Journal of Metals, Materials and Minerals. Vol.18 No.2 pp.83-87, 2008

Determining Biodegradability of Polylactic Acid under Different Environments

Yosita RUDEEKIT, Jaruayporn NUMNOI, Monchai TAJAN, Phasawat CHAIWUTTHINAN and Thanawadee LEEJARKPAI*

National Metal and Materials Technology Center
114 Thailand Science Park, Paholyothin Road, Klong 1, Klong Luang, Pathumthani 12120

Abstract

Received Nov. 17, 2008
Accepted Feb. 10, 2009

Determining biodegradability of polylactic acid (PLA) sheets were investigated under different environments. Under the waste water treatment conditions for 15 months, the small white spots could be visually observed on the surface of the PLA sheet. Under real conditions of the landfill, the PLA sheet changed from clear to white opaque. Moreover, the PLA sheet was deformed, became brittle, and was broken into coarse pieces and some disappearance after 15 months of the testing. Molecular weight of 17.31 kDa and 48.56 kDa were obtained for the PLA sheet under the landfill and the waste water treatment conditions, respectively. Under real composting conditions, no PLA residuals could be observed though visual inspection within 34 days. The molecular weight of the PLA sheet obtained from the composting conditions was reduced from 151.90 kDa to 4.45 kDa after 17 days. Moreover, the degree of biodegradation for PLA sheet was 86 % for 4 months under controlled compost conditions determined in the laboratory by a method based on ISO 14855-99. In conclusion PLA sheet would degrade completely under real and controlled composting conditions, whereas the degradation of the PLA sheet under natural landfill and waste water treatment would required a longer time.

Key words: Biodegradation, Polylactic acid, Composting, Landfill, Waste water treatment

Introduction

The production and the use of plastic materials increase the problem of waste disposal since they are extremely stable. The growing interest in environmental impact has directed research to the development of plastics that degrade rapidly, leading to a complete minerization. These materials offer a possible alternative to the traditional non-biodegradable polymers especially when their recycling is difficult or not economical.

Polylactic acid (PLA) is a linear aliphatic polyester, and it can be synthesized from renewable resources. It is widely studied as a sustainable biodegradable material for use product applications such as medical application, packaging materials and mulching film.

The aim of this study was to investigate the biodegradability of PLA after discarding in natural conditions, such as waste water treatment, landfill, and condition both in real and control in laboratory. The results can be used to determination of appropriate disposal environments for PLA packaging waste.

Materials and Experimental Procedures

Specimen

The PLA (Nature work®, (Cargill Dow)) sheets were prepared in a window mold 180x150x0.3 mm^3 dimensions and then placed in a compression molding machine (LAB TECH). They were using for degradation test under real environments.

Visual Inspection

Every time the PLA sheets were visually inspected for colour and shape after they were removed from the waste water treatment landfill, and composting plant. A Nikon D50 6.1 MegaPixel digital camera was used to take pictures.

*E-Mail: thanawl@mtec.or.th

Molecular Weight Analysis

Molecular weight analysis was conducted using a standard gel permeation chromatography (GPC) technique calibrated with polystyrene standard.

Biodegradation Testing

Real Environments

Waste water treatment conditions: The degradation of the PLA sheets were performed in waste water treatment of Supanburi Province, Thailand from April 2006 – July 2007 or 15 months. The sample was covered with meshes on metal frame and fixed in the waste water at a depth of about 1.5 meter.

Landfill Conditions: The landfill test was an outdoor experiment, which provides a realistic environment with seasonal changes. The test was carried out in landfill of Supanburi Province, Thailand from April 2006 – July 2007 or 15 months. The PLA sheets were buried at 1 meter depth from the landfill surface.

Composting plant conditions: A compost pile made of vegetables waste (32 wt%), wood chips (17 wt%), coconut shells (17 wt%), fruit peels (17 wt%) and old compost (17 wt%) were used for assessing the biodegradability of the PLA sheets. The PLA sheets were placed inside the compost pile, at a depth about of 1 meter. The temperature, moisture content, and pH of pile were range of 45-70°C, 40-55% and 4-8, respectively. The composting process was continued until fully stabilized compost is obtained (approximately 3 months).

The PLA sheets were taken out periodically from the real environment for visually inspected, and pictures were taken for visual evaluation of its biodegradation trend. The samples were washed in distilled water and dried at 35°C in a vacuum oven for 24 h. It was then allowed to equilibrate in a desiccator at least 24 h and kept in dark before testing. The testing of each sample was analyzed before and after degradation.

Controlled Composting Conditions in Laboratory

Biodegradation test under controlled compost conditions using the 2 liters reactor was conducted according to ISO 14855-99.[2] The compost had the following characteristics: total solids 52.5 wt%; volatile solids 28.24 wt%; pH 8.5. Its water content was raised to 50 wt% by adding water. Cellulose powder (Sigma, particle size 20 μm) was use as a positive control. The organic carbon content of the cellulose was 42.35% determined by elemental analysis. The PLA sheet was cut into pieces of 2 x 2 cm^2. The organic carbon content of the PLA was 46.40%, which was determined by elemental analysis. A mixture of mature compost (360 g, dry weight) and the sample (60 g, dry weight) were introduced and incubated at 58 + 2°C. The current system is comprised of six reactors; two blank, two positive controls (Cellulose), and two samples (The PLA sheet) placed in a temperature-controlled system. The air flow rate was controlled at 40 ml/min. CO_2 produced from the reactor was absorbed by 0.1 N barium hydroxide, and the amount was determined by titrating the solution with 0.1 N HCl.

Results and Discussion

The PLA sheets were subject in natural conditions, such as waste water treatment, landfill, and condition both in real and control in laboratory for variation of time.

Real Environments

Waste water treatment conditions: Figure 1 shows that the PLA sheets were slowly degraded after 1 month and the small white spots on the surface of the PLA sheet could be visually observed. There were some areas where the sheet unchanged. After that, the small white spots were found more distributed across the surface of the PLA sheet for 15 months. Molecular weight of the PLA sheet was reduced slowly. The molecular weight variation of the PLA sheet for a period of 15 months can be seen in Figure 2. The PLA sheet degrades slowly probably because of the slow rate of hydrolysis at 25-32°C which was waste water treatment conditions. It was suggested that PLA does not biodegrade readily at temperatures less than 60°C due to its ‘glass transition’ temperature being close to 60°C.[6]

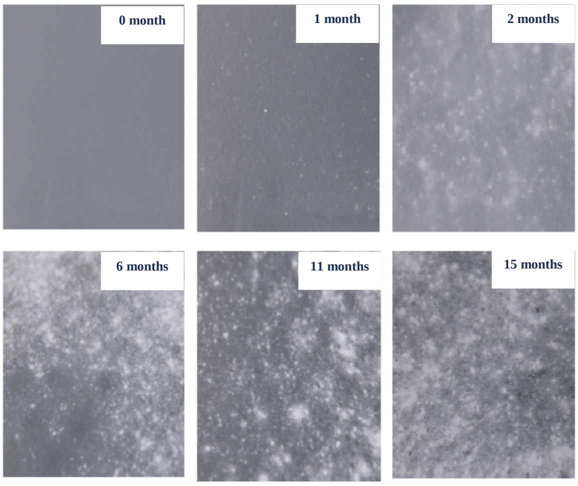
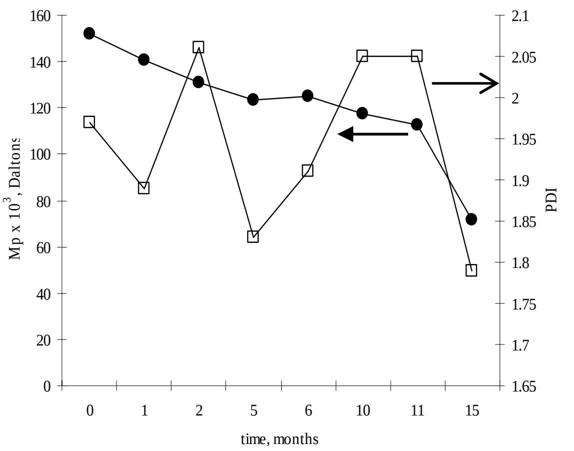


Figure 1. Degradation of the PLA sheets under real waste water treatment conditions.



Mp = peak molecular weight

Figure 2. The Variation of the molecular weight and polydispersity index (PDI) as a function of time for the PLA sheets under real waste water treatment condition.

Landfill Conditions: The PLA sheets were visually inspected. After 1 month, the PLA sheet was deformed and changed from clear to white opaque. After that, the PLA sheet became brittle and started breaking apart within 6 months. It was more brittle and was broken after testing for 11 months. After 15 months, the PLA sheet was broken into coarse pieces and some disappearance (Figure 3). Major fragmentation, which produces decomposition of the polymer chain into shorter oligomer chain was observed for 6 months onwards (Figure 4).

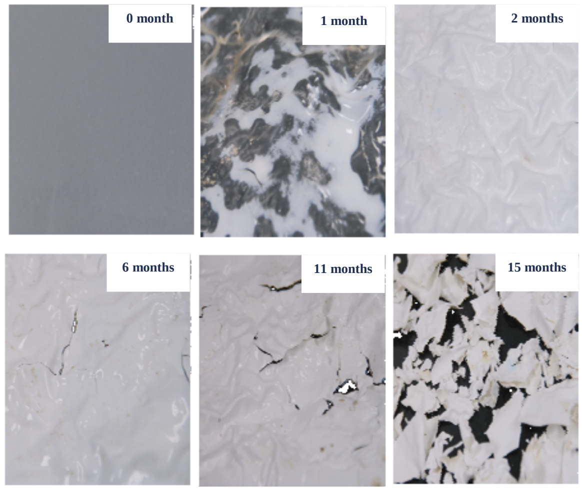


Figure 3. Degradation of the PLA sheets under real the landfill conditions.

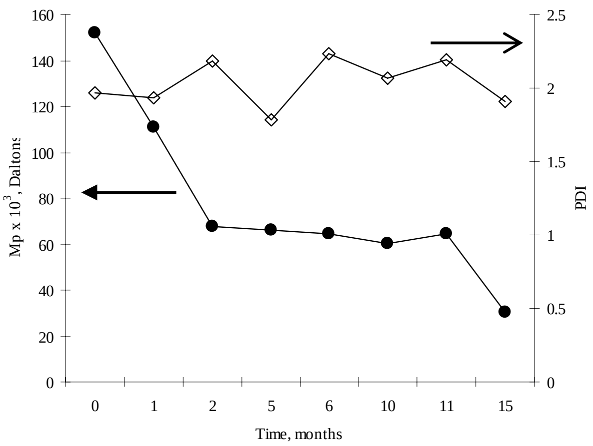


Figure 4. The Variation of the molecular weight and polydispersity index (PDI) as a function of time for the PLA sheets under real the landfill conditions.

Composting plant conditions: After 5 days at the testing, the changes in color and shape of the PLA sheet were observed. The shape changes could be attributed to distortion due to higher temperatures in the compost pile relative to the glass transition temperature of the PLA sheet (T_g = 59.2°C). In general, high temperature and humidity (50-60°C and RH > 60%) will cause PLA to degrade rapidly.[3] The PLA sheet became brittle and started breaking apart after testing for 8 days. Embrittlement of the PLA sheet occurs with reduction of molecular weight to around 23.27 kDa and 3.51 kDa (Figure. 6). The PLA sheet was broken into coarse pieces, and became more brittle and some disappearance of the PLA sheet was observed after 11 days and 14 days, respectively. Only few pieces of the PLA were observed after 17 days. After that, no the PLA residuals could be located though visual inspection for 34 days (Figure 5). Moreover, molecular weight of the PLA sheet was reduced for 5 days onwards. Random chain scission of the ester groups leads to a reduction in molecular weights and it was reported in Table 3. In summary, the moisture and heat in the compost pile attacks the PLA sheet chains and splits them apart, creating smaller polymer fragments, and finally, lactic acid. It was suggested that microorganisms found in active compost piles consume the smaller polymer fragments and lactic acid as energy source.[4] PLA degradability is driven by the hydrolysis and cleavage of the ester linkages in the polymer backbone (scheme 1).

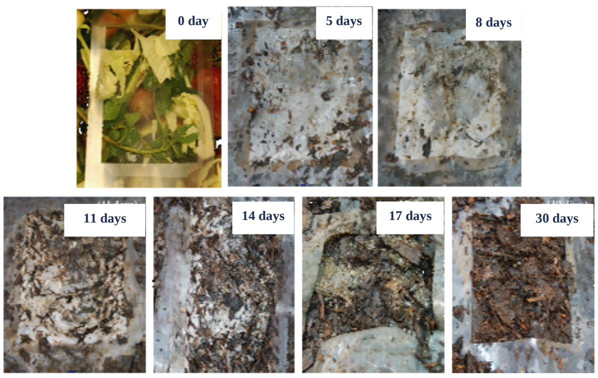


Figure 5. Degradation of the PLA sheets under real composting plant conditions.

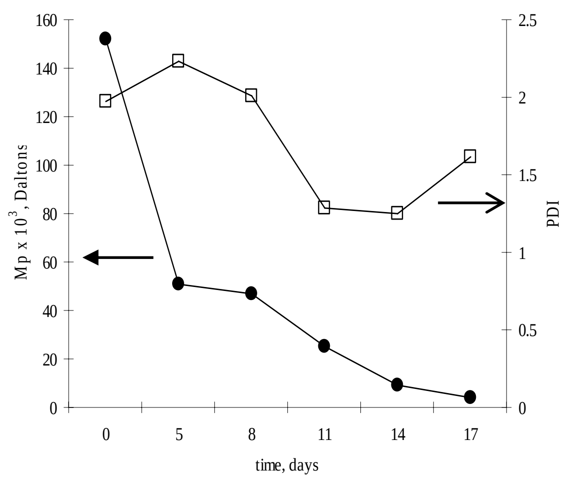
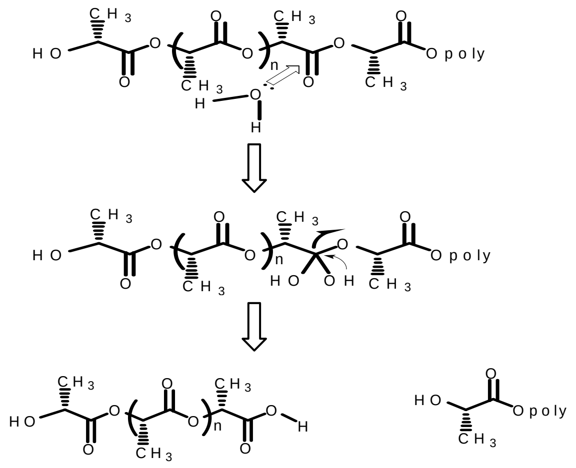


Figure 6. The Variation of the molecular weight and polydispersity index (PDI) as a function of time for the PLA sheets under real composting plant conditions.



Scheme 1 PLA hydrolysis and molecular weight loss

Controlled Composting Conditions in Laboratory

The biodegradation is calculated by using Eq. (1) according to ISO 14855-99, where $\Sigma(CO_2)_T$ is the amount of CO_2 evolved from the test material between the start of the test and time *t*, and $\Sigma(CO_2)_B$ is the amount of CO_2 evolved from the blank test reactor between the start of the test and time *t*, $ThCO_2$ is the theoretical amount of CO_2 evolved from the test materials assuming that all the carbon of the test material is transformed into CO_2.

$$\text{Biodegradation\%} = \frac{\left[\Sigma(CO_2)_T - \Sigma(CO_2)_B\right]}{ThCO_2} X100 \qquad (1)$$

This examination was valid because the biodegradability degree of the cellulose powder was over 70% at 45 days (ISO 14855-99). Cellulose, the standard material for comparison, was degraded by 87% (standard deviation (SD) + 2.5) compared to the PLA sheet which was degraded by 86% (SD + 7.4) after 120 days. Figure 7 shows that the biodegradation level in percent was determined from a degradation curve. By using the PLA, it was possible to distinguish a lag phase (0 to 14 days). The PLA undergoes a hydrolytic degradation process, causing a decrease of the polymer molecular weight. The portion of the polymer chains was broken down into small fraction (or oligomers) with low molecular weight in a biodegradation phase (14 to 96 days). The low molecular weight oligomers are consumed by microorganisms to evolve carbon dioxide.[3] In a plateau phase (96 days to the end of the test at 120 days), the biodegradation of PLA was ended.

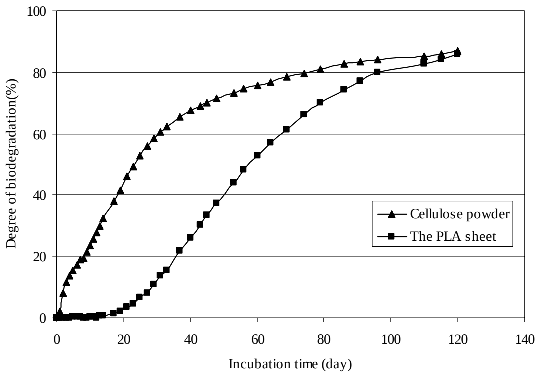


Figure 7. Biodegradation of the PLA sheet and cellulose powder under controlled composting condition by a method based on ISO 14855-99.

Conclusions

PLA biodegradation tests were carried out in waste water, landfill and real and controlled composting conditions. Variation in the degradation time frame can be attributed to the environment conditions. The degradation of the PLA sheet under natural landfill and waste water treatment would required a longer time than the composting conditions. Eventhough, the assessment of the biodegradability under real-life conditions can be used to study the behavior of the polymer. However, the quantitative measuring of polymer can be provided by testing in the controlled composting conditions in the laboratory.

Acknowledgment

This work was supported by the National Metal and Materials Technology Center (MTEC).

Reference

1. Gaurav, K., Rafael, A., Sher, P.S. and Ramani, N. 2007. The method biodegradability of polylactide bottles in real and simulated composting conditions. *J. Polym. Testing.* **26** :1049-1061.

2. International Standard ISO 14855, 1999. *Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions – Method by analysis of evolved carbon dioxide*. Geneva, Switzerland.

3. Kai-Lai, G.H., Pometto, A.L., III, Hinz, P.N. 1999. Efects of temperature and relative humidity on polylactide acid plastic degradation. *J. Environ. Polym. Degrad.* **7(2)** : 83-92.

4. The Sustainability of NatureWorksTM Polylactide Polymer and IngeoTM Polyactide Fibera: an Update of the Future. Initiated by the *1st International Conference on Bio-based Polymer (ICBR 2003), November 12-14 2003*. Saitama, Japan.

5. Li, S.M., Garreau, H., Vert, M., Structure-property relationships in the case of degradation of massive 1: poly (DL-lactic acid). *J. Mater. Sci.: Mater Med.* **1** : 123-130.

6. Environment Australia: Biodegradable plastics-development and environmental impact. October, 2002. Prepared in association with ExcelPlas Australia.