LOW TEMPERATURE SOLUTION DEPOLYMERIZATION OF PLA

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Abstract

A novel depolymerization method using low-temperature, low-pressure alcoholysis of PLA in a ternary solution is outlined in this work. Depolymerization kinetics are studied for the PLA/methanol/chloroform system at 57°C. Large changes in molecular weight can be achieved at relatively mild conditions. A tin catalyst is found to increase the reaction rate significantly. The method is well-suited to industrial recycling processes and is consistent with the concept of a 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, which is contrary to the principles of a circular economy [1]. It is thus incumbent upon society to recover as much of this value as economically viable. There are a number of ways available to accomplish this goal for plastics, as shown in Table 1.

Table 1. End-of-Life Value Recovery for Plastics

End-of-Life Option	Resources Recovered	Value
Landfilling	none	-
Incineration	thermal energy	+
Traditional Recycling	polymer for reuse or re-forming	++
Chemical Recycling	constituent chemicals	+++

Incineration recovers the fuel value of the polymer, while traditional (or primary) recycling reprocesses the material into an article with properties and value lower than the original article. For polylactic acid (PLA) in particular, primary recycling is problematic since the polymer is especially prone to thermal degradation compared to other components of the recycle stream (such as polyolefins, polyamides and aromatic polyesters). In chemical recycling, the polymer is broken down into constituent monomers or oligomers which can then be recovered, reprocessed and sold. Recovered monomers can be repolymerized directly into the original polymer, thereby maximizing value.

Chemical recycling processes for polyesters such as post-consumer PET to recover monomers by hydrolysis and alcoholysis have long been known in the industry [2, 3]. The same reactions for the chemical recycling of PLA have also been reported recently [4, 5, 6, 7, 8]. These chemical recycling processes are characterized by high-temperature reactions, high pressures and/or multiple phases. Recently, processes utilizing temperatures as low as 80°C and pressures up to 10 bar have been disclosed [9, 10, 11], thereby improving the economics for the chemical recycling of PLA. However, the overall depolymerization kinetics in many of the reported systems are limited by the need for interphase transport of the reactants.

In this present work, the results of experiments carried out for the alcoholysis of PLA in a ternary solution to recover oligomers and monomers at temperatures below 60°C are reported. The use of solution-based alcoholysis is expected to have a favorable impact on kinetics since there are no phase boundaries present to limit the overall reaction rate. A positive impact on economic viability is also expected compared to higher temperature processes by obviating the need for expensive pressure vessels and by lowering operating costs.

Materials and Methods

Table 2 below summarizes two of the solutions that can be used to depolymerize high molecular weight PLA into either methyl lactate or lactic acid monomers. The catalyst is not required to effect the depolymerization, but it greatly enhances the rate if utilized. For both of the tabulated systems, there is only one phase visible at the reaction temperature.

Table 2. Examples of Suitable Systems

Solvent	Reactant	Catalyst	Monomer Obtained
chloroform	methanol	tin(II) octanoate	methyl lactate
THF	water	tin(II) octanoate	lactic acid

The components of the system studied here are (in weight percent): 11% Purasorb® PL49 PLA (Corbion Purac); 63% chloroform (Acros Organics); 26% methanol (BDH Chemicals). This composition allows a large molar excess of methanol to ester linkages while maintaining a clear solution. No catalyst was used in the initial study.

The PLA polymer was first dissolved in the solvent at a temperature just below the boiling point in a 10 mL sealed glass vial. After cooling down to room temperature, the reactant was added to the vial and the

contents shaken to homogenize the mixture for 60 hours. The vial containing the ternary mixture was placed in an incubator set at 57°C for a specified amount of time - either 0 hrs, 2 hrs, 8 hrs, or 75 hrs. After the desired time had elapsed, the vial was cooled to room temperature. A PLA control dissolved in chloroform but containing no alcohol was left at 57°C for the duration of the alcoholysis experiment.

Subsequent to cooling, the vial was opened and placed in a fume-hood at ambient temperature for at least 14 days in order to dry the products without losing low molecular weight monomers or oligomers. The reaction products were then analyzed by determining the inherent viscosity (IV) in chloroform using an Ubbelohde viscometer. Selected samples were subjected to size exclusion chromatography (SEC) in a 300 x 7.8-mm Viscotek GMHHR-H apparatus with a Polymer Laboratories PLgel 300 x 7.5-mm 100 Å column and RI detector.

The same depolymerization experiment was repeated using amorphous 4042 PLA (NatureWorks,LLC) dissolved in tetrahydrofuran (THF)(Acros Organics). Methanol or water was used to depolymerize the PLA over 402 h.

The PL49 depolymerization experiment was repeated with the addition of 1% (by polymer weight) of tin (II) octanoate catalyst (American Elements) just before subjecting the mixture to the 57°C reaction temperature. The vial was removed after 7 h, cooled back down to room temperature, and the products dried as previously described.

The tin depolymerization experiment was repeated with a reaction time of 75 h. Without drying the sample, an aliquot of the solution along with a 97% methyl (S)-(-) lactate control (Acros Organics) was analyzed using Thermo GC-1310 with Flame Ionization Detector with the column TG-WaxMS 30 m x 0.25 mm x 0.25 μm.

Results

The results from a kinetic study of the PLA/chloroform/methanol system at 57°C are shown in Table 3. The IV of the PLA control was measured to be 4.0 dL/g after 75 h.

Table 3. IV Drop During the Reaction at 57°C

Time, h	IV (dL/g)
0	2.90
2	0.67
8	0.20
75	0.10

It can be seen from Table 3 that there is a significant decline in IV during the mixture homogenization process at room temperature from 4.0 dL/g for the PLA control to 2.9 dL/g for the ternary mixture after mixing for 60 h. After a further 75 h at elevated temperature, the IV drops dramatically, indicating significant depolymerization has occurred at the relatively low temperature of 57°C.

Figure 1 shows the SEC chromatograms for control PLA and for some reacted samples. The negative system peak at approximately 24 mL in the RI chromatograms required re-running the 75 h (blue curve) sample using a shorter run time. The chromatograms were then overlaid to give Figure 1. Clearly, the depolymerization reaction has resulted in a large drop in the PLA molecular weights.
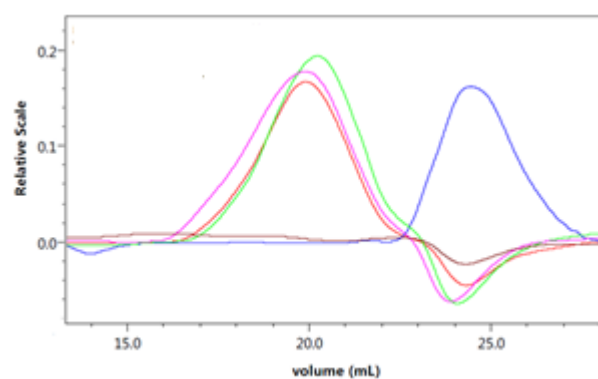

Figure 1. SEC chromatograms for selected samples. Red = PL49 control dissolved in chloroform; Violet = PL49 pellets as received; Green = reaction products after 0 h at 57°C; Blue = reaction products after 75 h at 57°C.

Table 4 tabulates the SEC results for selected samples. The molar mass averages for the PL49 Control, the reaction products after homogenization (i.e. 0 h at 57°C) and after 75 h at the same temperature mirror the IV results shown in Table 3. It can further be noted that the polydispersity index (PDI), defined as the weight average molecular weight divided by the number average molecular weight (M_w/M_n), does not change significantly throughout the reaction despite the drastic drop in molecular mass.

Table 4. SEC Results for Selected Samples

Sample Identification	Injection	Molar Mass Averages (g/mol)			M_w/M_n
		M_n	M_w	M_z	
PL49 Control (dissolved in chloroform)	1	179,400	413,200	866,500	2.30
	2	170,400	417,300	942,400	2.45
	Average	174,900	415,250	904,450	2.38
	Std. Dev.	6,364	2,899	53,669	0.10
Reaction products after 75 h @ 57°C	1	1,737	3,509	6,149	2.02
	2	1,814	3,598	6,278	1.98
	Average	1,776	3,554	6,214	2.00
	Std. Dev.	54	63	91	0.03
Reaction products after 0 h @ 57°C	1	137,000	333,200	699,400	2.43
	2	125,700	320,400	727,200	2.55
	Average	131,350	326,800	713,300	2.49
	Std. Dev.	7,990	9,051	19,658	0.08

It was of interest to see if the depolymerization process could be expanded to systems other than high molecular weight PL49 and the chloroform/methanol system. 4042 resin from Natureworks was selected and the IV at 0 h at 57°C was found to be 0.9 dL/g. The IVs of the products from the THF/methanol and THF/water systems after 402 h were found to be 0.6 dL/g and 0.4 dL/g, respectively.

In the experiment with 1% tin (II) octanoate catalyst, the reaction time was shortened to 7 hours. The IV of the recovered material in this case was indistinguishable from the blank, indicating that very low molecular weight product was obtained very quickly. In the 72 h tin catalyzed depolymerization experiment, the GC results indicated that 17% of the resultant mixture was methyl lactate. The theoretical percent of methyl lactate is expected to be 16%. The difference between the theoretical value and the actual value is attributed to solvent loss (evaporation) during the experiment.

Discussion

I) Depolymerization Kinetics

IV and SEC data show significant molecular weight reduction occurs during the solution-based methanolysis of PLA at an extremely low temperature of 57°C. This result is unexpected, since a chloroform and methanol system is commonly used to purify PLA. The PLA is dissolved into the chloroform, and excess amounts of methanol are used to precipitate the PLA out of solution and the entire system is heated under vacuum to dry. [12] It is likely that chain scission reactions occur at this low temperature because of the accessibility of the ester linkages in solution. In fact, it can be noted from the molar mass data in Table 5 that the PDI remains relatively constant around a value of 2 independent of reaction extent. This is an indication that the chain scissions are occurring in a random manner, which is consistent with a mechanism by which all ester linkages along the polymer chain are equally likely to be cleaved [13]. This result is to be expected for solution-based scission reactions.

For the case of random chain scission in PLA, Schindler and Harper [14] have proposed the following form of the Mark-Houwink equation to describe the drop in IV as a function of M_n:

$$[\eta] = K\Gamma(a + 2)M_n^a \qquad (1)$$

where $[\eta]$ is the IV (dL/g), M_n is the number average molecular weight (g/mol), a and K are constants, and $\Gamma(a+2)$ is the gamma function evaluated at $(a + 2)$. The values of a and K were determined from the experimental IV and M_n data for the following samples: resin pellets,

control PLA and reaction products after 75 h. Substituting for the experimentally-determined constants, Equation (1) becomes:

$$[\eta] = 3.3 \times 10^{-4} M_n^{0.77} \qquad (2)$$

For the depolymerization reaction studied here, the drop in M_n versus reaction time can be calculated using Equation (2). Figure 2 below summarizes the information graphically.
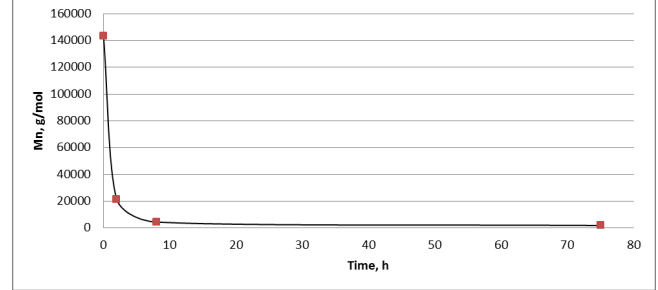
Figure 2. Drop in M_n during methanolysis of PLA.

It is well-known that the depolymerization of polyesters by hydrolytic or alcoholytic scission of ester linkages is an equilibrium reaction that initially follows a pseudo-first order rate model [15]. In the early stages of the depolymerization, the reverse reaction can be ignored, and the depolymerization rate constant can thus be calculated. The appropriate rate equation from Reference 15 is:

$$\frac{1}{1 - x} = e^{kt} \qquad (3)$$

where x is the reaction extent, k is the depolymerization rate constant (h^{-1}), and t is the reaction time (h). The reaction extent is defined as:

$$x = \frac{C - C_o}{C_p - C_o} \qquad (4)$$

where C is the concentration of chain ends (mol/L) at any reaction time t, C_o is the initial concentration of chain ends (mol/L), C_p is the total concentration of ester linkages (mol/L) susceptible to scission. The concentrations are readily calculated from the molecular weight data.

Equation (3) indicates that a plot of ln[1/(1-x)] versus reaction time should give a straight line with a slope of k for early reaction times This plot is shown in Figure 3.
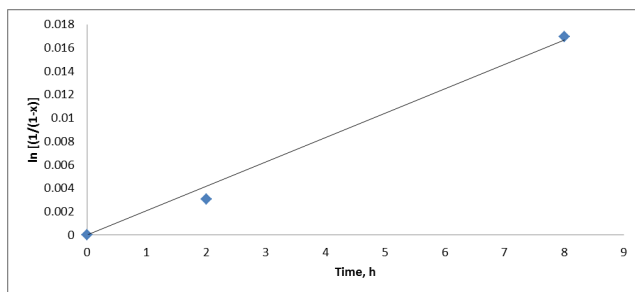
Figure 3. Log plot of Equation (3).

The kinetic model is seen to provide a good fit to the rate data collected in the first 10 hours of the experiment. The equation of the line is given by:

$$\ln\left(\frac{1}{1-x}\right) = 0.0021t \qquad (5)$$

The rate constant for chain scission is therefore 0.0021 h^{-1}.

In order for the depolymerization process to be of industrial interest, an improvement in the reaction kinetics would be required. For this reason, a suitable catalyst was found and tested. Tin (II) octanoate was selected as a catalyst because it is a well-known catalyst for the depolymerization of PLA into L-Lactide [16] and has FDA approval [17].   The presence of this catalyst drastically improved the reaction rate as indicated by the IV results after 7 hours. The product of the reaction was confirmed to be methyl lactate in high yields by GC.

II)	Scale-Up Considerations

The improved reaction kinetics and high yields make this system more attractive for implementation on an industrial scale, but there are other considerations that must be addressed such as handling commingled or diverse waste streams, isolating the methyl lactate, and recovering the solvent, reactant, and catalyst.   We are continuing to study these considerations in our laboratory.

Figure 4 presents a schematic diagram of a potential set-up currently under investigation for recovering and depolymerizing PLA.
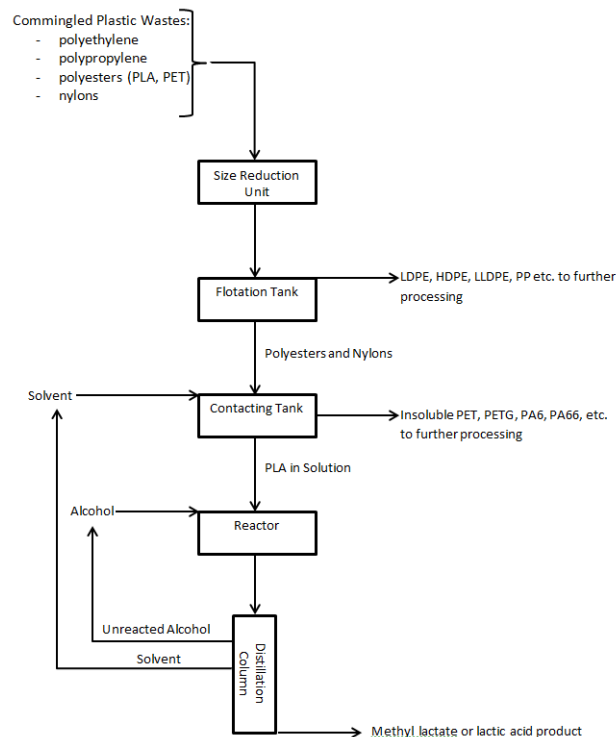

Figure 4. Schematic representation of a possible PLA depolymerization process.

After an initial washing step, the commingled plastic stream of postconsumer plastic waste 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 different plastics can be done in a variety of ways including electrostatic separation as well as flotation. The latter 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 to dissolve the PLA component. The undissolved PET can subsequently be dried and sent for further processing.   Additionally, the source of the PLA waste is not a concern as the process is capable of depolymerizing high molecular weight PLA intended for medical use or commercial grade PLA that may have other processing aids present.

The PLA in solution is now ready for alcoholysis. 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 mass transfer across an interphase boundary, as noted previously.   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 greatly increases the reaction kinetics at these mild conditions of temperature.

Since the depolymerization process occurs at low temperatures and atmospheric pressures, various 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, 143°C for methyl lactate, and 296°C for tin(II) octanoate) 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.

Conclusions

The low-temperature solution depolymerization process for PLA outlined in this work has been shown to have 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.

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 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.

References

1. https://www.ellenmacarthurfoundation.org/circular-economy (2017).
2. D. Paszun and T. Spychaj, *Ind. Eng. Chem. Res.*, **36**, 1373 (1997).
3. V. Sinha, M.R. Patel, J.V. Patel, *Journal of Polymers and the Environment*, **18**, 8 (2010).
4. K.K. Bhatia, US Patent 5136057 (1992).
5. H.E. Bellis, US Patent 5278256 (1994).
6. K. Nakamura, US Patent 7985778 (2011).
7. V. Thammonkol, N. Kaabbuathong, J. Junkasem, T. Thanpitcha, P. Lorjai, C. Katepetch, WO 2015112098A1 (2015).
8. G. Srinivisan, D. Grewell, US Patent 8895778, 2014.
9. P. Coszach, J.C. Bogaert, J. Willocq, US Patent 8481675 (2013).
10. P. Coszach, J.C. Bogaert, J. Willocq, US Patent 8431683 (2013).
11. P. Coszach, J. Willocq, US Patent 8614338 (2013).
12. S. Kaihara, S. Matsumura1, A.Mikos, & J. Fisher, *Nature Protocol*, **2**, 2771, (2007).
13. J.A.P.P. van Dijk, J.A.M. Smit, F.E. Kohn, Jan Feijen, *J. Polym. Sci.: Polym. Chem. Ed.*, **21**, 197 (1983).
14. A. Schindler and D. Harper, *J. Polym. Sci. Part A Polym. Chem.*, **17**, 2593, (1979).
15. J.R. Campanelli, M.R. Kamal, D.G. Cooper, *J. Appl. Polym. Sci.*, **48**, 443 (1993).
16. P.R. Gruber, US Patent 5274073 (1993).
17. D. Garlotta, *Journal of Polymers and the Environment*, **9**, 61 (2001).