PLLA Depolimerization Kinetics: A Preliminary Study

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Poly(L-lactide) (PLLA) which is produced from renewable plant resources, is recently increasingly utilized as an alternative to petroleum-based polymers in order to reduce their impact on the environments.
The monomer of PLLA is mainly produced from corn, which can also be utilized for food or to produce bioethanol or biofuels. Because of these reasons, the recycling of PLLA after its utilization, like other plastic material (PE, PP, or PET), must be carried out. For plastic material it is possible to carry out both a mechanical and chemical recycling: in the first case, the material is mechanically processed to obtain polymer pellets, while, in the second case, it is possible to obtain the monomer directly from the material depolymerization in order to reduce the consumption of renewable resources for the monomer synthesis.
One of the most important processes used to produce lactic acid (LA) from PLLA is based on hydro-depolymerization of PLLA at high temperature and under pressure.
In the present paper the hydrolytic depolymerization of pellets of PLLA in batch reactor at temperature near the melting temperature of the solid PLLA has been investigated and some preliminary experimental data are presented. Considering a residence time lesser than 120 minutes, a yield of lactic acid higher than 95% has been obtained at temperature equal to about 170-180°C, at pressure equal to water vapour pressure and with a water/PLLA ratio equal to about 20.

1. Introduction

Nowadays, attention has been paid to the so-called biodegradable polymers, made from biomass, because they can reduce environmental carbon dioxide emissions, which induces global warming, and their production does not require fossil resources, thus reducing the environmental load required to produce these plastics (Achmad et al., 2009).
Among the above-mentioned bioplastics, poly(L-lactic acid) (PLLA) is a biodegradable plastic which shows mechanical characteristics similar to those of polyethylene or polystyrene, has a higher transparency than other biodegradable plastics, and is superior in weather resistance, heat resistance and workability (Matsumura, 2008).
Even if it is commonly accepted that PLLA production and use leads to very low environmental burdens (Demirbas, 2007, Detzel & Krueger, 2006, Erwin et al., 2007), at least two critical issues must be taken under consideration:

1) The monomer of PLLA is mainly produced from corn, which is a provision and also its large fraction is used for producing ethanol fuel (Tsuji et al., 2008);

2) Polylactic acid is degraded to water and carbon dioxide with several years in the environment, or in a short period in compost facilities. Thus, there is the fear that a large amount of polylactic acid left outdoors may cause a new environmental problem (Matsumura, 2008).

Because of these reasons, the chemical recycling of PLLA to its monomer is crucial to reduce both the consumption of renewable resources for the monomer synthesis and the environmental impact related to its production and disposal. In particular, by producing lactic acid (LA) from PLLA wastes, rather than virgin material, is also achievable a considerable primary energy saving.

Several literature papers deal with the thermal PLLA depolymerization to the cyclic dimer (L-lactide) with or without the presence of catalysts (Tsuji et al., 2003, Noda and Okuyama, 1999). The presence of catalysts and the high temperatures required in the thermal depolymerization processes lead to high energy consumption and purification steps that impose large loads upon environment (Matsumura, 2008).

As alternative, in this work we propose the depolymerization of PLLA to LA by hydrolysis of PLLA in the solid state, in aqueous solutions, in absence of catalyst. The PLLA depolymerization was carried out in a batch reactor at temperature near the melting temperature of the solid PLLA. In the following, some preliminary experimental data are presented and a kinetic model is provided to their analysis.

2. Materials and Methods

The kinetic tests were performed in a batch reactor on suspensions of distilled water and solid PLLA, at concentrations of 5% by weight. In order to reach the desired temperature, the reactor was placed in an electric oven equipped with a temperature control system with an accuracy of ±1°C. The experimental runs were carried out at temperatures of 160 and 180 °C, while the pressure was kept constant and equal to about 1.5 MPa.

The fragments of PLLA, of average size of 2X3 mm (thickness 40 micron) were obtained by grinding commercial shells of PLLA (without pigments) provided directly by NatureWorks. The reaction apparatus (H=95 mm, Φ=10.5 mm) is made of stainless steel with sealed caps to withstand high pressures.

At the beginning of each run, the reactor was dried and weighted; successively it was filled with accurately weighted amounts of water and PLLA. Inside the reactor was always present a headspace which was filled with nitrogen, as inert gas. The amount of added water was calculated in such a way to reach the desired pressure value when the reactor reached the operating temperature. The oven was equipped with a motor driven shaft: the reactor was linked to the rotating shaft in order to ensure the mixing of the PLLA solution inside the reactor itself.

Each experimental run was characterized by a fixed value of reaction time (ranging from 30 to 150 minutes). This way it was possible to obtain a kinetic curve, i.e. the

amount of converted PLLA vs. time. It is worth noting that every point of the kinetic curves was obtained from a single experimental run.

Once the selected reaction time was reached, the reactor was removed from the oven and quickly cooled with fresh water. The liquid solution within the reactor was removed and centrifuged to separate any solid particles in suspension. The liquid phase was successively filtered by 25 micro pore filter in order to separate smaller solid particles eventually present in the liquid phase. The solid phase obtained from centrifugation ($\left(M_{PLLA}\right)_{centrifuge}$) and the solids deposited in the filter ($\left(M_{PLLA}\right)_{filter}$) were accurately weighed, after drying, in order to evaluate, by the difference with the mass of solid initially present in the reactor, the amount of PLLA reacted. Really also the amount of solids remained in the reactor ($\left(M_{PLLA}\right)_{precipitated}$) was evaluated by measuring the difference by weight of the reactor itself, before and after the test. The conversion of PLLA at each time was defined as :

$$X_{PLLA} = \frac{M_{PLLA}^{0} - M_{PLLA}}{M_{PLLA}^{0}} \tag{1}$$

where M_{PLLA}^{0} and M_{PLLA} stand for the mass of PLLA initially loaded inside the reactor and the mass of the non-reacted PLLA, respectively. In particular M_{PLLA} is given by:

$$M_{PLLA} = \left(M_{PLLA}\right)_{centrifuge} + \left(M_{PLLA}\right)_{filter} + \left(M_{PLLA}\right)_{precipitated} \tag{2}$$

Considering that the molecular weight of segment of PLLA and LA are 72 and 90 g/mol, respectively, it is also possible to evaluate the experimental conversion in lactic acid:

$$X_{LA} = \frac{90 \cdot M_{LA}}{72 \cdot M_{PLLA}^{0}} \tag{3}$$

where M_{LA} is the mass of lactic acid in the liquid solution.

3. Results

In Table I are reported the experimental runs carried out on PLLA depolymerization kinetics, at 160 and 180 °C and at initial concentration of PLLA equal to 5% by weight. Each experimental run was repeated for three times so the standard deviation for each operational condition was also calculated (see table I).

It is evident from Table I the influence of temperature on the depolymerization kinetics of PLLA. Indeed, we can see that after one hour the conversion of PLLA reaches about 5% at 160 °C and 90% at 180 °C.

The data seem to be in a quite good agreement with similar data reported by Tsuji et al. (2008). Indeed, by calculating the Average Absolute Deviation (AAD%) between our experimental data and those ones reported by Tsuji et al., both at 160 and 180°C for the same PLLA concentration, we obtain an AAD% equal to 2.6 and 3.2, respectively.

Table I: Experimental Runs

T (°C)	t (min)	PLLA Conversion (%)	LA Conversion (%)	Standard Deviation (%)
160	30	0.00	0.00	0.00
160	45	0.00	0.00	0.00
160	60	3.49	3.39	0.06
160	75	30.77	22.85	4.18
160	90	76.44	74,12	3.93
160	105	87.47	84.83	6.96
160	120	94.02	93.85	3.81
160	150	95.98	95.34	4.75
160	180	98.97	98.96	0.13
180	30	0.16	0.16	0.15
180	45	18.19	16.01	0.83
180	60	88.97	87.91	2.28
180	75	97.06	97.06	0.88
180	90	99.18	99.18	1.16
180	120	96.13	96.12	0.04
180	180	98.15	98.12	0.01

4. Discussion

In the modeling of the PLLA hydrolysis, a two-stage process was taken into account: the first occurring during the fast heating of the reactor from room temperature to the process temperature and the second one starting when the reactor reached the operating temperature. The first process is very fast, so kinetic analysis was carried out with an initial time (t_0=0) which coincides with the time for which the reactor reaches the required temperature.

Anyway during the heating phase, some very short chain (inside the PLLA molecules), with a free end along the chain direction, were cleaved from solid bulk with the formation of lactic acid molecules or oligopolymers; these molecules are characterized by a high solubility in aqueous phase. Therefore, it can be assumed that at t_0=0 in the reactor there is a non-zero concentration of lactic acid in the aqueous phase.

The hydrolytic depolymerization of PLLA occurs in the second stage and the kinetic modelling can be carried out assuming an autocatalytic mechanism, as also proposed by several authors (Tsuji et al., 2003 and 2008, Cha and Pitt, 1990):

$$(PLLA)_n + AL + H_2O \rightarrow 2AL + (PLLA)_{n-1} \tag{4}$$
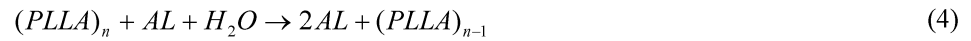
Therefore it is possible to write the depolymerization kinetic rate as

$$(-r_{PLLA}) = k \cdot c_{PLLA} \cdot c_{LA} \tag{5}$$

where

$$c_{LA} = c_{PLLA}^0 + c_{LA}^0 - c_{PLLA} \tag{6}$$

In previous equation c_{PLLA}^0 and c_{LA}^0 are the initial concentrations of PLLA and LA inside the reactor, respectively. It was impossible to measure this initial concentration of LA: therefore this parameter was assumed as an adjustable parameter to be evaluated from correlation of experimental data.

The mass balance applied to the batch reactor gives:

$$\frac{dc_{PLLA}}{dt} = -k \cdot c_{PLLA} \cdot (c_{PLLA}^0 + c_{LA}^0 - c_{PLLA}) \tag{7}$$

that, integrated with the obvious initial conditions, gives:

$$X_{PLLA} = 1 - \frac{1}{1 + a \cdot \exp(c_{PLLA}^0 \cdot k \cdot t)} \tag{8}$$

where a stands for the initial LA/PLLA concentration ratio. It is worth noting that eq. 9 has been obtained by assuming that $c_{PLLA}^0 >> c_{LA}^0$.

Figure 1 reports the comparison between the experimental and calculated kinetic curves at 160 and 180 °C, while in Table II are reported the obtained values of fitting parameters (least squares criterion) along with their asymptotic standard errors. The figure clearly show the good agreement between the experimental and calculated curves. In particular it is interesting to point out that all the experimental data are properly fitted by means of an almost constant value of the initial PLLA/LA concentration ratio (a) that is, as expected, very small (see Table II).
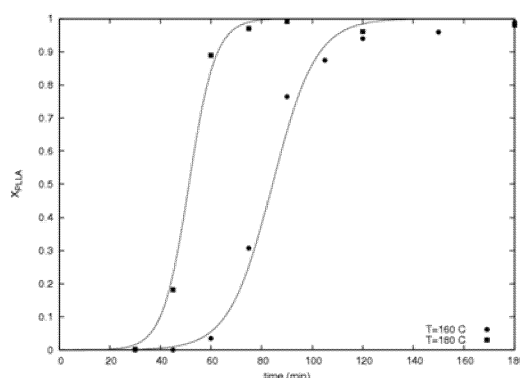

Figure 1: Experimental data (points) and theoretical PLLA depolymerization kinetic curves at 160 and 180 °C.

Table II: Fitted parameters values for all the kinetic curves reported in this work

T (°C)	a	k (l/mol s)
160	5.20e-5 +/- 6.5e-6	0.165 +/- 0.002
180	5.02e-5 +/- 7.7e-6	0.263 +/- 0.004

From Table II it is also possible to see that the temperature correctly influences the kinetic constant: the kinetic constant increases with temperature increasing. A value of activation energy equal to 1275.55 (cal/mol) and a pre-exponential factor equal to 10.95 (l/mol s) were obtained.

5. Conclusions

In this paper some experimental data about the hydrolytic depolymerization of PLLA in the solid state in water solutions and high pressure were presented. Some preliminary considerations can be derived from the obtained kinetic results:

1) More than 95% of PLLA was hydrolyzed to water-soluble LA within 120 min when hydrolyzed in the temperature range of 160-180 °C;
2) An autocatalytic reaction mechanism seems to be adequate for the fitting of experimental data obtained;
3) The kinetic constant is highly influenced by reaction temperature both for high and low initial PLLA concentration.

To conclude, the findings reported in this study can be useful to develop and optimize the depolymerization process of PLLA to obtain its monomer (LA).

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