

# Miscibility and hydrolytic degradation in alkaline solution of poly(L-lactide) and poly(methyl methacrylate) blends

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## Abstract

Poly(L-lactide) (PLLA) was melt blended with poly(methyl methacrylate) (PMMA) using a two-roll mill. The miscibility and hydrolytic degradation of the blend films were characterized. It was found that PLLA/PMMA blend has high miscibility in the amorphous state because only single  $T_g$  was observed in the DSC and DMA measurements. In alkaline solution, the hydrolytic degradation rate of the blends whose PMMA content is higher than 30 wt% was decelerated while the rate of the blends whose PMMA content is lower than 30 wt% was accelerated. That is, the hydrolytic degradation rate of the blends could be widely controlled by PMMA content in the blend. It was also found that only PLLA was hydrolyzed and eluted into alkaline solution, while PMMA remained during alkaline hydrolysis.

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*Keywords:* Polymer blend; Poly(L-lactide); Degradation

## 1. Introduction

Recently, much attention has been paid to poly(L-lactide) (PLLA) and its copolymer not only because they are biodegradable, but also because they can be made from renewable natural resources such as cornstarch. Therefore, utilization of PLLA will be one of the method to reduce consumption in fossil fuels. PLLA has various advantages such as high mechanical property and transparency. Somehow its brittleness and low heat resistance are shortages of PLLA in the case of being used as commodity materials.

Polymer blend has been widely utilized for the control of biodegradation as well as the improvement for the mechanical properties and the heat resistance. In the previous reports, the blends of PLLA with biodegradable polymers such as poly(D-lactide) (PDLA) [1,2], poly( $\epsilon$ -caprolactone) (PCL) [3,4], poly(3-hydroxybutyric acid) (PHB) [5,6], poly(ethylene oxide) (PEO) [7], and poly(vinyl alcohol) (PVA) [8] were studied because the biodegradability and the biocompatibility were required for some applications such as medical materials. But in some cases in other applications such as some part of car and electronic products, non-biodegradability is required.

Therefore, the blends of PLLA and non-biodegradable polymers with high mechanical properties are needed. It has been reported that PLLA is miscible with poly(*p*-vinyl phenol) (PVPh) [9,10], poly(vinyl acetate) (PVAc) [11], and poly(methyl methacrylate) (PMMA) [12,13], while it is immiscible with poly styrene (PS) [14] and poly(ethane-*co*-(vinyl acetate)) (EVA) [15]. The morphology and crystallization behavior of these blends have been widely studied, somehow there is a few researches for the degradability of these blends. It is desirable that PLLA is stable in use, and degraded rapidly after disposal, so the control of biodegradability is an important subject.

PMMA is a non-biodegradable polymer with high transparency and high  $T_g$ . Therefore, it is expected that the blends of PLLA and PMMA can be used as commodity materials in wide applications. In this study, the miscibility and hydrolysis behavior for the PLLA/PMMA blends were investigated.

It is well known that the biodegradability of PLLA is strongly related to its crystallinity, higher-order structure and morphology. It is also known that the crystallinity and structure of polymer blend are largely influenced by its blend ratio. That is biodegradability of PLLA/PMMA blend is varied depending on these two factors, i.e. crystalline structure and blend ratio. Because the two factors are not independent, the biodegradability of crystallized PLLA/PMMA blends is difficult to discuss. Therefore, we investigated the hydrolysis behavior of PLLA/PMMA blends in amorphous state to clarify the effect of blending with PMMA.

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## 2. Experiment

### 2.1. Materials

PLLA (Lacty#5000), with  $M_w = 3.2 \times 10^5$  was supplied by Toyota Motor Corporation. The melt index of the PLLA is 0.63 g/10 min and the optical purity is 98.3%. PMMA (Acrypet VH) with  $M_w = 1.0 \times 10^5$  was supplied by Mitsubishi Rayon Co., Ltd.

### 2.2. PLLA/PMMA blend

PLLA and PMMA were melt-blended in the various blend ratios. PLLA was dried at 120 °C for 3 h under vacuum before mixing. PLLA and PMMA were mixed together using a two-roll mill (Nishimura machinery Co., Ltd) at 180 °C for 15 min. The films with a thickness of about 0.5 mm were obtained from the resultant mixtures by compression molding method at 180 °C for 5 min under a pressure of 19.6 MPa using hot press (Technosupply Co., Ltd, Japan), followed by quenching in liquid nitrogen. Each of the blends was molded into the amorphous state. PLLA film and PMMA film were also prepared by the same procedure starting with pure PLLA and PMMA, respectively. The blend ratio and thermal properties of the films are summarized in Table 1. The specimens obtained are named as xx/yy where xx and yy denotes the blend ratio of PLLA and PMMA in wt%, respectively.

### 2.3. Measurements

#### 2.3.1. Differential scanning calorimetry (DSC)

Thermal analysis was carried out by DSC 8230 Thermo Pulus (Rigaku corporation). The sample of 4~5 mg in weight was sealed in an aluminum pan and was heated from 0 to 200 °C at the heating rate of 20 °C/min under nitrogen gas flow of 20 mL/min. DSC results were calibrated using In, Sn, and Pb as standards. The glass transition temperature ( $T_g$ ) was measured as midpoint value. The crystallinity of PLLA ( $\chi_c$ ), which is normalized by PLLA weight fraction ( $X_{\text{PLLA}}$ ), was calculated using the following equation,

$$\chi_c(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{X_{\text{PLLA}}} \quad (1)$$

where  $\Delta H_m$  (J/g) is melting enthalpy of PLLA and  $\Delta H_m^0$  is melting enthalpy of PLLA crystal having infinite crystal thickness, which value is 85.82 (J/g).

The weight fraction of PLLA ( $X_{\text{PLLA}}$ ) changes during degradation, because PLLA is hydrolyzed and PMMA is not hydrolyzed. The weight fraction of PLLA after hydrolyzed ( $X_{\text{PLLA}}^h$ ) was calculated by the following equation,

$$X_{\text{PLLA}}^h = \frac{X_{\text{PLLA}} - W_{\text{loss}}(\%)}{1 - W_{\text{loss}}(\%)} \quad (2)$$

where  $W_{\text{loss}}(\%)$  is the total weight loss of the samples, which is calculated by following Eq. (3) at section of hydrolysis test. The crystallinity after degradation, which is normalized by  $X_{\text{PLLA}}^h$  was also calculated by Eq. (1), replace  $X_{\text{PLLA}}$  by  $X_{\text{PLLA}}^h$ .

#### 2.3.2. DMA

Dynamic mechanical analysis was carried out by a DVA-200S (ITK Co., Japan). The size of test pieces was 5 mm in width, 30 mm in length, and 0.5 mm in thickness. This experiment was performed in a tension mode with 0.05% strain amplitude at a frequency of 10 Hz. The temperature ranged from 0 to 180 °C with a heating rate of 5 °C/min.

#### 2.3.3. Hydrolysis test

Alkaline hydrolysis test was performed using the films of  $0.5 \times 10 \times 10 \text{ mm}^3$  in 10 mL of 1 N NaOH aqueous solution (Kanto Kagaku Co., Ltd) of pH 12. The films were placed in vial filled with NaOH solution. The hydrolysis of the films was performed at 37 °C for a predetermined period of time. After hydrolyses, films were washed twice in distilled water at room temperature and wipe the NaOH solution off from the film surface, then it was rapidly weighed ( $W_{t-\text{asdeg}}$ ). Films were dried for a few hours at room temperature followed by being dried in vacuum for 2 days and weighed ( $W_{t-\text{dried}}$ ). The weight loss ( $W_{\text{loss}}$ ) and the water absorption coefficient ( $W_a$ ) were calculated by following Eqs. (3) and (4). ‘The water absorption coefficient’ means the ratio of the weight of NaOH solution to the weight of initial sample at each exposed time.

$$W_{\text{loss}}(\%) = \frac{W_0 - W_{t-\text{dried}}}{W_0} \times 100 \quad (3)$$

$$W_a(\%) = \frac{W_{t-\text{as deg}} - W_{t-\text{dried}}}{W_0} \times 100 \quad (4)$$

Table 1  
Thermal properties and crystallinity of PLLA/PMMA blends

Sample	PLLA (wt%)	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$\Delta H$ (J/PLLAg)	$\chi_c$ (%)
100/0	100	60.3	117.7	172.3	2.27	2.6
99/1	99	64.9	137.4	171.7	1.70	2.0
95/5	95	63.1	140.3	170.7	1.92	2.2
90/10	90	61.8	143.5	171.6	0.99	1.2
80/20	80	67.3	–	170.6	4.37	5.1
70/30	70	68.0	–	170.5	2.55	3.0
60/40	60	73.5	–	171.8	1.31	1.5
50/50	50	78.8	–	–	–	–
30/70	30	89.5	–	–	–	–
0/100	0	119.0	–	–	–	–

where  $W_0$  is the initial weight and  $W_{t-asdeg}$  is the weight of degraded film just wipe of the NaOH solution off from the film surface.  $W_{t-dried}$  is the weight of degraded film after drying in vacuum.

Hydrolytic degradation rate was calculated by Eq. (5). In this report, ‘hydrolytic degradation rate’ means not the molecular weight loss rate but the sample weight loss rate.

$$R(\%/h) = \frac{W_{loss-t}}{t} \quad (5)$$

where  $W_{loss-t}$  is the weight loss at the time, and  $t$  is exposed time in NaOH solution.

### 2.3.4. FT-IR

The FT-IR spectra of PLLA/PMMA films were measured by ATR reflection method, in which 64 scans were averaged at a resolution of  $4\text{ cm}^{-1}$ , using a FT-IR620 spectrometer (JASCO Corporation) equipped with Micro-20 and ATR-JC-Z microscope ATR unit (JASCO Corporation).

## 3. Results and discussion

### 3.1. Miscibility in PLLA/PMMA blends

Fig. 1 shows the DSC curves of PLLA, PMMA, and PLLA/PMMA blends. Each curve of the samples shows only one  $T_g$  in the temperature range from 60 to 120 °C. Fig. 2 shows the plot of  $T_g$  as a function of PMMA content (wt%). The  $T_g$  value increased with increasing PMMA content. The Gordon–Taylor

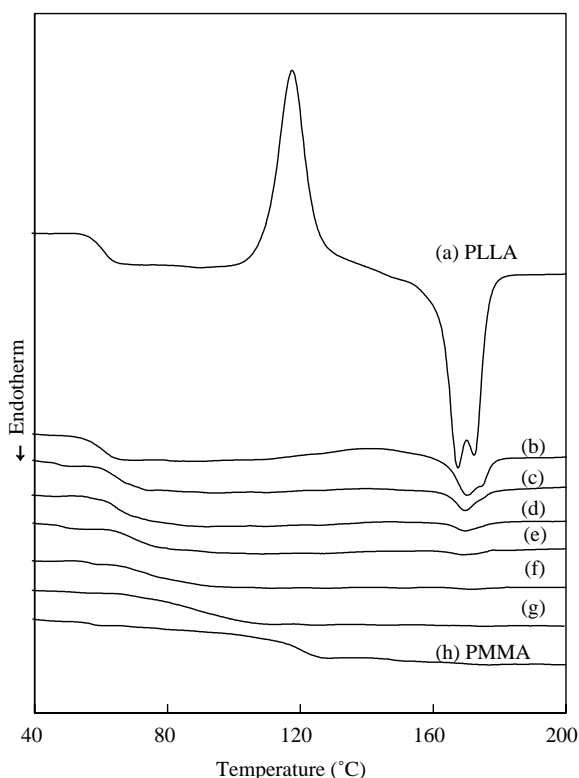


Fig. 1. DSC curves of PLLA, PMMA, and PLLA/PMMA blends; PLLA, (b) 90/10, (c) 80/20, (d) 70/30, (e), 60/40, (f) 50/50, (g) 30/70, (h) PMMA.

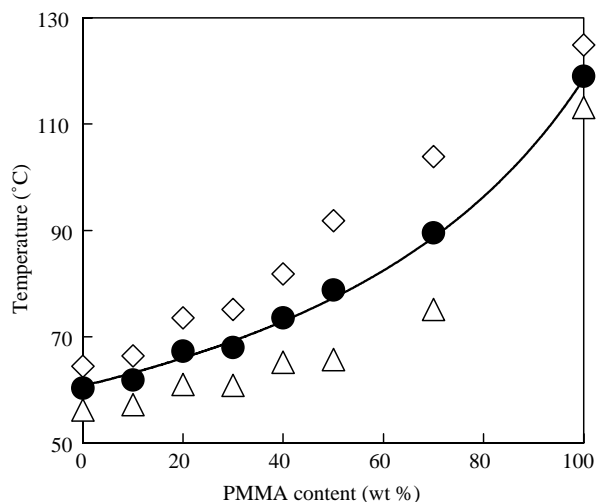


Fig. 2. Relationship between  $T_g$  and PMMA content; (●) midpoint  $T_g$  (□) onset  $T_g$  (◇) onset  $T_g$ .

equation [16] (6) has been one of the most often used to study the  $T_g$ -composition dependence in a polymer blend,

$$T_g^b = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (6)$$

where  $T_g^b$  is the glass transition temperature ( $T_g$ ) of the blend,  $T_{g1}$  and  $T_{g2}$  are the  $T_g$  of the component 1(PLLA) and component 2(PMMA), respectively. The  $w_1$  and  $w_2$  are weight fraction of component 1 and 2, respectively. Examination data is best fitted by this equation with  $k=0.4$ . This result supports that PLLA/PMMA blends have high miscibility in the amorphous state. Fig. 3 shows the temperature dependence of  $\tan\delta$  of PLLA, PMMA, and PLLA/PMMA blends. It shows only one  $\tan\delta$  peak for each blend sample due to the  $\alpha$ -relaxation in the temperature range between the two  $\tan\delta$

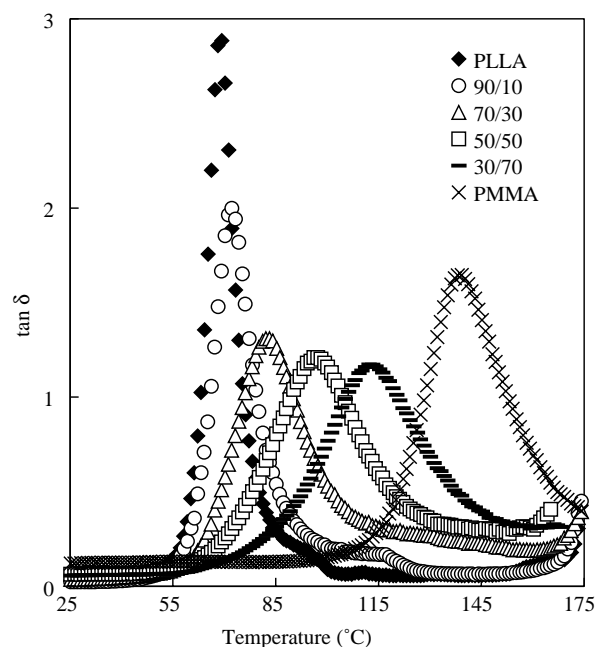


Fig. 3. Temperature dependence of  $\tan\delta$  of PLLA/PMMA blends.

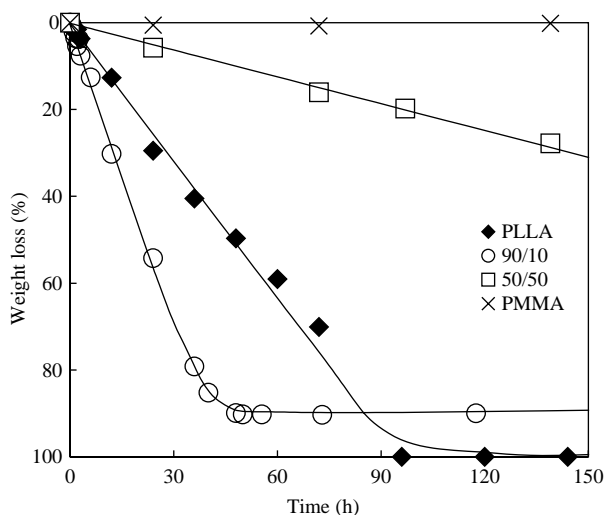


Fig. 4. Weight loss of PLLA/PMMA blends degraded with NaOH solution.

peaks for PLLA and PMMA. This result also supports the miscibility of the two polymers. Guobao Zhang et al. reported that PLLA/PMMA blends, which are mixed with solution/precipitation method, are miscible [14]. It was confirmed that PLLA/PMMA blends, which are mixed with a two-roll mill, are also miscible. Table 1 shows the thermal properties and the degree of crystallinity of each sample obtained from DSC thermograms. The blend samples in which PMMA content is higher than 30 wt% had no crystallization peak of PLLA in the DSC curves measured by heating scan at a heating rate of 20 °C/min. This result indicates that PMMA molecules, which are miscible with PLLA molecules, restrict the crystallization of PLLA in the blend [13].

### 3.2. Hydrolysis behavior of PLLA/PMMA blends

Fig. 4 shows the weight loss ( $W_{\text{loss}}$ ) of PLLA, PMMA, and PLLA/PMMA blends (90/10, 50/50) as a function of exposed time in hydrolysis test. The degradation of PLLA was completed in 90 h, while PMMA was not hydrolyzed at all. The PLLA/PMMA (50/50) blend was hydrolyzed slower than neat PLLA as expected. On the other hand, the PLLA/PMMA (90/10) blend was hydrolyzed faster than neat PLLA unexpectedly. The weight loss of PLLA/PMMA blends reached the ultimate values of 90 and 50% for the 90/10 and

50/50 blends, respectively. This means that all PLLA molecules in the PLLA/PMMA blend were degraded and eluted.

The 90/10 blend film, which was exposed to alkaline solution for 36 h became separated into the exfoliating part and the core part after it was dried at room temperature for a few hours as shown in Fig. 5(a). All PLLA component in the PLLA/PMMA (90/10) blend was hydrolyzed after exposed time of 48 h. The original square shape of the film was kept in alkaline solution, even if the fraction of 90 wt%, that is all PLLA, was eluted. During the drying process, the shape of the sample changed from square film to curved and shrunk film as shown in Fig. 5(b).

As shown in Fig. 4, the linear trend can be observed in the relation between the weight loss and the exposed time in the early stage. The hydrolytic degradation rate was defined as the initial slope in the plot of Fig. 4, and it was plotted against PLLA content as shown in Fig. 6. The hydrolytic degradation rate of PLLA/PMMA blends decreases as the increased in the PMMA content. Particularly, the hydrolytic degradation rate of the blend samples whose PMMA content is lower than 30 wt% is larger than that of neat PLLA. Thus, it is concluded that the hydrolytic degradation rate of PLLA/PMMA blend can be widely controlled by PMMA content. For more discussion, DSC, FT-IR, and water absorption test were carried out.

### 3.3. Thermal property of degraded samples

Generally, the biodegradability of PLLA decreases with increasing crystallinity, because the amorphous phase receives hydrolysis preferentially [17]. We investigated the hydrolysis behavior of PLLA/PMMA blends in amorphous state to clarify the effect of blending with PMMA. Therefore, it should be confirmed that the PLLA/PMMA blend sample is amorphous before and after hydrolysis test. Fig. 7 shows the DSC curves of PLLA/PMMA (90/10) blend exposed to hydrolysis test for each fixed time. In each thermogram of degraded sample, it shows endothermic peak at 70 and 170 °C, and exothermic peak at 140 °C. The endothermic peak at 70 °C is not originate from crystallization of PLLA during heating in DSC measurement but from enthalpy relaxation caused by physical aging. The enthalpy of fusion at 170 °C is almost same as that of crystallization at 140 °C, so it was confirmed that all of the

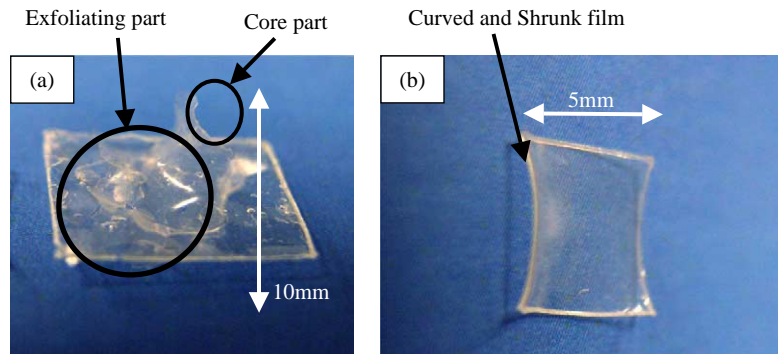


Fig. 5. Photographs of PLLA/PMMA samples; (a) degraded for 36 h, (b) degraded for 50 h.

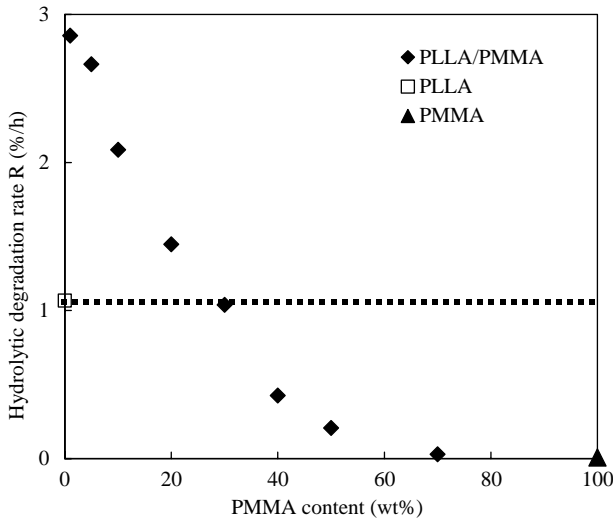


Fig. 6. Relationship between hydrolytic degradation rate  $R$  (%/h) and PMMA contents (wt%). The dotted line corresponds to  $R$  (%/h) of neat PLLA.

samples was almost amorphous before and after alkaline hydrolysis tests.

Thus in this study, it is not necessary to consider the influence of crystallization on the hydrolysis behavior. The  $T_g$  of original PLLA/PMMA (90/10) blend was 62 °C before hydrolysis test. After the alkaline hydrolysis degradation test for 48 h, the  $T_g$  of the sample changed to 120 °C, which is almost equal to the  $T_g$  of PMMA. This result indicates that the PMMA remains after complete degradation of PLLA in the PLLA/PMMA blend.

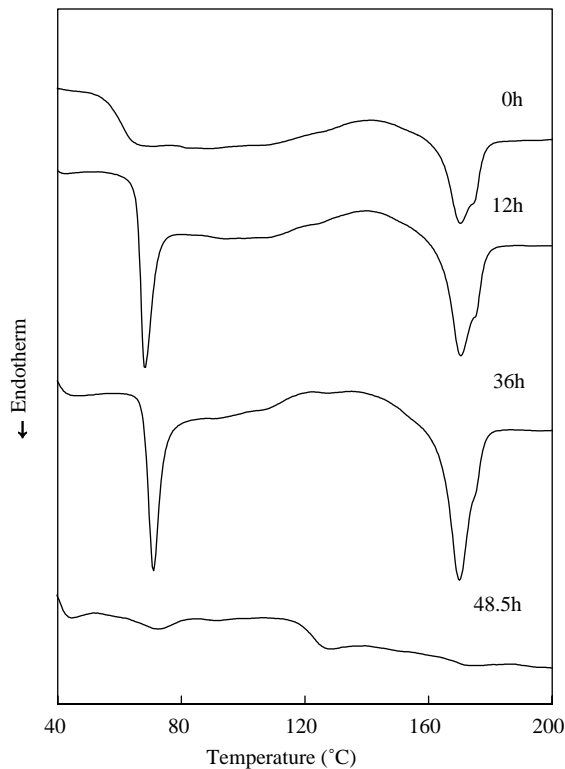


Fig. 7. DSC curves of degraded PLLA/PMMA (90/10) sample.

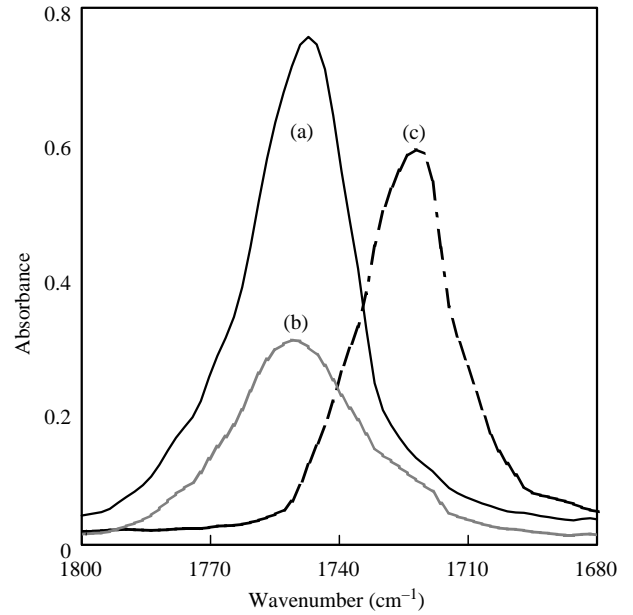


Fig. 8. FT-IR spectra of (a) PLLA, (b) PLLA/PMMA (90/10), (c) PMMA.

### 3.4. FT-IR

Fig. 8 shows the FT-IR spectra of the PLLA, PMMA, and PLLA/PMMA (90/10) films. The stretching vibration of carbonyl for PLLA is found at 1750  $\text{cm}^{-1}$ , while the same band for PMMA is found at 1720  $\text{cm}^{-1}$ . Two peaks for carbonyl bonds are observed at 1750 and 1720  $\text{cm}^{-1}$  for PLLA/PMMA (90/10) blend. The main peak at 1750  $\text{cm}^{-1}$  is attributed to PLLA and the shoulder peak at 1720  $\text{cm}^{-1}$  to PMMA. Fig. 9 shows the FT-IR spectra of the original and degraded PLLA/PMMA (90/10) blends. The original 90/10 blend film has the main peak around 1750  $\text{cm}^{-1}$  as shown in

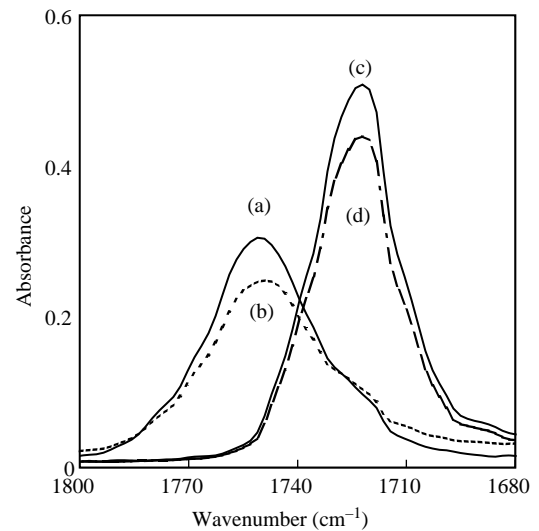


Fig. 9. FT-IR spectra of PLLA/PMMA blends; (a) original 90/10, (b) base part of degraded 90/10 film (36 h), (c) exfoliating part of degraded 90/10 film (36 h), (d) Curved and Shrunk 90/10 film (48 h).

Table 2  
Water absorption coefficient ( $W_a$ ) and weight loss ( $W_{\text{loss}}$ ) of degraded PLLA and PLLA/PMMA blend

Sample	Water absorption (%)	Weight loss (%)
PLLA	0.6	45.2
90/10	13.5	55.7
80/20	15.6	50.4
PMMA	1.8	0.5

Fig. 9(a). The FT-IR spectra of the core part and the exfoliating part of the PLLA/PMMA (90/10) blend film exposed to hydrolysis test for 36 h are shown in Fig. 9(b) and (c), respectively. The stretching vibration of carbonyl bond of exfoliating part is found at  $1720\text{ cm}^{-1}$  and that of core part is found at  $1750\text{ cm}^{-1}$ . These data show that the exfoliating part consists of PMMA, and the core part consists of the PLLA/PMMA (90/10) blend. Fig. 9(d) shows the FT-IR spectrum of the completely degraded PLLA/PMMA (90/10) blend and its carbonyl stretching band is found at  $1720\text{ cm}^{-1}$ , which is assigned to the carbonyl stretching band of neat PMMA. This result is consistent with the result of  $T_g$  change measured by DSC.

### 3.5. Water absorption

Table 2 shows the water absorption coefficient ( $W_a$ ) of each weight loss ( $W_{\text{loss}}$ ) of PLLA, PMMA, and PLLA/PMMA blend during alkaline hydrolysis tests. The degraded PLLA and PMMA samples had almost no water absorption. While the degraded PLLA/PMMA blend samples absorbed NaOH solution.

It was reported that hydrolysis of PLLA in phosphate buffer solution (pH 7) is much slower than that of PLLA in NaOH solution (pH 14) [18]. In phosphate buffer solution for 1 month, PLLA and PLLA/PMMA blend is almost no weight loss and no water absorption coefficient. Thus, it was recognized that only degraded PLLA/PMMA blend could absorb water.

Water absorption will be occurred with following mechanism. At surface layer, PLLA molecules of the blend are hydrolyzed and changed into low molecular weight. The low molecular weight PLLA molecules elute into NaOH solution, and only PMMA molecules remain in the surface layer of the blend. This generates the free volume in the surface layer and NaOH solution can remain in the space where PLLA molecules used to be.

Though more examination is needed, this water absorption mechanism may be one of the reasons for the hydrolysis acceleration of PLLA/PMMA blends whose PMMA content is lower than 30 wt%.

## 4. Conclusions

The following results were obtained on the miscibility and hydrolytic degradability of the PLLA/PMMA blends mixed with a two-roll mill and molded into amorphous state.

- (1) The glass transition behavior indicated the miscibility of PLLA and PMMA in an amorphous state.
- (2) The hydrolytic degradation rate of PLLA/PMMA blend can be widely controlled by PMMA content. In alkaline solution, the hydrolytic degradation rate of the blends whose PMMA content is higher than 30 wt% was decelerated while the rate of the blends whose PMMA content is lower than 30 wt% was accelerated.
- (3) In alkaline solutions, only PLLA was hydrolyzed into low molecular weight substance and eluted into alkaline solution, while PMMA did not elute. By the DSC curves and FT-IR spectra, it was confirmed that PMMA was remained after hydrolysis.
- (4) The degraded PLLA/PMMA blends absorbed alkaline solution in the space where PLLA molecules used to be. It may be one of the reasons for the hydrolysis acceleration of PLLA/PMMA blend whose PMMA content is less than 30 wt%.

## Acknowledgements

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