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Thermal degradation of poly(L-lactide): effect of alkali earth metal oxides for selective L,L-lactide formation

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Abstract

To achieve the feed stock recycling of poly(L-lactide) (PLLA) to L,L-lactide, PLLA composites including alkali earth metal oxides, such as calcium oxide (CaO) and magnesium oxide (MgO), were prepared and the effect of such metal oxides on the thermal degradation was investigated from the viewpoint of selective L,L-lactide formation. Metal oxides both lowered the degradation temperature range of PLLA and completely suppressed the production of oligomers other than lactides. CaO markedly lowered the degradation temperature, but caused some racemization of lactide, especially in a temperature range lower than 250 °C. Interestingly, with MgO racemization was avoided even in the lower temperature range. It is considered that the effect of MgO on the racemization is due to the lower basicity of Mg compared to Ca. At temperatures lower than 270 °C, the pyrolysis of PLLA/MgO (5 wt%) composite occurred smoothly causing unzipping depolymerization, resulting in selective L,L-lactide production. A degradation mechanism was discussed based on the results of kinetic analysis. A practical approach for the selective production of L,L-lactide from PLLA is proposed by using the PLLA/MgO composite.

Keywords: Thermal degradation; Poly(L-lactide); Racemization

1. Introduction

Poly(L-lactide), or poly(L-lactic acid) (PLLA) belongs to a group of biodegradable polymers and has received much interest because of its medical, pharmaceutical, and environmental applications [1–3]. Nowadays, PLLA and its related copolymers are attracting much attention as promising alternatives to the normal petroleum based commodity resins, because they can be derived from renewable resources, such as corn, potato and other agricultural products and have many useful properties, such as mechanical strength, transparency, and compostability [4,5]. However, whilst the biodegradability of PLLA is excellent in terms of its ability to be bioabsorbed, its microbial degradation is limited to a few species of microorganisms, such as *Amycolatopsis* and *Streptomyces* strains [6,7]. Any large-scale consumption of PLLA products will bring the associated problem of an excess of PLLA waste, which will be difficult to treat by biodegradation either in composting plants or in the natural environment. One possible approach to overcoming this difficulty is to regenerate the cyclic monomer, L,L-lactide, from the PLLA waste, using the well-known fact that PLLA can be changed into the monomer by thermal degradation [8–15]. However, the thermal degradation of PLLA has been reported to be more complex than the simple reaction that gives rise to lactide [11–15]. McNeill and Leiper investigated the degradation of PLLA under both controlled heating conditions and isothermal conditions [8,9]. They reported that the main products were cyclic oligomers, including lactide. Other lower boiling point products, such as carbon dioxide, acetaldehyde, ketene, and carbon monoxide were also produced. Kopinke and co-workers reported a multi-step process for PLLA pyrolysis. They found that the intra-molecular transesterification was a dominant degradation pathway, and that pyrolysis behavior was different between pure as opposed to Sn-containing PLLAs [11,12]. In addition, considerable racemization to

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meso- and D,D-lactides was observed during the pyrolysis of PLLA [11,12,16,17], which caused serious problems after the reproduction of PLLA, diminishing its crystallizability and some other useful properties [18–20]. Racemization during pyrolysis has scarcely been discussed in previously published works, except that of Kopinke et al., who proposed a racemization mechanism through an ester–semiacetal tautomerization occurring in a lactate unit in the chain under higher temperatures [12]. This speculation is reasonable as it explains the fact that more than two diastereoisomers were observed for each cyclic oligomer as pyrolyzates. Generally, temperature and catalyst are regarded as affecting the pyrolysis significantly. However, no detailed and quantitative discussion on these points has taken place so far. Thus, it is necessary to clarify the racemization mechanism in the pyrolysis, and find an appropriate approach for controlling the degradation reaction of PLLA so as to reproduce the optically pure L,L-lactide.

It has been reported that the blending of many kinds of metal compounds with PLLA greatly influences the pyrolysis behaviour [21,22]. Noda et al. evaluated the activity of a series of Al, Ti, Zn, Zr, and Sn compounds as intramolecular transesterification catalysts for the pyrolysis of PLLA oligomer, and reported that the activity of each metal was in the following order: Sn > Zn > Zr > Ti > Al [21]. Cam et al. also reported that compounds of metals, such as Sn, Zn, Al, and Fe, had a great influence on the pyrolysis behavior of PLLA [22]. Though the Sn compounds are effective catalysts for L,L-lactide production from PLLA [23], less toxic and more easily available catalysts should be used for feedstock recycling.

In our previous studies [24,25], it was found that the calcium salt end capped PLLA, PLLA-Ca, degraded through unzipping depolymerization to produce principally lactides. Alkali earth metal compounds are ideal catalysts for recycling, because of their lower toxicity and easy availability. Kinetic analysis of the pyrolysis process revealed that there was one selective L,L-lactide formation and two racemization reactions occurring in different temperature ranges each with its own specific mechanism [25]. At temperatures lower than 250 °C, a S_N2 attack from carboxylate anion on an asymmetrical carbon dominates, and at higher temperatures than 320 °C ester–semiacetal tautomerization occurs to produce *meso*- and D,D-lactides. In a temperature range of 250–320 °C, the unzipping depolymerization mechanism dominates, resulting in selective L,L-lactide formation. This temperature-dependent multiple mechanisms have been revealed as occurring in the pyrolysis of the homogeneous PLLA-Ca. If these multiple mechanisms are applied to heterogeneous composites of PLLA and inorganic compounds, then this approach will be usable for the practical feedstock recycling of PLLA.

In this paper, two alkali earth metal oxides, calcium oxide (CaO) and magnesium oxide (MgO), are blended with PLLA to prepare the PLLA/metal oxide composites. These metal oxides are naturally existing materials, and in particular MgO is commonly used in large quantities as a filler for plastics. The particle surfaces of these metal oxides are expected to have catalytic effects on the PLLA pyrolysis. The thermal degradation behavior of the composites is examined as a function of temperature. Consequently, the metal oxides in the composites markedly influenced the degradation temperature, kinetics, and racemization of the PLLA pyrolysis. A practical approach usable in controlling racemization and obtaining optically pure L,L-lactide is demonstrated.

2. Experimental

2.1. Materials

Monomer, L,L-lactide, was obtained from Shimadzu Co. Ltd. and purified by being recrystallized three times from dry toluene and one time from dry ethyl acetate. The vacuum dried L,L-lactide was stored in N_2 atmosphere. After the purification, no *meso*-lactide was detected by gas chromatography (GC). Polymerization catalyst, Sn(II) 2-ethylhexanoate, $Sn(Oct)_2$, obtained from Wako Pure Chemical Industries, Ltd. was distilled under reduced pressure before use. Calcium oxide (CaO, average diameter ≈ 10 μm, 99.0%) and magnesium oxide (MgO, average diameter ≈ 0.01 μm, 99.9%) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Other chemicals and solvents are used without further purification.

2.2. 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 ($0.6\ \mathrm{ml\ min^{-1}}$). 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 1 M-hydrochloric acid, and then measured by AA.

Thermogravimetric analysis (TG) was conducted on a Seiko Instrumental Inc. EXSTAR 6200 TG/DTA system in an aluminum pan under a constant nitrogen flow ($100\ \mathrm{ml\ min^{-1}}$) using about 5 mg of the PLLA film sample. Two heating program patterns were applied for pyrolysis of PLLA, which were, (1) dynamic heating and (2) isothermal heating. In the dynamic heating process, for each sample, prescribed heating rates ϕ of 1, 3, 5, 7, and 9 $\mathrm{K\ min^{-1}}$ were applied from room temperature to 400 °C. In the isothermal heating process, the sample was heated from 60 to 250 °C at a heating rate of 20 $°\mathrm{C\ min^{-1}}$ and kept at 250 °C for 10 min.

The pyrolysis data were collected at regular intervals (about 20 times K^{-1}) by an EXSTAR 6000 data platform, and recorded into an analytical computer system.

Gas chromatography (GC) measurements were recorded on a Shimadzu GC-9A gas chromatograph with a Varian cyclodextrine-β-236M-19 capillary column (30 m × 0.25 mm i.d.; film thickness, 0.25 μm) at 150 °C, using helium as the carrier gas. The peaks for *meso*-, L,L-, and D,D-lactide in the GC chromatogram were identified by comparison with the peaks for pure substances.

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 (30 m × 0.25 mm i.d.; film thickness, 0.25 μm). High purity helium at 100 ml min^{-1} was used as a carrier gas. A PLLA sample was put in the pyrolyzer and heated according to two heating program patterns, (1) dynamic heating and (2) isothermal heating. In the dynamic heating process, the PLLA sample in the pyrolyzer was heated from 60 to 400 °C at a heating rate of 10 °C min^{-1}. In the isothermal heating process, the PLLA sample was heated from 60 to 250 °C at a heating rate of 20 °C min^{-1} and kept at 250 °C for 10 min. The volatile pyrolysis products were conducted 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.

2.3. Preparation of PLLA/alkali earth metal oxide composites

PLLA was synthesized by the ring-opening polymerization of L,L-lactide catalyzed by $Sn(Oct)_2$ as described in the previous reports [24,25]. The obtained raw PLLA was purified by firstly extracting the catalyst and its residues from the PLLA/chloroform solution with a 1 M 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 (M_n 151,000, M_w/M_n 1.82, Sn content by AA analysis, 14 ppm—the order of the lower limit of detection under these experimental conditions). The purified PLLA was dissolved in chloroform and mixed with CaO or MgO (5 wt% as Ca or Mg to PLLA), and the mixture was vigorously stirred for 1 h to disperse the inorganic particles uniformly. The dispersed mixture was cast on a glass Petri dish. The obtained composite film was washed with methanol and then dried in vacuo for 48 h. Change in the molecular weight of PLLA was scarcely detected after the preparation (PLLA/CaO: M_n 158,000, M_w/M_n 1.82; PLLA/MgO: M_n 158,000, M_w/M_n 1.87).

3. Results and discussion

3.1. Dynamic pyrolysis of PLLA/CaO and PLLA/MgO composites

To examine effects of alkali earth metal oxides as catalysts for PLLA pyrolysis, CaO and MgO powder was blended with purified PLLA so as to contain 5 wt% of metal to PLLA, and thermal degradation of the composites was then conducted gravimetrically on TG/DTA in a N_2 flow. Fig. 1 shows the TG curves and differential thermogravimetric (DTG) profiles of PLLA/CaO (5 wt%) and/MgO (5 wt%) composites, which were measured at heating rate $\phi = 5$ K min^{-1}, and the results then compared with that of purified PLLA. The weight loss of purified PLLA started at about 270 °C and then proceeded smoothly to reach almost complete degradation at about 370 °C, reproducing the previous results [24]. On the other hand, the TG curves of composites shifted to rather lower temperature ranges. The TG curve of PLLA/CaO (5 wt%) showed the beginnings of degradation at about 180 °C and a smooth weight loss to 0.05 in the residual weight ratio, *w*, at about 260 °C. The weight loss of PLLA/MgO (5 wt%) began at about 210 °C and reached complete degradation at less than 300 °C, showing a rapid weight loss curve.

In DTG profiles, purified PLLA showed a main peak found at 357 °C in a higher temperature range of 320–375 °C and a shoulder at about 300 °C. PLLA/CaO (5 wt%) also exhibited a wide DTG profile in a temperature range of 180–300 °C, but had a sharper main peak at 242 °C, suggesting a rapid main degradation process after a

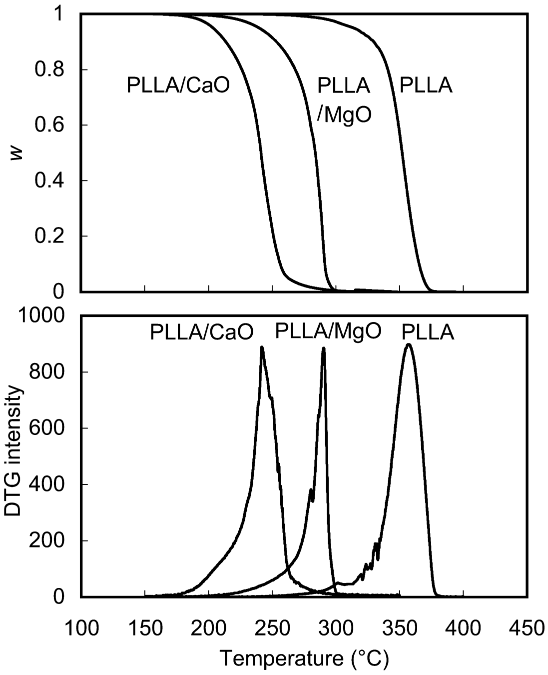


Fig. 1. TG (upper) and DTA (lower) profiles on pyrolysis of PLLA, PLLA/CaO (5 wt%), and PLLA/MgO (5 wt%) composites.

relatively slow initial process. Interestingly, PLLA/MgO (5 wt%) showed a pointed DTG profile peaking at 280 °C, which indicates a single and very rapid decomposition process. These results suggest that different decomposition pathways might be taken during pyrolysis in each case for purified PLLA, PLLA/CaO (5 wt%), and PLLA/MgO (5 wt%) composites.

3.2. Py-GC/MS analysis of pyrolyzates

Pyrolysis products of PLLA/CaO (5 wt%) and/MgO (5 wt%) composites in the temperature range of 60–400 °C were analyzed by Py-GC/MS. The results are illustrated in Fig. 2. For both the PLLA/CaO (5 wt%) and/MgO (5 wt%) composites, lactides were detected at 11.8 (meso-lactide) and 13.4 min (L,L-and D,D-lactide) as being the dominant pyrolysis products, and a small amount of cyclic oligomers other than lactide was detected in a range of 20–30 min. Quantitative summation of the peak intensities in the Py-GC/MS chromatogram showed that for both the composites the lactides comprised about 98% of the degradation products. In contrast, the pyrolysis of purified PLLA resulted in the production of a large amount of cyclic oligomers through a random degradation process as reported previously [24]. Thus, the selective lactide formation on the pyrolysis of the composites suggests that an unzipping depolymerization is the principal degradation route of PLLA/CaO (5 wt%) and/MgO (5 wt%) pyrolysis. In the previous report [25], it was assumed that the main pyrolysis process of a homogeneous material PLLA-Ca with a calcium salt end structure was the unzipping depolymerization. This proceeded through a back-biting attack from alkoxide ends upon carbonyl carbons in penultimate lactic units to produce lactide selectively. Similar reaction pathways may be the main pyrolysis process for the PLLA/CaO (5 wt%) and/MgO (5 wt%) composites.

3.3. Racemization of PLLA in pyrolysis of PLLA/CaO and PLLA/MgO composites

In Fig. 2, both pyrolyzates from PLLA/CaO (5 wt%) and/MgO (5 wt%) composites included *meso*-lactide, which is a cyclic dimer comprised of L- and D-lactate units. From quantitative calculations of the peak intensity in Fig. 2, the pyrolyzates were found to contribute 17.0 and 7.0% of *meso*-lactide to the total lactide for PLLA/CaO (5 wt%) and/MgO (5 wt%) composites, respectively. This *meso*-lactide formation is obviously due to racemization during the thermal degradation, because the original PLLA was composed of 100% L-lactate unit.

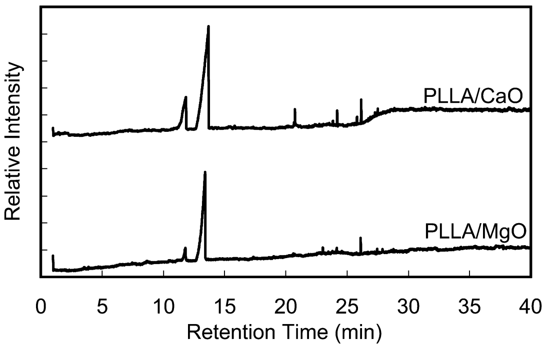


Fig. 2. Py-GC/MS chromatograms of pyrolyzates from PLLA/CaO (5 wt%) and/MgO (5 wt%) composites during a heating process at 10 °C min^{-1} from 60 to 400 °C.

As reported previously [24,25], the racemization behavior of PLLA-Ca varies markedly with temperature. To determine the racemization behavior in the pyrolysis of PLLA/CaO (5 wt%) and/MgO (5 wt%) composites, each pyrolyzate in different temperature ranges was collected and analyzed with Py-GC/MS. Results of *meso*-lactide formation in different temperature ranges are illustrated in Fig. 3, in which the *meso*-lactide content was calculated from the peak intensities at 11.8 and 13.4 min in Py-GC/MS chromatograms and the total weight loss derived from TG curves within the same temperature range. The pyrolysis of PLLA/CaO (5 wt%) showed a rather high ratio (10–20%) of racemization at temperatures lower than 250 °C, and a level of racemization lower than 2% in the temperature range 250–300 °C. In other words, in this temperature range L,L-lactide was formed selectively. Though an indication of the increase was found at 300–320 °C, no significant formation of lactides was observed at temperatures higher

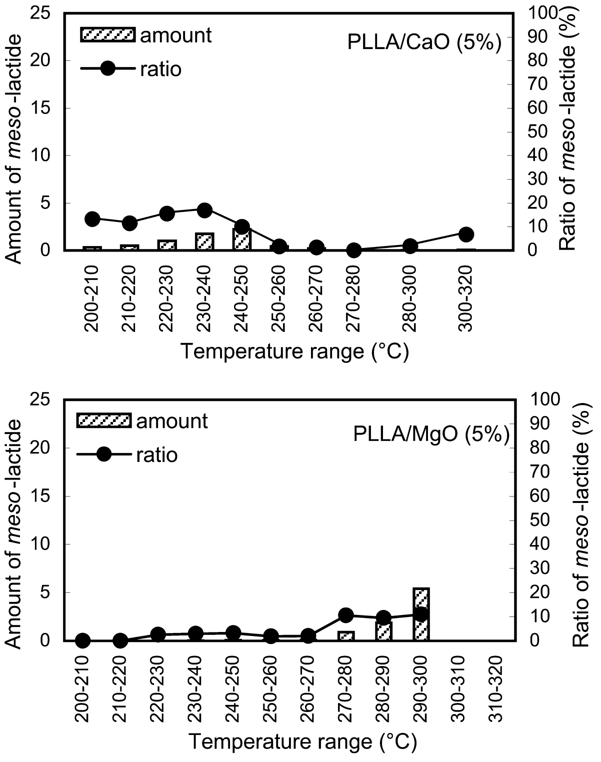


Fig. 3. Racemization on pyrolysis of PLLA/CaO (5 wt%) (upper) and PLLA/MgO (5 wt%) (lower) composites in different temperature ranges. Bar: amount of *meso*-lactide formed (integration value of TIC peaks); line: relative content ratio (%) of *meso*-lactide to total lactides.

than 300 °C, because the degradation of PLLA/CaO (5 wt%) finished at about 290 °C.

On the other hand, the pyrolysis of PLLA/MgO (5 wt%) composite exhibited a totally different racemization behavior compared to PLLA/CaO (5 wt%). At temperatures under 220 °C, volatilized pyrolyzates were scarcely observed. The lactide formation started at temperatures over 220 °C and the ratio of *meso*-lactide to the total lactide in the pyrolyzates was kept at a low level of less than 3% until 270 °C, showing selective L,L-lactide formation. Then, at temperatures over 270 °C, the *meso*-lactide ratio rose up to about 10% until the degradation was completed at about 300 °C.

The total *meso*-lactide content (7%) of PLLA/MgO (5 wt%) pyrolyzates was less than 18% of PLLA/CaO (5 wt%) pyrolyzates. This is considered to be responsible for the disappearance of the intensive *meso*-lactide formation at temperatures lower than 250 °C, which was apparent in PLLA/CaO (5 wt%) pyrolysis. The influence of temperature on the pyrolysis was examined in detail from a viewpoint of kinetics in following sections.

3.4. Kinetics of PLLA/CaO and PLLA/MgO composites pyrolysis: activation energy, E_a

To clarify the thermal degradation pathways of PLLA/-CaO (5 wt%) and/MgO (5 wt%) composites, a dynamic degradation method was carried out at different heating rates ϕ of 1–9 K min^{-1} in TG/DTA under N_2 flow.

At a certain fractional weight ratio w, the apparent activation energy E_a was determined from the slope of the log(ϕ) vs. 1/T plot according to the following equation [26, 27],

$$\frac{\mathrm{d}\log\phi}{\mathrm{d}(1/T)} = -\frac{bE_a}{R}$$

where E_a and R are the apparent activation energy of the thermal degradation and the molar gas constant, respectively. And, b is a constant in the Doyle's approximation equation [28]. Using this approach, results of E_a values for TG data of purified PLLA, PLLA/CaO (5 wt%), and PLLA/MgO (5 wt%) composites are plotted against w in Fig. 4. It should be noted that these E_a values are apparent values, because not only a variety of reactions but also a number of physical changes occur during the pyrolysis. Despite the values being apparent, the E_a value and its changes are effective in predicting the reaction, because the E_a value most likely reflects the main reaction occurring at each time and temperature.

The E_a values of purified PLLA steadily increased from 140 kJ mol^{-1} with a decrease in w to converge at about 180 kJ mol^{-1}, which is in accordance with previous results [24]. For PLLA/CaO (5 wt%), during the first half of the pyrolysis the E_a value increased from 147 to 160 kJ mol^{-1} with decrease in w, and then decreased to a final value of 125 kJ mol^{-1}, which is a value relatively near to that for the pyrolysis of PLLA-Ca (98–120 kJ mol^{-1}) [24]. This indicates that PLLA/CaO (5 wt%) composite changed its own physical and/or chemical conditions during the pyrolysis, finally approaching a similar structure to that of PLLA-Ca. On the other hand, the E_a value of PLLA/MgO (5 wt%) was kept at almost a constant value of 120–130 kJ mol^{-1} during the pyrolysis. Thus, the thermal degradation of PLLA/MgO (5 wt%) may proceed through a simple process.

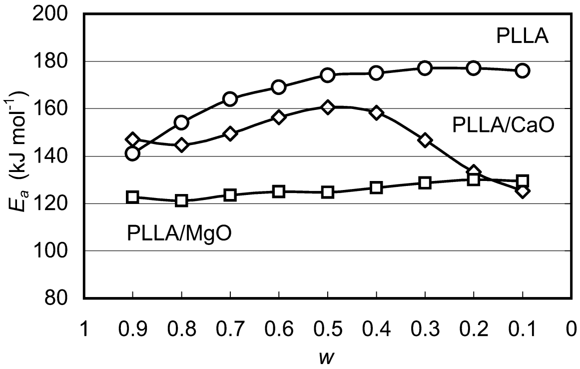


Fig. 4. Changes in E_a value during thermal degradation of PLLA, PLLA/CaO (5 wt%), and PLLA/MgO (5 wt%) composites.

In Fig. 5, the E_a values and the total of *meso*-lactide and cyclic oligomer contents were plotted against temperature. The three E_a curves for the PLLA/CaO (5 wt%), PLLA/CaO (1 wt%), and PLLA-Ca (Ca content: 210 ppm) pyrolysis look like one continuous curve changing with temperature (Fig. 5(a)). Further, this total combined curve just relates to the *meso*-lactide content of pyrolyzates in Fig. 5(b). These results demonstrate that the pyrolysis process of PLLA/CaO composite comprises at least three temperature dependent degradation stages, which are the frequent *meso*-lactide formation stage at temperatures lower than 250 °C, the dominant L,L-lactide formation stage in the temperature range of 250–320 °C, and the intensive racemization and oligomer formation stage at temperatures greater than 320 °C. Almost the same discussion was made about the pyrolysis process of PLLA-Ca alone in the previous report [25]. These results indicate that the degradation temperature shifts to a lower range because of the CaO content, whilst the degradation mechanism remains dependent on the temperature.

A similar relationship between the E_a values and *meso*-lactide and cyclic oligomer content is demonstrated on the pyrolysis of PLLA/MgO (5 wt%) and purified PLLA (Fig. 5(c) and (d)). In the case of PLLA/MgO (5 wt%) composite, it should be noted again that a few *meso*-lactide products are found at temperatures lower than 270 °C, however, both the E_a value and *meso*-lactide content gradually increased at temperatures over 280 °C and look like being linked to those of purified PLLA. The lower temperature shifts in the E_a value and content may reflect differences in the chemical properties between MgO and CaO. The production of cyclic oligomers was found only on the pyrolysis of purified

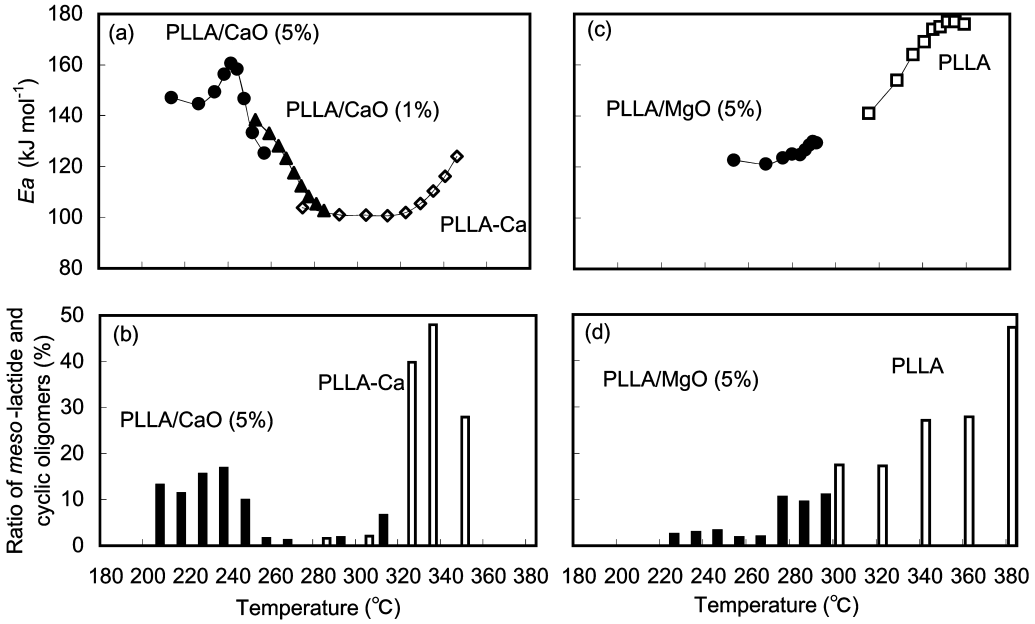


Fig. 5. Relations between E_a value and the total of *meso*-lactide and cyclic oligomers contents on pyrolysis temperature of PLLA/CaO (5 wt%), PLLA/CaO (1 wt%), PLLA/MgO (5 wt%), PLLA, and PLLA-Ca.

PLLA, because the volatilization of cyclic oligomers is mainly dependent on the temperature.

3.5. Kinetics of PLLA/CaO and PLLA/MgO composites pyrolysis: simulation analysis

Thermal degradation kinetics of the composites was studied by several analytical approaches [29–31]. In Fig. 6, the random degradation analysis plots of $\log[-\log\{1-(1-w)^{1/2}\}]$ vs. $1/T$ for experimental data of PLLA/CaO (5 wt%) (5 K min^{-1}) and model reactions are illustrated. It was observed that the degradation of PLLA/CaO (5 wt%) proceeds by an n^{th} order weight loss process at the beginning period ($1/T > 0.002$ K^{-1}, $T < 220$ °C), and is followed by a random degradation process ($L = 2-3$, where L is the least number of repeating units of oligomer not volatilized) ($1/T = 0.0020 - 0.00187$ K^{-1}, $T = 220 - 260$ °C). This process is similar to that of purified PLLA [24]. However, it should be noted that the random degradation curve gradually shifted out of the simulation lines for random degradation ($L = 2-3$) toward an end stage, in which the E_a value also approached that of PLLA-Ca pyrolysis as above mentioned. Thus, it was considered that the degradation of PLLA/CaO (5 wt%) started with a similar degradation behavior to that of purified PLLA, and then changed to approximate that of PLLA-Ca with a diffusion of CaO into the PLLA matrix and an increase in temperature.

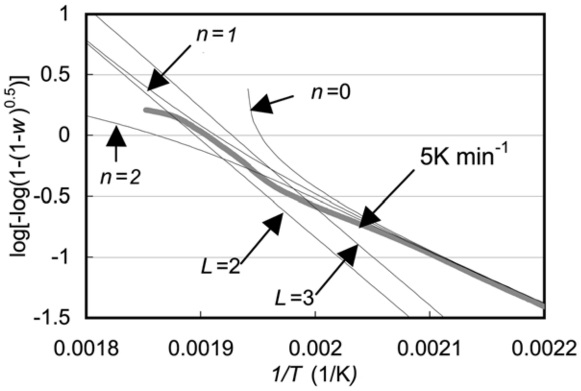


Fig. 6. Random degradation simulation for pyrolysis of PLLA/CaO (5 wt%) composite. Heating rate: 5 K min^{-1}.

In Fig. 7, the random degradation and integral analyses results of experimental data of PLLA/MgO (5 wt%) (5 K min^{-1}) were plotted along with model reaction simulations. The pyrolysis of PLLA/MgO (5 wt%) composite also started according to an n^{th} order weight loss process (Fig. 7(a)). Then, the degradation curve deviated from the n^{th}-order simulation by gradually accelerating as shown in the integral analysis plot (Fig. 7(b)). Considering the dominant L,L-lactide formation and the E_a value remained at 120–130 kJ mol^{-1} over the whole pyrolysis, it can be assumed that a simple degradation process of PLLA/MgO (5 wt%) underwent a gradual acceleration with the diffusion of MgO into the PLLA matrix.

These kinetic results indicate that both the inorganic materials and the temperature mutually interacted in the pyrolysis of PLLA composites in controlling the mechanism.

3.6. Mechanism of PLLA/CaO and PLLA/MgO composites pyrolysis

When PLLA/CaO (5 wt%) composite was heated in N_2 flow, the decomposition of PLLA chains will be started by

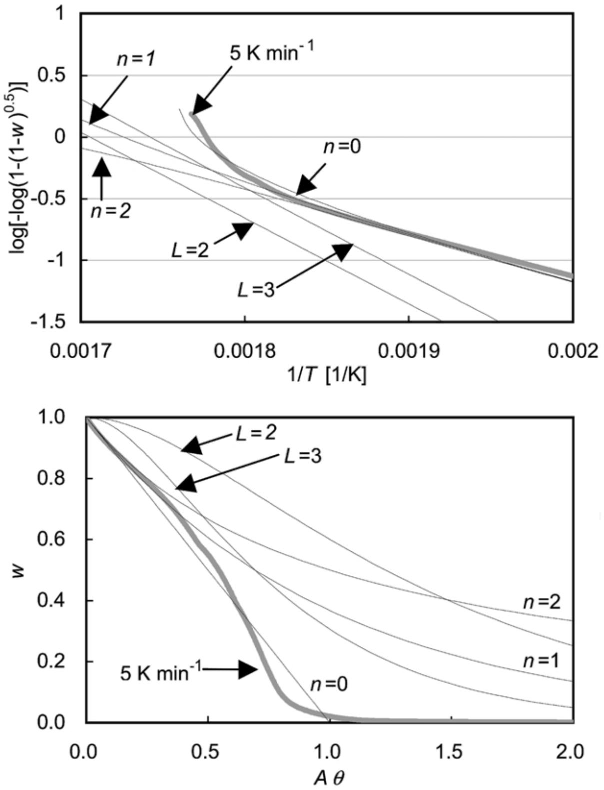
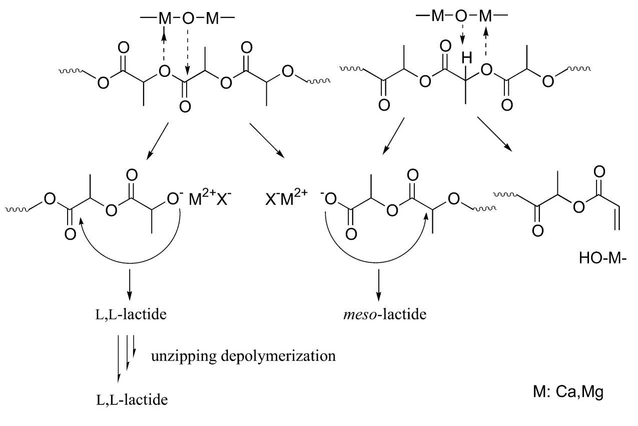


Fig. 7. Random degradation (upper) and integral (lower) simulations for pyrolysis of PLLA/MgO (5 wt%) composite. Heating rate: 5 K $\min^{-1}$.

reactions with CaO and followed by a backbiting reaction from chain-end anions as shown in Scheme 1. This may occur around the CaO particles in a lower temperature range. This reaction may correspond to the initial n th-order weight loss process in Fig. 6. Then, with increase in temperature, Ca species will diffuse into the PLLA matrix and cause extensive random degradation and subsequent backbiting reactions. The lower temperature may restrict the distillation of cyclic dimers, L,L- and *meso*-lactide. Further, it is considered that with increase in temperature, the unzipping depolymerization from alkoxy anion dominates so as to produce L,L-lactide preferentially.



Scheme 1. Expected degradation mechanism of PLLA/CaO and/MgO composites.

On the other hand, the weight loss of PLLA/MgO (5 wt%) composite started at 210 °C and continued in earnest over about 250 °C, which is 30 °C higher than PLLA/CaO (5 wt%). At this temperature, the unzipping depolymerization from alkoxy anion would be dominant and PLLA/MgO (5 wt%) would degrade smoothly through the depolymerization, resulting in a high yield of L,L-lactide.

It is considered that these differences between PLLA/-CaO (5 wt%) and/MgO (5 wt%) composites are due to the electronegativity of Ca and Mg, which are 1.00 and 1.31 eV, respectively [32]. Since Mg is of a lower basicity than Ca, the reaction between PLLA and MgO may merely occur at a lower level and the degradation may also slightly proceed at temperatures less than 250 °C, at which temperature CaO can form enough salt end structures to degrade the PLLA matrix. When the temperature becomes higher than 250 °C, the reaction between MgO and PLLA will be accelerated, and at the same time the unzipping depolymerization will be allowed to start, resulting in the rapid decomposition of PLLA/MgO (5 wt%) composite and the selective L,L-lactide formation.

Therefore, the thermal degradation of PLLA/MgO (5 wt%) composite can regenerate the L,L-lactide predominantly at temperatures lower than 270 °C, even when undergoing a heating process from ambient temperature. The *meso*-lactide formation experienced in the heating process of PLLA/CaO (5 wt%) composite can be avoided by using MgO instead of CaO.

3.7. Isothermal degradation of PLLA/CaO and PLLA/MgO composites

To confirm that the specific thermal degradation behavior is dependent on the temperature, the isothermal degradation of PLLA/CaO (5 wt%) and/MgO (5 wt%) composites was conducted in TG and Py-GC/MS. The same heating program: rapid heating from 60 to 250 °C at a heating rate of 20 °C $\min^{-1}$ and holding at 250 °C for 10 min, was applied to each. Both TG curves of the composites showed almost complete decomposition of PLLA under these conditions. Py-GC/MS profiles of pyrolyzates from the composites are illustrated in Fig. 8. The isothermal degradation of PLLA/CaO (5 wt%) at 250 °C resulted in the production of 12.1 and 1.7% of *meso*-lactide and cyclic oligomers, respectively (Fig. 8(a)), while the degradation of PLLA/MgO (5 wt%) showed the production of 2.6 and 1.3% of *meso*-lactide and cyclic oligomers, respectively (Fig. 8(b)). In these cases, the formation of D,D-lactide must be less than the *meso*-lactide formation. These results were determined through the GC analysis of the pyrolyzates on the isothermal degradation of PLLA/MgO (5 wt%) at 220 °C for 2 h in the glass tube oven. Fig. 9 shows that almost the same result was obtained with the pyrolyzates composed of dominant L,L-lactide, a small amount of *meso*-lactide, and a trace amount of D,D-lactide. This is in

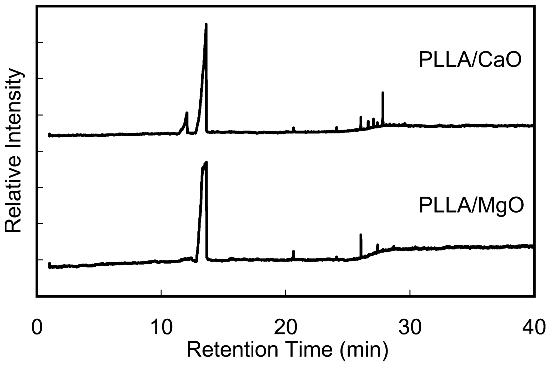


Fig. 8. Py-GC/MS chromatograms of pyrolyzates from PLLA/CaO (5 wt%) and/MgO (5 wt%) composites on a heating process: dynamic heating from 60 to 250 °C at heating rate of 20 °C min^{-1} and isothermal heating at 250 °C for 10 min.

accordance with our previous results in relation to the thermal degradation of the calcium salt end-capped PLLA-Ca [24,25]. Thus, the total yield of lactides in the isothermal degradation of PLLA/CaO (5 wt%) and/MgO (5 wt%) should be more than about 98% and the selectivity of L,L-lactide formation for these two composites should be more than about 80 and 95%, respectively.

4. Conclusions

In conclusion, the thermal degradation of PLLA/CaO (5 wt%) and/MgO (5 wt%) composites was studied, and compared with that of pure PLLA. Though the pure PLLA degraded with extensive racemization and production of oligomers other than L,L-lactide, the composites showed different thermal degradation behavior without the oligomers being produced and with limited racemization. CaO markedly decreased the thermal degradation temperature of the composite, but resulted in some racemization at lower temperatures of less than 250 °C. This is because of the formation of the calcium carboxylate end structure and the subsequent S_N2 attack from the carboxylate anion to the asymmetrical carbon atom in the penultimate unit. In the case of PLLA/MgO (5 wt%) composite, the reaction between MgO and PLLA may be limited at low temperatures of less than 250 °C, because of the lower basicity of Mg compared to Ca, resulting in the racemization experienced in PLLA/CaO pyrolysis being depressed. However, at temperatures higher than 250 °C, the reaction between PLLA and MgO occurred smoothly causing the unzipping depolymerization, and resulting in selective L,L-lactide production.

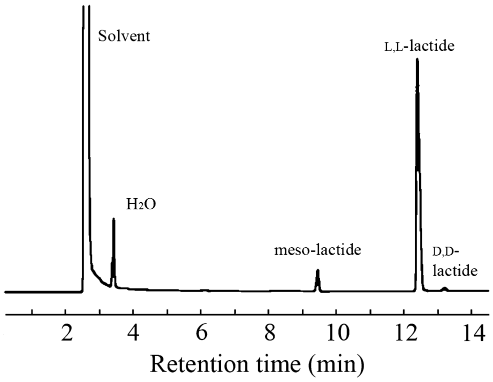


Fig. 9. GC chromatogram for volatile pyrolyzates of PLLA/MgO (5 wt%) at 220 °C for 2 h in a glass tube oven.

Therefore, a practical method for the feedstock recycling to L,L-lactide from PLLA waste will be possible by using the PLLA/MgO composite.

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