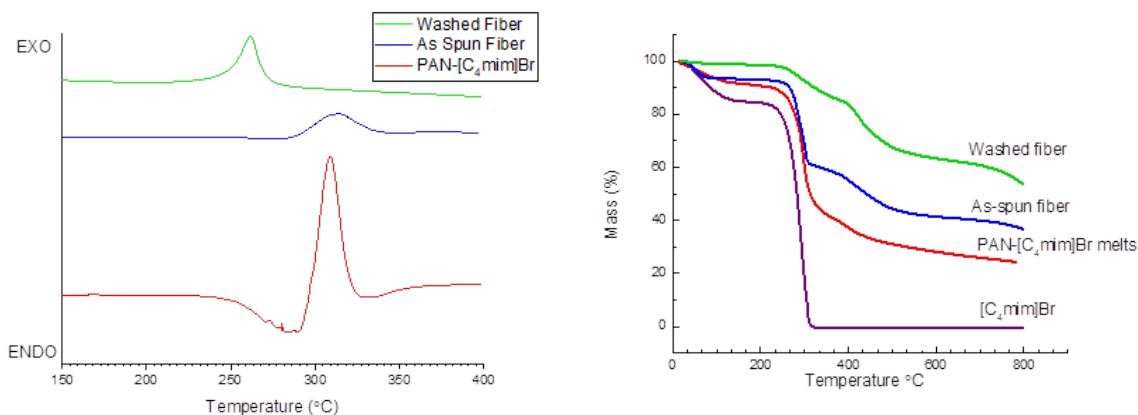


Figure 4. (Left) DSC curves for PAN-[C₄mim]Br composite melt (red), as-spun fiber (blue), and washed PAN fiber (green). (Once) TGA curves of [C₄mim]Br (purple), PAN-[C₄mim]Br composite melt (red), as spun PAN fiber (blue), and washed PAN fiber (green).

Table 3. Carbon Yield from TGA Curves for the PAN-IL Melts, As-Spun Fibers, and Washed Fibers

Fiber Sample	Melt	As-Spun Fiber	Washed Fiber
[C ₃ mim]Br	20.3	44.4	53.7
[C ₄ mim]Br	24.4	36.8	53.8
[C ₄ mim]Cl	13.1	29.3	45.0
[MPCNIm]Br	26.5	38.4	58.5
[MPCNIm]Cl	21.0	33.1	52.2

Techno-Economic Analysis of the Ionic Liquid Production

Cost drivers in the IL synthesis have been identified through a techno-economic analysis of IL production. Scale-up of the IL synthesis through minimization of the identified cost drivers was conducted to facilitate the melt-spinning task. The techno-economic analysis of IL production is summarized in Table 4.

Table 4. Techno-Economic Analysis of IL Production

IL Statistical Mixture Synthesis	Raw Material	Cost per metric ton	Cost per kg
One-pot synthesis	Formaldehyde (37% aqueous solution)	\$400 (Alibaba)	\$0.251
	2-chloroethylamine	\$450 (Alibaba)	\$0.271
	Methylamine (40% aqueous solution)	\$1,935 (molbase)	\$1.166
	Hydrochloric acid (37% aqueous solution)	\$88 (ICIS)	\$0.535
	Glyoxal (40% aqueous solution)	\$1,000 (Alibaba)	\$1.122
Purification (optional)	Ethyl acetate	\$978 (molbase)	\$1.210
Nitrile functionalization	Sodium cyanide	\$2,450 (Kemcore)	\$0.171
Total			\$3.516

CONCLUSIONS AND UPCOMING ACTIVITIES

In FY 2019, homogeneous melt-spun PAN fibers were prepared utilizing a selection of ILs. The fibers exhibited uniform cross sections, free from micro-voids, with smooth surface morphologies. The structural evolution from PAN powder to PAN-IL composite melts to PAN fibers as a function of ILs was investigated

utilizing DSC, TGA, and SEM. The removal of the IL from the fibers showed that the linear PAN polymer chains were partially converted into cyclized ladder structures through the formation of C=N, =NH, and C=C bonds. Scale-up of the IL synthesis was evaluated with techno-economic analysis.

In FY 2020, scale-up of the IL synthesis through minimization of the identified cost drivers will be conducted to facilitate the melt-spinning task. Cost drivers in the ionic liquid synthesis will be identified through a techno-economic analysis of ionic liquid production. We will continue to characterize the as-spun and washed PAN fibers using DSC, TGA, SEM, and Fourier transform infrared spectroscopy. The investigations on tensile modulus and tensile strength of as-spun and washed PAN fibers will also continue.

FY 2019 PUBLICATIONS/PRESENTATIONS

- S. Dai: 2020 Max Bredig Award in Molten Salt and Ionic Liquid Chemistry from the Physical & Analytical Electrochemistry Division of the Electrochemical Society
- S. Dai: 2019 Materials Research Society Fellow

FY 2019 PUBLICATIONS/PRESENTATIONS

1. S. Dai, “Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids,” presentation at 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting (AMR), Washington, D.C., May 1, 2019.
2. H. Martin, “Influence of Ionic Liquid Structure on the Melt Processability of Polyacrylonitrile Based Carbon Fiber Precursor,” oral presentation at Carbon Fibers and their Composites and Applications Symposium, Oak Ridge, TN, July 11–12, 2019.
3. H.J. Martin, H.M. Luo, and S. Dai, “Influence of Ionic Liquid Structure on the Formation of Melt Spun PAN Fibers” (manuscript in preparation).

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