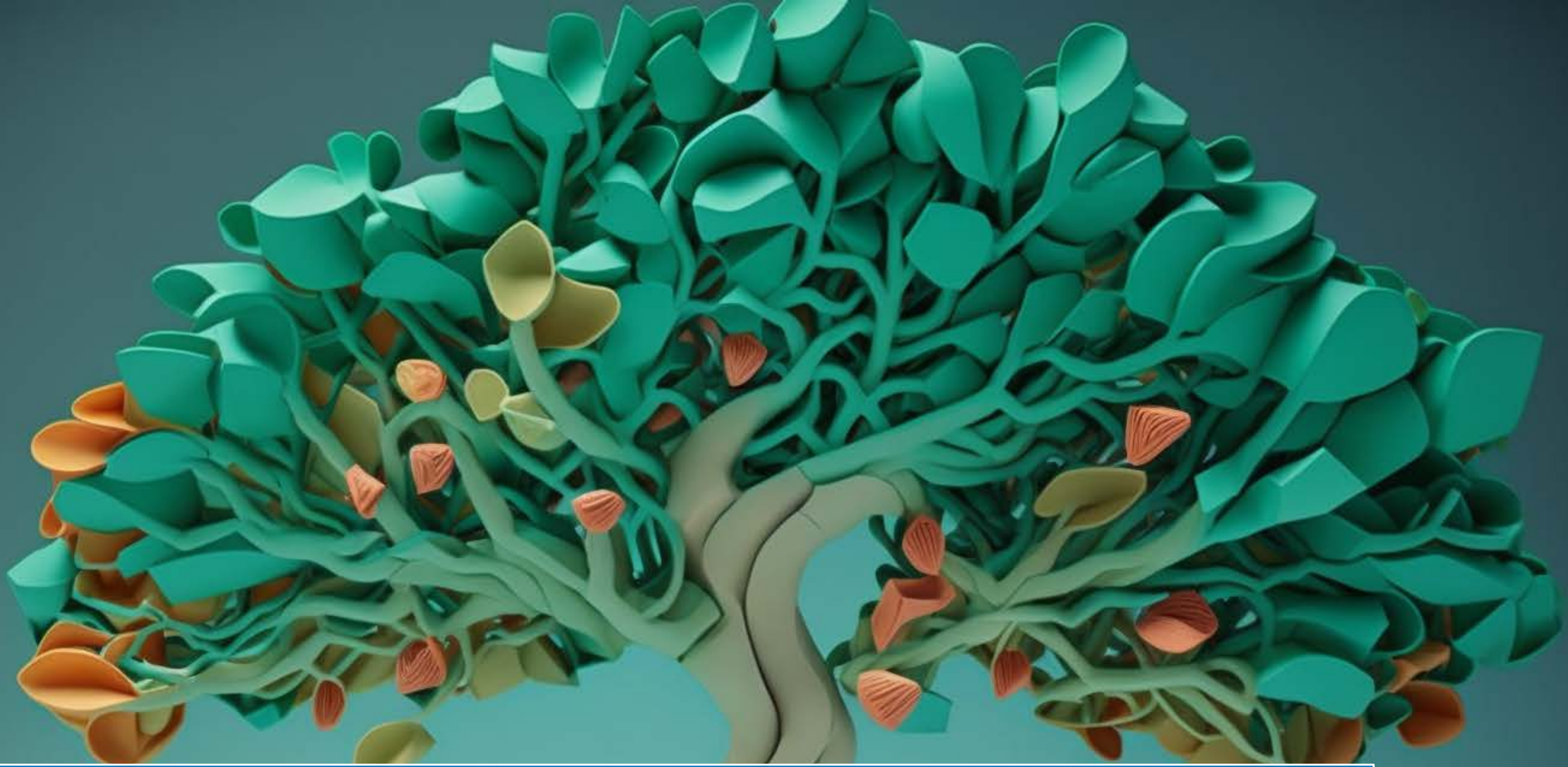

Converting poly(ethylene terephthalate) to rigid thermosets: Performance and recycling considerations

Nicholas A. Rorrer and Colleagues, National Renewable Energy Laboratory

Spring ACS Meeting – March 27, 2023 8:00a-8:25a

Acknowledgements

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
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bottle
we recycle

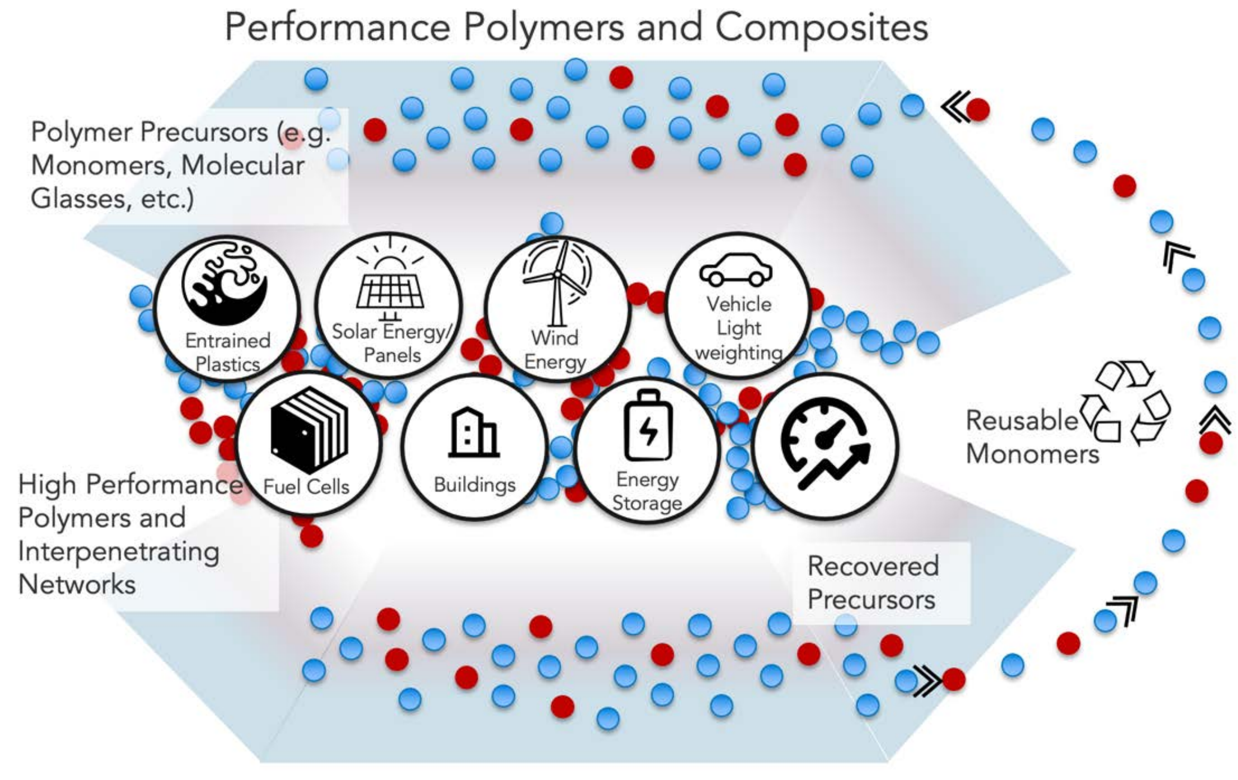
#TeamPolymers Over the Years

Collaborators and Colleagues

And Many More!!

Application of Engineered Polymers Designed for *Performance and End-of-Life* for Energy-relevant Applications

Goal: Align new materials innovation with the programmatic goals of various DOE offices

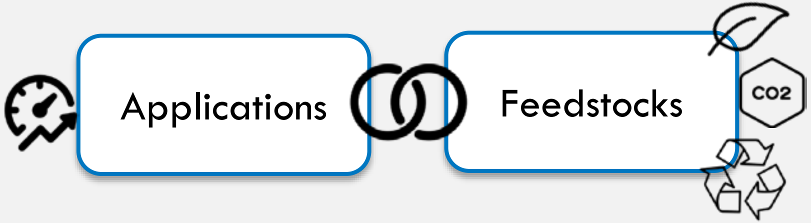


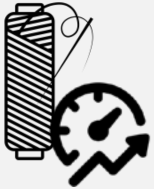
Creation through Application-specific Materials Innovation

Original NAR Images

Application of Engineered Polymers Designed for *Performance <u>and</u> End-of-Life* for Energy-relevant applications

Driving Research Questions





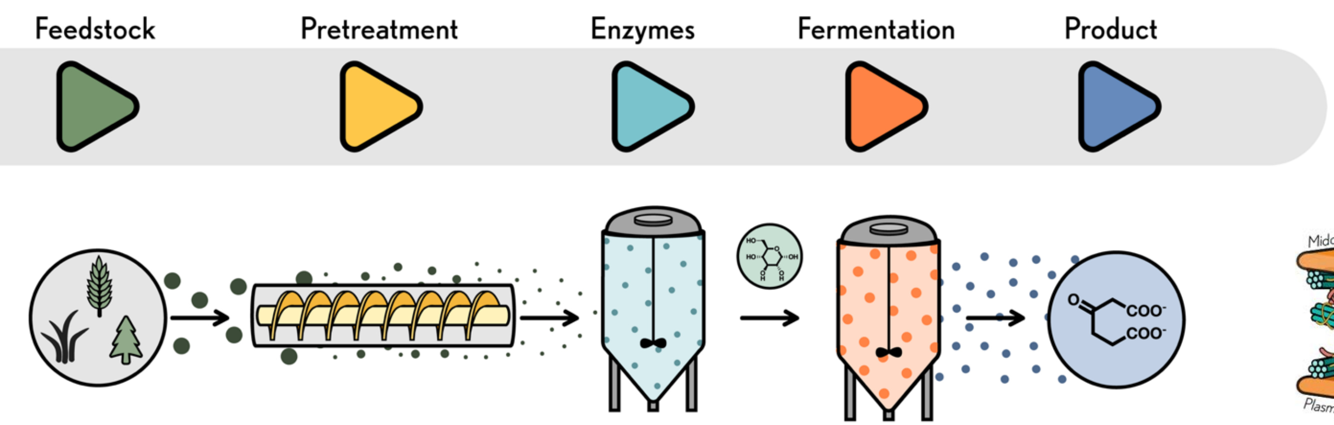
- Can we design and tailor high performance polymer and composite materials for energy relevant applications?

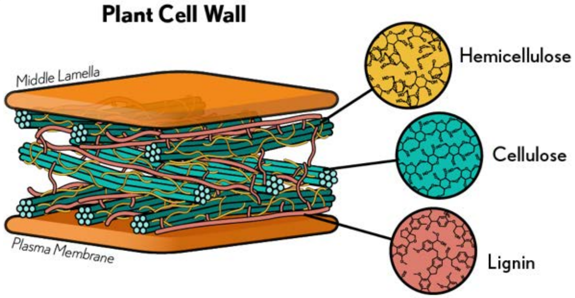
- Can we enable material circularity in a wide variety of energy relevant applications?

- Can we couple material performance and circularity with renewable feedstocks?

Original NAR Images

Coupling Performance and Feedstock





Images courtesy of Rita Clare, Formerly NREL

A Brief Aside: NREL History in Biomass to Polymer

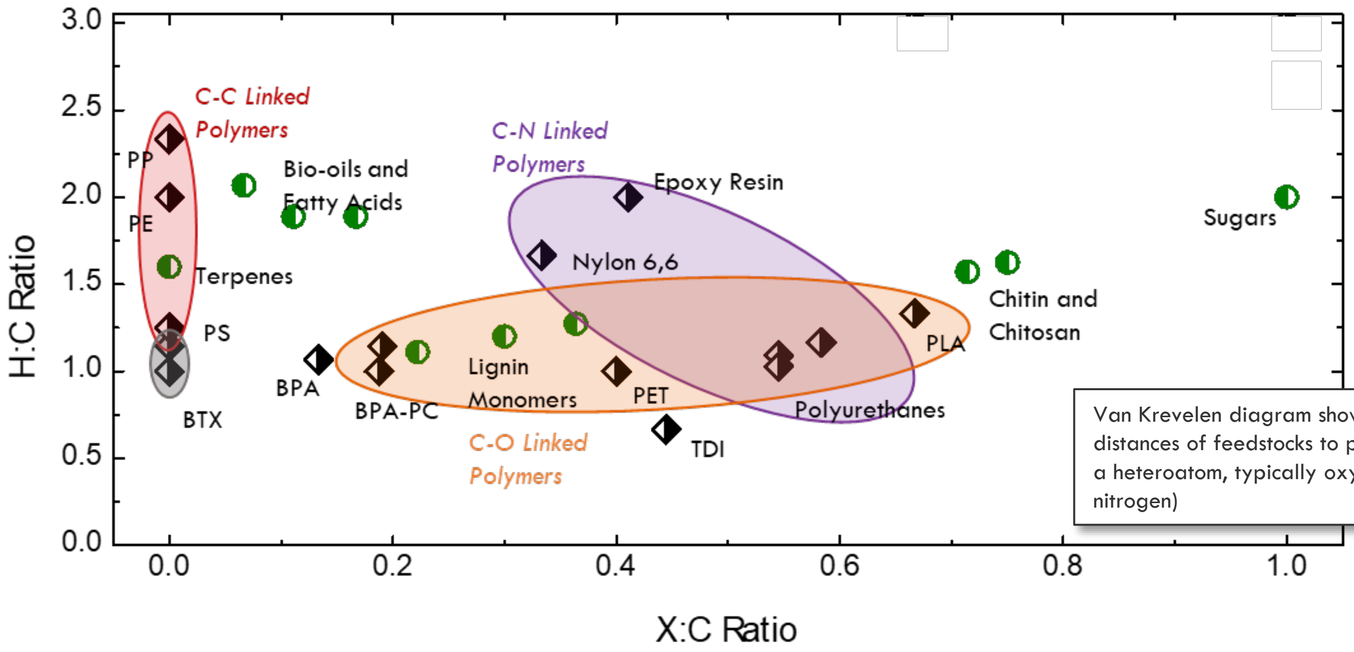
Our work attempts to enable the biorefinery by utilizing the entirety of biomass

- Recent work has also included the conversion of ‘waste’ plastics (e.g. PET) into the same monomers

Early work focused on direct replacements (e.g. Adipic and Terephthalic acid) however, as our worked evolved we started to target “*Performance Advantaged Bioproducts” (PABPs)*

- We classify performance advantages in three areas: **Manufacturing, Performance, End-of-Life**

Coupling Performance and Feedstock



Van Krevelen diagram showing chemical distances of feedstocks to polymers (X is a heteroatom, typically oxygen or nitrogen)

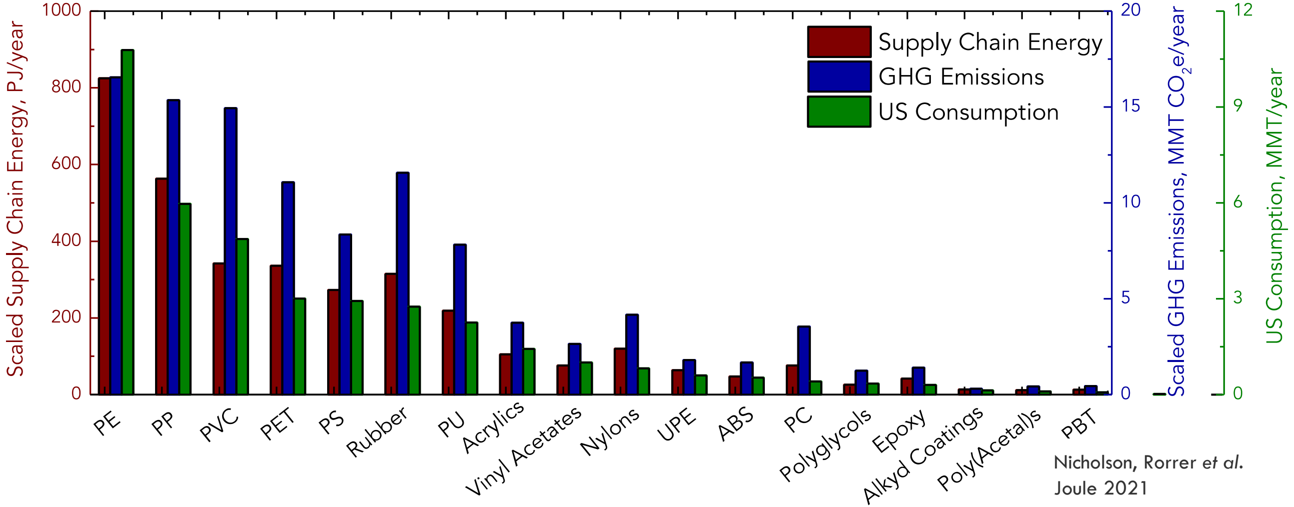
Maintaining Biomass' Functionality

Adding or removing functionality, especially heteroatom functionality, from chemicals (biobased or petrochemical) requires energy and emits GHG

- Thus, the heteroatom functionality of biomass makes it ideal for PABPs, notably performance polymers

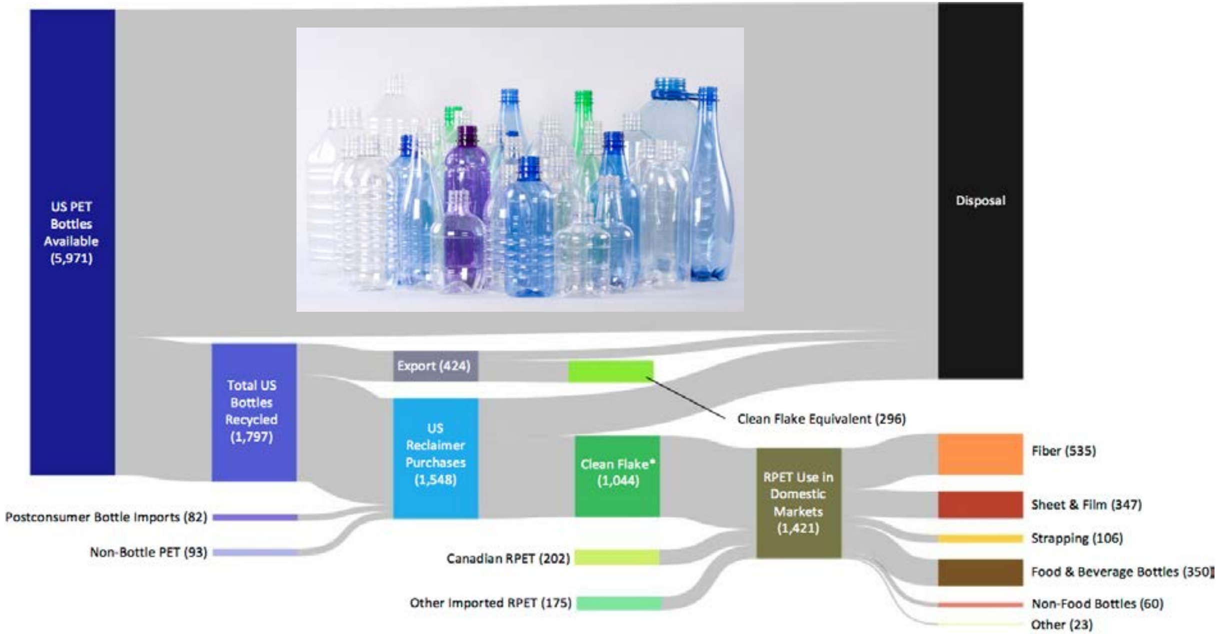
Plastics are Ubiquitous with Modern Life

US plastics consumption exceeds 360 MMT per year requiring 3.2 quads of energy and emitting 104 MMT a year



Nicholson, Rorrer *et al.*
Joule 2021

PET – An Engineering Polymer With Commodity Prices



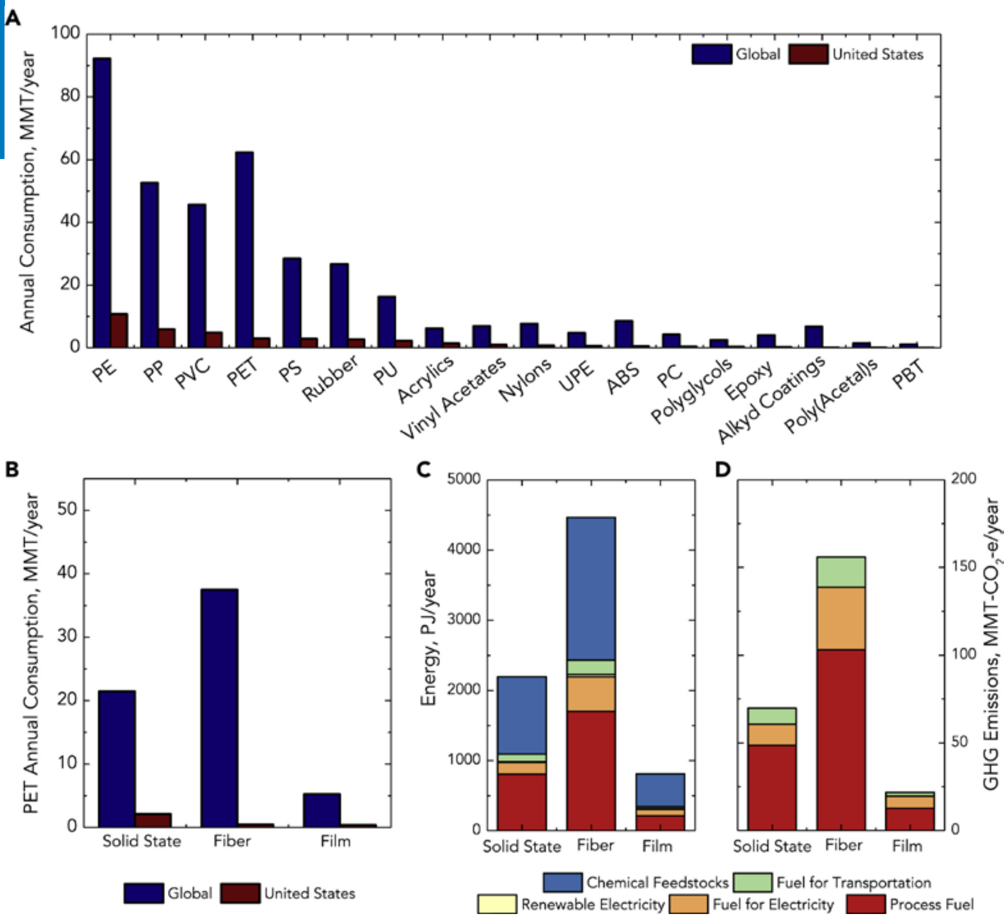
* This total represents all clean flake sold into end markets by US reclaimers. See figure 7 for detail on total flake produced by US reclaimers from bottles.

Even our most recycled plastics are not fully recycled

PET – An Engineering Polymer With Commodity Prices

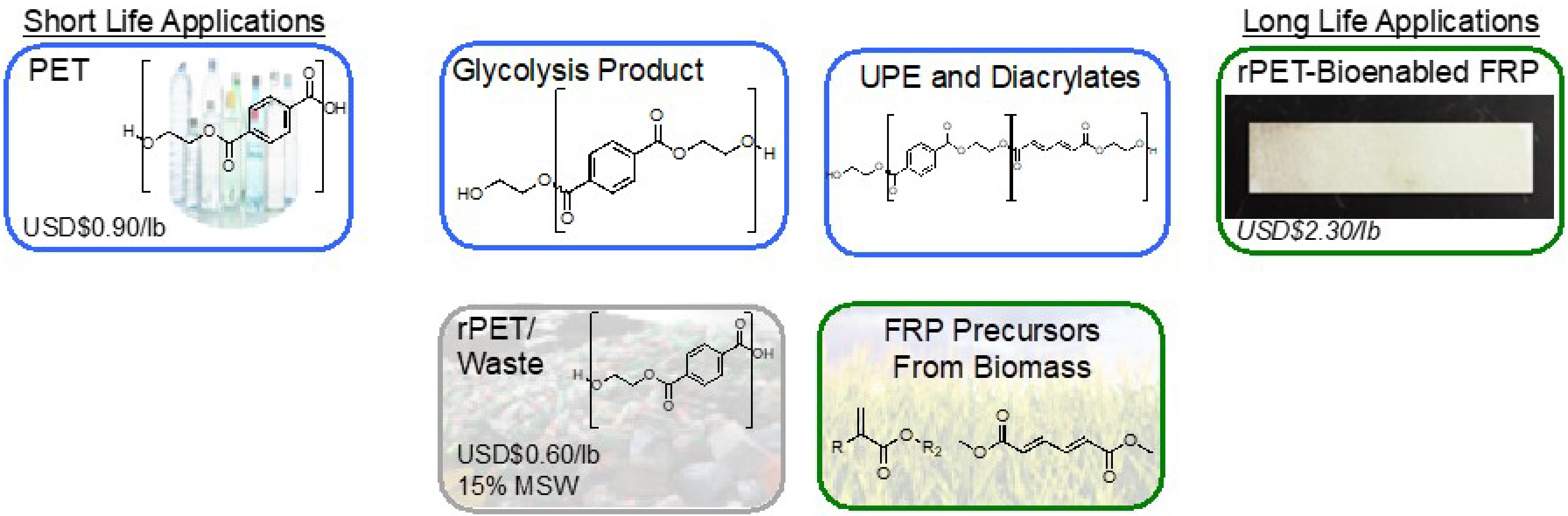
Recycling also depends on form factor leaving opportunities for further research into utilization

- When looking at a global picture across all PET uses, PET is the second largest consumed plastic annually
- This is main driven by textiles and the way that consumption is tracked
- Thus, there is still a huge opportunity to study PET recycling and re-use to keep carbon in the economy



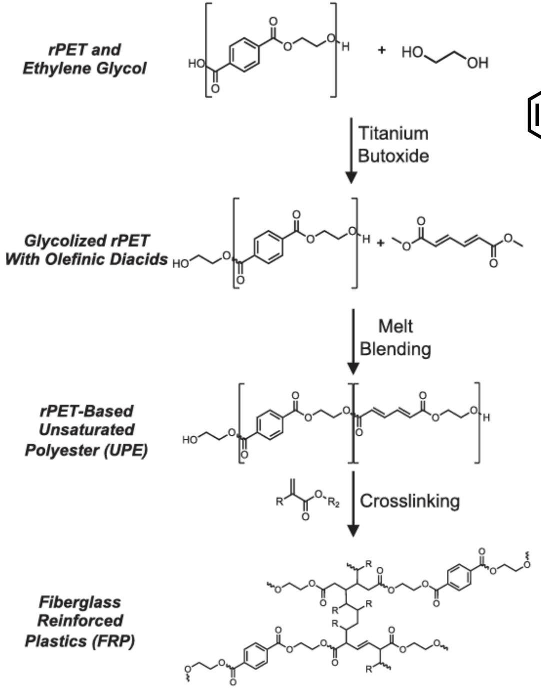
Nicholson, Rorrer *et al.* Joule 2021

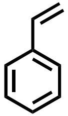
Unsaturated Polyesters from rPET

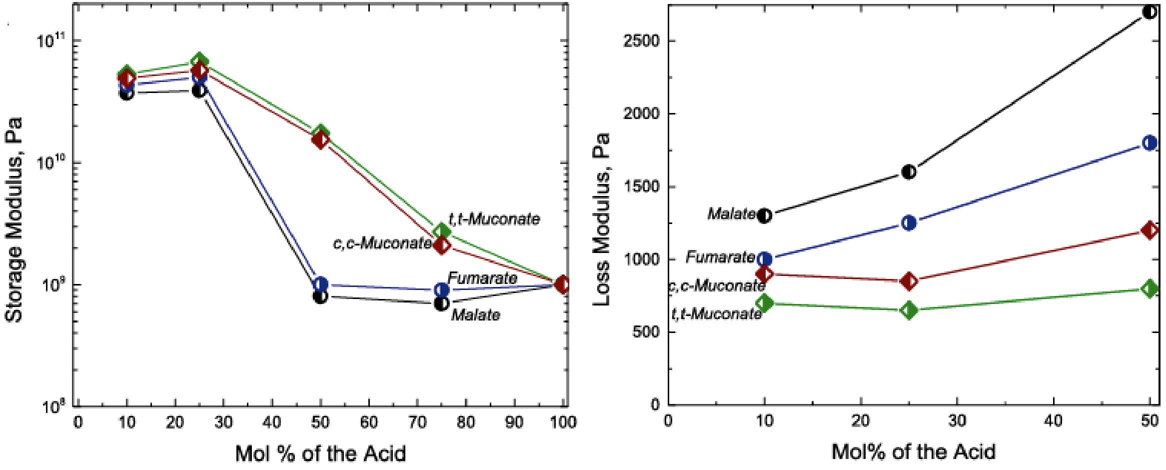


Driving Research Question: Can we selectively depolymerize PET and use it in subsequent second life applications?

Unsaturated Polyesters from rPET





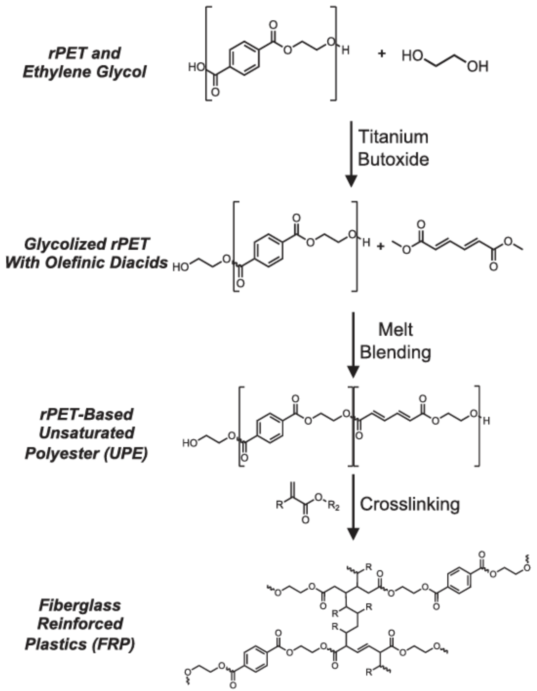


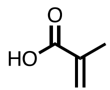
Muconate, a bioderived building block with two crosslinking sites, always performance better than its petrochemical counterparts

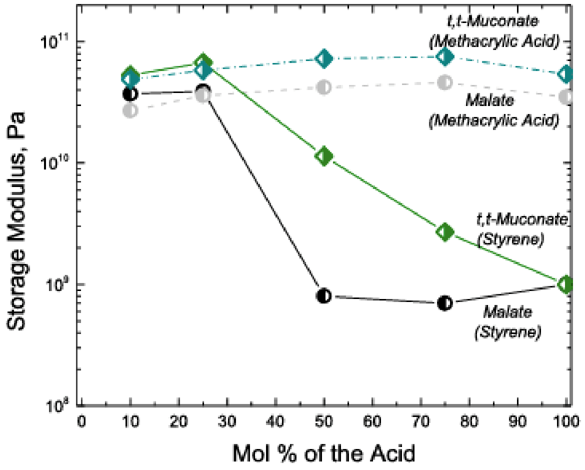
- Storage modulus tracks stiffness while loss modulus tracks fiberglass adhesion

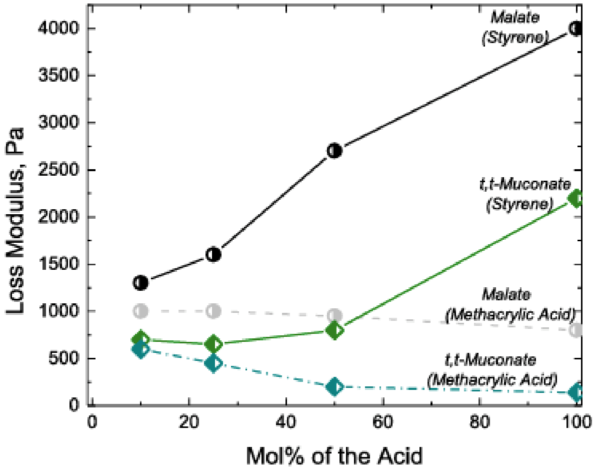
Rorrer *et al.* Joule 2019

Unsaturated Polyesters from rPET





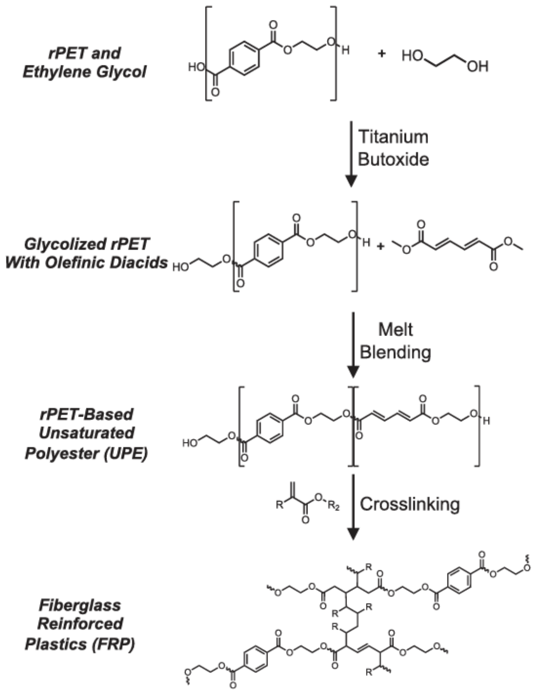


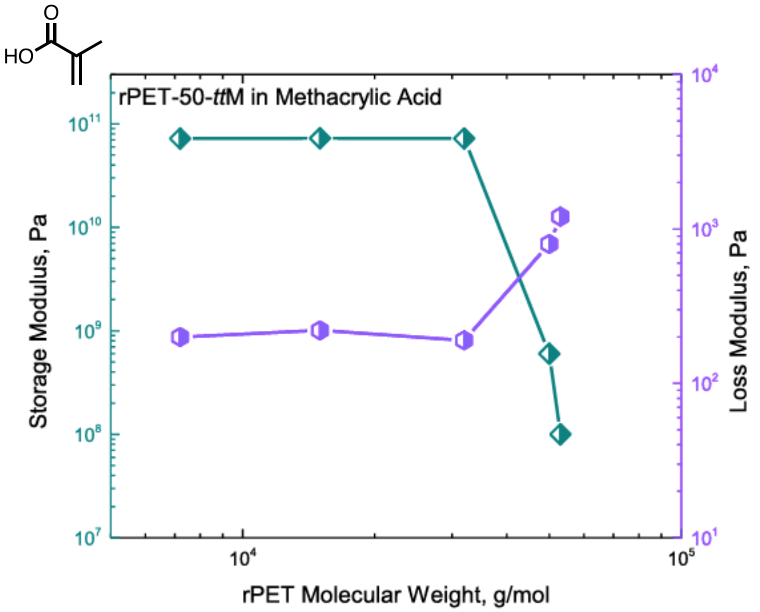


The FRPs with styrene exhibit poor compatibility at higher olefinic loadings, alongside an excess of crosslink sites. Methacrylic acid is more compatible with all UPEs

Cywar *et al.* Forthcoming

Unsaturated Polyesters from rPET

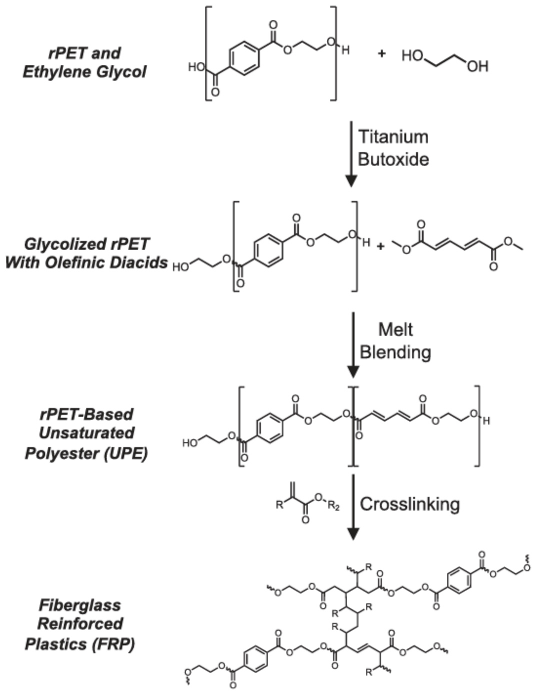


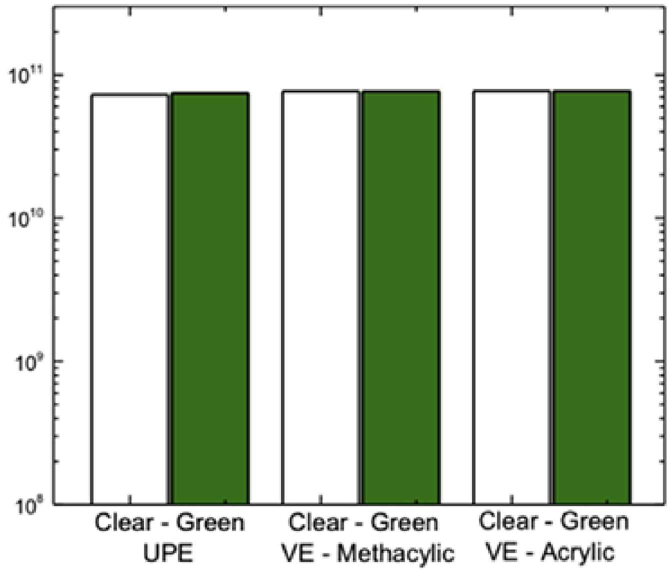


Properties are consistent with molecular weight, or extent of deconstruction, until the PET starts to exhibit gross incapability with the reactive diluent

Rorrer *et al*. Joule 2019

Unsaturated Polyesters from rPET

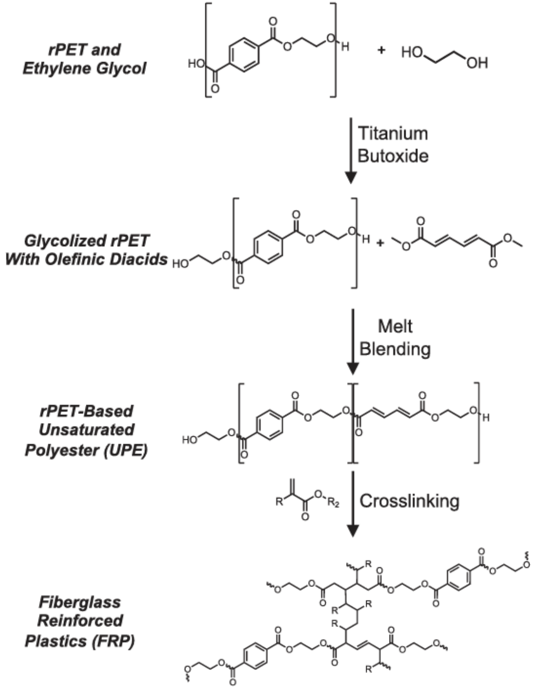


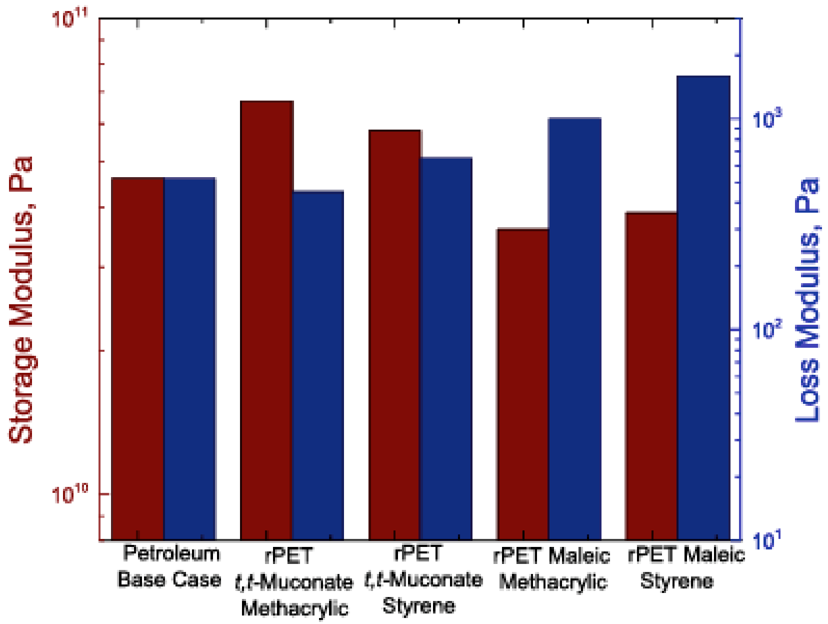


As thermosets don't have to crystallize and are already additive laden, their performance is constant regardless of starting feedstock

Rorrer *et al.* Joule 2019

Unsaturated Polyesters from rPET

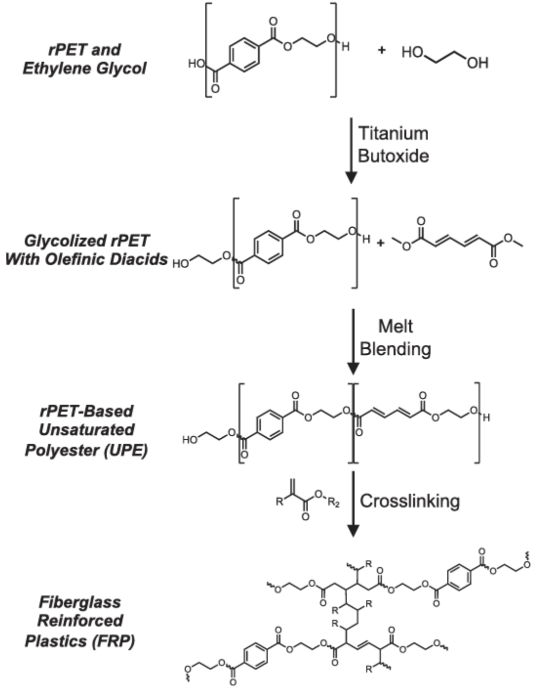


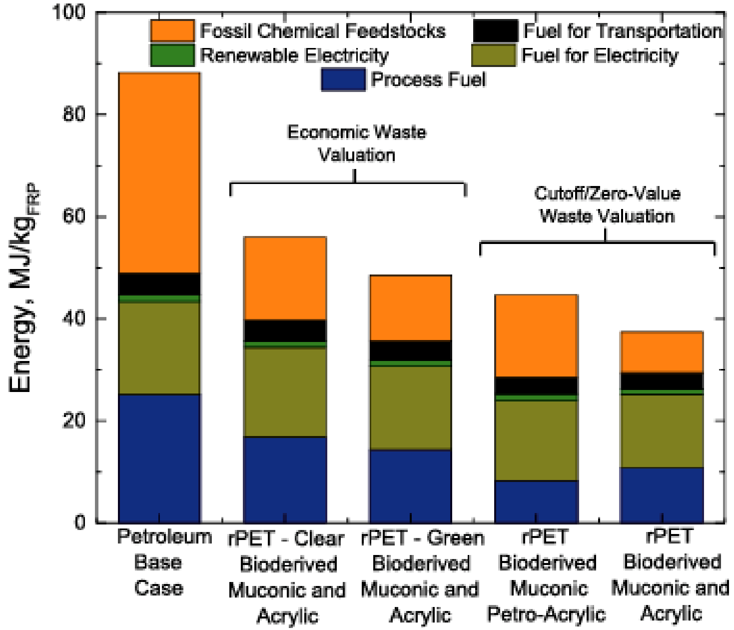


When both reclaimed plastics and bioderived monomers are used, performance can exceed the petrochemical incumbent in stiffness (storage modulus) and fiberglass adhesion (loss modulus)

Rorrer *et al.* Joule 2019

Unsaturated Polyesters from rPET



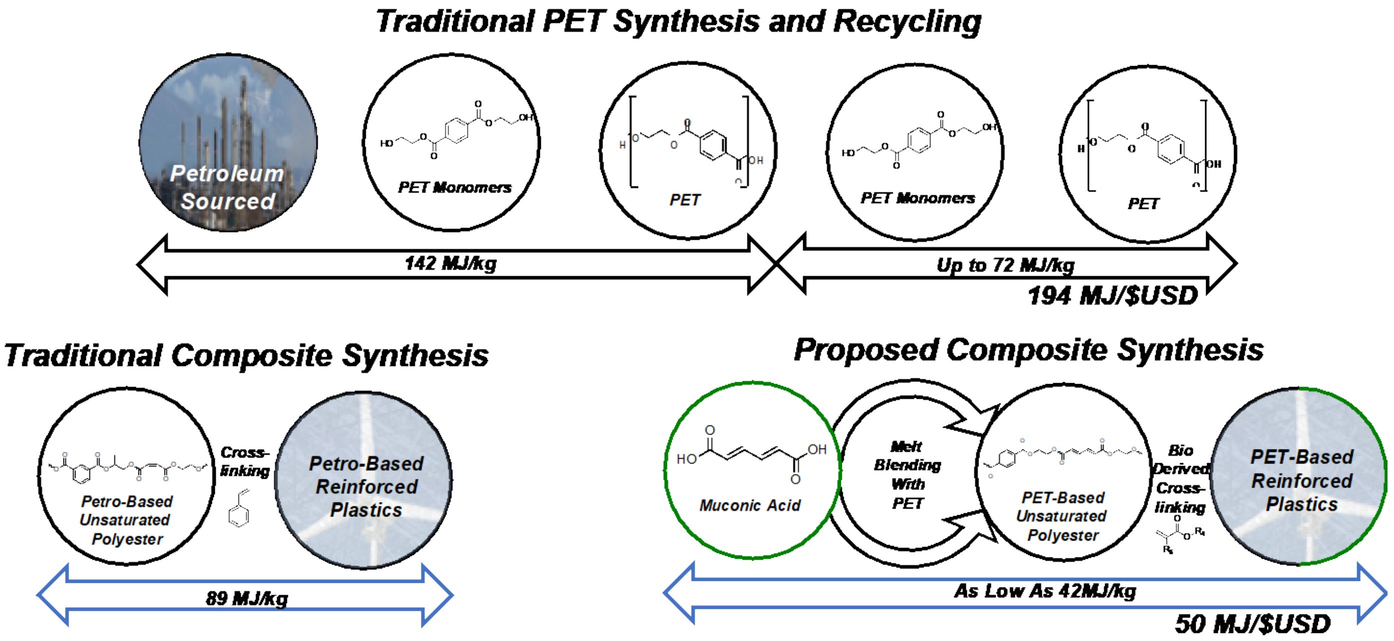


Process intensity can be reduced in all cases with the reduction depending on analysis technique, composition, and starting material

- GHG emissions follow similar trends to supply chain energy

Rorrer *et al.* Joule 2019

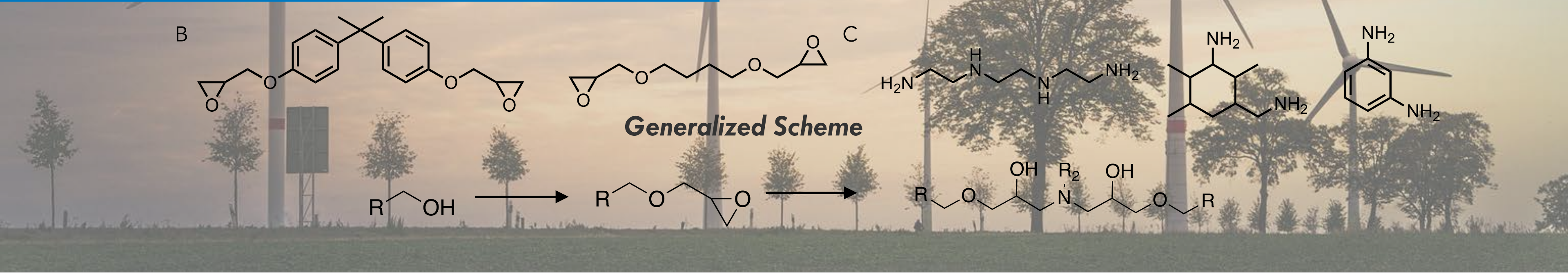
Unsaturated Polyesters from rPET



Carbon should be kept in the economy. Utilizing materials for their second life can enable lower GHG emissions and supply chain energies, alongside multiple profit avenues.

Rorrer *et al.* Joule 2019

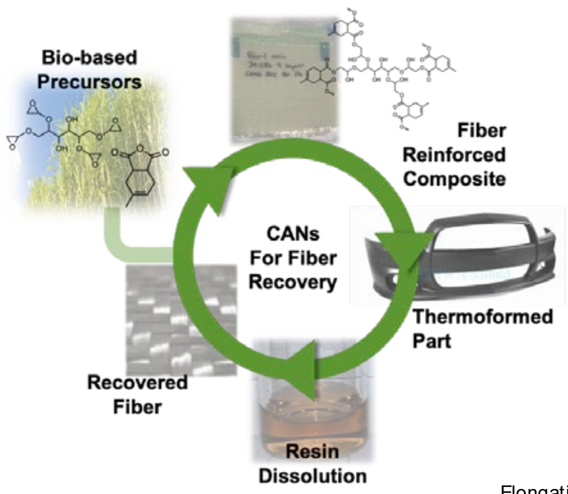
Targeting Other Thermosets

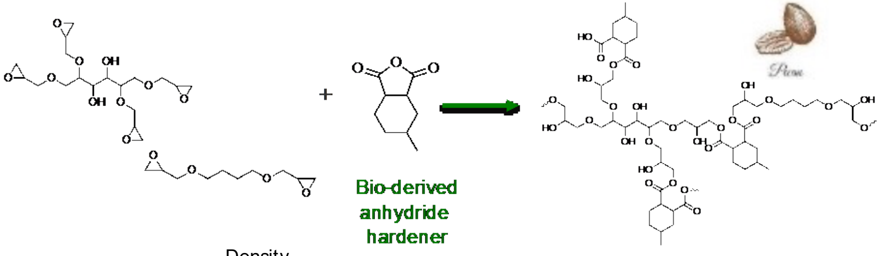


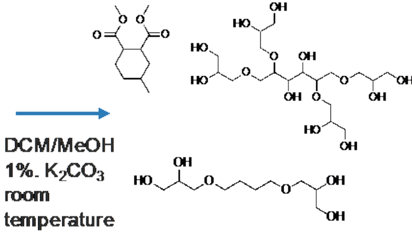
Today's energy-relevant thermosets are typically sourced from epoxy-amines

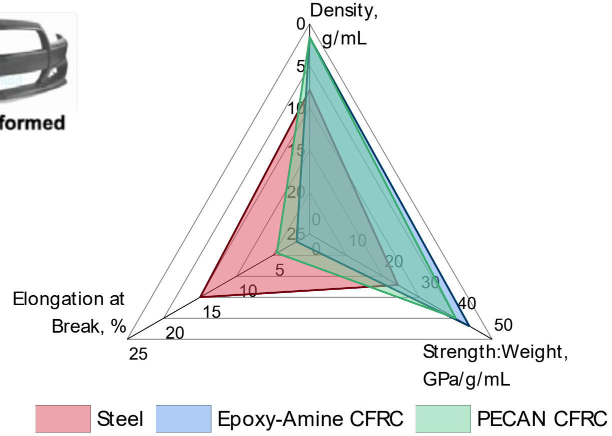
- This materials enable robust performance but can be easily cured at low to moderate temperatures
- Like UPE, these materials are used for long-lives but have minimal circularity options

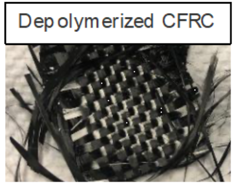
A Path to RBD Thermosets?









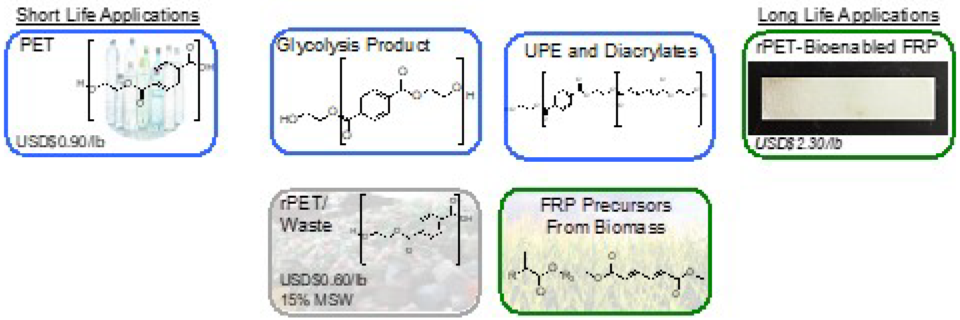


Consistent performance over 3+ lives

Epoxy-Anhydride chemistry has been demonstrated to enable circularity and performance in a wide variety of thermosets

Wang *et al.* Forthcoming, Rognerud *et al.* Forthcoming

Next Steps:



This work demonstrates the capability of using PET in multiple thermoset applications.

- Determine structure property relationships. Are amines or anhydrides superior performers?
- Formulate for application
- Explore other applications beyond thermosets (e.g. a return to multilayers)

Thank You!

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NREL/PR-2800-85240

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