

# OLIGOMERIZATION OF POLY(L-LACTIC ACID) BY HIGH-PRESSURE STEAM TREATMENT FOR FEEDSTOCK RECYCLING

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**Abstract:** High-pressure steam hydrolysis of a poly(L-lactic acid) (PLLA) / poly(bisphenol A carbonate) (PC) (50:50 wt/wt) immiscible blend was investigated as a pre-treatment process before feedstock recycling of the PLLA component, resulting in the selective oligomerization of the PLLA component. After the pre-treatment by steam, the PLLA component was preferentially hydrolyzed in a manner of autocatalytic random degradation, whereas the PC component showed no change in molecular weight. This characteristic hydrolysis behavior of the blend will facilitate the crushing of moldings and subsequent feedstock recycling of PLLA.

## 1. Introduction

In recent years, great interest has been shown in polymers derived from renewable resources. Poly(L-lactic acid) (PLLA), in particular, because of its high melting point, good transparency and superior biocompatibility has been considered as the most interesting of the biomass-based materials. However, its brittleness and low glass transition temperature have limited its practical application. Therefore, various approaches including copolymerization and blending with other polymers, such as polyethylene[1], have been employed to try to improve these limitations in PLLA's mechanical and thermal properties. Especially, a blend with poly(bisphenol A carbonate) (PC)[2], which has good transparency and high impact resistance, was able to correct the defects of PLLA and applied to a notebook computer in 2005.

Feedstock recycling is an attractive strategy for plastic waste management. Monomer recovery, especially, is an ideal approach, because it enables plastics to completely regenerate. The monomer recovery from PLLA to L,L-lactide[3] and L-lactic acid[4] has been developed by pyrolysis and hydrolysis approaches, respectively, giving a reasonable yield. When considering the total process of PLLA feedstock recycling, the oligomerization of PLLA moldings is an interesting pre-treatment process. This is because, before monomer recovery,

the oligomerization facilitates the crushing of molded products into flakes [5], which are in a convenient form for transporting and separating from other kinds of plastics.

Recently, it has been reported that PLLA oligomerization can be effectively achieved using high pressure steam up to the critical point [6], at which point the homogeneous random degradation process shifts into a heterogeneous decomposition process inducing easy crushing. In the present work, to confirm the pre-treatment effect of using high pressure steam, the hydrolysis behavior of PLLA/PC blend was investigated to achieve the selective oligomerization of the PLLA component.

## 2. Experimental

### 2.1 Materials and Preparation of PLLA/PC melt blend

PLLA (LACEA H-100J;  $M_n$  76,000 and  $M_w$  142,000) and PC (Iupilon S-3000;  $M_n$  18,500 and  $M_w$  36,100) were obtained from Mitsui Chemicals, Inc. and Mitsubishi Engineering-Plastics Corp., respectively, and used as received. PLLA/PC (50/50 wt/wt) blend film was prepared by a convenient solvent casting method from a chloroform solution (10 w/v-%) and subsequent compression molding at 200 °C for 5 min under a pressure of 8.0MPa to produce a blend film (10×10 mm<sup>2</sup>) with a thickness of 100-120 μm.

### 2.2 Hydrolysis of PLLA/PC blend film under high-pressure steam

Hydrolysis of blend films under high-pressure steam was carried out in an autoclave (Tomy autoclave model SS-325). The films were treated with steam at 100 (0.102), 110 (0.145), 120 (0.202), and 130 °C (0.276 MPa) for prescribed periods. The internal temperature of the autoclave was thermostated to within ± 0.5 °C. Temperatures of both the hydrolysis start and stop were controlled at 70 °C.

### 2.3 Measurements

Differential scanning calorimetry (DSC) thermograms were measured on a Seiko Instruments Inc. EXSTAR 6200 DSC system at a constant heating rate of 10 °C·min<sup>-1</sup>. Scanning electron microscopic (SEM) images were observed on a Hitachi S-3000N WET-SEM at an accelerating voltage of 5kV. Before observation, the sample films were fractured in liquid N<sub>2</sub>, and sputtered with Pt. Size exclusion chromatograms (SEC) were measured on a TOSOH HLC-8120 GPC system equipped with refractive index (RI) and ultra violet (UV) dual detectors at 40 °C using a TOSOH TSKGel Super HM-M column and a chloroform eluent (0.6 mL·min<sup>-1</sup>).

## 3. Results and Discussion

### 3.1 Morphology of PLLA/PC blend

Thermal properties of PLLA/PC (50/50 wt/wt) blend were determined using DSC and compared with PC and PLLA homopolymers. Transition temperatures of the blend were

observed at 59.4, 105.0, 169.3, and 231.8 °C as  $T_{g,PLLA}$ ,  $T_{c,PLLA}$ ,  $T_{m,PLLA}$ ,  $T_{m,PC}$ , respectively. These transition temperatures almost agreed with the transition temperatures of the PLLA and PC homopolymers. The  $T_{g,PC}$  around 150 °C was not determined due to overlapping with  $T_{m,PLLA}$ . From the results, it is clear that PLLA and PC are immiscible and thus both phases exist independently in the blend film.

Morphological structure of the blend was a key factor influencing its hydrolytic behavior. Therefore, the morphology of the blend film was observed with SEM before and after the high pressure steam treatment at 130 °C for 2 h. Fig. 1 shows the fractured surface images of blend film. In good agreement with the DSC result, the PC/PLLA blend was segregated in two phases with particle domains of 5-20 µm in diameter being dispersed in a matrix phase. The rough surface morphology of the original particles was changed to a smooth surface after the hydrolysis. Taking into account the melting at 200 °C, PLLA would form a continuous matrix with PC being dispersed as particle domains in the matrix.

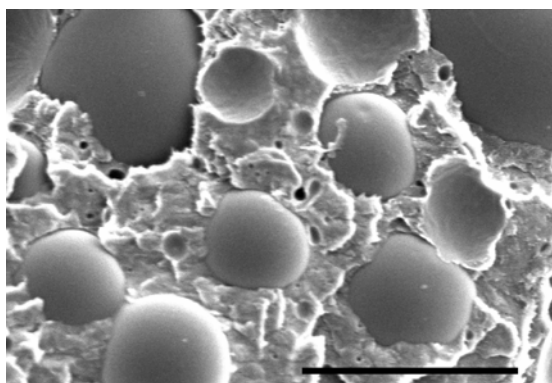


Fig.1 SEM images of fractured surfaces of the PLLA/PC blend film after high pressure steam treatment at 130 °C for 90 min. bar: 20 µm.

### 3.2 Hydrolytic behavior of the PLLA/PC blend

For evaluating the changes in molecular weight during the hydrolysis, SEC profiles were measured with the RI and UV dual detectors. The peak separation was carried out based on the contribution of each component. Each fraction of the SEC analysis was separated into two compositional sub-fractions then individual SEC profiles of the components were constructed by integration of the compositional sub-fractions.

To calculate the molecular weigh, all the response coefficients of components were taken into account for the composition calculation of each fraction. Expressions employed for calculating the weight sub-fractions of PLLA and PC components at elution point “*i*”:  $w_{i,PLLA}$  and  $w_{i,PC}$ , are as follows:

$$w_{i,PLLA} = \frac{A_{i,UV,mix} - R_{PC} \cdot A_{i,RI,mix}}{(A_{UV,PLLA} - A_{UV,PC}) - R_{PC} \cdot (A_{RI,PLLA} - A_{RI,PC})} \quad (1)$$

$$w_{i,PC} = \frac{A_{i,UV,mix} - R_{PLLA} \cdot A_{i,RI,mix}}{R_{PLLA} \cdot (A_{RI,PLLA} - A_{RI,PC}) - (A_{UV,PLLA} - A_{UV,PC})}$$

where  $A_{i,UVmix}$  and  $A_{i,RI mix}$  are the UV and RI responses of a fraction of the blend at elution point “ $i$ ”,  $A_{UV,PLLA}$ ,  $A_{RI,PLLA}$ ,  $A_{UV,PC}$ , and  $A_{RI,PC}$  are the response coefficients for PLLA and PC with the UV and RI detectors, and  $R_{PLLA}$  and  $R_{PC}$  are response ratios:  $A_{UV,PLLA}/A_{RI,PLLA}$  and  $A_{UV,PC}/A_{RI,PC}$ , respectively. All the coefficient values were determined by using the same polymer concentration ( $6 \text{ mg}\cdot\text{mL}^{-1}$ ).

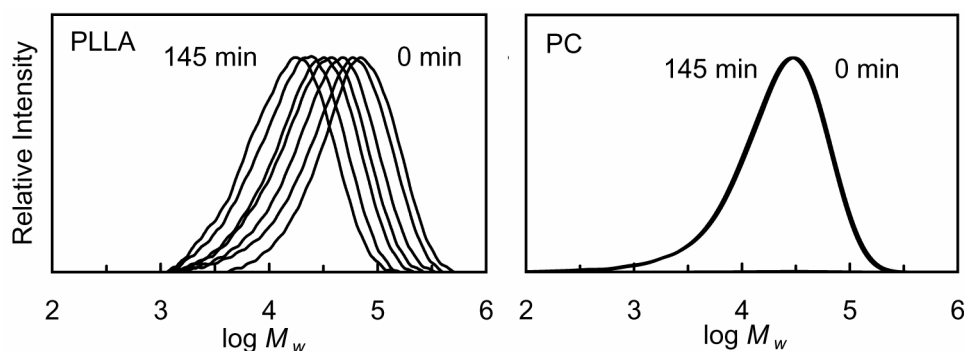


Fig. 2 Changes in SEC profiles of PLLA and PC components during high pressure steam hydrolysis at 130 °C.

Fig. 2 illustrates changes in the SEC profiles of PLLA and PC components, which were treated by steam at 130 °C. The SEC profile of the PLLA component gradually shifted into a low molecular weight range with time (Fig. 2a), whereas no shift in the profile of the PC component was observed (Fig. 2b). Similar results were obtained with time of steam treatments at 100, 110, and 120 °C. These results indicate that a selective hydrolysis of the PLLA component in the blend proceeded without any deterioration in the PC component.

To evaluate parameters: rate constant ( $k_h$ ) and activation energy ( $E_a$ ) values for the high-pressure steam hydrolysis of the PLLA component, the  $M_w$  value was employed. Previously, Mohd-Adnan et al.[6] reported that estimation using the  $M_w$  value was more reliable than when using the  $M_n$  value in the analysis of the hydrolysis process. In Fig.3, relationships between  $\ln M_w$  and hydrolysis time are plotted. A linear relationship was observed for each plot.[6] This linear relationship means that the homogeneous autocatalytic random degradation occurred during the treatment. The  $k_h$  values were calculated from slopes of the linear plots. The  $E_a$  value was estimated as being  $82.4 \text{ kJ}\cdot\text{mol}^{-1}$  using the Arrhenius plot from these  $k_h$  values. The steam hydrolysis of the PLLA homopolymer film was also examined as a reference and its  $E_a$  value was calculated as being  $82.8 \text{ kJ}\cdot\text{mol}^{-1}$  from its  $k_h$  values.

Nearly equal hydrolysis parameters:  $k_h$  and  $E_a$  values were shown for the PLLA component in the PLLA/PC blend and the PLLA homopolymer film. The PC domain had no effect on the hydrolysis of the PLLA matrix. Thus, the steam can easily diffuse in the matrix of the blend and hydrolyze the PLLA chains preferentially without any effect on the PC particle domain.

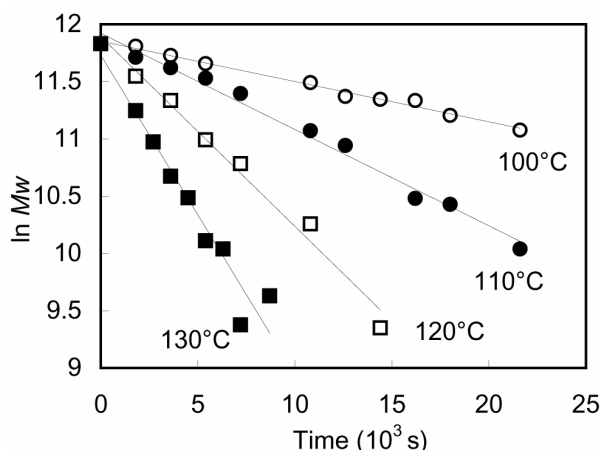


Fig. 3 Plots of  $\ln Mw$  vs. hydrolysis time for PLLA component under high pressure steam in a temperature range of 100-130 °C.

#### 4. Conclusion

The high-pressure steam treatment of PLLA/PC (50:50 wt/wt) immiscible blend induced the preferential hydrolysis of PLLA component as a matrix phase. The PLLA component was hydrolyzed in a manner of the autocatalytic random degradation into oligomers, whereas the PC component showed no change in molecular weight during the treatment. Obtained hydrolysis parameters:  $k_h$  and  $E_a$  values for the PLLA component were nearly the same as those of PLLA homopolymer film, suggesting no effect from the PC component.

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