



Feedstock Recycling of Flame-Resisting Poly(lactic acid)/Aluminum Hydroxide Composite to L,L-lactide

著者	Nishida Haruo, Fan Yujiang, Mori Tomokazu, Oyagi Naoko, Shirai Yoshihito, Endo Takeshi
journal or publication title	Industrial and Engineering Chemistry Research
volume	44
number	5
page range	1433-1437
year	2005-02-03
URL	http://hdl.handle.net/10228/00006733

doi: [info:doi/10.1021/ie049208+](https://doi.org/10.1021/ie049208+)

Feedstock recycling of flame-resisting poly(lactic acid) / aluminum hydroxide composite to L,L-lactide

Haruo Nishida,^{†,} Yujiang Fan,^{†,‡} Tomokazu Mori,^{†,§} Naoko Oyagi,[†] Yoshihito Shirai,[‡] and Takeshi
Endo^{†,£}*

Molecular Engineering Institute, Kinki University, 11-6 Kayanomori, Iizuka, Fukuoka 820-8555, Japan;
Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Fukuoka
808-0196, Japan; Faculty of Computer Science and Systems Engineering, Kyushu Institute of
Technology, Fukuoka, 820-8502, Japan; Faculty of Engineering, Yamagata University, Yamagata 992-
8510, Japan

E-mail: hnishida@mol-eng.fuk.kindai.ac.jp (H. Nishida)

RECEIVED DATE

TITLE RUNNING HEAD: Feedstock recycling of flame-resisting PLLA/Al(OH)₃

* Corresponding author. E-mail: hnishida@mol-eng.fuk.kindai.ac.jp Tel/Fax: (+81)-948-22-5706.

[†] Molecular Engineering Institute, Kinki University

[‡] Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology

[§] Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology

[£] Faculty of Engineering, Yamagata University

ABSTRACT: To achieve the chemical recycling of flame-resisting materials consisted of poly(L-lactic acid) (PLLA), a safer flame-resisting material, PLLA/aluminum hydroxide $\{Al(OH)_3\}$ composite, was investigated the feedstock recyclability to optically active monomer L,L-lactide. The thermal stabilization of the composite was improved compared to as-polymerized PLLA and $Al(OH)_3$ themselves, which makes the melt processing of the composite easier. Nevertheless, at temperatures lower than 300 °C the effective depolymerization of PLLA proceeded, without any racemization reaction, to selectively convert into L,L-lactide, with $Al(OH)_3$ acting as a catalyst for the depolymerization. This means that the PLLA/ $Al(OH)_3$ composite is capable of reconciling flame resistance with feedstock recycling of PLLA to cyclic monomer.

KEYWORDS: poly(lactic acid), flame resistance, aluminum hydroxide, feedstock recycling, lactide

Introduction

Polymer materials in many of their applications are required to be flame resistant. This is especially true in the electric and electronic fields, where organic bromides, phosphorous, and antimony compounds have traditionally been used, but are less used these days. For example, employing organic bromides as flame-retardants are less common nowadays because of Directive 2002/96/EC regulating waste electrical and electronic equipment (WEEE) and Directive 2002/95/EC restricting the use of certain hazardous substances (RoHS). At the same time as aluminium hydroxide $\{Al(OH)_3\}$ is gaining popularity as a safer flame retardant.¹ Poly(lactic acid) (PLLA) is also being introduced into electric and electronic equipments as a flame resisting housing material.² PLLA, a well-known biodegradable (especially bioabsorbable) and depolymerizable material, is an attractive raw material, which is produced from renewable resources such as corn,³ potato and garbage.⁴ Because of the advantage of having a carbon neutral, the use of PLLA in industrial fields has been rapidly increasing in the form of moulding parts for personal computers,⁵ portable disk players, and automobiles.^{6,7} However, to achieve

a high enough level of flame resistance for the PLLA/Al(OH)₃ composite, a large amount of Al(OH)₃ is required.² PLLA has poor biodegradability in certain environments⁸ but if the feedstock recycling of the PLLA molding parts to monomer could be achieved then no doubt it would become more widely used as a reasonable choice for a sustainable future society.⁹ Until now, the feedstock recycling of flame resistant polymer materials has been left untouched, because all the retardants have been thought to inhibit the thermal degradation of the polymer components. Here we demonstrate an effective way to feedstock recycle the flame-resisting PLLA/Al(OH)₃ composite material to cyclic monomer, L,L-lactide without the racemization to meso- and D,D-lactide (Scheme 1).

[**Scheme 1** is displayed here]

We have been demonstrating repeatedly that the choice of catalyst and the control of temperature are key factors in achieving a precise depolymerization of PLLA to cyclic monomer.¹⁰ Each active species in the degradation reactions can function effectively in an appropriate temperature range. For example, some PLLA materials containing Sn compounds as residual initiator show different degradation behaviors in specified temperature ranges according to the Sn content and their chemical structure at the polymer chain ends.¹¹

Though there is much information on the flame-resistance of PLLA/Al(OH)₃ composite, no report about the thermal degradation of the composite has been published.² A few reports about the thermal degradation of PLLA materials, including other types of aluminium compounds, have been published. Degée et al. reported that the thermal stability of as-polymerized É-alkoxyaluminium-PLLA with Al(isopropoxide)₃ was so stable as to be quite comparable to the purified PLLA.¹² Cam et al. suggested that an unknown inorganic salt of aluminium caused the lowering of the PLLA decomposition temperature.¹³ Noda et al. found that in the presence of Al(isopropoxide)₃ or Al(ethyl acetoacetate)₃ PLLA oligomer was depolymerized with accompanying marked racemization, resulting in the formation of large amounts of meso- and D,D-lactides.¹⁴ The racemization causes some serious problems, for example, a decrease in crystallinity, melting point, and useful mechanical properties.¹⁵ From these

previous results, we might never imagine the flame resistance and the feedstock recycling of PLLA materials with such aluminium compounds.

This is the first report indicating that the flame-resistance of PLLA/Al(OH)₃ composite is consistent with the feedstock recycling of PLLA materials to L,L-lactide.

Experimental Section

Materials

Monomer, L,L-lactide, obtained from Shimadzu Co. Ltd. was purified by recrystallizing three times from dry toluene and one time from dry ethyl acetate. The vacuum dried L,L-lactide was stored in a N₂ atmosphere. After the purification, meso-lactide was not detectable by gas chromatography (GC). Polymerization catalyst Sn(2-ethylhexanoate)₂ obtained from Wako Pure Chemical Industries, Ltd. was distilled under reduced pressure before use. Aluminium hydroxide, Al(OH)₃, was purchased from Wako Pure Chemical Industries, and was used without any further treatment. Solvents, chloroform and methanol, were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

Preparation of the PLLA/Al(OH)₃ composites

PLLA was synthesized by the ring-opening polymerization of L,L-lactide catalyzed by Sn(2-ethylhexanoate)₂ as described in previous reports.¹⁶ The obtained as-polymerized PLLA-ap was purified in a three stage process; firstly extracting the catalyst and residues from the PLLA-ap/chloroform solution with a 1M HCl aqueous solution, then washing with distilled water until the aqueous phase became totally neutral, and finally precipitating the polymer with methanol before vacuum drying. The PLLA-ap or purified PLLA-H was mixed with Al(OH)₃ in a prescribed weight ratio (Table 1) in a chloroform solution and vigorously stirred for 1 h to disperse the inorganic particles uniformly. Then the mixture was cast on glass Petri dishes.

Measurements

Molecular weight was measured by gel permeation chromatography (GPC) on a TOSOH HLC-8220 GPC system at 40°C using TOSOH TSKgel Super HM-H column and a chloroform eluent (0.6 mL min⁻¹). Low polydispersity polystyrene standards with M_n from 5.0×10^2 to 1.11×10^6 were used for calibration. The residual metal content in the PLLA samples was measured with a Shimadzu AA-6500F atomic absorption flame emission spectrophotometer (AA). The samples were degraded by a 25 % ammonia solution, dissolved in a 1M HCl aqueous solution, and then measured by AA.

Thermogravimetric analysis was conducted on a SEIKO EXSTAR 6200 TG/DTA 6200 system in an aluminium pan under a constant nitrogen flow (100 mL min⁻¹) using about 5 mg of the PLLA film sample. Pyrolysis-gas chromatograph/mass spectra (Py-GC/MS) were measured on a Frontier Lab PY-2020D double-shot pyrolyzer connected to a Shimadzu GCMS-QP5050 chromatograph/mass spectrometer, which was equipped with an Ultra Alloy⁺-5 capillary column. High purity helium at 50 mL min⁻¹ was used as a carrier gas. The gas chromatography (GC) measurements were recorded on a Shimadzu GC-9A gas chromatograph with a Varian cyclodextrine-2-236M-19 capillary column (0.25 mm × 50 m) using helium as a carrier gas. The column and injector were set isothermally at 150 and 220 °C, respectively. The sample (3 mg) was dissolved in acetone (1 mL) and a 1 µL aliquot of the solution was injected. The peaks for meso-, L,L-, and D,D-lactides were identified by comparison with pure substance peaks.

Thermal degradation

Dynamic pyrolysis of PLLA/Al(OH)₃ composites was conducted on TG/DTA in aluminium pans under a constant nitrogen flow (100 mL min⁻¹) using about 5 mg of the composite. For each composite, prescribed heating rates, β of 1, 3, 5, 7, and 9 °C min⁻¹ were applied from 60 to 400°C. The pyrolysis data were collected at regular intervals (about 20 times °C⁻¹) by an EXSTAR 6000 data platform, and recorded into an analytical computer system.

In the dynamic heating process with Py-GC/MS, about 0.5 mg of the composite was added in the pyrolyzer and heated from 60 to 400 °C at a heating rate of 10 °C min⁻¹. The volatile pyrolysis products were introduced into the GC through the selective sampler. The temperature of the column oven was first set at 40 °C. After the pyrolysis process had finished, the column was heated according to the following program: 40 °C for 1 min; 40-120 °C at 5 °C min⁻¹; 120-320 °C at 20 °C min⁻¹; 320 °C for 13 min. Mass spectrum measurements were recorded 2 times s⁻¹ during this period.

Isothermal pyrolysis of PLLA/Al(OH)₃ composites was carried out in a glass tube oven. A 150 mg sample of PLLA-H/Al(OH)₃=100/30 (wt/wt) composite was put into a Shibata GTO-350D glass tube oven. After the air was replaced by nitrogen in the chamber of the oven, the oven was heated rapidly to 280 °C and then kept at this temperature for 2 h to complete the pyrolysis. The distilled components were collected and analyzed by gas chromatography (GC).

Results and Discussion

In this study two kinds of PLLA, as-polymerized PLLA (PLLA-ap) and purified PLLA (PLLA-H), were used to prepare the composite films with Al(OH)₃ in feed ratios of PLLA-ap/Al(OH)₃=100/10~100/30 and PLLA-H/Al(OH)₃=100/10~100/60 (wt/wt) (Table 1). PLLA-ap, which was a just polymerized PLLA with Sn(2-ethylhexanoate)₂ as catalyst, included 388 ppm of Sn atom having number- and weight-average molecular weights (M_n and M_w) of 150,000 and 373,000, respectively. On the other hand, PLLA-H, which was a purified sample obtained in a solution-solution extracting method from a PLLA-ap/chloroform solution with a 1M HCl aqueous solution,¹⁷ included 17 ppm of Sn atom with its M_n and M_w being 279,000 and 530,000, respectively.

[Table 1 is displayed here]

The thermal degradation of the PLLA/Al(OH)₃ composite films was carried out by linear heating and isothermal processes in a temperature range of 60-400 °C with TG/DTA, pyrolyzer-gas chromatograph/mass spectrometer (Py-GC/MS), and a glass-tube oven.

Weight loss curves of PLLA-ap/Al(OH)₃ composites under a linear heating process of 5 °C min⁻¹ are shown in Figure 1a. The TG curve shifted into a higher temperature range with increasing content of Al(OH)₃ finally converging into a temperature range of 250~300 °C. Considering that the degradation of PLLA-ap itself proceeded in a temperature range of 180-280 °C, Al(OH)₃ functioned as a stabilizer of PLLA-ap, increasing the temperature range of degradation. Weight loss curves of PLLA-H/Al(OH)₃ composites under the same linear heating process at 5 °C min⁻¹ are shown in Figure 1b. The degradation of PLLA-H itself proceeded in a higher temperature range of 300~375 °C, however, the TG curve of PLLA-H/Al(OH)₃ composites shifted into a lower temperature range with increasing content of Al(OH)₃ and ultimately converged into the same temperature range of 250~300 °C as PLLA-ap/Al(OH)₃ composites. These results indicate that when the feed ratio of Al(OH)₃ was higher than PLLA/Al(OH)₃=100/30 (wt/wt), the degradation proceeded in a steady state in the range 250~300 °C, in which a Al(OH)₃-catalyzed degradation reaction must be a dominant reaction.

[Figure 1 is displayed here]

To determine differences in degradation behavior of PLLA/Al(OH)₃ at temperatures both higher and lower than 300 °C, degradation products at these differing temperatures were compared with each other. Figure 2 shows Py-GC/MS chromatograms of the pyrolysis products of the PLLA-H/Al(OH)₃=100/30 (wt/wt) composite, which were measured at a heating rate of 10 °C min⁻¹ in two temperature ranges of 60~300 and 60~400 °C. The peaks at 11.8 and 13.4 min in these chromatograms, by comparison with the standard chemicals, were identified as representing meso-lactide and D,D-/L,L-lactides, respectively. The groups of peaks appearing periodically after 20 min were assigned to higher cyclic oligomers than lactide, in which each oligomer peak showed two series of signals with $m/z = 72n \pm 1$ and $72n - 16$ (n: number of lactate unit).

[Figure 2 is displayed here]

Composition values of the volatilized degradation products were calculated from the total ion counts of peaks in the Py-GC/MS chromatograms. In Figure 3, the composition spectrum of products from PLLA-H/Al(OH)₃=100/30 (wt/wt) composite is illustrated for each different temperature range.

Interestingly, at temperatures lower than 300 °C, the volatized product was L,L- and/or D,D-lactides selectively. Over 300 °C, the amount of meso-lactide and cyclic oligomers higher than trimer gradually increased. Similar results were obtained in the case of the PLLA-ap/Al(OH)₃=100/30 (wt/wt) composite. The production of meso-lactide and cyclic oligomers at higher temperatures than 300 °C, which are produced via ester-semiacetal tautomerization and intramolecular transesterification, was previously reported.¹⁸

[Figure 3 is displayed here]

Composition of L,L- and D,D-lactides in the pyrolyzates from PLLA-H/Al(OH)₃=100/30 (wt/wt) composite was determined through gas chromatography (GC) analysis with a capillary column, cyclodextrin-2-236M-19, which splits the diastereoisomers in the pyrolyzates. The isothermal degradation of composite was carried out in a glass tube oven at 280 °C for 2 h. The GC chromatogram of the pyrolyzates showed the formation of L,L- (95.8 %) and D,D-lactides (0 %) at 12.42 and 13.17 min, respectively, and a small amount of meso-lactide (4.2 %) at 9.45 min. Therefore, at temperatures lower than 300 °C, Al(OH)₃ functions as an effective depolymerization catalyst of PLLA, resulting in preferential L,L-lactide formation.

In Figure 4, the TG/DTA profile of Al(OH)₃ itself indicated that 78 % of Al(OH)₃ was converted to inert Al₂O₃ in a temperature range of 220~270 °C, and complete conversion was found at 600 °C. This TG profile of Al(OH)₃ indicates that the residues in Figure 1 were predominantly Al₂O₃ that had been converted from Al(OH)₃, not only in the cases of PLLA-H/Al(OH)₃ but also in the cases of PLLA-ap/Al(OH)₃ (Table 1). Comparing the TG/DTA profiles of Al(OH)₃ to PLLA/Al(OH)₃ composites in Figure 1, it is suggested that the dehydration of Al(OH)₃ to Al₂O₃ was suppressed by PLLA, resulting in a shift to the range of 250~300 °C. This means that Al(OH)₃ in the composite must be thermally stable.

[Figure 4 is displayed here]

To clarify the activation energy, E_a , of the thermal degradation of PLLA/Al(OH)₃ composite, a dynamic degradation method was carried out at different heating rates of 1~9 °C min⁻¹. The E_a value at a certain fractional weight ratio, w , was calculated using Doyle's and Reich's methods.^{19,20} The calculated

E_a value was 120-135 kJ mol⁻¹, which was lower than that for the degradation of PLLA-H (Figure 5) at 180 kJ mol⁻¹.¹⁶ Such a lower E_a value is advantageous for the feedstock recycling of PLLA.

[Figure 5 is displayed here]

Conclusions

In conclusion, the above results from this investigation clarified three advantages of PLLA/Al(OH)₃ composite, adding to its well known flame resistance. These are: 1) the thermal stabilization of the composite compared to PLLA-ap and Al(OH)₃ themselves, which makes the melt processing of the composite easier, 2) the effective depolymerization of PLLA component to cyclic monomer L,L-lactide, occurring at lower temperatures than 300 °C, and 3) the decrease in the energy required for the monomer's recovery. These effects demonstrate that the flame-resistant PLLA/Al(OH)₃ composite is able to be reconciled with an efficient feedstock recycling of PLLA component to cyclic monomer L,L-lactide. Therefore, it was clarified that Al(OH)₃ as a flame retardant of PLLA is able to function as a catalyst for the depolymerization of PLLA to monomer independently in a different temperature range under controlled conditions (Figure 6).

[Figure 6 is displayed here]

Acknowledgement: This work was supported by the Special Coordination Funds of the Ministry of Education, Culture, Sports, Science and Technology, and the Japanese Government.

Literature Cited

- ¹ Kiuchi, Y.; Iji, M. Development of environmentally safe flame-retarding epoxy resin compounds without halogen and phosphorous derivatives and their application to printed wiring boards. *NEC Res. & Develop.* **2003**, *44*, 256.
- ² Sterzel, H.-J. Flammwidrig ausgerüstetes polylactid und copolylactid. DE Patent 4,325,849 A1, 1993.
- ³ Lunt, J. Large-scale production, properties and commercial applications of polylactic acid polymers. *Polym. Degrad. Stab.* **1998**, *59*, 145.
- ⁴ Shirai, Y.; Sakai, K.; Miura, S.; Ohara, H. Production of poly-lactate from kitchen refuse in Japan. In *International Symposium on Biotechnology for Recycling of Organic Wastes to Useful Resources* (ed Shirai Y.) 7-9 (Kyushu Institute of Technology, Kitakyushu, 2001).
- ⁵ NEC succeeds in development of flame resistant bio-plastic. *Mod. Plast. Int.* **2004**, *34*, 60.
- ⁶ Isobe, Y.; Ino, T.; Kageyama, Y.; Nakano, M.; Usuki, A. Improvement of heat resistance for bioplastics. *Special Publications. Soc. Automotive Eng.* **2003**, *SP-1763*, 103.
- ⁷ Riedel, U.; Nickel, J. Natural fibre-reinforced biopolymers as construction materials – new discoveries. *Angew. Makromol. Chem.* **1999**, *272*, 34.
- ⁸ Tokiwa, Y.; Jarerat, A. Microbial degradation of aliphatic polyesters. *Macromol. Symp.* **2003**, *201*, 283.
- ⁹ Fan, Y.; Nishida, H.; Shirai, Y.; Endo, T. Control of racemization for feedstock recycling of PLLA. *Green Chemistry* **2003**, *5*, 575.
- ¹⁰ Fan, Y.; Nishida, H.; Shirai, Y.; Endo, T. Racemization on thermal degradation of poly(L-lactide) with calcium salt end structure. *Polym. Degrad. Stab.* **2003**, *80*, 503.

- ¹¹ Nishida, H.; Mori, T.; Hoshihara, S.; Fan, Y.; Shirai, Y.; Endo, T. Effects of tin on poly(L-lactic acid) pyrolysis. *Polym. Degrad. Stab.* **2003**, *81*, 515.
- ¹² Degée, P.; Dubois, P.; Jérôme, R. Bulk polymerization of lactides initiated by aluminium isopropoxide, 3 Thermal stability and viscoelastic properties. *Macromol. Chem. Phys.* **1997**, *198*, 1985.
- ¹³ Cam, D.; Marucci, M. Influence of residual monomers and metals on poly (L-lactide) thermal stability. *Polymer* **1997**, *38*, 1879.
- ¹⁴ Noda, M.; Okuyama, H. Thermal catalytic depolymerization of poly(L-lactic acid) oligomer into L,L-lactide: Effects of Al, Ti, Zn, and Zr compounds as catalysts. *Chem. Pharm. Bull.* **1999**, *47*, 467.
- ¹⁵ Grijpma, D. W.; Pennings, A. J. (Co)polymers of L-lactide, 1 Synthesis, thermal properties and hydrolytic degradation. *Macromol. Chem. Phys.* **1994**, *195*, 1633.
- ¹⁶ Fan, Y.; Nishida, H.; Hoshihara, S.; Shirai, Y.; Tokiwa, Y.; Endo, T. Pyrolysis kinetics of poly(L-lactide) with carboxyl and calcium salt end structures. *Polym. Degrad. Stab.* **2003**, *79*, 547.
- ¹⁷ Fan, Y.; Nishida, H.; Shirai, Y.; Endo, T. Thermal stability of poly (L-lactide): Influence of end protection by acetyl group. *Polym. Degrad. Stab.* **2004**, *84*, 143.
- ¹⁸ Kopinke, F. D.; Remmler, M.; Mackenzie, K.; Moder, M.; Wachsen, O. Thermal decomposition of biodegradable polylactides-II. Poly (lactic acid). *Polym. Degrad. Stab.* **1996**, *53*, 329.
- ¹⁹ Doyle, C. D. Estimating isothermal life from thermogravimetric data. *J. Appl. Polym. Sci.* **1962**, *6*, 639.
- ²⁰ Reich, L. A rapid estimation of activation energy from thermogravimetric traces. *Polym. Lett.* **1964**, *2*, 621.

TABLE:

Table 1. Thermal degradation of PLLA/Al(OH)₃ composites with TG.

In feed		After thermal degradation ^a	
PLLA/Al(OH) ₃		Found residue	Calcd. residue ^b
(wt/wt)	Al(OH) ₃ (wt-%)	(wt-%)	Al(OH) ₃ →Al ₂ O ₃ (wt-%)
PLLA-ap/Al(OH) ₃		Conversion: 58 % ^c	
100 / 0	0	0.34	-
100 / 10	9.1	7.4	7.3
100 / 20	16.7	13.2	13.3
100 / 30	23.1	18.5	18.5
PLLA-H/Al(OH) ₃		Conversion: 78 % ^c	
100 / 0	0	0.13	-
100 / 10	9.1	7.5	6.6
100 / 20	16.7	12.3	12.2
100 / 30	23.1	17.8	16.9
100 / 40	28.6	20.7	20.9
100 / 50	33.3	24.6	24.3
100 / 60	37.5	27.1	27.4

^a Conditions: heating rate 5 °C min⁻¹ in a temperature range of 60-400 °C under N₂ flow (100 mL min⁻¹). ^b Calculated value based on the approximated conversion value. ^c Approximated value of the conversion of Al(OH)₃ to Al₂O₃.

SCHEME:

Scheme 1. Al(OH)₃-catalyzed feedstock recycling of poly(L-lactic acid).

FIGURE CAPTIONS:

Figure 1. TG profiles on pyrolysis of PLLA and PLLA/Al(OH)₃ composites with different PLLA/Al(OH)₃ weight ratios. a) PLLA-ap/Al(OH)₃, b) PLLA-H/Al(OH)₃.

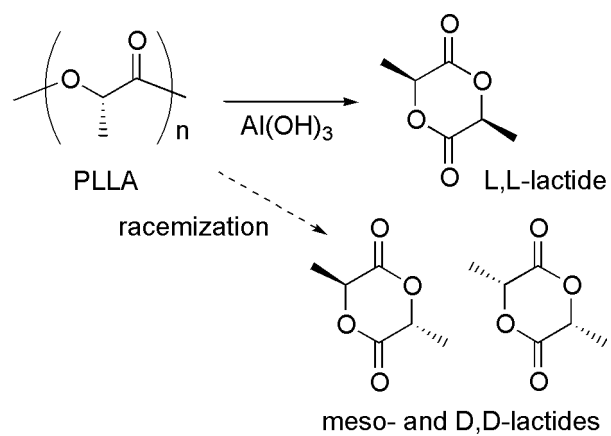
Figure 2. Py-GC/MS chromatograms of PLLA-H/Al(OH)₃=100/30 (wt/wt) in two different temperature ranges to determine differences in degradation behavior at temperatures both higher and lower than 300 °C.

Figure 3. Components of pyrolyzates of PLLA-H/Al(OH)₃=100/30 (wt/wt) composites in different temperature ranges. Contents were calculated from integration values of peaks in Py-GC/MS total ion chromatograms.

Figure 4. TG profile of Al(OH)₃. Conversion means the value of the reaction of Al(OH)₃ to Al₂O₃ at the residual weight.

Figure 5. Changes in E_a value during thermal degradation of PLLA-H and PLLA/Al(OH)₃=100/30 (wt/wt) composites.

Figure 6. Total view of functions of PLLA/Al(OH)₃ composite.



Scheme 1. Al(OH)_3 -catalyzed feedstock recycling of poly(L-lactic acid).

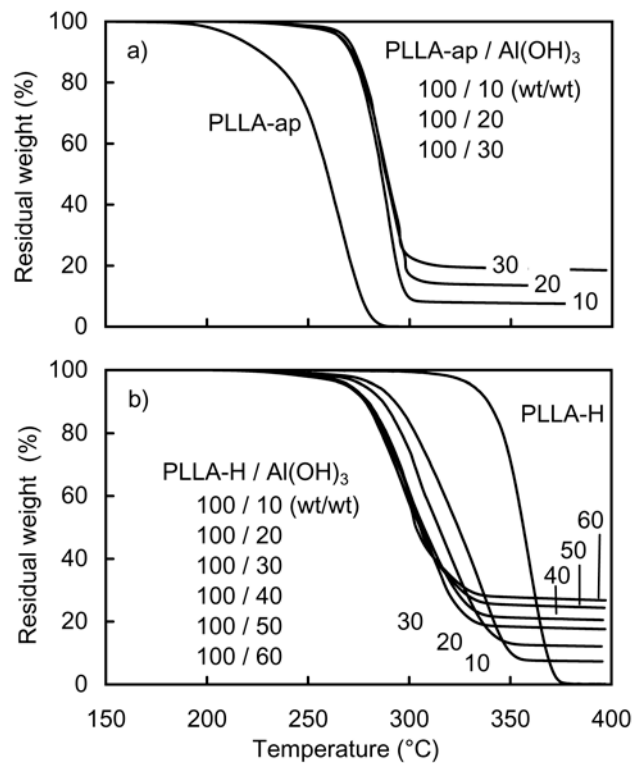


Figure 1. TG profiles on pyrolysis of PLLA and PLLA/Al(OH)₃ composites with different PLLA/Al(OH)₃ weight ratios. a) PLLA-ap/Al(OH)₃, b) PLLA-H/Al(OH)₃.

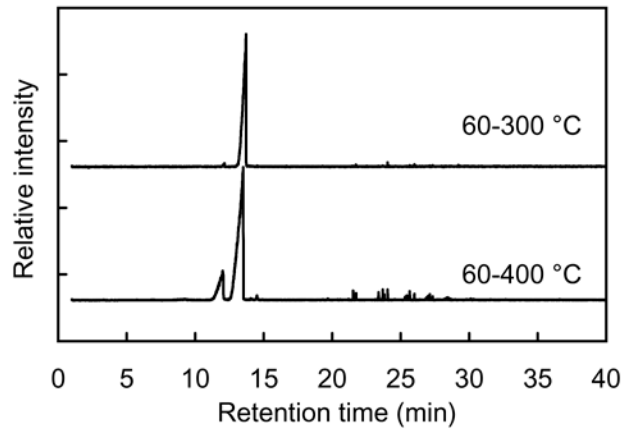


Figure 2. Py-GC/MS chromatograms of PLLA-H/Al(OH)₃=100/30 (wt/wt) in two different temperature ranges to determine differences in degradation behavior at temperatures both higher and lower than 300 °C.

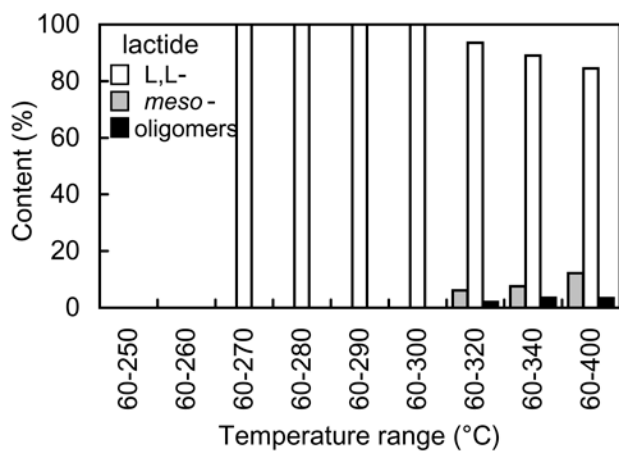


Figure 3. Components of pyrolyzates of PLLA-H/Al(OH)₃=100/30 (wt/wt) composites in different temperature ranges. Contents were calculated from integration values of peaks in Py-GC/MS total ion chromatograms.

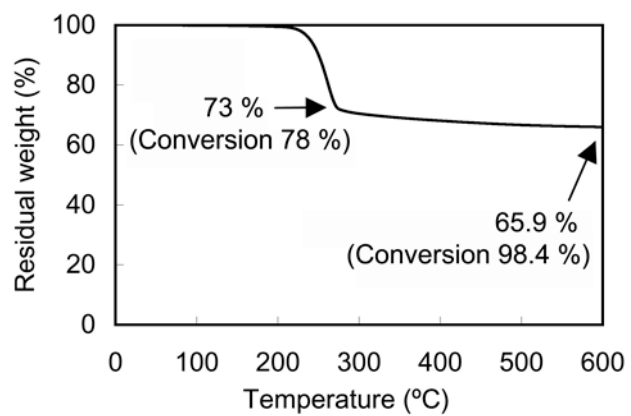


Figure 4. TG profile of Al(OH)₃. Conversion means the value of the reaction of Al(OH)₃ to Al₂O₃ at the residual weight.

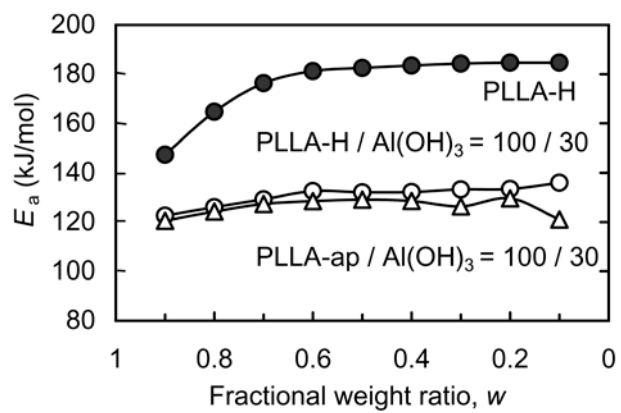


Figure 5. Changes in E_a value during thermal degradation of PLLA-H and PLLA/Al(OH)₃=100/30 (wt/wt) composites.

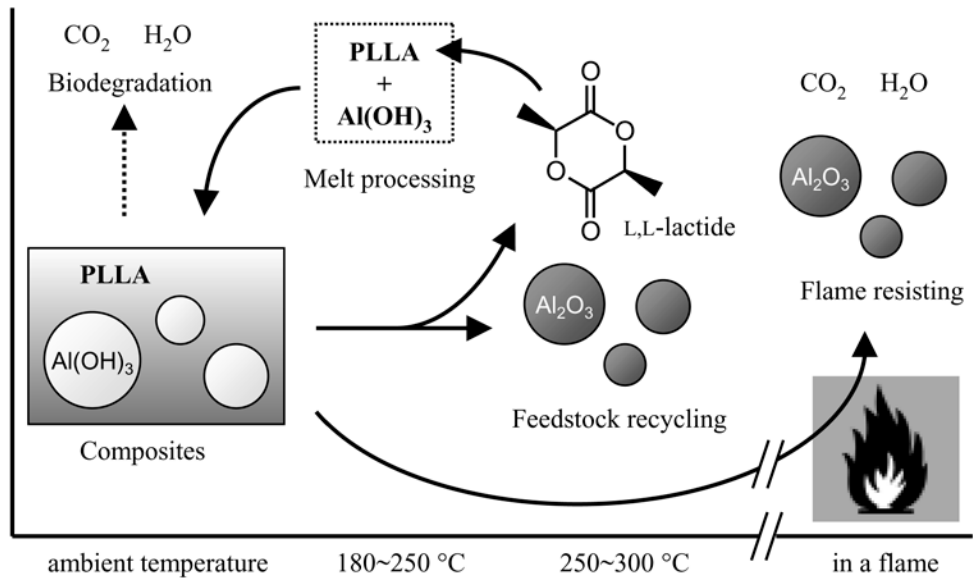


Figure 6. Total view of functions of PLLA/Al(OH)₃ composite.