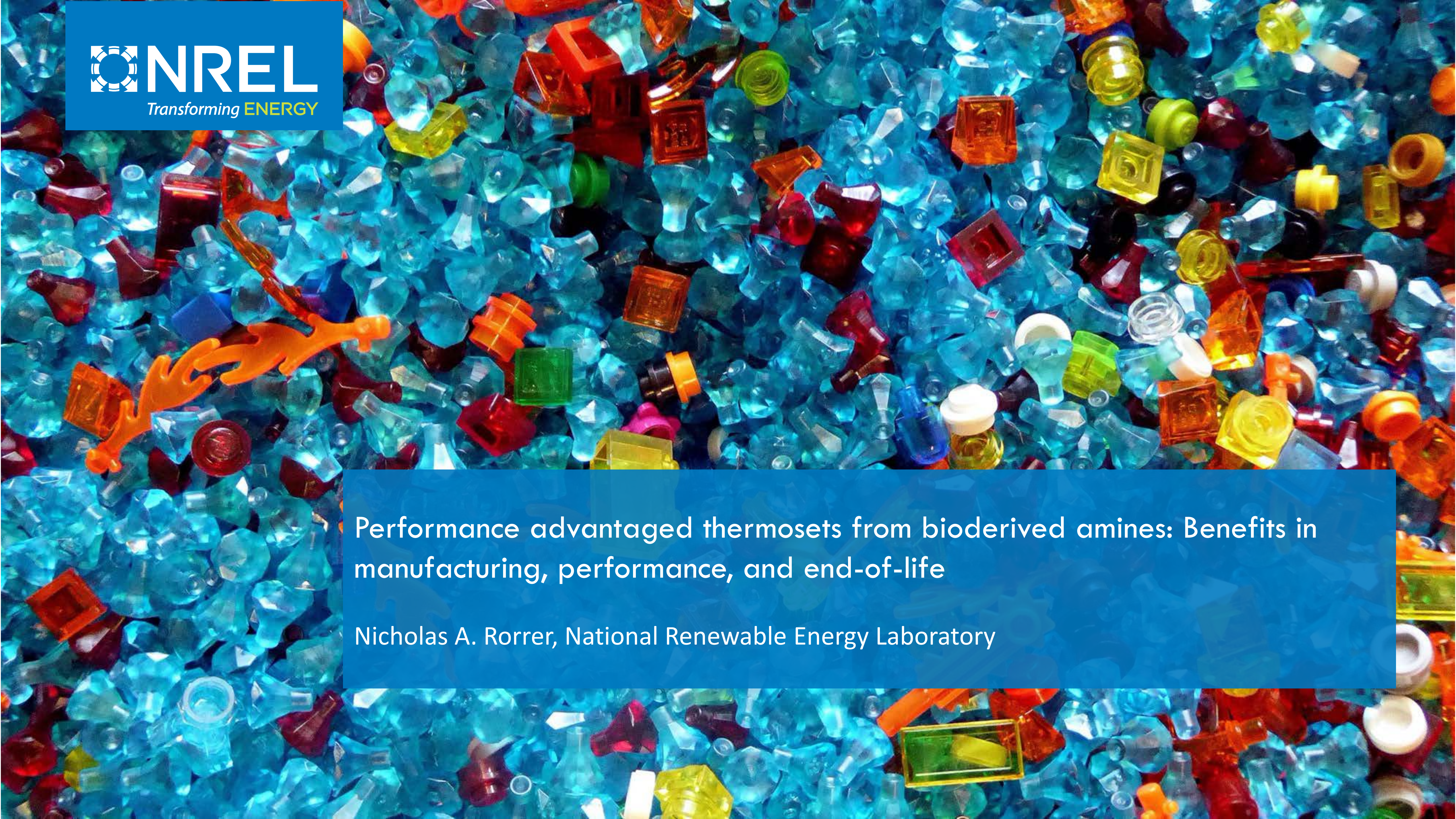

Performance advantaged thermosets from bioderived amines: Benefits in manufacturing, performance, and end-of-life

Nicholas A. Rorrer, National Renewable Energy Laboratory

Acknowledgements

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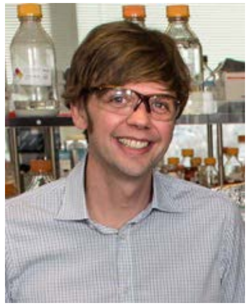
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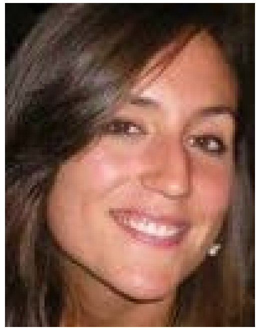
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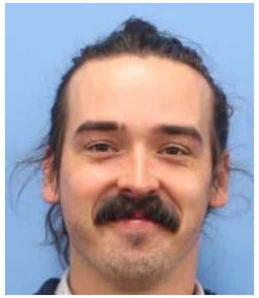
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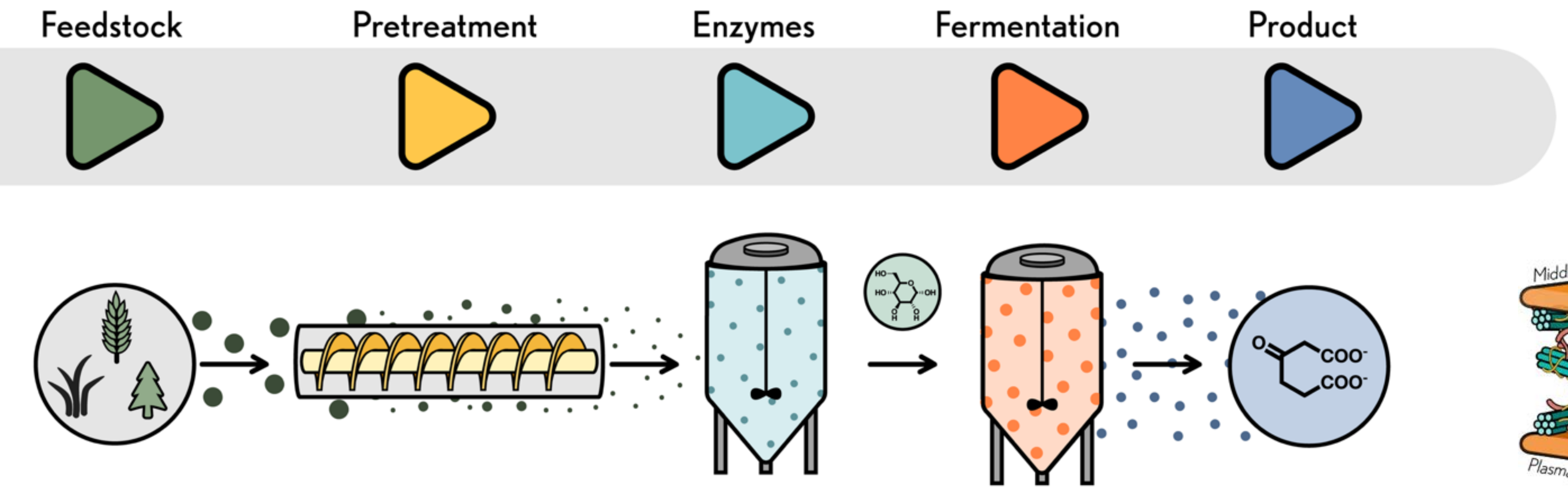
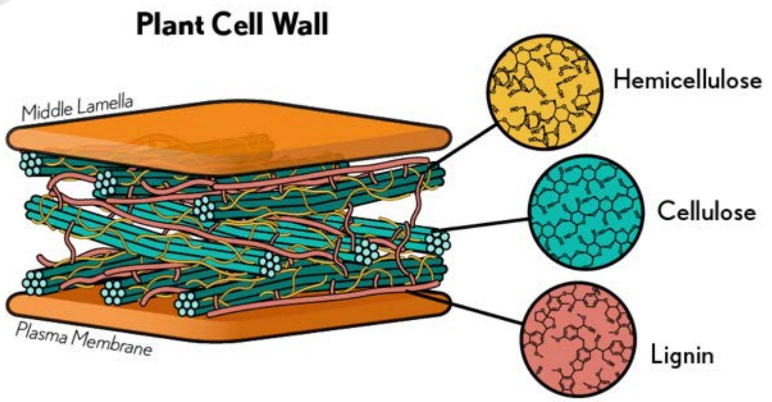
NREL's Approach to New Polymers





Images courtesy of Rita Clare, Formerly NREL

NREL Takes a Holistic Approach to Biomass Conversion

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**

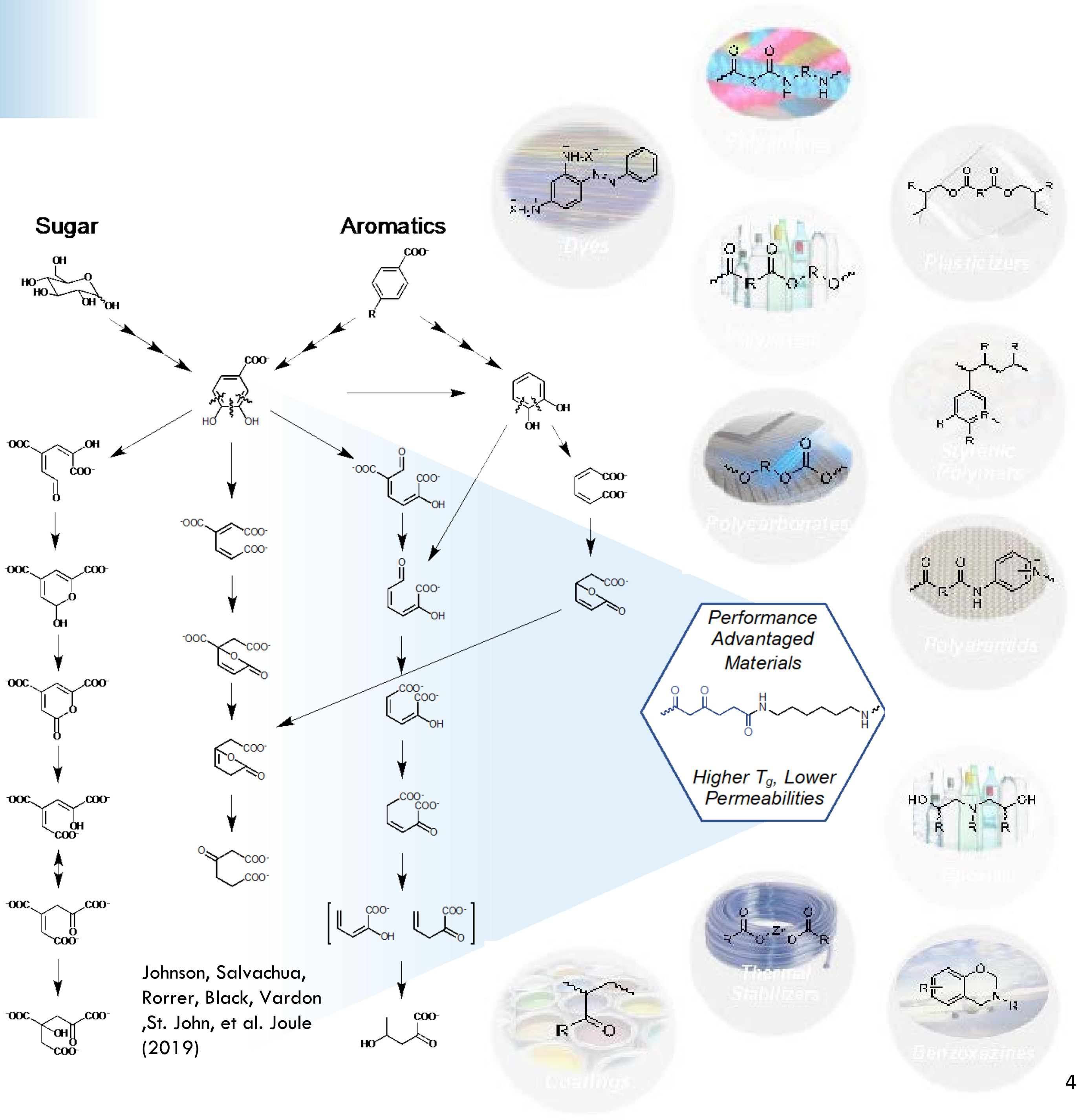
A Large Design Space

Chemical, biological, and hybrid transformation offer plenty of unique monomers

The transformation of biomass provides access to a wide variety of functionality such as:

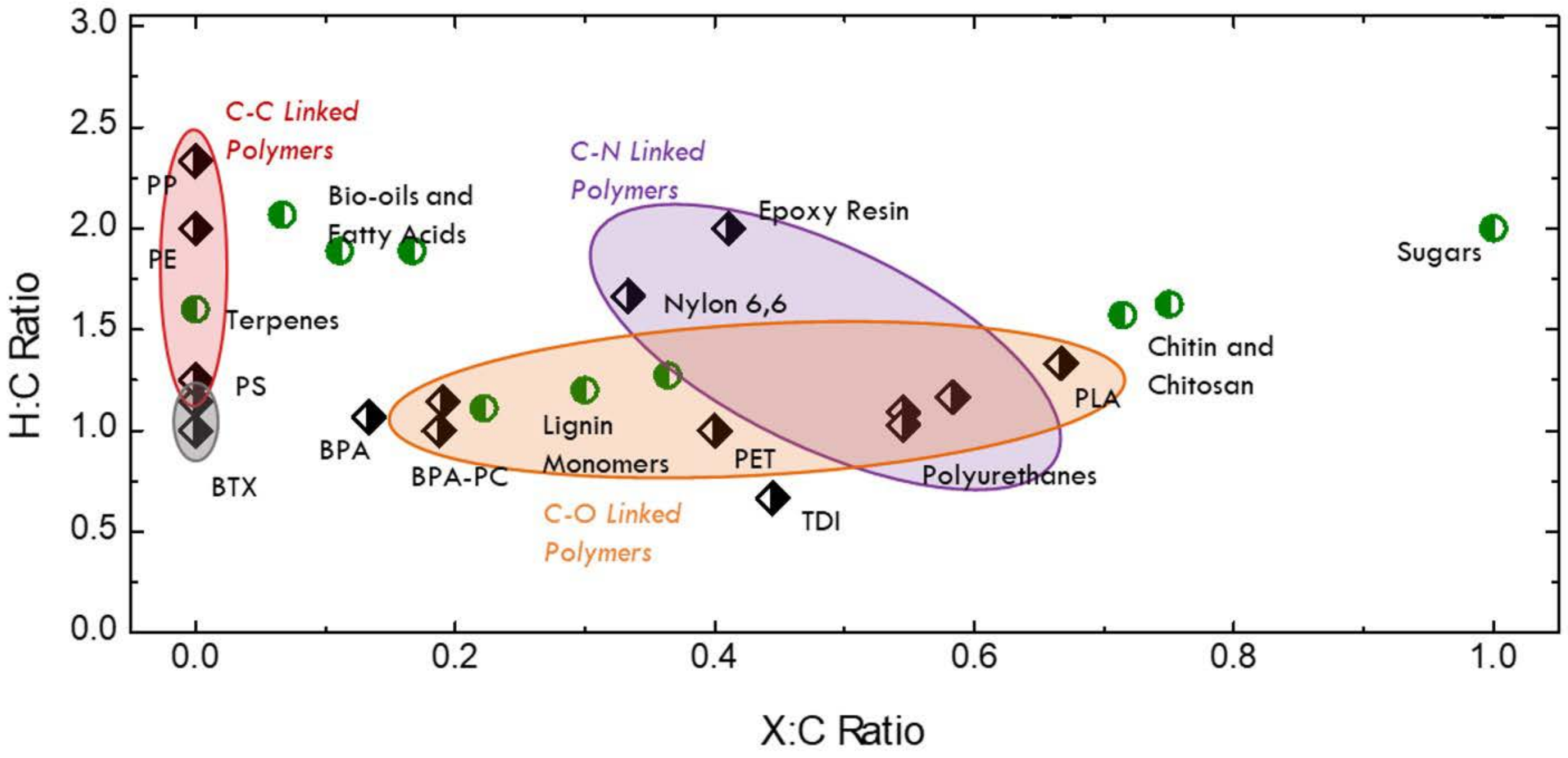
- Carboxylic Acids, including Diacids
- Anhydrides
- Alcohols, including diols and polyols
- Amines, including diamines and multifunctional amines
- Epoxies
- Styrenic Monomers
- Olefinc or Unsaturated Structures

These chemicals provide access to a wide variety of material classes and narrowing the chemical design space is a constant challenge



Johnson, Salvachua, Rorrer, Black, Vardon ,St. John, et al. Joule (2019)

Maintaining Biomass' Functionality to Target Engineering Plastics



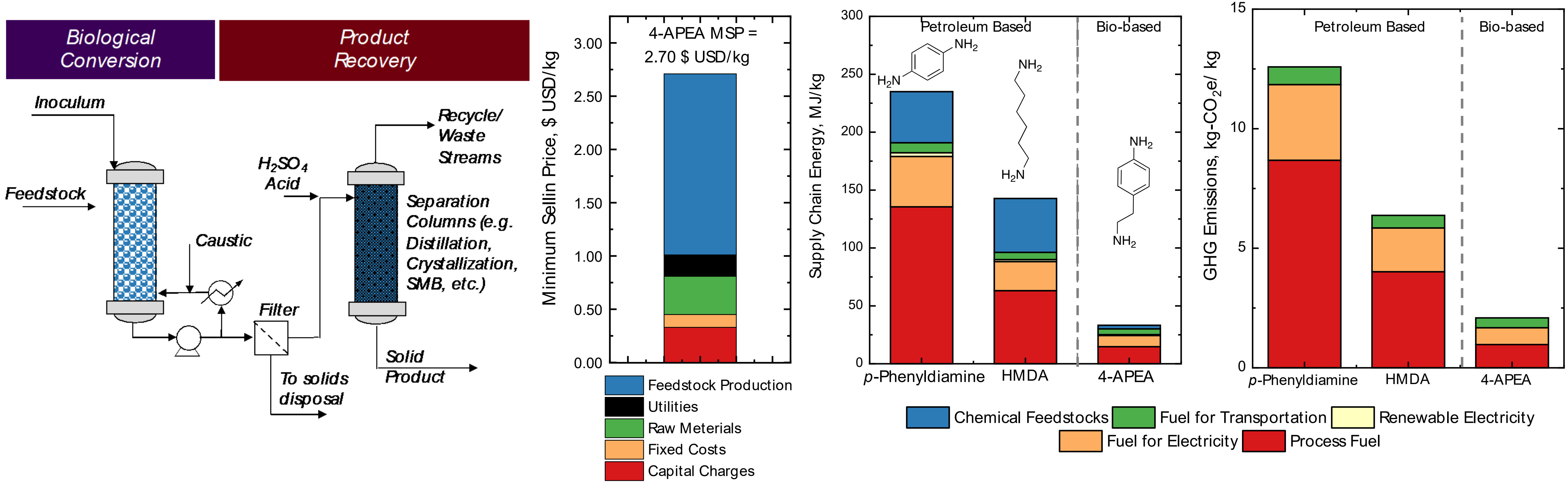
Van Krevelen diagram showing chemical distances of feedstocks to polymers (X is a heteroatom, typically oxygen or nitrogen)

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

Biomass-derived amines exhibit manufacturing benefits

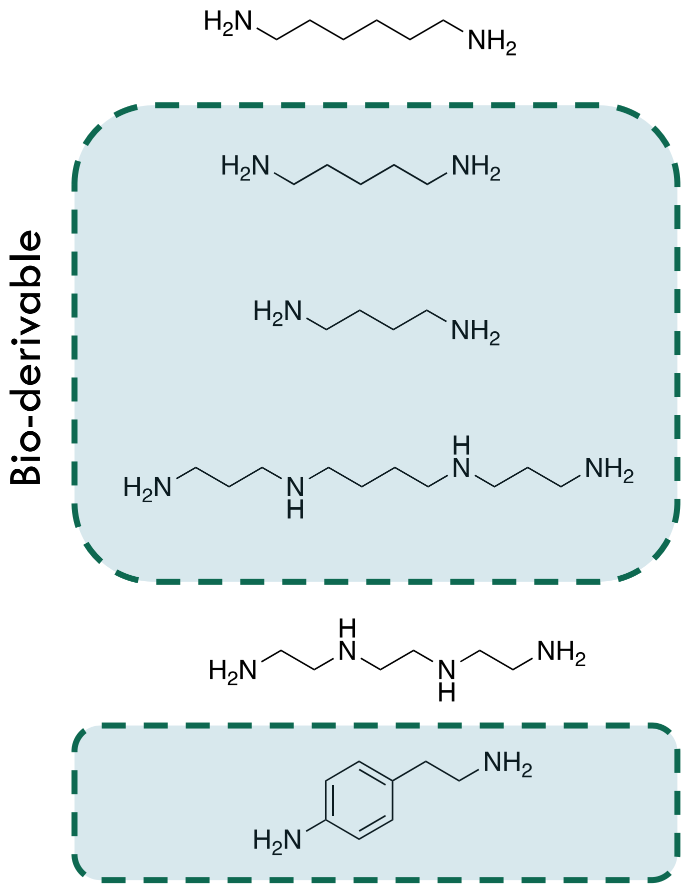


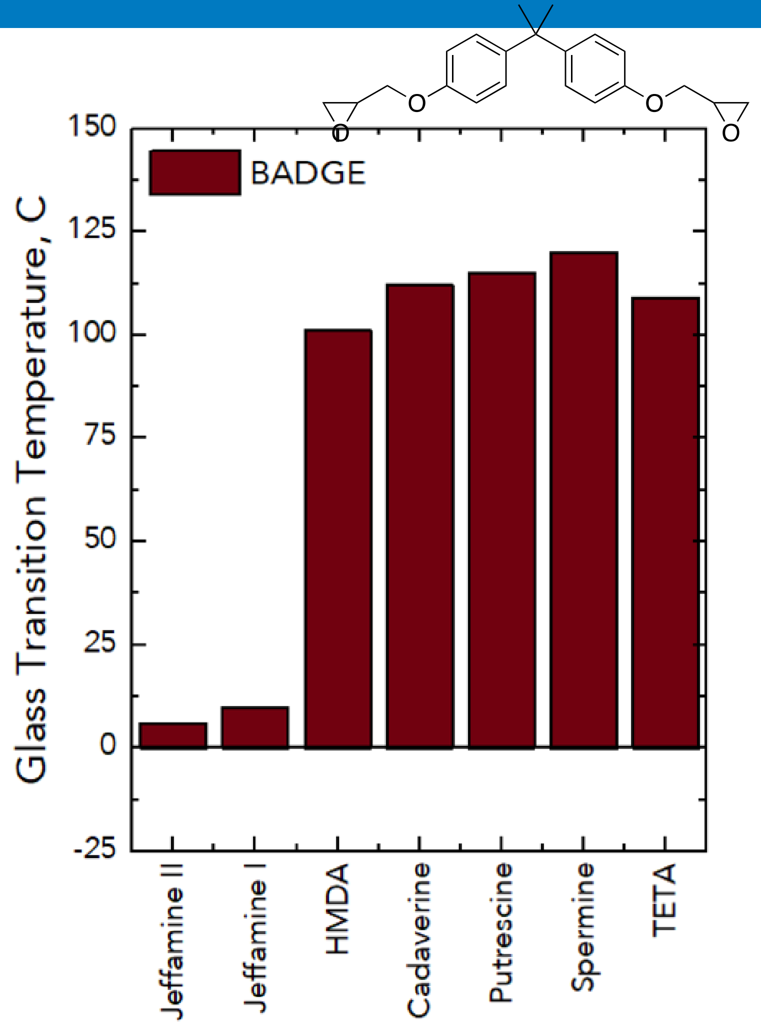
Amines from biomass can offer ≥85% reduction in supply chain energy and GHG emissions depending on comparison

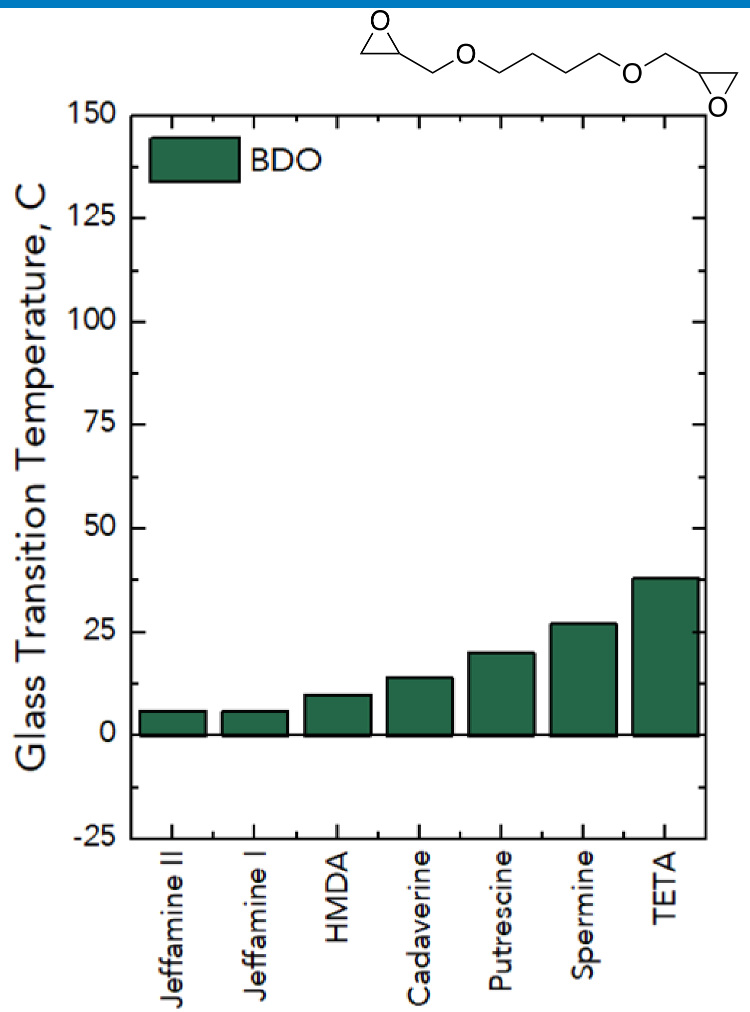
- Amines are intensive to make from petrochemical sources as they either rely on ammoxidation or nitrilation reactions
- The creation of amines from biomass uses significantly less heating than petrochemical processes
- Feedstock is a key contributor to cost – analysis is ongoing for reducing feedstock contribution

Hoyt *et al.* in preparation

Epoxy Amine Resins – Tunability via Expanded Formulation



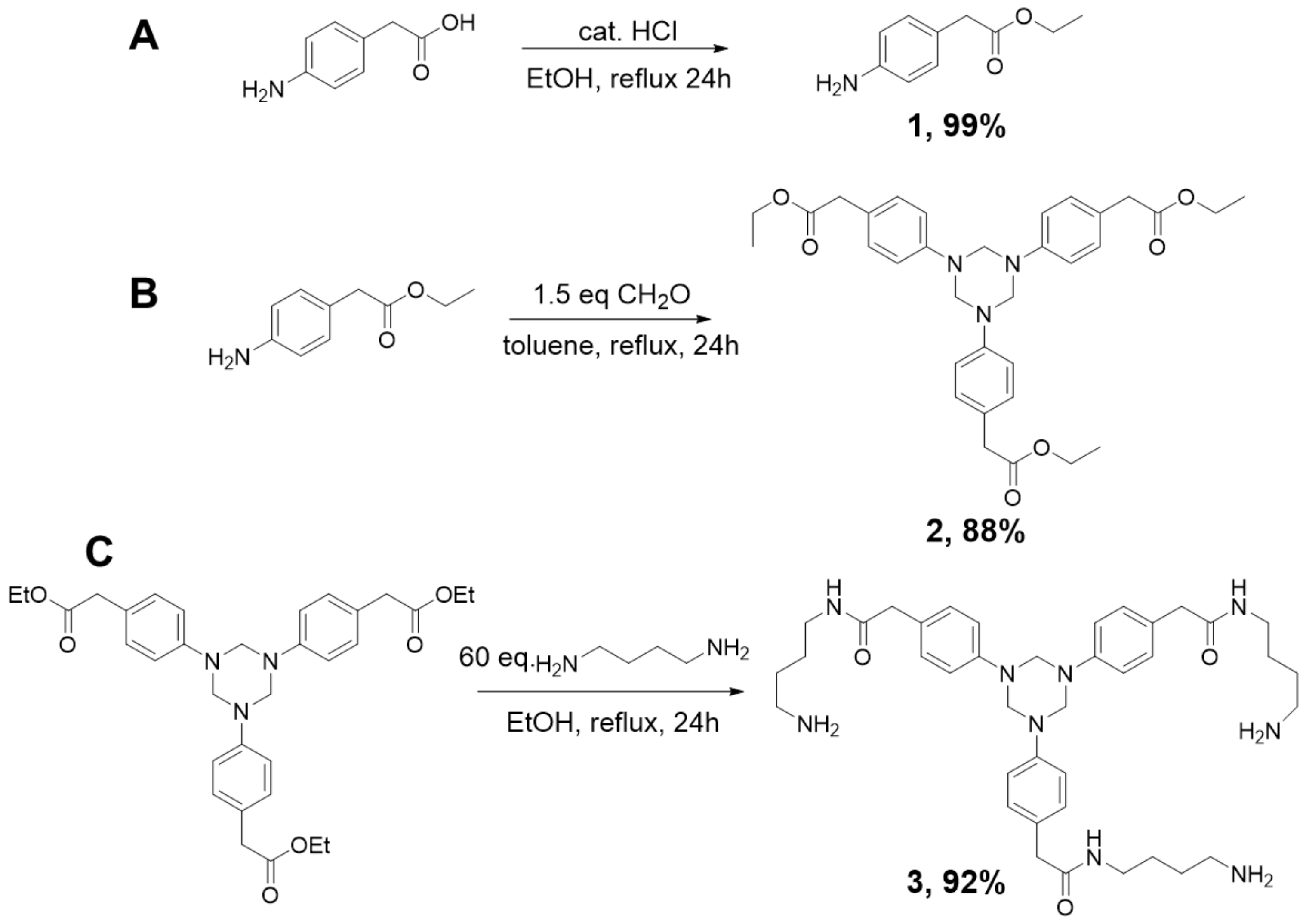




Diamines can be reacted with epoxies to form robust thermosets

- When implemented in epoxy resins the performance of the material is proportional to the spacing between amines
- Aside from lower GHG and SCE in monomer manufacture, benefits are minimal

Hybrid Epoxy Amine/Triazine Thermosets – Multiple Performance Advantages

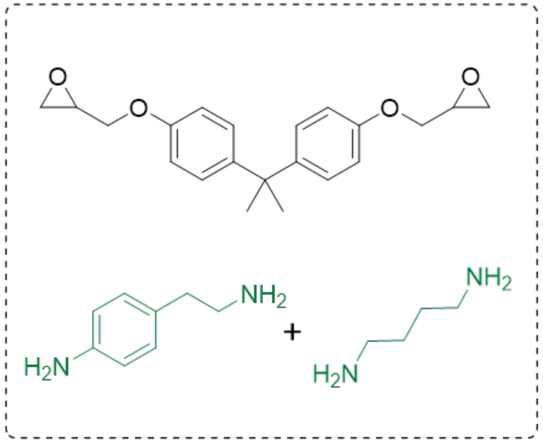


Triazine are another emergent application that relies on amines as they offer end-of-life recycling

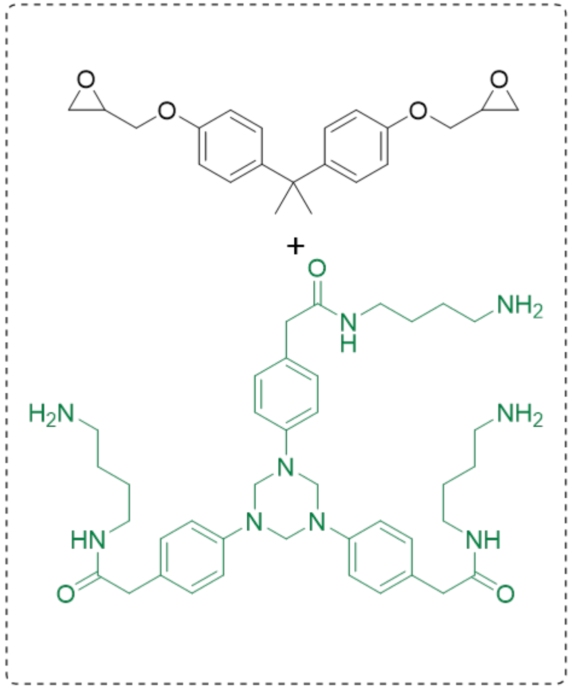
- Here, we implement APAA again to form amine hardeners with a central triazine
- The carboxylic acid of the APAA enables the controlled incorporation of triazines
  - Data that will not be shown today has indicated that controlled incorporation is needed and that the rate of triazine formation and epoxy ring opening are comparable
- The use of this hardener can enable the reaction with epoxies via the terminal amines and end-of-life options via the traizine

Hoyt *et al.* in preparation

Hybrid Epoxy Amine/Triazine Thermosets – Multiple Performance Advantages



PBND- Partially bio-based; *non-degradable*

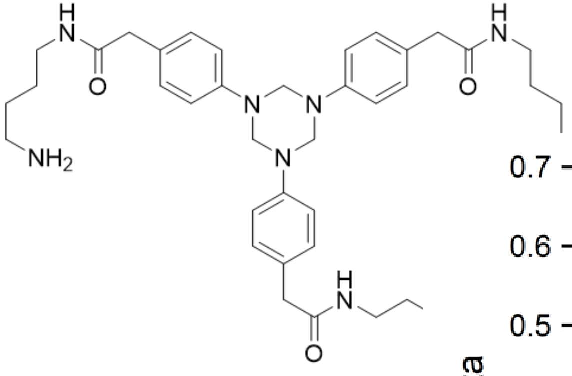


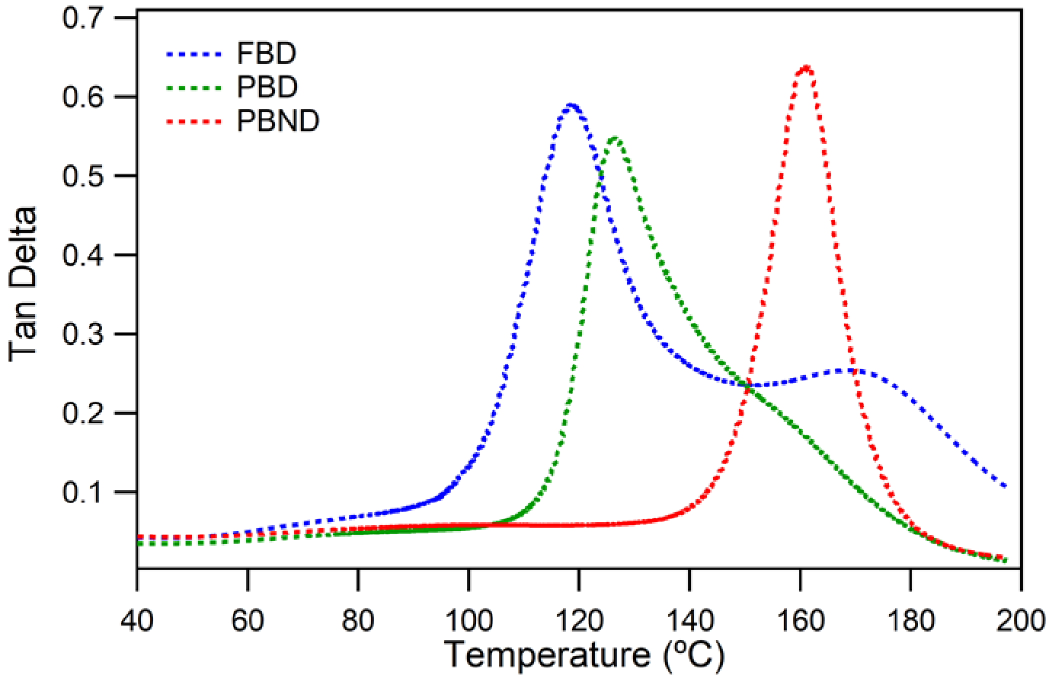
PBD- Partially bio-based; *degradable*

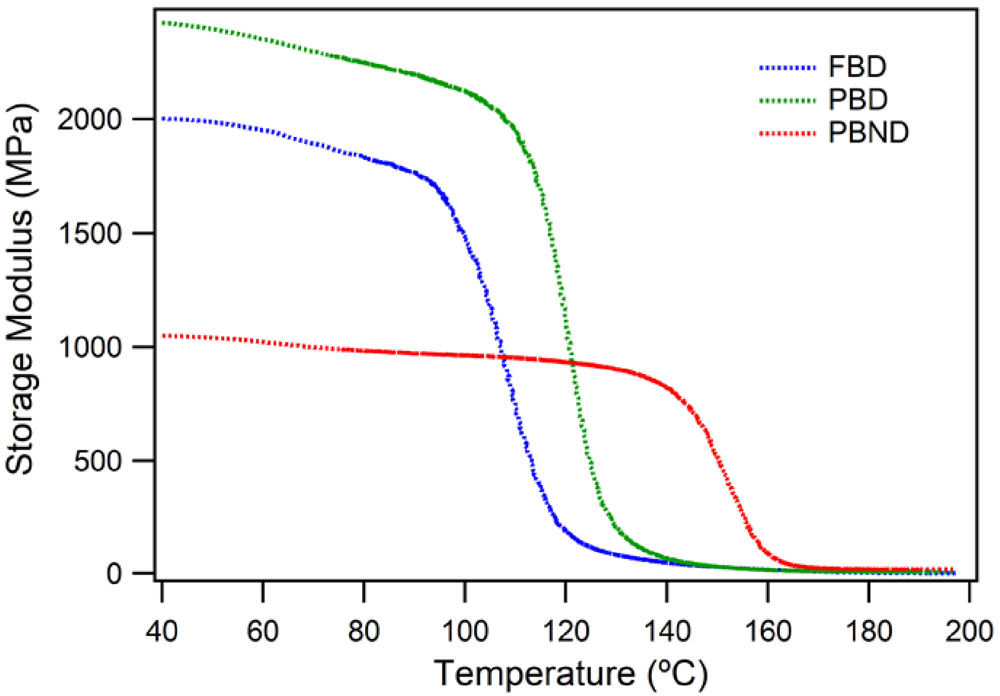
Control reactions to understand performance

- As the new hardener uses two bio-based amines, we designed an analogous non-degradable epoxy-amine resin with similar characteristics
- Additionally, we probed a bio-derivable epoxy from lignin sources
  - We expect that the bioderived epoxy may lead to plasticization but may have manufacturing based performance advantages

Hybrid Epoxy Amine/Triazine Thermosets – Multiple Performance Advantages







The triazine enables degrdataion increases

- The incorporation of the triazine increases free volume of the thermoset which leads to a lower glass transition temperature
- However, the triazine itself provides more rigidity leading to higher stiffness and storage modulus
- The bioderived epoxy also increases free volume alongside flexibility leading to reduced T_g and storage modulus

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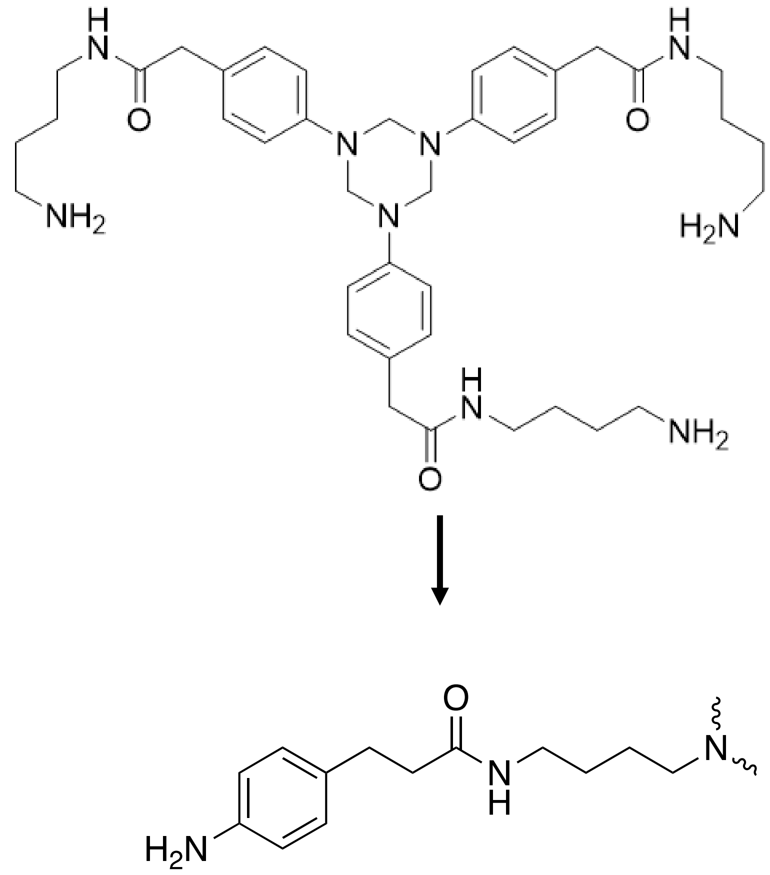
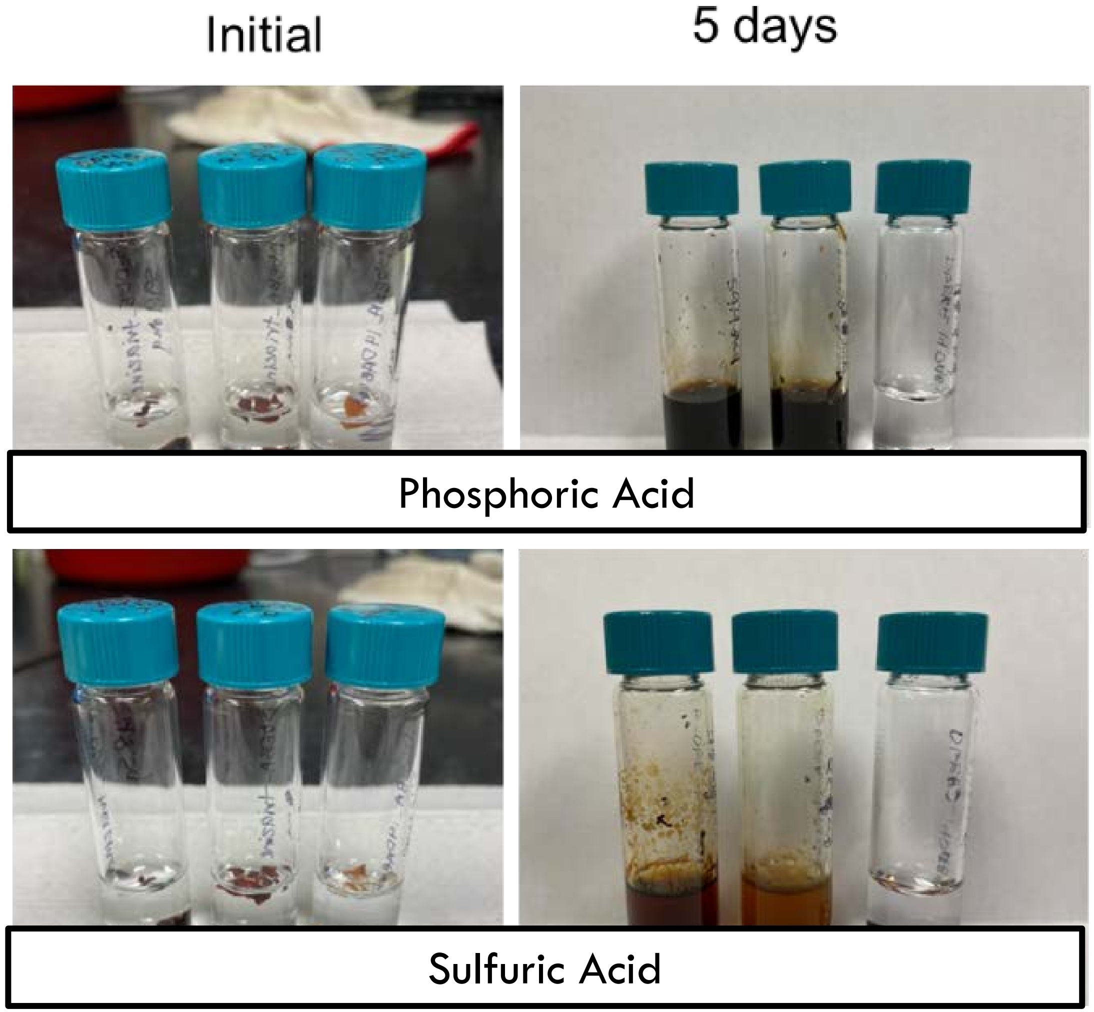
Hybrid Epoxy Amine/Triazine Thermosets – Multiple Performance Advantages

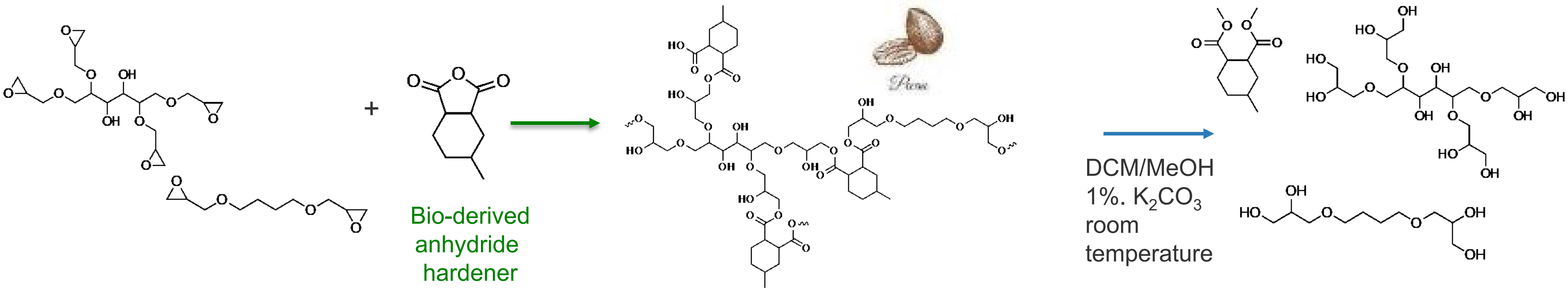




Controlled triazine incorporation depolymerization

- We have also made random **epoxy-amine/triazine networks and they do not degrade substantially**
- Thus, we can enable all three types of performance advantages when leveraging hybrid networks

Non-Amine Networks – Potential for Redesign



Virgin PECAN CFRC

Depolymerized CFRC

Epoxy-anhydrides can be used to redesign thermosets with easy to recycle ester linkages

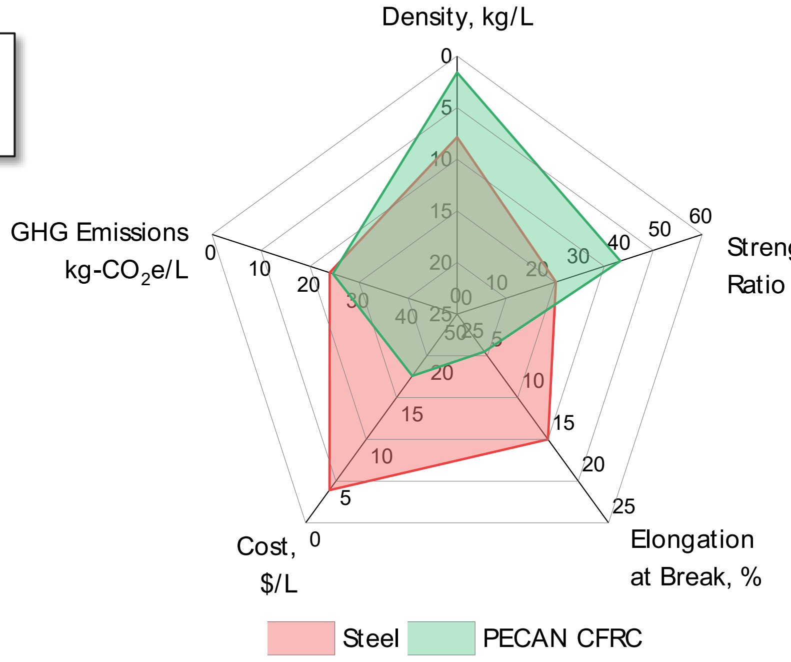
- Properties of the epoxy-anhydrides can be formulated to match or exceed epoxy amine resins. Currently, we have found minimal performance advantages however in the ***1st life*** manufacturing or lifetime performance
- Room temperature depolymerization can be implemented to maintain filler, here CF, properties

Non-Amine Networks – Potential for Redesign

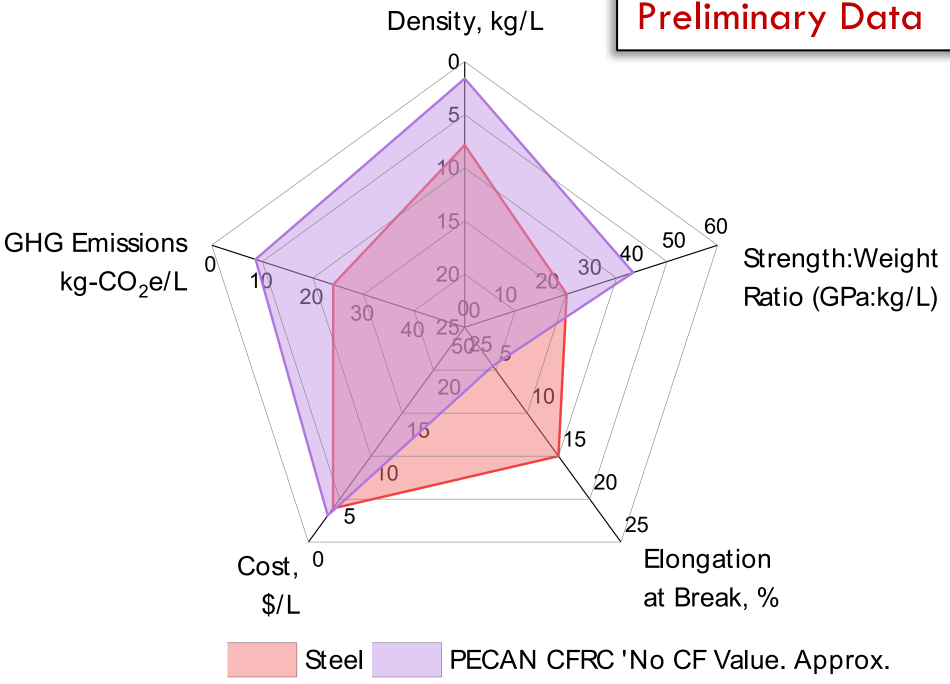
Fiber estimate price:
$21.5/kg (variable)

Hexion estimate
price: **≥ $2.03/kg**

Estimate initial selling
price: **≥ $2.17/kg**



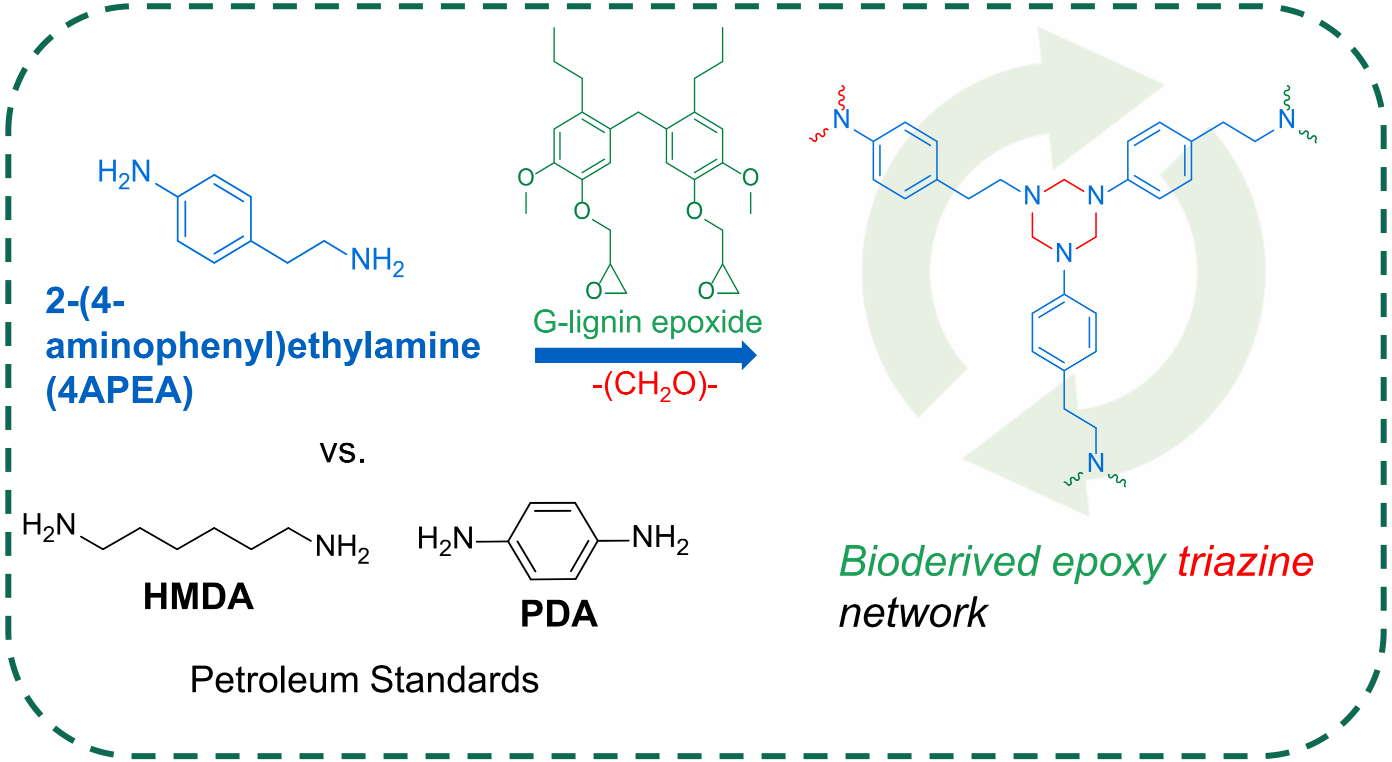
Preliminary Data



In the context of composites, recyclable systems exhibit multiple manufacturing performance advantages

- Virgin epoxy-anhydride CFRC synthesis is comparable to steel GHG emissions on a volume basis.
- When the first life of the CFRC is not accounted for, nor the recovery of monomers, the GHG impacts of all subsequent lives are ~10 kg/L.
  - Resin depolymerization and CF recovery accounts for 4.4 kg CO_2-e/kg_{CFRC} and cost \$1.70/kg_{CF}
  - TEA for depolymerization is still ongoing. Early economics are favorable and still need to account for the recover of the anhydride, which can be sold (\$2–\$4/kg) to bolster economics.

Conclusions – Finding Multiple Performance Advantages



Hoyt *et al.* in preparation

Nitrogen from biomass can enable multiple performance advantages can enable robust properties for engineering plastics

- Multiple thermoset materials leverage nitrogen-based compounds for there reactivity or performance
- Bio-derivable nitrogen containing compounds can be used to enable performance advantages in **Manufacturing, Performance, End-of-Life**
- There is still a parallel opportunity to avoid nitrogen through thermoset redesign

Thank You!

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