Efficient Synthesis of Kevlar and Other Fibers from Polyethylene Terephthalate (PET) Waste

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Organization: Pacific Northwest National Laboratory
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Project Overview

Timeline
- Project start date: 7/1/2020
- Project end date: 6/30/2023
- Percent complete: 20%

Barriers Addressed
- High cost of carbon fiber composites remains a barrier and technical challenge to achieving both near- and long-term goals
- There is potential for a wide number of uses with a range of weight reductions over steel up to 60–70% (carbon fiber [CF] systems). Key challenges include cost reduction (for precursor materials and CF conversion), Other opportunities include optimizing mass reduction and improved recycling of CF materials.
- Low-cost/high-volume manufacturing of CF replacements

Budget
- Total Budget Funding: $820k
- FY20 Funding: $20k
- FY21 Funding: $250k

Partners
- Collaborations in Year 2 for fiber production: UT Knoxville or WSU (through BioIn)
- PNNL Lead

Relevance

Impact

► Addresses R&D focused on low-temperature/low to intermediate-strength and high-temperature/intermediate to high-strength hybrid composite systems for vehicle components

► Replacement of high-cost carbon fiber (barrier)

► Reduce materials/energy costs

► Recycled plastic-based starting materials (supporting clean energy and a circular carbon economy)

► Reduce the current cost barrier to implementing aramid fiber composites in automotive applications

Objectives

► Demonstrate the synthesis of Kevlar-like polymers (aramids) and fibers from PET plastic waste

► Develop composites containing those fibers (overarching)

► Achieve PET deconstruction and repolymerization to make aramids in one step

► Develop mitigation strategies and alternative to aramid fibers
**Project Milestones (all regular, quarterly)**

<table>
<thead>
<tr>
<th>Milestone Number</th>
<th>Milestone Description</th>
<th>Deliverable</th>
<th>Status</th>
<th>Anticipated Quarter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Demonstrate PET deconstruction with any diamine</td>
<td>A yield of at least 85% based on PET consumption</td>
<td>Complete</td>
<td>FY21 Q2</td>
</tr>
<tr>
<td>2</td>
<td>Demonstrate the PET deconstruction with at least one aryl diamine</td>
<td>Generate a polymer with a Mw of 10kDa</td>
<td>On target* (75% complete)</td>
<td>FY21 Q4</td>
</tr>
<tr>
<td>Go/no go #1</td>
<td>Demonstrate suitable polymer formation from PET</td>
<td>A polymer with 40 repeating units will be synthesized on a 20g scale</td>
<td>On Target</td>
<td>FY21Q4</td>
</tr>
<tr>
<td>3</td>
<td>Demonstrate fiber formation from the polymers obtained</td>
<td>A fiber with a diameter smaller than 25µm</td>
<td>FY22 Q2</td>
<td></td>
</tr>
<tr>
<td>Go/no go #2</td>
<td>Establish fiber properties</td>
<td>A fiber with a tensile strength of at least 1500MPa</td>
<td>FY22 Q4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Demonstrate composite properties</td>
<td>Tensile modulus of 50GPa for unidirectional composite</td>
<td>FY23 Q3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Techno-Economic analysis of proposed process</td>
<td>Utilize unoptimized 20g scale process to demonstrate a 40% cost reduction of proposed aramid fibers versus Kevlar 29</td>
<td>FY23 Q4</td>
<td></td>
</tr>
</tbody>
</table>

* PET deconstruction and polymer synthesis accomplished through alternative route
Approach

- Direct depolymerization of PET waste and concerted repolymerization

\[
\text{Polyethylene glycol (PET waste)} \xrightarrow{\text{catalyst, solvent}} \text{Polyaramid (Kevlar fibers)}
\]

- Current process for aramid polymers production

\[
\text{Petroleum derived} \xrightarrow{\text{catalyst, solvent}} \text{Polyaramid (Kevlar fibers)}
\]

- Proposed route would provide a unique path to Kevlar-like fibers
- While also addressing our plastic problem
- Starting material cost would be substantially decreased, thereby reducing the cost of the fiber
Technical Accomplishments and Progress

Direct Route

- PET is insoluble in ALL practical organic solvents, making solution chemistry prohibitive
- PET has a high mp (above 270°C) and when depolymerization attempted in the melt in presence of amine, small fragments were obtained, but no polymer.
- Catalysts are still under investigation to accomplish direct depolymerization and repolymerization
- Disadvantages:
  - Reaction unlikely to go to completion and separation of insoluble starting materials and products would be extremely challenging (removing unreacted PET from aramid polymer)
  - The approach not feasible for mixed waste (impurities might interfere with catalyst)
  - Chopping of PET to a fine powder required for close contact of reactants is very expensive

Traditional Route to Aramids

- PET is first depolymerized to obtain terephthalic acid, then reacted with thionyl chloride at reflux to make reactive acid chloride; Thionyl chloride is recovered by distillation and can be reused
- Acid chloride reactive and can be subsequently reacted with any diamine
- Four polymers were prepared via this route (see back-up slides)
Technical Accomplishments and Progress

- Conversion varies from 70% to 100%, dependent on the size of the chopped PET
- This route allows for removing impurities from PET stream by filtration, followed by precipitation of the acid
- Reaction is robust and tolerant of impurities
- Inexpensive reagents and simple work-up; solvent and water use are minimal
- 30g of clean and fine PET yields 25g of terephthalic acid
- Sequence demonstrated with *mixed* PET waste
- Manuscript in final stages of editing

**Alternative Route**

\[
\text{PET} \xrightarrow{\text{NaOH, H}_2\text{O, EG, 100C}} \text{HOOC--COOH}
\]
Responses to Previous Year Reviewers’ Comments

Project was funded in FY21/end of FY20, and was not reviewed last year
Collaborations

- Collaborations were not envisioned during the first stages of the project since we have the know-how (synthesis, methodology development)
- We intend to reach out to WSU (Washington State University) to discuss fiber production. This will be facilitated by the BioIn (Bio Institute) which is a joint PNNL-WSU endeavor to tackle the plastic challenge
- Several polymers are investigated, not just diphenylendiamine analog. In year 2, once we have demonstrated scale-up and fiber formation, we will reach out to Honeywell, one of the largest users/producers of Kevlar
Remaining Challenges and Barriers

Polymer Solubility Challenges

- For spectral characterization
  - $^{1}$HNMR: products only soluble in H$_2$SO$_4$
- For molecular weight analysis
  - Most literature reports of aramid polymers only report viscosity of a given concentration of H$_2$SO$_4$ solution, not a molecular weight
  - One literature example reports running gel permeation chromatography (GPC) of Kevlar in H$_2$SO$_4$ as the solvent (DuPont)
  - GPC can be run with salted N-methylpyrrolidinone (NMP) or dimethylacetamide (DMAc) and salt (LiCl, CaCl$_2$) to aid solubility; however, we were not able to dissolve polymers in similar solvent systems.
- Many organic solvents were investigated: NMP, DMF, DMAc, HMPA

Fiber Production

- The solubility barrier will also impact making fibers
- This has not yet been attempted, it is part of Year 2 task
Proposed Future Research

- To resolve polymer solubility for characterization purposes and fiber formation
  - Investigate different salt additives
  - Heat up to 100-150°C, to the clearing point
  - Search for “solvents” which may be solid at room temperature, but have low melting point

- Prepare more polymers/aramids
  - With other amines which may impart solubility
  - Prepare co-polymers with two amines to improve solubility
  - *Milestone 2-deliverable due FY21 Q4: Generate a polymer with a Mw of 10kDa*
  - Although polymers were generated, proper solubility is required for molecular weight evaluation

- Thermal Analysis
  - DSC and TGA of all polymers

- Scale-up
  - Prepare 20g of the most soluble polymer identified (tbd)

| Go/no go #1 | Demonstrate suitable polymer formation from PET | A polymer with 40 repeating units will be synthesized on a 20g scale | On Target | FY21Q4 |

Any proposed future work is subject to change based on funding levels
Summary Slide

• Demonstrated PET deconstruction via basic hydrolysis with conversions varying from 70-100% depending on the reaction conditions (Achieved Milestone 1)

• Achieved high monomer recovery (terephthalic acid) independent of the PET feed utilized (clean versus mixed waste PET). Impact: important in providing starting material for aramid fiber production from realistic waste feeds

• First manuscript nearly finalized

• Prepared four polymers via traditional route (acid chloride) from terephthalic acid and several diamines (p-phenylene diamine, m-phenylenediamine, piperazine, 4,4’-oxydianiline) in small scales (1-2g). Impact: closing the gap towards generating aramid fibers and carbon fiber replacement

• Milestone 2 is 75% complete

• On target to generate cost efficient Kevlar-like fibers from PET waste
PET bottles were reduced to chips by mechanical chopping in a Battenfeld Gloucester Engineering Company, Inc. model 68 5 horsepower pelletizer.

Particle size distribution was evaluated according to the relevant portions of ASTM Standard D1921.

Chips were sieved to achieve desired size (1.4-0.85mm)
How can we run condensation of terephthalic acid and a diamine?

- **Higashi-Ogata** method is a direct polycondensation, but requires very dry reagents
- Reaction somewhat successful with less rigorous drying (spectroscopically appears to have low degree of polymerization)

**Melt polymerization**

- Challenges encountered:
  - Piperazine and phenylene diamines (para and meta) sublime around 100C;
  - TPA is a very high melting solid, at 300 C, that tends to sublime, not melt
  - Reaction takes place but sluggish, low degree of polymerization (low number of repeating units)
## Technical Back-up Slide: Reactions and Conditions to date

<table>
<thead>
<tr>
<th>NB#</th>
<th>Amine</th>
<th>conditions</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>60367-21</td>
<td>Phenylene diamine</td>
<td>TPP-2eq; Py; CaCl₂, LiCl, NMP, 100°C; 7h</td>
<td>Product precipitated out; difficult filtration; insoluble in everything but H₂SO₄</td>
</tr>
<tr>
<td>60367-24</td>
<td>Phenylene diamine</td>
<td>“melt” reaction in ambient; 200°C</td>
<td>TPA has a mp of 300°C, and amine sublimes at ~110°C, could not reach temperature</td>
</tr>
<tr>
<td>60367-25</td>
<td>Phenylene diamine</td>
<td>TPP-2eq; Py; CaCl₂, LiCl, NMP, 110°C; overnight</td>
<td>Slight modification of 21, more easily dissolved in H₂SO₄ for NMR, more easily filtered. Suspect lower Mw</td>
</tr>
<tr>
<td>60367-26-1</td>
<td>Phenylene diamine</td>
<td>250°C, bomb (to prevent sublimation/escaping of the amine); no cat; 4h</td>
<td>No rxn, darkening of the mixture</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>It did not appear glassy, as if it had reached a melt state</td>
</tr>
<tr>
<td>60367-26-2</td>
<td>Phenylene diamine</td>
<td>250°C, bomb (to prevent sublimation/escaping of the amine); DMAP (10mol%)</td>
<td>No rxn, darkening of the mixture</td>
</tr>
<tr>
<td>60367-27</td>
<td>Phenylene diamine</td>
<td>300°C, bomb (to prevent sublimation/escaping of the amine); DMAP (10mol%)</td>
<td>Mixture turned black, charred, no appearance of rxn</td>
</tr>
<tr>
<td>60367-29-1</td>
<td>piperazine</td>
<td>260°C; bomb; 4h</td>
<td>No rxn, no melting (solids were ground together before loading</td>
</tr>
<tr>
<td>60367-29-2</td>
<td>piperazine</td>
<td>260°C; bomb; 4h, catalyst</td>
<td>No rxn, no melting (solids were ground together before loading</td>
</tr>
</tbody>
</table>

![Diagram](https://via.placeholder.com/150)

HOOC-**̋**-COOH  \(\xrightarrow{200-240°C \text{ Catalyst, neat melt}}\)  H₂N-**̋**-NH₂  \(\rightarrow\)  aramide polymer

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</tr>
</thead>
<tbody>
<tr>
<td>60367-30</td>
<td>Phenylene</td>
<td>TPP-2eq; Py; NMP, 110C; overnight</td>
<td>Similar to 25, no salts. By HNMR, lower Mw polymer</td>
</tr>
<tr>
<td></td>
<td>diamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60367-36</td>
<td>Phenylene</td>
<td>TPP-2eq; Py; CaCl2, LiCl, NMP, 110C; overnight</td>
<td>Repeat of 25, slightly larger scale, similar HNMR</td>
</tr>
<tr>
<td></td>
<td>diamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60367-38</td>
<td>piperazine</td>
<td>DMAP; PEG (1ml), ambient; 250C</td>
<td>Amine starts subliming at 60C, discard experiment</td>
</tr>
<tr>
<td>60367-40</td>
<td>PET</td>
<td>Hydrolysis with mixed PET, chopped and sieved &lt;14</td>
<td>Clean terephthalic acid obtained, PET conversion 85%</td>
</tr>
<tr>
<td>60367-41</td>
<td>piperazine</td>
<td>NMP</td>
<td>Salt forms, isolated</td>
</tr>
<tr>
<td>60367-42</td>
<td>Propylene</td>
<td>NMP</td>
<td>Salt forms, isolated</td>
</tr>
<tr>
<td></td>
<td>diamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60367-44</td>
<td>pip-TPA salt</td>
<td>Bomb at 325C (with antioxidant)</td>
<td>Polymer product, but appears low MW</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bomb at 325C (no additive)</td>
<td>Low MW polymer and charred byproducts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bomb at 325C (catalyst)</td>
<td>Low MW polymer and charred byproducts</td>
</tr>
<tr>
<td>60367-50</td>
<td>PET-Pip</td>
<td>Bomb at 280C, Zr catalyst</td>
<td>Depolymerization takes place but no desired aramide detected; as much as 70% PET deconstructed or decomposed</td>
</tr>
</tbody>
</table>

Salt formation followed by polymerization is limited to primary and secondary amines, not phenyl amines.
Technical Back-up Slide: Successful Polymerizations

- Scalable process analogous to industrial practice has been demonstrated
- Can tune polymer properties by choice of amine or a combination of amines
- Simple polymer purification (water/methanol wash)
- Piperazine was included due to its cyclic structure, may impart interesting properties