

High Pressure Steam Hydrolysis for Chemical Recycling of Poly(L-lactic acid)

(九工大院・生命体)(学) Ahamad-Faris Mohd-Adnan
(九工大・ETC)(正) 西田治男*、(九工大院・生命体) 白井義人

Abstract

Poly(L-lactic acid) (PLLA) was treated with high pressure steam as a pre-treatment for chemical recycling. PLLA degraded smoothly with decrease in molecular weight. Using appropriate analytical models and mechanistic assumptions, the mode of hydrolysis was verified to proceed via an auto-catalytic random degradation. Exact rate constant (k_h) and activation energy (E_a) values were estimated to be 8.4×10^{-5} (100°C) to $7.2 \times 10^{-4} \text{ s}^{-1}$ (130°C) and 87.2 kJ mol⁻¹, respectively.

Introduction

Recently, biomass plastics have gained popularity as an alternative to conventional plastics. PLLA, which is produced chemically via the lactic acid fermentation from renewable resources¹, have been promoted as a 'green' alternative in the packaging industries. PLLA was originally conceived as a biodegradable plastic, degrading in the natural environment to CO₂ and H₂O. In many efforts to utilize natural resources efficiently, several recycling processes have been established to recover L-lactic acid and L,L-lactide by hydrolysis² and pyrolysis³, respectively. In this study, an effective method to hydrolyze PLLA by using high pressure steam is proposed as a pre-treatment process of the chemical recycling.

Materials and Methods

PLLA pellets (LACEA H-100J; Sn content: 40ppm; M_n 23700, M_w 56300; dimension: w3.92×d3.48×h4.52mm) were obtained from Mitsui Chemicals, Inc. and used as received.

Hydrolysis of PLLA pellets under high pressure steam was done in an autoclave (Tomy autoclave model SS-325 unobstructed capacity 55 L) for prescribed periods at 100°C (0.102MPa), 110°C (0.145MPa), 120°C (0.202MPa) and 130°C (0.276 MPa). Internal temperature of the autoclave was thermostated to within $\pm 0.5^\circ\text{C}$. After autoclaving, the PLLA samples were dried *in vacuo* at room temperature for one night and refrigerated at -30°C until following analysis.

Molecular weight (MW) of PLLA was measured on a size exclusion chromatograph (SEC) at 40°C using chloroform as an eluent. SEC traces were analyzed by universal calibration method

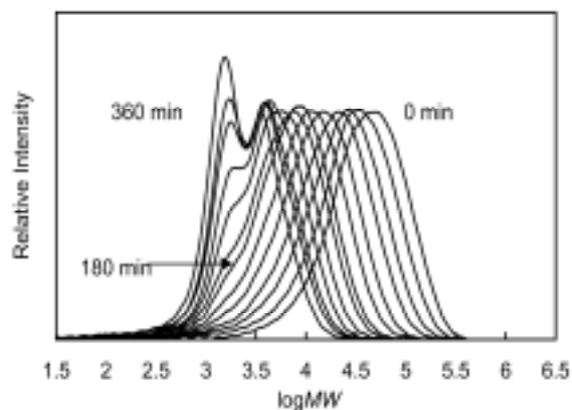


Figure 1. Changes in SEC profile of PLLA sample during the hydrolysis by high pressure steam at 110°C.

(UCM)⁴ using Mark-Houwink-Sakurada parameters for PLLA and polystyrene.

Results and Discussion

The pre-treatment of PLLA pellets under the high pressure steam resulted in the smooth hydrolysis with decrease in MW . SEC profiles gradually shifted from a uni-modal to a multi-modal shape with an appearance of a shoulder at a certain point (Figure 1). Critical point has been defined as a specific point, at which the random degradation changes from a homogeneous reaction to a heterogeneous one, exhibiting the changes in the shape in SEC profile as shown in Figure 1 and the departure of actual plots from the theoretical approximation lines as shown in Figure 2.

To determine exact rate constants (k_h) and activation energy (E_a) values for the high pressure steam hydrolysis of PLLA, relative MW values based on polystyrene standards were re-calculated into exact values MW_{UCM} by using UCM. To avoid the uncertain evaluation by M_n value alone, both values of M_n and M_w were used for the evaluation. Moreover, to determine the mode of hydrolysis, the MW_{UCM} data were applied into kinetic equations for several models.

As results, it was found that the mode of hydrolysis of PLLA under the high pressure steam was a typical autocatalytic random degradation. According to the appropriate kinetic model formulated by Nishida *et al*⁵, exact k_h and E_a values were estimated as being 8.4×10^{-5} (100°C) to $7.2 \times 10^{-4} \text{ s}^{-1}$ (130°C) and 87.2 kJ mol^{-1} , respectively.

Conclusion

In order to confirm the precise kinetics parameters: k and E_a values, PLLA hydrolysis was carried out under high-pressure steam and analyzed the MW changes by UCM without any influence of weight loss. The changes in molecular weight were successfully fitted with the simulation lines generated according to the auto-catalytic hydrolysis mechanism, resulting in the evaluation of exact k and E_a values.

References

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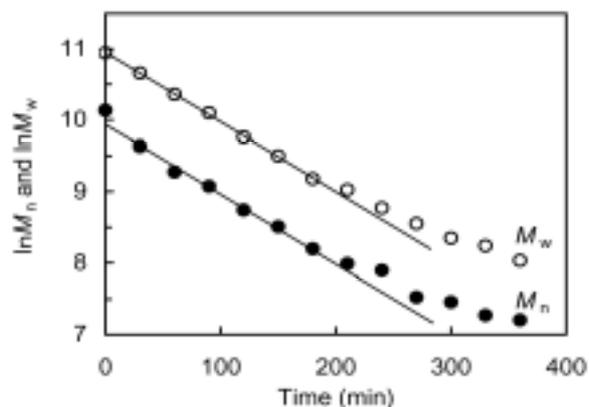


Figure 2. Plots of $\ln M_n$ and $\ln M_w$ of PLLA sample hydrolyzed at 110°C and theoretical approximations.