Degradation of Poly(lactic acid) under Simulated Landfill Conditions

***Chomnutcha Boonmee* [1*], *Charnwit Kositanont* [2] and *Thanawadee Leejarkpai*[3]**

[1] *Inter-department of Environmental Science, Graduate School, Chulalongkorn University, Bangkok 10330, Thailand*
[2]*Department of Microbiology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand*
[3]*National Metal and Materials Technology Center, Pathumthani 12120, Thailand*

Abstract

In this study, the physical and chemical properties change of poly(lactic acid) after burying in the mixture of soil and sludge under thermophilic (61 °C) oxygen limited conditions were investigated using various analytical techniques. The environmental factors under these setting conditions and microbial activities accelerated the degradation process of PLA. Under tested conditions, PLA loss their weight about 90% at the burying time of 90 days. During the degradation process, PLA samples were continuously broken to small fragile fragments and showed the size less than 1 mm at the end of degradation test. Change of the surface morphology change was revealed by scanning electron microscopy (SEM). Many pores, cracks and irregular roughness were presented on the PLA surface. Thermal decomposition was decreased from 387.8 to 289.2 °C. The percentage of carbon content in molecular structure decreased from 49.46% to 45.42%. In addition, the Fourier transformed infrared spectroscopy (FTIR) revealed the change of ester bonds. This study can be used for developing PLA waste management process.

Keywords: Poly(lactic acid)/ PLA/ Degradation/ Physical Properties

Received: 17 June 2016 Accepted:1 August 2016
DOI:

1. Introduction

The worldwide plastic consumption has been increased continuously according to the population and the economic growth (Biron, 2014). Plastic wastes are the large portion (16%) of municipal solid waste that regarded as non-degradable materials (Muenmee et al., 2015). Therefore, they are accumulated and caused environmental problems. Biodegradable plastics are expected to be the solution for the problems. Anyhow, at high volume of biodegradable plastics waste generated, the proper means for waste management are needed. Therefore, the understanding of their degradation behavior is necessary. Sanitary landfill is widely used as a common waste disposal method in many countries including Thailand. However, there is limited information on the biodegradable plastic degradation under the landfill conditions. The poly (lactic acid) or PLA is promoted as the environmental friendly material. Because of its property as a biodegradable plastics, PLA is designed to be used in applications such as medical devices, agricultural tools as well as packaging materials (Avérous, 2008; Gupta and Kumar, 2007; Sin et al., 2013). The good degradation rates of PLA was found at/or above glass transition temperature (Tg ~55-60°C) (Itävaara et al., 2002; Yagi et al., 2013). In our previous study, the optimal conditions of PLA degradation under simulated landfill conditions were 61 °C under oxygen limited conditions (unpublished data). In this study, the degradation behavior of PLA under these conditions was examined within 90 days of burying test.

2. Methodology

2.1 Poly(lactic acid) sheet casting

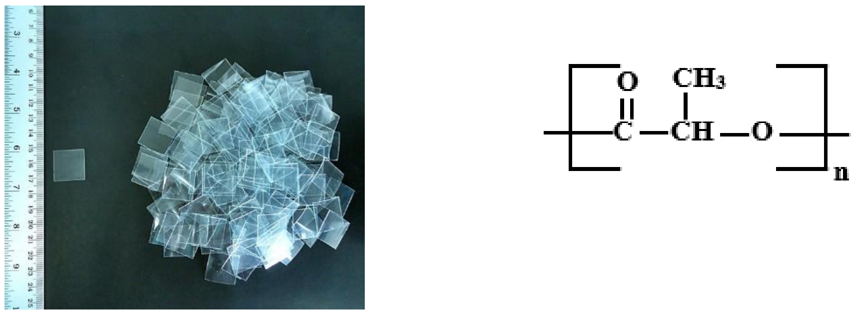
The poly(lactic acid) (PLA) that used in this study was obtained from National Metal and Materials Technology Center, Thailand (MTEC). PLA was molded by the cast sheet extrusion machine (HAAKELR 8906-02F). The average thickness of the sample was 0.5 mm. Before using in the experiments, the sheet of PLA was cut into square shape (2×2 cm2) as demonstrated in Fig. 1A. The plastic shape and size are set to follow the International standard ISO 15985, 2004 (Plastics-Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions). The chemical structure of PLA was showed in Fig. 1B.

2.2 Medium preparation

The mixture of land filling soil and sludge was used as medium. Soil was obtained from Suphanburi province municipal solid waste disposal landfill site. Sludge was received from the anaerobic wastewater treatment plant of fruit juice factory, Malee Sampran Public Company Limited, Nakhon Pathom province, Thailand. Both materials were collected and preserved at 4 °C until experimental used.

*Corresponding author:
E-mail: chomnutcha.b@gmail.com

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)



(A) (B)

Figure 1: (A) PLA sheet. (B) The chemical structures of PLA.

2.3 Experimental set-up

In this experiment, landfill soil and anaerobic sludge were mixed at the ratio of 50:50 (W/W) and used as the medium. 330 g of medium was weighted and placed in a 660 ml glass bottle. PLA samples were placed in a plastic net bag at 1.5% weight by weight of the medium then, bury in the medium. To achieve oxygen limited conditions, the glass bottles were capped with a rubber bung to prevent air transferring in the glass bottles. The tested bottles were incubated at 61 °C in dark conditions for 90 days. The experiment was conducted in triplicate.

2.4 Weight loss determination

For weight loss determination, the remaining of PLA samples was recovered from the tested bottles at 15, 30, 45, 60, 75 and 90 days of burying test. The PLA samples were rinsed with sterile water to washout the soil and sludge particles. PLA samples were kept in a desiccator at room temperature and weighted until the weight was constant. The percentage of PLA weight loss was calculated by following the equation (1).

$$Weight\ loss\ (\%) = \left[\frac{(W_i - W_f)}{W_i}\right] x\ 100 \qquad (1)$$

Where W_i represented the initial dry weight of plastic material (g) and W_f represented the dry weight of the recovery fragment of plastic material after the degradation (g). The percentage of weight loss was taken from the average of three samples.

2.5 pH analysis

The pH of medium samples was monitored by using pH meter (Consort, C862, Belgium). Ten g of soil was suspended in 50 mL deionized water. The solution was stirred during measurement.

2.6 Surface change and particle size analysis

The surface PLA samples before and after burying test were investigated by visual observations and by using Scanning Electron Microscopy (SEM) (model JSM-5410LVJEOL, Japan) at 2000x. For particle size analysis, the fragmented residuals of PLA samples were divided into three fraction sizes including greater than 2 mm, 2-1 mm, and less than 1 mm by using sieving method. Each size of PLA samples was separately collected and weighted for determining the percentage of weight fraction.

2.7 Thermal gravimetric analysis (TGA)

The thermal property of PLA samples before and after incubation were studied by TGA analysis, using Thermal Gravimetric Analyzer (NETZSCH thermos gravimetric balance, model TG 209F3, NETZSCH, Germany). The samples decomposition temperature (Td) in the range of 28 °C to 600 °C were determined under nitrogen atmosphere using 8-11 mg PLA**.**

2.8 Elemental analysis

The C, H, O contents of PLA samples before and after degradation were determined with an Elemental Analyzer (PerkinElmer model PE2400 Series II, PerkinElmer, USA**).**

2.9 Chemical characteristic changes

The chemical characteristic changes of the PLA samples were studied by using Fourier Transform Infrared Spectrometer (Spectrum One, PerkinElmer, USA). The IR wave number frequency range was 650 cm-1 to 4000 cm-1.

3. Results and Discussion

3.1Weight loss of PLA under tested conditions

The PLA degradation during 90 days of tested conditions is showed in Fig. 2. The result indicated that the weight of PLA samples was decreased when increased burying time. It was found that weight loss was approximately 90% at 90 days. The result was in accordance with the study of Yagi et al (2009) and Arrieta et al. (2014) reported the rapid disintegration of PLA at 90% of weight loss under thermophilic conditions.

Generally, PLA was degraded via hydrolytic and microorganism degradation process. The hydrolytic process depend on the temperature and humidity level (Lunt, 1997;

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

Mathew et al., 2005). In this case, high temperature conditions enhanced the break down of polymeric chain. Mixing the sludge in burial medium was not only increase in microorganism number but also the humidity in the system. The water absorption of PLA has been reported to accelerate the hydrolytic degradation, disintegration, and cleavage the ester linkages of polymeric chain resulting in weight loss of PLA (Lunt, 1997; Copinet et al., 2004; Mathew et al., 2005 ; Wang et al., 2008).

3.2 pH change

During the burying test, the pH of media was measured (Fig. 3). The pH of media was decreased from 7.3 ± 0.1 to 5.0 ± 0.2 within 90 days. The evidence of pH decreasing was also reported by Dong et al., (2013) who suggested that the carboxyl group (−COOH) and hydroxyl group (−OH) that occurred after PLA hydrolytic degradation had the effect on decreasing the pH of media**.**

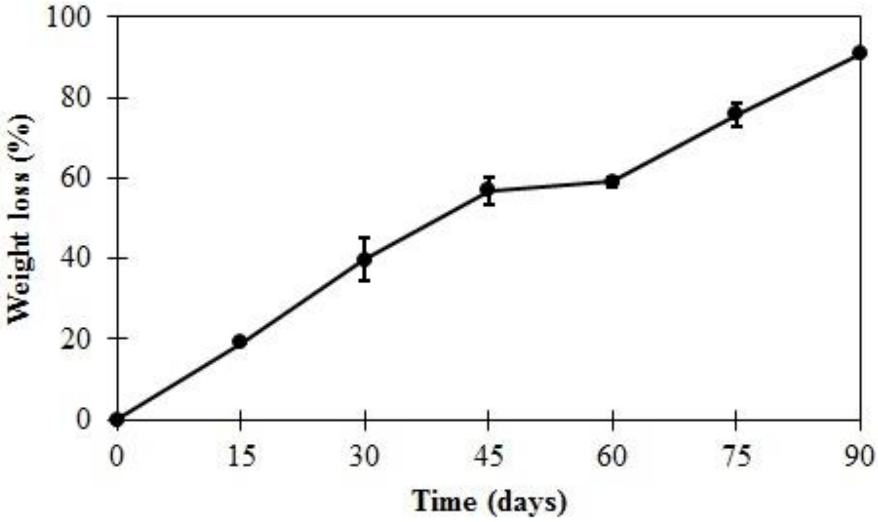


Figure 2: Weight loss (%) determination of PLA during 90 days of burying test.

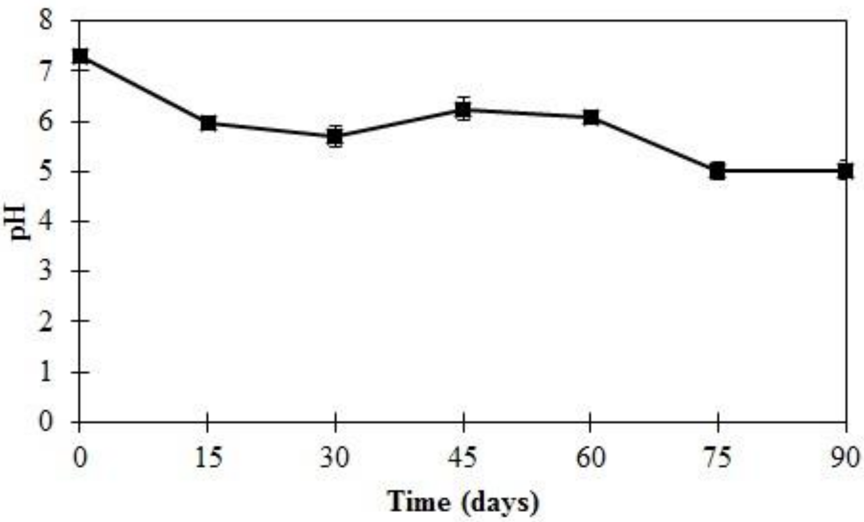


Figure 3: Change of pH in burial medium during PLA degradation test.

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

3.3 Changes in physical appearance and size of PLA after burying test

The degradation of PLA was confirmed by visual physical appearance observation and size measurement as a function of time. The sample size before and after the burying test were showed in Fig. 4. The color of PLA in the image before and after degradation process was changed from the clear color to opaque white. In this study, the disintegration/fragmentation was started after the day 15th and continuously disintegrated into small fragile size until 90 days. In the Fig. 5, from 15 to 30 days, the separation of PLA fragments started breaking into size greater than 2 mm and other smaller fractions. During 45 to 90 days, the number of smaller fraction was increased by the time of burying. At the end of burying test, the fraction greater than 2 mm was not founded and the fraction of less than 1 mm was the largest percentage. The increasing of smallest fraction (less than 1 mm) indicated the continuous degradation process of the test system.

The color change after the burying test related to the absorption of water from medium to the PLA matrix during the stage of hydrolysis (Arrieta et al., 2014). The similar result was reported by Ghorpade et al. (2001)

Lunt (1997) summarized the hydrolytic degradation of PLA as a function of time. At thermophilic temperature around 60 °C, the onset of disintegration started at 8.5 days. This temperature was close to the glass transition temperature (Tg) of PLA resulting in increasing the speed of the PLA degradation/disintegration. The slower disintegrations were found at the incubation temperature below its Tg (Rudnik and Briassoulis, 2011, Weng et al., 2013).

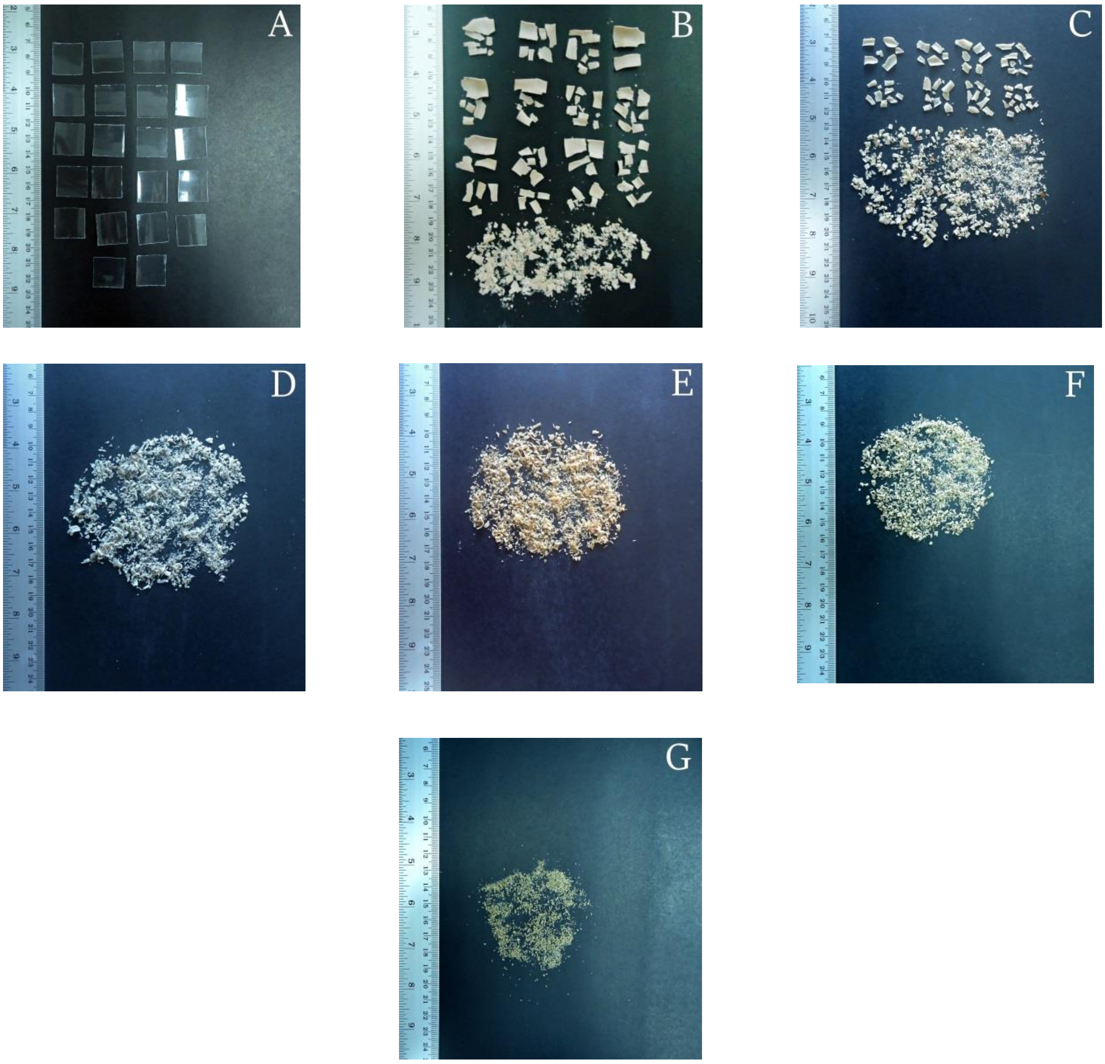


Figure 4: Appearance of PLA (A) before burying test; (B) after 15; (C) 30; (D) 45; (E) 60; (F) 75; and(G) 90 days of burying test at 61 °C

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

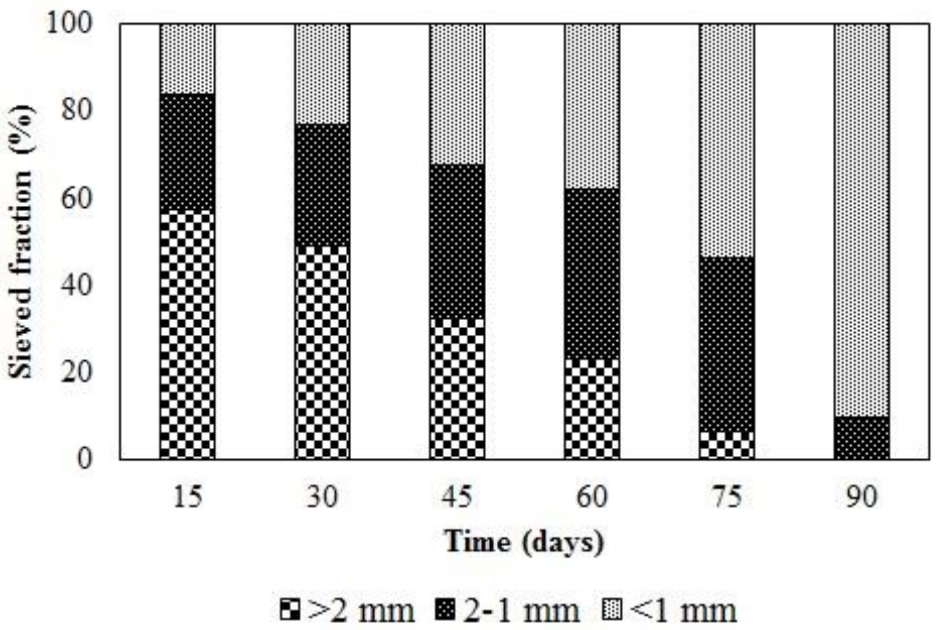


Figure 5: Particle size fractions of PLA after burying test.

3.4 Change of surface morphology

The change of surface morphology during the degradation process was examined by using scanning electron microscopy (SEM). The appearance of PLA surface after 30, 60 and 90 days of degradation were revealed at 2000x magnification as demonstrated in Fig. 6. Before the burying test, the PLA sample had smooth and clear surface (Fig. 6A). After 30 days, the roughness and small pores were appeared on the PLA surface as showed in Fig 6B. The drastic change on PLA surface was found after 60 days of degradation process showing big cracks and small pores as present in Fig. 6C. At the end of the burying test (90 days) PLA surface became totally roughed with many micropores (Fig. 6D).

Under tested conditions, PLA not only reduced in small size (Fig. 5.) but also changed on the surface morphology (Fig. 6.) However, the disintegration of PLA was found after 15 days while the crack on surface was obviously observed after 60 days of burying test. These evidences could be indicate that the degradation profile of PLA was started with the disintegration/ fragmentation and followed by the degradation on the surface.

3.5 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) provided information on the structure of the PLA samples by the mass loss steps. The result in Fig. 7 demonstrated the curves of PLA samples before and after burying test at 30, 60 and 90 days. At initial time of study, the maximum temperature for the decomposition was 387.8 °C, but after 90 days of burying test, the thermal stability of PLA is decreased to 289.2 °C. The decreasing of thermal stability of PLA during degradation time could be originate from the degradation of the long chain polymer to short chain and reduced molecular weight of PLA (Al-Itry et al., 2012).

3.6 Element content before and after degradation

The results of element analysis before and after degradation were summarized in Table 1. The carbon content in samples was continuously decreased while oxygen content in samples was increased due to the degradation process. The sample before degradation showed 49.46% of carbon content. After degradation at 30 60 and 90 days, the percentages of carbon content were decreased to 46.33, 46.35 and 45.42%, respectively. The similar tendency in decreasing in carbon content after degradation was reported by Weng et al. (2013).

3.7 Fourier Transform Infrared (FTIR) Examination

The changes of PLA functional groups before and after degradation were shown in Fig. 8. The peaks presented at wave number 2800-3000 cm-1 which associated with the C–H groups. The distinctive peak at 1722-1759 cm-1 indicated the C=O group of active ester bond for hydrolysis (Ndazi and Karlsson, 2011). Peaks located around 1300-1500 cm-1 related to the vibration of C-H in CH3 groups stretching vibrations. The intensive of peaks according to 1050-1250 cm-1 due to the C-O stretching vibration (Al-Itry et al., 2012; Pamula et al., 2001). The FTIR is useful for characterize the PLA base material, this result indicated that there were some peak around 1602 -1635 cm-1

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

increased after 30 days and accumulated until the end of burying test. This peak associated with the formation of carboxylate ions. Arrieta et al. (2014) found this peak after PLA degradation and summarized that the carboxylate ion was resulted from the degradation of lactic acid by microorganisms and leaved the carboxylate ion at the end of the chain.

Moreover, in this study, the shape of peaks according to C-O was slightly changed which indicated that the degradation of PLA could be occurred at this point. Our results were complied with the study of Weng et al. (2013)

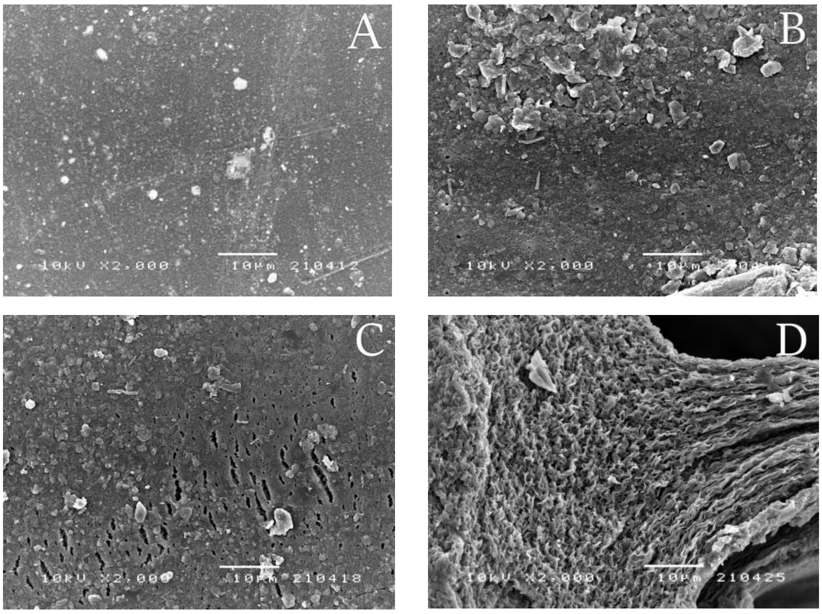


Figure 6: SEM micrographs (2,000x) of PLA (A) surface before burying test; (B) after 30; (C) 60; (D) after 90 days of burying test.

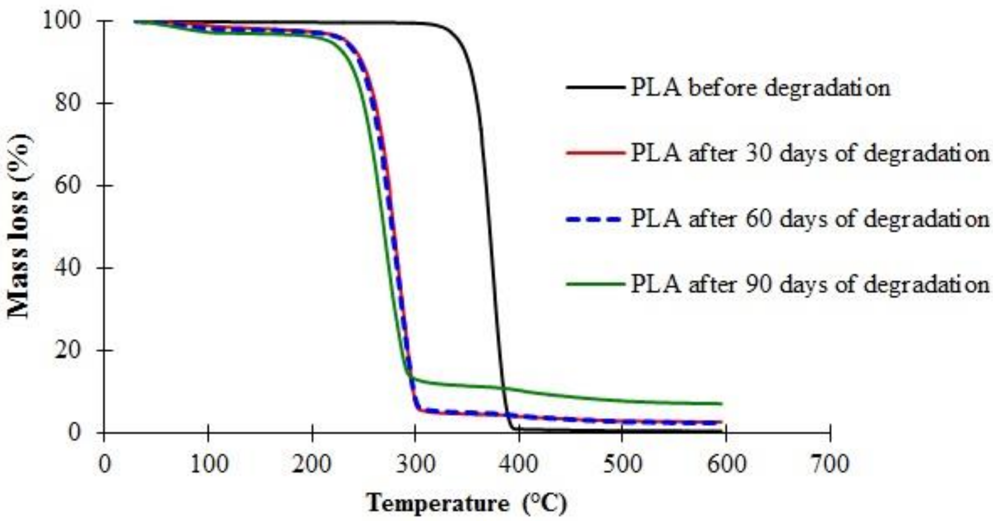


Figure 7: TGA curves of PLA

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

Table 1: Elements content of %C, %H and %O of PLA before and after degradation

Sampling date	%C	%H	%O
Original PLA	49.46	5.54	45.00
30 days	46.33	5.54	48.13
60 days	46.35	5.54	48.11
90 days	45.42	5.44	49.04

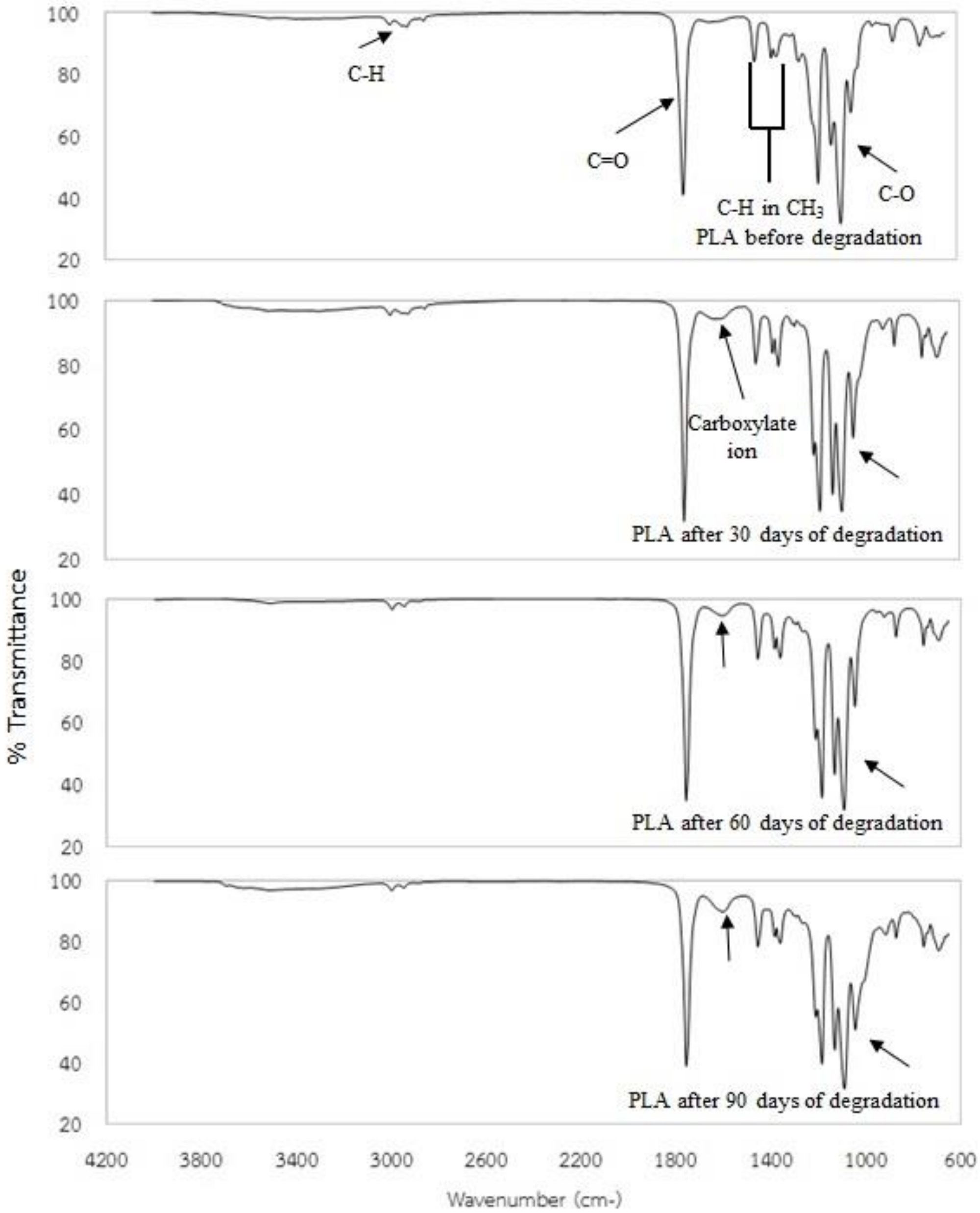


Figure 8 : FTIR spectra for PLA before and after degradation

4. Conclusions

In this study, the physical and chemical changes of PLA sheets during burying test under simulated landfill conditions were investigated. Landfill soil and anaerobic sludge was used as burying medium which have a diversity of microorganisms. Under setting conditions, the hydrolytic degradation process was occurred resulting in the change of PLA properties. These conditions enhanced PLA degradation up to 90% of weight loss in 90 days. The degradation of PLA was confirmed by visual examination and particle

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

size analysis. PLA samples were reduced to small brittle fragments as a function of degradation time. After the end of burying test, most of remained fragmented sizes were less than 1 mm. The occurrence of pores, cracks and irregular roughness was increased through the buried time. Moreover, the strength of PLA was continuously decreased during burying test as seen from lower decomposition temperature. Meanwhile, the percentage of carbon content in molecular structure also decreased during the degradation test. In addition, the change in chemical properties of PLA was tested by FTIR. The FTIR graph presented some peaks and changed in the shape of peak area.

5. Acknowledgments

This study was supported by the 90th Anniversary of Chulalongkorn University fund (Ratchadaphiseksomphot Endowment Fund).

6. References

Al-Itry R, Lamnawar K, Maazouz A. Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. Polymer Degradation and Stability 2012;97:1898-914.

Arrieta MP, López J, Rayón E, Jiménez A. Disintegrability under composting conditions of plasticized PLA–PHB blends. Polymer Degradation and Stability 2014;108:307-18.

Avérous L. Chapter 21-Polylactic Acid: Synthesis, Properties and Applications. In: Gemini MNB editor. Monomers, Polymers and Composites from Renewable Resources. Amsterdam: Elsevier; 2008. p. 433-50.

Biron M. The Plastics Industry: Economic Overview. In: Biron M. editor. Thermosets and Composites. 2nd ed. Oxford: William Andrew Publishing; 2014. p. 25-104.

Copinet A, Bertrand C, Govindin S, Coma V, Couturier Y. Effects of ultraviolet light (315 nm), temperature and relative humidity on the degradation of polylactic acid plastic films. Chemosphere 2004;55:763-73.

Dong W, Zou B, Yan Y, Ma P, Chen M. Effect of chain-extenders on the properties and hydrolytic degradation behavior of the poly(lactide) / poly(butylene adipate-co-terephthalate)blends.International Journal of Molecular Sciences 2013;14:20189-203.

Ghorpade VM, Gennadios A, Hanna MA. Laboratory composting of extruded poly (lactic acid) sheets. Bioresource Technology 2001;76:57-61.

Gupta AP, Kumar V. New emerging trends in synthetic biodegradable polymers – Polylactide: A critique. European Polymer Journal 2007;43:4053-74.

Itävaara M, Karjomaa S, Selin J-F. Biodegradation of polylactide in aerobic and anaero bicthermophilic conditions. Chemosphere 2002;46:879-85.

ISO 15985. Plastics-Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions. 2004.

Lunt J. Large-scale production, properties and commercial applications of polylactic acid polymers. Polymer Degradation and Stability 1997;59:145-52.

Mathew AP, Okasman K, Sain M. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). Journal of Applied Polymer Science 2005;97:2014-25.

Muenmee S, Chiemchaisri W, Chiemchaisri, C. Microbial consortium involving biological methane oxidation in relation to the biodegradation of waste plastics in a solid waste disposal open dump site. International Biodeterioration & Biodegradation 2015;102:172-81.

Ndazi BS, Karlsson S. Characterization of hydrolytic degradation of polylactic acid/rice hulls composites in water at different temperatures. EXPRESS Polymer Letters 2011;5(2):119-31.

Pamuła E, Błażewicz M, Paluszkiewicz C, Dobrzyński P. FTIR study of degradation products of aliphatic polyesters–carbon fibres composites. Journal of Molecular Structure 2001;596:69-75.

Rudnik E, Briassoulis D. Degradation behaviour of poly(lactic acid) films and fibres in soil under Mediterranean field conditions and laboratory simulations testing. Industrial Crops and Products 2011;33:648-58.

Sin LT, Rahmat Abdul R, Rahman Wan AWA. 3 - Applications of Poly (lactic Acid). In: Ebnesajjad S. editor. Handbook of Biopolymers and Biodegradable Plastics Boston: William Andrew Publishing; 2013. p. 55-69.

Wang S, Ma P, Wang R, Wang S, Zhang Y, Zhang Y. Mechanical, thermal and degradation properties of poly(d,l-lactide) /poly (hydroxybutyrate-co-hydroxyvalerate) /poly(ethylene glycol) blend. Polymer Degradation and Stability 2008;93:1364-9.

Weng Y-X, Jin Y-J, Meng Q-Y, Wang L. Zhang M, Wang Y-Z. Biodegradation behavior of poly (butylene adipate-co-terephthalate) (PBAT), poly(lactic acid) (PLA), and their blend under soil conditions. Polymer Testing 2013;32: 918-926.

Yagi H, Ninomiya F, Funabashi M, Kunioka M. Anaerobic biodegradation tests of poly(lactic acid) under mesophilic and thermophilic conditions using a new evaluation system for methane fermentation in anaerobic sludge. International journal of molecular sciences 2009;10:3824-35.

Yagi H, Ninomiya F, Funabashi M, Kunioka M. Thermophilic anaerobic biodegradation test and analysis of eubacteria involved in anaerobic biodegradation of four specified biodegradable polyesters. Polymer Degradation and Stability 2013;98:1182-7.

ISSN 1686-5456(Print)
ISSN 2408-2384(Online)