2021 DOE Vehicle Technologies Office Annual Merit Review

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

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Project ID #: mat208

Project Overview

Timeline

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

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

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

Light-Duty Vehicles Technical Requirements and Gaps for Lightweight and Propulsion Materials Workshop Report, February 2013

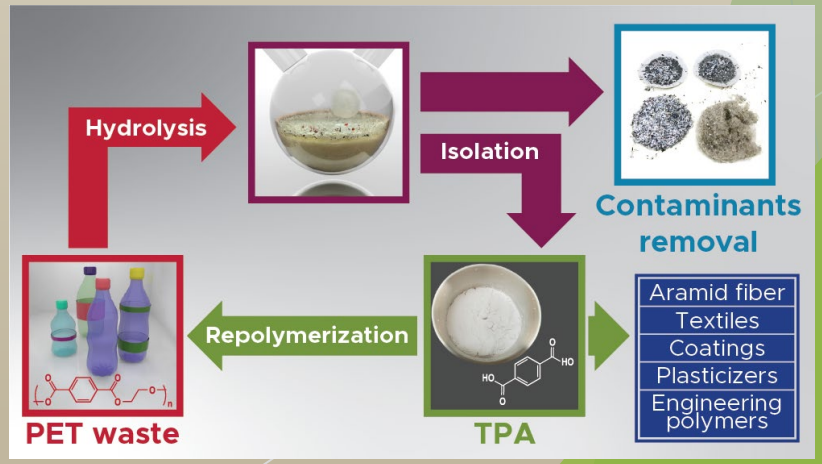
Relevance

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)

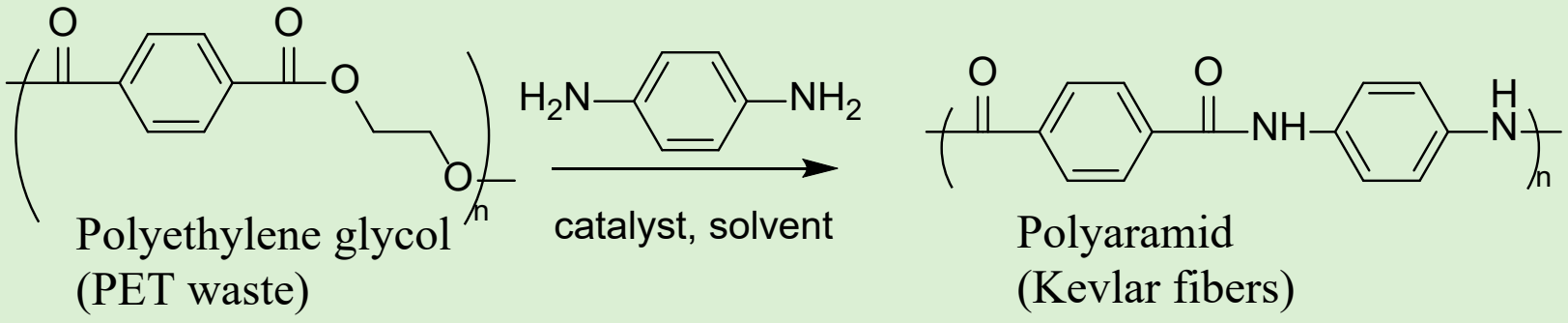
Table 1: Milestone Summary

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

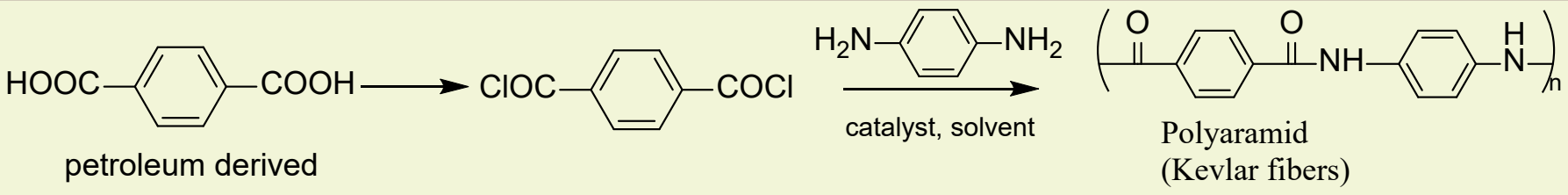
* PET deconstruction and polymer synthesis accomplished through alternative route

Approach

- Direct depolymerization of PET waste and concerted repolymerization



- Current process for aramid polymers production



- 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

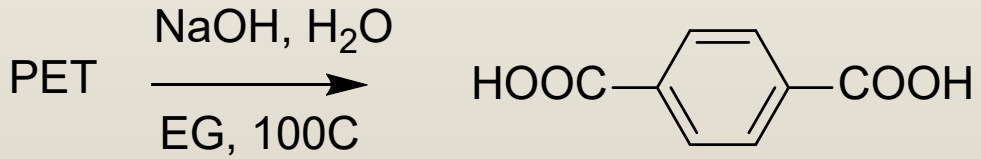
- PET is insoluble in ALL practical organic solvents, making solution chemistry prohibitive
- PET has a high mp (above 270°C) and when depolymerization attempted in the melt in presence of amine, small fragments were obtained, but no polymer.
- Catalysts are still under investigation to accomplish direct 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)

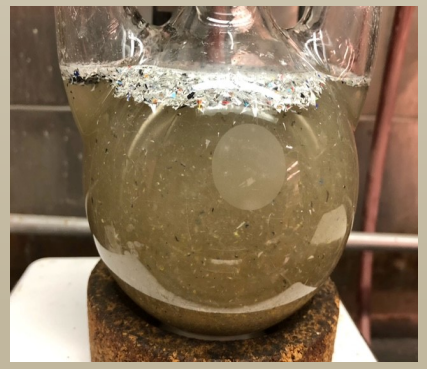
Technical Accomplishments and Progress

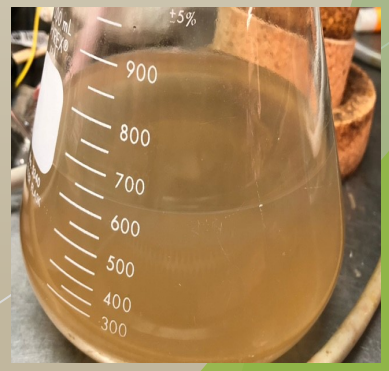
Alternative Route

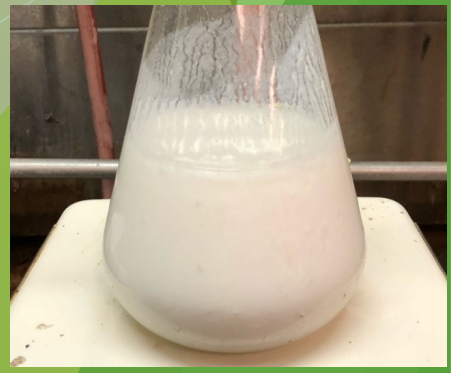


- Conversion varies from 70% to 100%, dependent on the size of the chopped PET
- This route allows for removing impurities from PET stream by filtration, followed by precipitation of the acid
- Reaction is robust and tolerant of impurities
- Inexpensive reagents and simple work-up; solvent and water 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









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_2SO_4
- For molecular weight analysis
  - Most literature reports of aramid polymers only report viscosity of a given concentration of H_2SO_4 solution, not a molecular weight
  - One literature example reports running gel permeation chromatography (GPC) of Kevlar in H_2SO_4 as the solvent (DuPont)
  - GPC can be run with salted N-methylpyrolidinone (NMP) or dimethylacetamide (DMAc) and salt (LiCl, CalCl2) 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

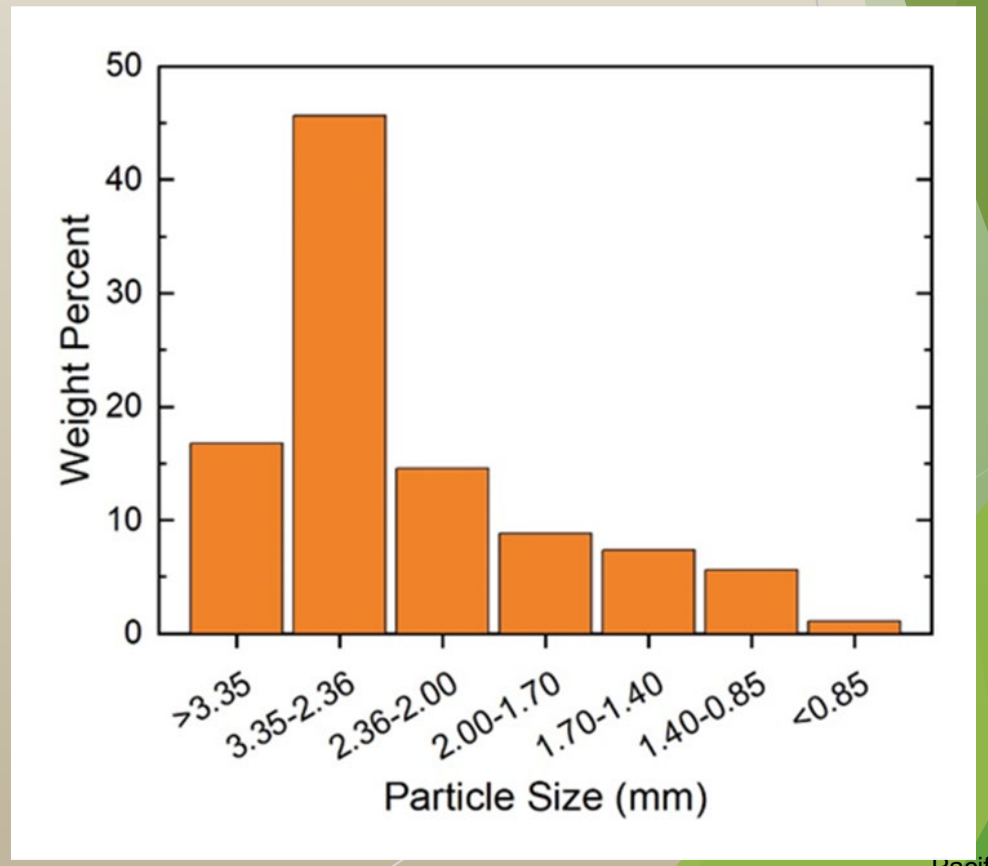
- Demonstrated PET deconstruction via basic hydrolysis with conversions varying from 70-100% depending on the reaction conditions (*Achieved Milestone 1*)
- Achieved high monomer recovery (terephthalic acid) independent of the PET feed utilized (*clean* versus *mixed* waste PET). *Impact: important in 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**

Technical Back-up Divider Slide

Technical Back-up Slide: Chopping/Particle Size

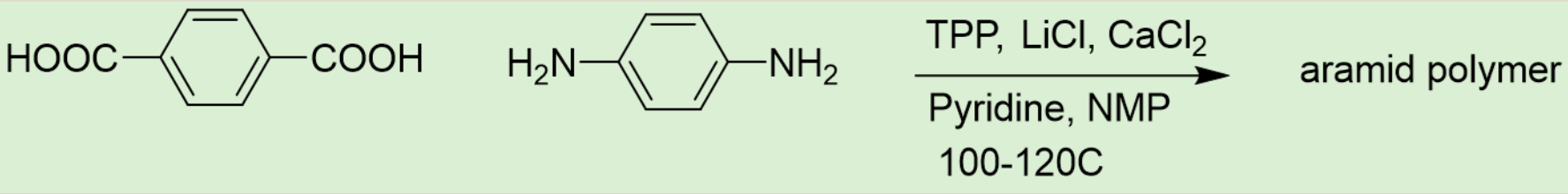
- PET bottles were reduced to chips by mechanical chopping in a Battenfeld Gloucester Engineering Company, Inc. model 68 5 horsepower pelletizer.
- Particle size distribution was evaluated according to the relevant portions of ASTM Standard D1921.
- Chips were sieved to achieve desired size (1.4-0.85mm)

Raw PET waste



Technical Back-up Slide: Alternative Approaches

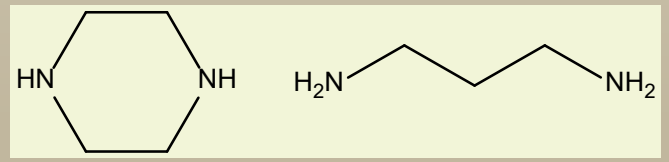
How can we run condensation of terephthalic acid and a diamine?



- **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)

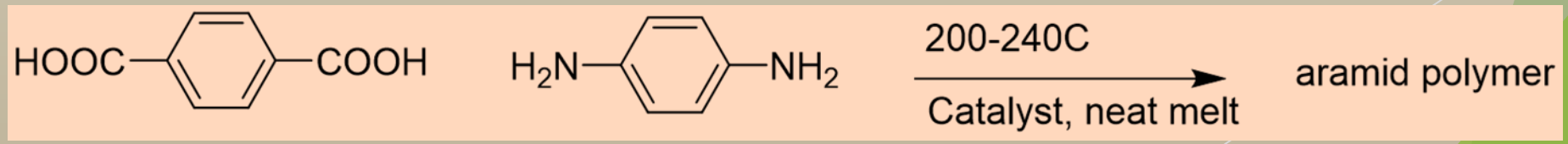
Melt polymerization

- 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

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



Technical Back-up Slide: Reactions and Conditions to date

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

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