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Thermal degradation behavior of poly(lactic acid) in a blend with polyethylene

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ABSTRACT: Poly(L-lactic acid) (PLLA) is a candidate for feedstock recycling materials, because it easily depolymerizes back into the cyclic monomer, L,L-lactide. In order to examine the recycling of PLLA from blends with other kinds of polymers, a polymer blend of PLLA and linear low-density polyethylene (LLDPE) was prepared and thermally degraded with a degradation catalyst: magnesium oxide (MgO) in a TG/DTA and Py-GC/MS. To clarify the influence of LLDPE ingredient in the blend, the thermal degradation data were analyzed kinetically using two simulation methods: integration and random degradation analytical methods. From the results, it was found that PLLA was effectively depolymerized in the presence of MgO into L,L-lactide with a low racemization ratio, and that LLDPE had no effect on the feedstock recycling of PLLA.

Introduction

To move towards the more sustainable society predicted for the near future, renewable resources will need to be used more effectively. In this regard poly(L-lactic acid) (PLLA) has been attracting the attention of many researchers because of its biomass-origin and recyclability based on its biodegradation, hydrolysis, and depolymerization functions. However, the biodegradability of PLLA is relatively poor because it is broken down by only a few kinds of microorganisms, such as, the *Amycolatopsis* and *Streptomyces* species[1,2] or a combination of chemical and bio-reactions in compost[3]; this is in contrast to the ease with which it depolymerises under heating. Thus, PLLA has potential as a feedstock recycling material suitable for use in a future sustainable society system.

The physical properties of PLLA are comparatively similar to polystyrene and polyethylene terephthalate in terms of transparency and mechanical properties.[4] Moreover, because of the characteristic advantage of its carbon neutral feature, PLLA has started being used in automobiles, as well as in electric and electronic equipment; for example, as a spare tire cover in automobiles[5,6], or for molding parts of portable disk players and personal computers.[7,8]

Although PLLA is synthesized from renewable resources such as corn, and sugarcane, the production of the polymeric form requires much processing, energy, and fuel. Typically, PLLA is being produced via starch saccharification, lactic acid fermentation, oligomerization, cyclic monomer formation, and ring-opening polymerization of the cyclic monomer. If the feedstock recycling of PLLA to the cyclic monomer, L,L-lactide, is able to be achieved effectively, it will then become possible to renew PLLA by the shortest, most energy efficient route. Once this is achieved there is no doubt that PLLA will become widely used as a basic material in a sustainable society.

Recently, the depolymerization behavior of PLLA has been investigated in detail. In many reports, depolymerization kinetics, catalysts, and the effects of chemical structures have been discussed. Fan *et al*. in particular, have been investigating alkali earth metals, such as magnesium oxide (MgO), as depolymerization catalysts for the feedstock recycling of PLLA, where in this case MgO acts as an

effective catalyst for the depolymerization of PLLA in a temperature range of 250-300 °C with slight racemization to *meso*-lactide (Scheme 1).[9] In the practical feedstock recycling of PLLA, it is difficult to avoid contamination from other kinds of polymers, especially polyolefins. Moreover, the polymer alloy is a common way to improve the property of PLLA.[10] Thus, to achieve the selective feedstock recycling of PLLA from such polymer blends, the influence of contaminants and blended polymers on the recycling of PLLA should be clarified. A blend of PLLA and polyethylene was the subject of a report by Raghavan and Emekalam[11], but there has been no discussion on the thermal degradation behavior of the PLLA ingredient.

In this paper, to clarify the influences of coexisting polyolefins on the feedstock recycling of PLLA, a blend of PLLA and linear low-density polyethylene (LLDPE) was prepared and thermally degraded with MgO catalyst. The degradation behavior of the blend was investigated kinetically and mechanistically, comparing it with the degradation behavior of PLLA homo-film.
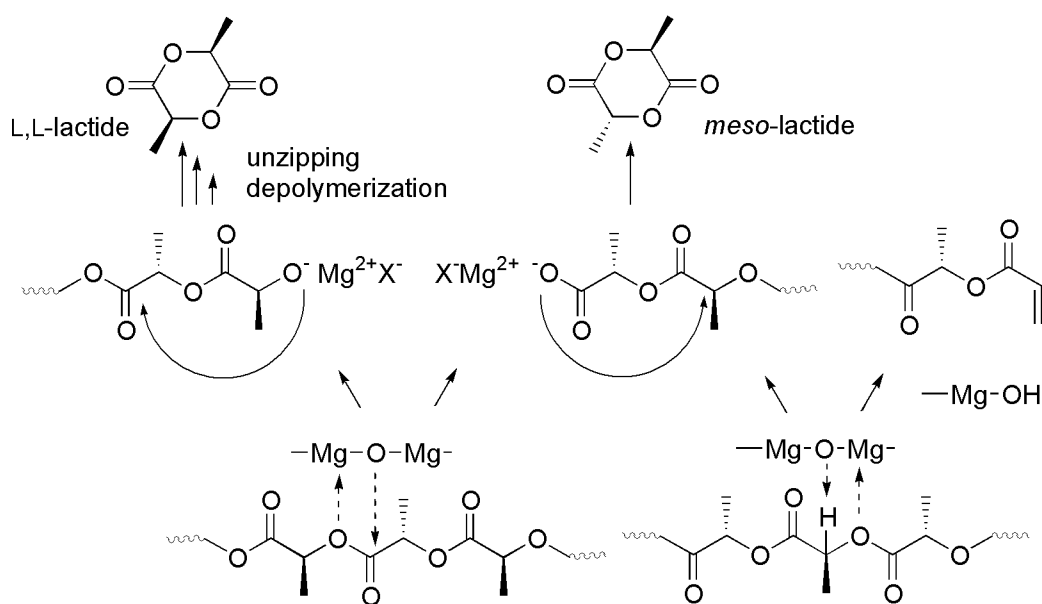
Scheme 1. Proposed depolymerization mechanism of PLLA with MgO.

Experimental Section

Materials

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Monomer L,L-lactide, was obtained from Shimadzu Co. Ltd. and purified by recrystallizing three times from dry toluene and one time from dry ethylacetate, it was then vacuum-dried, and stored in a N_2 atmosphere. After the purification, *meso*-lactide was not detectable by gas chromatography (GC). Polymerization catalyst Sn(2-ethylhexanoate)$_2$ [Sn(Oct)$_2$], obtained from Wako Pure Chemical Industries, Ltd., was distilled under a reduced pressure before use. Magnesium Oxide, MgO, was purchased from Wako Pure Chemical Industries, Ltd. and used after drying at 120 °C for 1 h. Linear low-density polyethylene (LLDPE, NEO-ZEX 2015M, MFI = 12 g·min^{-1}, T_m 122 °C) was purchased from Mitsui Chemicals, Inc. Other chemicals, chloroform (> 99.0 %), methanol (> 99.5 %), and xylene (> 80 %) were purchased from Wako Pure Chemical Industries, Ltd. and distilled before use.

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 PLLA 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.

Preparation of PLLA/LLDPE/MgO composite and PLLA/LLDPE blend films

PLLA was synthesized by the ring-opening polymerization of L,L-lactide catalyzed by Sn(Oct)$_2$ in the same way as described in a previous report.[12] After the polymerization, obtained raw product was purified by firstly extracting the residual catalyst 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 to obtain purified PLLA (M_n 349

000, M_w 568 000; Sn content by AA analysis 17.7 ppm, which was about the lowest limit of detection under the experimental conditions).

A mixture of the purified PLLA 200 mg, LLDPE 800 mg, and MgO 10 mg was added into xylene 30 mL. The mixture was vigorously stirred for 30 min at room temperature and for 1 h at 130 °C to completely dissolve the PLLA and LLDPE, and then cast on a glass Petri dish. Obtained composite film of PLLA/LLDPE/MgO in the weight ratio 20:80:1 (wt/wt/wt), PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)], was dried *in vacuo* for 24 h at room temperature. PLLA/LLDPE [20:80 (wt/wt)] blend film was prepared in a similar manner but without MgO.

Thermal degradation of blend and composite samples

Thermal degradation behavior of PLLA ingredients from the PLLA/LLDPE/MgO composite and PLLA/LLDPE blend samples was analyzed by the thermogravimeter (TG) and the pyrolysis-gas chromatograph/mass spectrometer (Py-GC/MS).

TG was conducted on a Seiko Instrumental Inc. EXSTAR 6200 TG/DTA system in an aluminum pan (5 mm φ) under a constant nitrogen flow (100 mL·min^{-1}) using about 5 mg of film sample. Dynamic thermal degradation of the sample was conducted at prescribed heating rates, φ, of 1, 3, 5, 7, and 9 °C·min^{-1} in a temperature range of 60 to 500 °C. The thermal degradation data were collected at regular intervals (about 20 times per degree) by an EXSTAR 6000 data platform and recorded into an analytical computer system.

Py-GC/MS was conducted on a Frontier Lab PY-2020D double–shot pyrolyzer connected to a Shimadzu GC/MS-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 was used as a carrier gas under a constant flow of 100 mL·min^{-1}. In the dynamic heating process with Py-GC/MS, about 0.5 mg of sample was added to the pyrolyzer and heated from 60°C to a prescribed temperature at a heating rate of 9 °C·min^{-1}. Volatile pyrolysis products were introduced into the GC through a 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, and 320 °C for 13 min. Mass spectrum measurements were recorded 2 times·s⁻¹ during this period.

Results and Discussion

Weight loss behavior

To clarify the thermal degradation behavior of PLLA ingredient in a polymer blend with a commodity polymer, linear low-density polyethylene (LLDPE), PLLA/LLDPE blend and PLLA/LLDPE/MgO composite films were prepared using a solution blending method with xylene as a solvent to obtain homogeneous films. In this study, the purified PLLA, which has a residual Sn atom concentration of 17.7 ppm, was used, because even a trace amount (60 ppm) of Sn influences the degradation behavior of PLLA.[13]

Thermogravimetric (TG) curves of PLLA, LLDPE, PLLA/LLDPE [20:80 (wt/wt)], PLLA/MgO [100:1 (wt/wt)], and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] films are illustrated in Figure 1. The TG curve of PLLA/LLDPE [20:80 (wt/wt)] blend film showed a 2-step degradation process, clearly reflecting each degradation process of the PLLA and LLDPE ingredients. Each degradation temperature range was in the same temperature range with that of the PLLA or LLDPE homo-films, and the weight loss ratio in each step was compatible with the composition ratio of each ingredient. These results suggest that the degradation of PLLA and LLDPE ingredients proceeded independently; that is, they did not influence each other.

In the TG curve of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] film, the degradation temperature range of PLLA ingredient shifted to a lower temperature range by about 70 °C to become consistent with the degradation temperature range of PLLA/MgO [100:1 (wt/wt)]; whilst the degradation temperature range of LLDPE ingredient remained in the same temperature range as that of the LLDPE homo-film. These

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results clearly indicate that MgO functioned selectively as a depolymerization catalyst of PLLA ingredient, but not for LLDPE ingredient.
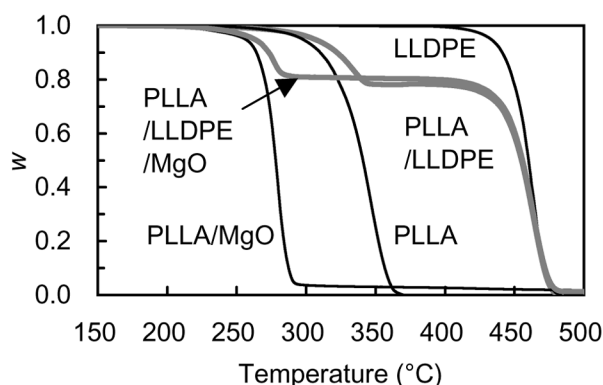

Figure 1. Thermogravimetric curves of PLLA, LLDPE, PLLA/LLDPE [20:80 (wt/wt)], PLLA/MgO [100:1 (wt/wt)], and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] films at 5 °C·min^{-1} in a constant nitrogen flow (100 mL·min^{-1}).

Changes in activation energy: E_a

Influences of LLDPE ingredient on the pyrolysis of PLLA ingredient in a PLLA/LLDPE blend were evaluated in terms of kinetic parameters. First, the activation energy, E_a, on the degradation of PLLA, LLDPE, PLLA/MgO [100:1 (wt/wt)], PLLA/LLDPE [20:80 (wt/wt)], and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] films was estimated by the dynamic heating method with TG under N$_2$ flow, in which different heating rates, φ, of 1, 3, 5, 7, and 9 °C·min^{-1} were applied for each sample. The E_a value at a certain fractional weight ratio, w, was calculated using Doyle's and Reich's methods.[14-16] In Figure 2, changes in E_a values of the PLLA, LLDPE, and PLLA/LLDPE [20:80 (wt/wt)] films are plotted against w. The E_a values on the thermal degradation of PLLA and LLDPE homo-films were 141~176 and 237-256 kJ·mol^{-1}, respectively. The E_a curve of PLLA/LLDPE [20:80 (wt/wt)] clearly showed a two-step reaction, where the E_a value in the first-step increased gradually from 128 to141 kJ·mol^{-1} in a range of w = 0.9-0.8, and in the second-step (w = 0.7-0.1) shifted into a range of 215-252 kJ·mol^{-1}, moving close

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to the E_a curve of LLDPE homo-film degradation. Thus, this result demonstrates that the thermal degradation of PLLA and LLDPE ingredients do not mutually influence one another during the pyrolysis of the blend film.
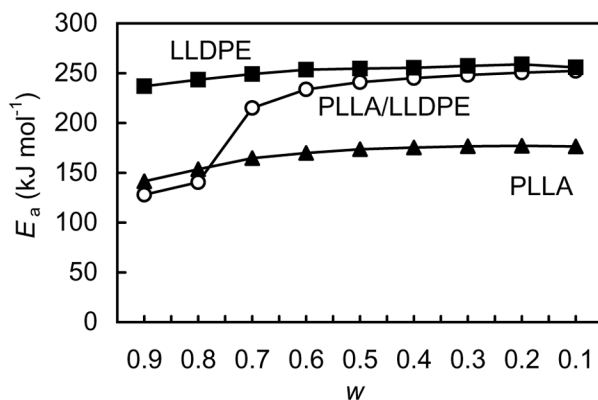

Figure 2. Changes in E_a values on pyrolysis of PLLA, LLDPE, and PLLA/LLDPE [20:80 (wt/wt)] blend films.

To clarify the effects of MgO on the thermal degradation of blend film, changes in E_a values on the pyrolysis of PLLA, PLLA/MgO [100:1 (wt/ wt)], PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)], and LLDPE films are plotted against temperature as shown in Figure 3. In the presence of MgO, the E_a value of the first step in the degradation of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] film was nearly constant at 116-122 kJ·mol^{-1} in a temperature range of 273-289 °C. This value was different from that of PLLA homo-film, being nearly the same value as that of PLLA/MgO [100:1 (wt/ wt)]. The E_a value in the second step at temperatures higher than 430 °C agreed with that on the pyrolysis of LLDPE homo-film. These results indicate that MgO selectively catalyzed the degradation of PLLA without influencing the LLDPE degradation.
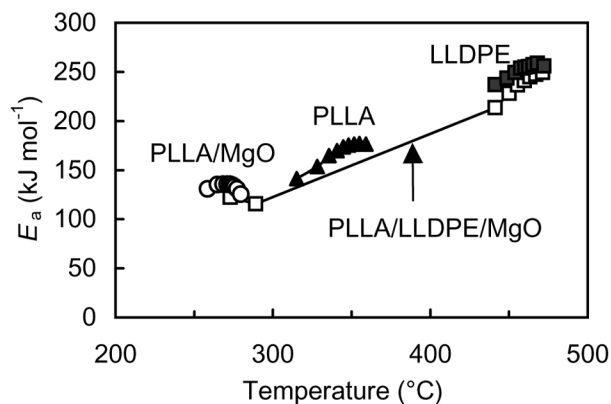
Figure 3. Changes in E_a values on pyrolysis of PLLA, PLLA/MgO [100:1 (wt/wt)], and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)], and LLDPE films.

Pyrolysis products

Pyrolysis products from PLLA/LLDPE [20:80 (wt/wt)] and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite films were analyzed with Py-GC/MS in temperature ranges of 60 °C to prescribed temperatures at a heating rate of 9 °C·min^{-1}. Total ion count (TIC) profiles of the Py-GC/MS measurement are illustrated in Figure 4. Since the weight loss in the 1st-step of PLLA/LLDPE [20:80 (wt/wt)] degradation started at around 300 °C and ended at 350 °C as shown in Figure 1, the TIC profile of the sample was recorded in a temperature range encompassing these values (Figure 4a). At temperatures over 300 °C, some peaks appeared in retention time ranges of 11-13 and 23-30 min, which were assigned to lactides and cyclic oligomers, respectively. In the profiles, the production of *meso*-lactide was clearly detected as a peak in a retention time range of 11-12 min, which may have arisen from racemization through the ester-semiacetal tautomerization at temperatures over 300 °C.[17] On the other hand, in the case of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite film, TIC profiles were measured in a range of 250 to 280 °C (Figure 4b), corresponding to the temperature range of the 1st-step weight loss of the sample in Figure 1. In the profiles, the peak of L,L-lactide in a retention time range of 12-13 min was dominant and the peak of *meso*-lactide also appeared with a weak intensity at 280 °C. Interestingly, in this temperature range, neither cyclic oligomers nor other pyrolysis products

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originating from LLDPE were detected. These results reveal that MgO functioned as a depolymerization catalyst of PLLA effectively and selectively to produce L,L-lactide even in the polymer blend with LLDPE.
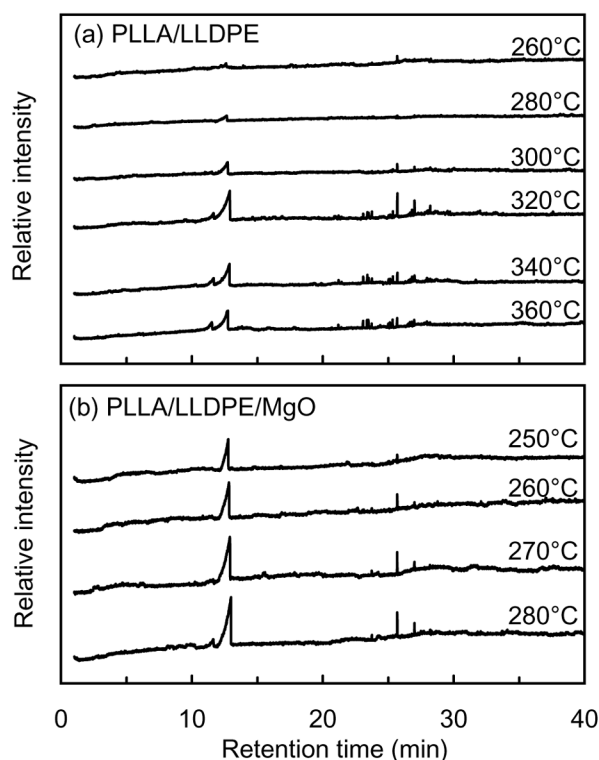

Figure 4.   Py-GC/MS chromatograms of pyrolyzates from (a) PLLA/LLDPE [20:80 (wt/wt)] and (b) PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] on a dynamic heating process at a heating rate of 9 °C min^{-1} from 60 °C to various prescribed temperatures.

A quantitative composition ratio of the volatile pyrolysis products was calculated from the TIC value of each peak in the Py-GC/MS profiles. The analytical results of pyrolysis products from the PLLA/LLDPE [20:80 (wt/wt)] and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] films in temperature ranges of 60 °C to prescribed temperatures are illustrated in Figure 5. In Figure 5a, PLLA/LLDPE [20:80 (wt/wt)] showed *meso*-lactide generation of about 10 % at 300 °C, with the sample beginning to decrease in weight beyond this temperature. Cyclic oligomers first detected at 300 °C, increased to reach about 20 % over 320 °C. On the other hand, from PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] film,

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L,L-lactide was generated selectively by 270 °C (Figure 5b). A small amount of meso-lactide was detected at 280 °C, but by this temperature the sample had already lost most of its weight as shown in Figure 1. These quantitative results revealed that MgO is able to work effectively as a depolymerization catalyst of PLLA even in the polymer blend.
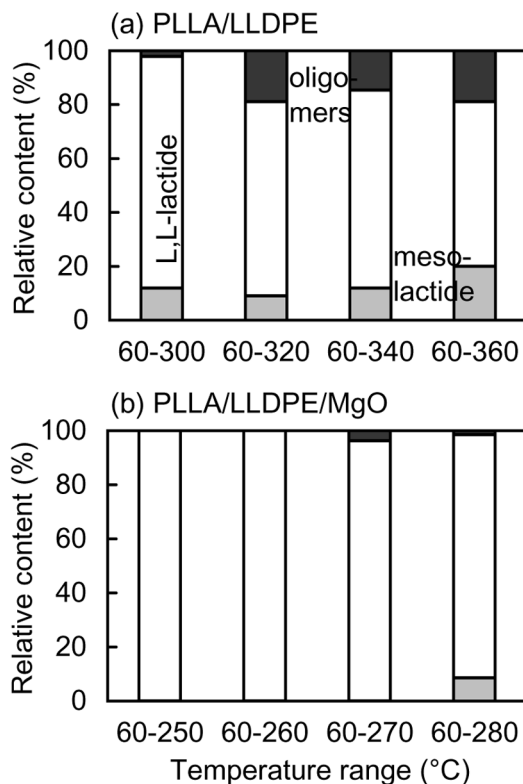

Figure 5. Pyrolysis products from (a) PLLA/LLDPE [20:80 (wt/wt)] and (b) PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] on a dynamic heating process in prescribed temperature ranges at a heating rate of 9 °C min^{-1}.

Simulation analysis of thermal degradation

To clarify the thermal degradation behavior of PLLA ingredient in PLLA/LLDPE blends, the kinetic parameters: n, L, and A were evaluated by using several analytical approaches: the random degradation analysis[18] and the integration methods[19], where n is the reaction order of an nth-order reaction, L is defined as the least number of repeating units of oligomer not volatilized, and A is the pre-exponential factor. The values of n and L were given for the nth-order and the random degradation reactions,

respectively. Generally, the L value increases with increase in pyrolysis temperature. The kinetic parameters were determined by comparing actual results with various simulation curves of model reactions, which were generated using the corresponding kinetic parameters: E_a, A, n, and L based on the methods reported by Ozawa[20] and Nishida et al.[21]

To simulate the degradation behavior of PLLA ingredient in the blend film, the random degradation analysis plots of $\log[-\log\{1-(1-w)^{0.5}\}]$ vs. $1/T$ for PLLA/LLDPE [20:80 (wt/wt)] (9 °C·min^{-1}) in a range of w = 1.0~0.8 together with model reaction simulations are plotted in Figure 6. The model reaction simulations for the random degradations exhibit almost linear plots. On the other hand, each nth-order model reaction simulation is represented by a characteristic curve. The simulation with the kinetic parameter values: activation energy E_a = 141 kJ·mol^{-1} and pre-exponential value A = 5.5 × 10^9 s^{-1} revealed that the experimental data plot conformed to the nth-order reaction simulations at the initial stage and then shifted to the random degradation with L = 3 ~ 4. The increase in the L value agrees with the higher oligomer production detected in the Py-GC/MS spectrum (Figure 5a). This result is basically the same as the behavior exhibited by purified PLLA in an initial stage of pyrolysis.[12]
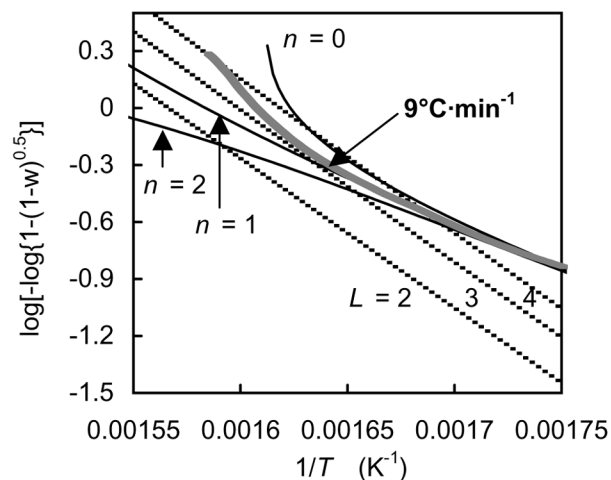

Figure 6. Plots of $\log[-\log\{1-(1-w)^{0.5}\}]$ vs. $1/T$ for thermogravimetric data of PLLA/LLDPE [20:80 (wt/wt)] in a range of w = 1.0-0.8 at a heating rate of 9 °C·min^{-1} and for model reactions using the

kinetic parameters: E_a = 141 kJ·mol^{-1} and A = 5.5×10^9 s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L = 2 ~ 4).

   To evaluate the degradation behavior of PLLA ingredient in the composite with MgO, PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite film was investigated by the integration method, through which a multi-step reaction can be easily analyzed.[22] In Figure 7, the weight fraction w is plotted against $A\theta$, where θ is defined as the reduced time: $(E_a/\varphi R)p(y)$ using the gas constant R, heating rate φ, and function $p(y)$.[20] Simulation curves are also plotted with kinetic parameter values: E_a = 118 kJ·mol^{-1} and A = 7.2 × 10^8 s^{-1}. The experimental curve in a range of w = 1.0~0.8 gave a straight line parallel to the simulation plot of the zero-order weight loss curve as a main process after the induction period. This induction period must be caused by a diffusion process of Mg^{2+} from the MgO powder surface to form an active species for the depolymerization as indicated in previous reports[9,23], which used various Ca and Mg compounds. The straight line, parallel to the zero-order weight loss curve, may be due to the acceleration effect of depolymerization[9] by the diffused Mg^{2+} and/or a combination of the unzipping depolymerization and a random intermolecular transesterification.[13] Thus, this degradation behavior of PLLA ingredient is no different from that of the PLLA/MgO composite[9], and indicates no influence of the coexisting LLDPE.
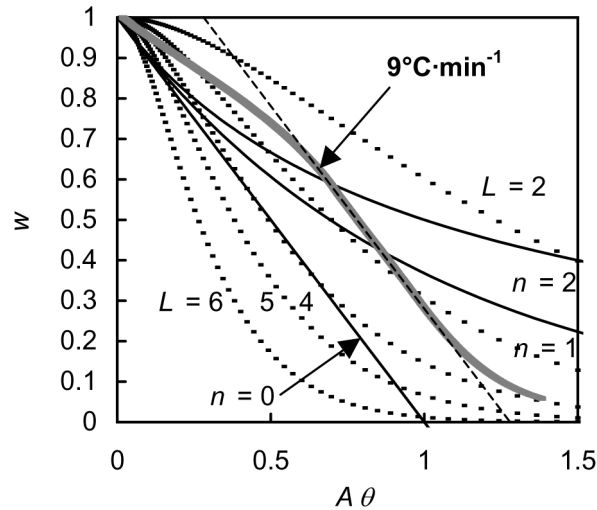
Figure 7. Plots of experimental $A\theta$ vs. w for thermogravimetric data of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] in a range of w = 1.0-0.8 at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: E_a = 118 kJ·mol^{-1} and A = 7.2×10^8 s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L=2-6).

Because no induction period was observed, the degradation behavior of LLDPE ingredient in PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite was also analyzed by the random degradation analysis method. In Figure 8, the experimental curve in a range of w = 0.7~0.1 and the simulation curves are plotted with the kinetic parameter values: E_a = 244 kJ·mol^{-1} and A = 3.8 × 10^{14} s^{-1}. As a result, it was found that the degradation of LLDPE ingredient proceeded by the random degradation (L = 6~7). Nearly the same kinetic result was obtained by the thermal degradation of LLDPE homo-film, in which the degradation was evaluated as the random degradation (L = 6~9) (Figure 9). Thus, these results revealed that there is no influence of PLLA and MgO on the LLDPE degradation.
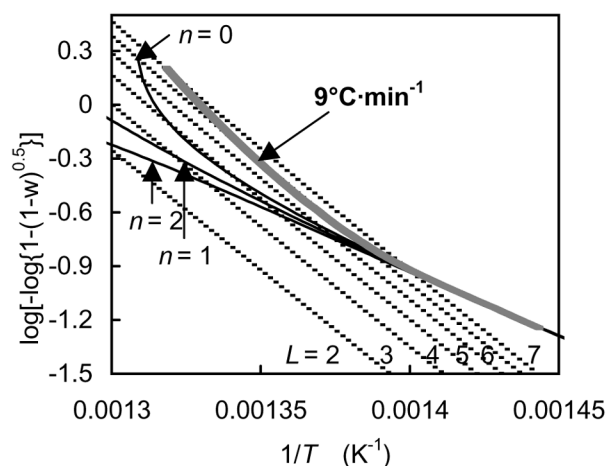
Figure 8. Plots of $\log[-\log\{1-(1-w)^{0.5}\}]$ vs. $1/T$ for thermogravimetric data of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] in a range of $w = 0.7\text{-}0.1$ at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: $E_a = 244$ kJ·mol^{-1} and $A = 3.8\times10^{14}$ s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L= 2 ~ 7).

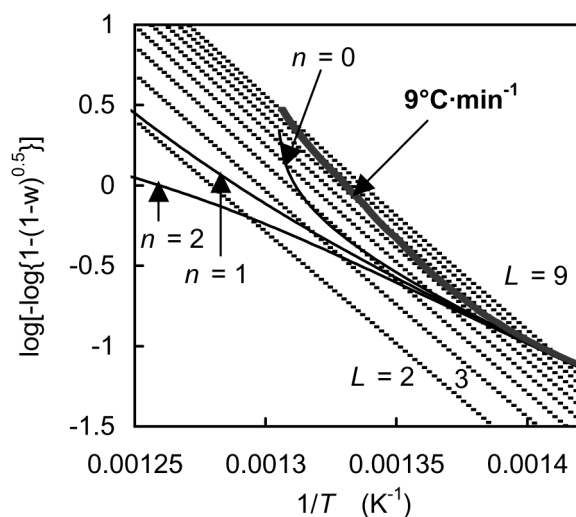**Figure 9**. Plots of $\log[-\log\{1-(1-w)^{0.5}\}]$ vs. $1/T$ for thermogravimetric data of LLDPE at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: $E_a = 255$ kJ·mol^{-1}, $A = 2.0\times10^{15}$ s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L= 2 ~ 9).

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Degradation mechanism

Based on the above-mentioned results, the PLLA ingredient in PLLA/LLDPE [20:80 (wt/wt)] film must be degraded randomly according to the many kinds of well-known degradation reactions to give not only L,L-lactide but also diastereoisomers and cyclic oligomers. On the other hand, the PLLA ingredient in the PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite film was depolymerized by the catalytic reaction of MgO to give L,L-lactide dominantly. It is considered that the thermal degradation of PLLA ingredient proceeded mainly according to the unzipping depolymerization in the presence of MgO as the degradation mechanism of the PLLA/MgO composite[9] as shown in Scheme 1. Moreover, the coexisting LLDPE must not participate in the degradation process of the PLLA ingredient.

Therefore, it is clear that MgO is an ideal catalyst for the feedstock recycling of PLLA when it forms a mixture with LLDPE.

Conclusions

To clarify the thermal degradation behavior of PLLA ingredient as a blend or when forming a mixture with other kinds of polymers, a polymer blend of PLLA and LLDPE was prepared and thermally degraded with the degradation catalyst MgO in a TG/DTA and Py-GC/MS. The thermal degradation of PLLA ingredient in PLLA/LLDPE 20:80 (wt/wt) blend proceeded randomly to give not only L,L-lactide but also *meso*-lactide and cyclic oligomers; while the PLLA ingredient in PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] composite depolymerized according to the unzipping reaction to produce the L,L-lactide dominantly. The kinetic analysis of TG data indicated similar parameter values to that of PLLA/MgO without LLDPE ingredient. Consequently, PLLA is effectively depolymerized by MgO to give L,L-lactide even when it forms a blend with LLDPE, meaning that LLDPE has no effect on the feedstock recycling of PLLA.

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Scheme and Figure Captions

Scheme 1. Proposed depolymerization mechanism of PLLA with MgO.

Figure 1. Thermogravimetric curves of PLLA, LLDPE, PLLA/LLDPE [20:80 (wt/wt)], PLLA/MgO [100:1 (wt/wt)], and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] films at 5 °C·min^{-1} in a constant nitrogen flow (100 mL·min^{-1}).

Figure 2. Changes in E_a values on pyrolysis of PLLA, LLDPE, and PLLA/LLDPE [20:80 (wt/wt)] blend films.

Figure 3. Changes in E_a values on pyrolysis of PLLA, PLLA/MgO [100:1 (wt/wt)], and PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)], and LLDPE films.

Figure 4. Py-GC/MS chromatograms of pyrolyzates from (a) PLLA/LLDPE [20:80 (wt/wt)] and (b) PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] on a dynamic heating process at a heating rate of 9 °C min^{-1} from 60 °C to various prescribed temperatures.

Figure 5. Pyrolysis products from (a) PLLA/LLDPE [20:80 (wt/wt)] and (b) PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] on a dynamic heating process in prescribed temperature ranges at a heating rate of 9 °C min^{-1}.

Figure 6. Plots of log[-log{1-(1-w)$^{0.5}$}] vs. 1/T for thermogravimetric data of PLLA/LLDPE [20:80 (wt/wt)] in a range of w = 1.0-0.8 at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: E_a = 141 kJ·mol^{-1} and A = 5.5×10^9 s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L = 2 ~ 4).

Figure 7. Plots of experimental $A\theta$ vs. w for thermogravimetric data of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] in a range of w = 1.0-0.8 at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: E_a = 118 kJ·mol^{-1} and A = 7.2×10^8 s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L=2-6).

Figure 8. Plots of log[-log{1-(1-w)$^{0.5}$}] vs. 1/T for thermogravimetric data of PLLA/LLDPE/MgO [20:80:1 (wt/wt/wt)] in a range of w = 0.7-0.1 at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: E_a = 244 kJ·mol^{-1} and A = 3.8×10^{14} s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L= 2 ~ 7).

Figure 9. Plots of log[-log{1-(1-w)$^{0.5}$}] vs. 1/T for thermogravimetric data of LLDPE at a heating rate of 9 °C·min^{-1} and for model reactions using the kinetic parameters: E_a = 255 kJ·mol^{-1}, A = 2.0×10^{15} s^{-1}. Model reactions: zero (n=0), 1st (n=1), and 2nd (n=2)-order, and random degradations (Random L= 2 ~ 9).