



A Combined Thermochemical and Microbial Process for Recycling Polylactic Acid Polymer to Optically Pure L-Lactic Acid for Reuse

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Published online: 19 March 2020

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Abstract

Poly(lactic acid) polymer (PLA) produced from renewable resources can be recycled at the end of life to constituent monomer, optically pure lactic acid (LA), by a combination of chemical and biological processes. Efficient application of this closed loop of LA-PLA plastics-LA can minimize accumulation of plastics waste that pollute land and oceans. Temperature-dependent hydrolysis of PLA in water to LA follows apparent first order decay kinetics after a short lag. A modified Gompertz equation can explain the overall hydrolysis process. Alkali increased the rate of hydrolysis of PLA and reduced the length of lag period compared to water alone. The stoichiometry of base added to LA released was 1.0. The highest lactic acid yield was 0.95 g g⁻¹ of PLA. D-LA in the syrup obtained after hydrolysis of PLA-plastics was removed using an engineered *Escherichia coli* to produce a L-LA syrup with an optical purity $\geq 99\%$. These results show that thermochemical hydrolysis of PLA-based plastics to LA with optimum amount of base followed by bio-based purification to L-LA is an effective method of recycling PLA-plastics for reuse.

Keywords Polylactide · Plastics · Chemical recycling · Engineered *E. coli* · Lactic acid syrup purification

Introduction

In 2017, 348 million metric tons of plastics was produced world-wide and this is projected to reach three times this value by 2050 consuming about 20% of world oil production [1]. In addition to the demand on non-renewable fossil resources, these recalcitrant polymers accumulate in the ecosystem creating an environmental and human health hazard in land, rivers and oceans [2, 3]. Many countries are attempting to ban single-use plastics to minimize plastics pollution that also endangers marine life [4]. Food stored in some of the plastics containers are known to be contaminated with container-derived chemical leachates making it unfit for human consumption [5].

To overcome these concerns, researchers have focused on bio-based plastics derived from renewable feedstocks that are biocompatible and also biodegradable [6–10]. Bio-based polymers reduce consumption of fossil resources and alleviate some of the environmental burden associated with it. Although bio-based plastics production capacity in 2017 was only about 2 million metric tons [11], this is projected to increase significantly. Among the various bio-based plastics, poly(lactic acid) (PLA) polymers derived from optically pure lactic acid (LA) produced by fermentation of sugars by microorganisms, is likely to be the largest plastics segment in the coming years [12].

PLA is commonly produced through a solvent-free process in which condensation of lactic acid, an α -hydroxy-acid, to lactide is the first step. Ring opening condensation of lactide leads to polymerization yielding PLA [9]. In this process, precise compositional control of the type and quantity of the lactide introduced dictates the final properties of PLA plastics in terms of rigidity and crystallinity [13]. The repeat unit of PLA contains one stereocenter: either L(S)- or D(R)-lactic acid linked to another by an ester bond. The common commercial polymer of PLA is PDLLA (poly (D-L-) lactic acid), a copolymer composed predominantly of L-lactide, with varying amounts of D- and *meso*-lactide to broaden the

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range of applications. Typically, the D-LA ratio is between 1 and 8% of the total LA in various commercial PLA polymers. This is generally achieved by blending PLLA (poly-L-lactic acid) and PDLA (poly-D-lactic acid) polymers into a stereocomplex [14]. PLA resins containing more than 93% of L-lactic acid are semi-crystalline whereas PLA composed of 50–93% L-lactic acid are amorphous [15].

Although PLA-based plastics can be completely biodegraded in nature, this is effective only under suitable conditions achieved at industrial composting sites; i.e. 55–65 °C (glass transition temperature, T_g , of the polymer) and 80% relative humidity with aeration [16]. Since PLA has mechanical properties that are similar to traditional polymers, PLA-based products do not biodegrade readily during conventional disposal [17, 18]. Biodegradation of PLA by microorganisms leads to almost complete oxidation of carbon to CO₂ except for a small amount that is conserved as cellular biomass. During this process, a significant fraction of the energy spent in generating LA during PLA production is lost. An alternative to biodegradation of PLA is hydrolysis of the polymer to monomer and reuse the monomer in the production of new polymer, also called chemical recycling [10]. This process can compete favorably on energy cost of generating lactic acid compared to production by fermentation [19]. The ability to recycle PLA plastics to lactic acid by hydrolysis could also reduce landfill volume. Due to the presence of varying amounts of D-lactic acid in PLA, the LA syrup generated by chemical recycling is expected to be a mixture of both isomeric forms of LA. This contaminating D-LA, although a minor component of the total LA, needs to be removed since optical purity is a critical factor for reusing this product [20]. Chiral chromatography is an effective, although expensive, method of separating the two enantiomers [21]. This method may not be as effective in separating small amounts of D-LA in a syrup containing high concentrations of L-LA. A bio-based method described recently [22] could be an alternative, cost-effective, method of purifying PLA-syrup to L-LA for reuse.

The mechanism of hydrolysis of PLA is covered in numerous reports [9, 15, 23–25]. While extensive literature is available on degradation characteristics of PLA polymers used in medicine [9], information on chemical recycling of PLA to monomer is minimal [10, 19, 24, 26, 27]. Hydrolysis of PLA proceeds in two steps; rehydration of the polymer followed by hydrolysis of the ester bond to release the LA. Rate of hydrolysis of PLA in water is temperature dependent and process temperatures higher than 250 °C leads to racemization and decomposition of the released LA [24, 28, 29]. To minimize the side reactions, various catalysts, such as, acid and base, and ionic liquids, and solvents, like acetone, ethanol and ethyl lactate, have been used to enhance the rate of depolymerization at lower temperatures [19, 24, 30–33]. Yagihashi and Funazukuri evaluated depolymerization of

PLA in NaOH and reported almost complete hydrolysis of PLLA in 20 min at 160–180 °C [24]. Due to the low concentration of PLA (0.8 mmoles of LA equivalent), stoichiometrically higher amount of base (1.2 mmoles) and a temperature near the melting temperature of PLA used in their study, critical evaluation of the effect of NaOH on hydrolysis of the polymer was found to be challenging. They also reported a time and temperature dependent racemization of L-LA to D-LA in water but not in an alkaline solution up to 180 °C.

This present study compares the kinetics of PLA hydrolysis in water and NaOH towards understanding the role of alkali in this process. Hydrolysis kinetics were evaluated using a modified version of the Gompertz equation [34, 35] to describe the thermochemical hydrolysis of PLA via a single equation relating the LA concentration as a function of time, rate of hydrolysis and lag phase duration. These results show that hydrolysis of PLA beads in the presence of NaOH is biphasic and follows a first order rate constant. The generated syrup was purified using an engineered *Escherichia coli* to an optical purity of $\geq 99\%$ L-LA that can be used for polymerization to PLA.

Materials and Methods

Materials

PLA beads (~ 2 mm in diameter) were purchased from NatureWorks® LLC (Ingeo biopolymer 3052D and 4032D) and were utilized without further treatment. These polymer grades represent a large portion of PLA used in food packaging in USA. PLA grade 3052D is designed for injection-molding applications whereas grade 4032D is typically converted into biaxially oriented films. In preliminary experiments, hydrolysis profile of the two grades were found to be similar. Grade 4032D had slightly higher crystallinity than grade 3052D and was therefore used in this study. Properties of PLA grade 4032D with 1.2 (± 0.2) % average D-LA content are as follows: M_w 155,000, number-average molecular weight (M_n) 93,200, T_m (melting temperature), 160 °C, T_g (glass transition temperature), 61 °C [36]. On the other hand, PLA pellet grade 3052D contained 4.15 (± 0.45) % D-LA and the T_m and T_g were 145–160 °C and 55–60 °C, respectively (NatureWorks® LLC). PLA beads were ground, as needed, using a laboratory mill (Thomas-Wiley Company model 4, Swedesboro, NJ, USA). The powder was sieved through the mesh of a bouillon strainer (WINCO model CCB-8R, China) before hydrolysis. Pure Na-L-LA and D-LA were purchased from Sigma Aldrich (St. Louis, MO, USA). PLA-based plastic cups were obtained from Kangaroo Convenience Stores, Gainesville, Florida and used after cutting them to about 0.5–1.0 cm².

Thermohydrolysis Conditions

Fifteen g of PLA beads were mixed with 15 g of liquid in a 200 ml sealed canister (Werner Mathis AG, Switzerland). A total of 24 canisters, prepared identically were heated to the desired temperature in a Mathis® oven (Werner Mathis AG, Switzerland). The Mathis® oven harbors a temperature probe that continuously measures the temperature in the canister. Canisters were locked onto a circular device rotating alternatively for 30 s at 60 RPM clockwise and counterclockwise, allowing mixing. Temperature of the canisters was increased by 6 °C per min. The contents of the canisters reached 160 °C in about 18 min in the pre-heated oven. At different time periods, individual canisters were removed from the oven and cooled in a water bath at room temperature.

Analyzes

After heating and cooling to room temperature, canisters were opened and the liquid and solid fractions were separated, weighed and a mass balance was obtained. After removing the liquid fraction, canisters were rinsed with distilled water and dried at 160 °C to obtain the weight of remaining solid bound to the canister. Water bound to the solids in the canister was included as part of the solid fraction. Particulates in the liquid fraction were separated by centrifugation (12,000×g; 10 min) before analysis of the hydrolysate. Weight of all three fractions, clear liquid, solids entrained in the liquid and solids bound to the canister were combined to obtain the mass balance of the PLA hydrolysis reaction. The pH of hydrolysate was measured using an Orion 420A pH meter (Thermo Scientific). Density of the liquid fraction was obtained gravimetrically. LA concentration in the syrup was determined by high-performance liquid chromatography (HPLC; HP 1090 chromatograph; Agilent Technologies, Santa Clara, CA.) equipped with a Bio-Rad Aminex HPX-87H ion exclusion column (45 °C; 4 mM H₂SO₄; flow rate, 0.4 ml min⁻¹) and dual detectors (UV detector at 210 nm and refractive index monitor, in series). Optical isomers, D- and L-lactic acid, were separated and determined by HPLC with a diode array detector set at 210 nm using a chiral column (Chirex 3126(D)-penicillamine, 150×4.6 mm; Phenomenex, Los Angeles, CA.) using 2 mM CuSO₄ as mobile phase (flow rate, 0.6 ml min⁻¹).

Rate of Hydrolysis, k' and Lag Phase Duration λ

For each hydrolysis condition tested, lactic acid concentration as a function of time of incubation was generated and

an Eq. (1) derived from Gompertz model [34, 37] was used to fit the data set. The equation used was as follows:

$$[\text{Lac}] = [\text{Lac}]_{\text{max}} \exp \left\{ -\exp \left[\frac{k'}{[\text{Lac}]_{\text{max}}} e^{(\lambda - t)} + 1 \right] \right\} \quad (1)$$

where [Lac] is the moles of lactic acid at time t, [Lac]_{max} is the maximum theoretical moles of lactic acid, k' is the rate of hydrolysis of PLA into LA (mmoles h⁻¹), t, time of incubation at the selected temperature (h), and λ, the lag phase duration (h). The constants [Lac]_{max}, k' and λ, were determined using the non-linear regression approach with the aid of R software for statistical computing and graphics (r-project.org), version 3.5.2.

Activation Energy E_a

The natural logarithm form of the Arrhenius equation was used to determine the activation energy for hydrolysis of PLA into LA (Eq. 2) [38].

$$\ln(k') = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (2)$$

where E_a is the activation energy (kcal mole⁻¹), k' is the rate of hydrolysis (h⁻¹), T is the absolute temperature in Kelvin, R is the universal gas constant (1.9858×10⁻³ kcal mol⁻¹) and A, is the frequency factor, a constant (relationship between temperature and rate coefficient).

Optical Purity Study

To evaluate the effect of heat and alkaline condition on racemization of LA, 7 g of water or 7 g of 1 M NaOH was mixed with 7 g of PLA syrup (6 M lactic acid), placed in a sealed canister and heated to 160 °C for 2 h. The PLA syrup used in this experiment (run in triplicate) was obtained after treating PLA at 160 °C for 150 min with water or NaOH. In another set of canisters, 7 g of 1 M L-LA solution was mixed with either 7 g of 1 M NaOH or 7 g of water and subjected to the same treatment (160 °C for 2.5 h). After heat treatment and cooling to room temperature, a sample from each canister was subjected to chiral HPLC and the D-LA content of the samples before and after treatment was determined.

Bio-Based Purification of PLA-Derived Lactic Acid Syrup

Escherichia coli K-12 derivative, strain DC1001 was previously described [22]. This strain lacking all L-lactate dehydrogenase activities (L-LDH, YkgE and other unidentified non-specific activity) while retaining membrane-bound D-LDH activity was derived after mutagenesis and metabolic

adaptation for higher growth rate in mineral salts medium with D-LA as sole C-source. Strain DC1001 was used for purifying lactic acid syrup generated in this study.

For removal of D-lactate from a PLA syrup containing both D- and L-LA, cells were grown in mineral salts medium containing D-lactate as the sole C-source in a shaker (200 RPM) at 37 °C. At mid-exponential phase of growth, cells were harvested by centrifugation (5000×g for 10 min at room temperature). Cells were resuspended in a salt solution of the same composition as the mineral salts medium. PLA syrup (56 µl; 30 g total LA) was added to 10 ml of cell suspension at a density of 1.4 mg dry weight per ml in a 125 ml Erlenmeyer flask. The culture was incubated in a shaker (200 RPM) at 37 °C and samples were removed periodically to determine the concentration of D- and L-LA in the culture medium.

Experimental Results and Discussion

PLA Hydrolysis in Water

Poly(lactic acid) polymer beads from NatureWorks were treated in water at 140 °C, 150 °C and 160 °C at 50% PLA by weight (Fig. 1). At all three temperatures, lactic acid was released from PLA after a short lag and the duration of this lag time was dependent on the temperature of incubation (2.75, 1.5 and 0.5 h at 140 °C, 150 °C and 160 °C, respectively) (Fig. 1a). During the lag period, the beads started to soften due to heat followed by swelling indicating water intake [26]. Increase in the solid fraction weight due to water intake reached its maximum (1.8-fold higher) by the end of the lag phase. This was followed by an exponential

release of lactic acid by hydrolysis. The rate of LA production increased with increasing temperature (0.38 g h⁻¹ at 140 °C, 0.66 g h⁻¹ at 150 °C and 0.99 g h⁻¹ at 160 °C).

During the mid-exponential phase of LA release, the beads had completely melted, and the remaining solid material was opaque and white. At the end of hydrolysis of PLA, solid material was not detected, and the syrup was clear with a slight yellow color. Density of the syrup was 1.162 and 1.191 for the 140 °C and 160 °C treated samples, respectively. The amount of time required for almost complete hydrolysis of PLA was also dependent on the temperature and at 160 °C, hydrolysis of PLA was complete at 2 h. At the end of hydrolysis, lactic acid titers were 182.5 ± 3.0, 197 ± 1.9 and 191 ± 10.6 mmoles of LA at the three temperatures tested (140 °C, 150 °C and 160 °C, respectively). These titers represent a yield of 88% (140 °C), 95% (150 °C) and 92% (160 °C) of LA from 15 g of PLA beads (208.3 mmoles of LA equivalent). The lower yield at 140 °C could be due to incomplete hydrolysis of LA oligomers at this temperature at 5.5 h when the experiment was terminated. Similar hydrolysis profiles were obtained with PLA beads 3052D and PLA strips obtained from cups treated at 160 °C (data not presented).

Release of LA from PLA, under the experimental conditions described here, followed first order reaction after a lag phase. After the lag phase, the rate of hydrolysis increased reaching a maximum value before decreasing until all the PLA was hydrolyzed. The experimental data fit well to a modified Gompertz model (Eq. 1; Fig. 1b). The parameter values and 95% confidence intervals that best fit the data for the 150 °C PLA hydrolysis were [Lac]_{max} = 200.23 ± 4.42 mmoles, k' = 219.55 ± 14.29 mmoles h⁻¹ and λ = 1.98 ± 0.03 h (Fig. 1b).

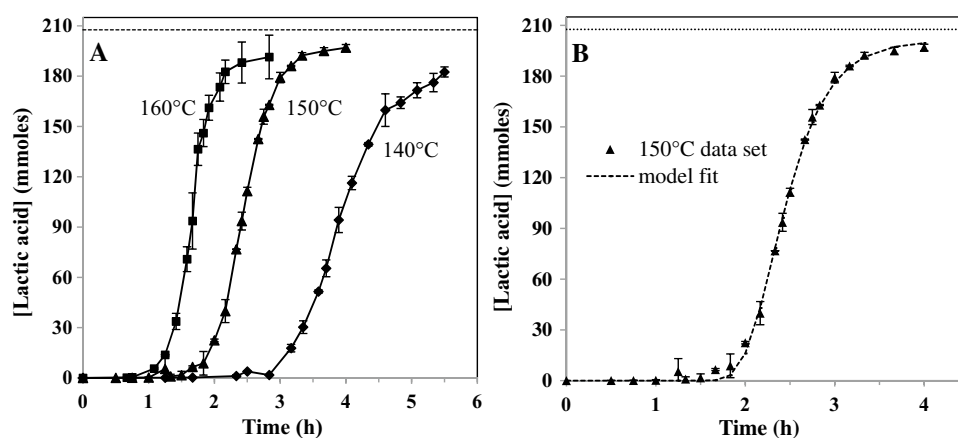


Fig. 1 Hydrolysis profiles of poly(lactic acid) polymer at different temperatures. PLA beads (15 g) were mixed with water (15 g) and heated at the indicated temperature. The amount of LA in soluble fraction was determined over time. **a** Hydrolysis profile. **b** Fitting the hydrolysis profile from 150 °C sample (solid triangles) to Gompertz

model predicted LA production profile (Eq. 1) (dashed line). In **a**, **b** the dotted line at the top represents the theoretical maximum LA concentration (208.3 mmoles) that can be obtained from 15 g of PLA. Average of three independent experiments with standard deviation are presented

These results are comparable to the ones reported by others although the rate of polymer hydrolysis varied depending on the temperature and type of material; beads, thin wires or films [25, 28, 39, 40]. Temperature dependence of the rate of PLA hydrolysis was also evaluated by Tsuji et al. in the range of 180–350 °C and they reported 90% of hydrolysis of PLA in 15 min at 350 °C [10]. The results presented in Fig. 1 show that 95% of PLA hydrolysis can be achieved at a significantly lower temperature of 160 °C, using a solid loading of 50% although a slightly longer hydrolysis time and a lag period were observed.

Siparsky et al. [41] suggested that the exponential increase in LA accumulation during PLA hydrolysis could support an autocatalytic mechanism of PLA hydrolysis and this has been further expanded [28, 31, 39]. Such an autocatalytic hydrolysis of PLA is dependent on the release of carboxyl groups during hydrolysis of the polymer that serves as a catalyst. In support of this mechanism, the rate of hydrolysis of COOH-terminated PLA was reported to be higher than regular PLA at 80 °C in phosphate-buffered saline at pH 7.4 [33]. To evaluate this further, hydrolysis profile of PLA beads at 50% loading was determined at 160 °C in the presence of LA syrup obtained from a previous PLA hydrolysis experiment (pH 2.0; LA concentration of syrup, 6.0 M). The hydrolysis profile of this sample was similar to that of hydrolysis in water, including a 1-h lag period suggesting that the presence of 0.46 M lactic acid in the reaction mixture had minimal effect on the rate of PLA hydrolysis (Fig. 2). Additionally, PLA hydrolysis profile determined in the presence of sulfuric acid (8N) did not exhibit significant difference in the lag phase duration or the

rate of lactic acid release compared to PLA hydrolysis in water (Fig. 2). With NaOH (8N) in the reaction mixture, 5.7 M lactic acid was released in the first 15 min after reaching 160 °C, about 70% of the total LA titer, due to the absence of a lag period that was observed with water or acid (lactic or sulfuric acid) treatment (Fig. 2). In addition to the absence of the lag period, the highest rate of release of LA from the PLA beads during the first 15 min with 8N NaOH (22.8 moles l⁻¹ h⁻¹) was about twice the rate of LA release in the presence of 8N H₂SO₄ (12.3 moles l⁻¹ h⁻¹) or water alone (10.0 moles l⁻¹ h⁻¹) (Fig. 2).

Based on autocatalytic model of hydrolysis, LA is expected to be released from the beads by surface erosion as the polymer melts in the presence of an acid as a catalyst and LA is expected to accumulate in the liquid fraction with minimal lag, as seen with NaOH. The similar lag period duration in the presence of added LA or sulfuric acid compared with hydrolysis in water (Fig. 2) plus the fact that there was a very good fit of the hydrolysis profile in water to the Gompertz model (Fig. 1b) and the inability to enhance the rate of hydrolysis by added acids suggest that the autocatalytic model of PLA hydrolysis requires further evaluation. It should be noted that Siparsky et al. hydrolyzed PLA in acetonitrile/water mixture and Pimonte and Gironi used water during the development of their kinetic models [39, 41]. An alternate possibility that the observed inability of added acids, lactic or sulfuric, to enhance the rate of PLA hydrolysis above the rate of hydrolysis in water, is due to a masked effect of nascent carboxylate groups released during hydrolysis, cannot be ruled out. However, under the present experimental condition, PLA hydrolysis is not influenced significantly by added lactic acid or sulfuric acid (Fig. 2), in agreement with the reported stability of several biodegradable polyesters to acidic conditions [42].

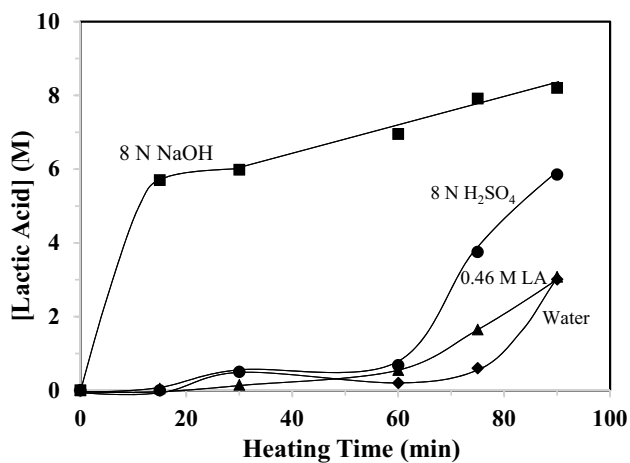


Fig. 2 Hydrolysis profile of PLA in acid or base. PLA beads were mixed with equal amount (by weight) of either H₂SO₄ (8N), lactic acid syrup from previous PLA hydrolysis (0.46 M total lactic acid), NaOH (8N) or water and heated at 160 °C for 90 min. Samples were withdrawn at the indicated times for determination of lactic acid released by hydrolysis of PLA. See “Methods” section for details

PLA Hydrolysis in an Alkaline Solution

PLA was hydrolyzed to LA in water at a rate that increased with temperature after an initial lag (Fig. 1). This higher rate of PLA hydrolysis at increasing temperatures also lowered the amount of time required for hydrolysis of PLA to higher than 95% (Fig. 1). To lower the reaction temperature without compromising the rate of hydrolysis, hydroxyl ion was evaluated as a potential catalyst since added acids failed to reduce the lag time (Fig. 2). Base had been reported to alter PLA hydrolysis profile without affecting the rate of hydrolysis over that of water alone at very low solid loading (80 mg PLA in 2 ml of 0.6 M NaOH) [24]. Other studies on hydrolysis of PLA film in NaOH in methanol reported an increase in polymer decomposition compared to water or methanol alone [30, 43]. These studies, in addition to the results presented in Fig. 2, suggest that NaOH is an inexpensive

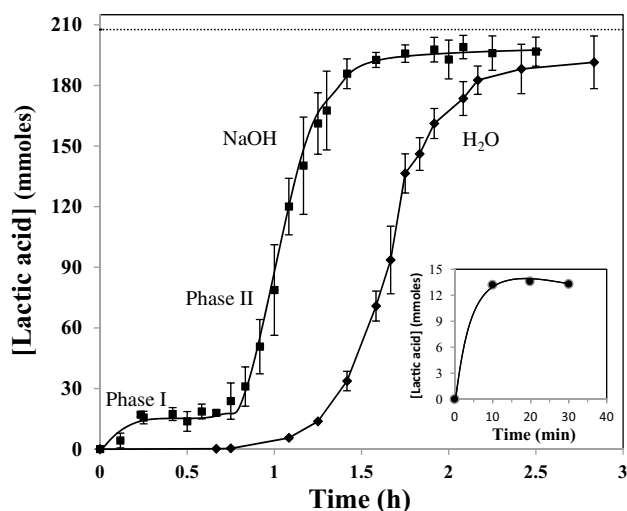


Fig. 3 Hydrolysis profiles of PLA in limiting concentration of NaOH. PLA beads (15 g) were hydrolyzed with water or NaOH (15 mmoles) at 160 °C. The dotted line at the top corresponds to the theoretical yield of LA (208.3 mmoles) that can be obtained from 15 g of PLA. Results are average of three independent experiments with standard deviation. (inset), Release of LA from PLA at 60 °C with NaOH

additive that has the potential to lower the temperature of PLA hydrolysis without affecting the rate of hydrolysis.

In the presence of NaOH at a molar NaOH to PLA ratio of 0.07, hydrolysis profile of PLA was biphasic (Fig. 3). There was an initial release of LA that reached a maximum of about 17 mmoles in the presence of 15 mmoles of NaOH in less than 15 min at 160 °C (Phase I) and this is about 8% of the total expected LA. A similar alkali-dependent initial burst of LA was also observed at 60 °C (Fig. 3, inset) but not at room temperature suggesting that melting of the polymer enhances hydrolysis by NaOH. It should be noted that the T_g for this polymer was reported to be 55–60 °C and the T_m as 155–170 °C (NatureWorks® LLC). At both 60 and 160 °C, this initial phase of LA release was within 15 min. When PLA was hydrolyzed with water at temperatures as high as 160 °C, the T_m for the polymer, this initial phase of LA production seen with NaOH at 60 °C was not observed (Fig. 3). These results suggest that added alkali directly interacts with surface-localized amorphous regions of the polymer. This requires heating the beads to soften the polymer for exposing these regions as well as to diffuse the hydroxyl ion into the swelling polymer. This is in agreement with the observation that solid beads of slightly smaller diameter can be detected in the canisters after 15 min of incubation with alkali and also with previously reported surface erosion hydrolysis of PLA under alkaline conditions [44]. After a lag of about 30 min, rest of the PLA was hydrolyzed in an exponential manner at 160 °C (Phase II), as seen with thermohydrolysis with water alone at this temperature

(Fig. 3). At 60 °C, the Phase II of LA release from the PLA was not observed even after 4 days of incubation in the presence of 15 mmoles of NaOH suggesting that the release of LA during Phase I is strictly base dependent. A reaction mechanism proposed by Tham et al. for base hydrolysis of PLA [43] is apparently the mode of action for base-dependent release of LA from PLA in this study (Fig. 3, inset).

Increasing the [NaOH] in the reaction increased linearly the amount of LA produced during the Phase I of PLA hydrolysis either at 60 or 160 °C (Fig. 4a). After this initial base-catalyzed release of LA (Phase I), a short lag in LA release was observed at 160 °C. This lag duration varied depending on the concentration of NaOH added to the reaction and the temperature of incubation (Fig. 4b, c). This reduction in the lag phase by increasing concentration of NaOH at 160 °C (Fig. 4b) is probably due to surface and bulk erosion from melted polymer at this temperature. Since at 160 °C, higher [NaOH] led to an overlap of the two phases of PLA hydrolysis (Fig. 4b; also Fig. 2), actual LA concentration released during Phase I could not be accurately determined. On a molar basis, the correlation between the amount of NaOH added and LA released into the liquid phase was 0.72 at 60 °C. Apparently, one molecule of OH^- reacts with one stereocenter of the polyester to release one molecule of LA as proposed by Tham et al. [43]. A ratio of 0.72 for LA released to base (less than 1.0) represents the presence of LA oligomers in the hydrolysate that are not included in this calculation. Effect of [NaOH] and temperature on the lag duration between Phases I and II was calculated using Eq. 1 derived from Gompertz model and the results are presented in Fig. 4b, c. However, it should be noted that addition of NaOH at limiting concentrations only shortened the lag phase before the remaining PLA hydrolysis started and it did not significantly alter the hydrolysis profile during Phase II. This is comparable to the results on PLA hydrolysis at temperatures higher than 160 °C that showed that NaOH shortened the lag phase [24]. Immediately following this lag, the remaining PLA beads were hydrolyzed to LA in an exponential manner until the total LA yield reached about 90% of the theoretical value, as seen previously with water-based hydrolysis (Fig. 3). The rate of hydrolysis in this reaction with the added base was slightly higher (1.23 g h^{-1}) compared to water-based hydrolysis (0.99 g h^{-1}). This slightly higher rate of hydrolysis could be a consequence of surface erosion of the beads during the initial base attack that reduced the size of the remaining beads suggesting that the bead diameter is an important component in determining the hydrolysis rate [44]. These results show that a judicious application of base and temperature can shorten overall hydrolysis time of PLA polymer to LA for reuse (Figs. 3, 4).

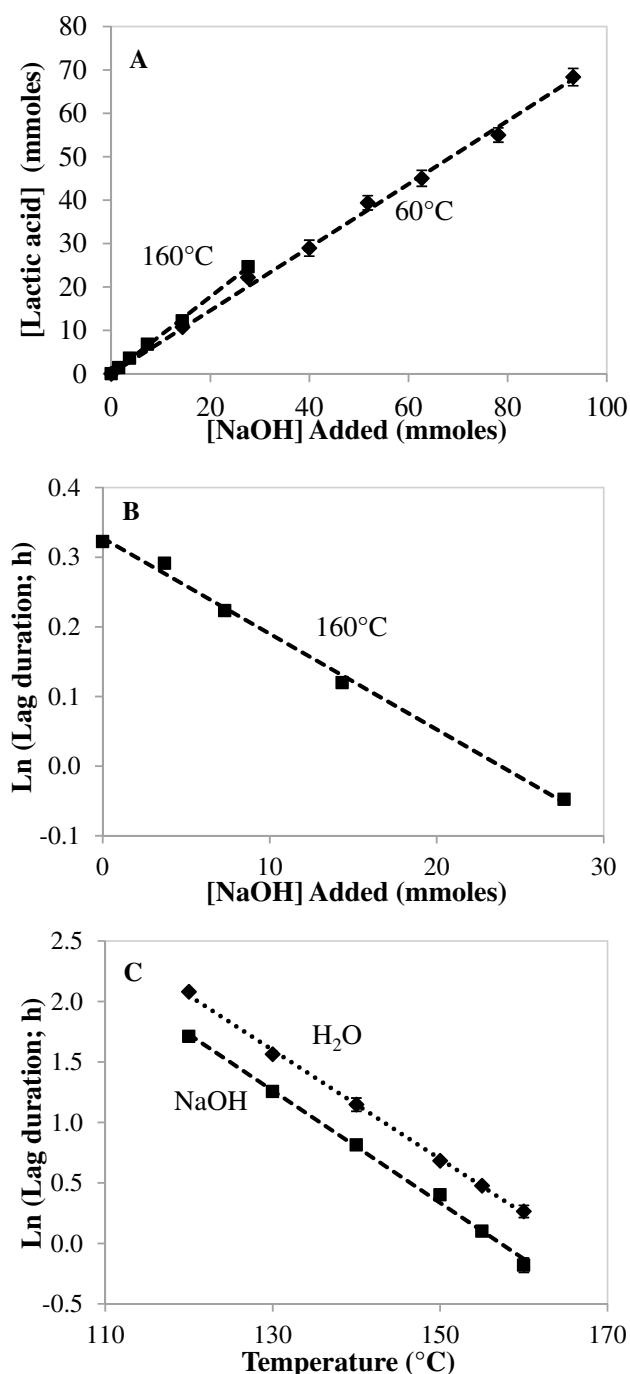


Fig. 4 Base-dependent hydrolysis of PLA to LA. **a** Effect of NaOH concentration in the reaction on the amount of LA recovered during Phase I of PLA hydrolysis at 160 °C ($R^2=0.999$) and at 60 °C, ($R^2=0.997$). **b** Natural logarithm of the lag duration (h) between Phases I and II as calculated using Eq. 1 as a function of initial NaOH concentration ($R^2=0.996$). **c** Natural logarithm of the lag duration (h) as calculated using Eq. 1 as a function of temperature (R^2 values were above 0.99). See text for details

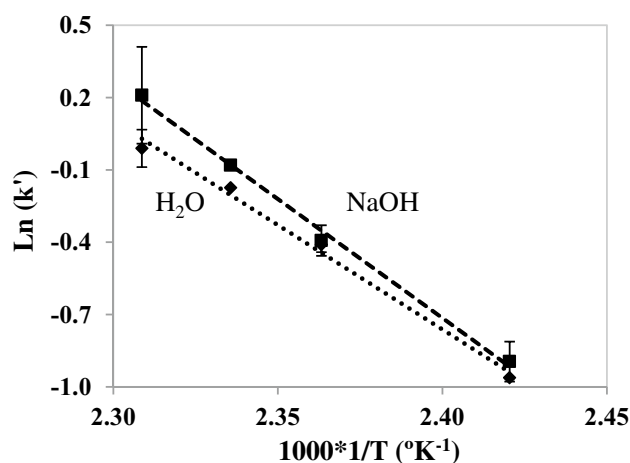


Fig. 5 Activation energy for hydrolysis of PLA in water or NaOH

Activation Energy of PLA Hydrolysis to LA

Addition of base to the hydrolysis reaction did not significantly change the activation energy of hydrolysis ($19.6 \text{ kcal mol}^{-1}$ with NaOH and $17.2 \text{ kcal mol}^{-1}$ with water alone) (Fig. 5). One possible explanation for the slightly higher activation energy in the presence of NaOH is that the base initially helps hydrolyze the amorphous regions of the beads leading to an increase in activation energy for hydrolysis of the remaining crystalline parts of the beads. This is in agreement with the previously reported higher energy to achieve hydrolysis of crystalline PLA compared to amorphous polymer [44]. These values for activation energy of hydrolysis of PLA beads are close to the $19.9 \text{ kcal mol}^{-1}$ reported for hydrolysis of PDLLA microcapsules and $20.0 \text{ kcal mol}^{-1}$ for PLLA microcapsules in the range of 21–45 °C [45]. On the other hand, values obtained in this study differ from the $12.2 \text{ kcal mol}^{-1}$ reported for temperatures ranging from 180 to 250 °C; this lower value probably represents the activation energy required to break down the polymers into oligomers as opposed to activation energy necessary for release of LA [25].

Particle Size of PLA on Hydrolysis

The results presented above suggest that the reactivity of NaOH with the PLA beads (2 mm diameter) is limited by the surface area of the beads. It is possible that increasing the surface area accessible to the hydroxyl ions would increase the amount of LA released per mole of NaOH added. To test this possibility, the 2 mm diameter PLA beads were ground, sifted and reacted with NaOH at 60 °C (Fig. 6).

In this set of experiments, 5 g of size-reduced PLA (70 mmoles of LA equivalent) was added to 25 g of aqueous solution containing 90 mmoles of NaOH at 60 °C

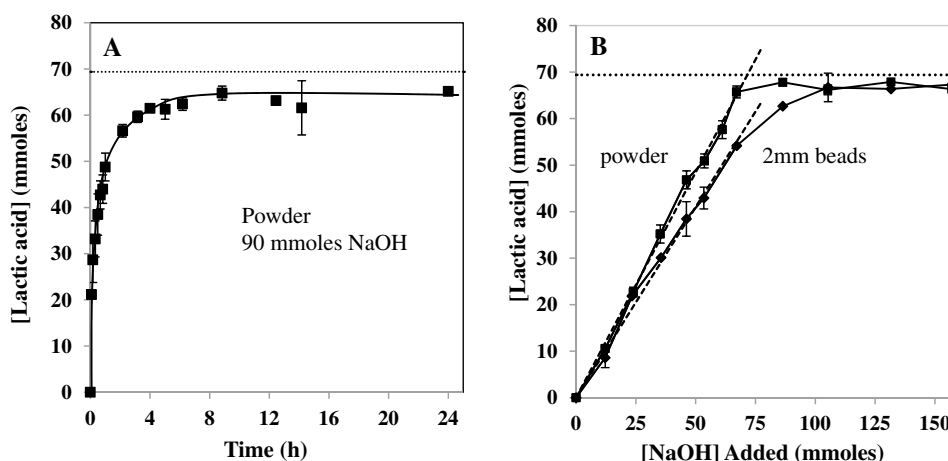


Fig. 6 Effect of particle size on PLA hydrolysis in NaOH. The dotted line at the top of the figures represents the theoretical yield of LA (69.4 mmoles). **a** Hydrolysis profile at 60 °C of PLA powder [17% (w/w)] in 90 mmoles of NaOH. **b** Effect of the amount of base added

to the reaction on hydrolysis of PLA powder or polished beads (2 mm diameter) at 60 °C. Total LA in solution was determined after 24 h. Average of three independent experiments with standard deviation are presented. See “Methods” section for other details

(Fig. 6a). At this ratio of NaOH to PLA, hydrolysis of PLA was monophasic and reached a maximum yield of about 90% within four hours. At [NaOH] below this value, the quantity of base added was limiting and the amount of total LA recovered was proportional to the initial amount of base added (Fig. 6b). When ground PLA was tested, 0.97 mol of LA was released from the polymer per mole of NaOH added as opposed to a ratio of 0.82 obtained for the 2 mm diameter PLA beads (Fig. 6b). This molar ratio of 0.97 suggests that hydroxyl ion is a reactant in hydrolysis of PLA polymer and is in agreement with the suggested mechanism of action of base on PLA hydrolysis [43]. This increase in molar ratio shows that the total surface area of the polymer accessible to hydroxyl ions is a critical factor in hydrolysis of PLA polymer. It is interesting to note that with the 2 mm PLA beads, the ratio of LA released to base added at 60 °C increased to 0.82 in this experiment compared to 0.72 seen before (Fig. 4a).

Racemization of Lactic Acid During Hydrolysis

During chemical recycling of PLA for reuse by the polymer industry, the LA produced needs to retain the enantiomeric ratio of the polymer. To investigate the isomeric stability of LA during hydrolysis, PLA grade 3052D reportedly containing about 4% of D-isomer (NatureWorks® LLC) was used in this experiment. The average ratio of D-isomer to the total LA obtained after hydrolysis at various temperatures with or without NaOH was 6.2 ± 0.3 (Table 1). Total LA yield in these experiments varied from 92 to 98% of the theoretical value. This observed 6% D-LA content of the syrup obtained from PLA stated to contain about 4% D-LA was unexpected since it has been reported that racemization did not occur during heat treatment of PLA polymer below 200 °C [10, 24, 25].

The observed increase in the D/L ratio (Table 1) could arise from limited racemization of LA during the production of PLA through ring-opening polymerization [9], or during hydrolysis. Racemization during hydrolysis could occur either at the time of release of LA from the polymer or in the syrup. To explore the possibility that racemization occurred

Table 1 D-LA fraction of PLA syrup from various temperatures with water or NaOH

Temp. (°C)	Water			NaOH		
	Time (h)	d/total LA (%)	LA yield (%)	Time (h)	d/total LA (%)	LA yield (%)
120	50.7	5.6	94.7	40.7	6.0	94.2
130	15.6	6.4	94.7	17.0	6.4	97.5
150	3.7	6.8	95.0	2.5	6.0	95.9
155	2.8	6.3	92.4	2.0	6.3	96.1

PLA beads (Ingeo biopolymer 3052D) at a LA equivalent of 104 mmoles were heated to the indicated temperature and time in either water or NaOH (7 mmoles)

Table 2 D-lactic content of PLA syrup or L-lactic acid solution after treatment for 2 h at 160 °C

Sample	Medium	0-time	2 h
PLA syrup	Water	6.26 ± 0.8	6.46 ± 0.9
L-LA solution	Water	UD*	UD*

Lactic acid syrup obtained after hydrolysis of PLA beads (3052D) or L-lactic acid solution (1 M) was heated at 160 °C for 2 h

*D-LA was undetectable

after the release of LA, LA in PLA hydrolysis syrup with 6% D-LA content or L-LA solution in water was incubated at 160 °C for 2 h. Results presented in Table 2 show that heating either PLA syrup or pure L-LA in water at 160 °C for 2 h did not alter the D-LA content. Based on these results, it appears that the observed higher than expected D-LA content of the PLA syrup (6% vs 4%), especially after hydrolysis with water (Table 1), is apparently introduced either at the time of hydrolysis of the polymer or preparation of the polymer. It is difficult to distinguish between these two alternatives since the listed D-LA content of the PLA grade 3052D (NatureWorks® LLC) is apparently based on the manufacturing process and may not represent the actual D-LA content of the beads. Evaluation of the potential of very low level of racemization during the release of LA from the polymer requires additional experimentation.

Even though NaOH in limiting amounts did not appear to affect racemization during hydrolysis of PLA (Table 1), base must be used with caution as excess NaOH remaining after hydrolysis and continued heating even at 160 °C could lead to racemization of the product as seen with an increase in racemization of LA in the presence of excess KOH and heat [46]. Ideally, the process chosen for chemical recycling of PLA must rapidly hydrolyze the polymer to completion while also not supporting racemization to minimize the need for separation of the two enantiomers before L-LA can be reused [20]. This can be achieved by judicious application of alkali, time and temperature during chemical recycling of PLA polymer for reuse.

Bio-purification of Lactic Acid Syrup

Since the LA syrup obtained after hydrolysis of PLA is expected to contain D-LA that was introduced intentionally during polymerization, this contaminating D-LA needs to be removed before the derived L-LA can be reused for polymerization. Although the two isomers can be separated by chiral ligand chromatography [21, 47], its application at industrial scale may not be practical due to the cost. As an alternative to chiral separation, the less than 10% content of D-LA in a syrup obtained from chemical recycling can be

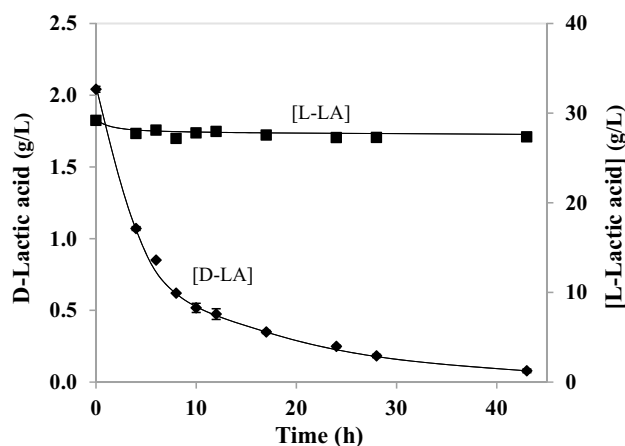


Fig. 7 Bio-based purification of lactic acid syrup using engineered *E. coli* strain DC1001. See “Methods” section for details

effectively removed from the bulk L-LA biologically without loss of L-LA.

Towards this objective, *E. coli* derivatives that selectively utilize D-LA were developed and described [22]. Further improvement and metabolic adaptation led to *E. coli* strain DC1001 that removed D-LA in a D- and L-LA mixture at a highest rate of 1.4 g DCW⁻¹ h⁻¹. At a cell density of 1.4 mg ml⁻¹, the rate of D-LA removal was 0.65 g l⁻¹ h⁻¹ [22] demonstrating the potential of bio-purification of LA syrup from chemical recycling of PLA. Strain DC1001 lowered the D-lactic acid content of a PLA syrup (31 g l⁻¹ of total LA) from 6.4% to less than 1% in about 24 h in mineral salts medium (Fig. 7). Further improvement of microorganisms coupled with efficient process conditions is expected to increase the rate of D-LA removal from PLA syrups and lower the time of treatment.

Conclusions

Chemical recycling of PLA is an effective way to broaden the afterlife of PLA based plastics in addition to reducing their environmental footprint. Although hydrolysis of PLA in water is effective, it requires higher temperature for effective hydrolysis in a shorter time. The rate of hydrolysis of PLA and the yield of LA can be enhanced at a lower temperature by inclusion of NaOH in the process. A bio-based process can serve as a cost-effective method to remove contaminating D-LA from the majority L-LA in the syrup obtained after hydrolysis of PLA polymer for reuse in the polymerization process.

Acknowledgements This work was supported by grants from the US Department of Agriculture (USDA) (2012-67009-19596; LOI) and Biomass Research and Development Initiative Competitive Grant

(2011-10006-30358) from the USDA National Institute of Food and Agriculture. This work was also supported by funding from the US Department of Energy's International Affairs under Award Number DE-PI0000031 and the Florida Department of Agriculture and Consumer Services.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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