QUARTERLY PROGRESS REPORT
October 2025 – November 2025

PROJECT TITLE: PLASTIC RECYCLING VIA REACTIVE MELT PROCESSING: ALIPHATIC POLYESTER RECOVERY

PRINCIPAL INVESTIGATOR(S):

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Research Description:

Given the complexities in reaction pathways, stereochemistry, and the effects of solvent and other additives, quantum calculations have been applied to gain an in-depth understanding for the impact of degradation kinetics on molar mass and architecture of molten PLA. We found the thermal radical induced beta-scission possess a large energy barrier at typical temperature of melt processing and therefore being kinetically inefficient for PLA thermal degradation. On the contrary, transesterification mechanism suggests an alternative pathway with the formation of PLA oligomeric rings. Through a systemic study corresponds to size, presence of metal ions, stereochemistry, and solvation, we found thermal stability of the rings can be regulated by the type and the state of metal ions. In particular, the configuration and the energy of transforming a linear segment of PLA into a cyclic form were shown to be strongly affected by the stereochemistry and the solvation. Further efforts are made to understand the presence of stabilizing hydrogen bonding under polar reaction environment. Once complete, these computational studies will provide molecular insight to design and engineer critical reactions for recycling of PLA via melt processing.

Experiments are designated for the effects of detailed formulation along with processing condition on the properties of recycled PLA. Model compound studies will be conducted to reconcile the aforementioned computational findings with experimentally determined kinetics. Trials of low molar mass PLA oligomer will be formulated and reacted under identical conditions as typical melt processing with the corresponding reaction outcomes quantified by NMR and GC/MS.

Life Cycle Assessment (LCA) will support development of polylactic acid (PLA) recycling technology by evaluating the environmental impacts of different recycling options (including reactive melt processing, composting, and mechanical recycling) and the business-as-usual approaches (incineration and landfill). The typical functional unit selected was 1 kg of waste PLA, and the system boundary was defined as cradle-to-gate. Furthermore, the technoeconomic analysis (TEA) will assess the feasibility and potential of the proposed reactive melt processing in comparison to other recycling/disposal pathways, providing a

comprehensive view that integrates experimental, environmental, and economic aspects of the process under our development.

Work accomplished during this reporting period:

For this reporting period, we are completing the computational study on degradation mechanism of PLA, initiated the experimentation on reaction profile and formulation design as well as life cycle assessment and technoeconomic analysis.

Computational Study on Degradation Mechanism:

Quantum chemistry was used to evaluate the degradation kinetics (chain scission and transesterification) and their impact on molar mass and architecture of molten PLA, which can hardly be acquired from experiments otherwise. Preliminary results from this study show there is a high energy barrier (>> RT = 4.2 kJ/mol, Fig. 1A) that much be overcome to break PLA at the chain end to produce small molecules (carbon monoxide and acetaldehyde) via the thermal radical induced beta-scission mechanism. The high energy barrier suggests that degradation by beta-scission from chain end be kinetically inefficient and thus unlikely under typical melt processing temperature of 500K. Alternatively, transesterification reaction, via the formation of PLA oligomeric rings, was of particular interest as these rings are hypothesized to be a stable PLA degradation product and can be leveraged to improve the mechanical strength of PLA.[1, 2] It was found later that the formation of these PLA rings is affected by the following factors: 1) ring size, 2) metal ions, 3) stereochemistry and 4) solvation.

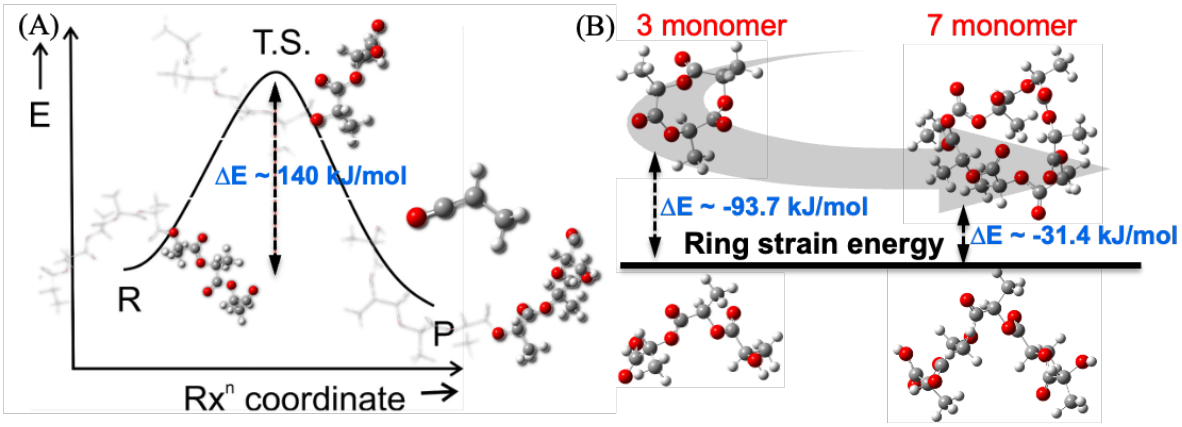

Fig 1. Computational studies reveal valuable mechanistic insights on the degradation of PLA. (A) The beta scission of chain end to small molecules (CO and acetaldehyde) is associated with high energy barrier and thus inefficient kinetics. (b) The computed ring strain energy (i.e., the energy difference between cyclic and linear PLA of identical size) decreases with size of PLA indicating a high probability to form macrocycles under thermal treatment.

As illustrated in Fig. 1B, larger size PLA oligomeric rings were found to possess higher stability as they showed a decrease in ring strain energy (i.e., energy required for forming ring from linear oligomer via loss of 1 or more monomer units) with number of monomers contained. This implies the probable formation of PLA macrocycles under thermal treatment. Additionally, we noted the presence of “even-odd effect" (i.e., alternating pattern in properties linked to the number of monomer units based on whether this number is even or odd)[3], where a consistent reduction in ring strain energy exist for PLA oligomer of even numbers of monomers.

The thermal stability of PLA oligomeric rings can be further regulated by the presence of metal ions with different types and charges. The association of metal ions, such as Li+, Na+, Mg2+ and Ca2+ ions, with PLA oligomeric rings resulted in a symmetric configuration and lower energy compared to those with no association. On the contrary, in the presence of Al3+, the oligomeric rings seemed unfavored and eventually giving rise to the destruction of PLA oligomer into small molecules. Such effects also vary with the ring size, suggesting a route for fine tuning the macromolecular architecture.

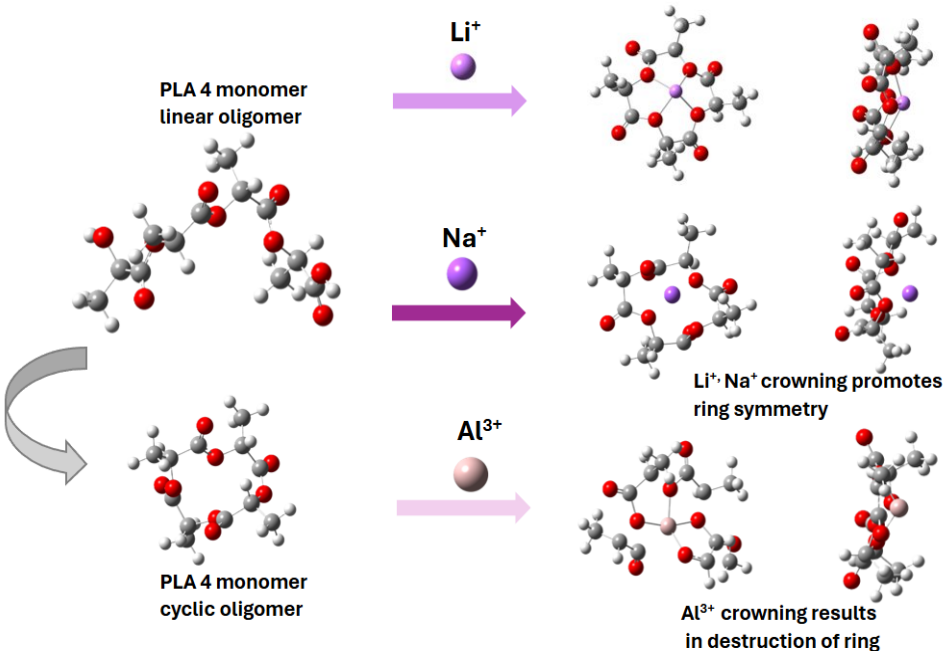

Fig 2. The stability and configuration of PLA cyclic structure is affected by the association with metal ions of different types and charges. Li+, Na+, Mg2+ and Ca2+ ions lead to a symmetric configuration with the cyclic oligomer whilst the association with Al3+ trends to be unfavored.

For stereochemistry, comparisons on the energy of both linear and cyclic PLA oligomers with varying constitution of L- and D-enantiomers were made. Oligomers of L- enantiomers showed predominately lower energy for all cases we studied regardless of the topology (i.e. cyclic or linear) than those of D-enantiomers. This is consistent with the abundance of PLLA in nature given the energetic preference. For large oligomers (i.e., those containing 7 or more monomer units), the difference in structures of varying type of enantiomers, become significant: The L- enantiomers displayed a coiled helical pattern, compared to the mixed structure (alternating L and D monomer units) of a zig-zagging pattern. More efforts are made to understand the mechanisms responsible for the observed steric difference.

Solvation effect also known to be a significant factor in the degradation of PLA. All previous degradation conditions were simulated under vacuum and are therefore subject to the addition of solvation model. The effects of hydrogen bonding are also under study by inserting water molecules along the PLA backbone.

Experimentation on Reaction Profile and Formulation Design:

Model compound studies are designed to validate and expand upon the findings from quantum calculations related to PLA degradation and structural reconfiguration kinetics. To gain experimental insight into the reaction profile of PLA degradation, design of experiments is structured to quantify the

influence of reagents and processing parameters, rather than attempting to optimize specific reaction outcomes. Formulations to begin with consist of few reagents and test under narrow range of processing parameters, gradually add and broaden design space based on results from prior trials.

As shown by Fig. 3, a low-molar mass oligomer of PLA is to be used for the consistency and ease for chemical analysis that conventional PLA of complex molecular characteristics would not provide. Master batches will be made composed of the PLA oligomer, along with additives of interests (from the aforementioned computations) including but not limited to triol, peroxide, dehydrated cerium salt, and citrate designated to act as the transesterification initiator, scission initiator, catalyst, and plasticizer respectively. To begin with, glycerol, dicumyl peroxide,[4] and Cerium(III) nitrate are selected, and water may also be included as another additive. After the preparation of the batch, aliquots are to be distributed into dry N_2 purged glass vials resealed with thermoresistant tape. These vials will be placed in high precision heating plate for designated conditions before quenching the reaction.[5]

Proton NMR and GC/MS analysis will be conducted by diluting aliquots in chloroform[6] to a 1:11 and 1:75 volume ratios for each test respectively.[5] Each vial, including one retrieved from the batch and never heated (i.e., negative controls), will be analyzed to collect data across the domain of reaction profile. The joint usage of NMR and GC/MS techniques are to quantify the reacted species and the corresponding molar mass respectively. The dual employment of these methods will provide demonstration data for design the further optimization of reactive melt processing at industrial relevant scale and processing unit.

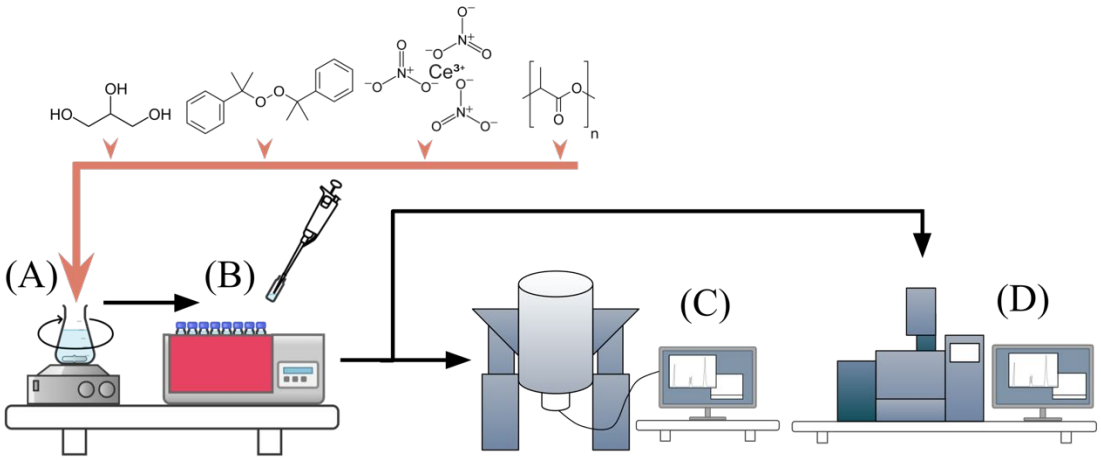

Fig 3. Illustration of model compound study on design of formulation and reaction profile for PLA melt-phase recycling. (A) Formations of well-mixed master batch consist of reagents and additives by experimental design. (B) Batch aliquots under precise control of reaction conditions are retrieved and quenched for quantitation. (C) Aliquot samples are fed into (C) NMR for protium spectra and (D) GC/MS for abundance spectra, respectively.

Life Cycle Assessment on PLA End of Life Pathways:

Polylactic acid (PLA) is a bio-based polymer that has increased demand for the dependency reduction on fossil resources and mitigation on climate change. The annual capacity for a typical major producer of PLA is 130,000–150,000 tons (metric)[7]. It is thereof major importance to investigate the end of life of this material, with a focus on the recycling and business-as-usual scenarios (BAU). As a useful tool to investigate the environmental impacts of a product or a process, Life Cycle Assessment (LCA) can be leveraged for decision-making on the environmental aspect between disposal and repurposing of PLA.

In comparison to petroleum-based plastics such as polypropylene (PP) and polyethylene (PE), PLA have shown lower levels of acidification and ecotoxicity, emphasizing its importance as biodegradable plastics and the corresponding impacts on their waste management scenarios [8]. The life cycle assessment of recycling options for PLA has been studied before, though primarily with a focus on understanding the environmental impacts of different PLA end-of-life scenarios, such as mechanical recycling, chemical recycling, solvent-based recycling, composting, incineration, and landfill [8-10]. The environmental gains of using biodegradable plastics in different percentages of waste treatment approaches (e.g., landfill, incineration, recycling, composting) were also assessed through the LCA development. Due to its production process, [8] PLA showed higher Global Warming Potential (GWP) among the scenarios evaluated in comparison to another biodegradable plastic, polyhydroxybutyrate (PHB).

To better compare the greenhouse gas emissions (GHG) for each end-of-life pathway, the functional unit, also known as the basis for the analysis, must be defined. A functional unit of 1 kg or 1 ton of residual or waste PLA was typically reported. [10-12] Such selection was justified by the fact that the recycling outputs of each technology vary with properties and quality, otherwise making a reasonable comparison impossible[10].

Previous studies by Maga et al. [10] found that recycling PLA and using it to substitute virgin PLA can reduce GHG emissions in comparison to incineration. The authors also reported that the quality of the recyclate via chemical recycling, is identical to virgin PLA, and thus the substitution of the same amount of virgin PLA with the recyclate saves 1480 kg CO_2-eq./FU. For chemical versus mechanical recycling, Cosate et al. [11] found that, electricity consumption shows the greatest impact as being used mainly for extrusion, granulation, drying, hydrolysis, and polymerization in these pathways. Among chemical recycling, mechanical recycling, and composting, the authors reported that mechanical recycling is the best waste management approach with the lowest environmental impacts. While chemical recycling stands for lower emissions in comparison to composting. Regarding emissions from the biodegradability (end-of-life) of PLA, Benevides et al. [13] found that, with the consideration of biodegradability (BD 60%) for PLA, the life cycle GHG emissions increase significantly (3.7 kgCO_2e/kg plastic), when comparing to composting with the same BD percentage or landfill without biodegradability consideration. These authors also reported the emissions for end-of-life were lower in composting than in landfill, due to lower CH_4 emissions in composting gas.

Overall, it is important to investigate the environmental impacts of PLA recycling for new technologies development. The understanding of plastic end-of-life pathways, such as reactive melt extrusion, has not been explored before, and is the aim of this work, to allow a technoeconomic analysis of challenges and opportunities for PLA recycling.

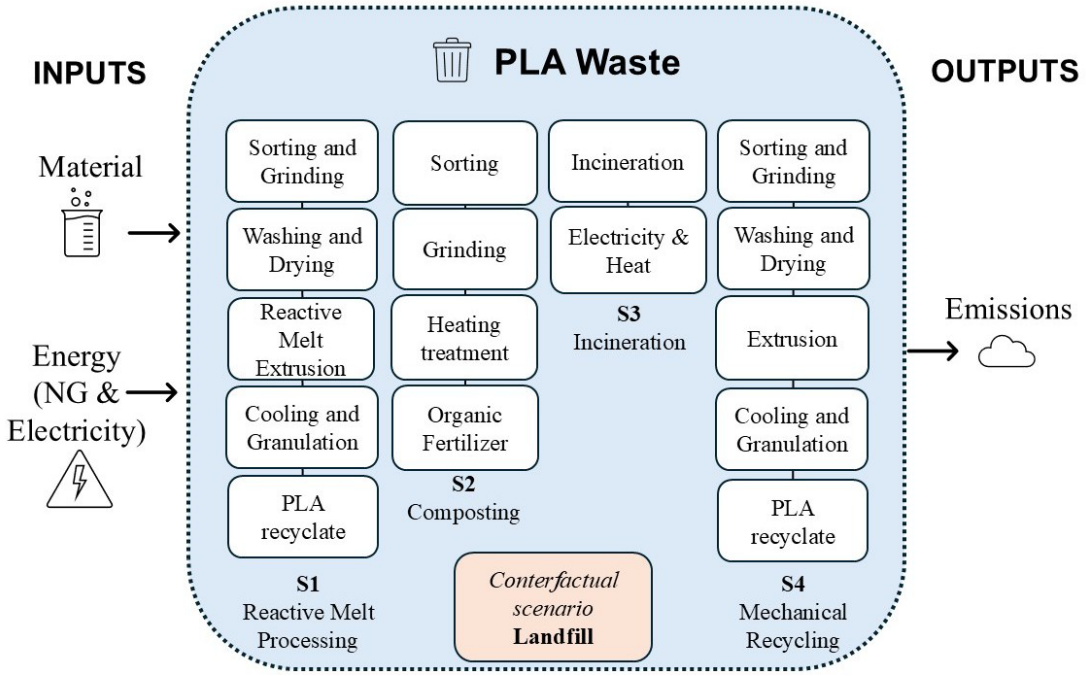

Fig 4. System boundary cradle-to-gate for LCA on PLA End of Life Pathways.

Here our life cycle assessment on comparing the end-of-life pathways of PLA waste will be performed in accordance with ISO 14040 and ISO 14044. The GREET 2024 Rev.1 software is being used to assess the simulation. The functional unit selected for this work is 1 kg of waste PLA, and the system boundary defined is cradle-to-gate, which accounts for environmental impacts from the raw material production through end-of-life pathways. The representation of the boundaries used can be seen below (Fig. 4). The scenarios analyzed in this work include reactive melt processing (S1), composting (S2), incineration (S3), and mechanical recycling (S4). For this study, PLA recyclate produced by the reactive melt processing (S1) was modeled to include steps of sorting, grinding, washing, drying, reactive melt extrusion, cooling, and granulation (Fig. 5).

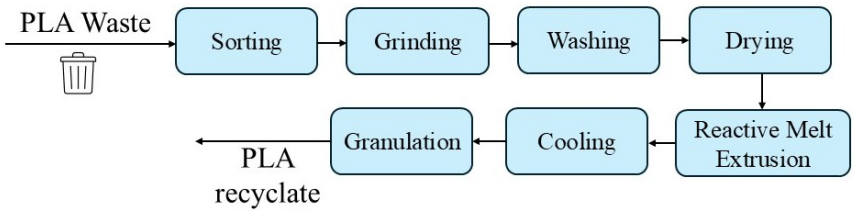

Fig 5. Block flow diagram for the reactive melt processing of PLA.

Technoeconomic Analysis for Development of PLA Recycling Technology:

For the TEA development, economic parameters and data based on literature are being collected for the scenarios studied. The software DWSIM chemical process simulator will be used to support some of our estimates. The economic performance will be compared considering the equipment prices, total capital costs (CAPEX), total project investment, operating costs (OPEX), utilities, and revenue generation, and the net present values (NPV).

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TAG meetings:

The 1st TAG meeting was held on Oct. 24. The full list of members is found at the website link. We were pleased to have ~ 14 of the TAG members be able to join. The website will be updated soon to reflect the meeting took place and the slides will be uploaded there.

Future Tasks:

Computational Study on Degradation Mechanism:

Next steps for the computation study include further investigation of the effect of stereochemistry as well as solvation models, with emphasis on water effect. Additional work includes refining all molecules with high level theory and finally gaining insight into the long chain degradation mechanisms and kinetics via ONIOM (Our own N-layered Integrated molecular Orbital and Molecular) modelling and greater single point energy readings using ORCA modelling software.

Experimentation on Reaction Profile and Formulation Design:

The next steps on model system-based reaction and formulation design include lab-scale testing for kinetics of moderate molecular weight PLA under industrial relevant processing conditions.

Life Cycle Assessment on PLA End of Life Pathways:

The next steps in the LCA development include the inventory definition. Mass and energy balances will be completed to allow simulation of the impacts for each scenario studied.

Technoeconomic Analysis for Development of PLA Recycling Technology:

The next steps in the TEA development include the collection of all the important inputs needed for all the scenarios studied, which include literature review and simulations.

METRICS REPORTING

1. Summarize input provided by the TAG during this period.

   We recently completed our kickoff TAG meeting. As mentioned above, we had ~ 14 TAG members present. After ~ 45 min presentation, TAG members asked ~ 5 questions, which helped us refine the explanations and scope of work. We anticipate also receiving feedback via email.

2. List research publications resulting from THIS Hinkley Center project. Has your project been mentioned in any research and/or solid waste publication/newsletters/magazines/blogs, etc.?

   None.

3. List research presentations resulting from (or about) THIS Hinkley Center project. Include speaker presentations, TAG presentations, student posters, etc.

   “Upcycling of Aliphatic Polyesters: Mechanistic Insight into Polylactic Acid Degradation” by N. Hall, S. Powell, E. Abudobaida, and W. Zou, 2025 AICHE Annual Meeting, Boston MA, Nov. 05.

   TAG meeting on 10/24/25.

4. List who has referenced or cited your publications from this project. Has another author attributed your work in any publications?

None.

5. How have the research results from THIS Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought? Please list all grant applications and grants and/or funding opportunities associated with this project. Indicate if additional funding was granted.

Multiple (pre)proposals on plastic upcycling via reactive melt processing are pending and/or in preparation. One is to EREF (pending), and others to DOE, NSF, and relevant industries are planned.

6. What new collaborations were initiated based on THIS Hinkley Center project? Did any other faculty members/researchers/stakeholders inquire about this project? Are you working with any faculty from your institution or other institutions?

None.

7. How have the results from THIS Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders? (1 paragraph maximum). Freely describe how the findings and implications from your project have been used to advance and improve solid waste management practices.

None.

PICTURES: The most recent pictures have been uploaded to the website (linked above).