

Depolymerization of Post-Consumer Polylactic Acid Products

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ABSTRACT: Presented in this study is a novel recycling strategy for poly(lactic acid) (PLA) in which the depolymerization is rapidly promoted by the base-catalyzed hydrolysis/ alcoholysis of the terminal ester bonds under mild conditions. Post-consumer PLA water bottles were cut into approximately 6 x 2 mm plastic chips and heated to 50–60°C in water, ethanol, or methanol as the depolymerization medium. A variety of carbonate salts and alkaline metal oxides were screened as potential catalysts. High-power ultrasound was also investigated as a means to accelerate the PLA decomposition. Both mass loss and HPLC analysis of the treated suspensions showed that the conversion of PLA to lactic acid/lactic esters was achieved with yields over 90% utilizing either ultrasonics or a hot bath. It was found that the most rapid decomposition occurred in solution of sodium hydroxide in methanol at 50°C, in which maximum depolymerization was complete in 5 min. It was also seen that the degree of crystallinity affected the rate of depolymerization.

KEYWORDS: Poly(lactic acid), high-power ultrasound, depolymerization, PLA recycling, crystallinity, energy efficiency, post-consumer water bottles

1 BACKGROUND

Poly(lactic acid) (PLA) is a polyester derived from corn that is renewable and compostable. Historically, it has been used for medical applications such as degradable sutures; however, over the past decade novel chemical pathways have allowed the production of quantities large enough for applications such as packaging and lawn care products. Although PLA continues to expand into other markets, the dominant market remains food packaging [1].

Poly(lactic acid) and ethanol are produced using similar methods: corn starch (polymerized sugar) is depolymerized through milling, cooking, and enzymatic hydrolysis to produce fermentable sugars. It is important to note that in climates where sugar cane can be grown, the process of extracting fermentable sugars is less intensive; however, this paper focuses on PLA derived from areas where this is not possible. The sugar is then fermented by microbes into lactic acid (LA), which is then polymerized into PLA by condensation [2].

While PLA is compostable in commercial composting systems that provide the necessary temperature and moisture content, home composting conditions are not conducive to the degradation of PLA [3]. It is also important to note that the degradation products of PLA include CO₂ and methane gas, both of which are known greenhouse gases. Moreover, the detrimental effects of methane are 21 times stronger than CO₂ [4]. In addition, there is no infrastructure in place to recycle PLA and there are concerns regarding PLA contaminating other plastic recycling streams if mixed together. Thus, while PLA is renewable and in principle biodegradable, a potentially better end-of-life treatment would be the depolymerization of PLA into lactic acid monomers that can be subsequently purified and reconverted into PLA as a virgin material. Hydrolytic depolymerization has been one of the popular techniques to depolymerize PLA, employing pressures of approximately 10 MPa (~1,500 psi), coupled with temperatures ranging from 120°C to 350°C for small quantities of PLA [5–7]. Although the inexpensive treatment media used in this technique are water or an alkaline solution, scale-up of such high-pressure processes makes the technique energy-intensive and costly. In addition, the typical batch-wise hydrolytic depolymerization of PLA makes scale-up and meeting the needs of the industry difficult

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to achieve. Other techniques that have been investigated include selective enzymatic depolymerization [8] and metal organic salt depolymerization [9]. These methods have limitations, such as slower conversion rates and a higher residue of metal ions, which make them unattractive as recycling techniques [6, 10].

If more energy-efficient techniques can be found, there would be the possibility that the development of collections techniques would be attractive to the industry, and PLA would be recycled without the requirement of virgin feedstock (corn or sugar cane) suitable for direct food contact. This would save the energy and emissions resulting from feedstock harvesting and conversion. It is estimated that the energy used to convert corn into PLA is 82.5 MJ/kg, of which 54 MJ/kg [11] is derived from fossil fuel. The overall emissions for PLA are 1.8 kg/kg PLA of CO₂-equivalent [12].

It is well known that ultrasonic treatment can accelerate chemical reactions through enhanced mass transfer. Some have reported that ultrasonics can increase chemical rates by many orders of magnitude [13, 14]. High-powered ultrasonics in a liquid medium results in cavitation and streaming that break down particle size, produce stable emulsions, and enhance mixing [11]. Historically, high-powered ultrasonics were limited to relatively low-power systems, such as cleaning baths (<1,000 W), and based on batch-type treatment. Recently, high-power systems (+5,000 W) have been introduced that are based on continuous flow system [15]. It is hypothesized here that the application of ultrasound to hydrolysis/transesterification reactions that drive the depolymerization of PLA would serve as an energy-efficient route to catalyze these reactions.

In this work it was shown that while ultrasound in this application is not efficacious; however, under mild heating the alcoholysis of terminal ester bonds proceeds rapidly under mild conditions, achieving the complete decomposition of post-consumer PLA bottles in under fifteen minutes [16]. The process requires no extensive pretreatment of the bottles, e.g., grinding to a fine powder or extraction of dyes or other additives. This method of depolymerizing PLA to lactic acid requires substantially less energy and produces less greenhouse gasses compared to producing lactic acid from corn. As the majority of PLA produced in the US is from corn and not from sugar cane, this work focusses strictly on corn-based PLA.

2 EXPERIMENTAL

2.1 Materials

Water bottles produced from PLA were supplied by Naturally Iowa® and were cut into approximately

6 × 2 mm chips and used with no further processing. The ultrasonic treatment media was water (de-ionized), methanol (reagent grade), or ethanol (reagent grade) together with various carbonate salts and metal oxides. Potassium carbonate (K₂CO₃), sodium hydroxide (NaOH), and aluminum carbonate (Al₂(CO₃)₃) were purchased from Alfa Aesar, MA; zinc carbonate basic [ZnCO₃]₂•[Zn(OH)₂]₃, magnesium oxide (MgO), and zirconium(IV)oxide (ZrO₂) salts were obtained from Fischer Scientific, Pittsburg, PA. All materials were used as received. Though indicated in literature, titanium-based oxides, which possess catalytic activity for depolymerization, were not used in the study because they were not found to be cost-effective chemistries.

2.2 Equipment

A Branson 2000ea series 20KHz ultrasonic system (2200 W) (Danbury, CT) was used to treat the samples. A booster with a gain of 1:0.6 (a reducing booster), and a horn (1:2.17 multiplying factor) with a 39 mm diameter flat face were used. The stack assembly produced an amplitude of 26μm_{pp} at 100% amplitude setting. All samples were treated in a 150 ml quartz beaker.

In order to determine the material composition, thermogravimetric analysis (TGA) was performed using a TA Instruments system, New Castle, Delaware. A heating rate of 10°C/min was used for TGA analysis. In addition, crystallinity was measured using a TA Instruments system at a heating rate of 5°C/min.

Further confirmation and quantification of lactic acid was completed with high-performance liquid chromatography (HPLC) using a Varian HPLC and Varian-356-LC Ri detector. The column used was Aminex HPX-87H Column #125-0140 for organic acids from Biorad. Standard chemical grade LA samples were used for calibration. The lactic acid concentration in treated samples was determined using a calibration coefficient based on the area of LA peaks of known concentration. The calibration coefficient had a reasonably good correlation with an r² value of 0.95. An example HPLC trace of a standard sample with known concentration of LA is shown in Figure 1.

2.3 Depolymerization

Each depolymerization experiment was conducted using 5 g of PLA chips in 50 ml solvent with the various catalysts. A full factorial experimental design was conducted to assess efficacious catalysts according to the screening experiments as described below. Suspensions were heated to 45, 55, or 65°C in a thermostated hot water bath; experiments were repeated

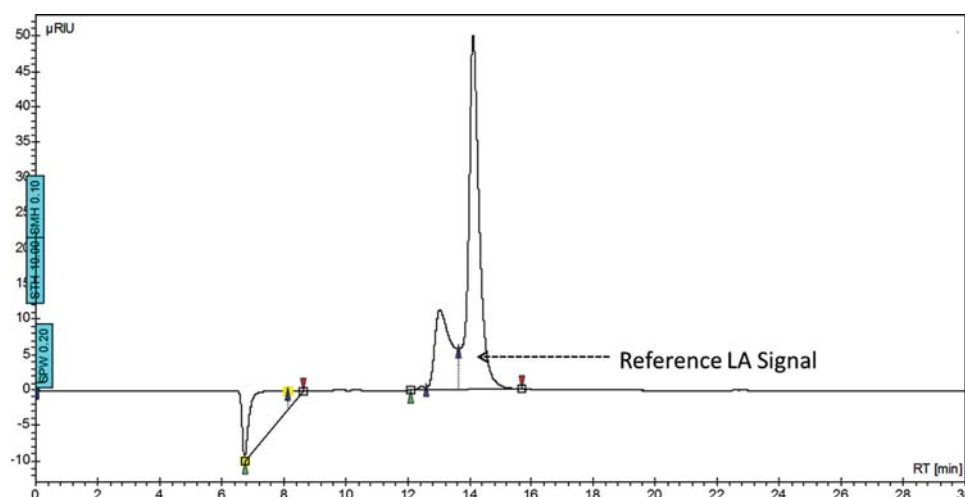


Figure 1 HPLC calibration curve for lactic acid.

both with (denoted US) and without (denoted HB) the use of ultrasonication in batch mode. The hot bath temperatures were determined based on temperatures observed during ultrasonic screening experiments resulting from cavitation. In addition, the experimental design was set near the T_g of PLA (55°C) to facilitate any chemical interaction between the mobile polymer chains. Experiments with ultrasonication employed a treatment amplitude of $16\ \mu\text{m}_{\text{p-p}}$ and were monitored for temperature changes throughout the treatment. Higher ultrasonication amplitudes were not investigated because the vapor barrier effects of the high vapor pressure solvents resulted in strong attenuation of the sound waves. The reactions were stopped by adding excessive amounts of water to the reagents. Successive depolymerizations were stopped at 2.5 min time intervals to quantify mass loss and evaluate the suspension medium; depolymerizations were allowed to proceed to a maximum time period of 20 min, or until 100% mass loss was reached. The HB trials were repeated once; the reported mass loss and conversion values represent the average of the two repetitions.

After treatment, the solid content (remaining PLA chips) was collected and its mass compared to the initial mass of the sample. The degree of depolymerization was measured and mass loss calculated according to Equation 1:

$$\% \text{ Loss} = \frac{(\text{Initial weight} - \text{Post ultrasonic treatment weight}) \times 100}{\text{Initial weight}}$$

Eq. 1

Conversion of PLA to lactic acid/lactic esters was determined with HPLC. An HPLC concentration calibration curve was constructed with a series of pure known concentration lactic acid standards in the

respective solvents. The HPLC-derived concentrations were used to calculate the degree of PLA conversion as per Equation 2:

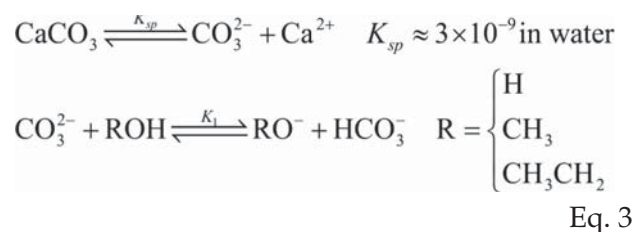
$$\% \text{ Conversion} = \frac{\text{Measured concentration of lactic acid} \times 100}{\text{Theoretical yield}}$$

Eq. 2

While mass loss was used as a first order approximation of PLA depolymerization, the products of the reactions were characterized with HPLC to confirm the presence of LA and to exclude partial depolymerization or solvation. In addition, the HPLC results were integrated as a function of time to confirm the mass conversion of PLA to LA monomers.

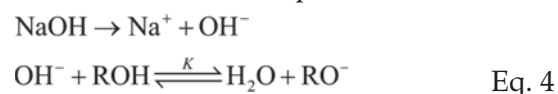
2.4 Catalyst Screening

Each of the catalysts studied (detail in the following text) are compounds that are basic to some degree; for example, calcium carbonate is very weakly alkaline as illustrated by the chemical equilibria as seen in Equation 3.



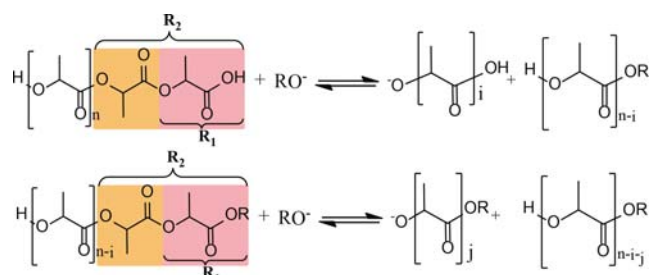
Eq. 3

Sodium hydroxide, on the other hand, is a strong base and will produce a mixture of nucleophiles in the alcoholic solutions, as seen in Equation 4.



Eq. 4

The depolymerization mechanism targeted in these experiments is simply the classical base-catalyzed hydrolysis/transesterification of the ester linkages in the PLA backbone as seen in Equation 5.



Eq. 5

In a transesterification reaction, the rate decreases substantially according to the size of the leaving group, and accordingly the rate of monomer production ($i = 1$) should be substantially greater than that for dimers and higher ($i \geq 2$). Note that while the first depolymerization product is a lactic acid alkoxide, subsequent products will vary according to the attacking R group ($R \in \text{H}, \text{CH}_3, \text{CH}_3\text{CH}_2$).

Based on solvent and salts' miscibility with the three solvents, the various experimental combinations are detailed in Table 1. To determine the relative effectiveness of each solvent, screening experiments were conducted at a constant treatment time of 15 min, with ultrasound applied at an amplitude 13 mm_{r-p} with 1 g of PLA chips in 0.125, 0.25, 0.5 g of each salt and 50 ml of each solvent. Our choice to meter the catalysts on a mass basis rather than on the molarity is

predicated primarily on the observation that the mass basis directly influences the cost of the process; our objective is to compare the efficacy of these materials from a cost-sensitive perspective since this will ultimately dictate commercial adoption. As detailed in the results section, a "+ve" indicates a variable effectiveness allowing the depolymerization of PLA, while a "-ve" indicates a variable not capable of depolymerizing PLA. The effectiveness was based on a significant weight loss of the chips (at least 20% wt).

3 RESULTS

The thermogravimetric analysis of the treated PLA chips shown in Figure 2 indicates that the presence of dye colorants and additives limited the conversion value to approximately 98%. This analysis shows only one decomposition at approximately 280–315°C, which is not in good agreement with the reported decomposition temperature of PLA [17], and it accounts for nearly all of the mass fraction of the PLA sample. Thus it was assumed in the balance of this work that the PLA was approximately 100% pure.

The screening experiments, Table 1 (highlighted combinations), identified methanol and ethanol as treatment media with sodium hydroxide and potassium carbonate as salt as effective in depolymerizing PLA, and therefore these combinations were selected as the design space for further optimization. Table 1 shows that K_2CO_3 is only effective in water, while NaOH is effective in all solvent media, even at relatively low mass (0.125 g). While it was assumed that

Table 1 Experimental conditions that determine the variable effectiveness of PLA depolymerization as a function of catalyst.

Media		[M], mmol/L	H ₂ O	MeOH	EtOH
Catalyst	Code		M	W	E
K ₂ CO ₃	K(1)	72.4	+ve	-ve	-ve
K ₂ CO ₃	K(2)	36.2	+ve	-ve	-ve
AlCO ₃	Al	21.4	-ve	-ve	-ve
Zn ₂ CO ₃	Zn	40.0	-ve	-ve	-ve
NaOH	Na(1)	250.0	-ve	-ve	+ve
NaOH	Na(2)	125.0	+ve	-ve	+ve
NaOH	Na(3)	62.5	+ve	-ve	-ve
ZrO	Zr	46.6	-ve	-ve	-ve
MgO	Mg	124.1	-ve	-ve	-ve
CaCO ₃	Ca	50.0	-ve	-ve	-ve
CuCO ₃	Cu	40.5	-ve	-ve	-ve

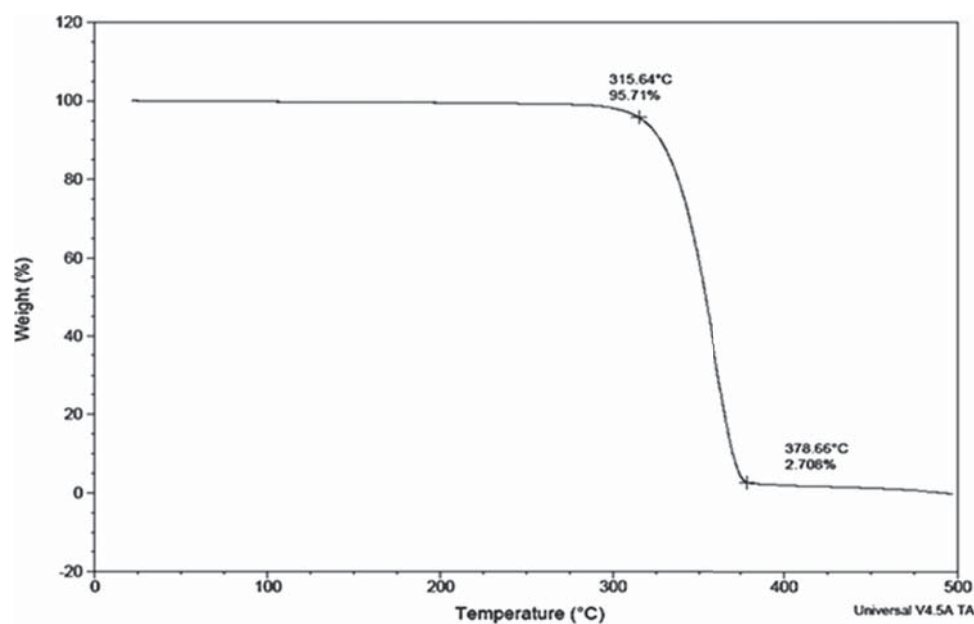


Figure 2 Thermogravimetric analysis of post-consumer PLA chips from water bottles.

other salts, such as Mg, Zr, Al, and Cu-based salts, would be effective in the depolymerization of PLA, the experiments showed that under the conditions studied they were ineffective.

3.1 Depolymerization of PLA

Samples of PLA were treated in hot bath (HB) and with ultrasonics (US) in a solution of MK (methanol and K_2CO_3). Figure 3 shows that independent of the treatment and conditions, the mass loss of PLA (conversion to lactic acid) asymptotically approached 100% as a function of time. It was seen that at 0.5 g of the salt the conversion time is approximately 15 min. There was reasonable agreement between mass loss (based on weight of remaining chips) and the conversion of LA, based on HPLC mass measurements. This suggests that the PLA was depolymerized by reactions at the polymer chain ends and was converted directly into LA monomers, supporting the expectation that the transesterification rate should favor monomer production. In addition, it was observed that for both hot bath and ultrasonic treated samples, the rate of depolymerization was affected by concentration/mass of salts ((1) = 0.5 g, (2) = 0.25g). An unexpected outcome was that there was no evidence that ultrasonic treatment promoted depolymerization. It is believed that the rate of cavitation erosion was significantly lower than the rate of chemical depolymerization for the two concentrations/masses of the salts. This theory was further supported by later SEM images.

A similar trend was observed for methanol and NaOH, as seen in Figure 4; however, here the conversion time was approximately 6 mins. It is important to note that the hot bath treatment temperature was set to approximately 55°C in order to match the temperatures observed during ultrasonic treatment.

Both Figures 3 and 4 indicate that ultrasonic treatment was actually less effective than hot bath treatment. This is attributed to the fact that the hot bath temperatures were based on the average temperature during ultrasonic treatment, and because the reagents formed a homogeneous solution and the enhanced mass transfer typically seen with ultrasonics with heterogeneous medium did not accelerate the chemical reaction.

Because simple heating of the chemical reagents appeared to be just as effective as ultrasonic treatment, additional experiments were conducted to study the temperature and mass loss as a function of time. In these studies, the solvents/liquid media and salts were preheated to selected temperatures and the PLA chips were added to the preheated solutions. The temperatures were controlled by a hot plate and monitored with a digital thermometer. Figure 5 (for the 0.5 g methanol NaOH solution) shows that depolymerization occurred rapidly and was over 90% complete within 5 min, and approximately 100% within 10 min, at temperatures at and above 55°C. Despite the addition of room temperature chips to the preheated solution, the temperature (right hand axis) remained relatively constant. While not reported here, the results

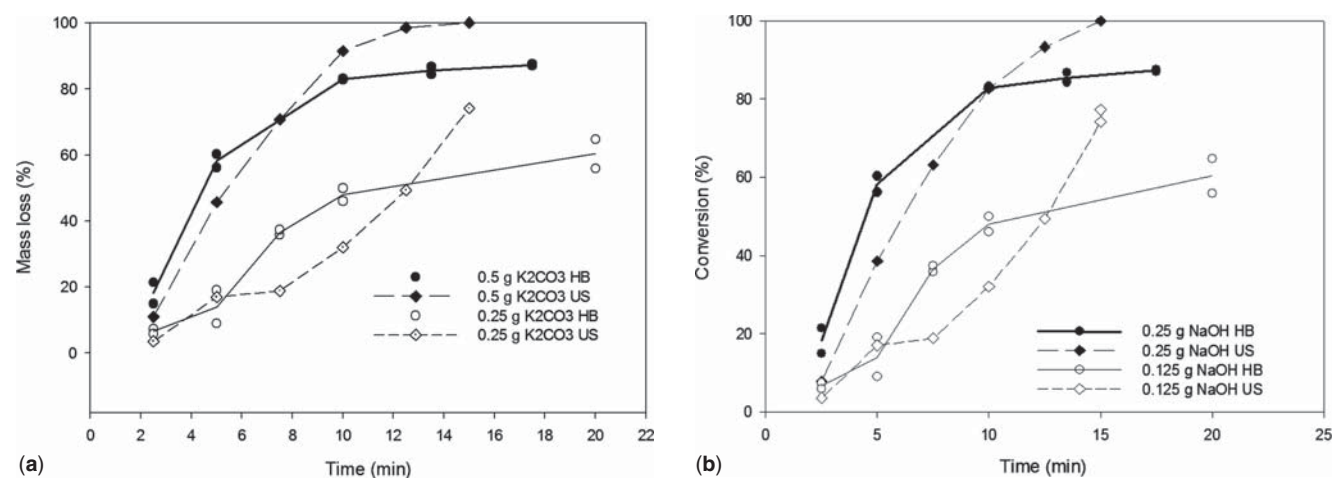


Figure 3 (a) Mass loss (%); (b) Conversion (%) in methanol using hot bath (HB) and ultrasonic (US) treatment with two masses of K₂CO₃ K, 0.5 g and 0.25 g, with 5 g of PLA in methanol.

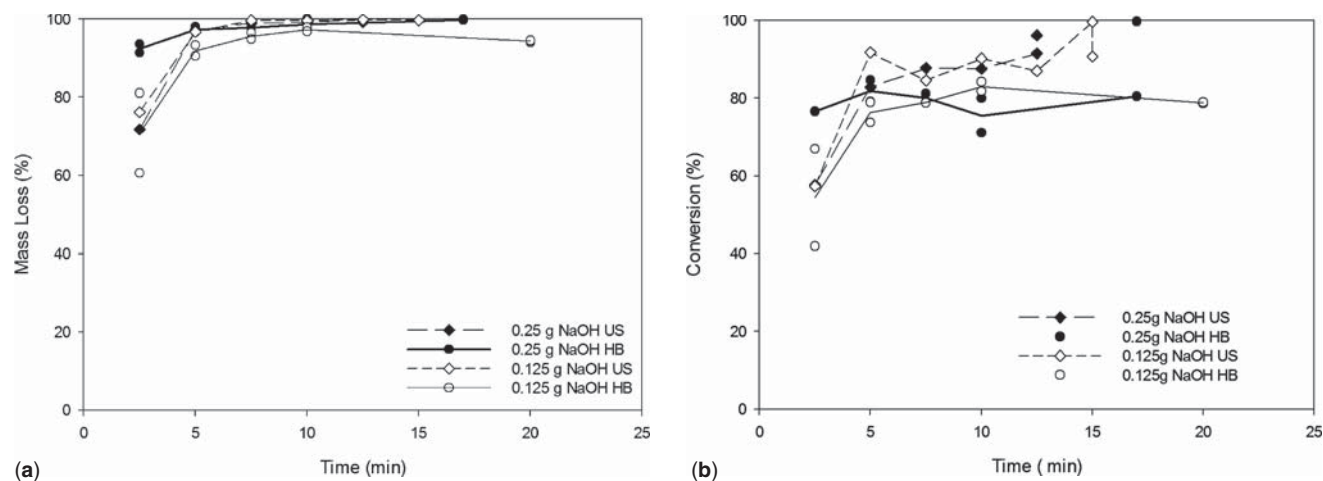


Figure 4 (a) Mass loss (%); (b) Conversion (%) in methanol with hot bath (HB) and ultrasonic (US) treatment for two masses of 0.125 and 0.25 g, respectively (5 g of PLA, NaOH catalyst).

of the other solvent/media and salts were similar to these findings.

Scanning electron microscopic images showed that the depolymerization was potentially affected by crystallinity. For example, Figure 6 shows that after 5 min of depolymerization, the surfaces of the 2 × 6 mm PLA chip face showed erosion in the direction of the axis of the bottle. Bottle flakes from this direction have a relatively high degree of oriented crystallinity, resulting from the injection molding process and from the subsequent blowing process that finalizes the bottles' shape. It is believed that the areas with maximum erosion (depolymerization) correlate to amorphous regions, while in contrast the less depolymerized areas correlate to crystalline regions. More detailed examinations showed that there was a very rough texture

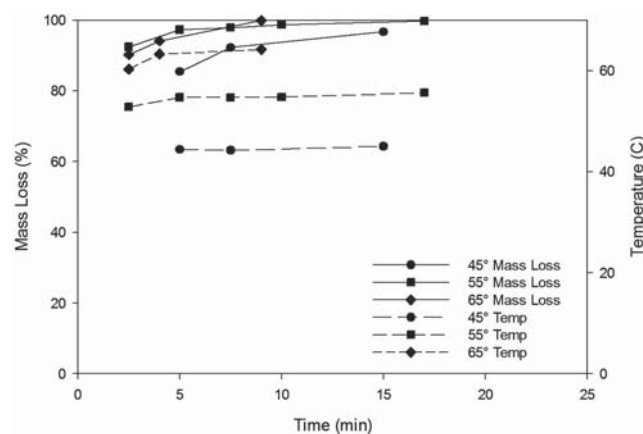


Figure 5 Effect of treatment temperature on relative mass loss as a function of treatment time for 0.5 g NaOH in methanol experiments using hot bath treatment (5 g of PLA).

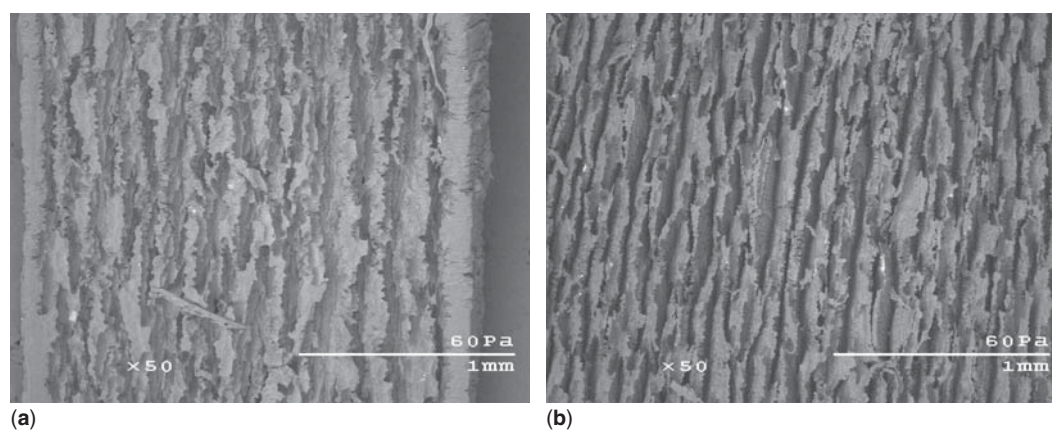


Figure 6 Treated PLA sample at 5 min with K_2CO_3 -0.5 g and methanol media (0.5 g); (a) ultrasonics and (b) hot bath.

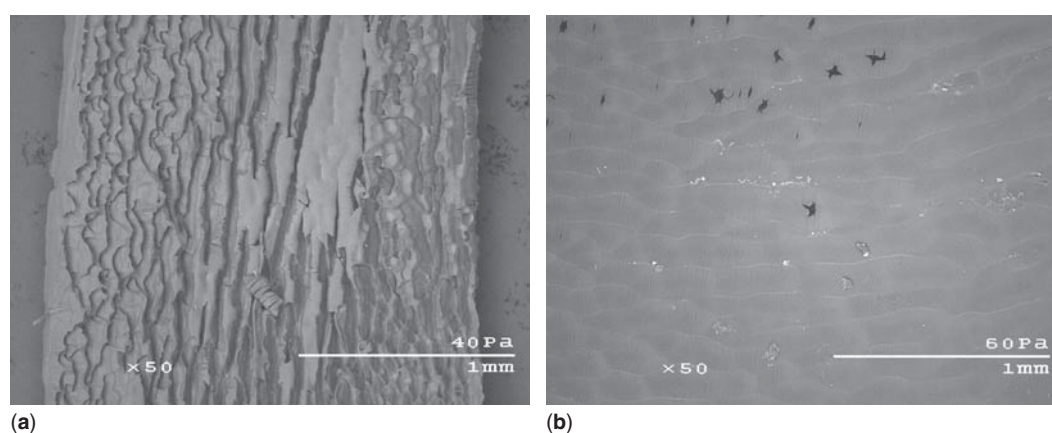


Figure 7 Treated PLA sample at 5 min with NaOH -0.25 g and methanol media; (a) ultrasonics and (b) hot bath.

on the surface, and the alignment of this texture corresponded to the stretch direction of the PLA bottle. This texture was more pronounced on the inner diameter of the bottle, where the degree of crystallinity is expected to be higher because of the slower cooling rate compared to the outer surface that is in contact with a chilled mold. This theory was further supported by studies comparing depolymerization of amorphous and crystalline samples detailed in a later section.

The PLA chips treated with NaOH -0.25g and methanol exhibited similar SEM images, as seen in Figure 7. However, at higher mass amounts of the NaOH (Figure 7b, 0.5 g), the samples are almost completely depolymerized, even showing holes through the sample. This is consistent with Figures 4 and 5 that showed mass loss exceeding 90% at 5 min of treatment.

3.2 Effect of Crystallinity

To characterize the effect of crystallinity on depolymerization, relatively crystalline and relatively amorphous samples of PLA were depolymerized under

optimum conditions using hot bath treatment. Two samples of PLA chips, each with a mass of 5 g, were prepared by heating them to 75°C for 30 min in a heated platen. The first 5 g samples were then quickly removed from the heater and rapidly cooled in dry ice and methanol. This rapid cooling reduced crystallization and resulted in samples that had a level of crystallinity of 24% as determined by DCS. The balance of the samples were then allowed to cool slowly by turning the platen heaters off in order to assure that the sample had a higher amount of crystallinity (32%). It took approximately 120 min for the platen heater (and PLA samples) to cool to room temperature. This slow cooling promoted crystallization of the samples, which were subsequently depolymerized for various lengths of time to study the depolymerization rate and the morphology of the samples during depolymerization. The actual degree of crystallinity was not measured because the intent of the experiment was to qualitatively confirm the findings of the previous work.

It was visually observed that rapidly cooled (more amorphous) samples depolymerized faster compared

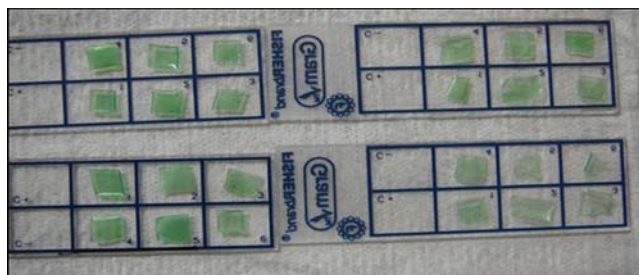


Figure 8 Photographs of PLA samples at different times of MK(1) hot bath treatment; (a) slowly cooled sample and (b) rapidly cooled sample (more depolymerization observed in lower samples).

to slowly cooled samples (see Figure 8), and the mass losses of the amorphous samples were higher than that in slowly cooled samples.

This suggests and is in agreement with the previous findings that the degree of crystallinity affected the rate of depolymerization. It is believed that in the crystalline samples there is less free volume between polymer chains, which limits the rate and depth of diffusion (penetration) of salts into the samples. In contrast, the amorphous samples had more free volume, thereby allowing the salts to penetrate into the bulk of the material. This exposed more reaction sites and caused higher rates of depolymerization.

3.3 Energy and Conversion Efficiency

Poly(lactic acid) as an alternative to petroleum for the production of plastics has a heating value of only 19 MJ/kg [18, 19]. The energy consumption for the production of PLA is 82.5 MJ/kg, of which 54 MJ/kg [9] are derived from fossil fuel. Though composting is considered an effective route, the production of new PLA will require further consumption of fossil energy (54 MJ/kg of PLA) and result in additional greenhouse gas (GHG) emissions.

The average amount of energy utilized during each ultrasonic treatment to achieve complete depolymerization ranged between 1.83 and 2.25 MJ/kg of PLA, depending on treatment parameters such as medium and salt concentration. In comparison, for the hot bath treatment and a combination of methanol as treatment medium and 0.25 g sodium hydroxide, the amount of energy required for depolymerization was calculated based on adiabatic heating. In more detail, a volume of 50 ml of the treatment medium methanol (40 g at a density of 0.79 g/cm³) corresponds to 1.25 moles of methanol. The specific heat or heat capacity (C_p) of methanol is 79 J/(mol K). The amount of energy required to raise the temperature of the methanol medium from 25°C to 55°C (depolymerization temperature) can be

calculated by Equation 3, where M is the number of moles and ΔT is the change in temperature

$$E_{(25-55^\circ\text{C})} = M \times C_p \times \Delta T \quad \text{Eq. 3}$$

From the above expression for a change in temperature ($\Delta T = 55-25^\circ\text{C} = 30 \text{ K}$), the energy required for depolymerization was determined as 0.26 MJ/kg of PLA (neglecting energy required to maintain constant temperature). Similar calculations for the high temperature, high pressure process (HTHP) with water as the medium ($C_p \text{ water} = 75.6 \text{ J}/(\text{mol K})$) and $\Delta T = 160-25^\circ\text{C}$ and assuming the same concentration of 12 g/50 ml (PLA/water), the energy consumption was 2.34 MJ/kg of PLA. Comparison of these energy requirements indicated that the newly developed hot bath process with methanol as treatment medium together with sodium hydroxide utilizes 10-fold less energy than the investigated ultrasonic treatment or the HTHP process developed by other researchers [3].

3.4 LA Recovery

Preliminary results for acid titration (HPLC) to produce salts and LA/LA-esters to fully recover the LA were obtained. In addition, distillation methods were studied to remove the solvents. The remaining chemistries were LA/LA-esters and salt. It is envisioned that future work will focus on complete recovery of the LA to a virgin form and further evaluation of the energy balance for its recovery.

4 CONCLUSIONS

This research was initially undertaken with the assumption that the use of ultrasonics would enhance and/or accelerate the depolymerization of PLA; and that ultrasonics would also decrease the energy required and/or reduce the time required to depolymerize PLA. However, this did not prove to be the case, and the effect of ultrasonics was insignificant compared to bulk erosion/depolymerization with appropriate media and salts over the range of treatment parameters studied.

The most significant finding of this work was the identification of bases (weakly basic K_2CO_3 and strong base NaOH) that depolymerized PLA within 5 to 7 min under mild conditions (60°C). This is in contrast to previously reported results that required long cycle times (30 min to 24 h [3–5]), and others that required intense conditions, including high temperatures and pressures [3–5]. Reducing the depolymerization time may allow the recovery of lactic acid from post-consumer PLA products, reducing greenhouse gas emissions (less demand to process biofeedstocks). The

research also showed that the depolymerization of PLA was accelerated by temperature and limited by the degree of crystallinity.

Other conclusions that can be drawn from this research include:

1. Water is not an effective medium/solvent for PLA depolymerization.
2. MgO, CuCO₃, CaCO₃, and ZnCO₃ are not effective salts for PLA depolymerization.
3. A mass of 0.25 g of salt, such as NaOH, in 50 ml of methanol and 5 g of PLA is sufficient to fully depolymerize PLA in 5 to 7 min.
4. Other salt, such as K₂CO₃, require higher concentrations to fully depolymerize PLA, and require depolymerization times between 10 and 15 min.
5. The combinations of K₂CO₃ or NaOH with methanol form a rapid depolymerizing chemistry for PLA.

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