

White Paper | Zeus Industrial Products, Inc.

A Novel Method for Chemical Recycling of PLA Under Mild Conditions

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ABSTRACT

*Monomers can be purified and used as feedstock to synthesize virgin **PLA** resin, thereby “closing the loop” on the **PLA** life cycle...*

A novel method for recycling PLA using low-temperature, low-pressure reactions with alcohol or water has been discovered by Zeus Research. PLA is used today in many applications ranging from food packaging to implantable medical devices.

Because of its sensitivity to thermal degradation, PLA is difficult to recycle and actually becomes a contaminant in the plastics stream of municipal solid waste. Using the newly discovered process, different grades of PLA can be removed from a stream of commingled plastics and broken down to give high value chemicals.

Some of these chemicals, called monomers, can be purified and used as feedstock to synthesize virgin PLA resin, thereby “closing the loop” on the PLA life cycle. The method has low capital and operating costs and is well-suited to industrial recycling processes. Moreover, it is consistent with the concepts of sustainability and of a circular economy.

CUSTOMER ISSUES

- Low-temp/pressure
- Tin Catalyst Utilization
- Helps Circular Economy

INTRODUCTION

Plastics retain a high added value throughout their life cycles. Much of this value is lost if a plastic article is discarded at the end of its useful life...

Zeus Industrial Products, Inc., is a manufacturer and processor of highly engineered polymers including bioabsorbable polylactide (PLA) and lactide copolymers catering to a variety of markets, including medical applications. Sustainability is a growing part of the Zeus culture and end-of-life issues are increasingly considered at the corporate level for all businesses. Recently, the Zeus Research team has developed a novel technology for recovering monomers from recycled PLA, whether present as clean industrial waste or commingled with other plastics. This depolymerization technology can be carried out efficiently at relatively mild conditions of temperature and pressure, and can be viewed generally as an effective enabling technology for dealing with PLA scrap economically.

As a biopolymer from renewable resources, PLA is one of the fastest growing plastics in commercial use today especially in the field of packaging. There is a growing impetus to finding economical methods of dealing with its end-of-life issues in a manner consistent with the principles of a circular economy [1]. In this paper, the Zeus depolymerization process for PLA is described in detail along with potential applications to commingled plastic waste streams.

PLA IN TODAY'S ECONOMY

Polylactic acid, PLA, is a plastic derived from plant starch (*usually corn*). In recent years, PLA has been growing in popularity as an alternative to petroleum-based plastics such as high density polyethylene, HDPE, low

density polyethylene, LDPE, polypropylene, PP, polystyrene, PS, nylon, PA, and polyethylene terephthalate, PET. This growth has been fueled in part by increased production efficiencies that have lowered costs, by improvements in polymer properties that have made PLA suitable for many packaging applications, and by consumer desire to utilize materials from renewable resources [2].

Everything from clamshells for fast food to bioabsorbable medical devices can be made from PLA, drastically reducing the carbon footprint in these industries. The demand for PLA has grown as society embraces the importance of sustainability and of a circular economy. Global production capacity of PLA is expected to grow by 50% by the year 2022 to over 250,000 metric tonnes, with the bulk of the production going towards packaging applications [3].

PRECEDENT

*Scientists estimate that a **PLA** bottle could take between **100 to 1,000 years** to decompose in a landfill.*

RECYCLING OPTIONS FOR PLA

The expected growth of PLA in consumer applications over the next five years means an increased presence of the resin in post-consumer waste streams. **Table 1** shows the alternatives available to recover the added value of PLA after its useful life.

There are important considerations to take into account before selecting an end-of-life strategy for PLA [4].

Although PLA does biodegrade, it does so very slowly in the environment. In a landfill, which is tightly packed and designed to exclude light and oxygen, the degradation process is even slower. Scientists estimate that a PLA bottle could take anywhere from 100 to 1,000 years to decompose in a landfill [5].

PLA may eventually break down into its constituent parts (*carbon dioxide and water*) within three months in a “controlled composting environment,” that is, an industrial composting facility heated to 140 degrees Fahrenheit and fed a steady stream of digestive microbes.

Unfortunately, there are only a few hundred industrial-grade composting facilities available across the United States.

Incineration recovers the fuel value of the polymer, while traditional (*or mechanical*) recycling reprocesses the material into an article with properties and value lower than the original article. PLA acts as a contaminant within a stream of mixed postconsumer waste plastics due to its propensity for thermal degradation during reprocessing compared to other constituents of the recycle stream (*such as polyolefins, nylons and aromatic polyesters*). It must therefore be removed using costly methods prior to mechanical recycling.

In chemical recycling, the polymer is broken down into constituent monomers or oligomers (*short chains of monomers*) which can then be recovered, reprocessed and sold. Recovered monomers can be repolymerized directly into the original polymer, thereby closing the loop.

Table 1 summarizes the end of life recovery options currently available for plastics.

| Table 1. End-of-Life Value Recovery Options for Plastics | | |
|--|---------------------------------|-------|
| END-OF-LIFE OPTIONS | RESOURCES RECOVERED | VALUE |
| Landfilling | none | - |
| Composting | biomass | + |
| Incineration | thermal energy | + |
| Traditional Recycling | polymer for reuse or re-forming | ++ |
| Chemical Recycling | constituent chemicals | +++ |

SUMMARY

Using recycled PLA frees up farmland to produce corn or other crops for human or livestock consumption.

CHEMICAL RECYCLING OF PLA

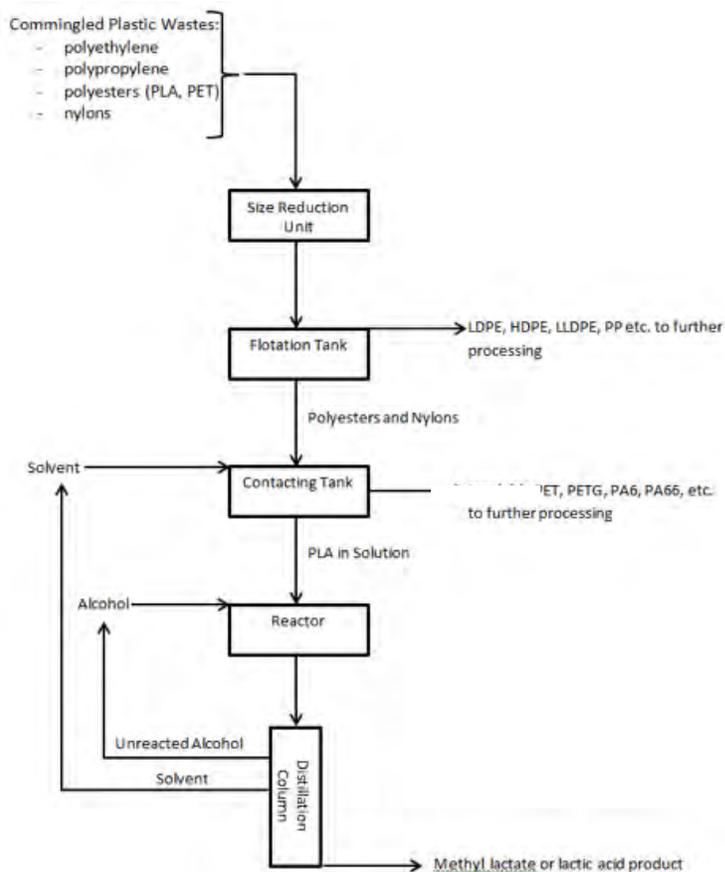
Resources in terms of energy and capital equipment are required to implement chemical recycling processes. In many jurisdictions, government incentives will also be available. For chemical recycling of a polymer to be viable, resource costs should be comparable to or lower than the costs of manufacturing the monomers or oligomers from raw materials. For each pound of PLA manufactured, 2.5 pounds of corn are required [6]. Therefore, the impetus for obtaining monomer from a waste source is certainly present. A further benefit of utilizing recycled PLA as a source of monomer is freeing up of farmland to produce corn or other crops for human consumption or for livestock.

There are a number of processes available for chemical recycling of PLA by hydrolytic or alcoholic depolymerization [7, 8, 9, 10]. However, these processes tend to be high-temperature, energy-intensive ones. Recently, processes utilizing temperatures as low as 80°C have been disclosed [11, 12, 13, 14], thereby improving the economics of chemical recycling. The Zeus process further enhances the economic viability of PLA depolymerization processes by using miscible systems of PLA/solvent/reactant to enable monomer recovery at even lower temperatures in an extremely efficient, environmentally-friendly manner.

THE ZEUS WASTE PLA DEPOLYMERIZATION PROCESS

Figure 1 below shows one possible configuration of unit operations in a depolymerization process to deal with a stream of commingled plastic post-consumer waste that includes scrap PLA according to the Zeus process.

Figure 1 shows a schematic representation of a depolymerization process.



SUMMARY_(cont'd)

*As long as the **PLA** remains dissolved, the **scission reactions** can occur without being limited by inter-phase transport of the reactant to the polymer.*

After an initial washing step, the commingled plastic stream is subjected to size reduction using common methods such as shredders and grinders to make flake-size granules that can be readily separated.

Separation of the various plastics can be done in a variety of ways including electrostatic separation, infrared techniques as well as flotation. This last method is easily carried out to separate polyolefins (*with specific gravity below 1*) from nylons and polyesters. The crucial part of the process is separating biodegradable plastics like PLA from reprocessable plastics like PET. In a mixed stream of polyesters, this separation can be carried out by contacting the stream with a solvent like chloroform to dissolve the PLA component. The undissolved PET can subsequently be dried and sent for further processing.

The PLA solution is then subjected to alcoholysis, or reaction with an alcohol. High molecular weight PLA can be dissolved to about 15% by weight into chloroform. Alcohol is then added in stoichiometric excess to favor depolymerization. As long as the PLA remains dissolved, the scission reactions can occur without being limited by interphase transport of the reactant to the polymer. Temperature can be increased to just below the boiling point of the mixture's lowest boiling component to speed up the reaction without necessitating high pressure equipment. The addition of a tin catalyst has been found to greatly increase the reaction kinetics at these mild conditions of temperature.

Since the depolymerization process occurs at low temperatures and atmospheric pressures, a variety of reactors can be used. Continuous stirred tank reactors or plug flow reactors are examples of the more common types. Stirred tank reactors can be used in series to make the process more efficient by increasing the concentration of alcohol in subsequent vessels to preferentially drive the reaction to monomer while maintaining solubility of the oligomers.

Separation of the solvent and alcohol from the resultant monomers is also easily accomplished. For the chloroform/methanol/methyl lactate system, the differences in boiling points of the components (*61°C for chloroform, 65°C for methanol and 154°C for methyl lactate*) make distillation a suitable process to remove the solvent and reactant from the product. The same is true of the THF/water/lactic acid system (*66°C for THF, 100°C for water and 122°C for lactic acid*). In each case, the solvent can be recondensed and returned to the contacting tank, while the unreacted methanol or water can be mixed with fresh reactant and returned to the reactor vessel.

SUMMARY_(cont'd)

*Solubility of the **PLA** in methanol or **THF** can be greatly enhanced by heating up the mixture to just below the boiling points of the respective solvents.*

Solubility of the PLA in methanol or THF can be greatly enhanced by heating up the mixture to just below the boiling points of the respective solvents. The respective reactants are subsequently added to the PLA solution at reaction temperature.

In experiments carried out just below 60°C and atmospheric pressure, molecular weight reduction of the PLA was evident in each solution within a few hours. Depolymerization extent was inferred by measuring inherent viscosity at different reaction conditions. Size exclusion chromatography was used to determine changes in molecular weight distribution for selected reaction conditions. It was found that polydispersity remains relatively unchanged as the reaction proceeds, indicating that random chain scission is the predominant mechanism in the single-phase systems [15]. The presence of significant amounts of methyl lactate monomer was confirmed for the case of the PLA/chloroform/methanol system by gas chromatography.

The resultant monomer, either methyl lactate or lactic acid, can be the used to synthesize

PLA again. There are several known routes to converting these monomers into PLA, including polycondensation, azeotropic dehydrative polycondensation, or a multistep route that leads to high molecular weight PLA [16, 17]. The multistep process polymerizes the monomer into low molecular weight PLA, also called a pre-polymer, that is then depolymerized to yield lactide.

The methyl lactate is not required to be converted into lactic acid prior to the pre-polymerization step [18]. The lactide undergoes ring opening polymerization, usually in the presence of a tin catalyst, to yield a high molecular weight PLA resin. Alternately, the pre-polymer can be coupled together using chain extending agents to produce a higher molecular weight PLA [16]. The preferred reaction route depends on the PLA characteristics needed in the end use application. The reintroduction of monomers back into the PLA life cycle completes the life cycle. **Table 2** below summarizes two of the ternary systems that can be used to depolymerize high molecular weight PLA into either methyl lactate or lactic acid monomers.

Table 2. Examples of Suitable Systems for PLA Depolymerization Process

| POLYMER | SOLVENT | REACTANT | CATALYST | MONOMER |
|---------|------------|----------|-------------------|----------------|
| PLA | chloroform | methanol | tin(II) octanoate | methyl lactate |
| PLA | THF | water | tin(II) octanoate | lactic acid |

CONCLUSION

*The process is versatile. Both commercial and medical grade **PLA** resins can be depolymerized.*

BENEFITS OF THE ZEUS DEPOLYMERIZATION PROCESS

The low-temperature solution depolymerization process for PLA outlined in this work has a number of advantages that would make it suitable for incorporation into industrial recycling operations.

The process is easy to implement and cost-effective to operate. No high pressure vessels are required, so capital costs are low. High temperatures are not needed in the reactor, so operating costs are low. The contacting tanks and reactors can be easily added to an existing post-consumer processing facility. A catalyst has been identified that greatly enhances the depolymerization reactions at mild conditions, and that can be reused for subsequent polymerization reactions.

The process is versatile. Both commercial and medical grade resins can be depolymerized. Strict control of PDI is possible throughout the reaction, so valuable intermediate products such as oligomers can be obtained. These could be useful as green solvents and coatings, or for pharmaceutical applications. Alternatively, different monomers can be obtained by driving the depolymerization reaction with either excess methanol or water to give methyl lactate or lactic acid, respectively. The process is not sensitive to other polymers present in the mixed waste stream, but successfully removes a problematic component of that waste stream.

The process supports sustainability initiatives. Using waste PLA to generate lactic acid, which is currently a corn-derived product,

frees up this valuable crop for other markets such as foodstuffs, livestock feed, and ethanol production. The process can also be used to generate lactide for high purity, high molecular weight medical-grade polymers.

The process adheres to the spirit of a circular economy. The inherent value of the waste biopolymer is largely recovered. Excess reactant and solvent can both be easily recovered to be reused in a closed loop process.

KEY BENEFITS

- Easy to Implement
- Cost-effective
- Supports Sustainability

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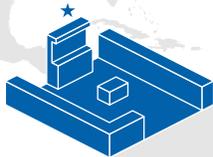
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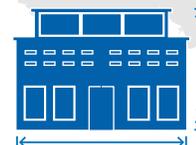
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