Research Article

Selective Depolymerization and Effects of Homolysis of Poly(L-lactic acid) in a Blend with Polypropylene

Haruo Nishida,¹ Yoshiro Arazoe,² Takayuki Tsukegi,¹ Wang Yan,² and Yoshihito Shirai^{1,2}

¹Eco-Town Collaborative R&D Center for the Environment and Recycling, Kyushu Institute of Technology, Hibikino 2-4, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0196, Japan

²Department of Biological Functions and Engineering, Kyushu Institute of Technology, Hibikino 2-4, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0196, Japan

Correspondence should be addressed to Haruo Nishida, nishida@lsse.kyutech.ac.jp

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Blends of poly(L-lactic acid) (PLLA) and polypropylene (PP), which are candidates for the practical use of PLLA, were investigated for selective degradation of PLLA, resulting in quantitative conversion of PLLA components into cyclic monomers, lactides, using magnesium oxide (MgO) as a depolymerization catalyst. Obviously, the catalyst MgO selectively accelerated only the PLLA depolymerization in the blends, dominantly generating L,L-lactide as a volatile product and separating the PP component. Expected effects of homolysis in the blend system were also determined as slight changes in activation energy of degradation for both the components and through the suppression of degradation by an antioxidant.

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1. Introduction

The move towards a future more sustainable society requires renewable resources to be used more effectively. One material derived from such resources, poly(L-lactic acid) (PLLA) has been attracting the attention of many researchers because of its biomass-origin [1] and recyclability based on its biodegradation [2], hydrolysis [3], and thermal depolymerization [4] functions. On the basis of its superior thermal degradation and hydrolysis, PLLA has potential as a feedstock recycling material ideally suited to a future sustainable society.

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, can be achieved more effectively, it will then become possible to renew PLLA by the shortest, most energy-efficient route. Once this is achieved, PLLA may become widely used as a basic material in a sustainable society.

Although PLLA has many useful physical properties, there are some shortcomings, such as brittleness and poor water barrier properties, which should be improved for actual uses. Use of polymer alloy is a common way to improve the properties of PLLA [5], but from the viewpoint of feedstock recycling it only brings attendant contamination problems. Therefore, for the selective feedstock recycling of PLLA from such polymer alloys and blends, it is necessary to clarify the influence of such blended polymers on the feedstock recycling of PLLA.

Polypropylene (PP) is a commonly used polyolefin in electric and electronic appliances due to its mechanical properties and processability by injection molding, thus PP has been alloyed with many kinds of materials by copolymerization, blending, lamination, and composite formation to improve its properties so as to suit particular applications. A blend of PP with PLLA is also being developed to apply to various household appliances in recognition of the environmental appeal of the carbon neutral feature of PLLA [6]. Improvements in the mechanical properties of the PLLA/PP blend have been achieved by the use of effective compatibilizers suited for the requirements of particular

applications. Since PP has a wide range of applications, the blend of PLLA and PP is a candidate for the practical use of PLLA.

Recently, the depolymerization behavior of PLLA has been investigated in detail. In some reports, depolymerization kinetics [7–9], catalysts [10, 11], and the effects of chemical structures [12] have been discussed. Depolymerization catalysts for the feedstock recycling of PLLA have been investigated by our group, which have paid particular attention to alkali earth metals, such as magnesium oxide (MgO) [10], which acted as an effective catalyst for the depolymerization of PLLA in a temperature range of 250–300°C with slight racemization to *meso*-lactide. However, selective depolymerization and thereby separation of PLLA component from polymer alloys has not been reported. There are few reports regarding other blends with commodity resins. Tsukegi et al., and Omura et al., already reported the selective depolymerization of PLLA component in PLLA/LLDPE [13, 14], PLLA/PS [15], and PLLA/PBS blends [16]. There is no information for the blend with PP in spite of the importance for practical uses of PLLA. However, influences of the PLLA thermal degradation to coexisting PP component are quite uncertain and must be important for the mechanical recycling of PP. The demand to the solution of this subject may gradually rise with increase in practical uses.

It is well known that PP decomposes randomly by homolytic chain scission via various mechanisms such as hydrogen abstraction, back biting, and β -scission [17–20]. Although the degradation of PLLA proceeds mainly in non-radical mechanisms [7, 9, 21], previous studies by McNeill and Leiper [22, 23], and Tsuji et al. [24] have suggested that the homolysis of PLLA occurs in a closed system. Södergård et al. [25, 26] have also suggested the stabilization of PLLA with various types of peroxides. However, the contribution of homolysis to the feedstock recycling of PLLA in a blend system has not been discussed in previous studies. If the radical mechanism significantly contributes to the depolymerization of PLLA, the generated radical species may affect PP degradation. Conversely, radical species originating from PP may also influence the degradation behavior of PLLA. In this paper, selective depolymerization of PLLA components in PLLA/PP blends with MgO was investigated. The effects of homolysis in PLLA/PP blends were discussed.

2. Experimental Section

2.1. Materials. PLLA (LACEA H-100J, M_n 88,000, M_w 170,000, Sn content: 52.7 ppm) and *isotactic* polypropylene (PP) (NOVATEC FY7HA, MFR = 1.7) were obtained from Mitsui Chemicals and Japan Polypropylene Corporation, respectively. Catalyst: magnesium oxide (MgO columnar crystalline, size $10 \times 10 \times 70 \mu\text{m}$) was purchased from Wako Pure Chemical Industries, Ltd. and used as received. Antioxidant: 2,2-bis(hydroxymethyl)-1,3-propanediol tetra[3-(4-hydroxy-3,5-di-*t*-butylphenyl)propanoate (BHPP) was purchased from Ciba Specialty Chemicals and characterized by ^1H NMR (purity ~100%).

2.2. Preparation of PLLA/PP, PLLA/PP/MgO, and PLLA/BHPP Blends. PLLA and PP were dried at 40°C for 2 hours at ca. 0.1 kPa in a vacuum oven just before melt processing. PLLA/PP, PLLA/MgO, PP/MgO, PLLA/PP/MgO, and PLLA/BHPP blends (see Tables 1 and 2) were prepared by melt blending with an Imoto Machinery Co., Ltd. twin-screw extruder model 160B (diameter 20 mm, L/D 25) equipped with an air vent under conditions of 180°C temperature and a screw rotational speed of 25 rpm.

2.3. Characterization. Molecular weights of the samples were measured by size exclusion chromatography (SEC) on a TOSOH HLC-8120 GPC system with a refractive index (RI) detector at 40°C using a TOSOH TSKgel Super HM-M column and chloroform eluent (0.6 mL min^{-1}). The calibration curves for GPC analysis were obtained using polystyrene standards with a low polydispersity (5.0×10^2 , 1.05×10^3 , 2.5×10^3 , 5.87×10^3 , 9.49×10^3 , 1.71×10^4 , 3.72×10^4 , 9.89×10^4 , 1.89×10^5 , 3.97×10^5 , 7.07×10^5 , 1.11×10^6 , TOSOH Corporation). The sample (12 mg) was dissolved in chloroform (2 mL) and the solution was filtered through a membrane filter with a $0.45 \mu\text{m}$ pore size.

Proton (^1H) NMR spectra were recorded on a 500-MHz JEOL JNM-ECP500 FT NMR system. Chloroform-*d* was used as solvent. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (TMS) in CDCl_3 unless otherwise noted.

Fourier transfer infrared (FTIR) spectra were recorded on a Perkin Elmer Spectrum GX2000R. Reflection spectra of as-pyrolyzed samples were measured on a Golden Gate Diamond ATR(10500) module with a germanium crystal, by the single-reflection ATR method.

Optical and scanning electron microscopy for PLLA/PP and PLLA/PP/MgO were performed with a KEYENCE digital microscope VH-5000 and a HITACHI S-3000N WET-SEM at an accelerating voltage of 15 kV.

2.4. Dynamic Pyrolysis in TG and Py-GC/MS. Thermal degradation behavior of PLLA/PP blends was analyzed by a 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 in diameter) under a constant nitrogen flow (100 mL min^{-1}) using about 5–6 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 ($30 \text{ m} \times 0.25 \text{ mm i.d.}$; film thickness, $0.25 \mu\text{m}$). 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

TABLE 1: Preparation of pellet samples with an extruder.

Entry	Melt-processed sample (wt ratio)	Molecular weight of PLLA component after preparation	
		M_n	M_w
1-1	PLLA	62 000	207 000
1-2	PP	—	—
1-3	PLLA/PP (20:80)	66 000	181 000
1-4	PLLA/MgO (100:5)	37 000	85 000
1-5	PP/MgO (100:5)	—	—
1-6	PLLA/PP/MgO (20:80:5)	8 000	15 000

TABLE 2: Preparation of PLLA/BHPP blends with an extruder.

Entry	PLLA/BHPP (wt/wt)	M_n	M_w
2-1	100/0	79 000	150 000
2-2	100/0.2	80 000	152 000
2-3	100/1	80 000	152 000
2-4	100/5	84 000	176 000
2-5	100/20	85 000	171 000

TABLE 3: Changes in weight and molecular weight of PLLA in PLLA/BHPP blends after heating at 300°C for 30 minutes.

Entry	PLLA/BHPP (wt/wt)	Weight loss (%) (SD ^(a))	M_n (SD)	M_w (SD)
3-1	100/0	14.6 (0.6)	5 500 (355)	18 800 (1095)
3-2	100/0.2	11.7 (0.4)	6 800 (338)	20 800 (645)
3-3	100/1	6.7 (0.9)	8 100 (929)	23 100 (1694)
3-4	100/5	7.9 (0.3)	8 100 (698)	20 800 (1319)
3-5	100/20	7.8 (0.3)	7 100 (118)	18 500 (1452)

^(a) Standard deviation. FIGURE 1: Thermogravimetric analysis of PLLA, PP, PLLA/MgO, and PP/MgO. $\varphi = 9^\circ\text{C min}^{-1}$.

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 Frontier Lab SS-1010E 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 minute, 40–120°C at 5°C min^{-1} , 120–320°C at $20^\circ\text{C min}^{-1}$, and 320°C for 13 minutes. Then, the separated pyrolyzates were analyzed directly with the quadrupole mass spectrometer (70 eV, electron impact ionization: EI). Mass spectrum measurements were recorded 2 times s^{-1} during this period.

Thermal degradation behaviors of related blends as references were also analyzed in the same manner as the PLLA/PP blend.

2.5. Isothermal Pyrolysis in Glass Tube Oven. About a 65 mg sample of PLLA/BHPP was put in a sample bottle and

set at the waiting position in a Shibata GTO-350D glass tube oven. The air in the oven chamber was completely exchanged with N_2 . The oven was heated rapidly to 300°C under a N_2 atmosphere. Then, the sample was moved to a heated position thermostated at 300°C and kept there for 30 minutes. After heating, the residual sample was quickly taken out from the reactor and quenched in an ice bath at 0°C. The recovered residual sample was dried, weighed, and its molecular weight was measured with SEC. Vaporized pyrolyzates were condensed in a chilled trap, collected by dissolving in acetone, and dried in a vacuum rotary evaporator to produce white solids. The obtained solid product was analyzed by GC for characterization.

The experiment was repeated 3 times in the same manner and the obtained results were averaged and listed in Table 3 with their associated standard deviations.

3. Results and Discussion

3.1. Thermal Degradation of Melt-Blended PLLA/PP and PLLA/PP/MgO. Melt-blended samples of PLLA/PP and PLLA/PP/MgO were prepared as pellets by hot extrusion molding at 180°C using an extruder with a pelletizer (Table 1). Melt-extruded samples of PLLA, PP, PLLA/MgO, and PP/MgO were also prepared as references in the same manner. From microscopic and SEM observations, PLLA and PP components showed a phase separation of the order of 10–20 μm and MgO powder dispersed homogeneously in the PLLA/PP matrix. The M_n values of PLLA and PLLA component in the PLLA/PP blend (entries 1-1 and 1-3 in Table 1) decreased, whereas M_w increased slightly compared with the values of original PLLA. These findings may result from a heterogeneous thermal degradation and

FIGURE 2: Thermogravimetric analysis ($\varphi = 9^\circ\text{C min}^{-1}$) of PLLA/PP and PLLA/PP/MgO blends. w : residual weight ratio of PLLA/PP components.

FIGURE 4: Pyrolysis-GC/MS analysis of PLLA, PP, and PLLA/PP. $\varphi = 9^\circ\text{C min}^{-1}$.

FIGURE 3: Pyrolysis-GC/MS analysis ($\varphi = 9^\circ\text{C min}^{-1}$) of PLLA/PP and PLLA/PP/MgO. Weight loss values of PLLA/PP components were estimated from TG analysis ($\varphi = 9^\circ\text{C min}^{-1}$).

condensation between carboxyl and hydroxyl groups during the extrusion [27]. In the case of samples including MgO, average values M_n and M_w of PLLA components decreased significantly. In particular, the PLLA component in PLLA/PP/MgO (entry 1–6) dramatically decreased, because of its higher concentration of the depolymerization catalyst MgO to PLLA component than that in PLLA/MgO.

Thermogravimetric analyses of the blends and homopolymers as references were carried out with a TG/DTA. In Figure 1, TG curves corresponding to polymer components in PLLA, PP, PLLA/MgO, and PP/MgO

measured at $\varphi = 9^\circ\text{C min}^{-1}$ are illustrated. The TG curve of PLLA/MgO was shifted to a lower-temperature range by 50°C compared with that of PLLA homopolymer. Since, in a previous report [28], PLLA (M_n 98,000, M_w 170,000)/MgO (100:5 (wt/wt)) prepared by mixing in a chloroform solution showed a similar TG curve in a temperature range of 250 – 310°C , the observed temperature shift in TG curve of PLLA/MgO must reflect a catalytic effect of MgO. On the other hand, when compared with that of PP homopolymer, no temperature shift of the TG curve of PP/MgO occurred except for a slight shift at the onset of the thermal degradation. These results indicate that MgO is an effective catalyst for PLLA-degradation, in which it has no appreciable effect on the thermal degradation of PP.

TG curves corresponding to polymer components in the blends, PLLA/PP = 20:80 (wt/wt) and PLLA/PP/MgO = 20:80:5 (wt/wt/wt), are plotted in Figure 2. Typical two-step weight loss behaviors were observed for both blends, reflecting the blend ratio of 20:80 (wt/wt). As shown in Figure 2, only the PLLA component in PLLA/PP/MgO shifted to the lower-temperature range by the catalytic effect of MgO in contrast to the PLLA component in PLLA/PP. At the same time, the PP component remained within the same range with nonblended PP shown in Figure 1. Obviously, the catalyst MgO selectively accelerated the degradation of only the PLLA component in the blend.

To investigate the interaction between both components during thermal degradation, volatile degradation products from PLLA, PP, PLLA/PP, and PLLA/PP/MgO blends were measured with Py-GC/MS. In Figure 3, the changes in the total ion count (TIC) spectra of pyrolyzates from PLLA/PP and PLLA/PP/MgO blends are illustrated within the temperature ranges of PLLA component degradation. From the PLLA/PP blend, many kinds of pyrolyzates including L,L-lactide, meso-lactide, and oligomers were detected at retention time ranges of 11–12, 9–11, and 19–28 minutes, respectively. In contrast, L,L-lactide was predominantly detected as a volatile product from the PLLA/PP/MgO blend. These results show the high selectivity of MgO catalyst for the PLLA depolymerization.

In Figure 3, it was observed that the detected pyrolyzates from PLLA/PP blend included other series of volatile products in a similar range to the well-defined cyclic oligomers composed of a lactate unit [29]. A typical TIC spectrum of pyrolyzates from PLLA/PP blend at 370°C is shown in Figure 4 in comparison with the TIC spectra of pyrolysis products from PLLA and PP homopolymers. The signals from the other series of products detected in Figure 3 agreed with those of the pyrolyzates from PP homopolymer at 400°C. In Figure 5, based on the TIC intensity-%, the changes in composition of pyrolyzates from PLLA/PP and PLLA/PP/MgO blends are shown with the corresponding degradation temperature. The pyrolyzates originating from PP component in the PLLA/PP blend were detected at 350°C and higher temperatures, despite the weight loss of PP homopolymer starting at 380°C under the same conditions. This result suggests that the degradation of PP component was accelerated by the degradation of PLLA component. However, in the degradation of PLLA/LLDPE blends [14], no interaction between the components was observed.

Considering the whole analytical results obtained, the highly selective depolymerization of PLLA component to L,L-lactide is possible from PLLA/PP blends, even when there is an interaction between both components during degradation.

To clarify the interaction between PLLA and PP components during the thermal degradation of the blend, the kinetic parameters for the degradation were evaluated. In Figure 6, changes in the activation energy (E_a) values of the thermal degradation of PLLA, PP, and PLLA/PP blend are plotted. PLLA and PP homopolymers showed characteristic E_a values of 115–165 [30] and 200–230 kJ mol⁻¹ [31] in separated temperature ranges of 320–360 and 410–460°C, respectively. The E_a plot for the PLLA/PP blend appeared over a wide temperature range of 310–460°C encompassing both the temperature ranges corresponding to PLLA and PP homopolymers. Although the E_a values of PLLA and PP components in the blend were in the same ranges as those for PLLA and PP homopolymers, it is noteworthy that the E_a plot for PLLA component in the blend shifted to a lower-temperature range by ~10°C in spite of having nearly the same molecular weight with that of PLLA homopolymer. Especially, during the initial period of the degradation, the departure from the plot of PLLA homopolymer was significant. This departure in E_a value between PLLA homopolymer and PLLA component in the blend may be induced by the melt-blending process and/or an interaction with the blended PP component.

When the E_a values were plotted against the residual weight ratio, w , of PLLA, PP, and both components in the blend, slight decreases of 5–10 kJ mol⁻¹ were observed for the PLLA and PP components, suggesting that both components influenced each other and induced minor reactions mutually accelerating the degradation.

In Figure 7, the E_a changes with temperature during the thermal degradation of PLLA/MgO, PP/MgO, and PLLA/PP/MgO blends are illustrated. Shifts to a lower-temperature range for PLLA component and into lower- E_a values for the PP component in the PLLA/PP/MgO

FIGURE 5: Composition ratios of pyrolyzates from PLLA/PP (80:20 wt/wt) and PLLA/PP/MgO (80:20:5 wt/wt/wt).

FIGURE 6: Activation energy, E_a , plots against temperature for thermal degradation of PLLA, PP, and PLLA/PP blend. $\varphi = 5^\circ\text{C min}^{-1}$.

FIGURE 7: Activation energy, E_a , plots against temperature for thermal degradation of PLLA/MgO, PP/MgO, and PLLA/PP/MgO blend. $\varphi = 5^\circ\text{C min}^{-1}$.

FIGURE 8: Thermogravimetric analysis of PLLA, PLLA/BHPP (0.2, 1.0, 5, and 20 wt%). $\varphi = 9^\circ\text{C min}^{-1}$.

blend were clearly observed in comparison with those of PLLA/MgO and PP/MgO, respectively. Plots against the residual weight ratio, w , of both components indicated a definite decrease in the E_a values of the PP component by 10–50 kJ mol^{-1} and a slight decrease for the PLLA component by $\sim 3 \text{ kJ mol}^{-1}$. This considerable decrease in the E_a value at the onset of the PP component degradation clearly indicates the influence of PLLA degradation, for example, H-radical abstraction, on an initial degradation mechanism of the PP component.

3.2. Thermal Degradation of Melt-Blended PLLA/BHPP. To determine active species taking part in the interaction between PLLA and PP components during the thermal degradation of the blend, effects of an oxidation inhibitor: BHPP on the thermal degradation of PLLA were investigated. Generally, oxidation inhibitors are added to PP to suppress its oxidative degradation by an amount less than 1 wt.-%. In

this study, BHPP was melt blended into PLLA at prescribed weight ratios of 0, 0.2, 1, 5, and 20 wt.-% to PLLA. After melt processing, M_w value of PLLA decreased by 20 000, but the decrease was suppressed by the BHPP (Table 2). Thermogravimetric analysis of the PLLA/BHPP blends was carried out with TG/DTA, resulting in TG curves illustrated in Figure 8. As shown by interpolation in Figure 8, the TG curve of PLLA shifted to higher-temperature ranges with increase in the dosage of BHPP, suggesting the inhibitive action of BHPP to PLLA degradation.

The changes in E_a values of PLLA/BHPP blends are plotted in Figure 9 against residual weight w . The E_a values of PLLA shifted from a range of 120 to 170 kJ mol^{-1} into higher ranges with increase in the addition of BHPP, especially, in the first half of the weight loss, resulting in an E_a range of 155 to 180 kJ mol^{-1} of PLLA/BHPP (1 wt.-%) blend. These results suggest that BHPP captured some of the active species responsible for accelerating the PLLA degradation, such as radical species.

To elucidate the inhibitive action of BHPP on the feedstock recycling of PLLA, changes in weight loss and molecular weight of the PLLA/BHPP blends were measured after heating at 300°C for 30 minutes under an N_2 atmosphere. Obtained results of the weight loss and the average molecular weights are shown with standard deviations in Figure 10. The largest decreases in weight and average molecular weights were observed for PLLA homopolymer without BHPP. The decreases became shorter with increase in the addition of BHPP up to 1 wt.-%. McNeill and Leiper [23] also found an inhibiting effect for diaminoanthraquinone (1 wt.-%) as a radical inhibitor on the volatilization of PLLA at 230°C. A BHPP addition of more than 1 wt.-% showed an increase in the weight loss and decreases in the average molecular weights. These decreases resulting from the addition of large amounts of BHPP may be due to the action of BHPP as a phenolic reactant. From the obtained results, it was assumed that BHPP acts not only as an oxidation inhibitor by reacting with radical species, but also as a phenolic reactant in breaking down the PLLA chains.

Volatile products from the samples were collected and characterized by ^1H NMR analysis as diastereoisomers of lactide (Figure 11). Interestingly, the addition of BHPP tended to suppress the racemization of products up to 1 wt.-% addition, resulting in the highest composition ratio of L,L-lactide occurring in the product from PLLA/BHPP. Based on mechanisms of PLLA homolysis previously submitted by Kopinke et al. [21] and Tsuji et al. [24], it is assumed that BHPP preferentially reacts with radical species to stop expected radical chain reactions (Scheme 1). According to this scheme, although the homolysis of PLLA chains induces the racemization of the resulting lactides as volatile products, BHPP suppresses not only the chain reaction of degradation by radical species, but also the racemization of the products.

From the above results, it was observed that the antioxidant BHPP affected the PLLA thermal degradation, suppressing some degradation mechanisms, which may induce a homolysis of PLLA chain bonds.

When considering the feedstock recycling of PLLA/PP blends, the antioxidant reagent in PP components may affect

SCHEME 1: Expected inhibitive mechanism on PLLA homolysis by BHPP.

FIGURE 9: Activation energy, E_a , plots against residual weight, w , of PLLA and PLLA component for thermal degradation of PLLA, PLLA/BHPP-0.2 wt%, 1 wt%, and 5 wt% blends.

the selective depolymerization of PLLA by MgO catalyst. When TG curves of PLLA/BHPP/MgO = 100:1:1 (wt/wt/wt) and PLLA/MgO = 100:1 (wt/wt) were compared, a slight increase in the degradation temperature range by $\sim 5^\circ\text{C}$ was found to occur on the addition of BHPP. Moreover, when the composition ratios of pyrolyzates from PLLA/MgO and PLLA/BHPP/MgO were compared, similar composition and its changes with temperature were observed for both samples. These results indicate that the function of MgO in the selective depolymerization of PLLA component was preserved even in the presence of BHPP.

4. Conclusions

The selective depolymerization of PLLA component in a PLLA/PP blend was investigated to determine influences of coexisting PP component. The TG curve of PLLA component

FIGURE 10: Weight loss values and average molecular weights of PLLA in PLLA/BHPP blends after heating at 300°C for 30 minutes. Bar: standard deviation.

shifted into a lower-temperature range upon the addition of MgO, while the TG curve for PP component retained its original position without any shift in the range. The catalyst MgO selectively accelerated the degradation of PLLA component in the blend. From Py-GC/MS analysis, L,L-lactide was dominantly detected as a volatile product from

FIGURE 11: Composition ratios of pyrolyzates evaporated from PLLA/BHPP during heating at 300°C for 30 minutes.

PLLA/PP/MgO, demonstrating the selective depolymerization of PLLA component by the catalytic action of MgO.

The E_a plot of PLLA component degradation in the blend shifted to lower temperatures and the E_a value of PP component also decreased by 10–50 kJ mol⁻¹. Py-GC/MS analysis of the blend showed the accelerated degradation of PP component. These results suggest that there are interactions between both components during the thermal degradation of the blend. From the suppression effects of antioxidant BHPP on PLLA degradation, the homolysis of PLLA chains by the contribution of radical species was expected.

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