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Final Report: Rheological Characterization of Polymer-Based Materials and Ionic Liquids at Xavier University of Louisiana

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6. AUTHORS

5d. PROJECT NUMBER

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Xavier University of Louisiana
1 Drexel Drive

New Orleans, LA 70125 -1098

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			Asem Abdulahad
UU	UU	UU	UU		19b. TELEPHONE NUMBER
					504-520-5405

RPPR Final Report
as of 07-Sep-2022

Agency Code: 21XD

Proposal Number: 78020MSREP **Agreement Number: W911NF-21-1-0212**
INVESTIGATOR(S):

Name: Asem Abdulahad
Email: aabdulah@xula.edu
Phone Number: 5045205405
Principal: Y

Organization: **Xavier University of Louisiana**
Address: 1 Drexel Drive, New Orleans, LA 701251098
Country: USA
DUNS Number: 020857876 EIN: 720635884

Report Date: 25-Jul-2022 Date Received: 19-Aug-2022

Final Report for Period Beginning 26-Apr-2021 and Ending 25-Apr-2022
Title: Rheological Characterization of Polymer-Based Materials and Ionic Liquids at Xavier University of Louisiana
Begin Performance Period: 26-Apr-2021 **End Performance Period:** 25-Apr-2022
Report Term: 0-Other

Submitted By: Asem Abdulahad Email: aabdulah@xula.edu
Phone: (504) 520-5405

STEM Degrees: 4 **STEM Participants:** 16

Major Goals: The rheological characterization and differential scanning calorimetry instrumentation purchased through this award were used to accomplish the following goals.

Project goal 1: determine the structure-property relationships of solid polymer electrolytes based on phosphonium ionenes for lithium ion batteries.

Project goal 2: optimize the interfacial compatibility in polymer-ceramic solid polymer electrolytes for lithium ion batteries.

Project goal 3: describe the temperature dependent molecular-level organization of imidazolium-based ionic liquids.

Project goal 4: teaching polymer chemistry through course-based research projects on the study of structure-property relationships of electroactive hydrogels.

Accomplishments: As indicated in the interim report, the instrument purchase was completed on June 16, 2021. The instrumentation was received from the manufacturer by July 15, 2021 and installation was completed over two visits from installation and service technicians from the manufacturer. The installation was completed by the second visit which was August 16, 2021.

Project goal 1: determine the structure-property relationships of solid polymer electrolytes based on phosphonium ionenes for lithium ion batteries

- Four different PEG-segmented phosphonium ionenes were synthesized with 10, 20, 30, and 40 mol % PEG incorporated into the ionene backbone and characterized for their thermal properties by DSC and their viscoelastic behavior using rheology. The properties of these copolymers were compared to a non-segmented phosphonium ionene (4P12). Thermal analysis using the DSC instrumentation revealed that the PEG-segmented phosphonium ionenes are most likely block copolymers that exhibit microscale phase separation. As shown in the uploaded document, increasing the mol % PEG incorporation increases the crystallinity and also decreases the overall glass transition temperature of the copolymer. Rheological characterization using a temperature ramp measurement along with analysis by time-temperature superposition shows significant evidence of a lower disorder-order transition within the copolymers that has not been previously reported for segmented copolymers.

Project goal 2: optimize the interfacial compatibility in polymer-ceramic solid polymer electrolytes for lithium ion batteries

- This project is still ongoing. Significant delays resulting from COVID-19 as well as Hurricane Ida during Fall 2021 delayed the preparation of the proposed solid polymer electrolytes. Training opportunities for the dielectric spectroscopy accessory also resulted in significant delays. Additionally, the initially proposed electrorheology accessory was not purchased due to an approved change in our purchased instrumentation. The funds initially budgeted for the electrorheology accessory and several measurement geometries was used to purchase the differential scanning calorimeter, which would support more projects. Our first data set from dielectric relaxation spectroscopy was obtained during July 2022, though we are unable to make draw conclusions without further study. This preliminary data is shown in the file accompanying file attachment.

Project goal 3: describe the temperature dependent molecular-level organization of imidazolium-based ionic liquids

- This project focused on describing a spectroscopic phenomenon observed in an FTIR spectroscopic study on imidazolium ionic liquids. Drs. Dutta, Riley, and Abdulahad published a manuscript that details the reorganization of 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]). FTIR spectroscopy showed an anomalous, temperature dependent red-shift in the FTIR spectrum of [EMIM][BF4]. Using differential scanning calorimetry, we were able to confirm that this shift was a result of an endothermic transition that is likely a result of molecular-level organization in the [EMIM][BF4] ionic liquid. Computational modeling provides insight into possible molecular configurations of the ionic liquid during the molecular reorganization.

Project goal 4: teaching polymer chemistry through course-based research projects on the study of structure-property relationships of electroactive hydrogels

- This project goal was modified due to a significant change in the purchased instrumentation. As stated previously (see Project goal 2), funds initially budgeted for the electrorheology accessory and several measurement geometries was used to purchase the differential scanning calorimeter, which would support more projects. In the absence of the electro-rheology measurements, we adapted a different educational research project that focused on the microencapsulation of essential oils within copolymers prepared by emulsion polymerization. Using differential scanning calorimetry, we were able to show successful microencapsulation of the essential oils. This work was disseminated at the Undergraduate Research Symposium during the 2022 ACS National Conference in San Diego, CA. This work was also presented during a special session on inclusive teaching at the BCCE 2022 conference in August 2022 at Purdue University.

Training Opportunities: Nothing to Report

Results Dissemination: Published journal manuscript:

Tran, L.; Rush, K.; Marzette, J.; Edmonds-Andrews, G.; Bennett, T.; Abdulahad, A.; Riley, K. E.; Dutta, S. Striking temperature-dependent molecular reorganization at the C-2 position of [EMIM][BF4]. Chemical Physics Letters 2021, 783, 138956. DOI: https://doi.org/10.1016/j.cplett.2021.138956.

In-progress journal manuscript:

Strong, K.; Muhammad, S.; Lewis, R.; Abdulahad, A.I. Rheological evidence of microphase separation in PEG-segmented phosphonium ionene block copolymers. ACS Polymers Au. In preparation.

Conference presentations:

Abdulahad, A.I. Incorporating inclusive teaching practices in the design of a course-based undergraduate research experience in polymer chemistry. Biennial Conference on Chemical Education, Purdue University, Lafayette, IN, 2022.

Muhammad, S.; Dibeh, J; Abdulahad, A.I. PEG-Segmented Phosphonium Ionenes as Solid Polymer Electrolytes for Lithium Metal Batteries. American Chemical Society National Meeting and Expositions, 2022.

Hixson-Wells, T.; Abdulahad, A.I. Structure-Property of Linear Phosphonium Ionenes for Solid-State Lithium Batteries. American Chemical Society National Meeting and Expositions, 2022.

Compton, J.; Abdulahad, A.I. Synthesis and Characterization of Hyperbranched and Branched Phosphonium Ionenes for Lithium Metal Batteries. American Chemical Society National Meeting and Expositions, 2022.

Lewis, R.; Abdulahad, A.I. Synthesis and characterization of microcapsules prepared by emulsion copolymerization of poly(methyl methacrylate) and poly(2-hydroxyethyl methacrylate). American Chemical Society National Meeting and Expositions, 2022.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Co-Investigator
Participant: Lamartine Meda
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Co-Investigator
Participant: Samrat Dutta
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Non-Student Research Assistant
Participant: Samirah Muhammad
Person Months Worked: 1.00 **Funding Support:**

Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Jazzniah Compton
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Trinity Hixson-Wells
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Ryanne Lewis
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Jenna Dibeh
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Non-Student Research Assistant
Participant: Ly Tran
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Kaiyah Rush
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Jordan Marzette
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Emanuela Riglioni
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Kirsten Grant
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Isaiah Washington
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Thea Nicholson
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Kayla Foy
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Sydney Green
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Kya Branch
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

RPPR Final Report
as of 07-Sep-2022

Participant Type: Undergraduate Student
Participant: Ayssia Crockem
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Asa Green
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Undergraduate Student
Participant: Kutemwa Masafwa
Person Months Worked: 1.00 **Funding Support:**
Project Contribution:
National Academy Member: N

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
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Volume: 783 Issue: First Page #: 138956
Date Submitted: 8/19/22 12:00AM Date Published: 11/1/21 5:00AM
Publication Location:
Article Title: Striking temperature-dependent molecular reorganization at the C-2 position of [EMIM][BF4]
Authors: Ly Tran, Kaiyah Rush, Jorden Marzette, Gabrielle Edmonds-Andrews, Timothy Bennett, Asem Abdulaha
Keywords: Ionic liquids, Imidazolium, C-D vibration, Infrared spectroscopy, Temperature-dependent
Abstract: Understanding the temperature-dependent structural evolution of imidazolium-based ionic liquids can facilitate their high-temperature applications. In this manuscript, we report an anomalous redshift and line-narrowing of the C-D vibration at the C-2 position of the imidazolium cation of the ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF4]), when compared to other investigated ionic liquids upon heating suggesting the possibility of structural ordering of this ionic liquid upon heating. Computational studies show that this ordering could arise due to the formation of strong hydrogen bonding conformers. Further infrared studies indicate the existence of a possible hidden transition in this liquid which was subsequently confirmed by calorimetric measurements.
Distribution Statement: 1-Approved for public release; distribution is unlimited.
Acknowledged Federal Support: **Y**

RPPR Final Report
as of 07-Sep-2022

Partners

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I certify that the information in the report is complete and accurate:
Signature: Asem Abdulahad
Signature Date: 8/19/22 5:53PM

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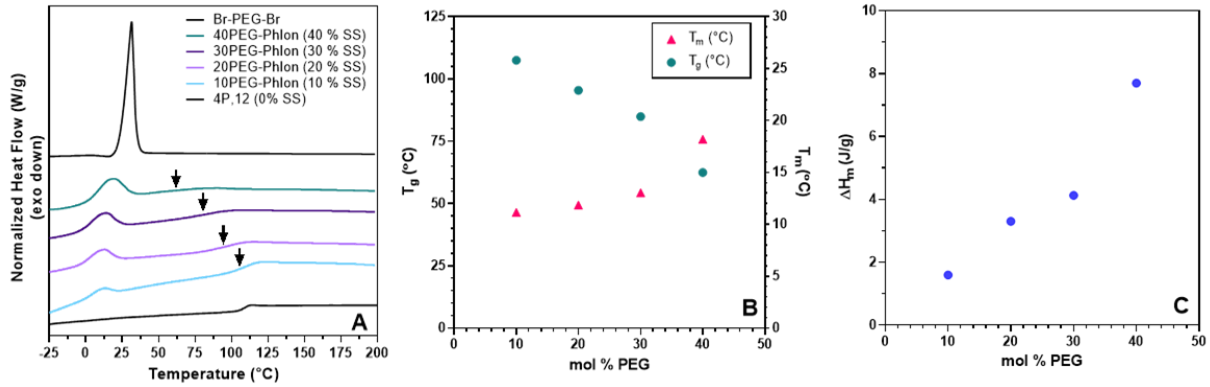

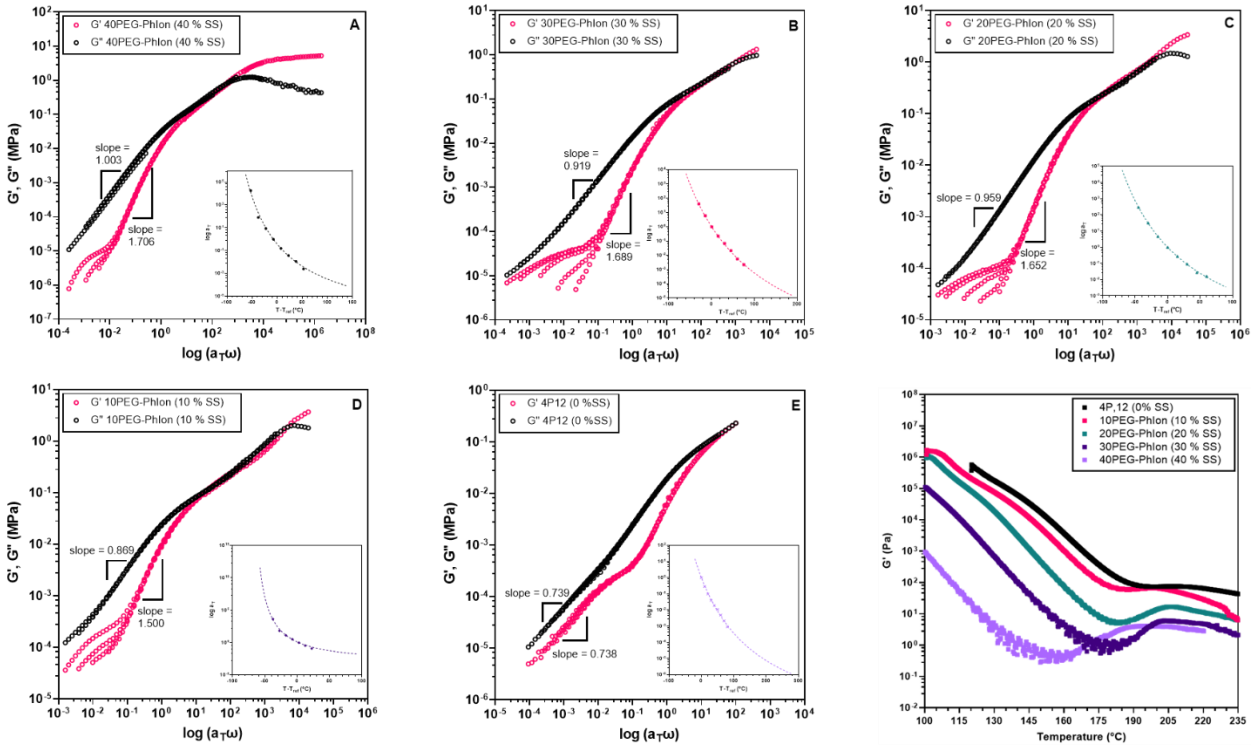

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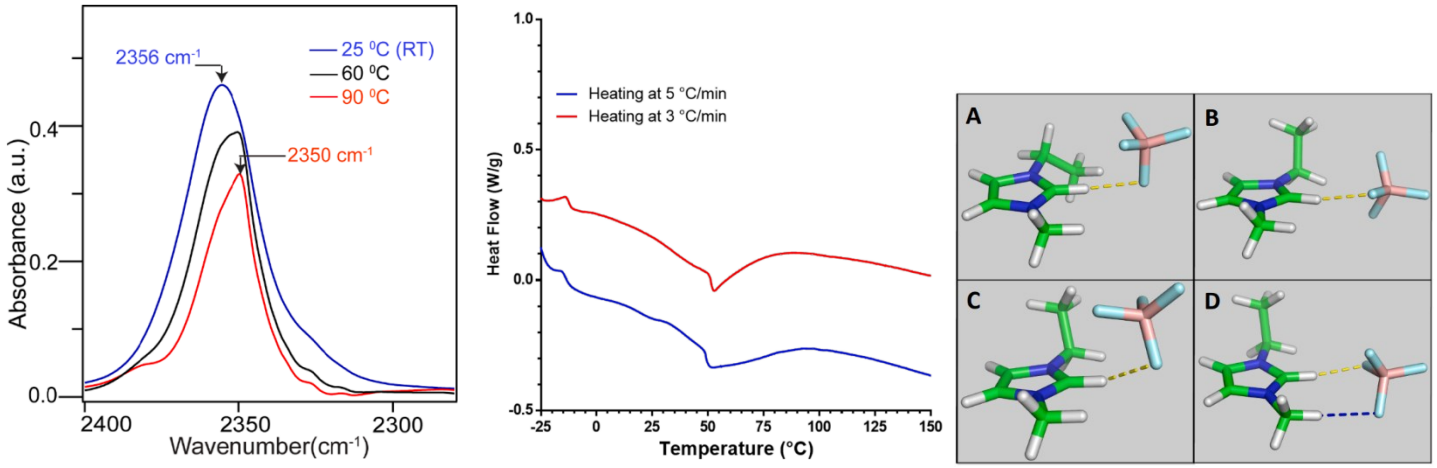

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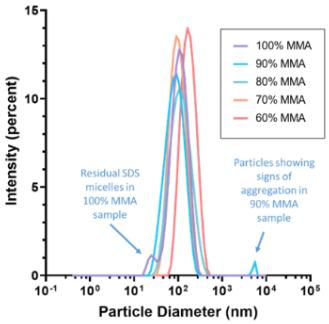
Intensity (percent)
Particle Diameter (nm)
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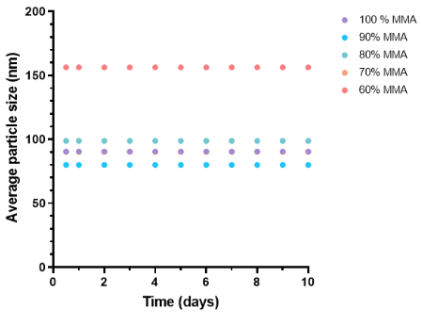
90% MMA
80% MMA
70% MMA
60% MMA
Residual SDS micelles in 100% MMA sample
Particles showing signs of aggregation in 90% MMA sample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90% MMA
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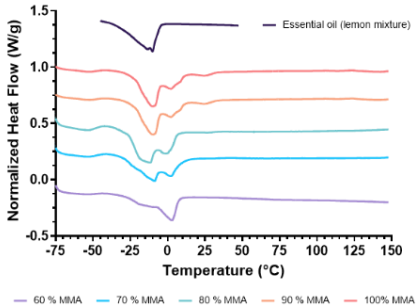
70% MMA
60% MMA


Normalized Heat Flow (W/g)
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Essential oil (lemon mixture)
60 % MMA
70 % MMA
80 % MMA
90 % MMA
100% MMA