QUARTERLY PROGRESS REPORT

December 2025 – February 2026

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

PRINCIPAL INVESTIGATOR(S):

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Research Description:

Further investigation of the polylactic acid (PLA) degradation mechanisms was undertaken using quantum calculations. Through this study, we found that specific degradation mechanisms, such as thermal radical induced beta-scission and mid-chain alpha scission, are kinetically unfavorable, due to their large energy barrier. Additionally, computational investigations on isomerism also show different energy profile and molecular configuration for L-enantiomers of PLA compared to that of its D and mixed counterpart.

Our ongoing computational study focus on the effect of solvation and water molecules as additives on PLA oligomers. Given the presence of ester linkages, understanding water-PLA interactions is critical to predict PLA stability in a hydrated environment. Quantum chemistry is therefore applied to investigate how bulk solvation (implicit continuum) and explicit hydrogen-bonding with a water molecule influence the configuration and stability of PLA oligomers. This is achieved using an implicit continuum solvation model with or without explicit water molecules to facilitate hydrogen bonding along the PLA backbone.

For the synthesis of PLA model polymer towards high molecular weight, two literature documented strategies have been proposed. Synthesized model PLA will serve as the base for future work involving the aforementioned design on formulation and reaction profile with the goal to structurally upgrade of PLA via melt processing.

While quantum calculations can generate many data effectively and at low cost, it alone cannot guarantee, nor explore the full extent of, reaction kinetics in a complex system such as polymer degradation. For this, a model compound study is needed on the mechanisms behind PLA, beginning with degradation kinetics This is primarily conducted through measuring 'snapshot' instances of a reaction underway using quantitative NMR spectra.

For the Life Cycle Assessment (LCA), the inventory for mass and energy data for Scenario 1, using Reactive Melt Processing of waste PLA, was defined. All the upstream materials were available in the GREET module, and the impact assessment category used in this assessment is Global Warming Potential (GWP) over a 100-year period. The stages covered in the LCA are collection, sorting, washing & drying, reactive melt extrusion, cooling, and granulation. The preliminary results show that electricity consumption is the major factor affecting greenhouse gas (GHG) emissions.

Capital expenditure (CAPEX) was estimated for on-site processing of biodegradable plastic (1041.7 kg/h), using the tools CAPCOST, CatCost, and Matches. All the costs will be extrapolated to the 2024 Chemical Engineering Process Cost Index (CEPCI).

Work accomplished during this reporting period:

For this reporting period, we are completing the computational investigation on degradation kinetics, the effects of stereochemistry, solvation and additive on the stability and configuration of PLA; conducting preliminary experiments and calculations for reaction profile and formulation design and life cycle assessment and technoeconomic analysis, respectively.

<u>Computational Study on Degradation Mechanism:</u>

Effect of stereochemistry. The stereochemical effects on stability and configuration of linear and cyclic PLA oligomers is modelled with varying constitution of L- and D-enantiomers. Oligomers of L-enantiomers showed predominately lower energy for most sizes (i.e. dimer to nonamer) we studied regardless of the topology (i.e. cyclic or linear) than those of D-enantiomers and alternating enantiomers (alternating L and D monomers). This trend appears to be consistent with the abundance of PLLA in nature given the energetic preference. For large oligomers (i.e. those containing 7 or more monomer units), significant differences on molecular configuration appear by varying type of enantiomers: The structure of pure L- enantiomers displayed a coiled helical pattern in contrast to the alternating structure (alternating L and D monomer units) of a zig-zagging pattern (Fig. 1). More efforts are currently being made to understand the mechanisms responsible for the observed chiral differences.

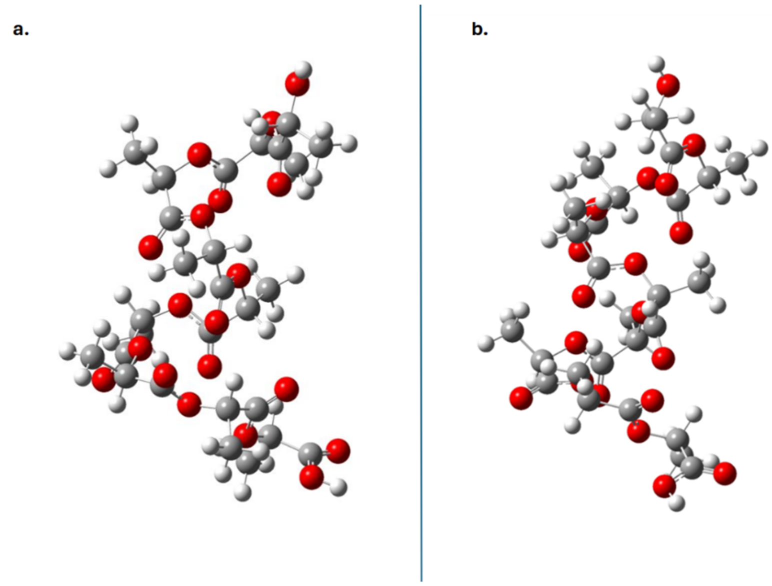

Figure 1. Chiral differences displayed in PLA isomers. a) Oligomer of pure L- enantiomers shows coiled helical pattern, in contrast to the zig-zagging pattern for (b) alternating structure (alternating L and D monomer units).

Degradation kinetics. Quantum chemistry was used to evaluate the degradation kinetics correspond to chain scission and transesterification. For mid chain alpha scission, PLA is cleaved at the alkyl C-O single bond in the ester group, resulting in the formation of 2 radical molecules with a particularly high energy barrier (156.2 kJ/mol). This suggests alpha-scission based degradation in the middle of the polymer backbone is kinetically inefficient at typical melt processing temperatures (i.e., 500 K). Further refinement using ONIOM (Own N-layered Integrated Orbital and Molecular) modelling and energy correction with higher-level theory might impact the kinetic data and overall outcome of reaction.

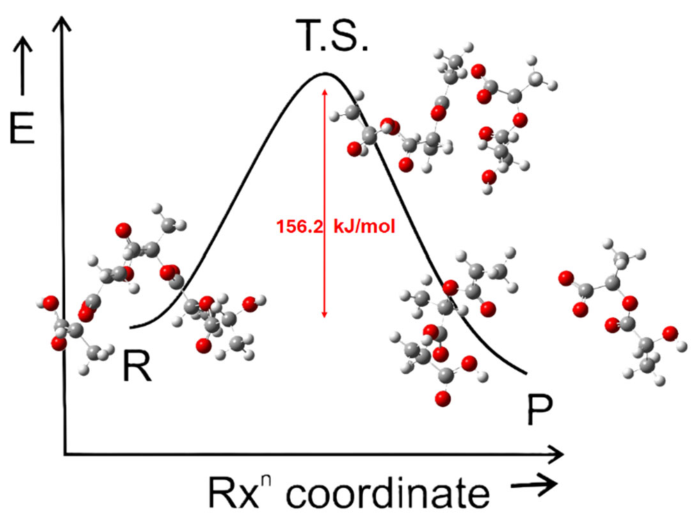

Figure 2. Computational studies reveal valuable mechanistic insights on the degradation of PLA. Mid-chain alpha scission to radical molecules is associated with high energy barrier of the transition state (T.S.) and thus suggests inefficient kinetics.

Effect of solvation. The effects of bulk solvation were quantified by using an ester solvent, methyl ethanoate, as a continuous dielectric medium surrounding the oligomer. Methyl ethanoate was selected as it provides a bulk environment with ester-like polar behavior similar to the repeating unit of PLA in chemical character[2]. The solvated oligomers showed small but consistent charge-redistribution along the oligomer (Fig. 3).

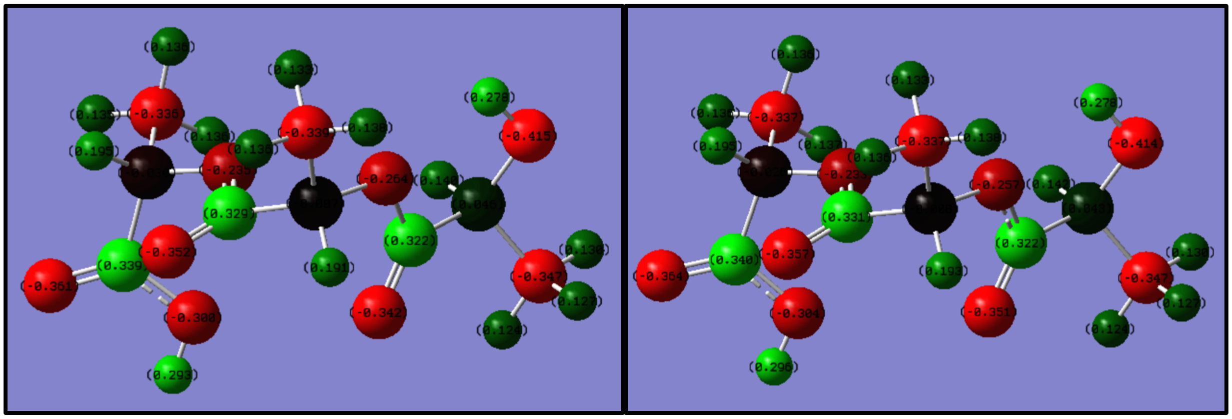

Figure 3. PLA oligomer before (left) and after (right) solvation, obtained using the Integral Equation Formalism Polarizable Continuum Model (IEFPCM) with methyl ethanoate. Partial atomic charges are shown, illustrating solvent-induced charge redistribution. The maximum partial charge difference was +0.009e on a carbonyl oxygen atom. All partial charge differences were on the order of 0.001–0.009 e (absolute value).

Effect of added water. Hydrolysis is a primary degradation pathway for polyesters via cleavage of ester bonds through reactions with water molecules, constituting a change in the molecular structure. Water molecules can also participate in hydrogen bonding to change PLA structure. To investigate such localized hydration effects, a single water molecule was introduced into the optimized solvated oligomer structures to trigger hydrogen-bonding, where water molecules are placed and later optimized near partial-negatively charged oxygen atoms within oligomer–water complexes.

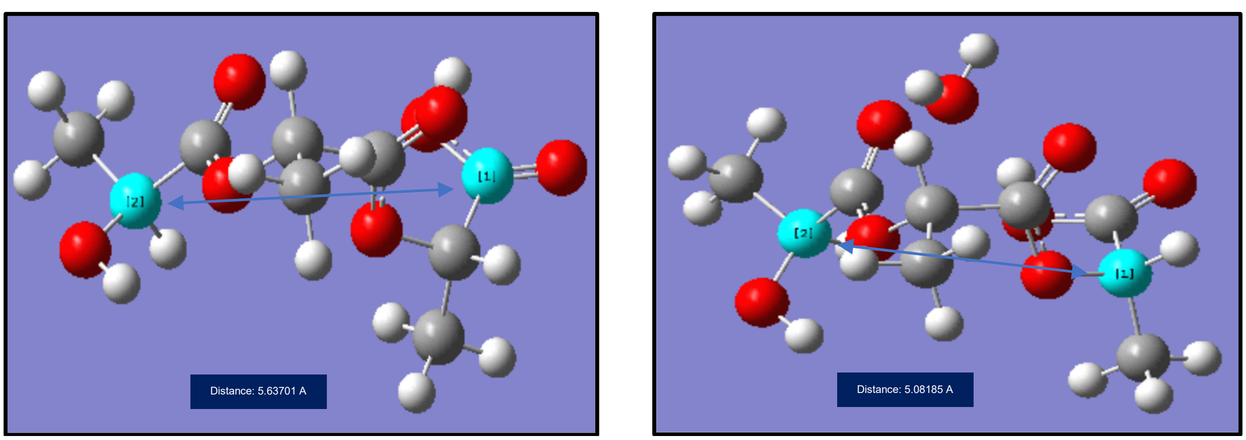

Figure 4. An optimized PLA oligomer geometry without (left) and with (right) a hydrogen-bonded water molecule. A hydrogen bond was formed and a 9.84% decrease in end-to-end length was observed (measured along the longest C-C chain), along with significant warping at the right terminal region.

Preliminary results (Fig. 4) showed a decrease in end-to-end oligomeric distance of approximately 7–10% relative to the corresponding solvated oligomer without water molecules, among PLA of both D- and L-isomers. Analysis of the optimized structures indicated that hydrogen bonding primarily involved carbonyl oxygen atoms, and localized backbone deformations were also observed. Overall, these findings indicate the significance of added/residual water molecules on affecting PLA oligomer structure.

Experimentation on Reaction Profile and Formulation Design:

Model compound study. Model compound studies are currently underway to validate and expand upon the findings on PLA degradation and structural reconfiguration kinetics from quantum calculations. Experimental procedures have been designed to account for the different physical properties of the reagents, and several revisions have been made due to high viscosity or volatility of certain reagents with standard sample preparation methods. A streamlined workflow has been established for instrumentation across three lab spaces on the USF campus. Trials have been conducted to verify the experimental procedure, ensuring safety practices, replicable and discernable outcomes. Among them, the NMR spectra for a representative sample containing a polypropylene-glycol (PPG) in place of PLA oligomers is illustrated in Fig. 5. A generic data collection format has also been established to account for different feedstocks and polymer systems.

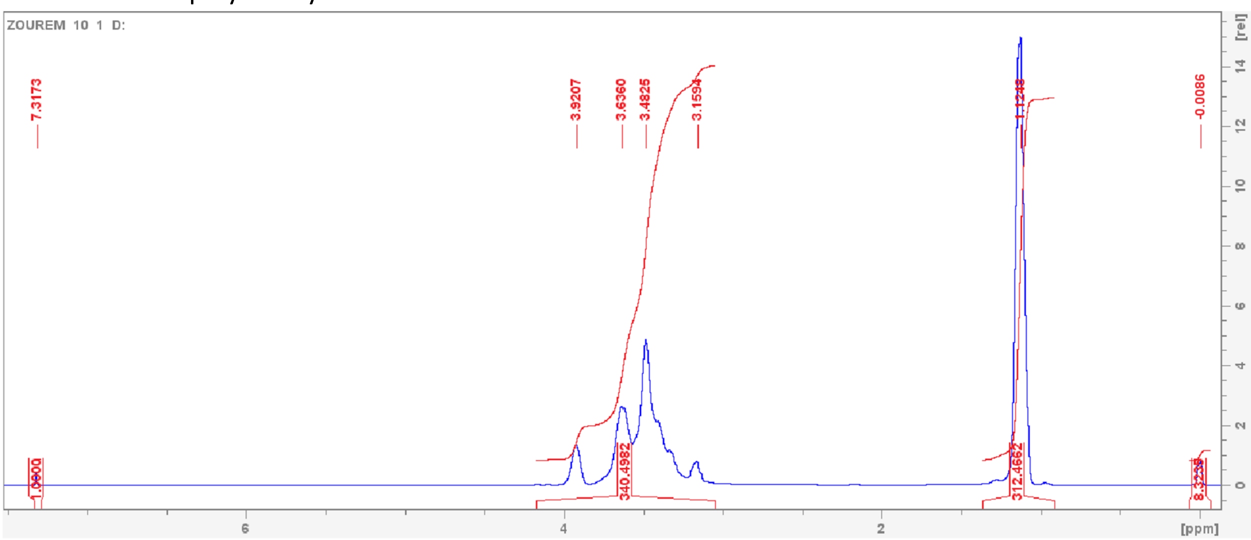

Figure 5. An initial NMR spectrum to verify that the experimental procedure can yield legible results. The small peaks on the far left and right of the spectrum denote chloroform and tetramethyl silane (TMS) standard respectively, and the large peaks between detonate chemical species found in PPG. From the known concentration of TMS in the sample, the concentrations of these chemical species can be determined.

Model Polylactic Acid Synthesis. A literature review was performed to find suitable synthetic pathways for PLA with various architectures and stereochemistry. As a good representative for commercial grade resin, the synthesized PLA would need to have an average molecular weight (MW) of (~30K g/mol) which is equivalent to ~300 monomers per polymer. This MW enables a well entangled regime with improved melt stability and resistance to hydrolysis, where flow properties will not be heavily impacted by minor degradation during processing [1,2]. Additionally, a well entangled system also possess better mechanical performance, as stress can be dissipated across a larger domain of the material via entanglements.[3]

Due to the use of low cost, low-toxicity $Sn(Oct)_2$ catalyst which can be easily removed from the product, the ring-opening polymerization (ROP) of lactide synthesis route as described in Kamber, N. E., et al 2007 is chosen.[3] The synthesis is shown to produce high MW up to 100K g/mol, with PDI ranging from 1.05-1.2 and mechanical properties of PLA comparable to commercial counterpart. Additionally, this synthesis method can be used to adjust and regulate MW, architecture, and physicochemical properties of the PLA.[1] The synthesis scheme is illustrated in Fig. 6. L-lactide need to be purified from ethyl acetate with reaction proceed under dry and inert environment. $Sn(Oct)_2$ and benzyl alcohol need to be added, and heated to 130 °C for bulk polymerization. The synthesized polymer can be extracted by chloroform and precipitate out with excess cold methanol.

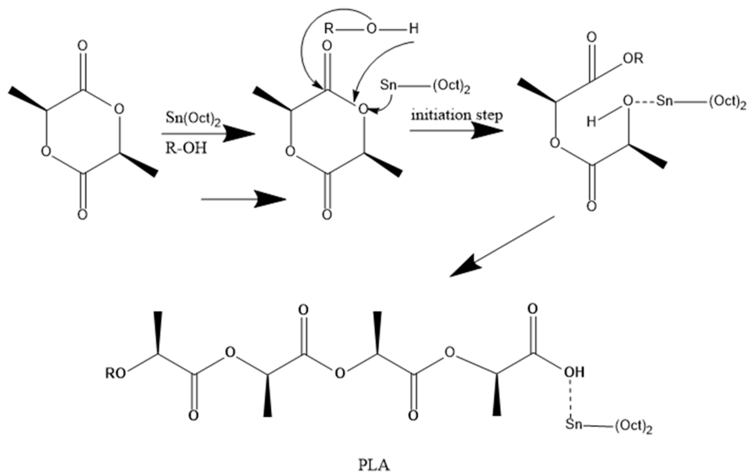

Figure 6. Organo-metal catalyst induced ROP of PLA

The stereochemistry of PLA can be tuned by selecting the appropriate ratio of lactide monomer to diastereomer (L-lactide, D-lactide, or meso-lactide)[3] as this impacts tacticity and crystallinity of the final polymer. For example, synthesizing separate batches of PLLA and PDLA and subsequently blending them creates a stereo-complex with a melting point exceeding 230 °C. Utilizing high-purity L-lactide with a non-racemizing catalyst like stannous octoate yields semi-crystalline PLLA, whereas a racemic mixture of monomers produces amorphous PDLLA.

<u>Life Cycle Assessment on PLA End of Life Pathways:</u>

Goal and Scope Definition. The GREET 2024 Rev.1 software is being used to assess the environmental impacts associated with the scenarios that process PLA waste. The functional unit selected for this work is 1 kg of waste PLA, and the system boundary is cradle-to-gate, which accounts for environmental impacts from the raw material production through end-of-life pathways. The scenarios analyzed in this work include reactive melt processing (S1), incineration (S2), and mechanical recycling (S3), and the counterfactual scenario (landfill). A cut-off approach is applied to avoid double-counting emissions, in a way that the environmental burdens from PLA production and waste generation are fully assigned to the original product, and recycling starts from waste treatment [1].

Life Cycle Inventory. The materials used for the inventory were present in the GREET module database. Biogenic CO_2 neutrality is assumed in all scenarios. Negative emission results are driven by avoided fugitive CH_4 emissions relative to the counterfactual scenario. It is assumed that the collection, sorting, washing, and drying stage of PLA waste is on-site. The impact assessment category used in this assessment is Global Warming Potential (GWP) over a 100-year period. The inventory for reactive melt processing is defined based on literature data and will be updated with experimental results. The inventory of important parameters and assumptions of scenario 1 (S1) is summarized in Table 1.

Table 1. Assumptions and Inventory Data for Scenario 1 (Reactive Melt Processing).

Process	Material/Energy source	Amount	Unit	Reference
Sorting step	Electricity	48	kWh/ton	[2]
Sorting step	Diesel for forklift	0.084	MJ/kg	[3]
Griding/ Shredding	Electricity for shredder and air separation	47.8	kWh/ton	[4]
Material loss	Dust	2.6	%	[2]
Washing step	2 % NaOH solution	0.4	L/ton	Calculated in this work
Washing step	Water	20*	L/ton	[2]
Washing step	Electricity	28.8	kWh/ton	[4]
Drying	Electricity	52.7	kWh/ton	[4]
Reactive Melt Extrusion	Transportation to plant	0	km	This work assumes on-site processing
Reactive Melt Extrusion	Waste PLA	1.01	kg	[5]
Reactive Melt Extrusion	Electricity for extruder	2	MJ/kg	[5]
Reactive Melt Extrusion	Electricity to extrude the waste PLA	0.00036	MJ/kg	This work based on [4]
Reactive Melt Extrusion	Filler (e.g., $CaCO_3$)	20	wt.%	[6]
Reactive Melt Extrusion	Dust (losses)	10	%	Assumption of this work
Cooling	Water	0.169	kg/kg	[7]
Granulation	Electricity	4.33	MJ/kg	[8]

Preliminary Impact Assessment and Interpretation The preliminary results found for scenario 1 (Fig. 7) show greenhouse gas emissions (GHG) of 0.55 $kgCO_2$ per kg waste PLA. As expected, the main contribution for environmental impacts is electricity consumption from the Reactive Melt Extrusion process (0.33 $kgCO_2$ per kg waste PLA). As a comparison, the process proposed by NatureWorks to produce virgin PLA results in a total net cradle-to-factory gate GWP is 0.62 $kgCO_2$ per kg PLA, considering biogenic carbon uptake credits from the corn production.

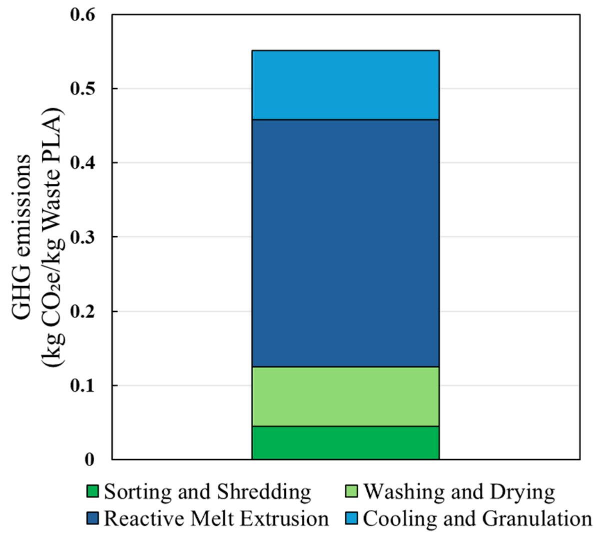

Figure 7. Greenhouse gas emissions of waste PLA Reactive Melt Extrusion.

<u>Technoeconomic Analysis for Development of PLA Recycling Technology:</u>

Capital Expenditure. CAPEX (e.g. equipment sizing, contingency cost) is estimated based on the material and energy balance as well as chemical engineering heuristics. The cost associated with equipment purchase was defined by considering the size and material needed using CAPCOST, the CatCost tool of the National Renewable Energy Laboratory (NREL), and Matches, all being widely used sources for technoeconomic analysis [9-11]. All the costs will be extrapolated to the 2024 Chemical Engineering Process Cost Index (CEPCI) (Table 2). The process flow diagram (PFD) of the proposed system is represented below (Fig. 8).

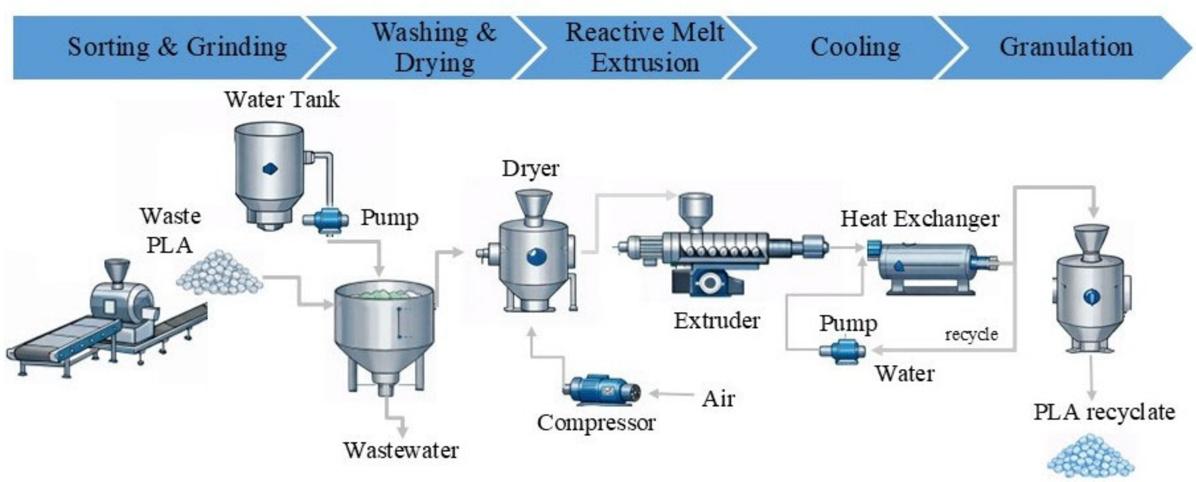

Figure 8. Process flow diagram of the proposed system. Disclosure: equipment figures generated with AI support.

Table 2. Equipment list needed for capital expenditure (CAPEX) calculation for on-site processing of biodegradable plastic (1041.7 kg/h).

Equipment	Cost ($)	Number needed	Year selling price	CEPCI in year listed	Reference
Shredder	56,000	2	2014	699.4	[12]
Conveyor belt	49,941	1	2010	532.9	[13]
Water tank	18,335	1	2013	567	[13]
Washing tank	22,918	1	2013	567	[13]
NaOH tank	24,752	1	2013	567	[13]
Truck dumper	33,000	2	2023	1005	[14]
Dryer	237,927	3	2013	567	[13]
Compressor	75,224	1	2010	819	[13]
Storage dome (pretreated PLA and recycled)	23,000	9	2017	684.4	[15]
Extruder	58,732	3	2010	532.9	[13]
Dust collector	87,225	2	2013	567	[13]
Pump for liquids	70,162	3	2013	567	[13]
Crystallizer	287,376	1	2013	567	[13]
Dryer	74,123	1	2013	567	[13]
Cooling Conveyor	4,020	1	2023	1,005	[16]
Shredder	10,000	1	2024	999.06	[17]

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TAG meetings:

No TAG meeting was held during this reporting period. 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 2nd TAG meeting is scheduled for April 22 at 2 pm. A calendar invite has already been sent. Many members have accepted.

Future Tasks:

<u>Computational Study on Degradation Mechanism:</u>
Degradation kinetics. Next steps for the kinetic study include refinement via ONIOM modelling and energy correction via high-level theory using ORCA software. Additional work will be done to obtain and refine kinetic data for other degradation mechanisms i.e. mid chain cyclization, mid-chain beta scission and intermolecular transesterification.

Effects of solvation and added water. The effect of water molecules will be further investigated with respect to stereochemistry, specifically D-, L- and mixed isomeric structure. More computational data will be generated to quantify hydrogen-bonding effects along the PLA backbone.

Model Polylactic Acid Synthesis. Next steps include setting up the Schlenk link, followed by the ring-opening polymerization of lactide synthesis route described by Kamber, N. E., et al 2007.3 The resulting polymer will be characterized using analytical measurements, i.e. NMR, FTIR, and triple detector GPC.

<u>Life Cycle Assessment on PLA End of Life Pathways:</u>

The next steps include the acquisition of inventory data for all the other scenarios, evaluation of impacts of carbon uptake credits, and conduction of sensitivity analysis in key important variables.

<u>Technoeconomic Analysis for Development of PLA Recycling Technology:</u>

The next steps include the use of Bare Module Factor to calculate the total capital of investment, as well as defining the equipment costs for other scenarios (all plastic being processed and mobile unit operation). The operating costs associated with the technology implementation will also be evaluated.

METRICS REPORTING

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

   No TAG meeting was held during this reporting period.

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.

   None. Several abstracts have been submitted.

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 in preparation. One is to NSF, and others to DOE, and relevant industries.

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).